Exp’t 10

Synthesis of Dibenzalacetone by Aldol Condensation

from K. L. Williamson, Macroscale and Microscale Organic Experiments, 2nd Ed. 1994, Houghton Mifflin, Boston. p 417; revised 9/22/03

PreLab Exercise

Calculate the volumes of acetone and benzaldehyde needed for this reaction, taking into account the densities of the liquid.

Introduction

![Chemical structure of benzaldehyde and acetone reacting to form dibenzalacetone](image)

Dibenzalacetone (1,5-diphenyl-1,4-pentadien-3-one)

MP 110-111 °C, $\lambda_{\text{max}}$ 320 nm, $\epsilon$ 34,300

The reaction of an aldehyde with a ketone employing sodium hydroxide as the base is an example of a mixed aldol condensation reaction, the Claisen-Schmidt reaction. Dibenzalacetone is readily prepared by condensation of acetone with two equivalents of benzaldehyde. The aldehyde carbonyl is more reactive than that of the ketone and therefore reacts rapidly with the anion of the ketone to give a $\alpha$-hydroxyketone, which easily undergoes base-catalyzed dehydration. Depending on the relative quantities of the reactants, the reaction can give either mono- or dibenzalacetone.

Dibenzalacetone is a fairly innocuous substance; its spectral properties indicate why it is used in sun-protection preparations. In the present experiment, sufficient ethanol is present as solvent to readily dissolve the starting material, benzaldehyde, and also the intermediate, benzalacetone. The benzalacetone, once formed, can then easily react with another mole of benzaldehyde to give the product, dibenzalacetone.

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 (benzaldehyde), one for a cospot (starting material and the reaction mixture), and one for the reaction mixture.

Synthesis of Dibenzalacetone

Obtain a sample of fresh pure benzaldehyde prepacked in a shorty vial from the hooded shelf or the stockroom. Weigh 0.212 g (2 mmol) of benzaldehyde directly into a 10 x 100 mm reaction tube. Add 1.5 mL 95% ethanol and 2 mL of 3M sodium hydroxide solution. Using a glass 1-mL calibrated pipet, a 3-mL plastic syringe, and a syringe-pipet connector, add the volume of acetone you calculated as equivalent to 0.058g (1 mmol) of acetone. Cap the tube immediately with a septum, and shake the mixture vigorously. Continue to shake the tube from time to time for the next 30 minutes. The benzaldehyde, initially insoluble, goes into solution, and a water-clear, pale yellow solution results. After a few minutes, it suddenly becomes cloudy, and a yellow precipitate of the product forms. Continue to shake the tube from time to time for the next 30 min. If the product fails to crystallize, open the tube and scratch the inside of the tube with a
glass rod.

**Isolation and Purification**

Remove the liquid from the tube using a Pasteur pipette by squeezing the bulb of the pipette, pressing the tip against the bottom of the tube, and bringing the liquid into the pipette, leaving the crystals in the tube (pipet filtration technique). Add 3 mL of water, cap, and shake the tube vigorously. Remove the water as before and wash the crystals twice more with 3-mL portions of water.

After the final washing, add 3 mL of water to the tube and collect the crystals on a Hirsch funnel using vacuum filtration. Use a few mLs of water to wash all the crystals into Hirsch funnel. Squeeze the product between sheets of filter paper to dry it, and then recrystallize the crude dibenzalacetone from 70:30 ethanol water. Insert a wooden boiling stick to promote even boiling. Remove the boiling solution from the hot sand bath, and place it in a beaker of glass wool to insulate it so it cools slowly to room temperature. Should the product separate as an oil, try to obtain a seed crystal, heat the solution to dissolve the oil, and add the seed crystal as the solution cools. If it continues to oil out, add a bit more ethanol. Collect the product on the Hirsch funnel or by removing the solvent with a pipette after cooling the tube for several minutes in ice. Wash the crystals once with about 0.5 mL of ice-cold 70% ethanol while the tube is in ice. Dry the product under vacuum by attaching the tube to an aspirator for a few minutes. Determine the weight of the dibenzalacetone and its melting point, and calculate the percentage yield. In a typical experiment, the yield would be 0.10 g, melting point 10.5-112°C.

**Analyses**

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

**Cleaning Up**

Dilute the filtrate from the reaction mixture with water, and neutralize it with dilute hydrochloric acid before flushing down the drain. The ethanol filtrate from the crystallization should be placed in the organic solvents container.

In the last step of the aldol condensation, loss of water from the b-hydroxyketone can form molecules in which the alkene hydrogen atoms are either cis or trans to each other. The name dibenzalacetone does not completely characterize the molecules made in this experiment. There are 3 isomeric dibenzalacetones, one melting at 100-110 °C, \( \lambda_{\text{max}} \) 330 nm, \( \epsilon \) 34,300; another melting at 60 °C, \( \lambda_{\text{max}} \) 295 nm, \( \epsilon \) 20,000; and a third, a liquid with \( \lambda_{\text{max}} \) 287 nm, \( \epsilon \) 11,000.

Both the melting points and the UV spectral data give some hints regarding the structures of these molecules. The first one is very symmetrical and can pack well into a crystal lattice. The long wavelength of the ultraviolet light absorption maximum and the high value of the molar absorbance indicate a long, planar conjugated system. The other two molecules are increasingly less able to pack nicely into a crystal lattice or to have a planar conjugated system. In your Final Report, include the structures of the three geometric isomers of dibenzalacetone (cis,cis; cis,trans; trans,trans), and assign each one to the three molecules described in the previous paragraph.

**Post Lab Questions**

1. Why is the C=O peak showing up at lower wavenumbers (1639 cm\(^{-1}\)) than standard C=O frequency (1715 cm\(^{-1}\))?
2. How would you change the procedures in this experiment if you wished to synthesize benzalacetone, $\text{C}_6\text{H}_5\text{CH}=\text{CHCOCH}_3$? Benzalacetophenone, $\text{C}_6\text{H}_5\text{CH}=\text{CHCOC}_6\text{H}_5$?

3. Write the detailed mechanism for the formation of dibenzalacetone from benzalacetone and benzoaldehyde.