Experiment #15: Carbonyl Chemistry: Thiamine-Mediated Benzoin Condensation of Furfural

Pre-Lab Preparation

1. Study the technique section in your lab manual regarding heating reactions at reflux, recrystallization (including use of activated charcoal for decolorizing), and 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: Furfural (2-furaldehyde) is considered toxic. It is not extraordinarily volatile, but should be handled with care. Some byproducts may have objectionable odors, and working in the fume hood is advised. Sodium hydroxide solutions can cause severe skin and eye damage. Handle with extreme care, and avoid contact. Other reagents and intermediate products present no unusual safety hazards, but should be handled with care.

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67. R. Breslow, *J. Am. Chem. Soc.* **1958**, *80*, 3719.

The reaction is too slow to allow its completion in a single laboratory session. During the first session, you will measure out reagents and set up the reaction. In the second laboratory session, ideally one week later, you will isolate, purify, and characterize the product.

Reaction

1. In a 25 mL round-bottom flask equipped with a magnetic stirring bar, dissolve, with stirring, 0.30 g of thiamine hydrochloride in a mixture of 0.45 mL of water and 3.0 mL of 95% ethanol. At this point, the reaction mixture should be clear and colorless.
2. Dropwise, add 0.90 mL of a solution of 8.0 g of NaOH in 100 mL of water (this solution will be prepared for you). This step should resemble a titration – each drop of NaOH should produce a bright yellow color, which disappears with stirring. When all of the NaOH solution has been added, there should still be a pale yellow color remaining. If the reaction mixture is colorless, you must add more NaOH solution, or the reaction may not work.
3. Add approximately 0.73 mL of furfural, mix thoroughly, seal with a septum and store in your drawer until the next lab period.

Workup and purification

4. Cool the reaction mixture in an ice bath, adding several mL of water to the cooled mixture to drive the remainder of the product from solution, then isolate the crude solid product by filtration. Pull air through the solid on the filter to dry it, then record the mass of crude product obtained.
5. Recrystallize the crude product from 95% ethanol.

Characterization

6. Record the yield and melting point range of the purified material.
7. Obtain an infrared spectrum of your recrystallized furoin.

Post-Lab Questions and Exercises

1. Describe the physical properties (color and state) of your crude furoin and your recrystallized furoin. Report the mass and percent of theoretical yield of both the crude product and the purified

68. C. K. Lee, M. S. Kim, J. S. Gong, and I.-S. H. Lee, *J. Heterocyclic Chem.* **1992**, *29*, 149.

material, as well as the percent recovery in the recrystallization step. If your yield was low, provide a plausible reason(s) for the low yield.

2. Report the melting point range for your recrystallized furoin and the reported melting point of furoin.
3. Attach your infrared spectrum of furoin to your report. Identify the significant features of the spectrum, suggesting when possible vibrational assignments for the observed absorption bands.
4. Calculate the atom economy for the reaction.
5. Perform an economic analysis for the preparation of your product.

Experiment Development Notes

This procedure was adapted from the original reports by Breslow [67], Lee, *et al.* [68], and Hanson [69]. In contrast to analogous procedures for the preparation of benzoin, which we have found to be erratically reproducible, the furoin condensation generally works well. Furoin may be readily oxidized to the corresponding α-diketone, furil, using a variety of mild oxidizing agents, an example of which is hoped to be included in the next edition of this text. This could provide a convenient opportunity for independent student investigation.

69. R. W. Hanson, *J. Chem. Educ.* **1993**, *70*, 257.