Mystery Product: The Acid-Catalyzed Reaction of Propionic Acid and Methyl Alcohol

by Kurt Rublein, Organic Instructional Laboratories, Revised 5/20/00

Ester syntheses are one of the more enjoyable experiments in organic chemistry, as one can't help but notice the pleasant odors. In contrast, the acids which are used in their syntheses usually have a rotten odor. The reverse reaction, hydrolysis of the ester, gives the alcohol and the acid from which it was synthesized. Because the hydrolysis can occur in the presence of sweat, esters are not used as perfumes. The ester from this particular reaction does not have a particularly pleasant aroma, but it is much better than the propionic acid, which smells a lot like vinegar.

\[
\begin{align*}
\text{HO} & \quad \text{C} \quad \text{H}_2 \\
\text{C} & \quad \text{CH}_3 \\
\text{O} & \quad + \\
\text{CH}_3\text{OH} & \quad \text{H}^+ \\
\end{align*}
\]

In this experiment, you should predict the product(s) of the reaction above and interpret your analysis data to confirm or negate your prediction.

Cautions
Propionic is corrosive and soaks into the skin quickly. Wear gloves when handling. Clean up any spills immediately. Concentrated sulfuric acid is also a corrosive hazard; wear gloves.

PreLab
Be sure to prepare a complete PreLab, following the guidelines in the Lab Guide for Synthetic Experiments. Include the hypothesized product in your Chemical Data Table. The product is in Aldrich, so you can use the Formula Index to locate the compound.

Include answers to the following questions in your PreLab:
1. Why should the sodium bicarbonate solution be added slowly? What by-product is generated?
2. Write balanced equations for all reactions that take place during the neutralization.

Procedure
Add 1.0 mL of propionic acid and 0.70 mL of methanol to a short-neck round-bottom flask from your microscale kit. Add three boiling chips the flask. Dropwise, add 6 drops of concentrated sulfuric acid. Attach the air-cooled condenser to the flask and heat the mixture. Once the mixture begins to reflux gently, continue refluxing for 35 min. During this time, make certain the methanol is condensing and running back into the reaction flask--if the solvent evaporates from the reaction (i.e., distills) then you are losing one of your reagents!

After the 35 min heating period, take the flask out of the sand bath and let it air cool for at least 5 minutes. During the cooling period, obtain 4 mL of 5% sodium bicarbonate solution in a beaker. Once the solution is cooled, add 1.25 mL of the sodium bicarbonate solution DROPWISE to the reaction mixture. After the bubbling has subsided, gently swirl the contents to mix the aqueous and organic layers. Use a pipet to transfer the mixture to one of your 13 x 100 test tubes. (Separation of two liquids
is easier when the interface between the two liquids is smaller in surface area.) Now use the pipet to remove the aqueous layer. (Which one is the aqueous layer?? You should do a drop test with additional sodium bicarbonate to be sure.) Repeat the sodium bicarbonate washing, once using 1.25 mL and then once using 1.50 mL; each time, remove the aqueous layer. After the third washing, add a little sodium sulfate to the tube to absorb any residual moisture. Mix gently and let it stand for 3 min. Using pipet filtration, transfer the dried organic layer to the long-neck round-bottom flask from your microscale kit; be sure to leave the drying agent in the tube. Distill the liquid using microscale simple distillation. You may find that loosely wrapping the distillation head with a piece of paper towel moistened with cold water will help to condense the product vapors. Record the temperature range over which the distillate is collected and transfer the distillate to a tared shorty vial.

**Cleaning Up**
The aqueous layers from the sodium bicarbonate washings can go down the drain with flushing water. The distillation residue should be discarded in the organic waste container.

**Analyses**
The product can be analyzed by NMR, GC, GC-MS, IR, or by refractometry. See your assignment strip for your assigned analysis.

**Questions**
Answers to the following should be included in your Final Report

1. Since methanol (methyl alcohol) is in excess, there should be some unreacted methanol remaining at the end of the reflux period. At what point is the methanol separated from the desired product?
2. What advantage might there be in using anhydrous methanol rather than the regular methanol that you used in the experiment?
Synthetic Experiment PreLab Grading Sheet

Name(s): ________________________________

TA: ________________________________

Date: ________________________________

PreLab For Exp't #: 89

Title: Mystery Product: The Acid-catalyzed Reaction of Propionic Acid and Methyl Alcohol

<table>
<thead>
<tr>
<th>Date, Name, Desk #, Experiment # &amp; Title(abbreviated after 1st pg), Section &amp; TA Name</th>
<th>Possible Points</th>
<th>Missed Points</th>
</tr>
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<tbody>
<tr>
<td>8</td>
<td></td>
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<tr>
<td>Summary</td>
<td>10</td>
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<td>Goals</td>
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<tr>
<td>Reactions, structures, diagrams</td>
<td>16</td>
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<tr>
<td>Completeness of Chemical Data Table(s)</td>
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<tr>
<td>PreLab Exercise</td>
<td>16</td>
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<td>Spectral Features Comparison (NMR, RI)</td>
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<tr>
<td>Work-up - Explanation of the product isolation and purification process</td>
<td>12</td>
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**TOTAL FOR PRELAB** 100

Date Handed in: ______________

General Comments: ______________

**Total Points:** ______
# Synthetic Experiment Final Report Grading Sheet

Name: ________________________________  
TA: ________________________________  
Date: ________________________________

Final Report For Exp't #: **89**

**Title:** Mystery Product: The Acid-catalyzed Reaction of Propionic Acid and Methyl Alcohol

<table>
<thead>
<tr>
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<tbody>
<tr>
<td><strong>Name, Date, Experiment Title (abbreviated after 1st page) and every page numbered</strong></td>
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<td></td>
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<tr>
<td><strong>OBSERVATION and DATA - Overall organization, readability, completeness</strong></td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Data: Weighing data, molecular weights, moles, density, volumes, analysis conditions (IR analysis type, NMR solvent, GC/GC-MS Conditions Sheet)</td>
<td>12</td>
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<tr>
<td>Yield: Show % yield calculations with limiting reagent clearly stated. Purity: boiling point, color, or other indicators of purity.</td>
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<td><strong>RESULTS AND DISCUSSION - Overall organization, readability, completeness</strong></td>
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<tr>
<td>Results: Achievement of goals, discussion of product</td>
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<tr>
<td>Product Analysis Data: Quality and Interpretation – Structure(s) drawn on each Spectrum or Chromatogram Assignment and discussion of major IR or all NMR absorptions or GC-MS chromatogram and major MS spectral features. RI, compared to literature, as a measure of purity Unknown Determination, Correct ID of the “Mystery” Product</td>
<td>24</td>
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<td><strong>POSTLAB QUESTIONS</strong></td>
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**Total Points:** ______