2nd 5. **Stephen Reduction:** Nitriles (alkyl cyanides) are partially reduced to corresponding imine with $SnCl_2$ and HCl, which on hydrolysis gives corresponding aldehyde. $SnCl_2$+HCl does not reduce C≡C and C=C bonds.

$$R-C\equiv N \xrightarrow[\text{(Partial Red}^{n}\text{)}]{SnCl_2+HCl,\ [H]} \underset{\text{Ecamine or Imine (Intermidiate)}}{[R-CH=NH]} \xrightarrow{H_3O^+} \underset{\text{(Aldehyde)}}{RCHO}$$

✓ $Sn + 2HCl \longrightarrow \underset{(+2)}{SnCl_2} + 2[H]$ This reagent will completely reduce nitriles to amines. (Stable)

but if we use $SnCl_2$ in HCl it gives limited amount of H_2 and only partial reduction will take place.

$$\underset{(+2)}{SnCl_2} + 2HCl \rightleftharpoons \underset{(+4)\text{(unstable) due to inert pair effect}}{SnCl_4} + 2[H]$$

6. **By Grignard Reagents:** Hydrogen cyanides or alkyl cyanides, when react with Grignard reagent yield an adduct which upon hydrolysis yield aldehyde or Ketone respectively.

$$R'/H-\overset{\delta+}{C}\equiv\overset{\delta-}{N} \xrightarrow{R^{\delta-}-Mg-X} \left[R'/H-\underset{R}{\overset{|}{C}}=N-Mg-X\right] \xrightarrow{H_3O^{\oplus}} \underset{R'/H}{\overset{R}{\diagdown}}C=O + Mg\begin{matrix}\diagup NH_2\\ \diagdown X\end{matrix}$$

Adduct

(Aldehyde/Ketone)

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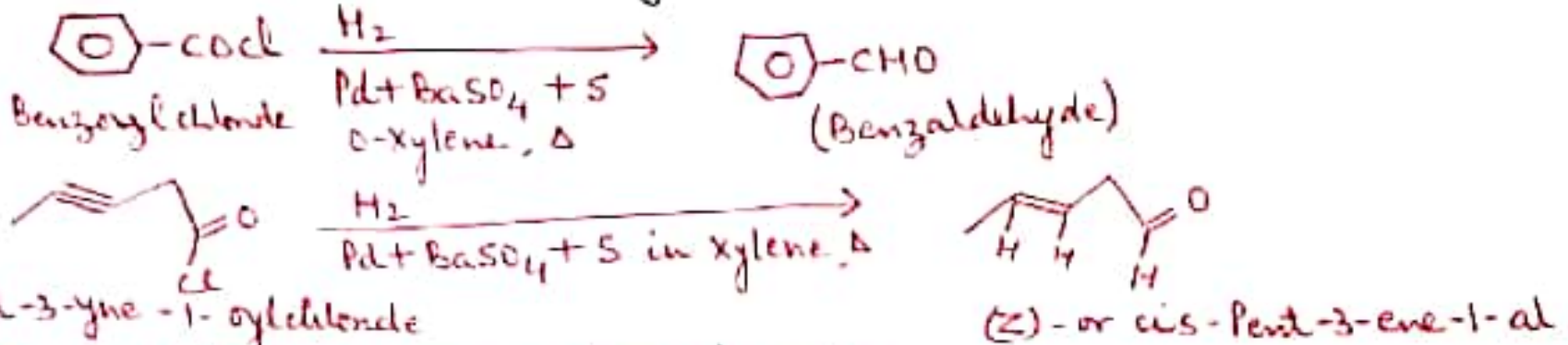
CLASSTIME

3. Rosenmund Reduction:

Partial hydrogenation of benzoylchloride with finely powdered Pd as catalyst in the presence of $BaSO_4$ and S or quinoline (act as poison) in boiling xylene (as solvent) gives benzaldehyde. The catalyst under above condition is also called Lindlar's Catalyst, also reduces C≡C & C=C in syn-addition.

Sulphur or quinoline retards the activity of Pd and reacts with small amount of H_2 to give H_2S or hydroquinoline, thereby limiting H_2 for further reduction of aldehyde to alcohol.



Pent-3-yne-1-oylchloride

(Z)- or cis-Pent-3-ene-1-al

4. Synthesis of Ketones from Acid chlorides:

$$2RLi + CuI \longrightarrow R_2CuLi + LiI$$

[Lithium dialkyl cuprate]
(Gilman Reagent)

$$R'COCl + R_2CuLi \longrightarrow R'COR + RCu + LiCl$$

(Ketone)

Similarly:

$$R_2Cd + 2R'COCl \longrightarrow 2\,RCOR' + CdCl_2$$

(Dialkyl cadmium)

Organic Chemistry (LS-2A)

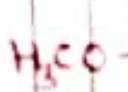
By: Dr. N. G. Gisi

1. Gattermann-Koch Aldehyde Synthesis:

Benzene or its derivatives on reaction with ($CO + HCl + AlCl_3$ or CuCl) gives benzaldehyde or substituted benzaldehyde.

eg:  + CO + HCl + Anhy. $AlCl_3$ or CuCl ⟶  -CHO (Benzaldehyde)

(Benzene)

 + CO + HCl + $AlCl_3$ (anhy.) ⟶  -CHO (p-Methoxybenzaldehyde)

Anisole

2. Hauben-Hoesch Reaction:

This reaction is acylation of highly reactive m-polyhydroxy compound with a nitrile in presence of HCl and anhydrous $AlCl_3$ or $ZnCl_2$. The ketemine produced is hydrolyzed with aqueous acid.