MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Department of Chemistry
5.310 Laboratory Chemistry

EXPERIMENT #1
THE PREPARATION OF FERROCENE AND ACETYLFERROCENE[1]

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, $(\eta^5\text{-}C_5H_5)_2Fe$, 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.

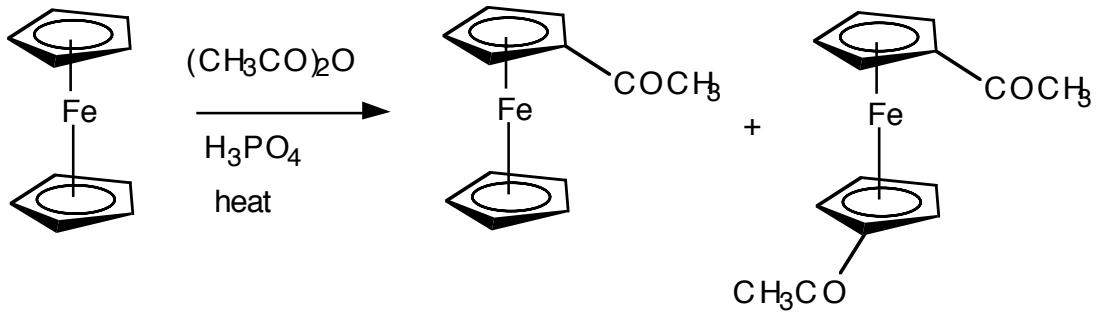
In the course of this synthetic sequence, the student will encounter operations such as sublimation, distillation, and execution of reaction under an inert atmosphere, all common techniques in synthetic chemistry.

Background:

Ferrocene is a historically important molecule. The recognition of the "sandwich" structure of $C_{10}H_{10}Fe$ 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 ($AlCl_3$, H_3PO_4) and the 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**).

[1] The experiment includes contributions from past instructors, course textbooks, and others affiliated with course 5.310 (Updated by John Dolhun Dec 2017).



1 **2** **3**

II. SAFETY

NOTES: 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, wash well with soap and rinse with plenty of water.

3. **Iron Chloride ($FeCl_2 \bullet 4H_2O$)**: Ferrous salts can be toxic. Handle with usual caution: do not ingest.

4. **Dimethyl sulfoxide [DMSO, $(CH_3)_2SO$]**: 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.

6. **Acetone (CH_3COCH_3)**: acetone is an organic solvent and should be treated with normal caution: keep away from flames and 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 [$(CH_3CO)_2O$]:** 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 ($CH_3CO_2C_2H_5$), dimethoxyethane ($CH_3OCH_2CH_2OCH_3$)**: 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 ($(\eta^5\text{-}C_5H_5)_2Fe$)**: 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 ($(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4(COCH_3))$)**: 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.

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.

- Boiling Point & Distillation — **MHS**, Chapter 12 pp. 173-205
- Heating & Cooling Methods — **MHS**, Chapter 6 pp. 73-86
- Reactions Under Inert Atmosphere — **MHS,** Chapter 7 93-103
  Setting Up Organic Reactions — **MHS**, Chapter 7 pp. 87-106
- Sublimation — **MHS**, Chapter 16 pp. 236-239
- Syringes, needles and septa — **JWZ** Chapter 8 pp. 64-65
- Thin layer and Column Chromatography — **MHS**, Chapter 18 pp. 255-267

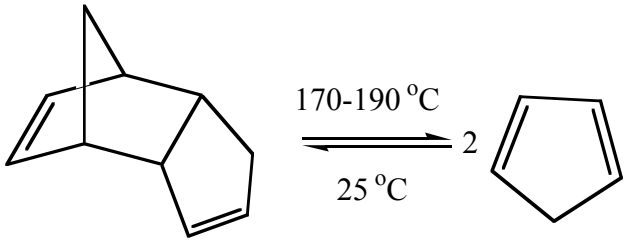
Required Videos: Digital Laboratory techniques Manual

#3. TLC basics
#7. Filtration
#8. Sublimation
#10. Column Chromatography
#11. Balances
#12. Melting Points

1. <u>Day 1 - Preparation of Ferrocene</u>

***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 Dimer[2]



dicyclopentadiene
density 0.98 g/mL
FW 132.20
b.p. 170 °C

cyclopentadiene
density 0.80 g/mL
FW 66.10
b.p. 41 °C

Cyclopentadiene monomer is not stable[3] 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. 75mL of commercial dicyclopentadiene have been added to the 250 mL distilling flask. The TA will crack the dimer as follows: first 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.

Then 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 the 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.**

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

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

Photograph by Mircea Gheorghiu. Used with permission.

Fig. 1. Cracking of dicyclopentadiene

1. Thermometer
2. Vigreux column
3. Heating mantle
4. 3 Necks round bottom flask
5. Condenser
6. Nitrogen bubbler
7. Variac
8. Ice-water

Preparation of Ferrocene[4]

Potassium hydroxide solution: To a 4-mL Assem Vial with septum (provided by TA), quickly add 0.75 g of finely powdered potassium hydroxide,[5] followed by 1.25 mL of dimethoxyethane. Adjust the nitrogen flow so 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

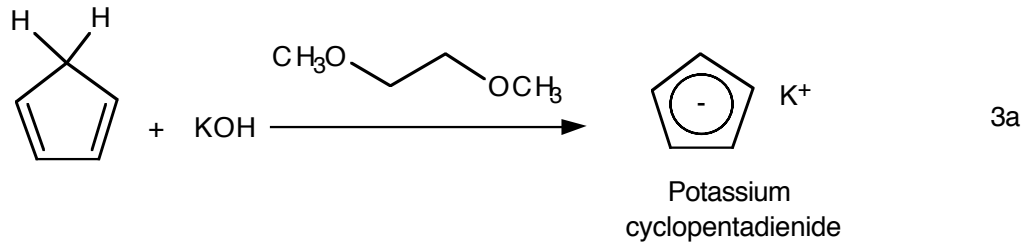
[4] Adapted from: **Keneth L. Williamson**, "*Macroscale and Microscale Organic Experiments*", 2nd Edition; D. C. Heat and Company, Lexington, MA, 1994.

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

nitrogen into the flask for about 1 min. to displace the oxygen present and create an inert atmosphere.[6]

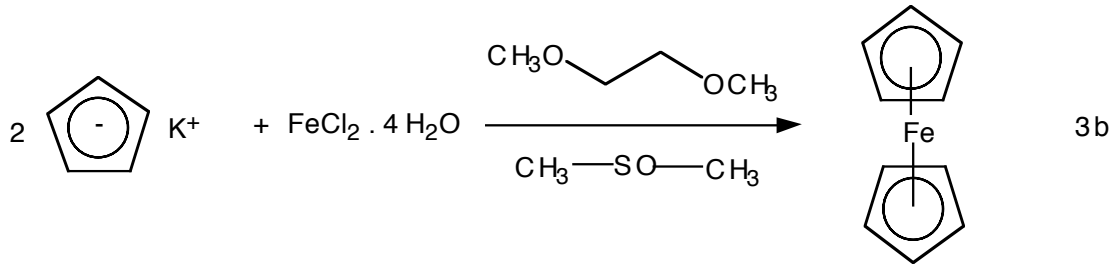
Remove the needles and shake the flask to dislodge the solid from the bottom and to help to dissolve it. Please note the KOH does not completely dissolve in this reaction.

WEAR PROTECTIVE GLOVES WHILE SHAKING THE FLASKS



3a

Potassium
cyclopentadienide



3b

Iron(II) chloride
tetrahydrate
MW 198.81

Ferrocene
MW 186.04
mp 172-174 °C

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 4 mL Assem Vial with septum (provided by TA). Cap the flask with the septum provided, insert an empty syringe needle through the septum and then insert the nitrogen inlet needle. Pass nitrogen into the vial for about 1 min to displace the oxygen present. Remove the needles. Shake the vial 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 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 form,[8] pierce the septum with an empty syringe needle to relieve pressure. Inject the iron (II) chloride solution contained in the Assem vial in six 0.25 mL portions over a 10-min period.

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[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.

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

Between injections remove both needles from the septum, put the flask back under a nitrogen atmosphere, 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 M HCl (prepared by each student; NOTE: concentrated HCl is 12 M) and a 30-mL beaker half filled with ice. Stir the resulting mixture thoroughly to dissolve and neutralize the potassium hydroxide. This in an exothermic reaction with heat released. 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.

The 4mL Assem vials used in this experiment are disposable. Please place the vial and its contents, into the special labeled glass vial waste container, set up under the hood.

2. Calibration of Melting Point Apparatus

A Mel-Temp® apparatus with a digital thermometer and a 90-mm melting point capillary is used to determine melting points. Calibrate the apparatus and the thermometer by taking the melting points of four pure compounds that melt over the range of 50-200 °C. Four pure melting point standards are provided in the laboratory. Prepare a graph of reported versus observed melting points for a particular Mel-Temp and digital thermometer. For future reference **record the identification number of the Mel-Temp and the digital thermometer**. Consult the Chemical Rubber Company HANDBOOK OF CHEMISTRY AND PHYSICS to verify the melting points of the standards used.

*****Students will be divided into teams. Each team will calibrate one Mel-Temp with each member of the team determining one point (i.e. melting point standard) on the curve for this instrument. You will use the same Mel-Temp apparatus for entire semester.**

To load the melting point capillary, push the open end into some of the crystals (which must be carefully dried beforehand), invert and tap the sealed end gently on the desk top until the crystals slide down. The crystals should not occupy more than 2-3 mm of the tube. If you have difficulty getting the crystals to go to the bottom of the tube, take a 65 mm, long stem funnel and place it upside down on the bench top. Drop the capillary

tube down the stem. The impact will not have enough force to break the tube, but it will force the crystals to the bottom.

If you have no previous knowledge of the melting point, it saves time to do a rough determination by scanning the 50-250 ºC range at a rate of 5 ºC to 10 ºC per minute. When the approximate melting range has been found, a new tube should be prepared and the run repeated using a much slower (<1 ºC per min) rate of temperature increase. Melting point ranges should not exceed four degrees for the former and two for the latter. Always recrystallize a product to constant melting point.

Determine the uncorrected melting point of your sample and compare to the calibration plot. Record in the notebook these results together with any pertinent observations made during heating i.e., evidence of decomposition, color changes, etc. When submitting your notebook pages, include a table showing yields and corrected melting points of the crude and purified products as well as the thermometer calibration curve.

3. Day 2 - Purification of Ferrocene and Acetylation 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.

Weigh and 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. Spread the sample out don't pile it up. Cover with the larger half of the culture dish and place it on a variable temperature hot plate. Slowly raise the temperature setting on the hot plate until the ferrocene sublimes to the upper half of the dish. The sublimation will proceed slowly. Cooling the top culture dish by placing a 600 mL 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.) Allow the dish to cool completely before removing from the hotplate, then, recover the sublimed ferrocene. This procedure may be repeated several times until all the ferrocene is purified.[9] Do not heat over 100 °C.

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).

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[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.

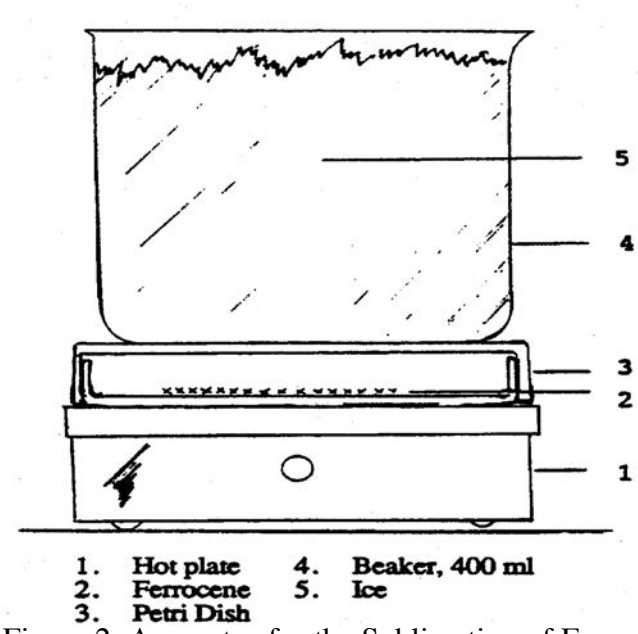

Figure 2: Apparatus for the Sublimation of Ferrocene

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 3x10 mm stir bar in a 10 mL round bottom flask (RBF). Prepare a 65°C water bath (use the red liquid thermometer and small crystallizing dish) and preheat the flask in the dish (temperature is critical higher temperatures may destroy your products). Then add, **in the following order**, 93±3 mg (0.5 mmol) of ferrocene, 0.5 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, insert 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 10 mL, round bottom flask (RBF) 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 (50+ drops, test with indicator paper around 40 drops and then each 5 drops to avoid excess base).

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.

4. Day 3 - Thin-layer Chromatography of Acetylation Product

First determine the weight and take the melting point 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 are available from the Stockroom. Applicators are micro-capillary tubes. Development is conveniently conducted in small jars (Fig. 3). A 5-1/2 cm diameter filter paper placed in the jar will 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), the dried acetylation product, and a control solution containing both ferrocene and acetylation product by placing a few (5 to 10) drops of methylene chloride CH_2Cl_2 in each of your three smallest sample vials. Add a small amount (one spatula-tip full) of ferrocene to one vial, the acetylation product to the second vial and a half spatula tip of both ferrocene and the acetylation product to the third vial (the control). The solution should be concentrated enough so that a dark spot is seen on the TLC plate when the sample is applied. Use the special micro capillary tubes to spot your plates. If you are unable to see the spots after developing, add more sample to the solutions.

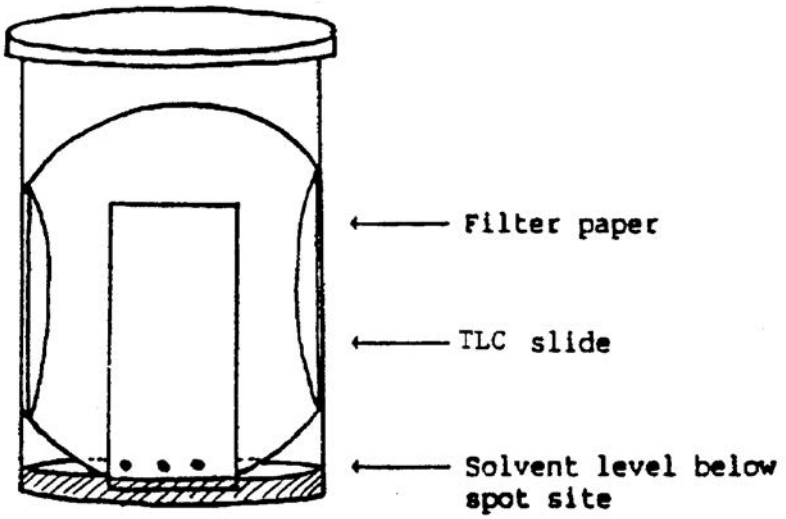

Figure 3. Apparatus for the Separation of Acetylation Products using TLC

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 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 following three solvent combinations 4:1, 1:1, and 1:4 ratios hexane : ethyl acetate. Students only need around 3mL of solvent (mobile phase) for each chamber. 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. Why? Include an explanation in your discussion. Save the remaining ferrocene and acetylation product/CH_2Cl_2 solutions for comparison by TLC with the purified products.

Column Chromatography

Based on your TLC results select a solvent system for use in the larger scale separation provided by column chromatography. Review your selection with your TA.

The semi-microscale column (MICROFLEX®, Williamson Microscale Kit), shown in figure 4, is used as a chromatographic column for separation of 20-200 mg mixtures. To separate the acetylferrocene from ferrocene (and 1,1-diacetylferrocene if present), prepare a column of acid washed alumina. Clamp the empty column in a vertical position. Note: Because this column has a built-in frit, unlike standard-scale columns, it is **not** necessary to tamp down a plug of glass wool and add sand on top of it, before adding alumina.

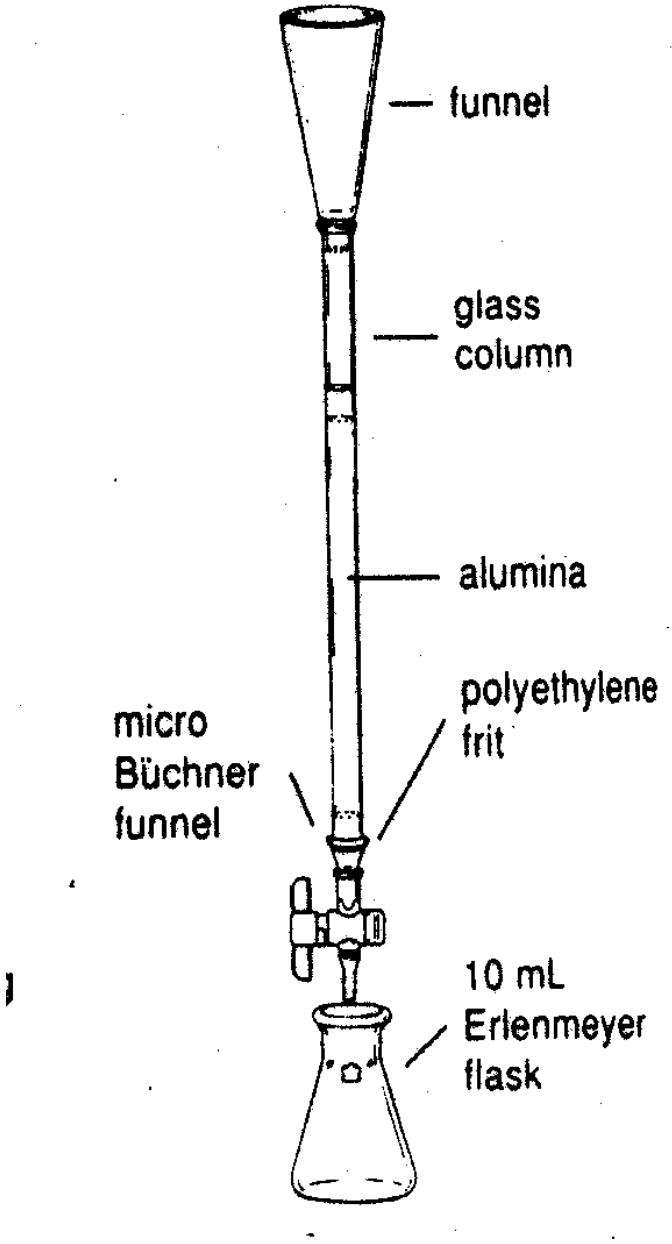

Figure 4. Packing of a column chromatography

Add about 7-8 cm of the acid washed alumina (which has been previously dried in a 100 °C oven for at least 24 hours). Tap the column gently to pack down the alumina. Add 5 mm sand on the top of the alumina.

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. Apply a 3 mm layer of sand to the top of the column. Add the solvent system chosen by TLC cautiously to avoid disturbing the sand; allowing it to pickup any particles adhered to the wall of the column (Note: The upper fitting serves as solvent reservoir). During the addition of solvent to your column keep

the stopcock open to allow air to escape. Collect the eluant containing the first colored component in a weighed 10 mL Erlenmeyer flask. Change flasks and collect the second colored component in a second weighed 10-mL Erlenmeyer flask. (Note: the solvent coming off the column, which does not contain colored product, may be collected separately from the colored products). Be careful not to permit the column to go dry during this process. Expect to remove the same number of fractions, as the number of colored spots observed moving on the TLC plate. (Note: With this synthesis diacetylferrocene, if present at all, will likely be present in such small amounts that it 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 a very gentle airflow. Dry the crystals in your desk until Day 4 of the next lab session.

5. Day 4-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 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. Check with your TA then safely discard all samples of ferrocene, acetylferrocene, and any other products into the appropriately labeled Ferrocene waste container.

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]

[10] P.J. Graham, R.V. Lindsey, G.W. Parshall, M.L. Peterson, and G.M. Whitman, *J. Amer. Chem. Soc.* **1957**, *79*, 3416.

[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.

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

1. Wilkinson, G. The Iron Sandwich. A Recollection of the First Four Months, *J. Organomet. Chem.* **1975**, *100,* 273.
2. Birmingham, J. "Synthesis of Cyclopentadiene Metal Compounds," *Adv. Organometallic Chem.* **1965**, *2*, 365.
3. Coates, G. E.; Greene, M. L. H.; Wade, K. *Organometallic Compounds*, vol. 2, Methuen and Co., London, 1968, pp 90-115.
4. Jolly, W. L. *Inorg. Synth.*, **1968**, *11*, 120
5. Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th Ed., Wiley: New York, 1988, p. 736.
6. M. Rosenbum, M. *Chemistry of the Iron Group Metallocenes*, Part one, John Wiley and Sons, Inc., New York, 1965.
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5.310 Laboratory Chemistry

Fall 2019