Chapter 20 Reaction Summary Reactions of Carboxylic Acids and Nitriles



Conversion to an Acid Chloride

• Subjecting a carboxylic acid to thionyl chloride (SOCl₂) converts it to an acid chloride.

$$\bigcup_{OH} \xrightarrow{SOCI_2} \bigcup_{CI} + SO_2 + HCI$$

Fischer Esterification

• In the presence of an acid catalyst carboxylic acids and alcohols react to form esters.

$$\underbrace{\bigcirc}_{OH} \underbrace{HO-R}_{H^{\oplus}} \underbrace{\bigcirc}_{O'}R + H_2O$$

- \circ Most commonly H₂SO₄, H₃PO₄, and HCl are used as the acid catalysts.
- The reaction equilibrium favors products when excess reagent (carboxylic acid or alcohol) is used or when water is removed as the reaction progresses.
- Methyl, primary, and secondary alcohols can be used. Tertiary alcohols don't generally work well due to steric hindrance.
- An intramolecular Fischer Esterification can occur when a molecule has both a carboxylic acid and alcohol functional group. Generally 5 or 6 membered rings (lactones) can be formed.

Reaction with a Base (Carboxylate Formation)

• Bases will react with carboxylic acids to form carboxylate salts.



• Common bases include: MOH, Grignard Reagents, and organolithium compounds.

Conversion to Amides

• Carboxylic acids can be converted to amides in the presence of an amine and DCC.



- NH₃, H₂NR (primary), and HNR₂ (secondary) amines work well while tertiary do not.
- DCC converts the alcohol into a good, aprotic, leaving group.

Preparation of Nitriles

• Nucleophilic Substitution: Alkyl Halides + NaCN

 $R \xrightarrow{NaCN} R \xrightarrow{CN} + NaX$

- This reaction is a useful method to add a carbon atom to a compound.
- \circ $\,$ Methyl, primary, and secondary halides work in this reaction.
- Nucleophilic Addition of NaCN to C=O produces a cyanohydrin.

$$\begin{array}{c} O \\ H \\ R(H) \end{array} \xrightarrow{NaCN} \begin{array}{c} OH \\ HCI \\ CN \end{array}$$

Reactions of Nitriles

Nitriles are considered carboxylic acid derivatives because they, like other carboxylic acid derivatives, can be hydrolyzed to carboxylic acids.

• Hydrolysis to a Carboxylic Acid: Subjecting nitriles to acid and water provides carboxylic acids. Base hydrolysis also works, but we didn't cover this in class.

$$R C_{S_N} \xrightarrow{H_2O} R OH$$

• Reduction to an Amine: Subjecting nitriles to LAH followed by water provides the amine product.

$$R C \sim N \frac{1. LAH}{2. H_2O} R NH_2$$

• Conversion to a Ketone: Subjecting a nitrile to an organometallic reagent such as a Grignard reagent or organolithium compound provides a ketone product.

$$R \frown C_{\gtrsim N} \xrightarrow{1. \text{R'-MgBr}} R \xrightarrow{R} O$$