March 28th, 2014

Experiment 5: Preparation of Benzoic Acid Using a Grignard Reagent

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Intro:

Purpose: To examine alkane and alkene reactivity and synthesize benzoic acid through the effective use of a grignard reagent.

Procedure:

1. All glassware to be used in the procedure was cleaned, dried and placed in an oven for approximately 15 minutes.
2. A Grignard reflux apparatus was assembled, and the drying tube was filed with a layer of $CaCl_2$ between two cotton balls.
3. 0.8g of magnesium turnings and two small crystals of iodine were placed in the 50mL round bottom flask of the reflux apparatus.
4. The mixture was allowed to sit for approximately 5 minutes.
5. A solution of 3.0mL of bromobenzene and approximately 20.0mL of anhydrous diethyl ether was prepared. Approximately half of the solution was added to the mixture in the round bottom flask of the reflux apparatus.
6. After approximately 5 minutes, a few small pieces of fresh magnesium was added to the round bottom flask.
7. Slowly, the remains of the bromobenzene - anhydrous diethyl ether solution was added to the reaction flask as to keep the mixture refluxing gently.
8. The reaction was allowed to sit until no more refluxing was observed, at such point the round bottom flask was clamped so that it within a hot water bath. The reaction was then left to sit for approximately 25 minutes.
9. The reaction mixture was slowly poured into a 100mL beaker congaing approximately 3g of dry ice. The mixture in the 100mL beaker was continuously stirred while the reaction mixture was added.
10. Approximately 30g of water ice, 20.0mL of water, 5.0mL of concentrated HCL and 15.0mL of diethyl ether were added to the 100mL beaker.
11. The resulting mixture was transferred to a separatory funnel. The 100mL beaker was rinsed with 15.0mL of diethyl ether and the resulting mixture was added to the separatory funnel.
12. The separator funnel was shaken and then the aqueous and organic layers that formed were separated into different beakers.

13. The extracted aqueous phase and 15.0mL of ether were added to the separatory funnel, and the aqueous phase was extracted, leaving the organic phase in the separatory funnel
14. The organic phase collected in step 12 was then added to the separatory funnel. 20.0mL of aqueous 10% NaOH solution were added to the separatory funnel, the aqueous phase was extracted, and added to a beaker.
15. Step 15 was repeated, and the two aqueous extracts collected were combined into one beaker.
16. Concentrated HCL was added drop wise until the combined aqueous extract solution become acidic. The mixture was then allowed to cool in an ice bath for approximately 10 minutes.
17. The crystals that formed were collected using suction filtration.

Observations/Data:

Experimental Procedure and Observations:

- Table 1: Reagent Table

	Molecular Weight (g/mol)	Density (g/mL)	Amount (g or mL)	Moles (mol)
Magnesium Turnings	24.30	1.74	0.8g	0.0329
Iodine	126.90	4.93	2 crystals	N/A
Bromobenzene	157.01	1.50	3.0mL	0.0287
Diethyl Ether Anhydrous	74.12	0.714	2.0mL	0.0193

- Table 2: Qualitative Observation of the Preparation of a Grignard Reagent

Initial Appearance of the Reaction Mixture	Appearance of the Heated Reaction Mixture
dark brown, translucent liquid	light yellow, translucent liquid.

- Table 3: Quantitative Observation of the Preparation of a Grignard Reagent

Time that the Reaction Mixture was Heated Without any Additional Aid (min)	Time that the Reaction Mixture was Heated with the Aid of a Hot Water Bath (min)
5:00	21:00

- *Table 4: Qualitative Observation of the Grignard - Carbon Dioxide Reaction*

Appearance of the Reaction Mixture During the Addition of the Grignard Reagent to Carbon Dioxide
Light yellow, translucent liquid. Contained a white precipitate.

- *Table 5: Qualitative Observation of the Isolation of Benzoic Acid*

Appearance of the Separatory Funnel During the HCL/Ether Extraction	**Appearance of the Separatory Funnel During the NaOH/Ether Extraction**	**Appearance of the HCL Induced Precipitate**
Top Layer: light yellow, translucent liquid Bottom Layer: clear, liquid	**First Extraction** Top Layer: light yellow, translucent liquid Bottom Layer: light brown, translucent, liquid **Second Extraction** Top Layer: light yellow, translucent liquid Bottom Layer: clear, liquid	Light yellow

- *Table 6: Observations and Quantitative Analysis any of Collected Product*

	Isolated Benzoic Acid
Weight of Vial (g)	0.19g
Weight of Vial + Product (g)	0.43g
Weight of Product (g)	0.24g
Melting Point Range (^{0}C)	122^{0}C - 123^{0}C
Appearance of the Dried Product	Light yellow flaky crystals

Mechanisms

-Generating the Grignard Reagent (Phenylmagnesium Bromide)

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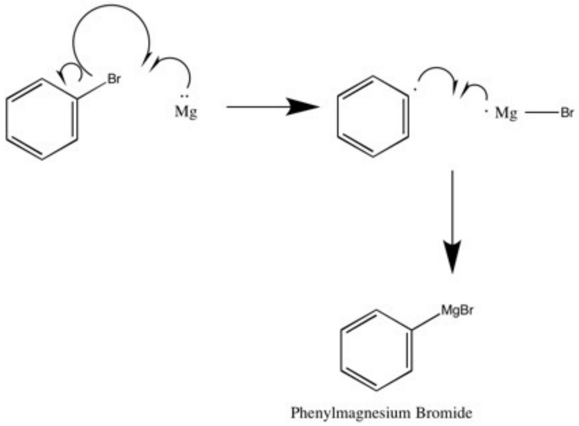
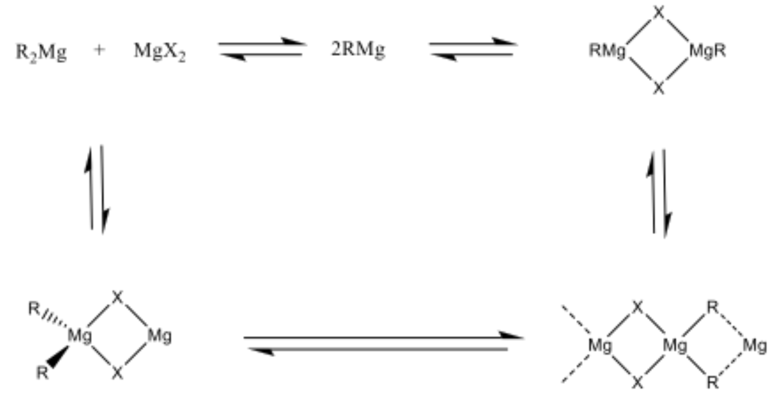
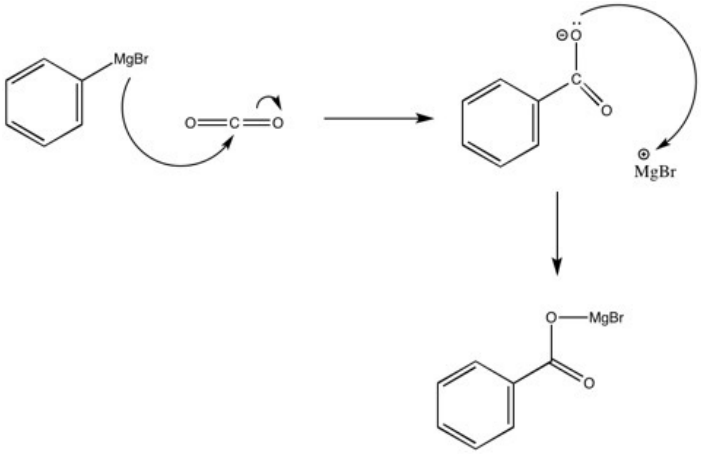


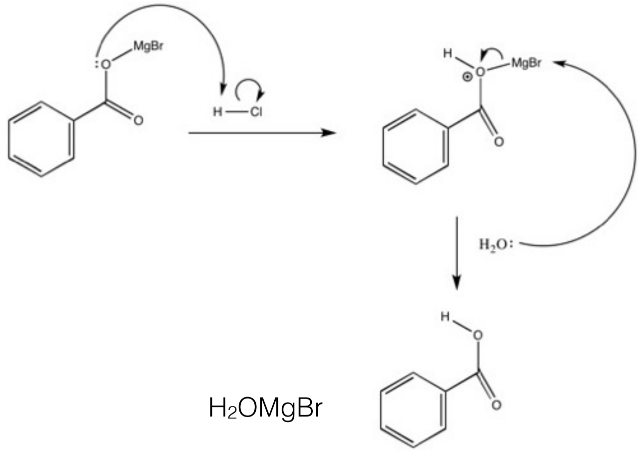
- *Equilibrium of Grignard Reagent*



- Reaction of Phenyl-magnesium Bromide with Dry Ice (CO_2)



- *Workup of Grignard Products using Acid Hydrolysis*



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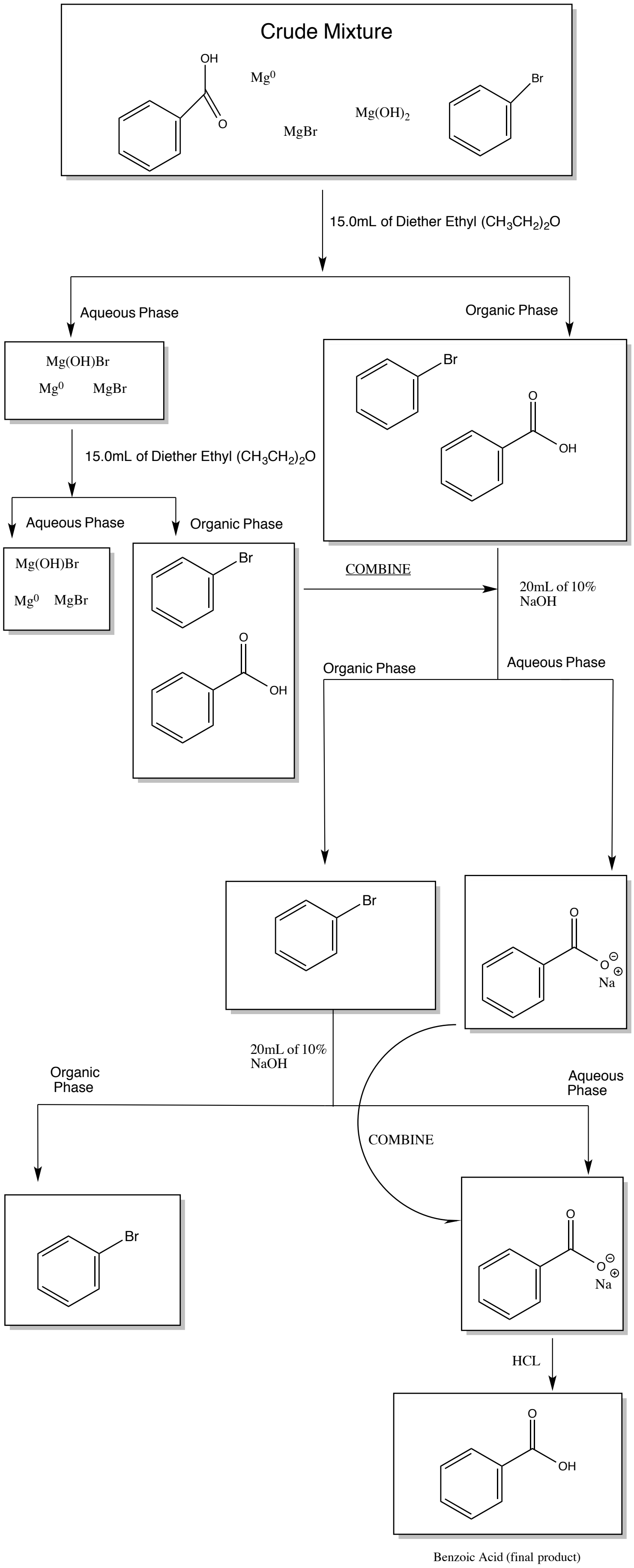
-Separatory Funnel Extraction Flowchart:



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Yield of Benzoic Acid

Reaction is given by:

$Mg_{(s)} + PhBr_{(l)} + CO_{2(s)} + HCL_{(aq)} \longrightarrow PhCOOH_{(l)} + Mg^{2+}_{(aq)} + Cl^{-}_{(aq)} + Br^{-}_{(aq)}$

*Note that bromobenzene is the limiting reagent, as all reactants and products are in 1:1 ratio, and bromobenzene is the lowest in amount of mols.

Theor. Yield = number of moles of benzoic acid * molar mass of benzoic acid
= mols of bromobenzene * [1 mol of benzoic acid/ 1 mol of bromobenzene]
= 0.0287 mols * (122.12 g/mol)
= 3.50g

Actual Yield = 0.24g

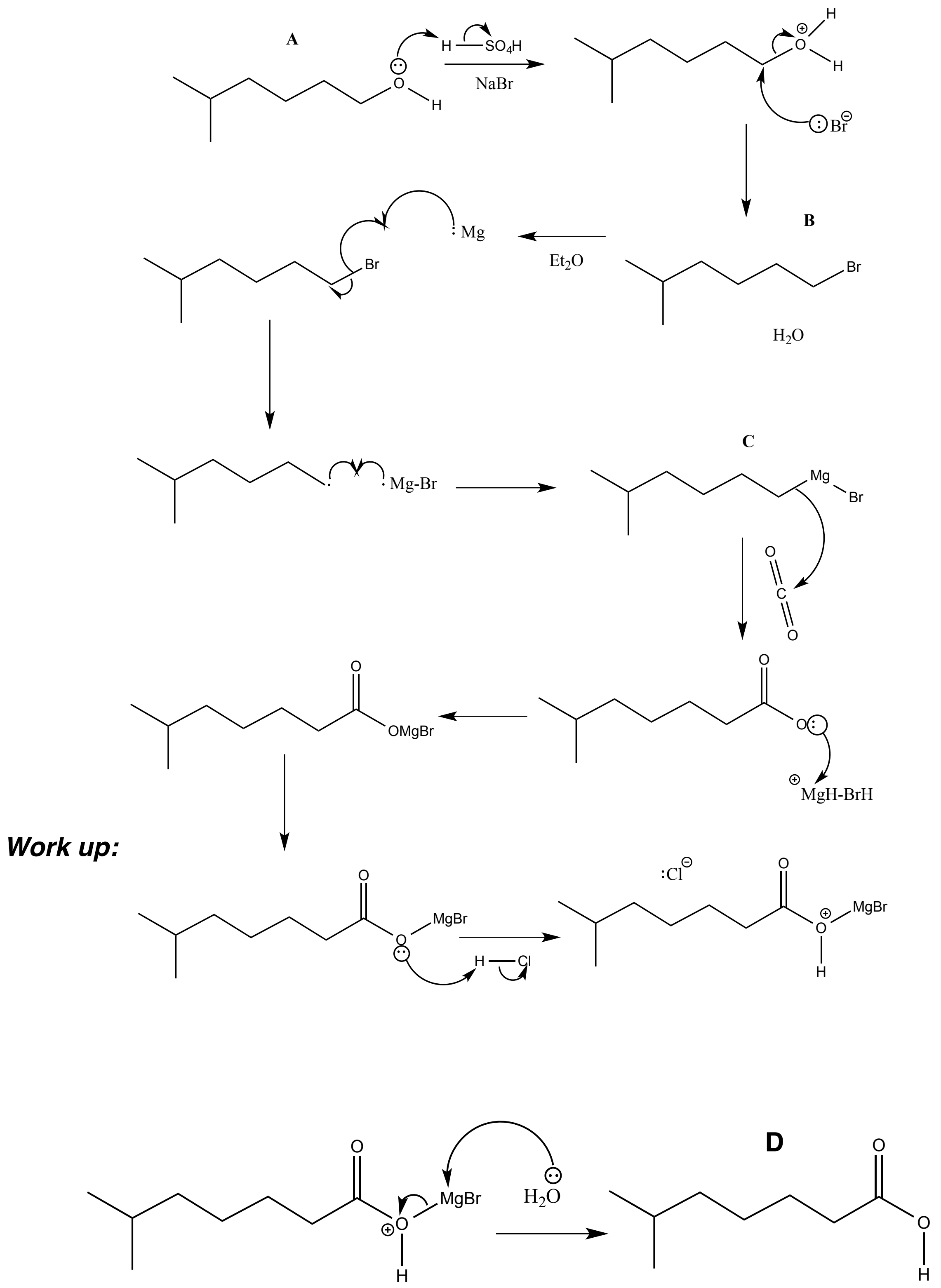
Percent yield = Actual yield/theoretical x 100%
= 0.24g/3.50g
= 6.9%

**See* Error Discussion *for explanation regarding the very low percent yield.*

Discussion*:*

Discussion Questions

1. a)



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b) Yield in the conversion from (A) to (B) = 65% = 0.65
Yield in the conversion from (B) to (D) = 75% = 0.75

Overall Yield of (D) of (A) is 75% of the yield of (B) from (D), which is 65%. So, Yield of (D) from (A) is (0.65)*(0.75) = 0.49 = 49%

Therefore the amount of (D) obtained from (A) is 49%.

c) Assuming that (A) and (D) are in a 1:1 ratio in the net reaction equation,

%yield of (D) from (A) * number of moles of (A) = number of moles of (D)
number of moles of (A) = 0.75mol/0.49
= 1.5 mols of (A)

Therefore, the number of mols of (A) required to produce 0.75 mols of (D) is 1.5 mols.

2. Grignard reagents are strong bases, and typically have pKa's of greater than 30. For this reason, any water present will undergo and acid-base reaction with the grignard, destroying the nucleophilic property of the carbon atom directly adjacent to the magnesium atom. This protonatation of the grignard reagent will interfere with the formation of the magnesium intermediate. For these reasons, anhydrous diethyl ether is used - firstly because it is "dry" (contains no water) and secondly, because it offers a protection against oxidation, as the highly volatile vapours of diethyl ether help prevent oxygen in the atmosphere from reaching the reaction solution (which contains the grignard reagent).

3. The reaction between the magnesium turnings and the bromobenzene is highly exothermic, and when the contents are first added to the round bottom flask, the heat produced is sufficient boil the the ether (which has a boiling point of 37^0C) and therefore the reflux will continue. As the magnesium gets consumed by the reaction, the reaction rate slows down and eventually there is no longer enough heat being released by the reaction to sustain the reflux. At which point, the round bottom flask was placed in a warm water bath, in order to provide the heat (thermal energy) necessary to continue the reflux. Specifically, a warm water bath was used in place of flames, as ethers are highly flammable (as well as other organic compounds used).

4. *See 'Reaction of Phenyl-magnesium Bromide with Dry Ice (CO_2)' in* **Observations** -> <u>Mechanisms</u> for the reaction of phenylmagneisum bromide and carbon dioxide.

See 'Workup of Grignard Products using Acid Hydrolysis' in **Observations** -> <u>Mechanisms</u> for the workup mechanism.

5. The dry ice must be freshly obtained and quickly added to the reaction mixture - this is because its extremely cold temperature (-78.5^0C) will cause any water that is in the atmosphere and comes close to the dry ice to condense, and leave a layer of moisture on

the ice. This layer of moisture, for aforementioned reasons, would interfere with the reaction.

General Discussion:

This experiment, by nature, required a strict set of precautionary steps in order to prevent the contact of water with the Grignard reagent. Briefly, all glassware used in the lab was heated in an oven in order to remove water residue. *Anhydrous* diethyl ether was used (as opposed to 'regular' diethyl ether) throughout the lab and, a drying tube containing a drying agent, calcium chloride ($CaCl_2$), was utilized to remove all water vapours prior to the reaction between bromobenzene and the grignard reagent. (**See Discussion Questions, #2 for more details - including why anhydrous diethyl ether is used and why water is avoided so intensely for this lab)*

Iodine is added in order to activate the surface of magnesium. Magnesium is highly oxidizing, so it reacts with oxygen to form a layer over top of the magnesium. Iodine converts MgO to MgI. The MgI floats away in solution, and we are left with a fresh layer of Mg.

During execution of the procedural steps, an exothermic reaction was observed after the mixing of iodine, magnesium, bromobenzene and *anhydrous* diethyl ether, providing the necessary heat to continue the reflux (for a short period of time). Placing the mixture in a hot water bath ensured the reflux continued (**See Discussion Questions, #3 for more details*). The Grignard reagent, phenyl magnesium bromide, then reacts with carbon dioxide in the form of dry ice and produces a magnesium salt that must be hydrolyzed by HCl (an acid) to remove the salts and eventually produce benzoic acid - this is the work up phase of this experiment (**See Discussion Questions, #4 for both mechanisms*).

Generally, benzoic acid is not soluble in water, therefore when diethyl ether was added to the mixture it dissolved in the ether phase (both *aqueous* and *organic*). To remove the water-soluble magnesium salts and other possible side products from the benzoic acid, an extraction was carried out and the aqueous and organic layers were separated. This separation was preformed twice, and another organic layer was extracted and collected. To further purify the benzoic acid, the combined organic layers consisting of ether and the side products were washed out with 10% NaOH. Only the benzoic acid dissolves in the NaOH, leaving the side products in the ether allowing the benzoic acid to now be collected. To reverse the reaction and restore the benzoic acid, excess HCl was added to the solution. The red coloration of the litmus paper induced by the solution indicated it's acidity. In the final steps of the experiment, the product was collected through suction filtration.

Error Discussion:

The limiting reactant was calculated to be bromobenzene (because there were only 0.0287 moles of it). This produces a theoretical yield of 3.50 g of benzoic acid. The

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experimental yield was measured in the lab to be g, which produces a percent, yield of 6.9% and an overall percent error of 93.1 % (**See* ***Observations ->*** *<u>Yield of Benzoic Acid</u> for more details including all calculations).*

We believe our major source of error during this lab occurred when we attempted to add the dry ice to the reaction mixture. More specifically, we did not add the dry ice *immediately,* rather, there was a short period off time between obtaining the dry ice from the container and adding it to the reaction mixture. We now realize that it was crucial to add the dry ice *immediately* after obtaining it from the container to avoid any possible water contamination - which would interfere with the Grignard reagent and significantly hinder the reaction process. (**See <u>Discussion Questions</u> #5, for more details on why its imperative to use 'fresh' dry ice).*

Throughout the execution of the procedural steps, *extreme caution* was taken in order to prevent water contamination that would have otherwise interfered with the Gringnard reagent (**See <u>General Discussion</u>, first paragraph for an explanation of these precautions).* As such, we conclude that the aforementioned, experimenter source of error, *is the major contributor* to our extremely low percent yield of 6.9%.

Conclusion:

0.24g of *benzoic acid* was synthesized from *bromobenzene* in this experiment, giving us a percent yield of **6.9%** and a percent difference of **93.1%**.