Purpose

This is the third step in the multistep synthesis from the original starting material of benzaldehyde. This is the final step before synthesizing the final product of hexaphenylbenzene.

Learning Objectives

To synthesize benzil

To understand co-oxidation

Theory and Background

This reaction uses a solution of ammonium nitrate, in the presence of a catalytic amount of copper(II) acetate, to oxidize benzoin to benzil. Many reactions in organic chemistry involve oxidation–reduction (redox) mechanisms, which simply means electrons are lost from one atom or molecule and gained by another. Typically, organic chemists refer to oxidation as the loss of carbon–hydrogen bonds (loss of hydride). Notice in the scheme below that going from benzoin to benzil results in the loss of a carbon–hydrogen bond. Cu2+ can accept an electron from oxygen while the acetate ion removes a hydrogen. To make the reaction catalytic in copper, a co-oxidant is used (ammonium nitrate) to regenerate the Cu_2^+ species.

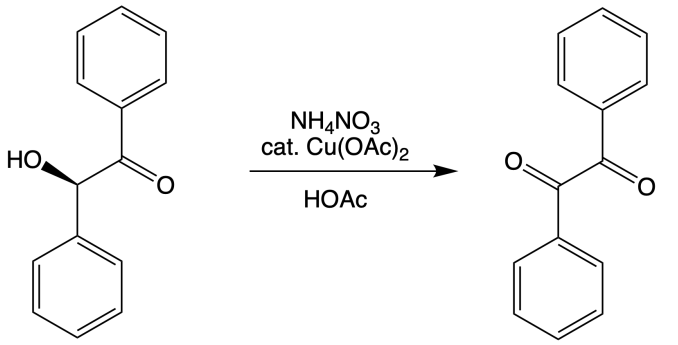

Figure 22B.1: Benzoin Synthesis with Cu oxidation.

Reagents

Table 22B.1: Table of Reagents

Reagent	Formula	Equiv	MW (g/mol)	Volume (mL)	Mass (g)	mmol	m.p. (°C)	b.p. (°C)
Benzoin	$C_{14}H_{12}O_2$	1.0	212.24					—
0.15 M $Cu(OAc)_2$ in $HOAc/H_2O$		0.12	181.5				—	—
NH_4NO_3 Source of NO_3^-		1.5	80.04				169 °C	210 °C
Benzil		1.0	210.23					—

Now you know...

There are many different oxidizing agents that could be used for this reaction. Chromium reagents, manganese oxides, as well as nitric acid (HNO_3) have been known to work as well as various similar forms of copper salts. Of the reactions available, the one employed in this lab is the least toxic.

Ammonium nitrate is used in this reaction as a co-oxidant. Why? It seems a bit redundant, right? Why not just add a full equivalent of copper(II) acetate? A quick search on Sigma Aldrich's website (one place from which to order chemicals) shows that copper(II) acetate is $156.00 for 100 g, whereas ammonium nitrate is $58.00 for 500 g.

After Cu_2^+ accepts an electron from benzoin, it becomes Cu_1^+. Under acidic conditions, nitrate can transfer an electron back to copper to regenerate Cu2+ and produce ammonium nitrite, which rapidly breaks down into nitrogen gas and water. What could be better by-products than nitrogen (>75% of the air in the atmosphere) and water?

Procedure

Preheat a hot plate and aluminum block to 150 °C. Add 200 mg (1.0 equiv) of benzoin to a clean 5.0-mL conical vial, equipped with spin vane, then add 0.15 M copper acetate acetic acid solution (0.12 equiv) and ammonium nitrate (1.5 equiv). Attach a reflux condenser and place the conical vial on the preheated aluminum block and reflux the reaction for 45 minutes. Take a TLC using CH_2Cl_2 as the mobile phase. If the reaction is not done, let it reflux for 15 more minutes and retake the TLC. Be sure to record your TLC results in your lab notebook.

Workup

Remove the reaction mixture from the heat source and allow it to cool to room temperature. Remove the reflux condenser and add ice-cold water (2.0 mL) and chill in an ice bath for 10 minutes. Collect the yellow crystals by vacuum filtration with a Büchner funnel by first wetting the filter paper with water. Wash with H2O (2̃ mL). After drawing air through the crystals for several minutes, further drying can be accomplished by blotting the solid dry with filter paper. The filtrate should be neutralized with 1 M $NaHCO_3$ until slightly basic and disposed of in the inorganic waste.

Purification

Recrystallize the benzil from hot ethanol (7 mL/g is about what it takes to get the benzil to dissolve completely). Place it in an ice bath to crystallize for about 5 minutes. Filter and wash with a very minimal amount of ice-cold ethanol. Test for the presence of unoxidized benzoin: Dissolve about 0.5 mg of the purified benzil in 0.5 mL of 95% ethanol 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 minutes, it indicates that the sample is free from benzoin. For comparison, acquire a small amount of benzoin from your TA and perform the same test to observe the color that develops. Note that if the contents are capped and shaken vigorously, the color momentarily disappears; when the solution is then left to stand, the color reappears.

Results

Calculate the percentage yield, and take a melting point and an IR. Compare your experi- mental data (IR and melting point) to the literature data for benzil. Obtain and interpret a ^{1}H-NMR and ^{1}3C-NMR spectrum for the product only (you already analyzed benzoin in the previous lab) from the course website. Include the labeled spectra in your notebook. Do not submit your product to the TA because you will use 100 mg of benzoin in a future experiment, but you should report the mass, m.p., and IR. If you failed to recover 100 mg, submit a request to your TA for additional starting material so that you will have 100 mg at the beginning of the next experiment.

Discussion

In addition to the lab report guidelines given, discuss the following questions in your lab report:

1. Calculate the percentage recovery from the recrystallization. If you took good notes in your observations, this question won't be a problem.
2. This reaction is quite complex. Write a legitimate mechanism for the reaction (just consider the copper and the benzoin; don't worry about how it gets re-oxidized with ammonium nitrate). To get you started, the first step is a single electron transfer from the carbonyl to Cu_2^+ to form a carbocation, a radical on oxygen, and Cu_1^+. The second step is removal of hydrogen by an acetate ion to form a carbon–carbon double bond. Show the whole sequence to benzil.
3. Benzoin can be reduced with reagents such as $NaBH_4$. What stereochemical products are possible if you are starting with a enantiomerically pure sample of benzoin? What if you are starting with a racemic mixture??
4. In the experimental procedure, it was mentioned that when benzoin is added to sodium hydroxide, a purple solution develops. What is the structure of this purple product? Why might it be so highly colored?

Waste Disposal

Any residual CH_2Cl_2 is put in a halogenated organic waste container. Nonhalogenated organic waste is put into the nonhalogenated waste container.