Exp't 121

Nitric Acid Oxidation of Benzoin to Benzil

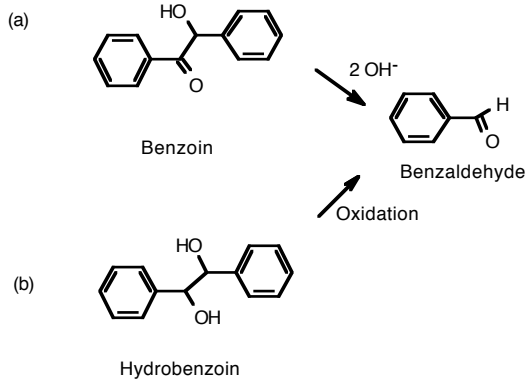
from K. L. Williamson, *Macroscale and Microscale Organic Experiments,* 2nd Ed. 1994, Houghton Mifflin, Boston. p494 Rev *4/8/99*

Prelab Exercjse

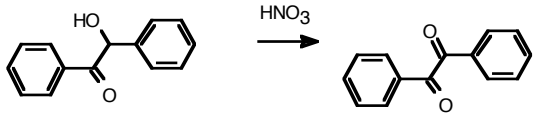
The UV spectra of benzoin shows a peak at λ_{max}^{EtOH} 247 nm. The extinction coefficient, $\in$, is 13,200. The concentration of the sample is 5.92 x 10^{-5} mol/L. The path length is 1 cm. What is the absorbance, A, of the chromophore at the λ_{max} wavelength? Please show all calculations. Refer to Lab Guide Chap 11.

Introduction

Benzoin can be oxidized to the _-diketone benzil very efficiently by nitric acid or by copper(II) sulfate in pyridine. On oxidation with sodium dichromate in acetic acid, the yield is lower because some material is converted into benzaldehyde by cleavage of the bond between two oxidized carbon atoms that is activated by both phenyl groups (**a**). Similarly, hydrobenzoin on oxidation with dichromate or perrnanganate yields chiefly benzaldehyde and only a trace of benzil (**b**).



Ultraviolet spectroscopy is used to help characterize aromatic molecules such as benzoin. The absorption band at 247 nm in the UV spectra is attributable to the presence of the phenyl ketone group C_6H_5-C=O, in which the carbonyl group is conjugated with the benzene ring. Aliphatic α, β-unsaturated ketones, R-CH=CH-C=O, show selective absorption of ultraviolet light of comparable wavelength. The IR spectrum of benzoin shows a peak at 1664 cm^{-1} for the conjugated carbonyl.



Benzoin
MW 212.24 MP 135 ^{o}C

Benzil
MW 210.23 mp 94-95 ^{o}C

Cautions

Handle concentrated nitric acid with care. Avoid contact with skin. Do the reaction in the hood as brown nitric oxide fumes are released.

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: Nitric Acid Oxidation of Benzoin

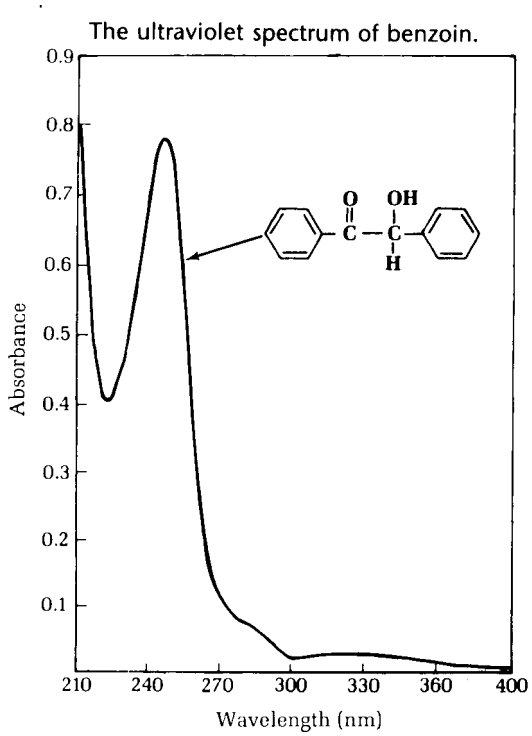
Heat a mixture of 100 mg of benzoin and 0.35 mL of *concentrated* nitric acid in a small beaker placed in boiling water for about 11 min. Carry out the reaction in the hood to avoid breathing evolved nitrogen oxides. Be sure all the benzoin gets washed down inside the tube and is oxidized. When reaction is complete, add 2 mL of water to the reaction mixture, cool to room temperature, and stir the mixture for a minute or two to coagulate the precipitated product.

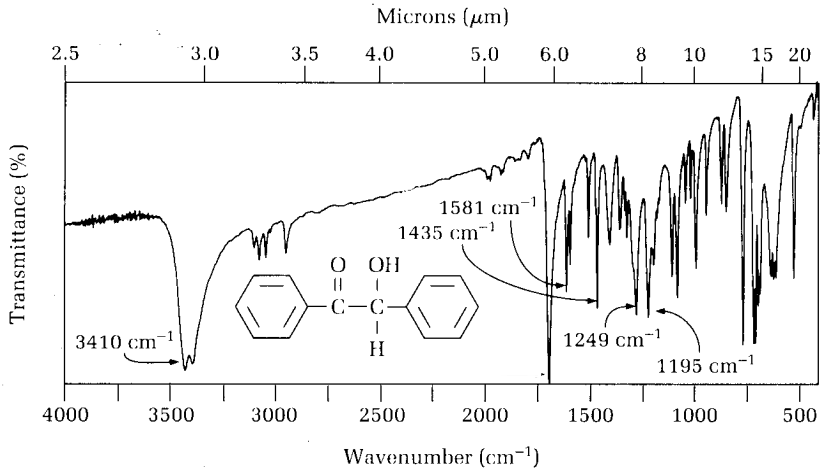
Remove the solvent with a Pasteur pipette, and wash the solid with 2 mL more water. Dissolve the solid in 0.5 mL of hot ethanol, and add water dropwise to the hot solution until the solution appears to be cloudy, indicating it is saturated. Heat to bring the product completely into solution, and allow it to cool slowly to room temperature. Cool the tube in ice, and isolate the product using the Hirsch funnel. Scrape the benzil onto a piece of filter paper, squeeze out excess solvent, and allow the solid to dry.

Record the percentage yield, crystalline form, color, and melting point of the product.

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 the Lab Guide.





IR spectrum of benzoin (KBr disk).

Test for the Presence of Unoxidized Benzoin

Dissolve about 0.5 mg of crude or purified benzil in 0.5 mL of 95% ethanol or methanol, and add one drop of 10% sodium hydroxide. If benzoin is present, the solution soon acquires a purplish color. If no color develops in 2 to 3 mm, an indication that the sample is free from benzoin, add a small amount of benzoin, observe the color that develops, and note that if the test tube is stoppered and shaken vigorously, the color momentarily disappears; when the solution is then let stand, the color reappears.

Cleaning Up

The aqueous filtrate should be neutralized with sodium carbonate, diluted with water, and flushed down the drain. Ethanol used in crystallization should be placed in the organic solvents container.

PostLab Questions

1. Why is it not a good idea to neutralize the nitric acid with a base when the reaction is complete?
2. Interpret the IR peaks whose frequencies are given for the IR spectrum of benzoin given above.
3. Give a plausible structure for the colored compound that is formed from benzoin by the addition of 10% NaOH.