Derivatives of Carboxylic Acids

Reactions of Acid Chlorides
And
Fischer Esterification

Carboxylic Acid Derivatives

Carboxylic acid derivatives include a variety of functional groups containing a heteroatom group other than –OH attached to a carbonyl group.

Examples include: –OR (esters), –OC(O)R (acid anhydrides), –NR₁R₂, (amides), –halide (acid halides)

All of these derivatives can be hydrolyzed to the carboxylic acid by a nucleophilic acyl substitution reaction.
Reactivity of Carboxylic Acid Derivatives

The reactivity of carboxylic acid derivatives toward acyl substitution is shown below:

Reactions of Acid Chlorides

Acid chlorides can be converted easily into esters, the carboxylic acid, and amides. You will examine two of these reactions today.
Fischer Esterification

\[
\text{PhC} - \text{OH} + \text{CH}_3\text{OH} \xrightleftharpoons{H^+} \text{PhC} - \text{OCH}_3 + \text{H}_2\text{O}
\]

7 The direct reaction of a carboxylic acid with an alcohol to form an ester will occur only in the presence of acid catalyst.

7 This reaction, called Fischer esterification, is an equilibrium reaction where the energies of the products are very close to the energies of the starting materials.

\[
K_{eq} = \frac{[\text{PhCO}_2\text{CH}_3][\text{H}_2\text{O}]}{[\text{PhCO}_2\text{H}][\text{CH}_3\text{OH}]} \approx 4.0
\]
**Increase Ester Formation**

\[
\text{PhC} - \text{OH} + \text{CH}_3\text{OH} \xrightleftharpoons{H^+} \text{PhC} - \text{OCH}_3 + \text{H}_2\text{O}
\]

\[K_{eq} = \frac{[\text{PhCO}_2\text{CH}_3][\text{H}_2\text{O}]}{[\text{PhCO}_2\text{H}][\text{CH}_3\text{OH}]} \approx 4.0\]

1. Remove one of the products as it is formed.
2. Use large excess of other starting reagent.

**Mechanism of Fischer Esterification**

7 Acid acts as a catalyst at two points in this mechanism.
Mechanism of Fischer Esterification

7 The second point of acid catalysis is in step 4.

Procedure

7 You WILL work in partners for this experiment.

7 Today’s lab has two parts. You will do the initial steps in both parts today, and complete them in lab next week.

7 Part I is the synthesis of methyl benzoate by Fischer esterification. You will run the reaction and isolate the crude product today. You will store the crude product until next week when you will distill the product and obtain an IR spectrum.
Procedure

In Part II today, you will run the reactions of benzoyl chloride with water (hydrolysis) and with ammonia (ammonolysis). Both reactions form solid products which you will isolate by filtration. Rinse the products well with water on the filter pad, because you are not going to do a recrystallization. You will store the crystals in your section’s sample drawer and obtain melting points next week.

Procedure – NEXT WEEK

Obtain m.p. values for your derivatives and complete classification tests. Use this data to determine the most likely structure of your unknown.

You need to write this structure in your lab note-book and get your TA to initial it before you take your infrared spectrum.

Obtain an infrared spectrum of your unknown.
Structure Deduction

7 Reference spectra for the various unknowns will be posted on the webpage for this experiment on the Thursday after the second week of this lab.

7 Use all of your data to deduce the structure that best matches that data. Explain your reasoning and any data that might appear inconsistent in your laboratory report.

Safety

7 Sulfuric acid is toxic and corrosive. It will burn skin and create holes in clothing. Flush with water and then with aqueous sodium bicarbonate.

7 Benzoyl chloride is a lachrymator (Quiz question!)

7 Ammonium hydroxide is a solution of ammonia gas in water and releases ammonia vapor (corrosive toxin).
Cleanup

7 Rinse all glassware used with benzoyl chloride with acetone in the hood into a waste bottle.

7 Aqueous phases may be disposed of in the sink.