Condensation: Tetraphenylcyclopentadienone

from K. L. Williamson, Macroscale and Microscale Organic Experiments, 2nd Ed. 1994, Houghton Mifflin, Boston. p461; revised 3/26/02

Introduction

Cyclopentadienone is an elusive compound that has been sought for many years but with little success. Molecular orbital calculations predict that it should be highly reactive, and so it is; it exists only as the dimer. The tetraphenyl derivative of this compound is to be synthesized in this experiment. This derivative is stable and reacts readily with dienophiles. It is used not only for the synthesis of highly aromatic, highly arylated compounds but also for examination of the mechanism of the Diels-Alder reaction itself. Tetraphenylcyclopentadienone has been carefully studied by means of molecular orbital methods in attempts to understand its unusual reactivity, color, and dipole moment.

The literature procedure for condensation of benzil, with 1,3-diphenylacetone in ethanol with potassium hydroxide as basic catalyst, suffers from the low boiling point of the alcohol and the limited solubility of both potassium hydroxide and the reaction product in this solvent. Triethylene glycol is a better solvent and permits operation at a higher temperature. In the procedure that follows, the glycol is used with benzyltrimethylammonium hydroxide, a strong base readily soluble in organic solvents, which serves as catalyst.

Prelab Exercise

Write a mechanism for the formation of tetraphenylcyclopentadienone from benzil and 1,3-diphenylacetone. To which general class of reactions does this condensation belong?

Synthesis of Tetraphenylcyclopentadienone

• Into a 10 x 100 mm reaction tube place 42 mg of pure benzil (free of benzoin; perform test at the end of handout), 42 mg of 1,3-diphenylacetone, and 0.4 mL of triethylene glycol, using the solvent to wash the walls of the tube. Clamp the tube over a hot sand bath, insert a thermometer, and heat the solution to 120°C and/or until the benzil is dissolved. Remove the tube from the heat, and then, using a 1 mL syringe, add to the solution 0.20 mL of a 40% solution of benzyltrimethylammonium hydroxide in methanol (Triton B) when the temperature of the solution reaches exactly 100 °C. Stir to mix. Crystallization usually starts in 10 to 20 s.

Isolation and Purification

Let the mixture cool to near room temperature, and then cool it in cold water. Add 0.5 mL of methanol, cool the tube in ice, and collect the product. If the crystals are large enough, collection can be done by inserting a Pasteur pipette into the tube and removing the solvent between the tip of the pipette and the bottom of the tube (pipet filtration). If the crystals are small collect them the Hirsch funnel. In any case, wash the crystals with ice-cold methanol until the washings are purple-pink, not brown. The yield of deep purple crystals is about 60 mg. If either the crystals are not well formed or the melting point is low, place the material in a reaction tube, add 0.6
mL of triethylene glycol, stir with a thermometer (You will need to use a mercury thermometer from one of the melting point apparati to do this. Please remember to put it back!), and raise the temperature to 220 °C to bring the solid into solution. Let it stand for crystallization (if initially pure material is recrystallized, the recovery is about 90%).

**Analysis:** Analyze sample according to Assignment sheet and instructions on Sample Preparation in Lab Guide.

**Cleaning Up:** Since the filtrate and washings from the reaction contain Triton B, they should be placed in the hazardous waste container. Crystallization solvent should be diluted with water and flushed down the drain.

**Test for the Presence of Unoxidized Benzoin**

Dissolve about 0.5 mg of crude or 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 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.

**Final Report**

1. Draw the structure of the Diels-Alder dimer of cyclopentadienone. Why doesn't tetraphenylcyclopentadienone undergo dimerization?
2. What is the function of the benzyltrimethylammonium hydroxide? Why is it better to use in this experiment than aqueous NaOH?
3. Why is cyclopentadienone so reactive? Hint: Compare these two carbo ions in terms of aromaticity.

![Diagram of Diels-Alder reaction](image)
# Synthetic Experiment PreLab Grading Sheet

Name(s): ____________________________

TA: ________________________________

Date: ______________________________

PreLab For Exp’t # 11

Condensation: Tetraphenylcyclopentadienone

<table>
<thead>
<tr>
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<th>Possible</th>
<th>Missed</th>
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<tbody>
<tr>
<td>Date, Name, Desk #, Experiment # &amp; Title (abbreviated after 1st pg), Section &amp; TA Name</td>
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<tr>
<td>Summary</td>
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<td>Goals</td>
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<tr>
<td>Reactions, structures, conditions, diagrams</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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<tr>
<td>- Mechanism of formation of tetraphenylcyclopentadienone (12)</td>
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<tr>
<td>- To what general class of condensation reactions does this condensation belong (4)</td>
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<tr>
<td>Chromatographic Behavior Comparison</td>
<td>12</td>
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<tr>
<td>Spectral Features Comparison</td>
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<tr>
<td>Work-up - Explanation of the product isolation and purification process</td>
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<td>TOTAL FOR PRELAB</td>
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Date Handed in: ______________________

General Comments:  

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

Name: _____________________________

TA: ________________________________

Date: ______________________________

### Final Report For Exp't # 11

Condensation: Tetraphenylcyclopentadienone

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<tr>
<th>Name, Date, Experiment Title (abbreviated after 1st page) and every page numbered</th>
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<tr>
<th>OBSERVATIONS and DATA - Overall organization, readability, completeness</th>
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<tr>
<td>Data: Weighing data, molecular weights, moles, density, volumes, Rf’s.</td>
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<td>Product analysis conditions i.e. weight of sample and KBr for IR; solvent and field strength for NMR; ionization mode for MS; solvent and wavelength range for UV/Vis,</td>
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<td>Yield: Show % yield calculations with limiting reagent clearly stated.</td>
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<td>Purity: Record melting points, color, or other indicators of purity.</td>
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<tr>
<th>RESULTS AND DISCUSSION - Overall organization, readability, completeness</th>
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<td>Product Analysis Data: Quality and Interpretation – Structure(s) drawn on each Spectrum or Chromatogram</td>
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<td>Interpret all major MS or IR peaks. Discuss all UV/Vis ( \lambda_{\text{max}} ) in terms of conjugation. Explain how spectra confirm product identity</td>
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**POSTLAB QUESTIONS**

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