Friedel-Crafts Acylation of Ferrocene and Column Chromatography of the Product

From the “Schedule of Experiments”: Read Chapt 32. Do Microscale Procedure, p. 440. Purify the product by column chromatography as follows: Column Chromatography. Read Chapt 9, pp. 185-190, follow procedures on pp. 200, 201 and p. 440, "Column Chromatography" and "Elution". (Basically, to purify the acetylferrocene do Exp 4, p. 200, but use the acetylferrocene that you prepared, not a 50:50 mixture as described in Exp 4.) Analyze final product by IR as a mull or directly with the ATR device.

Safety: treat all lab chemicals as if they are toxic. Most are. Keep them off your skin.

Reminder: this note is just to cover changes and suggestions. It is not a stand-alone experimental procedure. Base the prelab outline on the text and include these changes and suggestions.

Acetylferrocene (microscale). Chapter 32. Be sure to keep all reagents and equipment dry until water is purposely added at the end of the reaction. Overheating can cause decomposition and formation of by-products, so heat gently and for no longer than the prescribed time. When neutralizing with NaOH, mix the solution thoroughly after each addition before testing the acidity. Excess base can react with the prouct. After squeezing out as much water as possible with clean dry filter paper, save a small amount for a MP (taken only after it has dried thoroughly) and TLC and purify the remainder by column chromatography (as described in Chapt 9 and above). Do not leave the product in an open container for longer than needed – it too will sublime.

Waste Disposal. Place the neutralized filtrate into the container labeled as such. When you are finished with your product, place it into the Solid Waste container.

Column Chromatography – See page 196 – 197 (use the Slurry Packing Method)

Packing Your Column: See figure 9.2 on page 188 for a final picture of what the column should look like. First, place a small amount of cotton (not glass wool) into column and press into bottom neck with stopcock closed. Add a small amount of sand. This is used to keep the bottom if adsorbent level. Now, use slurry method on pp. 189.

To add your sample follow "Adding the Sample" on page 189. Use a 10 mL Erlenmeyer in which to dissolve your sample. Be careful to NOT overheat the sample as it will decompose. After adding the adsorbent to the dichloromethane solution, you need to carefully evaporate the solvent without overheating. Do this by carefully rolling the flask containing the damp sample over the surface of the sand, avoiding any bumping of solvent. Bumping indicates overheating which may lead to decomposition. If your sample turns dark, decomposition has happened. Note that dichloromethane boils at a very low temperature and does not need much heat to evaporate.

Isolate unreacted ferrocene and acetylferrocene as described. There may be a band of diacetylferrocene remaining on the column. How might you go about eluting this byproduct? If the band is present, try eluting it. Analyze the crude reaction product from the acetylation and the isolated chromatographed product(s) along with the unreacted ferrocene by TLC. Check the MP of crude and purified product and take the IR spectrum of pure material as a mull (see pp. 232, 233) or directly with the ATR device.

Waste Disposal. Place solvents used for the chromatography into the Nonhalogenated Liquid Waste container. Place leftover alumina into the container labeled as such. When you are finished with your product, place it into the Solid Waste container.

Important for a successful reaction next week!! In preparation for the Grignard experiment, Week 3, before leaving lab during week 2, you must thoroughly clean the glassware for the Grignard experiment. You will receive specific instructions on the day of the lab.

Postlab Questions.

1.) Using structural formulas, show the mechanism of formation of the electrophilic intermediate in the acylation reaction.

2.) If excess acetic anhydride is used and the reaction mixture heated, a second acetyl group will add to the acetylferrocene. Draw the structure of this diacetylferrocene and explain the regioselectivity.

3.) Draw the structure of the monosubstitution product that would result from reaction of ferrocene with propanoyl chloride.

4.) For a mixture of three compounds, each having different polarities, devise a strategy for separating the three by column chromatography. You have only hexane and ether available as elution solvents.