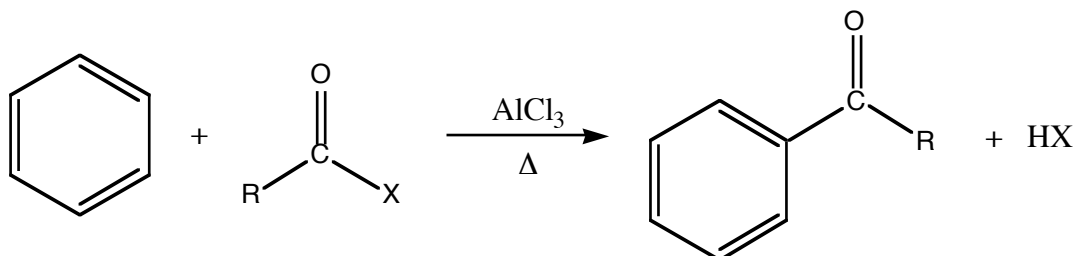
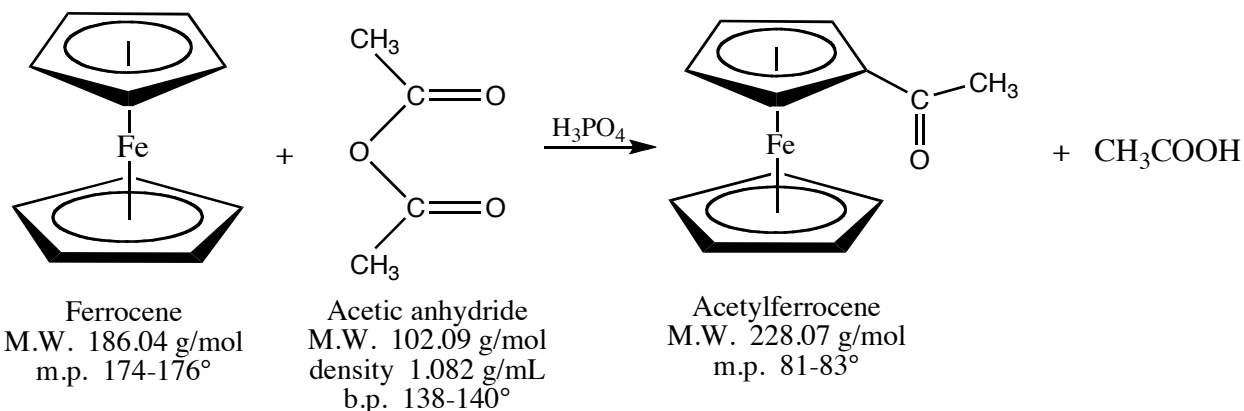


Experiment 14: The Friedel-Crafts Acylation of Ferrocene

A Friedel-Crafts acylation is an electrophilic aromatic substitution reaction that introduces an acyl group onto an aromatic ring. The electrophile is an acyl cation that is often coupled to a Lewis acid catalyst, such as aluminum chloride. In order for the reaction to take place, the aromatic ring system must be very electron rich and thus cannot contain any electron withdrawing groups.



Ferrocene was discovered by accident in 1951 and is an example of the now well-known metallocene or “sandwich” compounds. The highly electron rich cyclopentadienyl rings in ferrocene are aromatic and undergo many of the same reactions as benzene. In fact, most metallocenes are more reactive toward electrophilic reagents than is benzene, which indicates that the electrons are more readily available. Thus, while the Friedel-Crafts acylation of benzene requires aluminum chloride as a catalyst, ferrocene can be acylated by acetic anhydride under milder conditions using phosphoric acid as the catalyst.



In addition, the second ring may also be acetylated to give 1,1'-diacetylferrocene, $\text{Fe}(\text{C}_5\text{H}_4\text{COCH}_3)_2$. The highly colored acyl derivatives are easily separated by thin layer chromatography (TLC). You will use TLC not only to analyze the product(s) but also to follow the course of the reaction. Review Chapter 18, pp 255-269, in *LTOC*.

Outline the steps of the following procedure:

The glassware used for the reaction must be very dry. Clean a 10x100 mm reaction tube from the microscale kit, then dry it in an oven briefly before beginning the experiment. Insert a short length of Teflon tubing (1-2 inches) into a rubber septum that fits on a 10x100 mm reaction tube.

Begin heating a beaker of water on a hot plate.

Acetic anhydride is corrosive and a lachrymator (tear gas). Its fumes are highly irritating, and it can react violently with water. Wear gloves and dispense the liquid under a hood; avoid contact, do not breathe its vapors and keep it away from water.

Phosphoric acid can cause serious burns, particularly to the eyes; do not allow it to contact your eyes, skin or clothing.

Place 0.28 g of ferrocene in the dry reaction tube. Using the markings on the reaction tube, add 1.0 mL of acetic anhydride to the ferrocene. Mix the contents of the tube thoroughly to dissolve as much of the solid as possible. Obtain a *narrow* silica gel TLC plate and spot this initial reaction mixture on the left-hand side of the plate. Next, add 0.3 mL of 85% phosphoric acid, H_3PO_4 , using a pipet plus syringe assembly to measure the amount. Place the septum containing the piece of Teflon tubing on the reaction tube, and shake the bottom of the tube back and forth to mix the contents. If the ferrocene does not dissolve, use a small glass rod to break up any clumps.

Clamp the reaction tube such that just the bottom of the tube is immersed in the boiling water bath, and agitate the mixture to finish dissolving the ferrocene. Heat for 5 minutes after all the ferrocene has dissolved. Remove the rubber septum and spot the reaction mixture on the right-hand side of the TLC plate. When this plate is developed, it will allow you to compare the status of the mixture at this stage of the reaction with that of the initial reaction mixture spotted earlier. Replace the rubber septum *immediately* after spotting the TLC plate (it is important that the reaction mixture not be exposed to the atmosphere for very long). Place the reaction tube back in the boiling water and continue to heat for *only* another 5 minutes. If the reaction is heated too long, decomposition of the products and reactants will occur. Place the tube in ice and cool to at least room temperature.

Place 1.5 mL of ice water in a 25 mL Erlenmeyer flask. Pour the reaction mixture from the reaction tube into the flask. Add 1.5 mL of 3 M NaOH to the *residue* in the *reaction tube*, and stir vigorously with a stirring rod. Add this mixture of solids and liquid to the contents of the 25 mL Erlenmeyer flask. Check the pH of the reaction mixture with Alkacid paper. If the pH is not neutral, add 3 M aqueous sodium hydroxide solution dropwise with mixing until neutralization has occurred. Avoid adding an excess of base (dilute HCl solution will be available, if you overshoot the neutralization point). Collect the solid product by vacuum filtration on a Hirsch funnel, wash it thoroughly with water and press it dry between sheets of filter paper. Save a small amount of this crude product for TLC.

Clean the reaction tube with acetone, and pour the mixture into the **Byproducts** jar labeled Ferrocene Residue.

You will purify your product by recrystallizing it from hexane. Place the crude product in a 25 mL Erlenmeyer flask. Add 5 mL of **hot** hexane (**flammable!**). Heat on a steam bath, (not a hot plate!) and swirl to dissolve the solid. Add more hot hexane if necessary to completely dissolve the product, but some insoluble material is likely to be present. Add a small amount of decolorizing charcoal (enough to cover the rounded end of a spatula) and swirl.

Filter the mixture through a filter pipet. Be sure the plug of cotton is packed *tightly* into the constriction of the pipet. Holding the filter pipet over a 25 mL Erlenmeyer flask, transfer the *hot* mixture with the decolorizing charcoal into the filtering pipet such that it passes through the cotton and into the flask. To speed up the filtration, it is permissible to place a pipet bulb on the filter pipet and gently squeeze the solution through the cotton. Place the filtered solution on ice until crystals appear. If crystals fail to appear, concentrate the solution by evaporating some of the hexane using a steam bath. Collect the crystals by vacuum filtration on a Hirsch funnel and

wash with small portions (less than 1 mL) of **ice cold** hexane. Obtain the mass and melting point of your product next week.

Dissolve very small samples of the crude reaction product and the recrystallized product each in a few drops of toluene. A solution of pure ferrocene dissolved in toluene will be provided. Spot the three solutions on a *wide* silica gel plate. Develop this plate and the one used to monitor the progress of the reaction with a 30:1 toluene-absolute ethanol mixture. Visualize the spots under UV light. **Warning! Do not look directly into the UV lamp!** Make the necessary measurements to calculate the R_f 's, and sketch the TLC plates in your notebook.

Name _____ Date _____

T. A. _____ Lab period _____

Results and Calculations (to be handed in two days after the next lab period)

Calculate the percent yield of acetylferrocene using the mass of purified product.

Melting range for acetylferrocene _____

Calculate the R_f values for all spots seen on the thin layer chromatograms. Indicate the color of the spot that corresponds to each R_f .

Interpret the thin-layer chromatograms. Comment on the progress of the reaction after addition of the phosphoric acid catalyst and 5 minutes heating. Do you detect unreacted ferrocene in the crude product or a spot that might be attributed to diacetylferrocene?