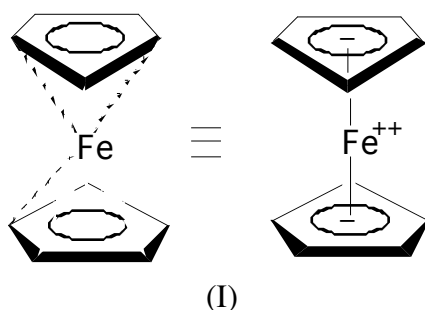


**FRIEDEL-CRAFTS ACETYLATION & COLUMN CHROMATOGRAPHY**

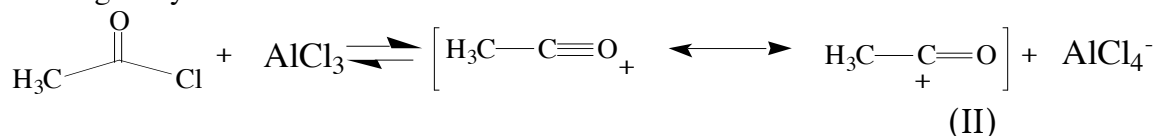
The purpose of this experiment is to acetylate ferrocene, an aromatic compound, and to purify the product mixture, which will contain both mono- and di-acetylated ferrocene. Purification will be achieved using column chromatography.

Ferrocene (I), is a compound which contains an iron (II) ion sandwiched between two flat cyclopentadienyl anions (see p. 643 of Bruice).

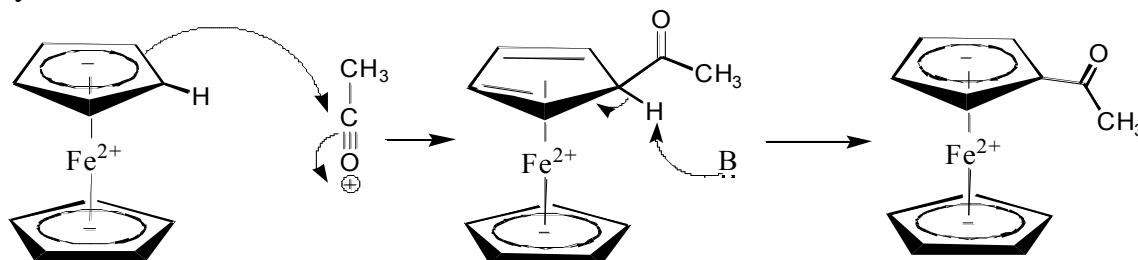


In the cyclopentadienyl anion component of ferrocene, the electron density is dispersed equally among the five carbons. These anions contain a cyclic cloud of six  $\pi$  electrons and are, therefore, aromatic. Hence ferrocene, like other aromatic systems, will undergo electrophilic aromatic substitutions such as Friedel-Crafts.

Acetylation will be carried out by the acylium ion (II), which can be generated by reacting acetyl chloride with aluminum chloride.



The electrophilic acylium ion, will then attack an aromatic cyclopentadienyl ring of ferrocene and form a diene. The diene will then lose a proton to regenerate the aromatic system.



In your reaction, we will use a 2:1 molar ratio of acetyl chloride to ferrocene so both mono- and di-acetylation will occur; these products will be separated by using column chromatography (Technique 19 of PLKE).

• **Pre-lab:**

**Read:** This handout and Technique 19 of PLKE,

**Prepare for class on Wednesday, April 18:** “Purpose” and “Materials and methods”

Decide which acid chloride you want to use. **Write the chemical reactions** of your synthesis after the “Purpose” section, including all reagents. Note that this is a multi-step synthesis.

**Pre-lab calculation:** Calculate the theoretical yield of the di-acetylated product, given 1.1 mmol of the acid chloride (show the steps of the calculation, please). **Confirm that ferrocene is in excess in this experiment.** This should be written near the chemical equation above.

You may tape the procedure on the next several pages into your notebook (right-hand page only).

• **During lab:**

Since this is a lab about color, in the “Data” section, you should writing your observations of what occurs at which step of which part. Of course, you should take notes about yields and melting points (a table format for this would be nice).

Sketch the TLC plate(s) results in this section and record the optimal elution fluid composition for the column chromatography part.

• **Post-lab:**

Since there is no published melting point for the benzoyl chloride or adipoyl chloride product, make sure you talk to another person who used the same acid chloride to check for consistency. Of course, a tight melting point range is always nice.

• **Lab Result Report: (Due Wednesday, April 25 at the beginning of lab)**

**Photocopy** the non-procedure parts of this lab.

No conclusion is required. An abstract is required, though.

**Abstract:**

- attach this to the **front** of your report
- must be **word-processed** on a **separate sheet of paper**

Your name, North Seattle Community College  
NAME OF LAB

Write a 75 to 100 word abstract, first describing the reactant and the product, then the efficacy of your synthesis (use your yield information here) and the purity of your product based on the melting point. Note how much mono-acetylated product was obtained compared to the diacetylated product.

You do not need to mention specific gram amounts (apart from stating that the reaction was done on a “microscale” level), nor do you have to mention the apparatus or details of the procedure. You should, however, mention that column chromatography was used in the product isolation, and note the composition of the elution fluid.

**Note:** Work individually. The column chromatography will begin on the second lab meeting for this experiment.

**Procedure:** Flame dry, in the hood, a 5 mL conical vial equipped with a spin vane, air condenser and drying tube containing calcium chloride desiccant (do **not** use the connecting caps to connect your 5 mL conical vial and air condenser). Let your apparatus cool and add 150 mg (1.1 mmole) of anhydrous aluminum chloride and 2.0 mL of methylene chloride to the conical vial. Then add, with swirling, 0.08 mL (1.1 mmole) of acetyl chloride\* (density 1.1 g/mL). To this mixture, add dropwise, with stirring, a solution of 100 mg of ferrocene dissolved in 1.0 mL of methylene chloride. (A deep violet color should appear after the addition of all the ferrocene). Be sure to promptly replace the air condenser and drying tube after each addition of reagent.

\*You may substitute benzoyl chloride or adipoyl chloride for acetyl chloride—see last page of the experiment for details.

Let the reaction proceed at room temperature for 15 minutes. At the end of this time, transfer the reaction solution to a 15 mL glass centrifuge tube (with cap) containing 5 mL of ice water. Cool the resulting solution in an ice bath and neutralize to pH 7, using 25% sodium hydroxide solution (about 0.5 mL). Use pH paper to confirm neutrality. If the solution is too basic, this will cause aluminum salts to precipitate but you will still be able to continue on to the next step.

To isolate your product you will perform a microscale extraction using your capped 15 mL centrifuge tube. Extract your product mixture 2 times with 3 mL portions of methylene chloride. Be sure to mix well and to periodically vent the centrifuge tube. If the layers do not easily separate, you may use a centrifuge to aid in the separation (be sure to counterbalance the centrifuge). Combine the methylene chloride extracts in a 25 mL Erlenmeyer flask.

The methylene chloride extracts are dried by adding about 100 mg of anhydrous sodium sulfate and letting the solution stand for 15 minutes. Also at this time, take 10 drops of the solution and save it in a vial. This will be used later for TLC analysis. At the end of

15 minutes, add the dried solution to a tared 50 mL Erlenmeyer and wash the remaining sodium sulfate with 2 ml of methylene chloride. The rinse is then combined with the rest of the dried methylene chloride solution.

At this point you may stop and leave this solution to evaporate in your drawer. If time permits, you may continue on by evaporating your solution in the hood using a stream of air and starting your TLC analysis (see next page). Once the methylene chloride has evaporated, weigh the product obtained.

**Waste Disposal:** All solids and solutions from above can be placed in the aqueous waste jug. TLC plates (below) can be placed in the trash cans. Silica gel, used during the next lab period, should be placed in the solid waste once it has been used. Solvent used in chromatography can be placed in the organic solvent waste jug

**TLC analysis:** With the small amount of solution saved from before, run a few TLC plates using various proportions of hexane/acetone as developing solvent. This will help you determine which will be the best solvent system to purify your product mixture using column chromatography (see sec 20.6, p. 785 of PLKE for more details). In essence, the solvent system that best resolves your spots and gives  $R_f$  values for the products between 0.2 and 0.5 would be the system of choice for column chromatography\*. There will be standards of mono- and di-acetylated ferrocene and of unacetylated ferrocene (you may have starting material left over).

\*Columns tend to "run" faster than TLC plate so it is recommended that you lessen the percentage of polar solvent by 10% (e.g., if you found that the best solvent system for TLC was 60/40 hexane/acetone, then use 70/30 hexane/acetone for your column)

**Column Chromatography:** Prepare about 50 mL of your solvent system of choice. Columns can be checked out from your instructor. To the column add a cotton plug followed by 0.5 cm of sand, and finally 15 mL of your solvent system. You are now ready to prepare your silica absorbent. You will use the "slurry" method. **Please read p. 767 of PLKE text for a better understanding of the following procedure.** In an Erlenmeyer flask, slowly add 5 g of silica gel to 30 mL of your solvent system. Heat may be liberated as you add the silica and any solvent that evaporates can be replenished. Swirl the solution a couple of minutes to ensure that slurry is relatively free of trapped air bubbles. At this point place a beaker below the column, open the stopcock, and add in portions the slurry to the column, making sure to swirl the slurry before each addition. As you add, tapping on the side of the column with a pencil (the wooden part) will aid in the packing of your absorbent. Note: Always keep the solvent level above the adsorbent -- add extra solvent when needed.

Once the adsorbent has settled in the column and a well-defined top has formed, add solvent from the collecting beaker to your column and let it run through 2 or 3 more times to ensure a tight pack. The column should not contain any air pockets at this point. Finally, carefully add 0.5 cm of sand to the top of the silica and adjust the solvent level so that it is just above the silica (1-2 mm). Close the stopcock!

The next step is to apply your sample to your column. Dissolve your product mixture in about 1 ml of methylene chloride and, with a pipet, add this solution down the sides of the column so as to not disturb the surface of the silica (the sand acts as a protective layer). Carefully open the stopcock to allow the solution to absorb onto the silica – be sure not to let the solvent fall below the silica surface but to keep it right at the same level as the silica surface. Now add 1 mL of hexane down the sides of the column and again drain until the surface of the silica is just at the same level as the solvent. Repeat this procedure 2 more times. At this point all of your compound should be bound on the silica in a tight band. Now carefully fill the column with solvent (the first few milliliters should be pipetted in to avoid disturbing the silica surface). Once the column is filled, you may begin your elution. Collect only the colored fractions and add solvent as needed. You may recycle fractions that are colorless.

Collect the colored fractions in separate, tared Erlenmeyer flasks. You may leave these in your drawer to evaporate or if time permits, evaporate the solvent in the hood. To remove silica gel from your column when are done, attach amber tubing to the tip or the column and push it out with air pressure (hook it up to your hood's airline). Any small amount of silica sticking to the sides of the column can be washed out with tap water and rinsed down the drain. Do this in your own hood and not out by the waste hood. Put spent silica in the solid waste jug.

Weigh and take melting points of the separated products. Acetyl ferrocene has a mp of 81-83°C, diacetyl ferrocene mp 125-127°C.

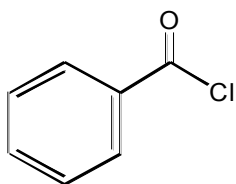
### Substituting different acetyl chlorides

You may substitute benzoyl chloride or adipoyl chloride for acetyl chloride in the first step of the reaction. This will give a different and perhaps more interesting ferrocene chromophore (color).

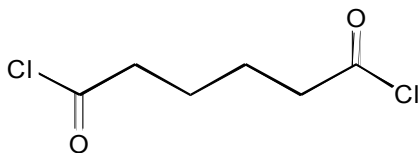
To substitute with benzoyl chloride you would add 0.12 mL (155 mg = 1.1 mmole) of benzoyl chloride.

To substitute with adipoyl chloride you would add 0.16 mL (201 mg = 1.1 mmole) and 300 mg of aluminum chloride (2.2 mmole — you need twice as much as adipoyl chloride has two acid chloride groups to react.)

The melting points of benzolated and adipoylated ferrocene are unknown.



Benzoyl chloride



Adipoyl chloride