

**Title: Synthesis of Acetylferrocene**

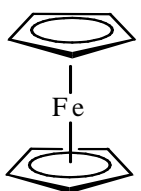
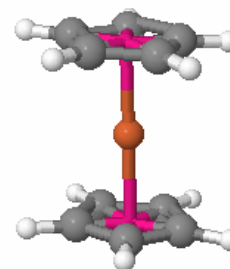
*New tricks:* C1, E7, F4, F8

*New principles:* gravity column chromatography, thin layer chromatography

*Instrument Operation:* Fisher-Johns melting point apparatus  
Midac FT-IR spectrometer, FT-NMR

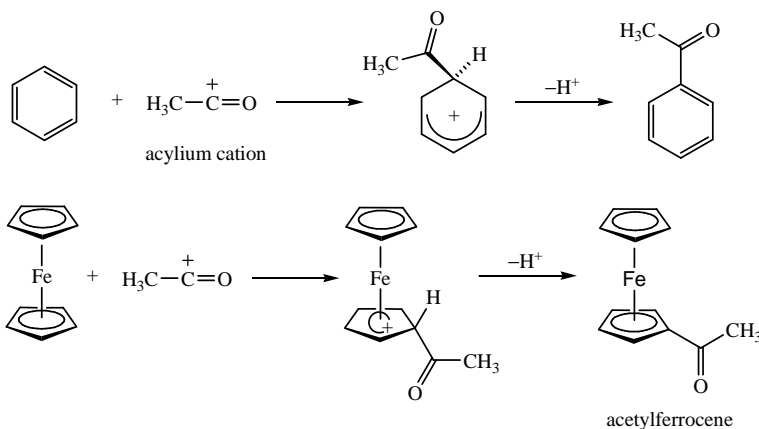
*Introduction:*

The structure of the organometallic compound ferrocene,  $\text{Fe}(\text{C}_5\text{H}_5)_2$ , is shown on the right. Two planar five-membered rings sandwich an iron atom between them. Each ring in ferrocene has six delocalized pi electrons and a formal  $-1$  charge; the iron atom has a formal  $+2$  charge. With a planar structure and six delocalized pi electrons in each ring, ferrocene is *aromatic* and has many properties similar to benzene and its derivatives. Thus, ferrocene is unreactive to many of the reagents that commonly react with alkenes. A special reaction that aromatic compounds undergo, and which you will carry out in this

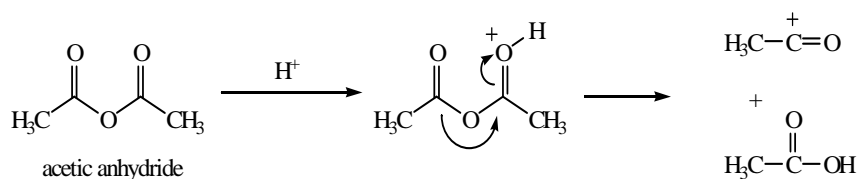


ferrocene

experiment, is the Friedel-Crafts acylation reaction. This reaction, involving the *acylium cation*, is outlined below for both benzene and ferrocene.



The reaction involves the addition of the acylium cation to one of the carbon atoms of benzene or ferrocene followed by loss of a proton (to solvent). The acylium cation is not a stable species. It is produced from acetic anhydride as shown below.



One of the complications of the Friedel-Crafts reaction is that acylation can occur twice, once on one ring, then on the other. That's a problem, because it results in the formation of a byproduct, diacetylferrocene. In this experiment you will learn how chemists separate the desired product from left over starting material and byproducts using a technique called *column chromatography*. In addition, in this experiment you will see how chemists monitor chemical reactions using a very common technique, *thin layer chromatography*.

*Green aspects:*

Use of phosphoric acid and acetic anhydride constitutes much milder and less toxic reaction conditions than use of the usual reagents, acetyl chloride and  $\text{AlCl}_3$ . This experiment demonstrates running a reaction with no solvent as well as the use of a catalyst.

**PRE-LAB QUESTIONS:**

You should read about both column chromatography and thin layer chromatography in the Tricks of the Trade section of your lab manual prior to answering these questions.

1. Write the balanced chemical equation and calculate the atom economy for the reaction you are doing today.
2. What impurities are removed by washing the final product with water?
3. Explain the basic principles involved in thin-layer and column chromatography.
4. Which compound, ferrocene, acetylferrocene, or diacetylferrocene, will travel *fastest* on a TLC plate? Which will be slowest?
5. If, following the procedure, you isolated 0.30 g of crude product and then, after chromatography as described, you ended up with 0.10 g of pure acetylferrocene, what would your percent yield be? [HINT: the correct answer is between 28% and 33%.]

**ANALYSIS AND DISCUSSION**

1. How do you know you made acetylferrocene?
2. Explain the IR and NMR spectra as best you can. Do you see any ferrocene or diacetylferrocene in the NMR spectrum?

*Procedure:*

In a 10-mL round-bottom flask place 0.32 g of ferrocene and 1 mL of acetic anhydride. To this mixture add 5 drops of 85% phosphoric acid with stirring. Attach a water-cooled condenser and heat the reaction mixture for 20 minutes in a 90 °C water bath on a **hotplate**.

Pour the reaction mixture into a 25-mL beaker containing 4 g of crushed ice. After the ice has melted, add enough solid NaHCO<sub>3</sub> to neutralize the mixture (pH=5-6; until the CO<sub>2</sub> stops bubbling off). About 1-2 g are necessary for this neutralization. Use pH paper to determine neutrality and add about 0.25 g at a time.

**Suction filter** and wash the product with cold water until the filtrate is pale orange. Dry the product until the next laboratory prior to chromatographic separation.

Perform **thin-layer chromatography** on your product using an ethyl acetate-hexanes mixture assigned by your instructor. Be sure to *cospot* with a sample of ferrocene dissolved in hexanes.

Prepare a gravity chromatography column using 8 g of activity grade III alumina or silica gel for the solid and ethyl acetate-hexanes as the liquid phase. Chromatograph 0.25 g of your product dissolved in 1.0 mL or less of ethyl acetate, eluting with a 10% solution of ethyl acetate in hexanes.

Evaporate the solvent using a **rotary evaporator**. Check the purity of your material using thin-layer chromatography, again *cospotting* with a sample of ferrocene.

Determine the **melting point** of your acetylferrocene (mp 83-85° reported). Weigh the solid product and determine the **percentage yield for the reaction**, taking into account the fact that you only chromatographed 0.25 g of your product. Obtain and analyze **NMR (CDCl<sub>3</sub>)** and **IR** (mull) spectra.

*Acetic anhydride is corrosive and a lachrymator; handle carefully in a hood. Phosphoric acid is corrosive.*

*These mild conditions will reduce the amount of tars that are formed by heating at higher temperatures.*

*Stir well after each addition, as extra NaHCO<sub>3</sub> will contaminate the product and cannot be removed later without significant loss of the water-soluble product.*

*Ice cold water is needed to prevent the product from dissolving and being lost. Don't use too much water, as acetylferrocene is somewhat water soluble.*

*Ethyl acetate is a flammable liquid and an irritant.*

*Think about how the fact that you only used a portion of your crude product in the chromatography affects this calculation. You need to consider what fraction of the crude product was used in the chromatography.*

*Deuteriochloroform is toxic and a cancer suspect agent. Use it only in the hood.*