Functional Group Reactions - CHEM 263

Acyl chlorides

1. Reduction

$$R \xrightarrow{\begin{array}{c} O \\ \hline CI \end{array}} \begin{array}{c} 1. \text{ LiAIH}(O-t-Bu)_3, Et_2O, -78^{\circ}C \\ \hline 2. \text{ H}_2O \end{array} \qquad R \xrightarrow{\begin{array}{c} O \\ \hline H \end{array}}$$

2. Reaction with lithium dialkylcuprates

3. Hydrolysis

$$R \xrightarrow{O} H_2O \longrightarrow RCO_2H$$

4. Ammonolysis

$$R \xrightarrow{O} NH_3 \qquad R \xrightarrow{O} NH_2$$

$$R \xrightarrow{O} R'NH_2 \qquad R \xrightarrow{O} NHR'$$

$$R \xrightarrow{O} R'_2NH \qquad R \xrightarrow{O} NR'_2$$

5. Alcoholysis

$$R \xrightarrow{O} R'OH R \xrightarrow{O} R$$

6. Friedel - Crafts acylation

7. Synthesis of anhydrides

$$R \xrightarrow{O} R'CO_2^- R \xrightarrow{O}$$

Alcohols

1. Reaction with SOCl₂, PX₃ or HX

2. Dehydratation

$$\begin{array}{c|c}
 & H \\
 & H_2SO_4 \text{ or } H_3PO_4 \\
\hline
 & \Delta
\end{array}$$

3. Reaction with Li, Na or K

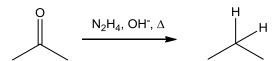
ROH
$$\longrightarrow$$
 RO-M+ + 0,5H₂

Aldehydes and ketones

1. Reduction

Clemmensen:

Wolff-Kishner:



2. Grignard reagents

3. Oxidation

$$R \xrightarrow{\begin{array}{c} O \\ H \end{array}} \xrightarrow{\begin{array}{c} KMnO_4, OH^{-} or \\ [Ag(NH_3)_2]^{+} \end{array}} R \xrightarrow{\begin{array}{c} O \\ O^{-} \end{array}} R \xrightarrow{\begin{array}{c} O \\ OH \end{array}}$$

4. Hhaloform reaction

$$R \xrightarrow{O} X_2, OH^- R \xrightarrow{O} + CHX_3$$

5. Formation of cyanohydrins

6. Formation of imines

7. Wittig reaction

$$O + (C_6H_5)_3P \longrightarrow + (C_6H_5)_3P = O$$

8. Halogenation

O
$$CI_2$$
, Br_2 or I_2
OH⁻ or H_3O^+

9. Aldol addition

10. Reductive amination

 X_2/Δ or hv RX

Alkanes

1. Halogenation

RH

Alkenes

1. Hydrogenation

2. Addition of HX

3. Oxymercuration

4. Hydroboration

$$\begin{array}{c|c} H \\ \hline \\ CH_3 \\ \hline \\ 2. \ H_2O_2, \ OH^- \\ \hline \end{array}$$

5. Addition of halogen

6. Addition of X₂/H₂O

$$\begin{array}{c|c} & & X_2, H_2O \end{array}$$

7. Addition of carbenes

$$\begin{array}{c|c} CH_2N_2/\Delta \text{ or hv} \\ \hline \\ RO^-, CHX_3 \end{array}$$

8. Ozonolysis

$$\begin{array}{c|c} & 1. O_3 \\ \hline & 2. Zn, H_2O \end{array} \longrightarrow O \longrightarrow \left(\begin{array}{c} \\ \end{array}\right)$$

9. Formation of oxacyclopropanes

Alkyl halides

1. Reduction

2. Corey - Posner, Whitesides - House reaction

RX
$$\frac{1. \text{Li}}{2. \text{Cul}}$$
 $R_2\text{CuLi}$

$$R_2CuLi$$
 $\xrightarrow{R'X (1^\circ) \text{ or } ArX}$ R-R or R-Ar

3. Finkelstein reaction

4. Williamson synthesis

5. Dehydrohalogenation

6. Reaction with ammonia and amines

$$RX \xrightarrow{NH_3} RNH_2$$

7. Reaction of primary alkyl halides with CN-

$$RCH_2X \xrightarrow{CN^-} RCH_2CN$$

Alkynes

1. Alkylation of terminal alkynes

$$R - - - H - \frac{1. \text{ NaNH}_2}{2. \text{ R'X (1^0)}} R - - - R'$$

2. Hydrogenation

3. Addition of halogens

$$\times$$
 \times \times \times \times \times \times

4. Addition of HX

$$H \longrightarrow HX \longrightarrow HX \times X$$

5. Addition of water

Amides

1. Hofmann degradation

$$R \xrightarrow{O} \frac{OH^{-}}{Cl_{2} \text{ or } Br_{2}} RNH_{2}$$

2. Hydrolysis

$$R \xrightarrow{O} \begin{array}{c} 1. \text{ OH}^-, \Delta \\ \hline 2. \text{ H}_3\text{O}^+ \\ \hline \text{ or } \text{H}_3\text{O}^+, \Delta \end{array} \longrightarrow \text{RCO}_2\text{H}$$

Amines

1. Reaction with derivatives of carboxylic acids

$$R \xrightarrow{O} R'NH_{2}$$

$$CI \qquad NHR'$$

$$O \xrightarrow{O} Q \qquad R'_{2}NH \qquad O \qquad NR'_{2}$$

$$R \xrightarrow{O} R'_{2}NH_{2}$$

2. Reaction with nitrous acid

ArNO₂
$$\xrightarrow{\text{NaNO}_2, \text{HX}}$$
 ArN₂⁺

Anhydrides

1. Hydrolysis

$$\begin{array}{c} & & & \\ & & \\ & & & \\ & & & \\ & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & &$$

2. Ammonolysis

3. Alcoholysis

4. Friedel – Crafts acylation

Aromatic rings

1. Nitration

$$ArH \xrightarrow{HNO_3/H_2SO_4} ArNO_2$$

2. Sulfonation

ArH
$$\frac{\text{H}_2\text{SO}_4/\text{SO}_3}{\qquad}$$
 ArSO₃H

3. Halogenation

4. Alkylation

5. Acylation

$$R$$
 O
 O
 $R = R \text{ or Ar}$
 O
 ArH
 $AlCl_3$

Carboxylic acids

1. Reduction

RCO₂H
$$\frac{1. \text{ LiAlH}_4/\text{Et}_2\text{O}}{2. \text{ H}_2\text{O/H}_2\text{SO}_4} \Rightarrow \text{RCH}_2\text{OH}_2$$

2. Reaction with SOCl₂, PCl₃ or PCl₅

3. Hell-Volhard-Zelinski Reaction

Esters

1. Reduction

$$\begin{array}{c|c}
O \\
\hline
 & 1. \text{ LiAlH}_4/\text{Et}_2\text{O} \\
\hline
 & 2. \text{ H}_2\text{O/H}_2\text{SO}_4
\end{array}$$
RCH₂OH + R'OH

2. Grignard reagents

$$R'$$
 O $\frac{1. \text{ RMgX}}{2. \text{ H}_3\text{O}^+}$ R $\frac{R'}{R}$

3. Hydrolysis

$$OR \xrightarrow{OH^- \text{ or } H_3O^+} O$$
or OH
$$OR \xrightarrow{O} O$$

4. Ammonolysis

5. Trans esterification

$$\begin{array}{c|c} O & & O \\ \hline & R'OH, H_3O^+ \\ \hline OR & & OR' \end{array} + ROH$$

Nitriles

1. Reduction

OH
$$\begin{array}{c}
\text{OH} \\
\text{1. LiAlH}_4 \\
\text{2. H}_2\text{O}
\end{array}$$

$$\begin{array}{c}
\text{OH} \\
\text{CH}_2\text{NH}_2
\end{array}$$

2. Hydrolysis

OH
$$H_3O^+, \Delta$$
 OH CO_2H