

Guided – Inquiry GC/MS Lab C122

1st week

Introduction to GC/MS
Introduce the problem

2nd week

Grignard synthesis
Characterize the product using IR

3rd week

Dehydration experiment
Collect data

4th week

Analyze the data
Explain the results
Verify using computational data
Prepare a research report

Guided – Inquiry: Kinetic vs. Thermodynamic Control in the Dehydration of 2-methyl-1-phenyl-cyclohexanol

Outline of Experiment

1. Students are asked few questions (such as what methods are available for the formation of new C-C bonds?) and guided to develop answers.
2. Students follow a predetermined procedure to synthesize a tertiary alcohol (Exposure to IR technique).
3. Students are posed a question to think about dehydration of this alcohol
 - What are the possibilities?
 - Which they may expect as major product and why?
 - Does stability of alkene contribute to the formation of products?
 - What role temperature would play?
4. Students form groups and carry out the dehydration experiment at two different temperatures (RT and reflux in toluene) and collect data (Ratios of alkenes with time).
5. Students share the data, analyze and draw conclusions.
6. Students, using the software package Spartan, optimize the structures of two alkenes (Instructor Guided) and calculate the energy difference.
7. Students prepare their research report.

PROCEDURE

The Grignard Reaction:

Preparation of 2-Methyl-1-phenylcyclohexanol

As with any Grignard reaction, care should be taken to assure the use of dry glassware and solvent. A magnetic stir bar, 0.47 g of magnesium turnings, and 15 mL of anhydrous ether are placed in a 100-mL, two-necked round-bottom flask fitted with a reflux condenser and an addition funnel containing 2.0 mL of bromobenzene in 5.0 mL of anhydrous ether. A drying tube filled with calcium chloride is connected to the top of the reflux condenser. The bromobenzene solution is then added dropwise at a rate of 1 drop per second with stirring. The appearance of a cloudy reaction mixture signals the initial reaction of magnesium with the halide. The reaction is refluxed after all the bromobenzene has been added. During this time, a solution of 2.0 mL of 2-methylcyclohexanone in 10 mL of anhydrous ether is placed in the addition funnel. After refluxing for 30 min., the heat source is removed and the ketone solution is added dropwise at a rate of 1 drop per second to the Grignard. The heat given off allows the reaction to continue refluxing on its own and a green solution results. After all the ketone solution is added, the heat source is used to continue the reflux for an additional 15 min. The mixture is then cooled in a warm water bath; additional cooling in an ice bath follows. An ether/ethanol solution is made by mixing 1.5 mL of ethanol and 10 mL of ether. While the reaction mixture is still in the ice bath, the ether/ethanol solution is placed in the addition funnel and added slowly (ca. 1 drop per second) to the reaction mixture. This causes formation of a precipitate of magnesium salts. The resulting solution is greenish yellow. Next, 20 mL of a 1 M sulfuric acid solution is placed in the addition funnel and added dropwise to the reaction mixture (still in the ice bath) to dissolve the magnesium salts. The stir bar is removed, and the contents

of the flask are transferred to a separatory funnel. The lower aqueous layer is removed and extracted twice with 15 mL portions of ether. All three ether layers are combined and dried with anhydrous sodium sulfate. Gravity filtration of the drying agent yields a clear yellow solution. The ether and ethanol are removed using a rotary evaporator (or alternatively via simple distillation) to give a slightly viscous yellow liquid. The crude alcohol product can be analyzed by GC/MS or IR to verify the formation of an alcohol. The product is stored in a sealed vial and saved for the dehydration portion of the experiment.

Kinetic vs. Thermodynamic Control: The Dehydration of 2-methyl-1-phenylcyclohexanol

A magnetic stir bar, 0.64 g of the alcohol from the Grignard reaction, 20 mL of toluene, and 0.05 g of p-toluenesulfonic acid are placed in a 50 mL two-necked flask fitted with a reflux condenser and a ground glass stopper. One batch will run reaction at room temperature. The second batch will place the flask in a heating mantle and reflux the solution with stirring. After 15 min., 4 drops of the reaction mixture are removed via disposable pipet and placed in a microcentrifuge tube containing 0.5 mL of dichloromethane and 0.5 mL of 10% sodium bicarbonate. The reaction solution forms a brown layer at the top of the microcentrifuge tube, giving three layers in total. The microcentrifuge tube is capped and the contents are vigorously shaken. Upon settling, two layers form in the tube: an aqueous layer on top and a clear brown organic layer on the bottom. A GC syringe is used to take a 1 mL sample from the lower dichloromethane layer. This sample is then analyzed by GC/MS. Additional samples are taken from the reaction mixture in a similar manner every 15-20 minutes for a total of 2 hours. The samples need not be analyzed immediately, since the sodium bicarbonate solution was used to neutralize the toluenesulfonic acid.

GC/MS CONDITIONS

Instrument used:

Column used:

GC conditions: Initial temp.:

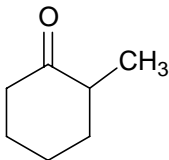
Final temp.:

Rate:

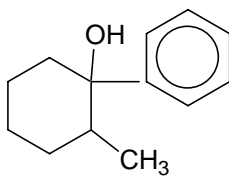
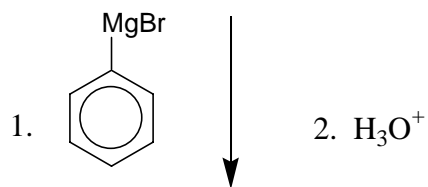
Total time for each run:

Table 1

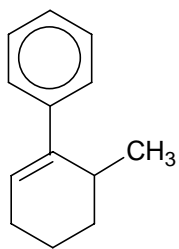
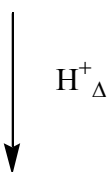
Time (Minutes)	Ratio of Products (based on retention time)	
	<u>3</u>	<u>4</u>
15		
30		
45		
60		
75		
90		
105		
120		



1

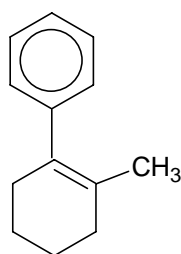


2



3

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4