The Friedel-Crafts Reaction: Anthraquinone

from K. L. Williamson, Macroscale and Microscale Organic Experiments, 2nd Ed. 1994, Houghton Mifflin, Boston p449; revised 10/10/00

Prelab Exercise
Write a mechanism for the formation of anthraquinone from 2-benzoylbenzoic acid, indicating clearly the role of sulfuric acid. What is the name commonly given to this type of reaction?

Introduction

The Friedel-Crafts reaction of phthalic anhydride with excess benzene as solvent and two equivalents of aluminum chloride proceeds rapidly and gives a complex salt of 2-benzoylbenzoic acid

in which one mole of aluminum chloride has reacted with the acid to form the salt $\text{RCO}_2^- \cdot \text{AlCl}_2^+$ and a second mole is bound to the carbonyl group.

On addition of ice and hydrochloric acid, the complex is decomposed and basic aluminum salts are brought into solution.

Treatment of 2-benzoylbenzoic acid with concentrated sulfuric acid effects cyclodehydration to anthraquinone, a pale-yellow, high-melting compound of great stability. Because anthraquinone can be sulfonated only under forcing conditions, a high temperature can be used to shorten the
reaction time without loss in yield of product; the conditions are so adjusted that anthraquinone separates from the hot solution in crystalline form, which favors rapid drying.

**Precautions**

Use caution when using sulfuric acid. It will spatter on contact with water and other liquids.

**TLC**

You are required to run a TLC to monitor the progress of the reaction. Plates should have three spots (or lanes) on the origin: one for the main organic starting material that is being transformed, one for a cospot (starting material and the reaction mixture), and one for the reaction mixture.

**Procedure: Anthraquinone**

In a reaction tube dissolve 100 mg of 2-benzoylbenzoic acid in 0.5 mL of concentrated sulfuric acid by gently heating and stirring. Warm the sand bath to about 150 °C. Immerse a thermometer in the reaction mixture, and heat it at 150 to 155 °C in the sand bath. Perform a TLC analysis after 10 min. If the reaction hasn’t reached completion heat for another 10 min. Remove from sandbath when reaction is complete as determined by TLC.

Allow the tube to cool to below 100 °C, and then, using extreme caution, add a very small drop of water to the mixture. Mix the contents of the tube, and continue adding water in minute drops to the mixture. This will cause the product to crystallize, and if done slowly enough, the crystals will be large enough to collect easily by filtration.

Fill the tube with water, and collect the product by filtration on the Hirsch funnel. Return the damp product to the reaction tube, and boil the product with 0.5 mL of concentrated ammonium hydroxide to remove unreacted starting material. Filter, then wash the product well with ice water. Recrystallize from ethanol or toluene using Norit pellets for decolorization, dry, determine the weight and melting point.

The resulting anthraquinone should be purified by sublimation in a 13 x 100 mm test tube. The product should be yellow in color after sublimation. Calculate % yield after sublimation.

Take a melting point after sublimation (compare with crude). Calculate % yield.

**Vapor Pressure vs. Temperature behavior of anthraquinone.**

<table>
<thead>
<tr>
<th>T °C</th>
<th>Vapor Pressure (mm Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>1.8</td>
</tr>
<tr>
<td>220</td>
<td>4.4</td>
</tr>
<tr>
<td>240</td>
<td>12.6</td>
</tr>
<tr>
<td>260</td>
<td>33.0</td>
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</tbody>
</table>

**Analysis**

In addition to TLC analysis, you may be instructed to analyze your final product by IR or UV-Vis. Analyze your sample according to your Assignment sheet and the instructions on Sample Preparation in Lab Guide.

**Cleaning Up**

The aqueous filtrate, after neutralization with sodium carbonate, is diluted with water and flushed down the drain.

**Post Lab Questions**

1. Describe the function of ammonium hydroxide in this experiment
2. Which of the two reactions shown below is expected to occur more readily?
CH₃O + CH₃CH=CH₂ → CH₃OCH₃

NO₂ + CH₃CH=CH₂ → NO₂CH₃