Aldehydes & Ketones – 02

Preparation of Aldehyde

① Rosenmund Reduction:

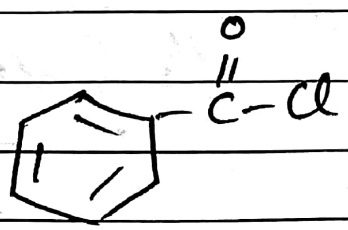
Acid Chloride $\xrightarrow[\text{Catalyst}/H_2]{\text{Lindlar's}}$ Aldehyde

Lindlar's Catalyst → $Pd/BaSO_4$
Poisoned by Sulphur or Quinoline
⇓
partial reduction

$$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[Pd/BaSO_4]{H_2} R-\overset{O}{\overset{\|}{C}}-H$$

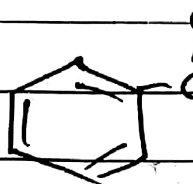
$$CH_3-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[Pd/BaSO_4]{H_2} CH_3-\overset{O}{\overset{\|}{C}}-Cl$$

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + H_2 \xrightarrow{Pd/BaSO_4} CH_3-\overset{O}{\overset{\|}{C}}-H + HCl$$



Benzoyl chloride

$+ H_2 \xrightarrow{Pd/BaSO_4}$



$+ HCl$

Benzaldehyde

* Formaldehyde can't be prepared as $H-\overset{O}{\overset{\|}{C}}-Cl$ is unstable

② Stephen's Reduction

Alkyl cyanide (nitrile) $\xrightarrow[ii)\ H_2O/H^+]{i)\ SnCl_2/HCl}$ Aldehyde

$R-C\equiv N \xrightarrow[HCl]{SnCl_2} R-CH=NH \xrightarrow[H^+]{H_2O} R-CHO$

cyanide (nitrile) → imine → aldehyde

$CH_3-C\equiv N \xrightarrow[HCl]{SnCl_2} CH_3-CH=NH \xrightarrow[H^+]{H_2O} CH_3-CHO$

ethanenitrile → ethanimine → ethanal

Mechanism:

$$SnCl_2 + 2HCl \longrightarrow SnCl_4 + 2H^+$$

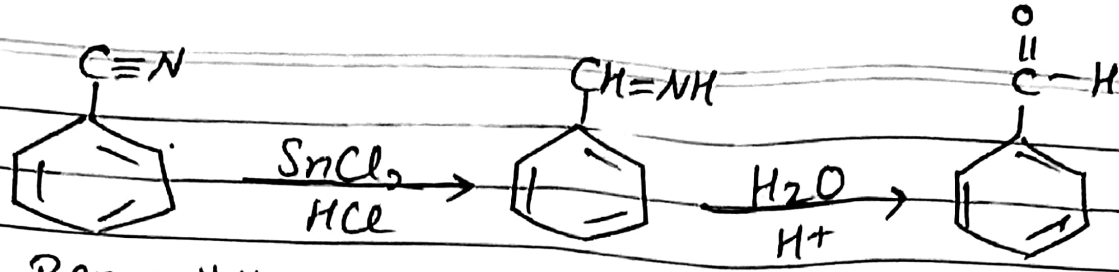
$$\overset{+2}{Sn}Cl_2 \longrightarrow \overset{+4}{Sn}Cl_4$$

$$Sn^{2+} \longrightarrow Sn^{4+} + 2e^-$$

$$CH_3-C\equiv N \xrightarrow{2e^-} CH_3-\overset{\ominus}{C}=N^{\ominus} \xrightarrow{2H^+} CH_3-\underset{H}{C}=NH$$

$$CH_3-\underset{H}{C}=NH \xrightarrow{H_2O} CH_3-\overset{O}{\overset{\|}{C}}-H$$

$$-NH_3$$



Benzonitrile

$-NH_3$

Benzaldehyde

③ Using DiBAL-H :

diisobutyl Aluminium Hydride

$\left(CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2\right)_2Al-H$ OR $AlH(i\text{-}Bu)_2$

$$R-C\equiv N \xrightarrow[ii)\ H_2O/H^+]{i)\ DiBAL-H} R-CHO$$

nitrile

$$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[ii)\ H_2O/H^+]{i)\ DiBAL-H} R-CHO$$

acid halide

$$R-\overset{O}{\overset{\|}{C}}-OR' \xrightarrow[ii)\ H_2O/H^+]{i)\ DiBAL-H} R-CHO + R'OH$$

$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow[ii)\ H_2O/H^+]{i)\ DiBAL-H} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H + C_2H_5OH$$