Experiment #16: Solid-Phase Photochemistry

Pre-Lab Preparation

1. Study the technique section in your lab manual regarding melting point determination.

2. Carry out pre-lab preparations as described in Chapter 11, section 11.6A, or as called for by your instructor.

Experimental Procedure

SAFETY PRECAUTIONS: Cinnamic acid presents no unusual safety hazards, but should be handled with care. Tetrahydrofuran and toluene are volatile and flammable; avoid open flames and undue contact or inhalation.

This experiment is very quick to set up and to work up, but requires several weeks of irradiation.

Reaction

1. Place 1.5 g of trans-cinnamic acid in a 125 mL Erlenmeyer flask and add approximately 2 mL of tetrahydrofuran (THF).

2. Gently heat the mixture in order to dissolve the acid. Remove the flask from the heat source and gently rotate the flask while the solution cools in order to coat the walls of the flask with crystalline cinnamic acid. If the resulting coating is very uneven, reheat and try again. Once the coating is sufficiently dry, clamp the flask upside down for 30 minutes to allow the solvent vapor to escape.

3. Stopper the flask, label it with your name, and place it, upside down, in a beaker on a window ledge (with southern exposure if possible) or, if more appropriate, under a sunlamp. After 1 week, rotate the flask to expose the opposite side.

Workup and purification

4. After the second week of irradiation, transfer the solid to a 25 x 100 mm test tube or a small Erlenmeyer flask. Add 15 mL of toluene and warm to ca. 40 °C to dissolve any remaining cinnamic acid. Isolate the insoluble solid by filtration, rinsing with 10 mL of toluene, and continue to pull air through the product until it is dry.
Characterization

5. Air dry and weigh the product, and record the percent yield and melting point. (The literature value is 286 °C).

Post-Lab Questions and Exercises

1. Describe the physical properties (color and state) of your product. Report the mass and percent of theoretical yield of the product. If your yield was low, provide a plausible reason(s) for the low yield.

2. Report the melting point range for your product.

3. Draw the structures of the six diastereomers of the truxinic acids and the five diastereomers of the truxillic acids, clearly showing the stereochemistry. Present only one enantiomer for any chiral dimers, but bear in mind that in the photodimerization, chiral dimers are obtained as racemates.

4. Calculate the atom economy for the reaction.

5. Perform an economic analysis for the preparation of your product.

Experiment Development Notes

This experiment is based on reports in the primary literature and on an elegant experiment presented by Bell, et al. [70]. The latter presents this reaction as the first of a multi-step sequence of investigations designed to allow the determination of the structure of the photodimer by a combination of chemical and spectroscopic techniques. While the additional reaction chemistry required to deduce the structure does not illustrate any new green principles (and for that reason, is not included in this preliminary edition’s presentation of the experiment), the sequence reported by Bell, et al. is very appealing.