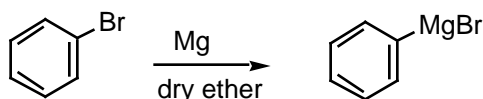


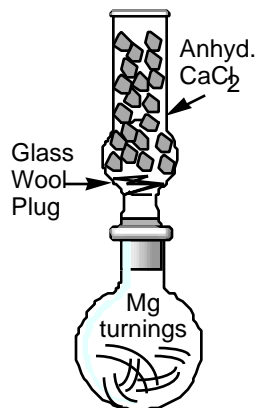
# PREPARATION OF CARBOXYLIC ACIDS VIA CARBOXYLATION OF GRIGNARD REAGENTS

**READ:** Landgrebe, Experiment 40 pp (493-496)

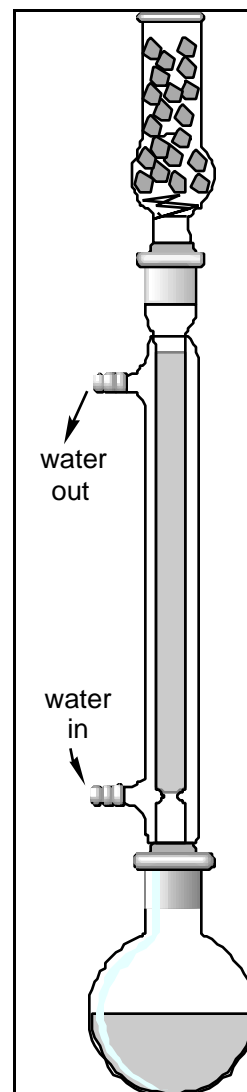
## I. Preparation of the Grignard Reagent, Phenylmagnesium Bromide



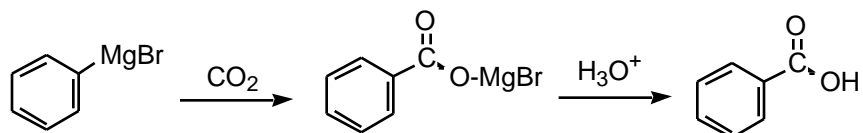
The Grignard reagent is prepared by first fitting a dry 250 mL round-bottom flask with a  $\text{CaCl}_2$  drying tube. The magnesium to be used ( $2\text{g} = 0.082$  moles of magnesium turnings) is placed in the flask, the calcium chloride tube is attached directly, and the flask is heated thoroughly with a large heating mantel and rheostat. Adjust the controller for a large heating mantel to setting '6' and heat the flask until it is too hot to touch with your finger. The flask on cooling pulls dry air through the calcium chloride. Remove the heating mantel and cool to room temperature (the flask should feel just slightly warm to your hand, or cooler) before proceeding.



Remove the calcium chloride drying tube and pour into the 250 round bottom flask 15 mL of absolute ether and 9 mL ( $13.5\text{g} = 0.086$  moles) of bromobenzene. Replace the  $\text{CaCl}_2$  drying tube. If there is no immediate sign of reaction, ask your lab instructor to initiate the reaction by crushing some of the magnesium turnings. This is done by inserting a dry stirring rod with a flattened end and carefully crushing a piece of magnesium firmly against the bottom of the flask under the surface of the liquid, giving a twisting motion to the rod. When this is done properly the liquid becomes slightly cloudy, and rapid bubbling commences at the surface of the compressed metal. At this point add 25 mL more of absolute ether and attach a reflux condenser to the flask and the  $\text{CaCl}_2$  tube to the top of the reflux condenser as shown at right. Don't start running water through the condenser until ether vapors have wet the joint at the top of the condenser. When necessary, cool the flask by touching the bottom of the flask with an ice-bath to slow the reaction, but don't use it unless it is necessary. It is necessary only if ether vapors are exiting from the top of the drying tube. If you do have to cool the reaction be careful not to slow the reaction down too much or it may stop and not start again when the ice is removed. Swirl the flask vigorously every sixty seconds. Once the reaction begins, spontaneous boiling in the diluted mixture may be slow or become slow. If so, add a few additional mLs of bromobenzene to the flask. The reaction is complete when the ether quits bubbling and only a few small remnants of metal remain. Mark the ether level in the flask using a small piece of masking tape. During the reaction, check to see that the volume of ether has not decreased. If it has, add more dry ether. When the Grignard reaction has completed, let the flask cool to room temperature. Since the solution of the Grignard reagent deteriorates on standing, the next step should be started at once.



## II. Condensation of the Grignard Reagent with Carbon Dioxide.



As the Grignard reaction flask cools, weigh out about 22 g of dry ice, wrap this in a dry towel and crush this with a small hammer. Immediately transfer this dry ice to a dry 400 mL beaker and **slowly and carefully!** pour your Grignard solution over the dry ice. There will be much bubbling as the dry ice quickly sublimates. Allow the reaction to stand until all of the dry ice has evaporated. Pour the reaction mixture carefully<sup>1</sup> into a 250mL Erlenmeyer flask containing 50 mL of 10% sulfuric acid and about 25g of ice. Use a few mL's of ordinary (non-anhydrous) ether and a few mL's of the 10% sulfuric acid to rinse the reaction flask. Add these washings to the Erlenmeyer flask. Swirl well to promote hydrolysis of the addition compound; basic magnesium salts are converted into water soluble neutral salts and the benzoic acid is distributed into the ether layer (benzoic acid is soluble in hot water and ether, but is insoluble in cold water). An additional amount of ether (ordinary) may be required if your original ether layer has become too low through evaporation. Pour this mixture into your separatory funnel, separate the ether from the aqueous phase and extract the aqueous phase with two 25 mL portions of ether. Combine **all** the ether extracts and re-extract with three 25 mL volumes of saturated sodium bicarbonate solution. Combine the sodium bicarbonate extracts and carefully add conc. HCl (**!!Caution Foaming!!**) until the solution is acidic. A white precipitate of benzoic acid will result. Filter the precipitate, wash with some ice cold water, and allow to air dry for at least 24 hours. Weigh and take a melting point of your product, report mp (compare with literature value) and per-cent yield.

## V. Report

1. Cover sheet.
2. Observation sheet including all measures.
3. Show a balanced chemical equation for the reaction.
4. Show calculation of theoretical and percent yield
5. Attach annotated IR
6. Write a summary half page describing why you think your product is benzoic acid.

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<sup>1</sup> When the unconsumed Mg metal comes in contact with the acid there will be a vigorous evolution of hydrogen gas and the reaction mixture may froth over if addition is too rapid.