

GRIGNARD REACTION: SYNTHESIS OF TRIPHENYLCARBINOL

Note: ALL glassware must be completely clean and dry. Moisture is detrimental to the desired reaction. Reagents have been stored over molecular sieves to keep them dry in storage, but you should also keep containers closed as much as possible.

PURPOSE: To prepare a Grignard reagent and use it to demonstrate a classic and versatile type of organic reaction.

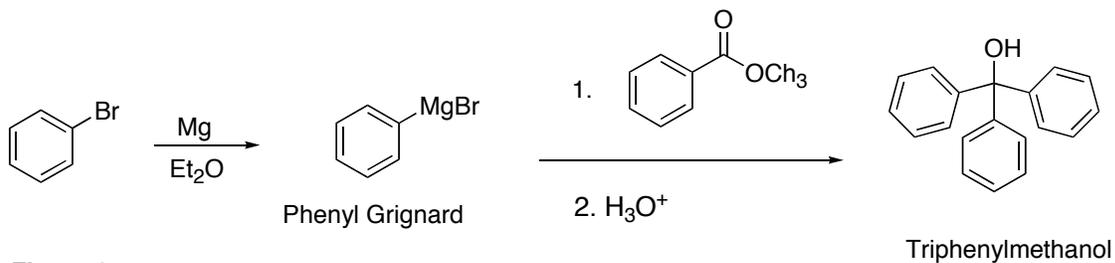


Figure 1.

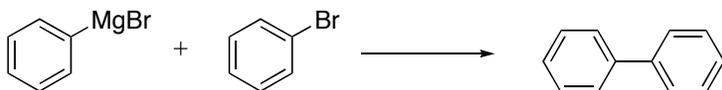


Figure 2.

EQUIPMENT:	ring stand	small graduated cylinder
	clamps	100 mL round bottom flask
	hoses	* (may be in oven-hot)
	pan or beaker for ice	125 mL separatory funnel
	flask heater	125 mL Erlenmeyer flask
	cork ring	250 mL Erlenmeyer flask
	rubber stopper/parafilm	150 mL beaker
	medium Buchner funnel	Tared 250 mL round bottom flask
	iron plate	
	unpacked condenser	

REAGENTS:	acetone
	absolute ethyl ether (dry)
	bromobenzene (dry)
	fresh shiny magnesium turnings
	iodine
	methyl benzoate (dry)
	10% sulfuric acid
	triphenylmethanol (product)

PROCEDURE:

Make sure that your round-bottomed flask, reflux condenser and graduated cylinder are absolutely dry. Clamp a clean, dry 100 mL round bottom flask securely to a ring stand. Do not use a ring and allow enough room to slide an ice bath under the flask. Though you may not need it, have a pan or beaker of ice water ready in case you need to control the exothermic reaction with cooling. Place 1.0g of dry, shiny magnesium turnings in the round bottom flask. Do not use magnesium that is dark and oxidized and do not touch it with your fingers. The TA may also lightly crush some of the turnings in a mortar and pestle. Next attach an unpacked reflux condenser onto the neck of the flask (see fig. 3).



Figure 3.

Add 8 mL absolute ethyl ether and 5 mL bromobenzene to the flask by pouring carefully down the condenser. Warm the flask by placing the palms of your hands around the outside of the flask. Be patient, but if a visible reaction has not started within 10 minutes, see your TA. The TA may initiate the reaction with iodine which activates the reactive surfaces of the magnesium. In the exceptional case that the reaction becomes too vigorous, cool the flask with the ice bath, but note that too much cooling can quell the reaction.

When the reaction has clearly begun, noted by cloudiness and bubbling around the magnesium, swirl the flask to provide fresh surfaces for the reactants and then add 12 mL more ethyl ether down the condenser. Let the reaction proceed until most of the magnesium is consumed and the solution turns the cloudy, brownish color that is characteristic of a Grignard reagent. Without much delay at this point, combine 2.5g methyl benzoate and 8 mL ethyl ether in a 125 mL separatory funnel and mix well. Cool the r.b. flask briefly with the ice bath, place the stem of the funnel inside the top of the condenser, and slowly add the ether/methyl benzoate solution drop-wise down the condenser. ('Slowly' is important here to promote the reaction of bromobenzene with magnesium rather than with already created Grignard reagent forming the impurity biphenyl as in fig. 2). Cool only as necessary to control the mildly exothermic reaction. An intermediate product may separate at this point as a white solid. Swirl the flask until it is at room temperature and the reaction has subsided.

Gently reflux your reaction mixture for 25 minutes. Transfer your mixture into a 250 mL Erlenmeyer flask containing 30 mL of 10% sulfuric acid and 15g of ice. Rinse the reaction flask with approximately 15mL ether (diethyl *or* MTBE) and add this rinse to the Erlenmeyer. Swirl well. The acid hydrolyzes the addition product, neutralizing the basic magnesium salts so they become water soluble, and the triphenylcarbinol disperses in the organic ether portion. Transfer the liquid contents to a 125 mL separatory funnel, rinse the flask with approximately 15mL of ether, and then also transfer this rinse to the separatory funnel. (Note: Give the r.b. flask containing remaining magnesium and solid residue to your TA at this point for treatment with HCl and disposal.) Shake the funnel using proper safe techniques (ask TA if not sure) and remove the aqueous layer. Shake the organic phase with additional 10% sulfuric acid solution to further remove magnesium salts using no more acid solution than half the volume of the ether phase. Again draw off the aqueous layer, add a similar quantity (<1/2 vol) of saturated sodium chloride to dry the ether layer. Pour the remaining ether layer out the neck of the funnel into a 125 mL Erlenmeyer flask, add a few grams of anhydrous sodium sulfate, swirl occasionally for 5 minutes or so, and decant the solution into a tared (pre-weighed) 250 mL round bottom flask. Roto-

evaporate to dryness and weigh the flask containing the solid product. Determine the yield and collect a melting point.

Don't forget to clean and dry your glassware, and place the clean 100 mL round bottom flask in the oven so that it is dry for the next lab.

Pre-lab Question

1: If the methyl benzoate contains water, what by-product will be formed?

Post-lab.

1. Determine the percent yield.
2. How does your melting point compare to literature reported values?
3. If there were time to recrystallize the product, predict how its melting point might change.