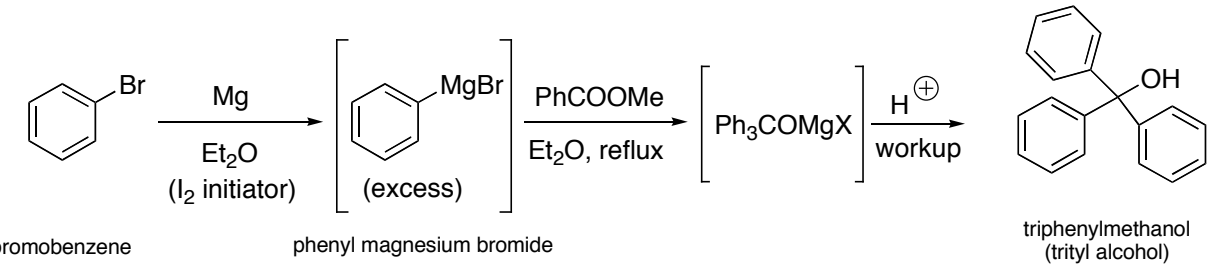
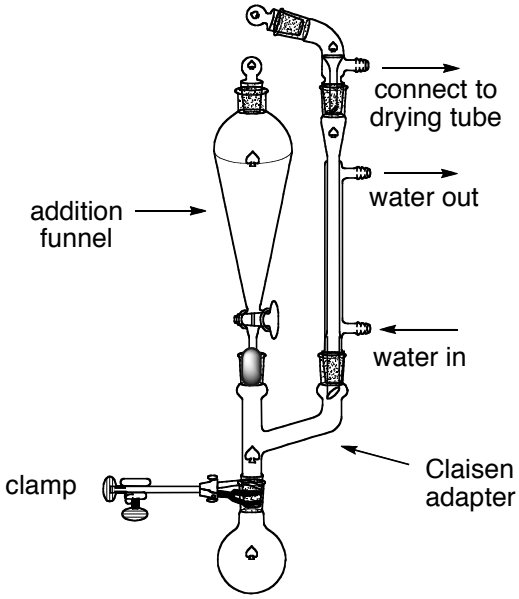
LAB 6 GRIGNARD REACTION: PREPARATION OF TRIPHENYLMETHANOL



Use your time properly to finish the lab on time!
Cans of anhydrous diethyl ether should be capped at all times (except when you pour into 25ml Erlenmeyer flask). For all heating steps – temperature controller setting should be <1.5!! (Et_2O is extremely volatile… and flammable.)



SET UP: (see Grignard setup picture 1) . All glassware must have been cleaned and air-dried at the end of last week. **Crush** (mortar and pestle) 0.5 g of Mg turnings and place in the 25 mL reaction flask. Make sure the stopcock on the addition funnel has been properly greased or moves easily – and is closed.

Plug in the heating mantle (power controller on 1 or 2: very little heat is necessary). No need to place the reaction flask deep in the sand.

REACTION.

1. Formation of phenyl magnesium bromide. Have an ice bath ready in case the reaction gets too violent. Use dry reagents, and keep to a minimum the time the set-up is open to air when adding the reagents. Keep the reagent bottles closed! Use a drying tube to protect the reaction. To minimize biphenyl formation, keep the temperature down during addition of bromobenzene, and keep swirling to prevent local hot spots. Avoid adding PhBr too fast.
Get 8 mL of an anhydrous ether solution containing 2.4 mL PhBr (solvent pump, solution prepared by TA). Place in addition funnel – make sure the stopcock is closed.
Add ~0.5 mL of this solution to the turnings and stir (picture 2. dropwise PhBr addition). Must become cloudy or observe the formation of bubbles (see also picture 7. cloudy as Mg is reacting). There is an initiation period. Warm the flask with your hand. Do not add more reagent. If after ca. 15 min, nothing happens, try heating GENTLY on the heating mantle for a few minutes while swirling. **VERY LITTLE HEATING IS REQUIRED!** (This is true for all the subsequent heating steps.) If the reaction still has not started, add either a crystal of iodine. (See picture 3. swirl after I2 addition.) You may need to heat very gently (and briefly) at that stage (see picture 4. after I2 addition, gentle heating), then swirl again. Add 5 mL anhydrous ether through the top of the condenser, swirl and heat again until a smooth reflux is observed. Stop heating.
Once the reaction is started (the iodine color disappears and the reaction mixture becomes milky, Mg appearance changes: see pictures 5, 6 and 7. after I2, Mg reacts to give a milky mixture). GENTLY heat the mixture so the solvent refluxes smoothly or add the PhBr solution slowly in order to maintain reflux. (The ring of ether condensation should not be above the bottom 1/3 of the condenser) Add the PhBr solution **DROPWISE** and control the rate of addition in order to maintain a smooth reflux. No additional heating is required, as the reaction should maintain the reflux on its own). Addition should take 5-10 min. Once the addition is complete, heat gently for

about 15 min. Most of the magnesium (but usually not all) should have disappeared. Let the reaction cool down.

2. Reaction with methyl benzoate. During this cooling time, get 7 mL of an anhydrous ether solution containing 1.2 mL of methyl benzoate (solvent pump, solution prepared by TA). Place the solution in the addition funnel. (Closed stopcock!) Cool the Grignard solution with an ice/water bath. Add the methyl benzoate solution slowly. (See picture 8. after PhCOOMe addition.) Once the addition is complete, reflux gently for 30 min.

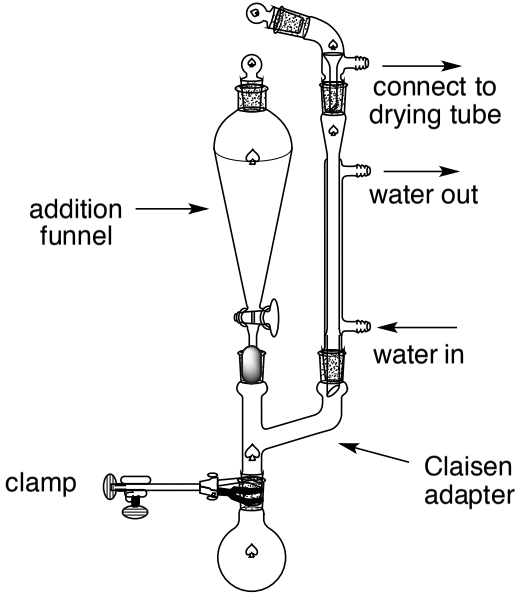
WORK-UP. Gloves! Prepare a mixture of 10 mL cold 6 M H_2SO_4 and 5-10 g ice in a beaker. If the reaction mixture contains some white solid, you may need to add a little bit of ether to the flask. Pour reaction mixture slowly into the beaker and rinse with ether (2-3 mL). (Technical grade ether is used from this point on.) Check that aqueous layer is acidic.

Add 20 mL of ether (the total amount of ether should be about 20 mL at that stage) and transfer to a separatory funnel. As usual make sure you **VENT OFTEN** during the subsequent extraction steps. Wash with 5 mL of 3 M H_2SO_4 [dispose of the acid layer into the appropriate waste container], then two times with 5 mL sat. aq. $NaHCO_3$ (Warning: a lot of CO_2 can evolve during the wash with the first portion: VENT!!), and finally 5 mL sat. aq. NaCl. Dry the organic layer with Na_2SO_4 (or $MgSO_4$). Filter or decant into a 50 mL RBF (weigh the flask before that to determine crude yield after ether has been removed). Distill the ether using simple distillation (place a boiling chip) – KEEP AN EYE on the distillation: it should not take very long to distill! But you can wash some glassware during that time. Do not distill to dryness, leave a penny or quarter size, disassemble the distillation set-up, and then pipette-out remaining solution onto a pre-weighed watch glass, let it dry and measure the crude amount obtained, calculate the yield; there is no need to measure the m.p. at this point.
Measure crude yield.

PURIFICATION. Purify the crude triphenylmethanol by recrystallization. Dissolve into a minimum amount of boiling cyclohexane (~less than 10 mL/g). Once everything is in solution, evaporate cyclohexane until small crystals form. Let the flask cool slowly to room temperature. Then cool in ice. Collect by vacuum filtration and air dry. Weigh and calculate the yield. Measure the melting point. Turn in the product.

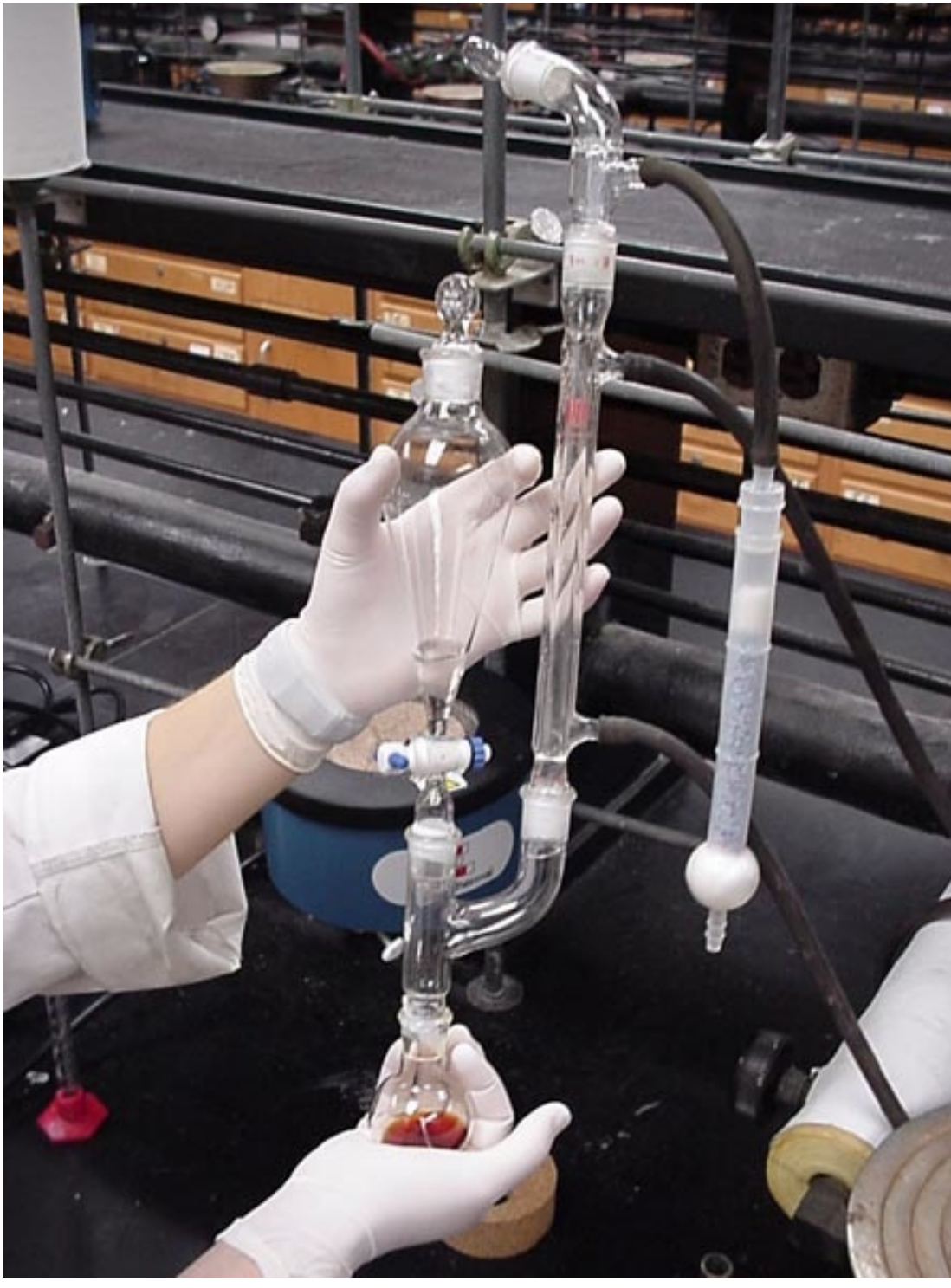
Pictures for the Grignard Lab

1 SETUP:

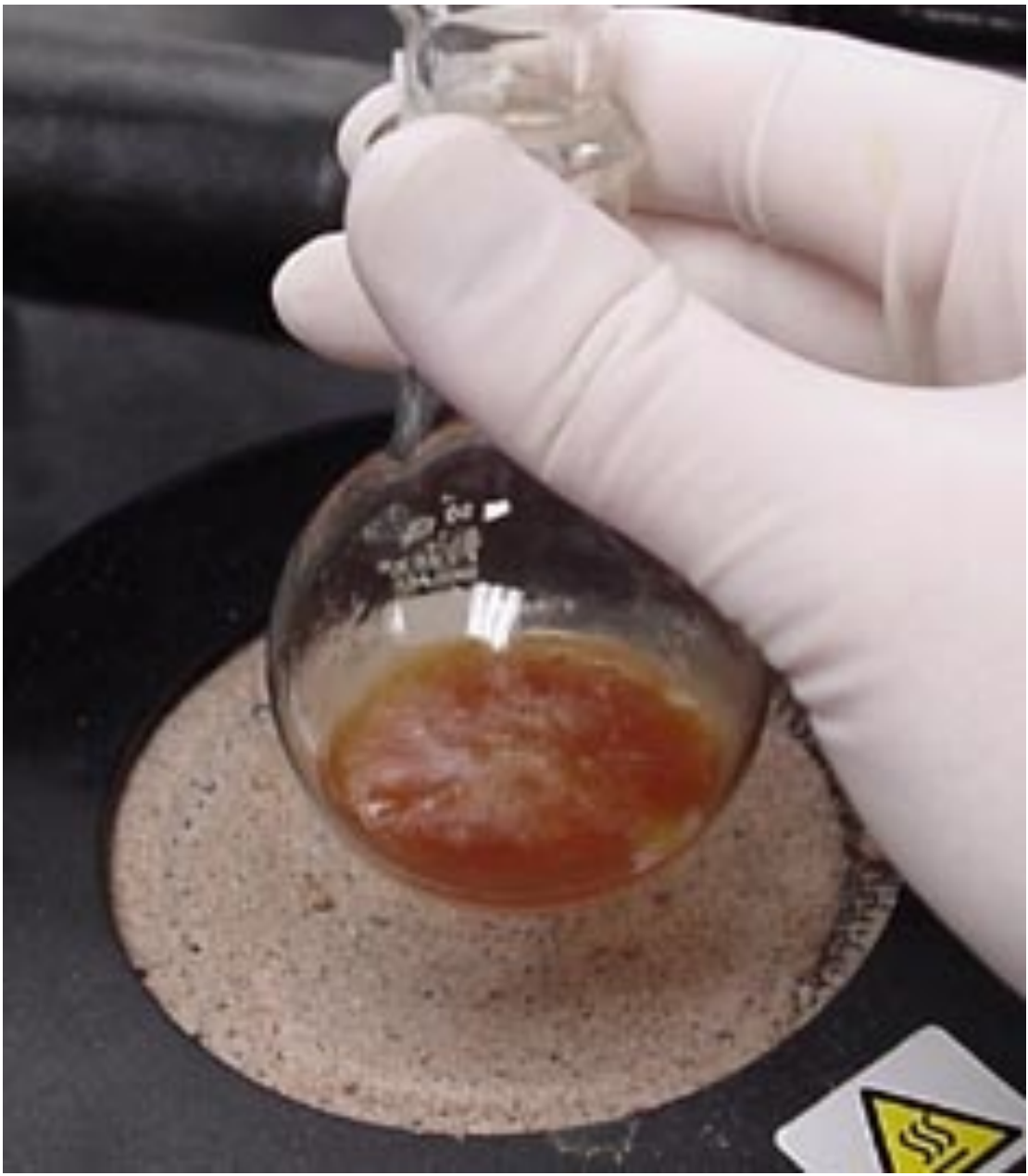


2 DROPWISE ADDITION OF BROMOBENZENE

3 SWIRL AFTER IODINE ADDITION



4 GENTLE HEATING AFTER IODINE ADDITION



5 MAGNESIUM REACTS AFTER IODINE ADDITION

6 MAGNESIUM CONTINUES TO REACT, THE REACTION BECOMES MILKY

7 MAGNESIUM IS REACTING

8 AFTER ADDITION OF METHYL BENZOATE