

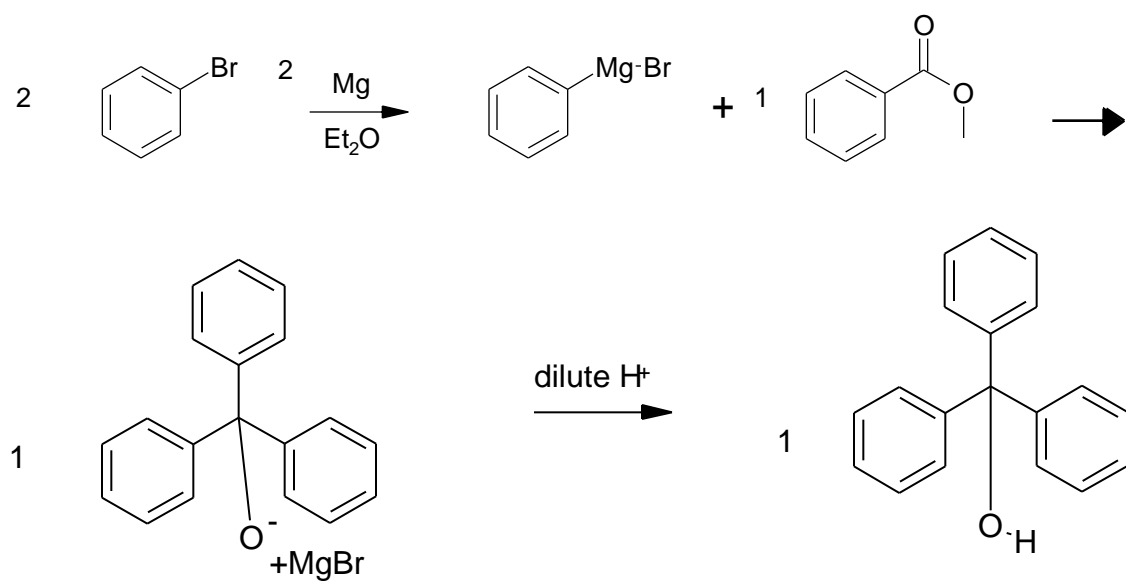
Triphenylcarbinol: A Grignard Synthesis

Chemistry 233L/234L
October 1, 2002
Laura Meraz

Purpose:

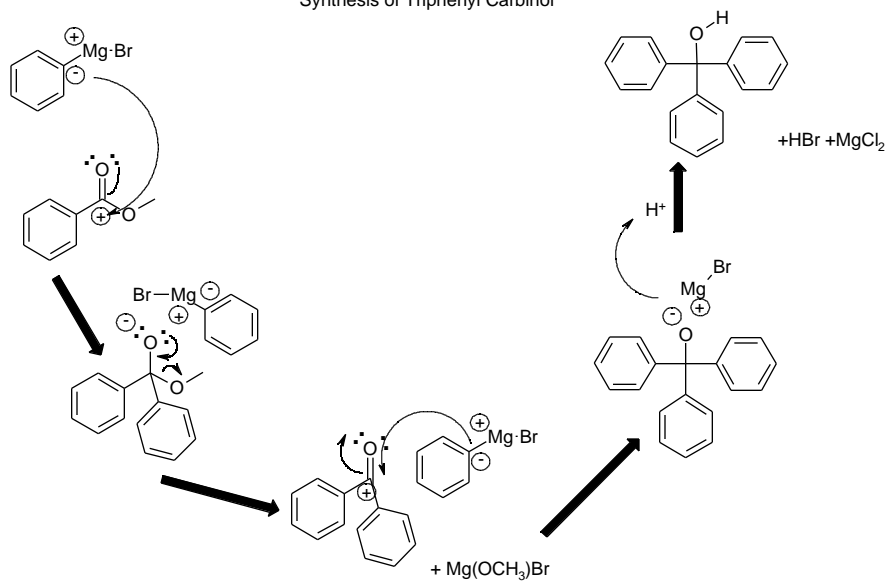
In this experiment, phenylmagnesium bromide (a Grignard reagent) was prepared and used to produce triphenylcarbinol (a tertiary alcohol) by reacting with methyl benzoate. Extraction was used in order to isolate the product and then purified through recrystallization from the short path distillation of a ligroin-diethyl ether mixture. The percentage yield and purity were calculated as well as the FTIR, HNMR, CNMR, and MS spectra analyzed and compared to the actual spectra.

Main Reaction:

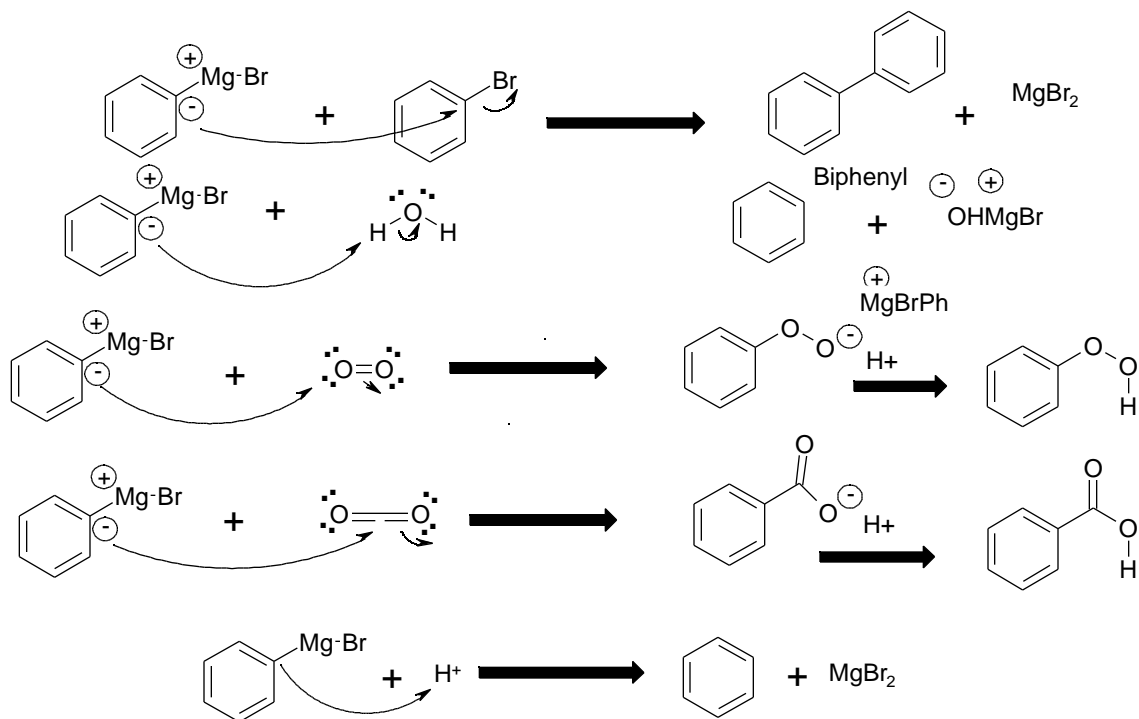


Reaction Mechanism:

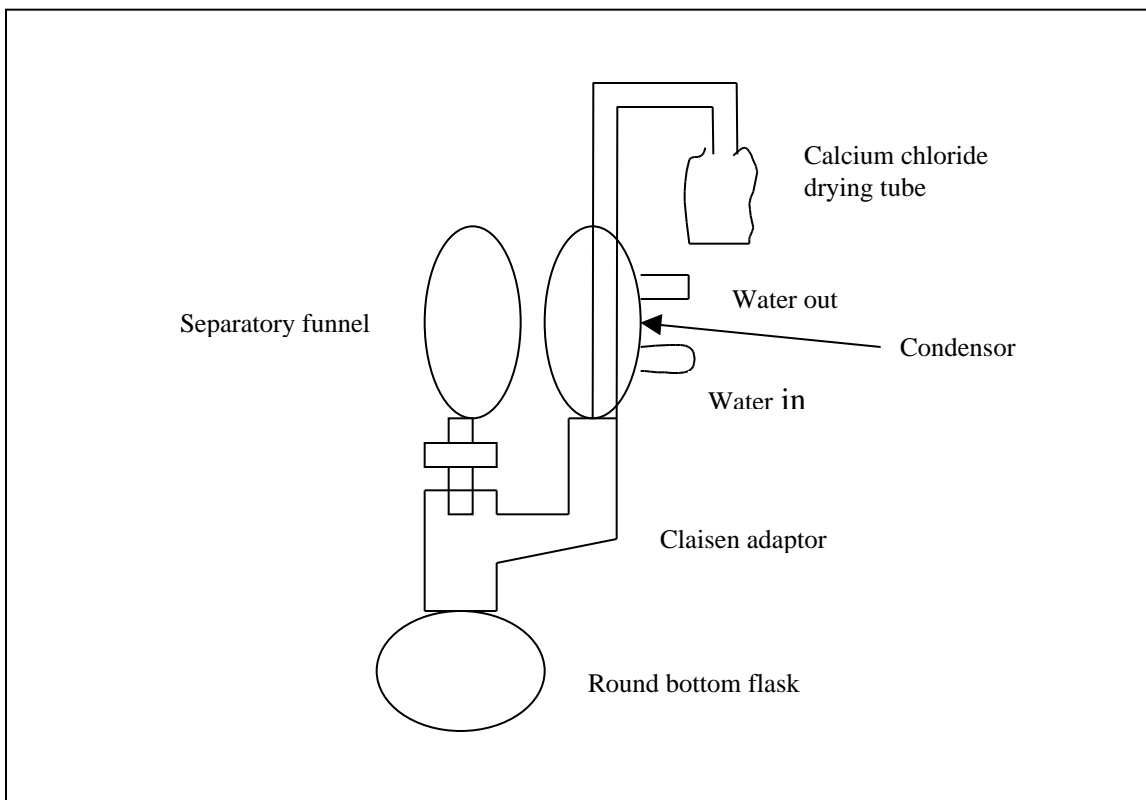
Synthesis of Triphenyl Carbinol



Side Reactions:






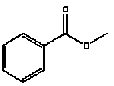
Special Set-Up:

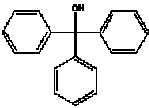


Safety:

- Diethyl ether is extremely volatile and its vapors are flammable and explosive. No flames can be present when any ether is being used in the rooms.
- The reaction of the Grignard reagent with methyl benzoate is exothermic and the ether solution may begin to reflux rapidly. The following precautions must be taken when refluxing:
 1. Never reflux an enclosed system
 2. Never reflux when the round bottom flask is more than 2/3 full.
 3. Never have reflux ring rise higher than 1/3 of the length of the condenser.
 4. Never reflux without a boiling chip.
 5. Never reflux without the condenser water running.
 6. The reaction mixture cannot get lower than the lowest boiling component, in this case, diethyl ether boils at 35°C.

Data Table:

Step 1								
Reactants	grams	molar mass	mole	mole ratio		MP	BP	miscellaneous
				Theoretical	Actual			
Bromobenzene 	10.0	157.0	0.064	1	1.03	-30°C	155°C	d=1.485
Magnesium (limiting reagent)	1.5	24.3	0.062	1	1			
diethyl ether	solvent						35°C	d=0.71; very flammable
Products								
Phenylmagnesium bromide 	11.2	181.4	0.062	1	1			
Step 2								
Reactants	grams	molar mass	mole	mole ratio		MP	BP	miscellaneous
				Theoretical	Actual			
Phenylmagnesium bromide 	11.2	181.4	0.062	2	2			
Methyl benzoate 	4.1 mL (4.5 g)	136.2	0.033	1	1.1	-12°C	200°C	d=1.094
Products								

Triphenylcarbinol 	3.50	260.33	0.0134	1	1.00	157-159°C (lit 163 ³)	
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Theoretical Yield Calculations:

Step 1:

$$10.0 \text{ g Bromobenzene} \times \frac{1 \text{ mol}}{157.01 \text{ g}} = .0637 \text{ mol bromobenzene}$$

$$1.5 \text{ g Mg(s)} \times \frac{1 \text{ mol}}{24.31 \text{ g}} = .0617 \text{ mol Mg(s)}$$

$$\frac{.0637 \text{ mol bromobenzene}}{.0617 \text{ mol magnesium}} = 1.03$$

Step 2:

$$.0637 \text{ mol bromobenzene} \div 2 = .0319 \text{ mol methyl benzoate}$$

$$.0617 \text{ mol Grignard} \times \frac{1 \text{ mol triphenylcarbinol}}{2 \text{ mol Grignard}} = .0309 \text{ mol triphenylcarbinol}$$

$$.0309 \text{ mol triphenylcarbinol} \times \frac{260.33 \text{ g}}{1 \text{ mol}} = 8.03 \text{ g triphenylcarbinol should be produced with MG}_{(s)} \text{ as LR.}$$

Conclusion:

Grignard reagents are well suited for use in organic chemistry since they are easily prepared by reaction of an alkyl or aryl halide with magnesium metal in a dry ether solvent. In this experiment, the Grignard reagent phenylmagnesium bromide was produced from the reaction of bromobenzene with magnesium. Phenylmagnesium

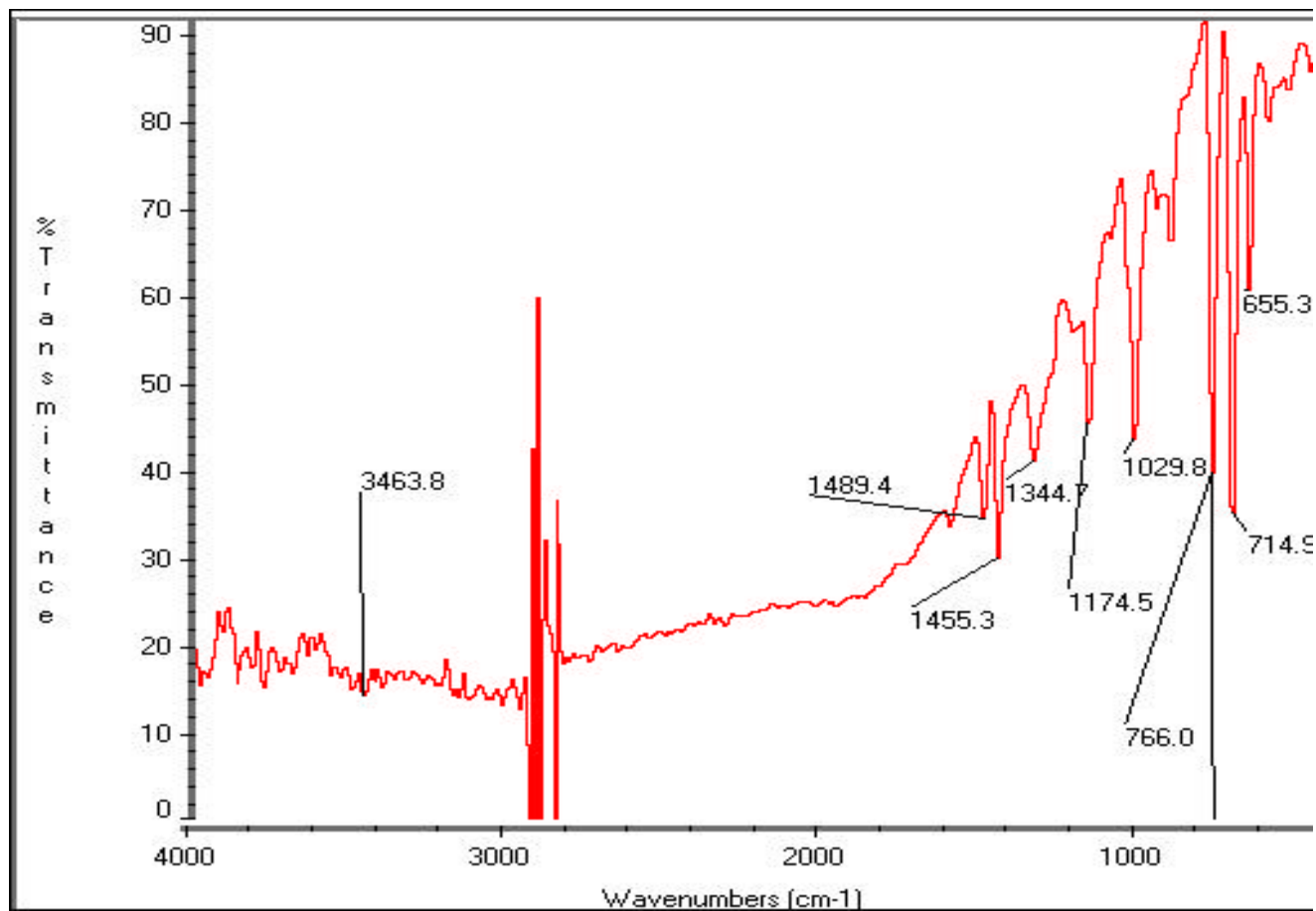
bromide then underwent the Grignard reaction to produce a tertiary alcohol by reacting with methyl benzoate.

The synthesis was successful with isolation of 3.5 grams of triphenylcarbinol in a 100% yield. These are the numbers that were reached after weighing and calculating, however, these are surprising values. The sample was no longer available to be re-weighed in the case that it was not completely dry when it was weighed or there was a mistake in the reading, therefore the numbers may be slightly incorrect. After recrystallization from ligroin, triphenylcarbinol was isolated as a slightly beige, off-white solid crystallization with a melting point of 157-159°C (lit. 158–160°C). Considering the wide range of side reactions possible, the carrying out of this reaction was good and produced a decent yield. Bi-phenyl was produced from the reaction between phenylmagnesium bromide and bromobenzene, which was completely reacted preventing its interaction with magnesium. The nonpolar biphenyl was removed in the final crystallization step of triphenylcarbinol after having been dissolved in ligroin.

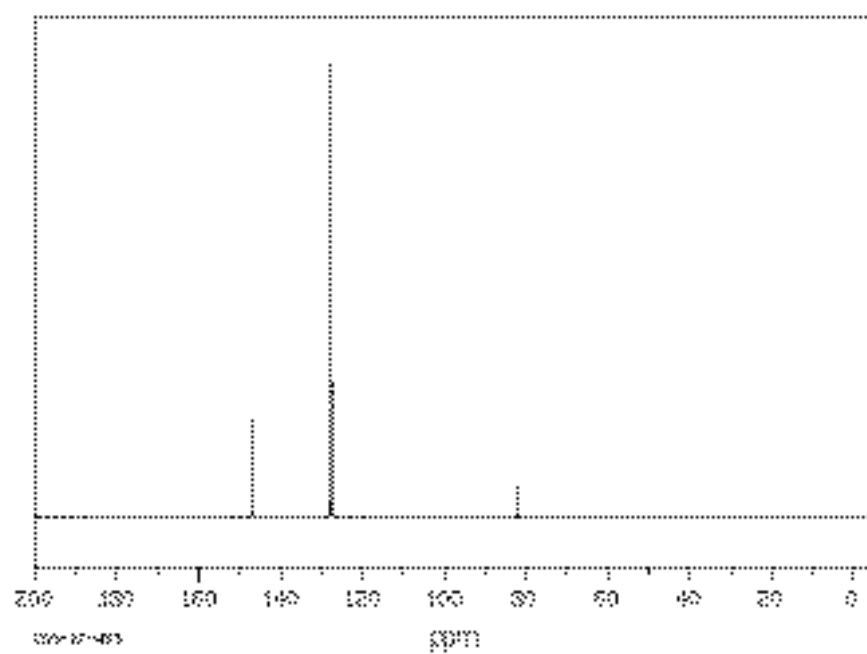
The experimental FTIR spectrum for triphenylcarbinol matched the actual spectrum very closely supporting the isolation of pure triphenylcarbinol. Both spectrum showed a strong, broad peak around 3463 cm⁻¹ representing the O-H group. They also shared a weak, sharp peak around 3072 indicating the =C-H bonds in the benzene rings. Finally, both spectra showed moderate, sharp peaks at 1450-1550 for the C=C bonds from the rings and around 1175 for the C-O bond.

Specific Functional Group	Observed Frequency Vibration (cm ⁻¹)	Intensity	Shape
Alcohol O-H	3463.8	Strong	Broad
=C-H stretch (benzene ring)	3072	Weak	Sharp
C=C (benzene ring)	1450-1550	Moderate	Sharp
C-O (3° alcohol)	1174.5	Moderate	Sharp

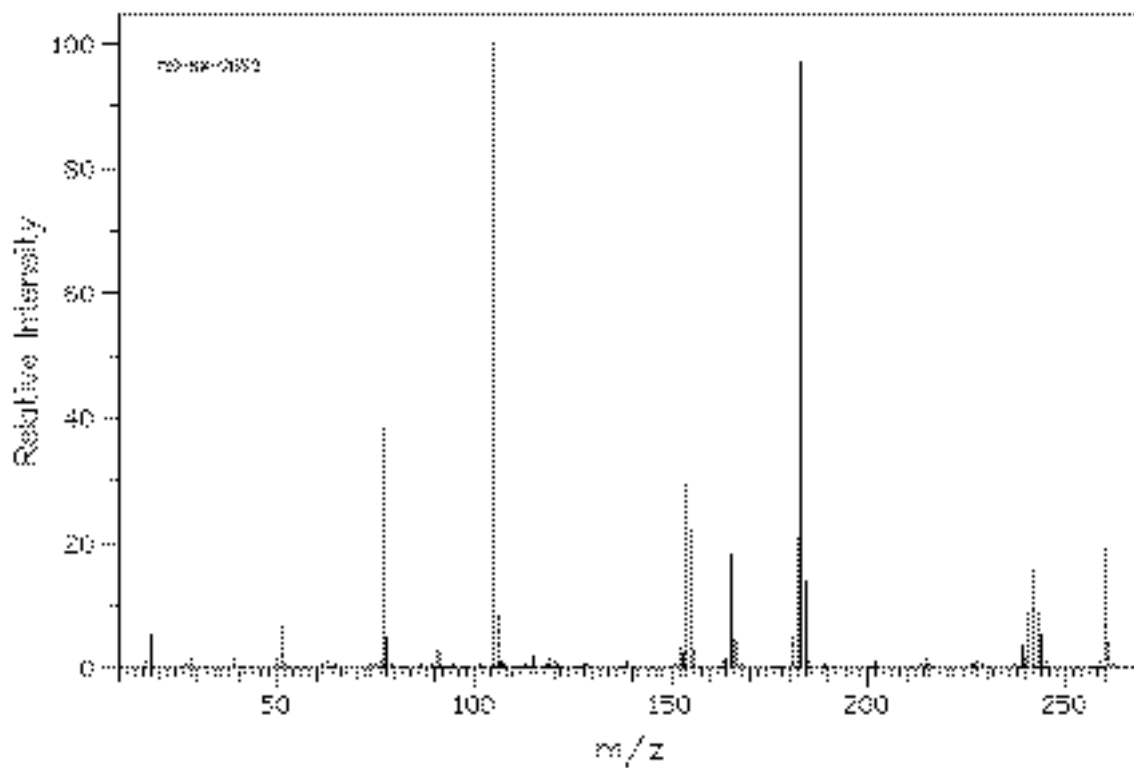
Experimental FT-IR Spectrum



Actual FT-IR Spectrum for triphenylcarbinol:



Actual Mass Spectrometry for
triphenylcarbinol:



The Mass spectrum showed a base peak at 105 m/z. In this spectrum, the molecular ion was obviously not the base peak. The molecular ion was at 260. By observing the tallest peaks and their positions, it was possible to determine the structures that they represent. For example, the entire molecule showed a peak at 260, it's molecular weight; however, as the compound was broken apart through mass spectrometry, it formed the most stable fragments. The first fragment that was formed was an oxonium ion, a result of losing one phenyl group. The fragment produced a peak around 183 m/z with a double bond resonating between the carbinol carbon and the hydroxyl oxygen. The next fragment indicated the presence of the acylium ion, triphenylcarbinol having lost two phenyl groups and a hydrogen and having a molecular weight of about 105. This fragment included resonance between the carbinol carbon and the oxygen from a double to triple bond.

Final Four Questions:

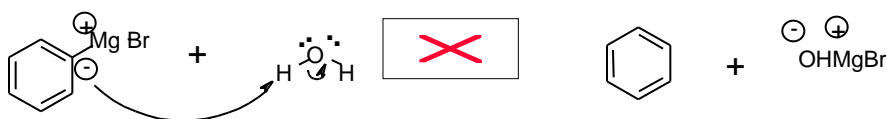
1. In this activity I reacted bromobenzene with magnesium to produce a Grignard reagent, phenylmagnesium bromide, which in turn reacted with methyl benzoate to produce triphenyl carbinol, a tertiary alcohol.
2. In this activity I saw solid magnesium dissolve in bromobenzene, as well as the reaction solution change color from clear to green to yellow to brown to orange and finally to an egg white color. In addition, I saw ether boil demonstrating the exothermic nature of part B of this activity.
3. In this activity I learned how to assemble a dropping funnel and how to rid it of any water. I also learned how important it is to keep Grignard reagents

exclusive of any water and in completely anhydrous reaction conditions. Finally, I learned that this reaction is best carried out continuously, rather than drawn out over several class periods.

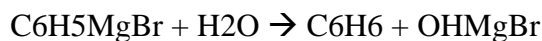
- Next, I would like to listen to an explanation of exactly how each of the steps in the experiment relates to a lecture on the Grignard reaction. That is, I would like the theoretical to be applied to the particular experiment that I just performed, simply as a final overview and to ensure correct understanding of the reaction.

Post Laboratory Questions:

- Benzene was produced as a side reaction when phenylmagnesium bromide reacted with water. The negative charge on the carbon attacked the partial positive charge of the H in water and underwent the elimination reaction.



The balanced equation for its formation is:



- Ligroin was used instead of a solvent like ethanol because it consists of mostly hexanes and is non-polar allowing it to dissolve other non-polar substances. Ligroin also does not contain oxygen as does ethanol. In addition Ethanol would probably dissolve the triphenylcarbinol and not allow it to recrystallize.
- Diethyl ether is a common solvent for Grignard reactions. It is a polar aprotic solvent and is capable of dissolving salts. It differs from petroleum ether

because it contains an oxygen in its molecular structure while petroleum ether is a mixture of aliphatic hydrocarbons. Diethyl ether is more polar than petroleum ether as a result of the oxygen and thus better able to dissolve polar compounds.

4. Alkyl bromides react more readily with Grignard reagents than alkyl chlorides.
5. Care must be taken to have all moisture excluded from the apparatus, solvents, and reagents before preparing a Grignard because any acidic protons will cause a reaction with the carbanion and allow for the formation of by-products. The Grignard reagent must be protected from air and water because it reacts with water, CO_2 , and oxygen.
6. It is necessary to have an ice-water bath available at all times during the preparation of the Grignard reagent because it is an exothermic reaction and could produce too much heat. The ice-bath could serve to cool the reaction down and keep the reaction from over-heating and boiling over.
7. The solution of bromobenzene is added dropwise to the magnesium to prevent the reaction from becoming too exothermic.
8. The visible signs of initiation one should look for are bubbling and turbidity after approximately five minutes.
9. In part A, the limiting reagent was magnesium. This was determined by comparing the number of moles of magnesium used (.0625), to those of bromobenzene used (.0637); and smaller of the two is the limiting reagent.

10. In part B the limiting reagent was phenylmagnesium bromide. There was .0625 moles of phenylmagnesium used compared to .0318 moles of methyl benzoate; however, the mole ratio was 2:1. $.0318 * 2 = .0636$ which is greater than .0625 making phenylmagnesium the limiting reagent.
11. The unreacted Grignard that remains in the reaction mixture after addition of the ester forms byproducts.
12. The biphenyl major by-product produced in this reaction was soluble in ligroin and was removed in the final crystallization step of triphenylcarbinol.
13. Saturated aqueous sodium chloride was used to remove residual hydrochloric acid from the ethereal solution during the work-up procedure rather than water because it was necessary to reduce the amount of water present by as much as possible. In the next step the anhydrous sodium sulfate was used for further drying, so we did not want to add more water to only have to be dried and removed in the next step.

Bibliography:

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