5. Acylation of Ferrocene

M. Jones: Ferrocene, 12.7, structure on page 572.

J.R. Mohrig, C.N. Hammond, and P.F. Schatz: Technique 15, 15.1 – 15.8, pgs 177 – 189
Technique 17, 17.1 – 17.7, pgs 190 – 226

This procedure has been adapted from the microscale procedure described in the third edition of *Macroscale and Microscale Organic Experiments* by Kenneth L. Williamson (Houghton Mifflin, Boston, 1999).

Background

Ferrocene. In this laboratory, you will acylate ferrocene (Figure 1). Ferrocene is an organometallic compound, which behaves like an aromatic compound. As one would suppose, an organometallic compound contains both a hydrocarbon and a metal. Sometimes this molecule is referred to as a "sandwich" complex because the iron is "sandwiched" between two rings.

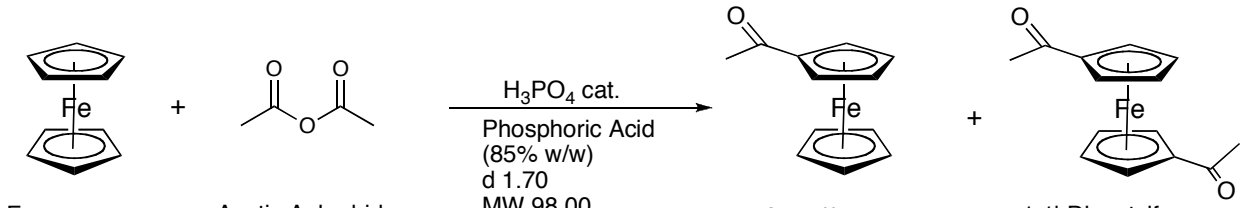

Figure 1. The overall reaction for the acylation of ferrocene.

One way to look at this molecule is to think of it as containing two cyclopentadienyl anions (formal -1 charge per each ring) and an iron atom with a +2 charge. Cyclopentadienyl anion is an aromatic compound, and its π electrons bond to the iron to yield an overall neutral complex.

The reactivity of ferrocene is similar to other aromatic compounds. Therefore, it can undergo electrophilic aromatic substitution in a very similar mechanism to that of benzene.

In this experiment, ferrocene is acylated using acetic anhydride with a catalytic amount of phosphoric acid. There are two possible products, acetylferrocene and 1,1'-diacetylferrocene, which will be identified at the end of this reaction.

Cautions:

-Take extra care when handling the acetic anhydride and phosphoric acid.
-Make sure to use a clean spatula and reaction tube. The reaction tubes should be cleaned with soap, water and a brush first, rinsed thoroughly, and dried (if needed rinse with acetone).
-Make sure to return the top to the bottles.

Experiment

Add 200 mg of ferrocene, 1.0 mL of acetic anhydride, and 0.3 mL of phosphoric acid to a large reaction tube and stir. Heat the tube to a gentle reflux using a water bath with constant stirring for 10 minutes. Note the color during the reaction. Cool the reaction tube to room temperature. Add dropwise 1.5 mL of ice water, followed by 3M NaOH solution until the resulting product mixture tests neutral (pH paper). Collect the solid via vacuum filtration. Dissolve the dark solid in a minimal amount of methylene chloride (CH_2Cl_2).

Purification. You will purify your product using column chromatography with alumina as your stationary phase. First, take your product dissolved in methylene chloride and add a small amount of alumina to it. Then, gently evaporate off the methylene chloride to a dry residue. For your column, load 3 g of alumina to the column (fitted with a frit). Then, add your product residue to the top of the column. You will first start with hexanes as your eluent followed by 50:50 hexanes:*tert*-butyl methyl ether. Note the colors of the compounds on the column. Collect all of the fractions (yellow, orange, and red) into separate, labeled, preweighed vials. Evaporate off the solvent. Weigh the vials. Take a melting point of the products. Perform a TLC of your products against your starting material using the silica plates as your stationary phase and 50:50 hexanes:*tert*-butyl methyl ether as your mobile phase.