

EXPERIMENT #2: *Ferrocene and Acetylferrocene*

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MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Department of Chemistry
5.310 Laboratory Chemistry

EXPERIMENT #2 THE PREPARATION OF FERROCENE AND ACETYLFERROCENE¹

I. PURPOSE AND BACKGROUND OF THE EXPERIMENT

The principal aims of this experiment are:

1. To provide experience in the synthesis of a relatively simple covalent compound, bis(pentahaptocyclopentadienyl) iron, ($\eta^5\text{-C}_5\text{H}_5$)₂Fe, whose trivial name is ferrocene (**1**).
2. To become familiar with inert atmosphere techniques.
3. To introduce the use of thin-layer chromatography as an analytical tool and column-chromatography as a means of purification.

In the course of this synthetic sequence, the student will encounter operations such as recrystallization, distillation, and execution of reaction under an inert atmosphere, all common techniques in synthetic chemistry.

Background:

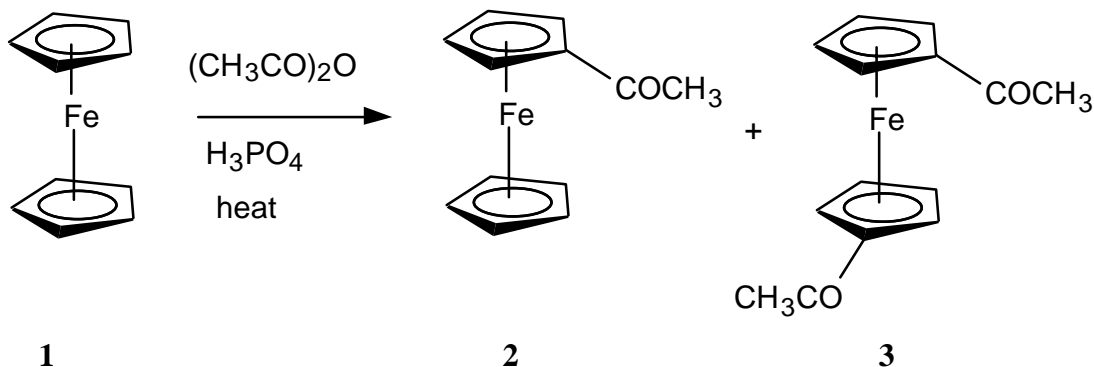
Ferrocene is a historically important molecule. The recognition of the "sandwich" structure of C₁₀H₁₀Fe in 1951 spawned transition metal based organometallic chemistry. This field is still developing and has produced a huge number of compounds in which saturated, unsaturated, and aromatic organic fragments are bonded directly to metal centers.

Ferrocene exhibits the properties of a typical aromatic molecule. The compound is stable to more than 500 °C. It does not react readily with acids or bases; however, it is sensitive to oxidizing agents. All the carbon atoms in the two cyclopentadiene rings are bonded equally to the central ferrous ion by the π electrons of the two rings. Ferrocene does not undergo addition reactions typical of cyclopentadiene, but is readily subject to electrophilic aromatic substitution. Depending upon the catalyst (AlCl₃, H₃PO₄) and the

¹ Modified by M D. Gheorghiu to use Ac₂O / H₃PO₄ for acetylation and to accommodate microscale quantities of the chemicals. The experiment includes contributions from past instructors, course textbooks, and others affiliated with course 5.310.

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reaction conditions, either the monosubstituted product (2) or the disubstituted product (3) is the major product of acetylation. For a particular set of reaction conditions, the student will determine whether the major product is the orange acetylferrocene (2) or the red 1,1-diacetylferrocene (3).



II. SAFETY

NOTES: The first use of a chemical is designated in the procedure with an asterisk. Additional information about the chemicals will be found in Appendix A.

The organic liquids used in quantity in this experiment: **dimethyl sulfoxide**, **dimethoxyethane**, **cyclopentadiene**, and **dicyclopentadiene** are volatile and possess noxious vapors. Avoid inhalation. Carry out operations with these organic liquids in the hood.

1. **Dicyclopentadiene:** Noxious liquid. Handle with usual caution: do not ingest. If it is spilled on skin, rinse well with water.
2. **Potassium hydroxide (KOH):** Very caustic chemical. Handle with caution and keep away from skin and clothing. If it spills, rinse with plenty of water.
3. **Iron Chloride (FeCl_2):** Ferrous salts can be toxic. Handle with usual caution: do not ingest.
4. **Dimethyl sulfoxide [DMSO, $(\text{CH}_3)_2\text{SO}$]:** Not considered toxic. However, it increases the permeability of the skin to other substances. Therefore, it may render other chemicals more hazardous by allowing entry through the natural skin barrier. Substances ordinarily regarded as harmless on the skin can become dangerous when the nonpermeability of the skin has been altered by application of DMSO. If DMSO is spilled, wash well with soap and plenty of water.
5. **Hydrochloric acid (HCl):** Very acidic liquid. Contact with skin will cause burns. If any gets on you or your clothing, remove affected clothing, rinse immediately with water.

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6. **Acetone (CH_3COCH_3):** acetone is an organic solvent and should be treated with normal caution: keep away from flames, dispose as organic waste. It has the ability to increase the permeability of skin and should not be spilled on hands, etc.
7. **Phosphoric acid (H_3PO_4):** Concentrated solutions are irritating to the skin and mucous membranes. Essentially nontoxic, the compound is used to flavor foods and for many other commercial applications.
8. **Acetic anhydride [$(\text{CH}_3\text{CO})_2\text{O}$]:** Combustible organic liquid. Strong acetic odor. Reacts with alcohol to form ethyl acetate, water to form acetic acid. Avoid contact with skin and eyes, as the compound produces irritation and necrosis of tissues
9. **Methylene chloride (CH_2Cl_2):** Common organic solvent. It is flammable and volatile. Prolonged exposure causes liver damage. Use in the hood; avoid prolonged breathing of vapor. If spilled soak up with vermiculite and dispose of as organic waste.
10. **Hexane (C_6H_{14}), ethyl acetate ($\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$), dimethoxyethane ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$):** Common organic solvents, handle accordingly: keep away from flames, do not ingest or inhale, dispose of as organic waste.
11. **Chloroform (CHCl_3):** Properties similar to methylene chloride, handle accordingly. Suspected carcinogen.
12. **Alumina (Al_2O_3):** Common chromatographic support. It is not considered hazardous except when inhaled or ingested in large quantities.
13. **Ferrocene ($(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}$):** An organometallic compound of moderate toxicity. Handle with the usual caution. Prevent ingestion, inhalation and skin contact. Chronic exposure may cause liver damage. Heating to decomposition emits acrid smoke, irritating fumes.
14. **Acetylferrocene ($(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4(\text{COCH}_3))$):** Highly toxic organometallic compound. Handle with caution. Prevent ingestion, inhalation and skin contact. Heating to decomposition emits acrid smoke, irritating fumes.

III. EXPERIMENTAL PROCEDURE

In the directions that follow the student should adhere closely to the amounts of materials used in each step. The yields given for each preparation, although not necessarily optimal, correspond to a competent execution of each preparation. Yields substantially lower indicate poor technique, and may necessitate repetition of the step.

It is important to carefully study the experiment before beginning it in order to maximize efficient use of laboratory time. Because of the instability of the cyclopentadiene monomer, it must be used immediately after distillation in the preparation of ferrocene. The total preparation of ferrocene requires about four hours.

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References - These provide background information on the techniques and are provided to improve your understanding of the techniques and provide practical hints that may help you avoid mistakes that may prove costly in terms of laboratory time.

- Fractional Distillation **MHSM**, Chapter 11.4 pp. 118-121
- Heating Mantles and Powerstats (Variacs) **MHSM**, Chapter 6.2 pp. 42-43
- Reactions Under Inert Atmosphere **TM** 10:44 - 10:47
- Lubrication of Ground Glass Joints **MHSM**, Chapter 2.2 pp. 18-19
- Clamping and Support of Reaction Apparatus **MHSM**, Chapter 7.1 pp. 48-50
- Sublimation **MHSM**, Chapter 12 pp. 133-135
- Syringes, needles and septa **JWZ** Chapter 8 pp. 63-65
- Thin layer and Column Chromatography **MHSM**, Chapter 15 pp. 153-160, 162
MHSM, Chapter 17 pp. 178-189

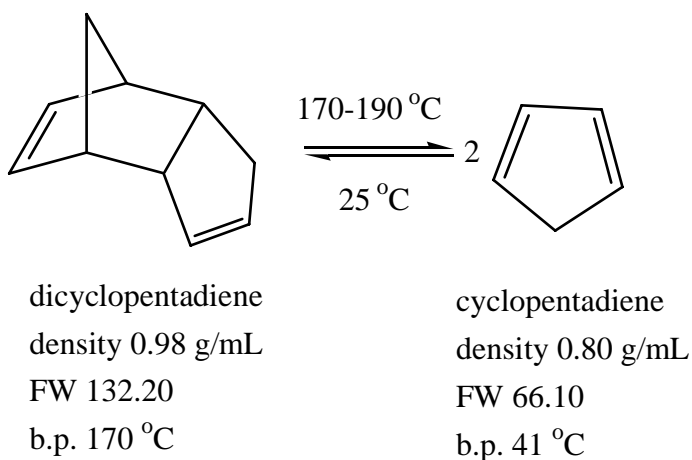
1. Day 1 - Preparation of Ferrocene

*****Additional pre-lab assignment.** In your lab notebook:

- 1). Determine the limiting reagent for the synthesis of ferrocene. **SHOW ALL WORK.**
- 2). Calculate the theoretical yield of ferrocene. **AGAIN SHOW YOUR WORK.**

Note: You will need to recalculate the theoretical yield once you have made the ferrocene to account for the quantity of reactant actually used.

"Cracking" of Cyclopentadiene Dimer²



² Adapted from: **Keneth L. Williamson**, "Macroscale and Microscale Organic Experiments", 2nd Edition; D. C. Heath and Company, Lexington, MA, 1994.

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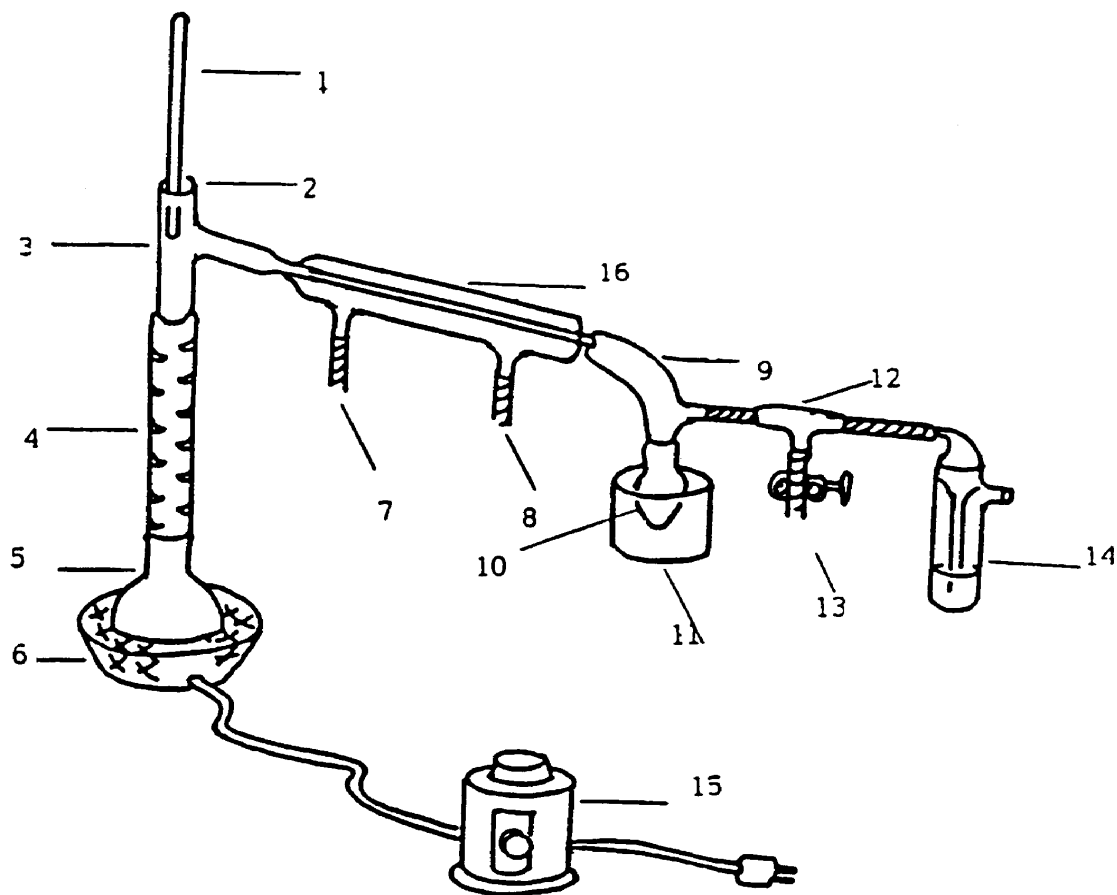
Cyclopentadiene monomer is not stable³ and undergoes spontaneous Diels-Alder addition to produce the dimer and higher polymers. Commercial dicyclopentadiene must be thermally degraded to the monomer, which is used in the preparation of ferrocene.

The apparatus shown in figure 1 is preassembled in the hood. Commercial dicyclopentadiene*15 mL of have been added to the 25 mL distilling flask. The TA will connect the heating mantle to a Variac, and turn on the water flow to the condenser. Check that all joints are well sealed and that the apparatus is stable and tight. Insert a syringe needle into the septum of the receiving flask, flush the system for 1 min with nitrogen. After 1 min remove the vent syringe needle.

Begin the cracking process by heating the distillation flask until it is hot to the touch (Variac setting 80-90), and then reduce the heating (Variac setting ~ 50) to avoid "flooding" the Vigreux column. During this time the liquid in the flask will begin to froth and the plates in the Vigreux column will become wet with condensate, indicating that the cracking process is taking place. The temperature at the top of the column should rise to 39 °C and condensation of the vapor should begin in the condenser. Collect cyclopentadiene monomer boiling at 39-41 °C. Maintain a rate of distillation that does not exceed 2-3 drops/sec of monomer passing from the water condenser to the receiver flask. During this time the rate of cracking may decrease. In this event a periodic increase in the Variac setting may be required. The TA will use a syringe to give each student 0.3 mL of cyclopentadiene monomer. The monomer must be used immediately or the cracking and distillation procedure will have to be repeated. **Make sure the iron chloride and the potassium hydroxide solutions are ready BEFORE obtaining the monomer.**

³ At room temperature, cyclopentadiene is 8% dimerized in 4 h and 50% dimerized in 24 h.

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- | | |
|--|---|
| 1. Thermometer | 9. Vacuum adapter $\bar{\Phi}$ 14/20 |
| 2. Thermometer Adapter | 10. Pear shape flask, 10 ml.
Mark level of 3.5 ml on
outside of flask |
| 3. Adapter, distillation, $\bar{\Phi}$ 14/20
with 10/18 Thermometer adapter | 11. Ice bath |
| 4. Vigreux column, $\bar{\Phi}$ 14/20 | 12. T-Shape tube |
| 5. Round bottom flask, 25 ml | 13. Nitrogen inlet, rubber |
| 6. Heating mantle | 14. Gas bubbler with nujol |
| 7. Water Outlet on condenser, $\bar{\Phi}$ 14/20 | 15. Variac |
| 8. Water inlet on condenser | 16. Condenser |

Figure 1

Preparation of Ferrocene⁴

Potassium hydroxide solution: To a 4 mL conic vial, quickly add 0.75 g of finely powdered potassium hydroxide*,⁵ followed by 1.25 mL of dimethoxyethane*. Cap the flask with a red 14x20 septum. Adjust the nitrogen flow by means of the pinch clamp so

⁴ Adapted from: **Keneth L. Williamson**, "Macroscale and Microscale Organic Experiments", 2nd Edition; D. C. Heath and Company, Lexington, MA, 1994.

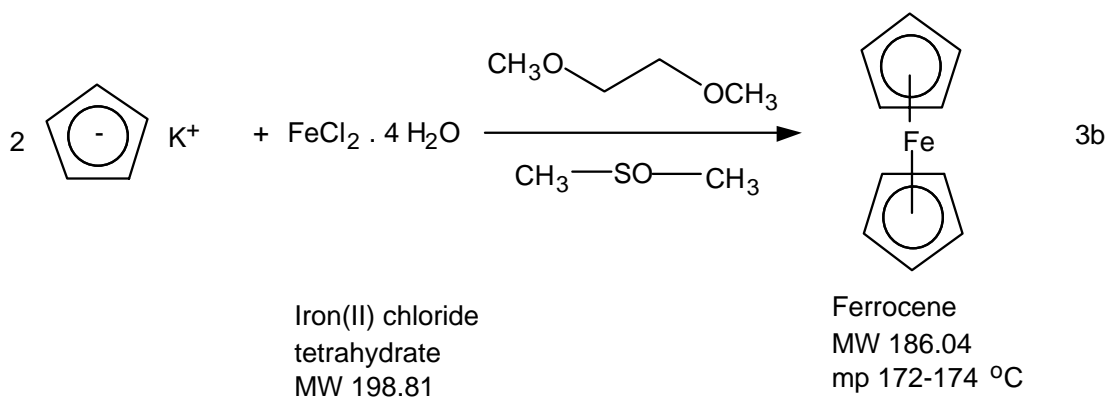
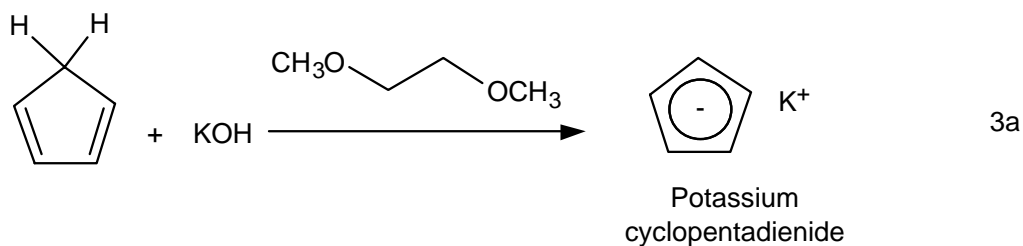
⁵ Potassium hydroxide is ground into a fine powder by employing an ordinary food blender.

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that one bubble every 2-3 sec. rises through the nujol. With the nitrogen flow adjusted, insert an empty syringe needle through the septum of the flask as an outlet and then insert the nitrogen inlet needle. Pass nitrogen into the flask for about 1 min. to displace the oxygen present and create an inert atmosphere.⁶

Remove the needles and shake the flask to dislodge the solid from the bottom and to help to dissolve it.

WEAR PROTECTIVE GLOVES WHILE SHAKING THE FLASKS



Iron(II) chloride solution: Add 0.35 g of finely powdered green iron(II) chloride tetrahydrate* and 1.5 mL of dimethyl sulfoxide* to a 5 mL pear shape flask. Cap the flask with a red 14x20 septum, insert an empty syringe needle through the septum and then insert the nitrogen inlet needle. Pass nitrogen into the flask for about 1 min to displace the oxygen present. Remove the needles. Shake the flask vigorously to dissolve the iron chloride.

Using the syringe, inject 0.30 mL of freshly prepared cyclopentadiene into the vial containing the potassium hydroxide.⁷ **WARNING:** Do not grasp the body of the

⁶ The anion of cyclopentadiene rapidly decomposes in air, and iron(II) chloride although reasonable stable in solid state is readily oxidized to the iron(III) (ferric) state in solution.

⁷ The mixture of cyclopentadiene monomer and potassium hydroxide slurry should appear pink but may turn either dark green or black. This dark coloration is due to oxidation of small amounts of the cyclopentadiene anion and is not detrimental to this particular procedure. Pure cyclopentadiene solutions are colorless. In other organometallic preparations more scrupulous efforts to eliminate oxygen must be followed.

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syringe because the heat of your hand will cause the cyclopentadiene to volatilize. Stir the mixture vigorously. After waiting about 5 min for the anion to form⁸, pierce the septum with an empty syringe needle to relieve pressure. Inject the iron(II) chloride solution contained in the pear shaped flask in six 0.25 mL portions over a 10-min period. Between injections remove both needles from the septum and shake the vial vigorously. After all the iron(II) chloride has been added, rinse the empty flask with 0.25 mL more dimethyl sulfoxide and add this to the vial. Continue to shake the solution for about 15 min to complete the reaction.

Pour the dark slurry of ferrocene into a mixture of 4.5 ml of 6 N HCl* and 5 g of ice in a 30 mL beaker. Stir the resulting mixture thoroughly to dissolve and neutralize the potassium hydroxide. This is an exothermic reaction. It is important that this mixture remain cold (near 0 °C) during the addition and subsequent stirring. If the temperature starts to rise, slow down the rate of addition and/or add more ice. Some of the Fe(II) will be oxidized to Fe(III) resulting in the formation of the blue (green, brown) ferrocenium salt.

Collect the resulting precipitate on a Hirsch funnel. Wash the ferrocene with four 1.5 ml portions of water, press out excess water, and squeeze the product between sheets of filter paper to aid drying. Dry the crystals on a watch glass in your drawer until the next laboratory. The filtrate is blue because of dissolved ferrocenium ion.

2. Day 2 - Purification of ferrocene

Ferrocene is a crystalline, diamagnetic material that is extremely stable to air, moisture and light. It is moderately to extremely soluble in practically all-nonpolar or weakly polar solvents. It may be purified by sublimation.

Take a mp of the dried crude ferrocene. [NOTE: All melting points must be taken in melting point tubes sealed off with parafilm. Ferrocene sublimes below its melting point and would be lost from an unsealed tube.]

Sublimation may be conducted in a 100 x 15 mm culture dish as shown in figure 2 or with the apparatus demonstrated by your TA. Transfer ferrocene to the "bottom" of the culture dish to cover the center of the dish to a thickness of about 5 mm. Cover with the larger half of the culture dish and place it on a variable temperature hot plate. Slowly raise the temperature until the ferrocene sublimes to the upper half of the dish. The sublimation will proceed slowly. Cooling the top culture dish by placing a beaker filled with ice water on top of it will facilitate the sublimation (WARNING: Slide the beaker off the top of the culture dish. Lifting it may lift the upper culture dish off and cause it to fall or disturb the sublimed ferrocene resulting in a loss of ferrocene.) Remove the dish from the heat, allow it to cool and recover the sublimed ferrocene. This procedure may be repeated several times until all the ferrocene is purified.⁹ Do not heat over 100 °C

⁸ Among simple hydrocarbons, cyclopentadiene is relatively acidic: pKa=15.5.

⁹ Acetone* may generally be used to clean glassware during this synthesis. A concentrated solution of KOH in water may be used to clean the petri dishes after sublimation.

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Determine the melting point of each batch of ferrocene sublimed. Place the final product in a weighed vial, determine the yield and report this along with the melting point. Calculate and report your actual percent yield. The melting point should equal or exceed 171 °C (lit., 173-174 °C).

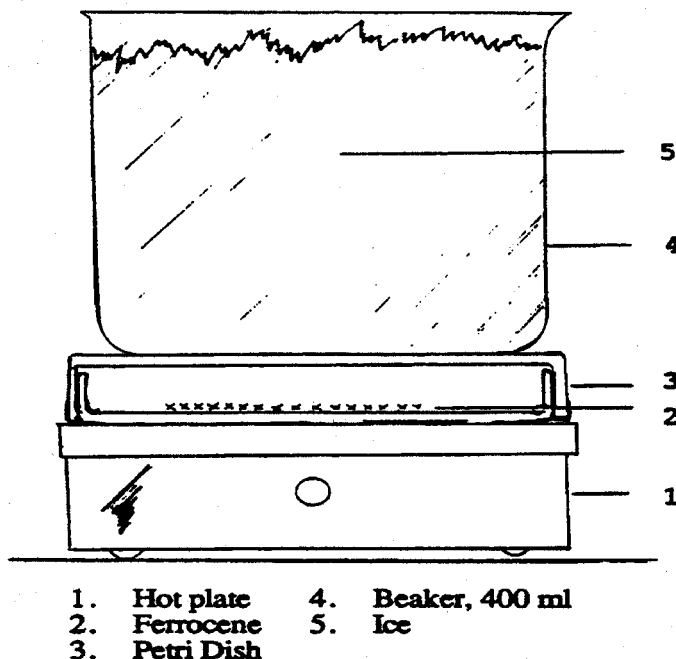


Figure 2: Apparatus for the Sublimation of Ferrocene

3. Day 3 - Acetylation of Ferrocene

Ferrocene will be acetylated by the action of phosphoric acid* and acetic anhydride*. The number of products in the reaction mixtures will be determined by thin-layer chromatography and the products isolated by column chromatography.

Acetylation Reaction

Place a 3x10mm stir bar in a 10 mL round bottom flask (RBF). Prepare a 65 °C water bath (use the red liquid thermometer) and preheat the flask in the bath. Then add, **in the following order**, 93±3 mg (0.5 mmol) of ferrocene, 0.35 mL of acetic anhydride, and 0.1 mL of 85% phosphoric acid. (WARNING: changing the order of addition will likely result in a brown goo resulting from the decomposition of the ferrocene, careful measurement of all quantities involved is also crucial to the success of this reaction) Cap the RBF with a red 14x20 septum bearing an empty syringe needle, and warm it in the water bath while agitating the mixture to dissolve the ferrocene. Heat the mixture for 30 minutes.

Cool the vial thoroughly in an ice bath. Carefully add to the solution 0.5 mL of ice water. Mix thoroughly. Add dropwise 3 M aqueous sodium hydroxide solution until the mixture is neutral (20-30 drops, test with indicator paper to avoid excess base).

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Collect the product on a Hirsch funnel, wash with 4x1.0 mL of water, and press it as dry as possible between sheets of filter paper. Dry the crystals until the next lab session. Place alumina in the oven according to the directions in the section on column chromatography.

4. Day 4 - Thin-layer Chromatography of Acetylation Product

First determine the weight of the dried crude acetylation product.

Procedure for TLC

To determine the product distribution of the reaction mixture, an aliquot will be analyzed by thin-layer chromatography. TLC plates of aluminum oxide may be obtained from Lab Supplies. Applicators are micro-capillary tubes. Development is conveniently conducted in plastic snap-top jars (Fig. 3). A 5-1/2 cm diameter filter paper placed in the jar will serve to saturate the chamber with solvent vapor. Be certain that the solvent level is below the point where the plate was initially spotted.

Prepare solutions of ferrocene (sublimed) and the dried acetylation product by placing a few (5 to 10) drops of methylene chloride* CH_2Cl_2 in each of your two smallest sample vials. Add a small amount (one spatula-tip full) of ferrocene to one vial and the acetylation product to the other vial. The solution should be concentrated enough so that a dark spot is seen on the TLC plate when the sample is applied. If you are unable to see the spots after developing, add more sample to the solutions.

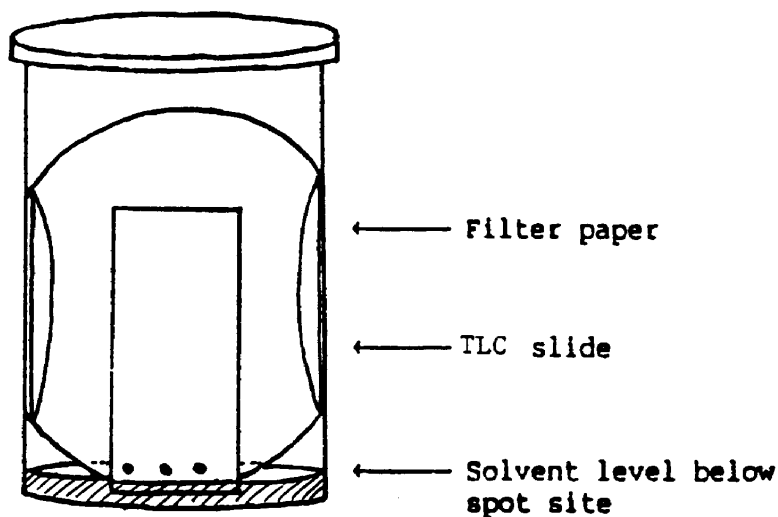


Figure 3. Apparatus for the Separation of Acetylation Products using TLC

The goal of this portion of the experiment is to find the solvent system that most effectively separates the various ferrocene species. This is determined by examining the migration of reaction products in a variety of solvents of varying polarity. The following

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solvents will be used to analyze the ferrocene products: **(1) hexane*** and **(2) ethyl acetate***

Begin by preparing a chamber as shown in figure 3 for each of the pure solvents listed above. Plates should be developed until the solvent front is within 1 cm of the top of the plate. It should then be removed and the solvent line marked. If the progress of the solvent front is monitored closely, it is also acceptable to draw start and stop lines on the plate before the chromatogram is run (A pencil should be used because ink is soluble). This prevents inaccuracies that occur when the solvent evaporates before the final solvent front can be marked. Sketch the chromatograms in your lab notebook. Calculate R_f ("ratio to front") values for each spot on the chromatograms. (R_f = distance a component travels/distance the solvent front travels.)

It is possible to optimize separation of reaction products by varying the polarity of the solvent systems. This is accomplished by adding hexane (non-polar) to ethyl acetate (polar). Make solutions of 4:1, 1:1, and 1:4 ratios of hexane:ethyl acetate. (If a greasy brown spot remains at the starting point no matter which solvent is used, be aware that this is an impurity and not diacetylferrocene.) Carry out TLC as above using these solvent mixtures.

By selecting a solvent that carries all products but still affords a clear separation, TLC can be used to quickly determine the qualitative makeup of a sample. However, when attempting column chromatography with a short column, such as one made from a Pasteur pipet, solvents that only carry one component at a time are preferred. Compare separation of the spots in each solvent system. Consider the solvent systems to be used for the column chromatography in the following section. Why were these solvent systems chosen for purification? Why might they be ill suited for a simple determination of product composition via TLC, but well suited for use in column chromatography utilizing a short column? Save the remaining ferrocene and acetylation product/ CH_2Cl_2 solutions for comparison with the purified products.

Column Chromatography

A Pasteur pipet, shown in figure 4, is used as a chromatographic column for separation of 10-100 mg mixtures. To separate the acetylferrocene from ferrocene (and 1,1-diacetylferrocene if present), prepare a column of acid washed alumina.* With a copper wire, place a tiny plug of cotton at the bottom of a Pasteur pipet. Clamp the empty column in a vertical position. Add 4 cm of the acid washed alumina (which has been previously dried in a 100 °C oven for at least 24 hours). Tap the pipet gently to pack down the alumina. Add 5 mm sand on the top of the alumina.

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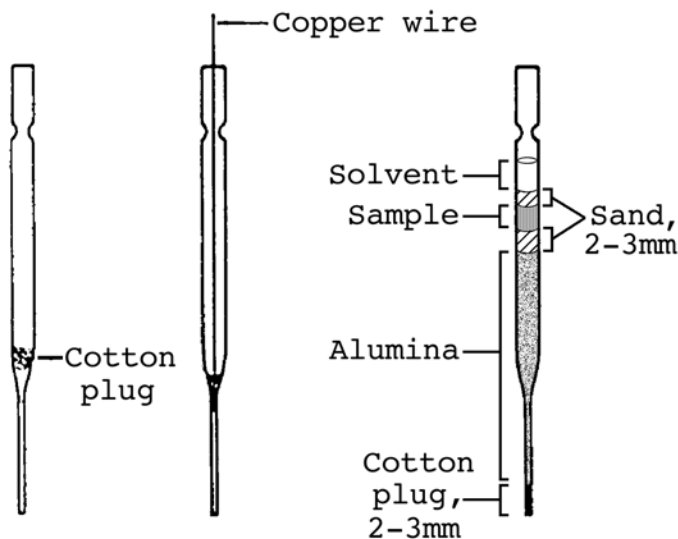


Figure 4. Packing of a pipet for use in column chromatography

Apply the crude acetylation product to the column using the “dry-loading”. Dissolve the entire dry acetylation product in a minimum of methylene chloride (just a few drops) in an Erlenmeyer flask. Add about 50 mg of dry alumina and stir. In the hood evaporate the solvent completely until a fine, smooth flowing powder remains. Add this powder to the top of the column. Use a small amount of hexane to wash down any powder adhering to the sides. Apply a 3 mm layer of sand to the top of the column. Add 5 mL of hexane cautiously to avoid disturbing the sand; a band of yellow material (ferrocene) will be eluted down the column. Collect the eluant containing the ferrocene in a weighed 10 mL Erlenmeyer flask. If necessary, add more hexane to complete the elution of ferrocene.

Once the band of yellow material has been separated and without permitting the column to go dry, carefully add a mixture of 1:4 hexane:ethyl acetate. Collect the eluant containing the orange component (acetylferrocene) in a weighed flask. Diacetylferrocene will appear as a red band if it is present in significant quantity. Only if a third spot appeared on the TLC indicating the presence of diacetylferrocene, elute diacetylferrocene into a weighed Erlenmeyer flask with ethyl acetate. (Note: With this synthesis diacetylferrocene, if present at all, will likely be present in such small amounts that cannot be recovered from the column).

Check the colored fractions by thin-layer chromatography to verify that each contains a single component. Evaporate the solvents in the hood using very gentle airflow. Dry the crystals until the next lab session.

5. Determination of Purity and Calculations

Determine the weight of each component and verify its identity by determining the melting points of the isolated components. If a component is not of satisfactory

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purity, it should be recrystallized. Acetyl ferrocene is recrystallized from hexane; diacetylferrocene from chloroform*-hexane.

Calculate the percent yield of each isolated component from the acetylation reaction. Submit all samples of ferrocene, acetylferrocene, and any other products in appropriately labeled vials to your teaching assistant.

Table I Melting Points of Acetylferrocene Compounds

Compound	mp (°C)	Ref.
Acetylferrocene	84.0 - 84.5	10
Diacetylferrocene	127.5 - 128.5	11
	130 - 131	12

IV. GENERAL REFERENCES: The following references are relevant to the preparation and properties of ferrocene and related metallocenes.

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2. J. Birmingham, "Synthesis of Cyclopentadiene Metal Compounds," *Adv. Organometallic Chem.* **2**, 365 (1965).
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¹¹ M. Rosenblum and R.B. Woodward, *J. Amer. Chem. Soc.* **1958**, *80*, 5443.

¹² R.B. Woodward, M. Rosenblum, and M.C. Whiting, *J. Amer. Chem. Soc.* **1952**, *74*, 3458.