Week 2. Friedel-Crafts Acylation of Ferrocene and Column Chromatography of the Product (rev 2/12)

(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.

CAUTION: treat all lab chemicals as if they are toxic. Most are. Keep them off of 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 product. 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.

Prepare your column so it is about 1/3 full of adsorbant. More than this will cause the elution to be unnecessarily slow. This is ok for this separation. For separations of mixtures having components of similar polarities, more adsorbant would be needed.

See p. 189, "Adding the Sample": use a 10 mL Erlenmeyer, not a vial. Be careful to NOT overheat the sample. It will decompose. After adding the dichloromethane solution to the adsorbant, ypu 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, as indicated by darkening of the sample. Note that dichloromethane boils at a very low temperature and does not need much heat to evaporate.

When turning the plastic valve on the microscale chromatography column, use two hands - one to hold the valve and the other to turn it open and closed. Some valves are very tight and require excessive pressure to open and close. Check yours beforehand and if it is too tight to turn easily, exchange it for another. Be careful to never allow solvent to run below the level of the top of the column. This will adversely affect the separation.

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.

**** 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.