Experiment #18: The Friedel-Crafts Reaction: Acetylation of Ferrocene

Pre-Lab Preparation

1. Study the technique sections in your lab manual regarding thin-layer chromatography, recrystallization (including hot filtration and the use of decolorizing charcoal), 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: Phosphoric acid and acetic anhydride are corrosive, and acetic anhydride is also a lachrymator; avoid contact or undue exposure to vapors.

Reaction

1. Place 1.5 g of ferrocene in a 20 mL round-bottom flask containing a magnetic stir bar. If a steam bath is not available, prepare a hot water bath, heating the water to nearly the boiling point while preparing the following reaction mixture.

2. In a fume hood, add 5.0 mL of acetic anhydride and 1.0 mL of 85% phosphoric acid to the flask. The reaction mixture should heat up and darken in color. Swirl the flask, heating occasionally in a hot water bath, if necessary, until all the ferrocene dissolves.

3. Attach a reflux condenser equipped with a calcium chloride drying tube, then heat the reaction mixture, with stirring, on a steam bath or in the hot water bath prepared in step 1. Heat for 19 minutes, during which time a purple color may develop.

Workup and purification

4. Pour the reaction mixture onto 25 g (ca. 60 mL) of ice in a 200 mL beaker, rinsing the flask with two 5 mL portions of ice water. (A black residue may remain in the flask.) Stir the orange-brown mixture with a glass rod for a few minutes. Any insoluble black material present will be removed in the following steps.
5. Add 37.5 mL of 3M aqueous NaOH solution, then carefully add solid sodium bicarbonate in small portions until the remaining acid has been neutralized (about 7 - 8 grams). (Use great care to avoid excessive foaming during this bicarbonate addition. This step can be done with magnetic stirring, but make sure to use a stirring plate that is not hot.) Stir well and crush any lumps, affording a dark-brown suspension.

6. Allow the mixture to stand for 20 minutes, then collect the crude product by vacuum filtration and continue to pull air through the product for a few minutes to dry it. Finish the drying process by pressing the solid product between two sheets of filter paper or paper towels. Save a bit of this crude product for TLC analysis.

7. Transfer the solid and a stir bar to a small Erlenmeyer flask and add 20 mL of hexanes. Boil for 5 minutes with stirring, then decant the dark-orange solution into another Erlenmeyer flask, leaving behind a black gummy substance.

8. To the hot solution, add a spartula-full of decolorizing carbon. (Use of too much carbon will reduce your yield.) Heat with swirling, then perform a hot filtration to remove the decolorizing carbon.

9. Set the flask aside to cool slowly. Red-brown needles of acetylferrocene should begin to form. Once the flask has reached room temperature, cool it in ice. Collect the crystalline product by vacuum filtration, washing with a small quantity of cold hexanes, and dry it by continuing to pull air through it for a few minutes.

**Characterization**

10. Record the yield and melting point range of your recrystallized acetylferrocene. (The melting point has been reported as either 82 - 83 or 84 - 85 °C.)

11. Analyze your crude and recrystallized products by TLC. Separately dissolve very small amounts of pure ferrocene, the crude product, and the recrystallized acetylferrocene in a few drops of toluene. Spot the solutions on silica gel plates and develop with 30:1 toluene/absolute ethanol. Visualization is simple — each of the compounds is brightly colored.

**Post-Lab Questions and Exercises**

1. Describe the physical properties (color and state) of your crude product.
2. Report the color and melting point range of your recrystallized product. Report the mass and percent of theoretical yield of the recrystallized product.

3. Report the results of your TLC analyses, including $R_f$ values and discussing any differences between the crude and recrystallized products.

4. Calculate the atom economy for the reaction.

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

Experiment Development Notes

This experiment represents an adaptation of a procedure reported by Fieser and Williamson [73]. The contrast of the reaction conditions called for in this experiment with those of more conventional Friedel-Crafts acylation reactions is striking, and if conditions allow, it may be instructive to allow students to explore this contrast experimentally. In addition to the differences in solvents and reagents, students carrying out such explorations should note that other experimental procedures for the acylation of ferrocene, using more vigorous acylation conditions, tend to afford mixtures of mono- and diacylated products.