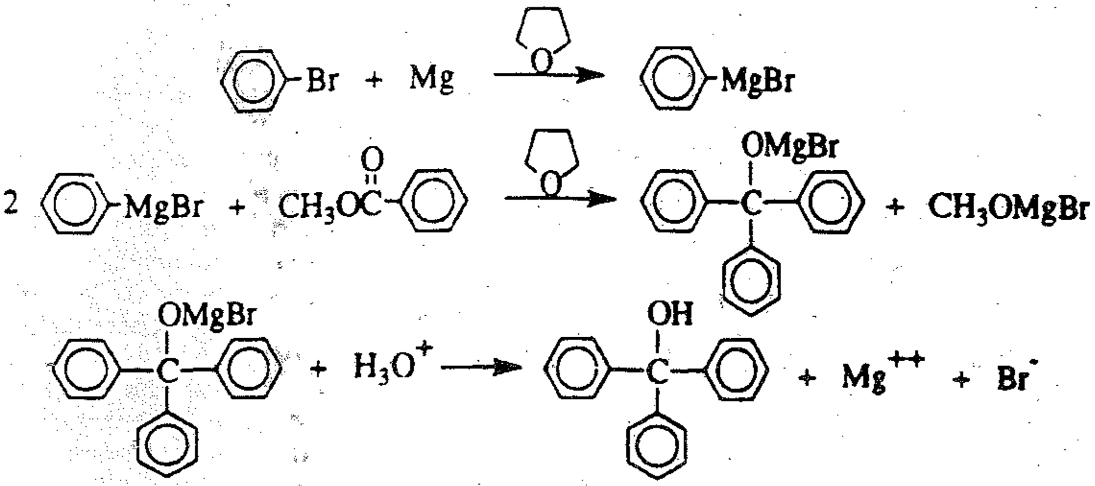
CHAPTER

17

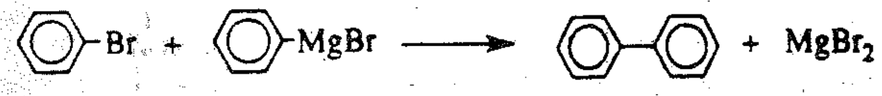
Grignard Reactions

Triphenylmethanol or Dicyclohexylphenylmethanol

In this experiment a Grignard reagent is prepared either from bromobenzene or from chlorocyclohexane. It is then treated with an ester to form a tertiary alcohol. This is one of many syntheses that can be carried out with the versatile Grignard reagent, and this topic should be reviewed in your textbook.



The most significant side reaction in the synthesis of triphenyhlmethanol is a coupling between bromobenzene and phenylmagnesium bromide to give biphenyl.



Isolation of the final product involves removal of volatile impurities by steam distillation. The nonvolatile triphenylmethanol crystallizes from the residue. The theory of steam distillation was discussed in Chapter 5 and should be reviewed. The steam distillation can be carried out using an external source of steam or the steam can be generated from water added continuously to the distillation mixture as described in the procedure below.

17.1 - The Synthesis of Triphenylmethanol

17.1-1. Preparation of the Grignard reagent. Phenylmagnesium bromide. Assemble the apparatus shown in Figure 17.1 using a 50 mL round-bottom flask as the reaction flask. Do not run water into the condenser jacket yet. It is imperative that all of the glassware be *clean* and *dry*. The drying tube connected to the top of the condenser should be filled with anhydrous calcium chloride (Figure 17.2). The drying tube is inverted and attached by means of a U-shaped tube as shown, rather than directly to the straight adapter, to prevent finely powdered calcium chloride from dropping into the reaction flask and to prevent vapors which may condense in the drying tube from washing drying agent into the reaction flask.

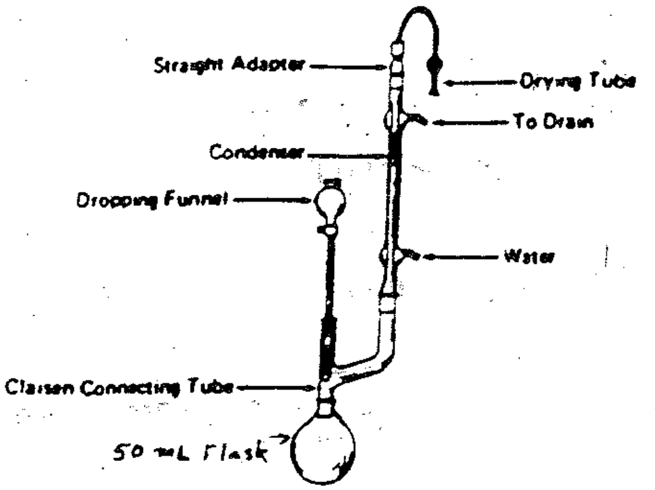


Figure 17.1. Apparatus for Refluxing with Simultaneous Addition of a Liquid

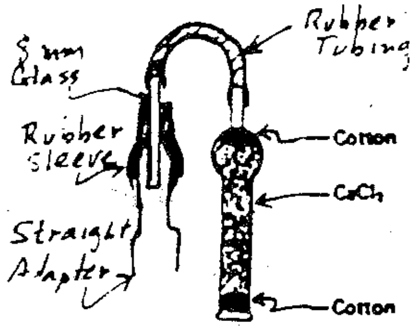


Figure 17.2. Drying Tube

Place 1.0 g of magnesium turnings and 1 or 2 tiny crystals of iodine in the reaction flask. Detach the drying tube and the dropping funnel and see that there is no water standing in the condenser jacket. Flame the apparatus by warming it with a Bunsen burner flame. Use a cool, almost oxygen free[1], flame and rotate the burner in a circular fashion starting from the bottom of the reaction flask and working up the condenser. No water should be in the condenser jacket during the flaming. This procedure drives traces of water vapor from the walls of the glassware and fills the apparatus with iodine vapor. When flaming is complete, replace the drying tube and the dropping funnel. Close the stopcock and and allow the apparatus to cool to room temperature. If available, arrange the hot plate-stirrer under the reaction flask and place the magnetic stirring bar in the flask with the magnesium.

Prepare a solution of 6.3 g of bromobenzene in 15 mL of tetrahydrofuran (THF) and place the solution in the dropping funnel. Have an ice-water bath in readiness to cool the reaction flask in case the reaction becomes too vigorous; *but do not use the ice-water bath unless absolutely necessary.* Check to see that water is running through the condenser (bottom to top).

Add approximately 5 mL of the bromobenzene solution from the dropping funnel to the magnesium in the reaction flask. Briefly swirl the mixture by hand or stir gently with the magnetic stirrer. The reaction should start promptly as shown by the generation of heat and clouding and then clearing of the solution. If the reaction does not begin easily, warm the reaction flask briefly by immersing in a beaker of hot water or with the hot plate. *Do not add any more of the bromobenzene solution until the vigorous reaction has started and then subsided.* Discontinue heating once the reaction starts. The reaction is strongly exothermic and does not need to be heated once it has started. If the reaction ever becomes too vigorous and threatens to flood the reflux condenser or to erupt through the top of the condenser, immediately cool the reaction flask in the ice-water bath for a few moments. Once the too vigorous reaction has subsided, remove the ice-water bath. If the reaction does not start after the mixture has been heated for a few minutes, it is probable that your apparatus was not dried adequately. Consult your laboratory instructor for advice on how to proceed.

Once the reaction has begun, add the remainder of the bromobenzene solution through the dropping funnel at a rate sufficient to keep the solution gently refluxing without application of external heat. After the addition is complete, heat the mixture so that it refluxes gently. Continue heating it until only a small quantity of finely divided magnesium remains, but no longer than 15 minutes. *The preparation cannot be stopped at this point. The Grignard reagent cannot be kept until another laboratory period . It must be used at once.*

17.1-2. The reaction of phenylmagnesium bromide with methyl benzoate. Triphenylmethanol. Place a solution of 2.80 g of methyl benzoate[2] in 10 mL of tetrahydrofuran in the dropping funnel, and while the Grignard solution is still warm, add the methyl benzoate solution dropwise, with vigorous swirling or stirring[2], over a period of about 10 min. No heat is applied during the addition of the methyl benzoate, since this reaction is also spontaneous and exothermic, and the reaction mixture should reflux gently from the heat of the reaction, without the application of any external heat. Allow the reaction mixture to stand for 15 to 20 minutes after the addition is complete.

Cool the reaction mixture and pour it slowly, with swirling, into a beaker containing approximately 25 g of ice, 10 mL of cold water and 1.5 mL of concentrated sulfuric acid. Leave as much of the unreacted magnesium behind as possible, although no harm is done if some if it gets into the acid mixture. Transfer the mixture to a 250 mL round-bottom flask and allow it to warm to room temperature. The preparation may be interrupted at this point, if necessary, or the steam distillation may be carried out immediately.

2nd week

Attachments:

17.1-3. Purification of Triphenylmethanol. ~~Assemble the apparatus~~

Grignard Procedure

1. Extract your solution with ether (not THF).
2. Separate out and collect ether layer (on top).
3. Dry with drying agent (e.g. Na2SO4).
4. Evaporate ether on steam bath.
5. Add some ligroin/petroleum ether (this is hexane not actual ether). Stir to dissolve impurities (methyl benzoate, bromobenzene, biphenyl side product). Hopefully yellowish product should become whiter and whiter.
6. Decant off hexane.
7. Recrystalize product in ethanol.