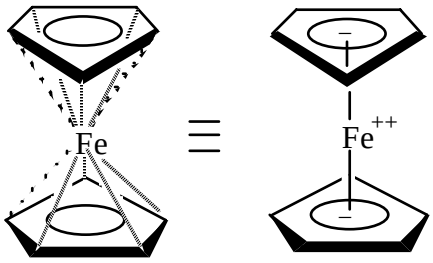
FRIEDEL-CRAFTS ACETYLATION & COLUMN CHROMATOGRAPHY

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.

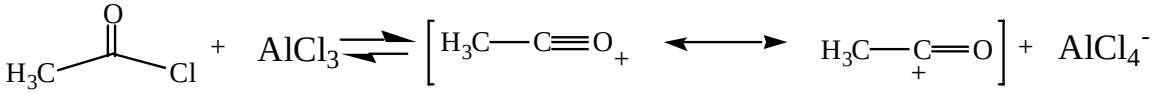
Ferrocene (I), is a compound which contains an iron (II) ion sandwiched between two flat cyclopentadienyl anions (see pg 643 of Bruice).



(I)

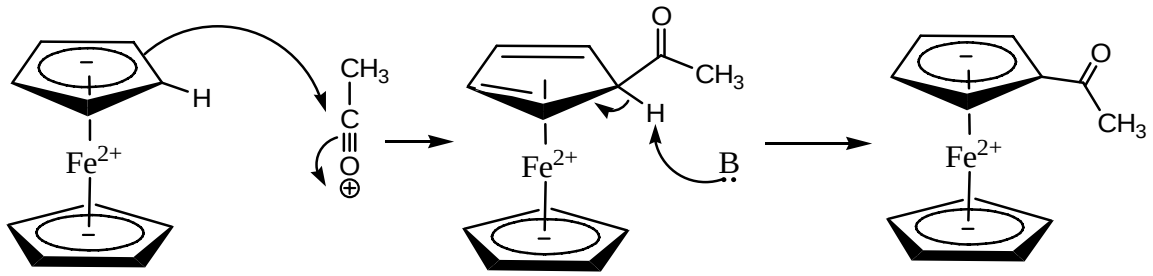
In the cyclopentadienyl anion component of ferrocene, the electron density is dispersed equally among the 5 carbons, and moreover these anions contain a cyclic cloud of 6 pi electrons and are, therefore, aromatic. Hence ferrocene, as other aromatic systems, will undergo electrophilic aromatic substitutions 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.



(II)

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 all a 2:1 molar ratio of acetyl chloride to ferrocene so both mono and di acetylation will occur and these products will be separated by using column chromatography (technique 19 of PLKE).

Note: Work in pairs**.** 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 choride 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 of anhydrous aluminum chloride (1.1 mmole) 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 counter balance the centrifuge). Combine the methylene chloride extracts in a 25 mL Erlenmeyer flask.

The methylene chloride extracts are dried by adding approx. 100 mg of sodium sulfate and letting the solution stand for 15 minutes. Also at this time, take 10 drops of the solution and save 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 place 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 solution saved from before, run TLCs 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, pg. 785 of PLKE for more details). In essence, the solvent system that best resolves your spots and gives R_f values 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 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 approx. 50 mL of your solvent system of choice. Columns can be checked out at the stockroom. To the column add a cotton plug followed by 1/2 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 pg 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 absorbant --add extra solvent when needed.

Once the absorbent 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 1/2 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).

The next step is to apply your sample to your column. Dissolve your product mixture in approx 1 ml of methylene chloride and with a pipet, add this solution down the sides of the column 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 mLs should be pipetted in as 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 you 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 hoods 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 you own hood and not out by the waste hood. Put spent silica in the solid waste jug.

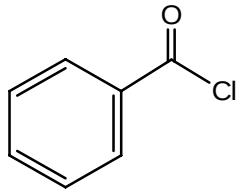
Weigh and take melting points of the separated products. Acetyl ferrocene mp 81-83, diacetyl ferrocene mp 125-127

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

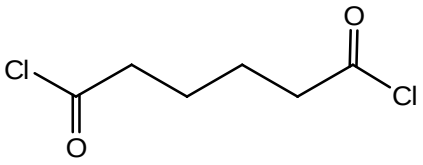
To substitute with benzoyl chloride you would use 0.12 mL (155 mg :1.1 mmole) of benzoyl chloride.

To substitute with adipoyl chloride you would use 0.16 mL (201 mg :1.1 mmole) and 300 mg of aluminum chloride (2.2 mmole—you need twice aluminum chloride as much as adipoyl chloride has 2 acid chloride groups to react.)

The melting points of benzolated and adipoylated ferrocene are unknown.



Benzoyl chloride



Adipoyl chloride