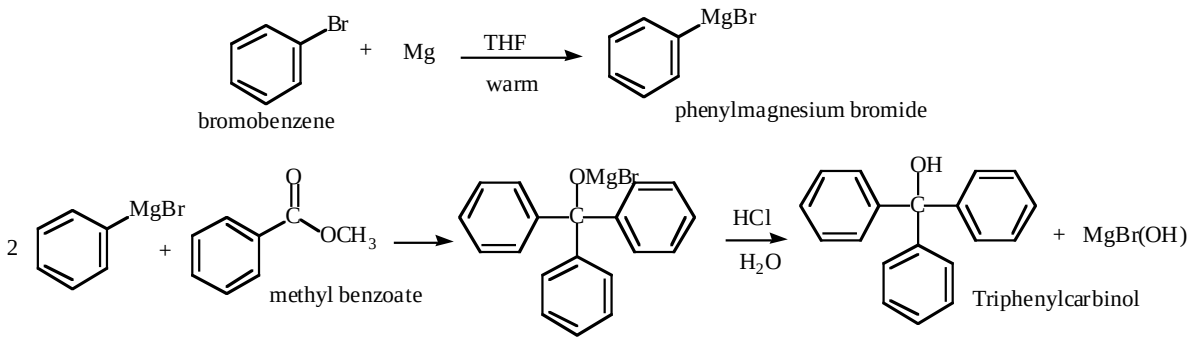
Experiment 12
Grignard Reaction; Preparation of Triphenylcarbinol

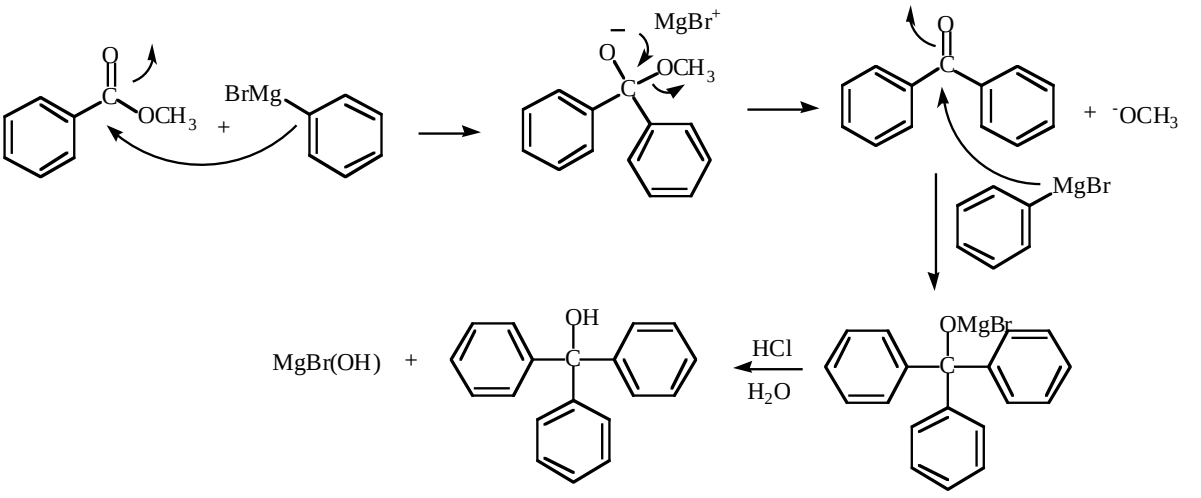
In this experiment we will perform a Grignard addition to an ester. First we will form the Grignard reagent from magnesium and bromobenzene and then we will add it to methyl benzoate to produce triphenylcarbinol (also called triphenylmethanol). The overall sequence is shown in Figure 12.1 and the mechanism for the addition is shown in Figure 12.2.

Figure 12.1 Grignard Addition to Methyl benzoate



Since we are using an ester as our electrophile in this reaction, the nucleophilic Grignard reagent, prepared from the bromobenzene and magnesium, will add to the carbonyl two times to give the triphenyl adduct that on treatment with aqueous acid gives the free alcohol. Note that we have a ketone intermediate. This is even more reactive than the starting ester (why?) and reacts again with the Grignard reagent.

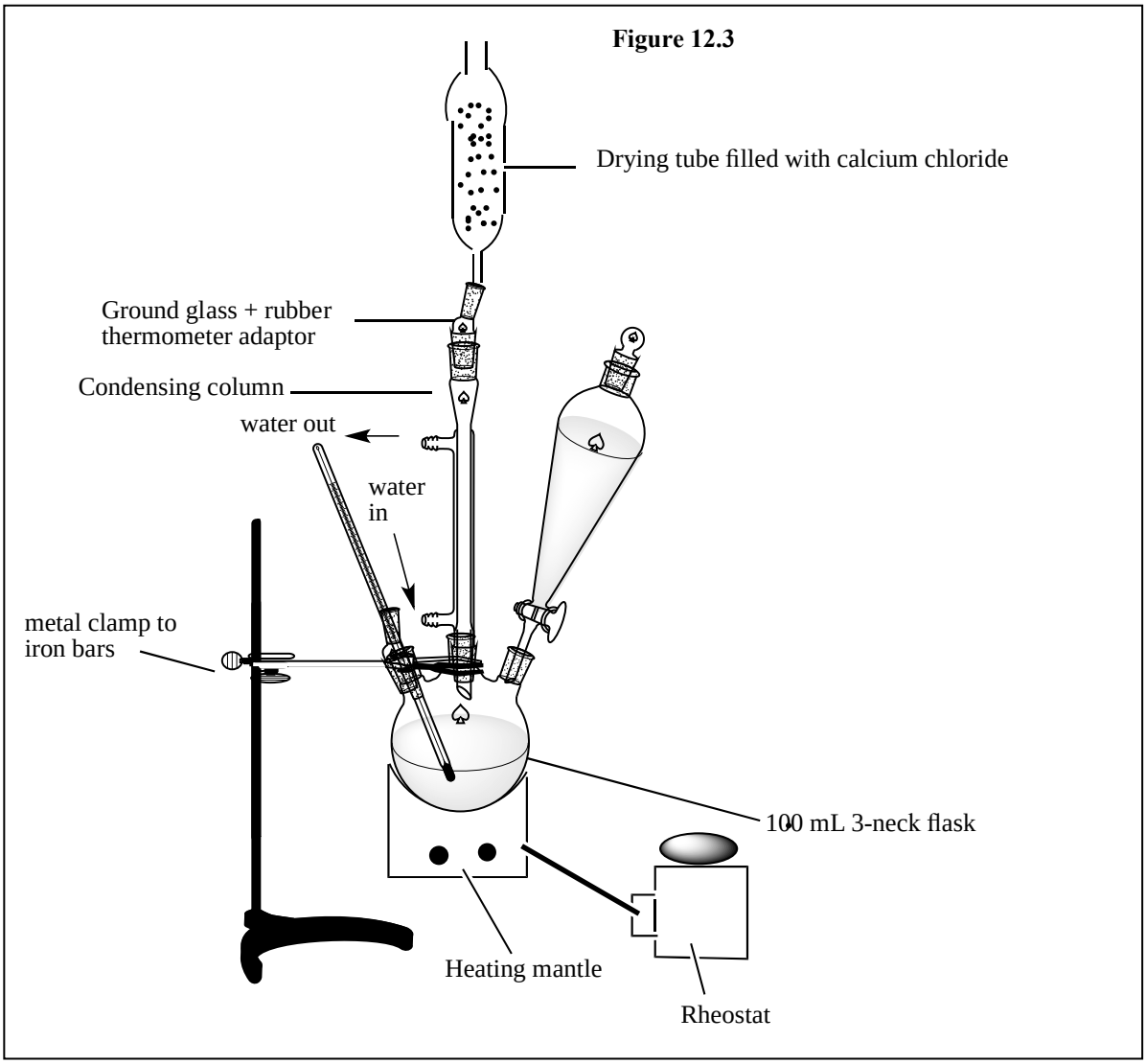
Figure 12.2 Mechanism for Grignard Addition



Physical Constants

Compound	Mol. Wt (g/mol)	Density (g/mL)	b.p. (°C)	m.p. (°C)
Bromobenzene	157.02	1.491	156	-31
Methyl benzoate	136.15	1.094	198-199	-12
Magnesium	24.31	1.740	-	648
Triphenylcarbinol	260.34	solid	360	160-163
Tetrahydrofuran (THF)	72.11	0.889	65-67	-108

Figure 12.3



Procedure:

The set-up for this experiment is shown in Figure 12.3. Grignard reagents are very strong bases and are very sensitive to water and humid air. We need to use a calcium chloride drying tube. The purpose of the tube is to remove moisture from the atmosphere. We can not just use a ground glass stopper because we do not want to heat a closed system since pressure will build up as the heated gases inside expand. Use of the drying tube creates a system that is open to the atmosphere. This allows pressure inside the heated flask to escape and

allows air from the atmosphere to re-enter the flask. The $CaCl_2$ removes any water that may be contained in the air. Moisture would react with our highly basic Grignard reagent to destroy it.

We also need to make sure our glassware is dry. It is a good idea to flame dry your glassware using your Bunsen burner. Do this carefully using a low, blue flame. Remove all the stoppers and the stopcock from your separatory funnel and there should of course be no reagents inside separatory funnel or the 100 mL flask. Do not have the water hoses connected to your condensing column and also remove the drying column. Start at the bottom of the 100 mL round bottom, moving the flame back and forth for a few seconds and working your way upward. Water vapors should be visible rising up the inside of the glassware. Chase these vapors with the flame. You do not need to get the glassware extremely hot and be careful not to melt or burn the plastic covers on the metal clamps. (You should have a clamp that has flame resistant-fabric coating the prongs).

After flame drying, reattach your drying tube, stoppers, etc. while the glass is still hot and allow the glassware to cool before proceeding.

Weigh out 1.3 g of magnesium chips and place them inside the round bottom flask. Add 1-2 small crystals of iodine using your spatula. Add 5.0 mL bromobenzene in 15 mL of dry tetrahydrofuran (THF) to the separatory funnel, which is being used as an addition funnel. Note that your separatory funnel has a ground glass stopper (unlike the one pictured in figure 12.3) and will fit with an air-tight seal into your 3-necked reaction flask. Make certain that the two compounds are mixed well, because bromobenzene is much denser than THF and tends to settle on the bottom of the separatory funnel, unless you stir or shake it.

Prepare an ice-water cooling bath.

Introduce just enough of the bromobenzene/THF solution into the 100 mL round bottom to cover the magnesium chips. About 2-3 mL should be enough. Warm the bottom of the flask with your heating mantle with the rheostat set to about 40 V. You should see the reaction begin to initiate within a few minutes. Once you see that the reaction begins, **remove the heating mantle**. The reaction is exothermic and should maintain itself without heating. You should see the THF begin to boil and continue boiling after removing the heating mantle.

Continue adding the rest of your bromobenzene-THF solution in small portions (a few drops at a time) at such a rate that you maintain a gentle reflux of the THF in the condensing column. This is a little tricky. If you add way too much you can quench the reaction – it will stop – and you may have to heat it up again but you must be careful because then if it initiates it can be very hot and boil too vigorously. If this does occur, then use your cooling bath to moderate the reaction but **DO NOT STOP IT COMPLETELY.** The addition should take 15-20 minutes.

When all of the bromobenzene has been added, apply a gentle heat (50 – 60 volts on rheostat) and reflux until most of the magnesium has been consumed. You can tell that the reaction is proceeding by noting that the magnesium is slowly being consumed. Much of it – but not all – will disappear by the end of the Grignard formation. The solution will slowly become dark and grayish in color. If you do not see the magnesium being consumed, you may have to add more iodine and to continue heating. Consult with your instructor.

After most of the magnesium is gone, remove the heat and cool the flask, first slowly to room temperature, and then in an ice bath so that the internal temperature is 20-25 °C. **DO NOT DISASSEMBLE YOUR GLASSWARE OR EXPOSE YOUR GRIGNANRD TO THE ATMOSPHERE.**

Place 3.0 mL of methyl benzoate and 15 mL of tetrahydrofuran in the separatory funnel and add this solution slowly drop-by-drop over **10 minutes** with swirling to the Grignard solution in the flask. Do not add the methyl benzoate all at once. The reaction is exothermic and the electrophilic reagent must be added slowly. Keep the contents of the reaction flask from overheating, using the cooling bath to maintain the temperature between about 20 and 25 °C.

When all of the methyl benzoate has been added, remove the cooling bath and allow the reaction mixture to stand at room temperature for 15 minutes.

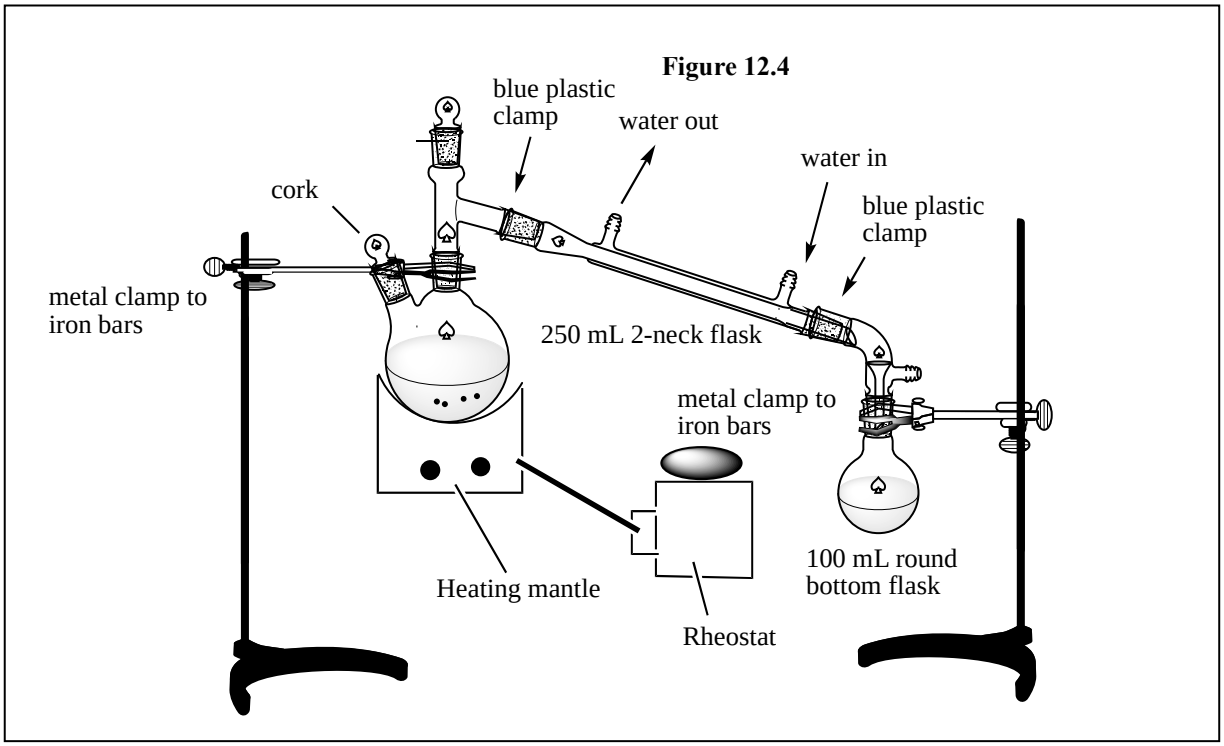
Work-up

Add 20 mL 3N HCl slowly through the top of the condenser. Add 2 mL at first and then swirl the flask in the ice bath to mix the contents. Continue adding 2 mL portions until all of the HCl has been added. Once all of the HCl has been added you need to wait 20 minutes for the hydrolysis to be complete. If there is still some solid magnesium remaining, additional 3 N HCl until the pH is acidic. Note, that if there is excess magnesium still remaining, the HCl will be consumed by reaction with the HCl and the pH can change. The reaction mixture must be acidic before you begin the distillation step described below. If you are in doubt, check the pH again. If the pH is not acidic, add more concentrated HCl by pipette in small increments until the mixture is acidic. Be sure to stir the mixture each time you add more HCl and to wait a minute or two for the neutralization reaction to proceed.

This is a convenient place to stop if you are running out of time. Stopper the flask using corks or greased ground glass stoppers and leave it in your bench until the next laboratory period.

Decant the reaction mixture away from any solid unreacted magnesium into your 250 mL round bottom flask. Add 40 mL of H_2O and set up for a simple distillation as shown in Figure 12.4. You will need a rheostat setting of 70-80 V. **Be sure to add boiling chips.** Collect about 30 mL of distillate. This is waste. Your product remains behind in the 250 mL three-necked distillation flask. Most of the impurities will distill over,

Figure 12.4



along with water, while the triphenylcarbinol remains behind in the reaction flask. The product is a yellow solid. If you reduce the volume of the liquid in your flask too much you may begin to see white magnesium salts begin to precipitate out as well. If this happens, add 10 mL more water.

When you have distilled over about 40 mL, remove the heating mantle and allow the reaction flask to cool first to room temperature and then in an ice bath. Collect the solid product that is left in the reaction flask by suction filtration. Remove the crystals from the Buckner funnel, spread them on the watch glass and let them dry until the next laboratory session. Weigh the dry solid, determine the melting point range and the percent yield. Turn in your Yield Report Sheet.