

Organic Chemistry II Lab Manual

Caitlyn Bailey

A Senior Thesis submitted in partial fulfillment
of the requirements for graduation
in the Honors Program
Liberty University
Fall 2019

Acceptance of Senior Honors Thesis

This Senior Honors Thesis is accepted in partial fulfillment of the requirements for graduation from the Honors Program of Liberty University.

Alan B. Fulp, Ph.D.
Thesis Chair

Lauren E. Brynteson, M.S.
Committee Member

David E. Schweitzer, Ph.D.
Assistant Honors Director

Date

Abstract

This project aims to supply a full lab manual and grading key for Organic Chemistry II, a class often taken by sophomores in Liberty University's science degree programs.

Properly applied laboratory experiments create a beneficial learning environment for science students by using hands-on procedures to transform intangible lecture concepts into concrete demonstrations. Lab work also fosters the development of problem-solving and critical-thinking skills that students need in research and the workplace. Thus, having a comprehensive lab manual is critical to students' success and understanding in this upper-level class. This project adds to the experiments of Organic Chemistry II lab through procedural updates, conceptual introductions to experiments, and supplemental information for the students. Additionally, weekly grading keys for teacher's assistants have been created for better assessment of each student's knowledge.

To prevent lab experiments from becoming isolated without a practical application, an introduction was written for each week that creates a clear connection between lab work and class concepts. Supplemental information was created to suggest review topics, lab technique cautions, and areas of data discussion required for success in weekly assignments. The main goal of this was to improve the comprehension, and consequently the grades, of students in their notebook and formal lab report assignments.

An answer key for weekly assignments was also designed for standardized grading among teacher's assistants. Objective answers for notebook assignments were included such as safety hazards for reagents, literature values and calculations for reagent tables, product theoretical yields, and expected results for analytical techniques.

Organic Chemistry II Laboratory

First Edition

Caitlyn Bailey

Department of Biology & Chemistry

Liberty University

Table of Contents

| | |
|------------------------------------------------------------------------|------------|
| 1. Infrared Spectroscopy | 6 |
| 2. Nuclear Magnetic Resonance Spectroscopy | 7 |
| 3. Grignard Reaction Week 1 | 9 |
| 4. Grignard Reaction Week 2 | 13 |
| 5. Diels-Alder Reaction | 16 |
| 6. Friedel-Crafts Acylation of Ferrocene | 20 |
| 7. Column Chromatography of Ferrocene and Acetylferrocene | 22 |
| 8. Wittig Reaction | 25 |
| 9. Polymer Chemistry: Synthesis of Nylon and Polyester | 27 |
| 10. Aldol Reaction | 30 |
| 11. Appendix: Keys | 325 |

Infrared Spectroscopy

Introduction

Identifying the structure of organic compounds is an important skill in organic chemistry, and one common way of accomplishing this is infrared (IR) spectroscopy. In this type of spectroscopy, a molecule's functional groups are shown by the way it absorbs infrared radiation.¹ Lecture will provide more information on the theory behind this technique, and the worksheet in lab this week requires application of that knowledge.

Table 1. Key information for interpreting IR spectra.¹

| Bond | Stretching Frequency (cm ⁻¹) and Characteristics |
|------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| C–H | 2800 - 3000 for <i>sp</i> ³ 3000 - 3100 for <i>sp</i> ² 3300 and sharp for <i>sp</i> |
| C–C | 1200 |
| C=C | 1640 - 1680 for isolated 1620 -1640 for conjugated Approx. 1600 for aromatic |
| C≡C | <2200 and sharp signal for terminal, weak or absent for internal |
| C–N | 1200 and stronger than C–C |
| C=N | 1660 and stronger than C=C |
| C≡N | >2200 and stronger than C≡C |
| C–O | 1100 |
| C=O | Approx. 1735 and strong for a carboxylic ester 1725 and strong for an aldehyde 1710 and strong for a ketone or an acid Approx. 1685 and strong for a conjugated carbonyl 1640-1680 and strong for an amide |
| O–H | 3300 and broad/rounded for an alcohol 3500-2500 and broad for an acid |
| N–H | 3300 and broad with spikes |

Nuclear Magnetic Resonance Spectroscopy

Introduction

To continue the topic of identifying the structure of organic compounds, this week's worksheet provides an opportunity to practice interpreting spectra from nuclear magnetic resonance spectroscopy (NMR). This powerful type of spectroscopy can reveal the nature of a molecule's protons based on how it behaves in a magnetic field.¹ Lecture will provide more information on the theory behind this technique, but a quick reference may be found in the tables below.

Table 2. Key aspects of an H-NMR spectrum.²

| Quality of the Molecule | How Quality Translates to the Spectrum |
|-----------------------------------------------|--------------------------------------------------------------------------|
| Number of types of non-equivalent protons | Number of signals |
| Number of protons within each type | The more equivalent protons, the greater the integration of that signal |
| Chemical shifts of the types of protons | Where the signal falls from 0-10 δ (ppm) (see Table 3 for values) |
| Number of non-equivalent, neighboring protons | Signal splitting pattern using the N + 1 rule |

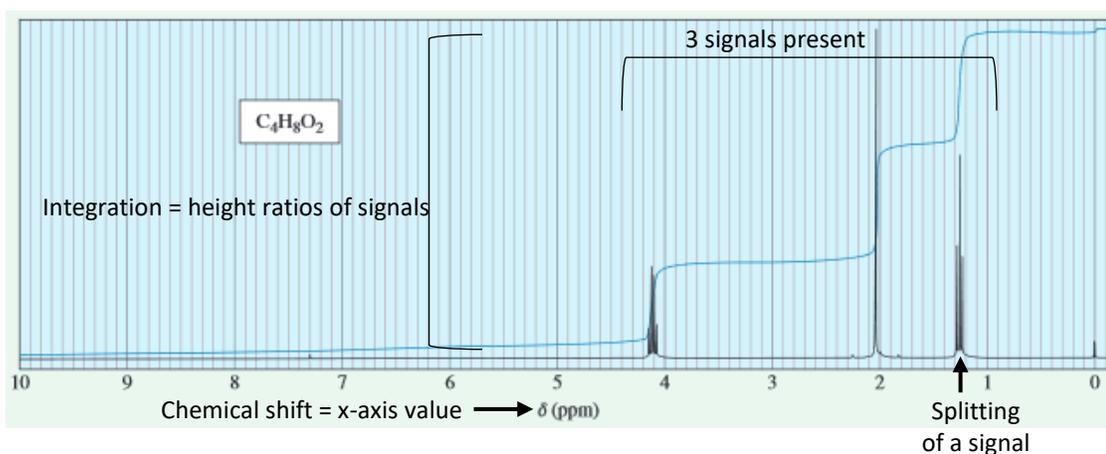


Figure 1. Example of how the qualities of a molecule translate to the spectrum.¹

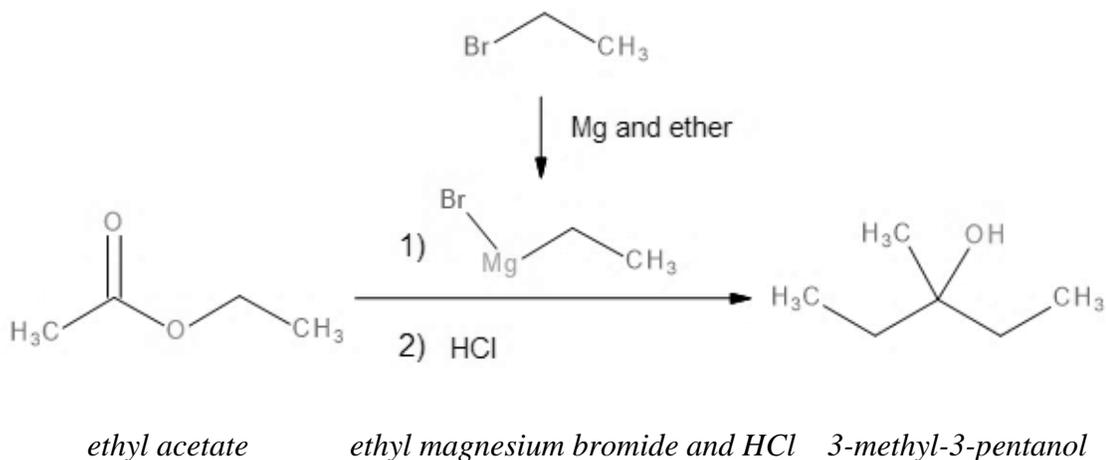
Table 3. Expected chemical shifts for various proton types.¹

| Proton Type | Approx. δ | Proton Type | Approx. δ |
|---------------------------------------|------------------|----------------------------------------------------------|--------------------------|
| CH ₃ | 0.9 | Aromatic | 7.2 |
| CH ₂ | 1.3 | Benzylic | 2.3 |
| CH | 1.4 | Aldehyde | 9-10 |
| Methyl ketone | 2.1 | Carboxylic Acid | 10-12 |
| C \equiv CH | 2.5 | Alcohol | ~2-5 (variable) |
| CH ₂ -X (X = halogen or O) | 3-4 | Phenol | ~4-7 (variable) |
| Vinyl | 5-6 | Amine | ~1.5-4 (variable) |
| Allylic | 1.7 | *These values do not account for additional substituents | |

Grignard Reaction Week 1

Introduction

Grignard reactions serve an important role in organic chemistry as a source of new carbon-carbon bonds. Relevant applications of this reaction can be found in sections 14-15, 18-9, and 21-9 in Wade and Simek's *Organic Chemistry: Ninth Edition* textbook. This week, the goal in lab is to perform the first steps of the Grignard reaction. Specifically, this involves the creation of a Grignard reagent (ethyl magnesium bromide) and a subsequent reaction of the Grignard reagent with an ester (ethyl acetate) to form a tertiary alkoxide. As discussed in lecture, starting this process requires magnesium metal, an alkyl halide, and the presence of an ether. When these reagents are combined, carbanion Grignard reagents are formed.³ Once ethyl acetate is added, these carbanions can then initiate nucleophilic attacks on the partially positive end of the ester's carbonyl, thus creating new carbon-carbon bonds.³ Following the first attack, a tetrahedral intermediate is formed, but this collapses to a ketone before the second attack. The reaction yields a tertiary alkoxide that is ready to be protonated to form a tertiary alcohol. This reaction can be seen in Scheme 1, including the protonation step that is going to take place next week.

Scheme 1. Grignard reaction between ethyl acetate and ethyl magnesium bromide.**Supplemental Information**

To succeed in this lab, the technique for setting up a reflux apparatus with an addition funnel must be understood (seen in Figure 2). Concepts that would be helpful for comprehending what happens in this lab include the polarity of carbonyls and organometallic compounds as well as the mechanism for a Grignard reaction which can be found in Key Mechanism 10-1 in Wade and Simek's *Organic Chemistry: Ninth Edition* textbook (note: this week does not include protonation of the alkoxide).

A caution to consider is that contamination by water will result in side reactions and a less successful Grignard reaction. Additionally, the flammability and volatility of ether should be remembered at all times. Since the product is to be stored for one week, a descriptive label is important for not losing this week's work. The label should appear as follows: "name, date, lab section, chemical or product name, and any relevant hazards (e.g., flammable)."

During the experiment, qualitative data indicates the success of the reaction.

Keeping an eye on bubbling and color changes is key.

Procedures⁴

Dry a 100 mL round bottom (RB) flask and a stir bar as per the instructor's directions.

The flask is best dried in an oven, but the instructor may choose to flame dry the flask.

Due to volatility and flammability, ether and other organic reagents should not be removed from the hood while a flame is being used to dry glassware. Allow the flask to cool to room temperature on a cork ring. Have a condenser ready for reflux with hoses attached and be sure the inner tube is absolutely dry. Weigh out 1.3 g (54 mmol) of magnesium turnings and place them into your dry RB flask with an appropriately sized stir bar. Next, add 14 mL of anhydrous ether into the flask containing the magnesium turnings. Measure out 4 mL of ethyl bromide into a dry graduated cylinder. Once entirely ready for the next two steps, add the 4 mL of the ethyl bromide to your reaction and immediately attach the Claisen adapter, addition funnel, and reflux condenser to the RB flask. After bubbling starts, cool the reaction in a water bath and allow reaction to stir for 10 minutes after the bubbling has stopped. Close the stop cock of the addition funnel and add 2.2 mL (22 mmol) of ethyl acetate and 5 mL anhydrous ether to the addition funnel. Swirl to mix. Slowly add the solution dropwise from the addition funnel. After addition is complete, rinse the addition funnel with 1 mL portions of ether twice. Stir the reaction for 30 minutes, then add a stopper to the flask, label it correctly, and store it for next week's lab.

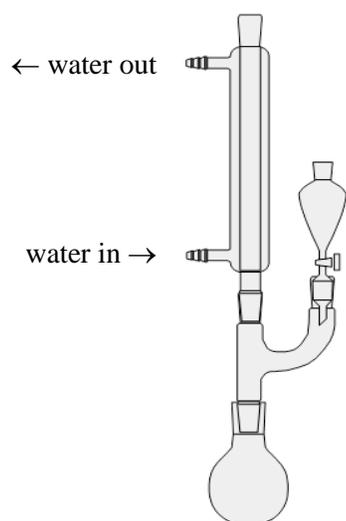


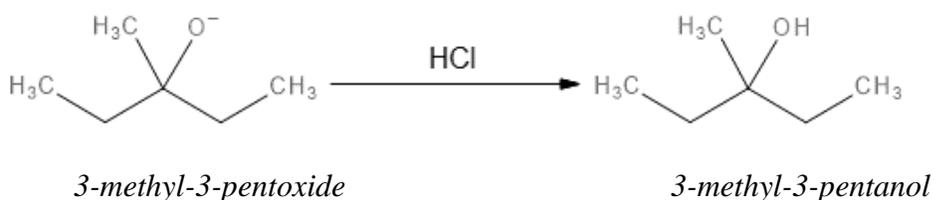
Figure 2. Glassware set-up for reflux with an addition funnel.

Grignard Reaction Week 2

Introduction

This week's goal is to finish the reaction started in last week's lab. Ultimately, the selected procedure yields a tertiary alcohol when treated with water or an acid, as seen in Scheme 2. This addition protonates the alkoxide that was created during the reaction of the Grignard reagent with an ester. Once this tertiary alcohol is formed, it needs to be isolated from other organic compounds by extraction and distillation. Analysis of this purified product by infrared spectroscopy can then reveal the success of the past two weeks of lab work. As discussed in lecture and demonstrated in Lab 1, IR spectroscopy shows the vibrations of bonds and reveals what functional groups are present in a tested substance.¹ Therefore, analyzing the product and overlaying its spectrum with that of the ester starting material should reveal whether the desired functional group change took place. The carbonyl starting material should show up as a strong peak at about 1735 cm^{-1} , while the desired alcohol product should show up as a broad stretch at 3300 cm^{-1} .

Scheme 2. Protonation of alkoxide to form tertiary alcohol.



Supplemental Information

Reviewing the concepts of extraction with ether and drying with anhydrous magnesium sulfate will be helpful for this lab. Additionally, knowing how to set up a simple distillation apparatus is required.

Attentiveness is advised during the extraction process so that the aqueous phase and ether phases are not mixed up, resulting in a potential loss in product. It is best to delay disposal of any phase until after the product is confirmed through analysis.

Qualitative data is useful in this lab for confirming a successful distillation (and consequently a successful collection of a pure product) because a distinct smell of ether should be present in a particular flask yet absent in the other. Additionally, qualitative data in the form of IR spectroscopy can tell the successfulness of the Grignard reaction by revealing any change in functional groups. Finally, the percent yield provides quantitative data about the quality of the reaction.

Procedures⁴

Record the initial appearance of the product. With the RB flask in a water bath with stirring, slowly add about 50 mL of 2 N hydrochloric acid in small portions until the white precipitate dissolves. Pour the solution slowly into 40 mL of water in an Erlenmeyer flask while stirring. Pour the entire mixture into a 125 mL separatory funnel and separate the layers by draining the water phase. Extract the aqueous phase two more times with 15 mL of ether each. Place the combined ether phase back into the empty separatory funnel, wash with 10 mL brine, drain the water phase, and pour the organic phase into a dry Erlenmeyer flask. Add 0.5 g (or more) of anhydrous magnesium sulfate until dry (until free-flowing particles are seen). Weigh a round bottom flask with stir bar and then set up a simple distillation apparatus. Filter the dried solution into a RB flask, and distill off the filtered ether solution. The distilled ether will be collected in the receiving flask, and the remaining liquid in the original RB flask should be your product.

Record the mass and calculate percent yield. Analyze the product by color, smell, and IR.

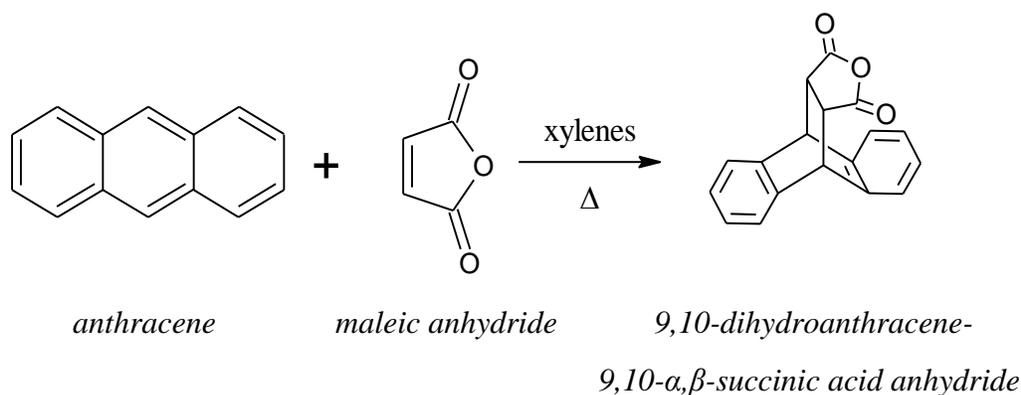
Overlay the product with the starting material to compare spectra.

Diels-Alder Reaction

Introduction

The Diels-Alder reaction creates a cyclohexene ring by the reaction of a diene with an alkene (dienophile). Like the Grignard reaction that was explored in the last two weeks of lab, the Diels-Alder reaction forms new carbon-carbon bonds, but it also provides stereochemical control.⁵ Using this basic concept, this lab's goal is to synthesize a complex product: 9,10-dihydroanthracene-9,10- α,β -succinic acid anhydride. This reaction uses the center ring of anthracene as the diene and the C-C double bond of maleic anhydride as the dienophile, as seen in Scheme 3. After attempting the Diels-Alder reaction and allowing the product to dry for one week, the product is to be analyzed by melting point, thin-layer chromatography, and IR spectroscopy. These methods can provide a thorough analysis of the purity and identity of the Diels-Alder product.

Scheme 3. Diels-Alder reaction between anthracene and maleic anhydride.



Supplemental Information

Given the nature of the second half of this lab, reviewing techniques for melting point analysis and TLC would be helpful. Another important concept to know is the interpretation of peaks at various regions of an IR spectrum. Specifically, peaks that would differentiate between the reactants and the Diels-Alder Product should be well understood.

Caution should be taken when preparing for vacuum filtration because substantial product can be lost if crystals are not clearly and abundantly present in the flask prior to filtering.

For week one, crystal product appearance is an important piece of qualitative data. After week two, many more pieces of data are available for evaluation. A percent yield can be obtained to quantitatively gauge the success of the reaction, while qualitative data from UV and IR spectra sheds light on whether there is a clear difference between the starting materials and the end product. At the same time, TLC can show any clear differences quantitatively through R_f values and qualitatively through plate visualization. Finally, the melting point value and range can describe the purity of the product when compared to literature values.

Procedures⁶**Week 1**

To a round bottom flask, add 0.5 g of anthracene, 0.2 g of maleic anhydride, and 20 mL of xylenes. Heat the reaction to reflux in a sand bath. After 1 hour, cool the reaction to room temperature for 10 minutes. Next, cool the reaction in an ice bath until crystals

form, taking care not to disturb the mixture. After crystals have formed, collect crystals by vacuum filtration. Wash with cool solvent and then dry the crystals by pulling air through them using a vacuum filtration apparatus. Take caution not to over-wash and dissolve the crystals. Record the mass of the reaction product, and store in an open top container for one week.

Week 2

Observe the product and record its appearance. Record the mass of the product again, and then proceed with the other analysis techniques.

UV Spectroscopy

Obtain UV spectra for the reactants and product per the professor's instructions. Compare the spectra to determine similarities and differences.

Melting Point

Obtain a melting point for the product from your Diels-Alder reaction using the MP90 Melting Point System per the professor's instructions.

IR

Obtain an IR spectrum for anthracene, maleic anhydride, and the product from your Diels-Alder reaction. Overlay these spectra to determine if you isolated a new product.

TLC

Prepare your TLC developing chamber with a 4:1 mixture of petroleum ether and ethyl acetate (leave your completely assembled TLC chambers in the hood for the next lab section). Prepare the TLC spotting solution of anthracene, maleic anhydride, and the product of the Diels-Alder reaction by dissolving a small sample (approximately 1mg) of

each in 1 mL of ethyl acetate. Make 4 spots on your TLC plate: 1 spot per sample and a final co-spot of all 3 samples (as seen in Figure 3). Visualize your TLC plate using a UV light, take a picture of your results, and calculate R_f values.

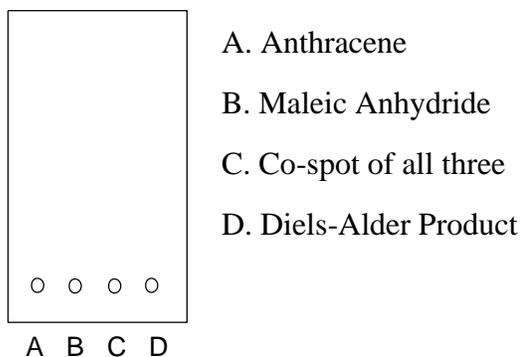


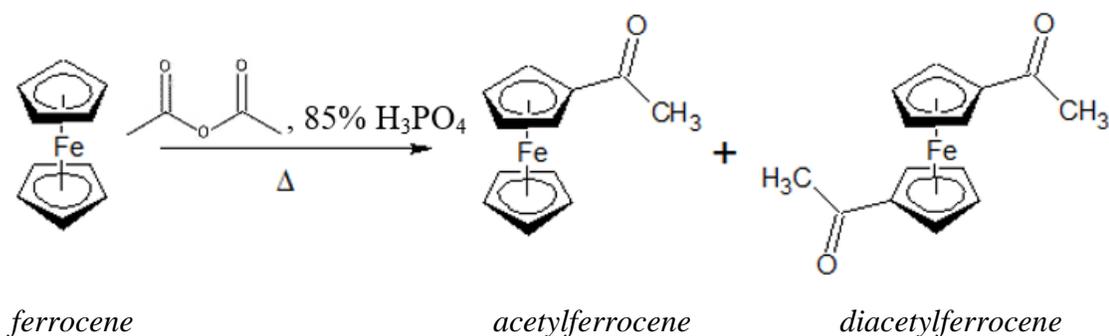
Figure 3. Example of TLC spotting technique.

Friedel-Crafts Acylation of Ferrocene

Introduction

This week's lab explores an electrophilic aromatic substitution reaction called the Friedel-Crafts acylation reaction. The key players in this reaction include a Lewis acid catalyst (H_3PO_4), an aromatic ring (ferrocene), and an acylating reagent (acetic anhydride).⁷ During the reaction, the Lewis acid catalyst causes the acylating reagent to become an acyl cation that acts as an electrophile and is attacked by the electron rich aromatic ring. This acylation turns ferrocene into acetylferrocene, and only one acyl group per aromatic ring can be added in this process since the newly added acyl group is deactivating.⁷ Ultimately, not all the ferrocene will react and over-acylation to diacetylferrocene can occur, so the final product from this lab is impure and needs to undergo purification in the next lab.

Scheme 4. Friedel-Crafts Acylation using ferrocene, acetic anhydride, and H_3PO_4 .



Supplemental Information

Lab techniques should be familiar for this week, but reviewing the mechanism of Friedel-Crafts acylation may assist in understanding what is taking place in lab.

Caution should be taken when preparing the water bath because overheating can destroy the products.⁸ Additionally, reagents must be added in the instructed order or the ferrocene will decompose.⁸ Finally, acetylferrocene is highly toxic, and extreme care must be used when handling it.

During the experiment, qualitative data helps to indicate the success of the reaction. Keeping an eye on color changes is significant.

Procedures⁹

Prepare a water bath to 65° C. In a 25 mL RB flask, add 1.5 g of ferrocene and 5 mL of acetic anhydride followed by 1 mL of 85% phosphoric acid. These need to be added in this exact order to avoid ruining the reaction, and record colors throughout the procedure.⁸ Heat the mixture while stirring for about 30 minutes. Then, pour the mixture onto 20 g of ice in a large beaker with stirring. Add enough water to melt the ice. Next, add small portions of sodium bicarbonate until no more CO₂ evolves. Measure the pH to ensure the mixture is neutral. Place the beaker on an ice-bath, allow to cool, and isolate the solids through vacuum filtration. Wash with water and then dry for at least 15 minutes on vacuum. Weigh the dried crystals and store with a label (as per instructions on page 9) until next week.

Column Chromatography of Ferrocene and Acetylferrocene

Introduction

Since the product collected from last week's Friedel-Crafts reaction consists of acetylferrocene contaminated with residual ferrocene, a purification technique must be used to isolate pure acetylferrocene. Column chromatography, a three-dimensional version of TLC, can be used to accomplish this. Conceptually, column chromatography is identical to TLC. A mobile phase travels along a stationary phase, and compounds are separated based on their individual polarity and interactions with either phase¹⁰. However, rather than a mobile phase that travels up a TLC plate, column chromatography uses gravity to pull the mobile phase down through a tube packed with silica gel. Mixture components separate out as they travel down the tube at different speeds, creating distinct layers of compounds. Since the mobile phase containing these compounds must be drained from the tube, this technique actually allows for the fractions to be collected in test tubes and further analyzed. This data can then determine the success of last week's reaction and of this week's purification.

Supplemental Information

Knowledge on how to set up a column for running column chromatography is necessary for success in this lab. If detailed pictures of each step are desired, chem.libretexts.org has a useful page called Macroscopic Columns. It would also be helpful to review the techniques used in running a TLC since this will be used on the separated fractions. Finally, understanding and applying the concepts of intermolecular

forces between different compounds based on their polarities will be needed to determine the identity of each layer.

A general caution is to carefully layer the silica and sand properly since this is a common source of error. To avoid cracks in the silica and disruption of compound separation, the column must never run dry, so care must be taken to keep the solvent level above the layer of silica. Additionally, maintaining distinct fractions by keeping different colored fractions separated is critical to obtaining a pure product.

Data from the column itself is mostly qualitative as the elution order and colors of the fractions speak to the identity of the compound within the fraction. Correctly identifying which layer is ferrocene and which layer is acetylferrocene is required. Quantitative data comes from the subsequent TLC analysis which provides R_f values that can indicate whether the reaction was successful and how pure the product is.

Procedures⁴

Take the weight of the crude product from last week, and then weigh out approximately 100 mg of the crude acetylferrocene in a crystallization dish. Make up 100 mL of an 80:20 mixture of petroleum ether/ethyl acetate. Once you have completely prepared your column, dissolve the crude acetylferrocene in approximately 2mL of your solvent mixture.

Set up the column using Figure 4 as a guide. Begin by weighing out 6g of silica gel and combining it with 30 mL of your solvent mixture. Use caution with the dry silica gel as it is hazardous if inhaled. Then, slurry pack your column with the silica gel and solvent by swirling the flask and quickly pouring it into the column. Use more solvent as needed and

drain solvent as needed. The solvent used to load and pack the column can be reused.

After the column is packed, and with the solvent level near the top of the column, add a small layer (~5mm) of sand to protect the top of the column. Once this protective layer is in place, drain the solvent level to the top of the sand. Add the acetylferrocene dissolved in 2 mL of the solvent to the top of the column slowly without disrupting the sand.

Slowly drain the solvent level to the top of the silica gel, but don't let it run dry. Rinse the sides of the column with an additional 2 mL of the solvent mixture and drain the solvent again to the top of the silica gel.

Carefully, fill the column with solvent and begin collecting fractions as you drain the column. Fill test tubes with approximately 5mL of a fraction in each. Continue to add solvent to the column when it gets near the top of the silica to keep the column from running dry. Collect 10 test tubes or until your instructor tells you to stop. When collection is complete, run a TLC on the colored fractions using the same developing solvent as your column. Take a picture of your results and calculate R_f values. Determine the identity of each colored band and evaluate the purity of the isolated product. Store the uncovered tubes with the desired compound until next week.

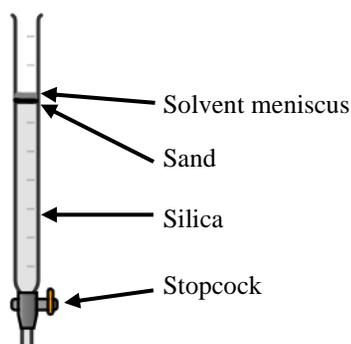


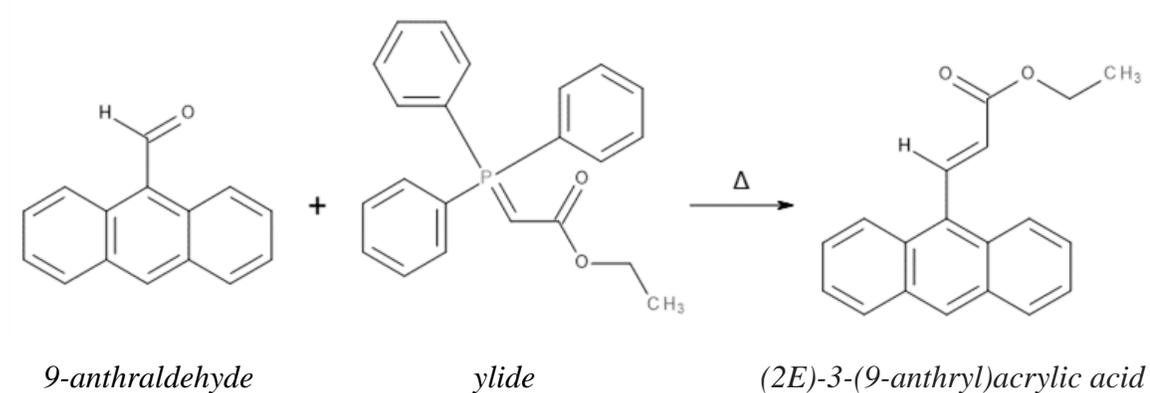
Figure 4. A macroscale column chromatography set-up.¹¹

Wittig Reaction

Introduction

Continuing in the exploration of reactions that yield new carbon-to-carbon bonds, this week's lab focuses on the Wittig reaction. In this reaction, an aldehyde or ketone is combined with an organophosphorus ylide to join the molecules and create a carbon-carbon double bond. Most significantly, the double bond's location is completely fixed when this reaction is used.¹² In the selected procedure, an aldehyde (9-anthraldehyde) reacts with a substituted ylide ((carbethoxymethylene)triphenylphosphorane) to yield (2E)-3-(9-anthryl)acrylic acid. As seen in Scheme 5, the new carbon-carbon double bond is formed between the carbon that was the carbonyl carbon on the aldehyde and the carbon that was double bonded to the phosphorus on the ylide.

Scheme 5. Wittig reaction using 9-anthraldehyde and ylide.



Supplemental Information

For lab, it would be helpful to review technique for recrystallization. Conceptually, it would be beneficial to review the mechanism for the Wittig reaction so as to better visualize the product.

Caution should be taken to not overheat the sand bath since it requires considerable time to cool down. To best utilize time in lab, heat it gradually so that it is easily maintained at the desired temperature.

During the experiment, qualitative data suggests the success of the reaction. Keeping an eye on color is significant. Additionally, quantitative data from the melting point and the percent yield can reveal the quality of the reaction.

Procedure⁹

Preheat a sand bath to 120° C over a hot plate. Add 103 mg of 9-anthraldehyde and 184 mg of (carbethoxymethylene)triphenylphosphorane to a 25 mL round bottom flask with a stir bar. Insert the round bottom into the sand bath once the temperature of the sand bath is holding steady at 120° C. Watch for the solid to melt. Once melted, continue stirring the reaction mixture for an additional 15 minutes before removing the flask and cooling it to room temperature. Add 3 mL of hexanes to the flask and stir for several minutes.

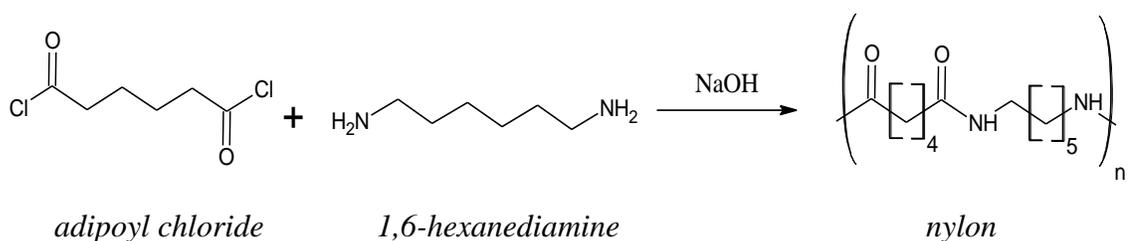
Using a filtering pipette, remove the solvent and place it into a clean flask. Add an additional 3mL more of hexanes, stir again, and then remove the solvent and add it to the previously collected solvent. Concentrate the solution, and if time allows, recrystallize in 1 mL of hot methanol. Vacuum filter, weigh the product, and analyze by melting point.

Polymer Chemistry: Synthesis of Nylon and Polyester

Introduction

This week's lab serves as an introduction to polymer chemistry. Both reactions include nucleophilic acyl substitutions of monomers to create a polymer product.¹ The diversity of properties among polymers makes them interesting to study since the interactions between chains dictates whether a polymer will be thin and flexible, like in plastic wrap, or highly durable, like in Kevlar.¹³ In the selected procedure, monomers of 1,6-hexanediamine and adipoyl chloride come together to form a common textile polymer called nylon. This process joins the monomers between the nitrogen of the amine and the carbonyl carbon of the acid chloride, thus creating an amide polymer with HCl as a byproduct (seen in Scheme 6). Additionally, this lab includes the synthesis of a polyester polymer by crosslinking a diacid anhydride (phthalic anhydride) with glycerol (seen in Scheme 7).¹

Scheme 6. Synthesis of nylon 6,6.



Procedure**Nylon⁶**

Add 10 mL of a solution of 5% m/v 1,6-hexanediamine (dissolved in 3% m/v sodium hydroxide) to a 50 mL beaker. If a colored product is desired, add food coloring. Next, being careful not to disturb the 1,6-hexanediamine solution, slowly add 10 mL of a 1.5% v/v solution of adipoyl chloride in cyclohexane to the beaker. After a film begins to form, pull strands of nylon from the reaction using a metal spatula. Wash the nylon strands with water and dry with a paper towel. Record the mass of the nylon.

Polyester⁴

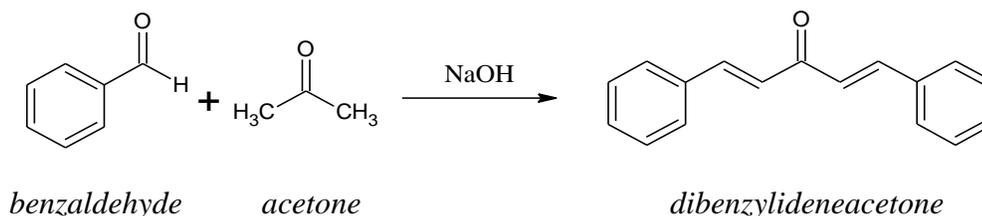
Select a test tube and weigh it. Add 2 g of phthalic anhydride, 0.9 g glycerol, and 0.1 g of anhydrous sodium acetate into the test-tube. Using a Bunsen burner, slowly heat the mixture to a boil and continue heating until the solution turns light orange (3-5 minutes). Allow the solution to cool and thicken for one minute. Attempt to draw out fibers from the polyester you have made. Record observations and weigh the product in the test tube.

Aldol Reaction

Introduction

In this week's lab, the Aldol reaction concludes the CHEM 302L exploration of reactions that yield new carbon-to-carbon bonds. This reaction gets its name from the product it creates prior to dehydration: a molecule with both a carbonyl and β -alcohol functional groups.¹⁴ In the selected procedure, acetone is converted to an enolate in the presence of NaOH. The enolate can then act as a nucleophile and attack the electrophilic carbonyl carbon of benzaldehyde. A subsequent protonation yields the aldol product. Afterwards, the aldol product undergoes dehydration, removing the hydroxyl group and leaving behind a double bond. A benzaldehyde can attach to both available sites of acetone enolate, yielding dibenzylideneacetone (seen in Scheme 8).

Scheme 8. Aldol reaction between benzaldehyde and acetone.



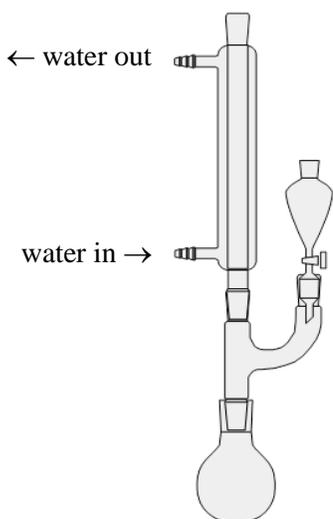
Supplemental Information

Given the two-part mechanism (reaction and dehydration) involved in this procedure, it may be valuable to review these steps to fully grasp what is taking place in lab. A reflux set-up with an addition funnel is needed (seen in Figure 5), so understanding this technique is required.

The percent yield and melting point provide quantitative data for evaluating the successfulness of this reaction.

Procedures⁶

In an Erlenmeyer flask, dissolve 0.6 g of sodium hydroxide in 6 mL of water. Next, add 4 mL of 95% ethanol to the flask slowly, and then allow the solution to cool to room temperature. Into a 50 mL round bottom flask, add 8 mL of benzaldehyde and a magnetic stir bar. Add the previously prepared sodium hydroxide solution to the round bottomed flask. Fit the round bottom flask with a Claisen head, reflux condenser, and an addition funnel. With the stopcock closed, add 3 mL of acetone to the addition funnel, and start circulating water through the reflux condenser. Over the course of five minutes, add the acetone dropwise to the reaction. Allow the exothermic reaction to stir for 30 minutes. After stirring for 30 minutes, collect the crude dibenzylideneacetone by vacuum filtration. Wash the crude product with 10 mL portions of water until the pH of the filtrate is neutral. After all washes are completed, dry the crude dibenzylideneacetone by



pulling air through the solid for 20 minutes using the vacuum filtration apparatus. If enough time remains, recrystallize the crude dibenzylideneacetone using a minimal amount of hot 95% ethanol. Measure the mass and determine a melting point for the product.

Figure 5. Glassware set-up for reflux with an addition funnel.

References

- (1) Wade, L. W.; Simek, J. W. *Organic Chemistry: Ninth Edition*; Pearson: Glenview, IL, **2017**.
- (2) Hardinger, S. Proton Nuclear Magnetic Resonance Spectroscopy H-NMR [PDF]. https://www.chem.ucla.edu/~harding/notes/notes_14C_nmr02.pdf (accessed Sep 29, 2019).
- (3) Bodner Research Group at Purdue University. Grignard Reagents. <http://chemed.chem.purdue.edu/genchem/topicreview/bp/2organic/grignard.html> (accessed Aug 20, 2019).
- (4) Fulp, A. Liberty University, Lynchburg, VA. Personal communication, 2019.
- (5) Azman, A. Diels-Alder Reaction. *Chem Eng News* **2011**, 89, 34.
- (6) Hemric, M. *Organic Chemistry Exploration: Organic Chemistry Laboratory*; Academx: Sagamore Beach, MA, 2013.
- (7) Antic, D. picoSpin™ 80: Microscale Friedel-Crafts Acylation of Ferrocene: Acetylferrocene [PDF]. <https://assets.thermofisher.com/TFS-Assets/CAD/Vector-Information/pS80-Friedel-Crafts-Acylation-of-Ferrocene.pdf> (accessed Aug 23, 2019).
- (8) MIT Department of Chemistry. The Preparation of Ferrocene and Acetylferrocene [PDF]. https://ocw.mit.edu/courses/chemistry/5-310-laboratory-chemistry-fall-2017/labs/MIT5_310F17_Ferrocene_Lab.pdf (accessed Aug 24, 2019).
- (9) Korn, M. *CHEM 302 Organic Chemistry 2 Laboratory*; Academx: Bel Air, MD, 2016.

- (10) Coskun, O. Separation techniques: Chromatography. *North. Clin. Istanbul*. **2016**, *3*, 156-160.
- (11) Gung, B. How to run column chromatography [PDF].
<http://chemistry.miamioh.edu/gung/CHM244/pdfs/column.pdf> (accessed Aug 26, 2019).
- (12) Organic Chemistry LibreTexts Supplemental Modules: The Wittig Reaction.
[https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Supplemental_Modules_\(Organic_Chemistry\)/Aldehydes_and_Ketones/Reactivity_of_Aldehydes_and_Ketones/The_Wittig_Reaction](https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Supplemental_Modules_(Organic_Chemistry)/Aldehydes_and_Ketones/Reactivity_of_Aldehydes_and_Ketones/The_Wittig_Reaction) (accessed Aug 26, 2019).
- (13) Harris, F. W. Introduction to Polymer Chemistry. *J. Chem. Educ.* **1981**, *58*, 837-843.
- (14) Hunt, I. The Aldol Reaction of Aldehydes.
<http://www.chem.ucalgary.ca/courses/350/Carey5th/Ch18/ch18-3-4.html>
(accessed Aug 28, 2019).
- (15) Royal Society of Chemistry, *The Merck Index: An Encyclopedia of Chemicals, Drugs, and Biologicals*; RSC Publishing: Cambridge, UK, 2013.
- (16) SciFinder Substances. <https://scifinder-cas-org> (accessed Sep 2, 2019).
- (17) Fisher Scientific Safety Data Sheets.
<https://www.fishersci.com/us/en/catalog/search/sdshome.html> (accessed Aug 23, 2019).
- (18) Sigma Aldrich Safety Data Sheets. <https://www.sigmaaldrich.com/safety-center.html> (accessed Aug 23, 2019).

- (19) Wichert, M. "Synthesis of 9,10-dihydroanthracene-9,10- α,β -succinic acid anhydride," ETH Zurich, 2004.
- (20) PubChem Compound Summary. <https://pubchem.ncbi.nlm.nih.gov/> (accessed Aug 23, 2019).

Appendix: Keys

[Grading keys for each lab have been removed for curriculum security.]