CHEMISTRY 344 - Organic Chemistry Laboratory II – Spring 2012
Lab #2: Grignard Reaction: Preparation of Triphenylmethanol (two weeks)

In this lab you will study the Grignard Reaction, a classic reaction in organic chemistry, and will be applying this procedure to the synthesis of triphenylmethanol from simpler starting materials. You will purify your product by crystallization, and characterize it by melting point.

Pre-lab Reading: You are expected to read the procedure attached to this outline. You will recrystallize the product, and characterize it by melting point.

Pre-Lab Notebook Preparation: Complete the following information in your lab notebook before your pre-lab recitation. Use the numerals and headings as given.

Table of Contents: You will need to update the Table of Contents for each new lab with the date and brief title of each experiment, and the notebook page number on which the lab begins.

I. Title of the Experiment and Date.

II. Purpose of the experiment: One- or two-sentences describing what you are going to do and why. State your experimental goals.

III. Equations: Write the balanced equation for this reaction, ***including structures***.

IV. Table of Reagents: In your lab notebook create a table, like the one shown below, for the following reagents used in this lab: **diethyl ether, bromobenzene, benzophenone.** Your table must include the name, structure and all physical data. You can find this information in the Aldrich Chemical Catalog, the Merck Index, or on-line from the **ChemIndex** web site. The link to ChemIndex and instructions can be found on Dr. Brush's Lab web site: **http://webhost.bridgew.edu/ebrush/CH343%20Lab.htm**.

Chemical name and formula	structure	molecular mass (g/mole)	melting point (solids) (^{o}C)	boiling point (liquids) (^{o}C)	density (liquids) (g/mL)

V. Procedure: Summarize the lab procedure in your notebook. Do not copy the procedure word-for-word.

VI. Health, Environmental, and Waste disposal: Look up and summarize some of the health and environmental hazards for **bromobenzene** at the MSDS database: **http://hazard.com/msds/index.php**

***Laboratory Book*: The following should be completed before leaving lab, initialed and dated by you.**

VII. Data and Observations: Record a rough transcript of your experimental method in your lab notebook, indicating what you actually did and what you actually observed. Do not prepare this section in advance. This section should be written in a paragraph format and include: **experimental procedure, all reagent mass and volume measurements, observations, crude and pure product mass or volume, % yield calculations, and product analysis by melting point, chromatography analysis, or instrument analysis.** You will be judged on the depth of your observations and technical success (yields, purity, etc.).

VIII. Discussion and Conclusions: A brief, but critical evaluation of your results, and the success of your experiment. Address the experiments goals and purpose!

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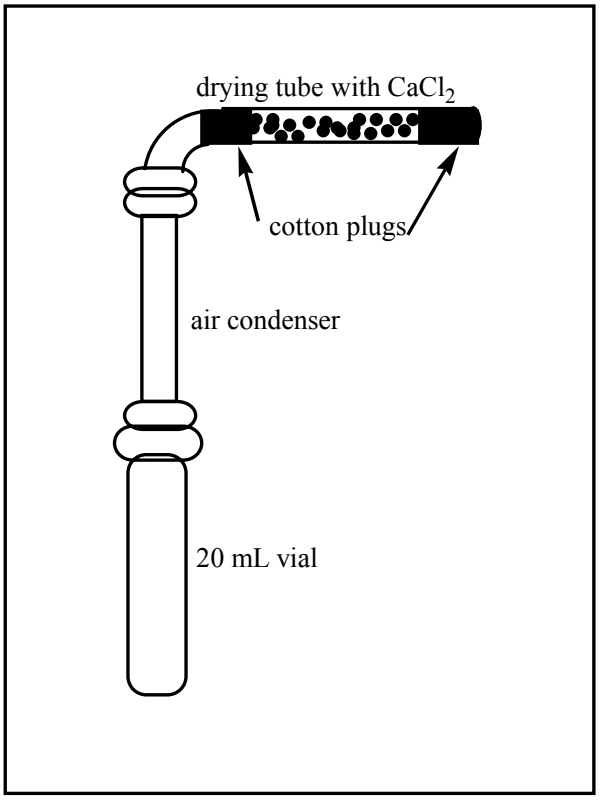
Experimental Procedure

The following **dry** glassware may be found in the desiccated cabinet located near the balances: drying tube, air condenser, 20 mL screw top vial, 25 ml Erlenmeyer flask, glass syringe, and a Pasteur pipette. **DO NOT wash this glassware!** This glassware has already been oven-dried, as traces of water on the glass surface will react with the Grignard reagent. Prepare a calcium chloride drying tube using cotton plugs. Assemble the drying tube, air condenser, and 20 mL vial as shown in the picture below.

Lab #2 is scheduled as a two-week lab. You should try to complete as much as possible in week #1, but should stop after Step II.

I. Formation of the Grignard Reagent. Keep all glassware dry! Obtain about 0.25 grams of Mg ribbon, and scrape off any white, oxidized MgO from the surface with a spatula to reveal the shiny metal underneath. Wipe the strip(s) with a paper towel to remove oil and dirt from your fingers or gloves, and cut the strip(s) into small pieces (0.5 cm or less). Add the Mg to your pre-weighed 20 mL reaction vial, and determine the exact mass of the Mg pieces (final mass must be between 0.19 - 0.2 g). Record the mass of the vial + Mg. Using the dry glass syringe carefully add 1.20 g of bromobenzene to the vial. Using the dry Pasteur pipette add about 5 mL of diethyl ether to the vial (ca. five additions from a Pasteur pipette). Mark the liquid level in the vial with a marking pen. The ultrasonic bath (sonicator) is in a hood and should contain tap water at approximately 30^0C. Place your vial in the test tube rack in the sonicator. The reaction should start within five minutes as the mixture will begin bubbling and take on a gray color. If no reaction begins in 10 minutes, your reaction has become contaminated with water and you need to start over. As the bubbling becomes more vigorous the reaction mixture eventually turns brown. If you estimate that more than 50% of the ether evaporates, you may need to remove the drying tube and add an additional 2-3 mL of ether from a Pasteur pipette. The reaction is complete in 45 minutes, or when nearly all the Mg has been consumed. Remove your vial containing the Grignard reagent from the sonicator bath and cool to room temperature. DO NOT remove the drying tube at this time.



II. Addition of benzophenone. This step must be done quickly to avoid contamination by water! In this step it is imperative that you do not allow any water to enter the reaction vial. Obtain 1.40 grams of benzophenone in a dry 3 mL reaction vial, and dissolve in 2 mL of diethyl ether. Remove the air condenser from the reaction vial and slowly add the benzophenone dropwise to the Grignard reagent over a 5 minute time period, while stirring with a spatula. Do not add the benzophenone too quickly or the heat from this exothermic reaction may cause the mixture to boil. The mixture may turn a pink or red color, and may even solidify as the alkoxide salt of triphenylmethanol forms. You DO NOT need the drying tube any more.
Stop here for the 1st week.

III. Isolation of crude triphenylmethanol. Cool the reaction vial containing the alkoxide salt in an ice bath. Obtain 5 mL of 6 M HCl (CAUTION!) and add this solution dropwise to the cold reaction mixture, while stirring with a spatula. Two reactions are occurring, protonation of the alkoxide salt (which is exothermic), and H_2 gas being released as excess Mg is oxidized to Mg^{+2} with reduction of H^+. You can now work with the reaction mixture at room temperature. Using pH paper, verify that the mixture is acidic (add more HCl if not). Now add 5 mL of ethylacetate, and stir with a spatula. You should now have two distinct layers with the triphenylmethanol dissolved in the ethylacetate layer. If you do not see two layers (emulsion), pipet the entire reaction mixture into a centrifuge tube and centrifuge for 1 minute. Carefully transfer the organic layer into a test tube. Add 2 mL of ethylacetate to the remaining aqueous solution, stir for 1 minute, and combine this organic layer with the first organic extract. Now add magnesium sulfate, $MgSO_4$, to dry the organic layer, mix with your microspatula, and leave the mixture for at least 10 minutes (with occasional mixing) at room temperature.

While waiting for the organic layer to dry, clean and dry your 25 mL Erlenmeyer flask, and obtain its empty mass. Pipet the dry organic layer into theflask, being careful to leave the $MgSO_4$ behind. Wash the remaining $MgSO_4$ by adding 1-2 mL of fresh ethylacetate, stir, and allow the solid to settle for at least one minute. Transfer this portion to the flask. If you are careful, you should be able to tilt the test tube without disturbing the $MgSO_4$, and recover additional ethylacetate solution. Evaporate for 30-40 minutes the volatile organic solvents, and obtain the mass and melting point of your crude triphenylmethanol.

IV. Crystallization from 2-propanol. Place a round spin bar in your 25 mL Erlenmeyer flask, and add 1 mL of 2-propanol (isopropanol) for every 0.1 g of crude product. Heat the mixture, with stirring, to 80^oC. If undissolved solid remains at 80^0C, add additional 2-propanol (5 drops at a time) until the solid just dissolves (no more than 20 extra drops). Record the total volume of 2-propanol added. Allow the hot, saturated solution to cool slowly at room temperature. If no solid forms in 10 minutes, scratch the inside bottom of the flask with a glass rod. Once crystallization has begun place the flask in an ice bath for 5 minutes. Isolate the product by filtration on a Hirsch funnel, and wash with 1-2 mL of **ice-cold** 2-propanol. Scrape the crystallized triphenylmethanol onto a watch glass, and dry the product in an 80^0C oven for 15-20 minutes. Obtain the mass and melting point of the dry, purified triphenylmethanol.

Don't forget to record the following information in your notebook:

- Mass of Mg used in the reaction
- Mass of bromobenzene used in the reaction
- Mass of benzophenone used in the reaction
- Mass of dry, crude product
- Melting range of dry, crude product
- % Yield of dry, crude product
- Total volume of isopropanol used for recrystallization
- Mass of dry, crystallized product
- Melting range of dry, crystallized product
- Literature melting range
- % Yield of dry, crystallized product
- Mass and volume of the waste you collected

Name:_____ **Lab Partner**_____

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Lab Report Grade _____(100 points)

The following questions are based on your pre-lab reading and the results of your experiment. You and your lab partner are encouraged to work together, but you must each turn in your own report! Answer each question in the space provided, and **show all calculation work below or on a separate sheet of paper**.

1. The Grignard reaction consists of three steps: preparation of the Grignard reagent; the reaction between the Grignard reagent and a carbonyl compound to form an alkoxide salt; and neutralization of the salt to form the alcohol product. Write three balanced equations for the synthesis of triphenylmethanol from bromobenzene, Mg, and benzophenone:

(a) Synthesis of the Grignard reagent.

(b) Reaction of the Grignard reagent with benzophenone:

(c) Neutralization of the alkoxide salt with aqueous H_3O^+

2. The Grignard Reagent is "very sensitive to water". What does this mean? Write the chemical equation for the reaction between water and the Grignard reagent from above.

3. Crude Product.

Mg used in the reaction: mass_____ moles_____

Bromobenzene used in the reaction: mass_____ moles_____

Benzophenone used in the reaction: mass_____ moles_____

What is the limiting reagent? _____

Theoretical yield: mass _____ moles _____

Crude product: mass_____ moles_____

% Yield of crude product: _____

Melting range of crude product: _____

Literature melting point for triphenylmethanol: _____

4. Recrystallized Product.

Mass of crude triphenylmethanol used in the recrystallization step: _____

Total volume of isopropanol used: _____

Dry, recrystallized triphenylmethanol: mass_____ moles_____

% Yield of recrystallized triphenylmethanol: _____

Melting range of recrystallized product: _____

Literature melting point for triphenylmethanol: _____

5. Yield. If your %Yield of crystallized product is less than 75% OR greater than 100%, provide an explanation. A short paragraph is expected.

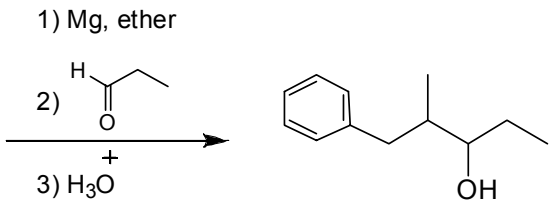
6. Melting Range. If the melting point of your crystallized product is more than 3^{o}C below the literature value of pure triphenylmethanol, or the melting range is more than 3^{o}C, provide an explanation. A short paragraph is expected.

7. Evaluation. Was your experiment a success? Consider your goals, observations, mp, and yield data. A short paragraph is expected.

8. Grignard Reactions. Complete each reaction shown below with the structure of the expected product.

(a) 

(b) 

(c) 

(d)