Experiment 4

Synthesis of Triphenylmethanol

Objectives

- To use the Grignard reagent in a water free environment.
- To react the Grignard reagent with a ketone and an ester.
- To purify the product via recrystallization.
- To assess the purity of the product by determining its melting point.
- To perform a cost-analysis of the two reactions.

In the Lab

- Students work in pairs

After Lab

- Complete the Chem21 assignments

Waste

- Place aqueous solutions (from the separatory funnel) in the waste container labeled **Aqueous Waste** located in the Instructor's hood.
- Place organic solutions (ligroin and isopropyl alcohol) in the waste container labeled **Organic Waste** located in the Instructor's hood.

Safety

- Students must wear goggles for this experiment.
- Students must wear gloves when handling the Grignard reagent.
- Diethyl ether is extremely flammable – No Flames!!

Experiment 4 • *Triphenylmethanol (TPM)*

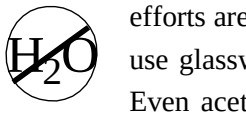
A chemical company has approached the Chemistry Department at Lee University and asked us to supply them with 50 lbs of triphenylmethanol per week. After researching the chemical literature, two methods (A & B) of producing triphenylmethanol were found. The question that you will answer in this lab is "which method gives the greatest profit margin to the Lee University Chemistry Department?" All of the chemicals can be purchased from the Aldrich Chemical Company as follows:

Benzophenone (500 g)	$18.40
Methylbenzoate (500 g)	$13.55
Bromobenzene (500 mL)	$21.30
Magnesium turnings (250 g)	$85.00

Assume that the amounts of the other reagents are similar in the two methods and will not affect the final outcome. You will use the stoichiometry of the two processes, the percent yield of each method, and the costs of the chemicals to determine which method provides the greatest profit to the Lee University Chemistry Department. Because the Grignard reagent is very reactive and difficult to store, it will be made for you so you can start two labs:

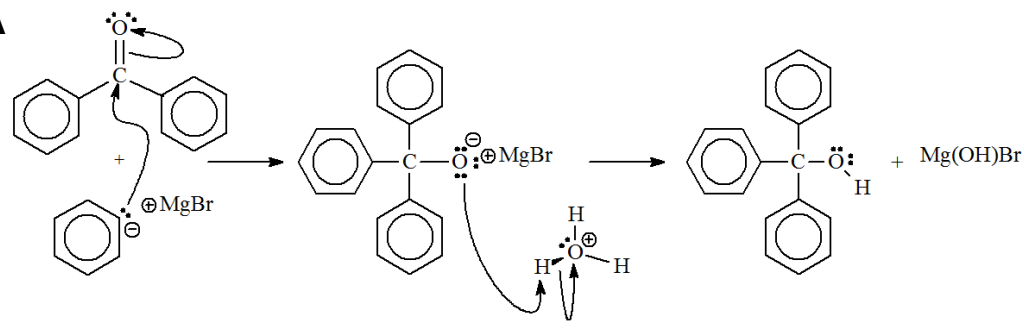
- **Lab 4 Method A** - Phenylmagnesium bromide + Benzophenone (ketone)
- **Lab 4 Method B** - Phenylmagnesium bromide + Methylbenzoate (ester)
- **Laboratory 5** - Phenylmagnesium bromide + Carbon dioxide (CO_2)

One of the most destructive environments for the Grignard reagent is one that contains even the slightest amount of water. Therefore, it is imperative that meticulous efforts are made to exclude water from coming into contact with this reagent – if the choice is to use glassware that is dry but dirty or recently cleaned, **choose the dry but dirty glassware!!** Even acetone, a commonly used solvent to remove water from glassware, will react with the Grignard reagent to form a tertiary alcohol. If acetone is used to dry glassware, make sure all traces are removed by pulling air through the glassware with a vacuum line or aspirator.



Mechanism

Method A



Method B

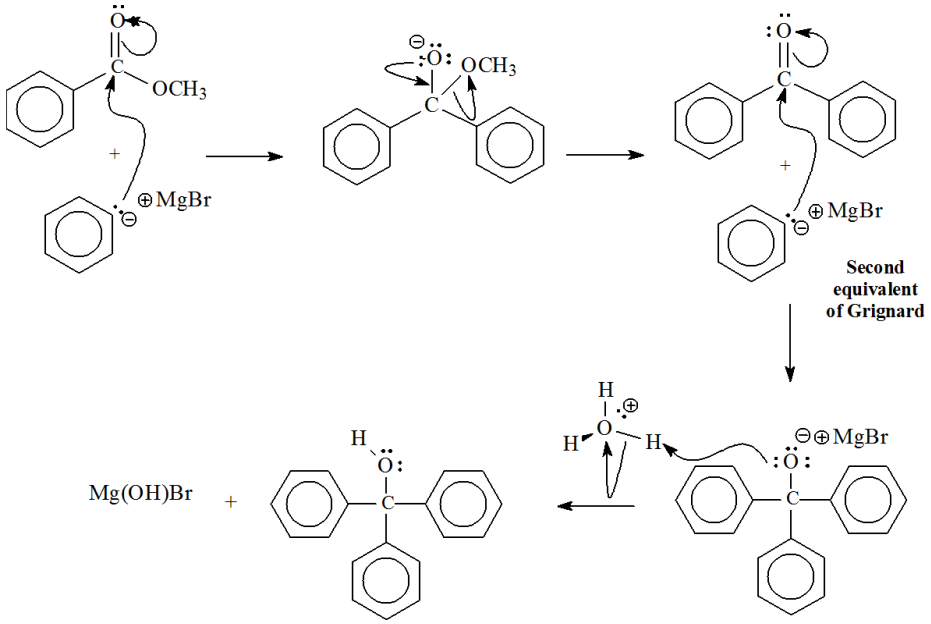


Table of Physical Constants

Chemical Name	Chemical Formula	Molecular Weight	Melting Point	Boiling Point	Density	n_D^{20}
Benzophenone	$(C_6H_5)_2CO$	182.22	48-49			
Methyl Benzoate	$C_6H_5CO_2CH_3$	136.15		198-199	1.094	1.5170
Ether	$(C_2H_5)_2O$	74.12		34.6	0.715	1.3530
Hydrochloric Acid	HCl	36.46			1.190	
Sodium sulfate	Na_2SO_4	142.04	884		2.680	
Petroleum Ether [Ligroin]	C_5H_{12}			60 - 80	.656	1.3760
Calcium Chloride	$CaCl_2$	110.99			2.150	
Triphenylmethanol	$(C_6H_5)_3COH$	260.34	160-163			
Magnesium	Mg	24.31				
Bromobenzene	C_6H_5Br	157.02	C*	156	1.491	

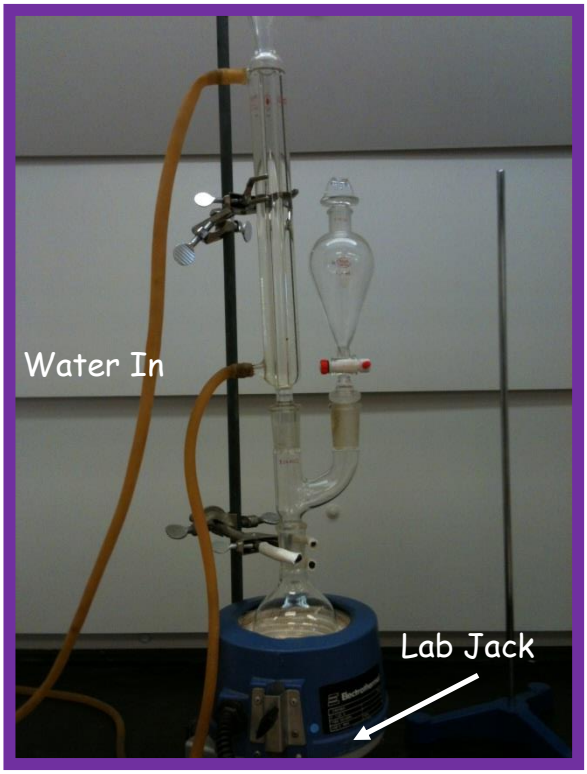
Table 1

Day 1 –Grignard (Lab 5)

1. **Wear Gloves**!! Start Lab 5 first.

Day 1 –Grignard (Lab 4)

2. Set up the apparatus show below using a 250 mL RBF. Turn on the water.



Making TPM (Method A)

3. In the hood, obtain 40 mL of the Grignard reagent in a dry 50 mL graduated cylinder.
4. Place 20 mL of the Grignard reagent in the separatory funnel and open the stopcock so it pools in the RBF.

- **Place a small beaker (inverted) over the graduated cylinder to prevent exposing the remaining Grignard to the atmosphere.**

5. Add 10 mL diethyl ether to the separatory funnel, invert twice and add the ether to the RBF.
6. Place 4.3 g ± 0.1 g [**Data Sheet**] of benzophenone and 15 mL of anhydrous ether in the separatory funnel (**use the separatory funnel "as is" (don't wash it), stopcock closed**). Swirl until the benzophenone completely dissolves.
7. Add the benzophenone solution to the Grignard reagent in the RBF at a rate that keeps this **EXOTHERMIC** reaction controlled (should take about 5 minutes). During the addition, gently move the entire ring stand to stir the reaction.
8. Next, add 5 mL ether to the separatory funnel, swirl, invert and add to the RBF.
9. Heat the solution at reflux (**liquid will drip from the condensor**) for 5 minutes.
10. After 5 minutes, remove the heat and place the RBF in a beaker in the back of the hood.

Making TPM (Method B)

11. Clamp a dry 250 mL RBF in the place of the **Method A** 250 mL RBF.
12. Place the remaining 20 mL of the Grignard Reagent in the separatory funnel and open the stopcock so it enters the RBF.
13. Add 10 mL diethyl ether to the graduated cylinder and then add this liquid to the separatory funnel, invert twice and add the ether to the RBF.
14. Add 5 mL diethyl ether to the separatory funnel, invert twice and add the ether to the RBF.
15. Place 1.61 g ± 0.1 g [**Data Sheet**] of methyl benzoate (**weigh it in a beaker**) in the separatory funnel (**use the separatory**

funnel "as is", stopcock closed). Add 10 mL anhydrous ether to the beaker that contained the methyl benzoate, swirl and add it also to the separatory funnel (invert several times to mix the methyl benzoate and ether).

16. Add the methyl benzoate solution to the RBF over a 5 minute period. Move the entire ring stand during the addition to ensure proper mixing.
17. After adding all the methyl benzoate, add 5 mL ether to the separatory funnel, invert, and add to the RBF.
18. Heat the solution and maintain reflux for 5 minutes. Remove the heating mantle after 5 minutes.

Acid Work-Up (Method B)

19. Leave the Method B RBF attached to the assembly and add 20 mL 6 M HCl to the separatory funnel (**stopcock closed!!**). Add ~ 1 mL of the acid and swirl the RBF by moving the entire ring stand. Add the remaining HCl in ~ 1 mL portions with swirling. **Keep any reflux ring in the lower third of the condenser.**

20. **Repeat Step 19 with the RBF from Method A.**

Day 2: Isolating / Purifying the TPM

21. Transfer the contents of the RBF from **Method A** to a separatory funnel. Rinse the RBF with 5 mL ether and add this to the separatory funnel. There should be two distinct clear layers in the flask – if not, add 5 mL ether and 5 mL 6 M HCl, shake twice, vent, and let stand for 5 minutes.

- **Set the separatory funnel in a ring clamp.**
- **Make sure the stopcock is closed before pouring in the solution!**
- **Use a stopper that fits snugly and doesn't leak.**
- **Make sure the funnel is pointed away from people when it is vented.**
- **When draining, the stopper must be out, or it will not drain.**
- **Always keep all layers in labeled beakers until the end of lab!**

22. Once both layers are clear (clear is not the same as colorless), separate the layers into 2 different labeled beakers.
23. Place the aqueous layer back into the separatory funnel. Add 10 mL of ether to the RBF, swirl, and place this ether in the separatory funnel with the aqueous layer. Shake the solution and allow the layers to separate and then drain off the lower water layer.
24. Place the top ether layer into the beaker containing the ether layer from the first separation (from **Step 22**).
25. Dry the ether solution by adding 1 g ± .05 g anhydrous sodium sulfate. Swirl, and allow it to sit for five minutes.
26. Decant the ether solution from the drying agent by pouring the liquid slowly into a **dry** 250 mL beaker - take care to leave the solid drying agent in the bottom of the original beaker.
27. Rinse the drying agent with 2 mL of ether and place this liquid in the 250 mL beaker from **Step 26**.
28. Place this 250 mL beaker in on a hot plate in the hood (setting 3 - 4). Allow the

ether to evaporate until there is ~ 5 - 10 mL left in the beaker (don't allow all the ether to evaporate or spattering will occur).

29. Add 25 mL high boiling petroleum ether (ligroin) to the beaker and place the beaker back on the hot plate until the volume decreases to ~ 25 mL (you essentially only have ligroin in the beaker since all the ether, with a boiling point of 40ºC, has evaporated).

30. Place the beaker in an ice bath for 5 minutes – take steps to ensure that the beaker does not "**tip**" over.

31. Collect the crystals by vacuum filtration on a Büchner funnel.

- **Place the Büchner funnel with its rubber stopper on top of the filter flask.**
- **Secure the top of the filter flask with a clamp.**
- **Attach the hose from the vacuum "trap" to the side of the filter flask.**
- **Place an appropriately sized filter paper in the Büchner funnel and turn the vacuum on.**
- **Seat the filter paper with Ligroin.**
- **Transfer the crystals to the filter paper - use 5 mL of cold ligroin to aid in the transfer.**
- **As soon as the filtrate has collected in the filter flask, rinse the crystals with 5 mL of cold ligroin.**
- **Once this ligroin has exited the crystals, TURN THE VACUUM OFF.**

32. Weigh and record the mass of TPM produced in Method A[**Data Sheet**].

33. **Repeat Steps 21 – 32 for Method B – it is not necessary to rinse out the separatory funnel**.

34. After weighing and recording the mass of Method B crystals, combine them with the Method A crystals – **you do not need to weigh the mixed crystals**.

35. Place the crystals on a watch glass and put them in the drying oven for 10 minutes.

36. Remove the crystals from the oven and pack a melting point tube with them. Label the melting point tube "Impure TPM".

Purifying TPM

37. Recrystallize the impure TPM (the combined crystals) from a minimal amount of hot isopropyl alcohol (IPA).

- **Place 5 mL IPA in a test tube and cool in an ice bath.**
- **Place your TPM in a 100 or 150 mL beaker.**
- **Add 20 mL IPA (not the 5 mL cooling in the ice bath!!).**
- **Heat to boiling for 20 seconds.**
- **If ≥ 95 % of the crystals have dissolved, place the beaker on the lab desk to cool. If < 95% of the crystals have dissolved, add 10 mL IPA and heat to boiling again.**
- **Repeat the previous step until more than 95% of the crystals have dissolved.**
- **After cooling for 5 minutes on the lab desk, place the beaker in an ice bath for 5 minutes.**
- **Collect the crystals by vacuum filtration (seat the filter paper with room temperature IPA).**

- **Wash the crystals with 5 mL ice-cold IPA**.

38. Place the triphenylmethanol in a labeled, uncapped vial and place it in the oven for 10 minutes.
39. Remove the TPM from the oven and allow it to cool for 5 minutes. Pack a melting point tube and label it Purified TPM.
40. Place a cap snugly on the vial, affix the provided label and turn it in to your Instructor.
41. **Go to Lab 5 and complete Steps 4 – 18.**

Day 3 – Analyzing the TPM

42. Prepare a melting point of the
    - **Impure TPM**
    - **Purified TPM**
    - **Pure TPM (from Instructor)**
43. Record the melting point range of each sample. The first number in the range is the temperature when the crystals just begin to melt, the second number in the range is the temperature when 90% of the crystals have melted) [**Data Sheet**].
44. Take a picture of the melting point apparatus (the picture must include the melting point tube and the digital readout) when the **Purified TPM** just begins to melt.
45. Take a picture of the melting point apparatus (the picture must include the melting point tube and the digital readout) when the **Purified TPM** is ~ 90 % melted.
46. Send these images to your email and save them on your computer. During the online lab submission, you will upload these images to Chem21Labs.
47. Place the used melting point tubes in the glass trash.

Lab Report

Once you have turned in your Instructor Data Sheet, lab attendance will be entered and you will have access to enter your lab data online and begin the lab submission process. In the hallway, enter you lab data by accessing www.chem21labs.com with your phone or computer.

Lab 4
Triphenylmethanol
Name: _____
Mass: _____ **g**

Synthesis of Triphenylmethanol

Student Data Sheet

Mass of Benzophenone (Method A) (~4.3 g)	______ g
Mass of Methylbenzoate (Method B) (~ 1.61 g)	______ g
Mass of Triphenylmethanol (TPM) (Method A)	______ g
Mass of Triphenylmethanol (TPM) (Method B)	______ g
Melting Point Range of Impure TPM	___ - ___ ºC
Melting Point Range of Recrystallized TPM	___ ___ ºC
Melting Point Range of Pure TPM	___ - ___ ºC

✂ -

Name:______________________

Partner:____________________

Synthesis of Triphenylmethanol

Instructor Data Sheet

Mass of Benzophenone (Method A) (~4.3 g)	______ g
Mass of Methylbenzoate (Method B) (~ 1.61 g)	______ g
Mass of Triphenylmethanol (TPM) (Method A)	______ g
Mass of Triphenylmethanol (TPM) (Method B)	______ g
Melting Point Range of Impure TPM	___ - ___ ºC
Melting Point Range of Recrystallized TPM	___ ___ ºC
Melting Point Range of Pure TPM	___ - ___ ºC