CHM 1321

Work Sheet – Experiment 4

<u>Experiment Title:</u>

Preparation of Benzoic Acid using a Grignard Reagent

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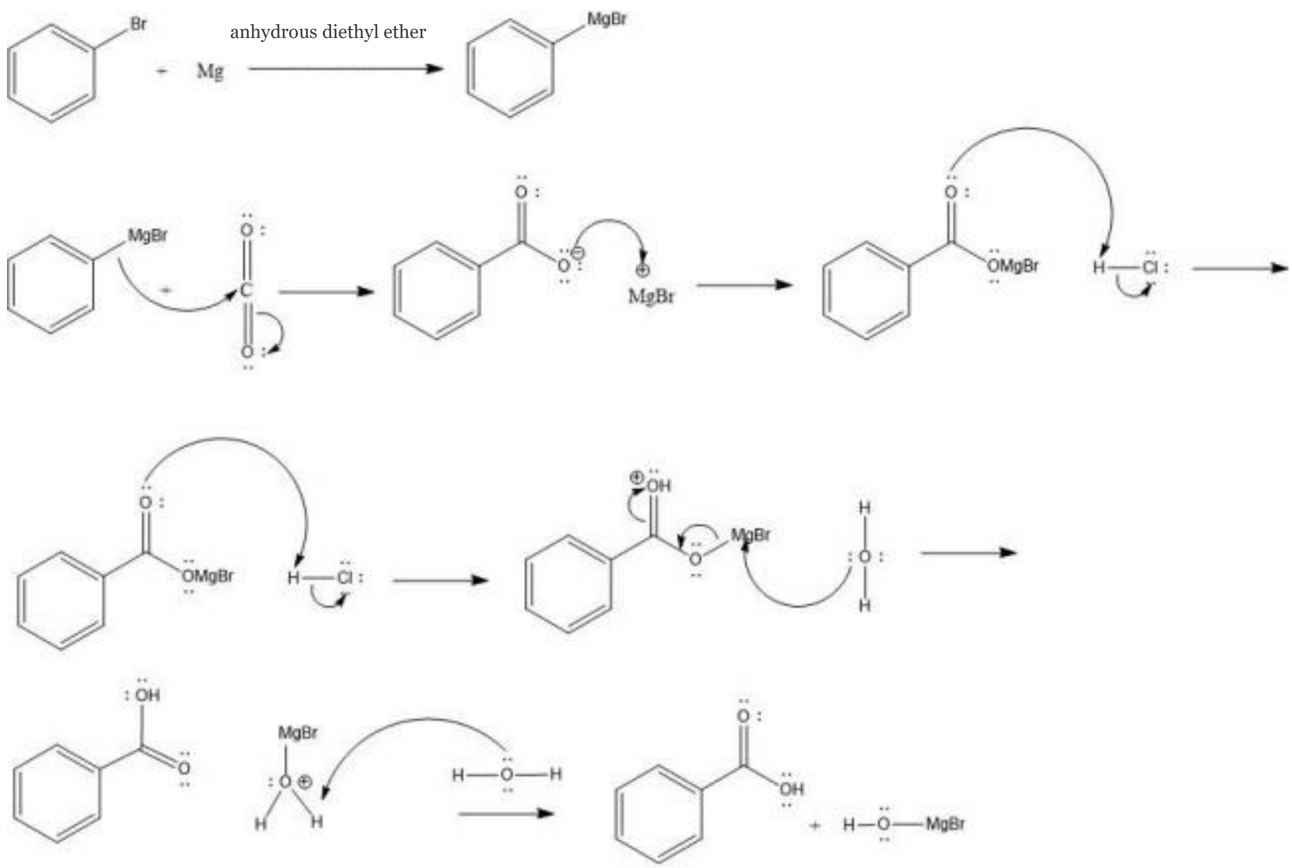
<u>Sample Data Set Number:</u>

[L4-Data1]

(Please note that if the sample data set numbers are not included, you will not receive a grade for the results as the TAs who are correcting the reports will not know which data sets you received)

Introduction:

The purpose of this laboratory was the preparation of benzoic acid using a Grignard reagent. The general formula, RMgX, is used for a Grignard reagent. R symbolizes an organic group while X represents a halogen (Li et al., 2018). A Grignard reaction contains Grignard reagents, which can have any of several different types of compounds, such as ketones, aldehydes, or esters. These Grignard reagents yield a variety of products, such as alcohols. Materials must be dry during such reactions as water could protonate the Grignard carbon as it is a nucleophile. If this were to happen, a hydrocarbon would be formed rather than the completion of the reaction. During the first step of this reaction, solid magnesium is added to bromobenzene which will allow for the formation of the Grignard needed for this reaction. The next step involves carbon dioxide, which is added to the Grignard reagent to form a carbonyl group. HCL is then added to protonate the reagent and following this, ice/water is added to rid of any unwanted aqueous ions. The following reaction mechanism illustrates this:



Procedure:

As outlined in the Introductory Organic Chemistry Lab Manual, Experiment 4 (Durst, Scaiano, Ogilvie, & Flynn, 2013)

Table of Reagents:

Table 1 – Reagent Table for the Grignard Reaction

Reagent	Molecular Weight (g/mol)	Density (g/ml)	Amount (g or ml)	Mol	Equiv.
Bromobenzene	157.01	1.491	3.0 mL	0.0287	1.0
Magnesium Turnings	23.21	1.738	1.0 g	0.043	1.5
Iodine	253.81	4.94	0.20 g	0.00079	0.028
CO_2	44.01	0.00198	2.5 g	0.057	2.0
Diethyl Ether	74.12	0.71	20.0 mL	N/A	N/A

(ChemicalBook)

Calculations:

Table 2 – Using the names for the TLC plates from *Figure 2* (see *Results and Discussion*), *Table 2* gives the calculated R_f value for each spot of each TLC plate.

	R_f Spot 1 (Ref.)	R_f Spot 2 (Co.)	R_f Spot 3 (R)	R_f Spot 4 (P)	R_f Spot 5 (Co.$_2$)	R_f Spot 6 (R_2)
TLC Plate 1	0.68	0.68	0.73	N/A	0.25	0.25
TLC Plate 2	0.69	0.69	N/A	0.22	0.22	N/A

Table 3 – Table of results for the Grignard reaction.

Compound	Molar Mass (g/mol)	Mass Obtained (g) (Mass Yield)	Moles of Product Obtained (mols)	% Composition (Percent Yield)	Melting Point
Benzoic acid	122.12	3.1	0.025	89.1%	117-121°C

Example of R_f calculations using TLC Plate 1 (see *Table 2*):

d 1 = 3.0 cm   d s = 4.4 cm

R_f = d1 / ds

R_f = 3.0 / 4.4

R_f = 0.68

Therefore, the R_f value for Ref. spot on TLC Plate 1 is 0.68.

Calculation of percent yield of reaction:

1 mole benzoic acid = 122.12 g

x moles benzoic acid = 3.1 g

1 mole bromobenzene = 157.01 grams

x moles bromobenzene = 3.0 grams

density of bromobenzene = 1.491 g/ml

% yield = (moles of product / moles of reagent) *100%

% yield = [(3.1 g / 122.12 g/mol) / ((3.0 ml * 1.491 g/ml) / (157.02 g/mol))] *100%

% yield = (0.02538 / 0.02848) *100%

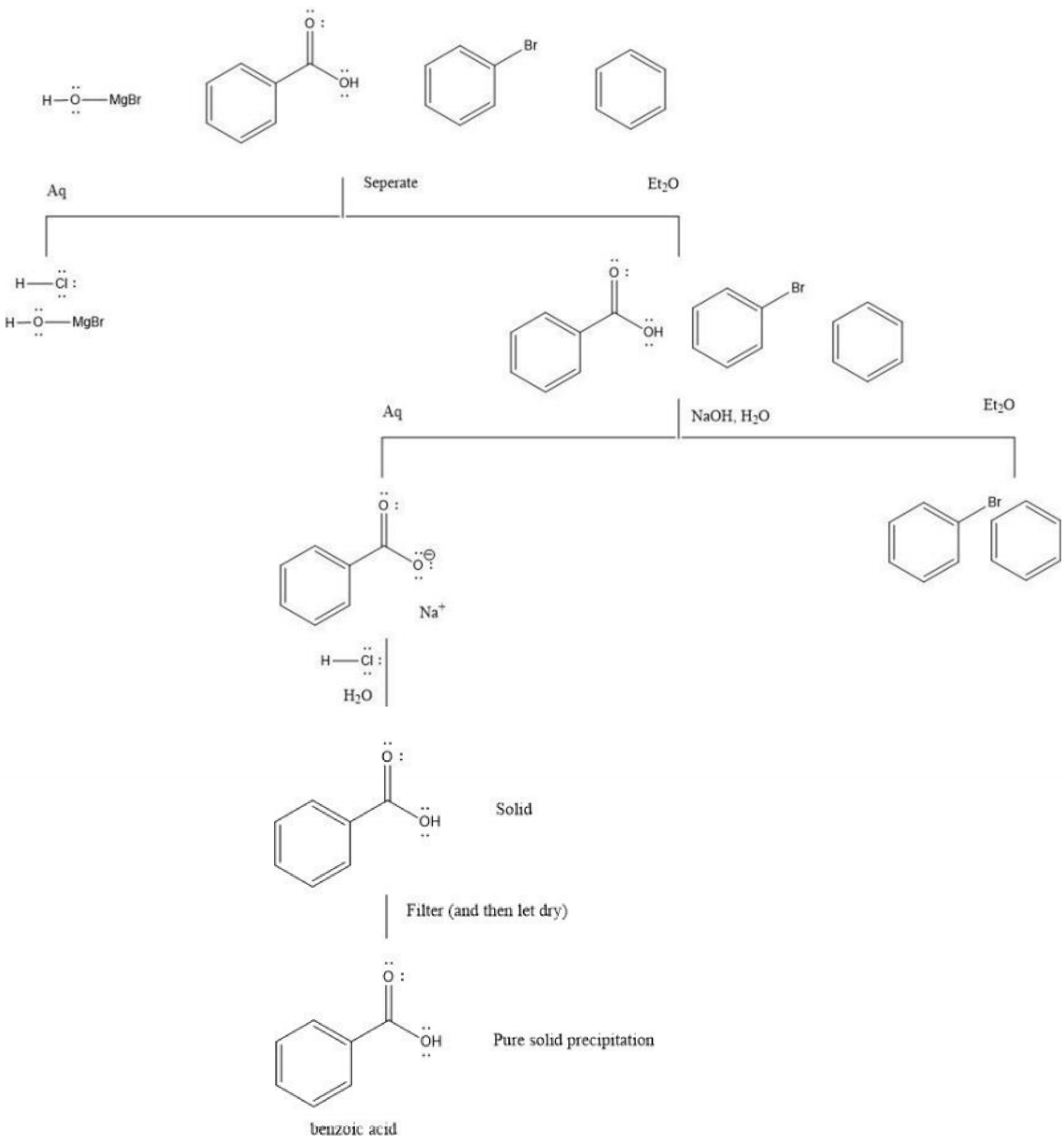
% yield = 0.8911 *100%

% yield = 89.1 %

Therefore, the percent yield of the reaction is 89.1%.

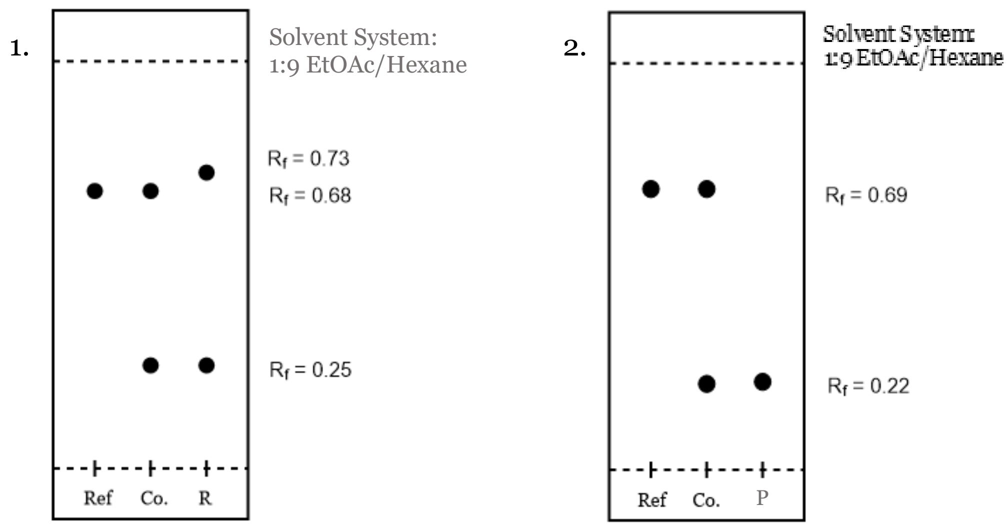
<u>Flowchart</u>:

Figure 1 – Flowchart depicting extraction process performed during this lab.



Results and Discussion:

Figure 2 – TLC plates for *Isolation of the product*. *Ref* represents the starting material, *Co* represents the co-spot, *R* represents the organic layer, and *P* represents the product.



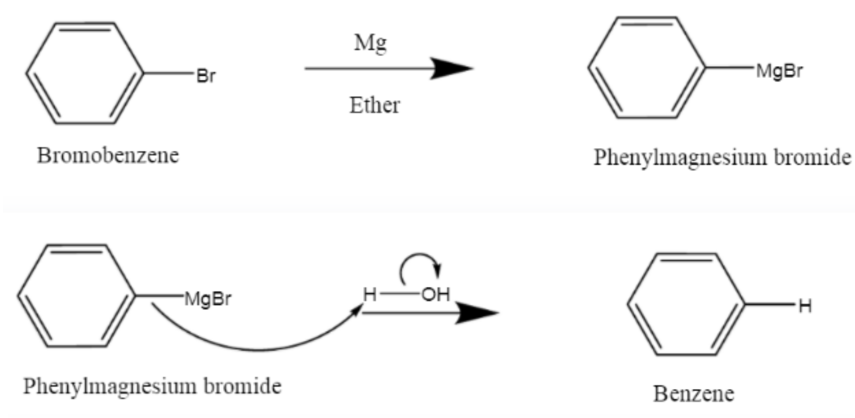
- The emphasis on this lab was to isolate benzoic acid using a Grignard reagent.
- At the beginning of the lab, it was important to make sure that the glassware was fully dry as the presence of water could ruin the reaction by forming a hydrocarbon and giving false results. During the Grignard reaction, the use of anhydrous diethyl ether was very important as it is aprotic and has no traces of water.
- The bromobenzene/anhydrous diethyl ether solution was added into the round bottomed flask, containing magnesium pieces and iodine crystals, in two portions, during the first part of this lab. It was added in two portions as, if this solution were added all at once, it would have caused the formation of an unwanted product, biphenyl. This would take away from the product mass. This also allowed for the maintenance of a low temperature which kept the ether from boiling over, as it has a low boiling point, favoring the Grignard reaction. It was crucial to let the mixture come to a boil on its own to start the exothermic reaction.
- Adding a small amount of iodine to the reaction will result in the breaking of a protective layer on magnesium oxide, releasing the oxide layer to interact with the solution and react quickly.
- Once the Grignard reaction was completed, dry ice was added, which would result in the formation of benzoate.

- 20-30 g of ice, 25ml of 2.5M HCl, and 15ml of ordinary diethyl ether were then added into the mixture to see separation of layers.
- There were then two extractions performed in the lab. The first used the reaction mixture (Grignard product + HCl + ice + ordinary diethyl ether) and ordinary diethyl ether was utilized as a solvent. This was performed twice to ensure that the aqueous phase was completely separated of all organic extracts. Following these extractions, a first TLC plate was performed. TLC plate 1 (see *Figure 2*) consisted of the organic layer as the sample and starting sample as the reference.
- A second extraction using NaOH was necessary as the results of TLC plate 1 demonstrated the presence of both aqueous and organic solvents. NaOH was used on the organic phase and was then added to the separation funnel to ionize the benzoic acid, forming the aqueous phase. To ensure that the aqueous phase was as pure as possible, this extraction was also performed twice.
- HCl was then added to the second extraction of the aqueous phase to acidify the aqueous extracts. Once this solution was proven to be strongly acidic, the mixture was put into an ice bath to cause benzoic acid to precipitate out.
- A gravity suction filtration technique was then used to dry the product and allow for the collection of the final product. A final product mass was taken of 3.1 g and the final precipitation yield found was 89.1% (see *Calculations*).
- A second TLC plate that was performed which consisted of a sample of the final product (precipitation = benzoic acid) and the starting material as the reference. The results from this plate proved that benzoic acid was indeed produced. Spot *P* on TLC plate 2 (see *Figure 2*) has a relatively low R_f value (0.22) which indicates that this indeed is benzoic acid as benzoic acid is slightly polar due to a carboxylic group (Summers, 2018) and will not travel far up the TLC plate.
- TLC plate 2 also shows that one of the co-spots and the reference spot align at a R_f value of 0.69, indicating that these spots are bromobenzene as it is a non-polar compound, leaving benzoic acid as the spot *P*, lower on the TLC plate.
- In conclusion, this lab was successful as benzoic acid was prepared using a Grignard reagent. The final product was significantly pure as the percent yield of the reaction was 89.1%.
- To obtain future success, it would be wise if additional water were used as little as possible as benzoic acid is soluble in water, resulting in loss of product mass. This will help in achieving a higher percent yield.

Questions:

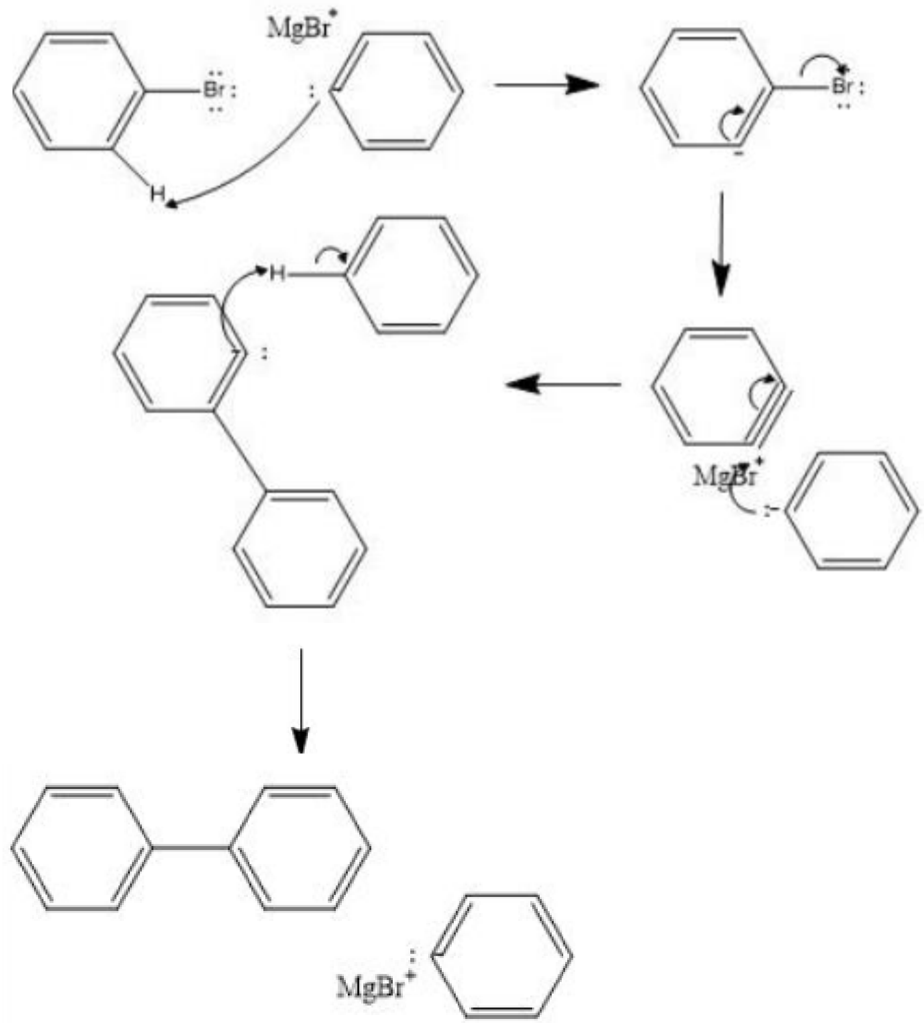
1. **During your Grignard formation, a small amount of benzene is formed. Provide a brief explanation and mechanism to explain this observation.**

The formation of benzene likely occurred due to the small amount of water in the system. This water would react with the Grignard reagent and would protonate it. This means that hydrogen replaces the magnesium bromide from the phenylmagnesium bromide, as indicated in the mechanism below:



2. **During your Grignard formation, a small amount of biphenyl is formed. Provide a brief explanation and mechanism to explain this observation.**

Bromobenzene reacting with the Grignard reagent, phenylmagnesium bromide, caused the formation of biphenyl. This can be seen in the mechanism below:



3. **What mass of water would be required to destroy the Grignard reagent that you prepared in this experiment? What volume does this represent?**

Water and phenylmagnesium bromide react with a 1:1 ratio. With this knowledge, one can calculate the mass of water required to destroy the experiment:

density $_{Bromobenzene}$ = 1.491 g/ml   m $_{Bromobenzene}$ = 1.491 g/ml * 3.0 ml = 4.473 g

n = m/M   = 4.473 g / 157.01 g/ml   = 0.0285 mol $_{Bromobenzene}$ = 0.0285 mol $_{Water}$

m $_{Water}$ = n * M   = 0.0285 mol * 18.02 g/mol   = 0.51 g $_{Water}$ = 0.51 ml $_{Water}$

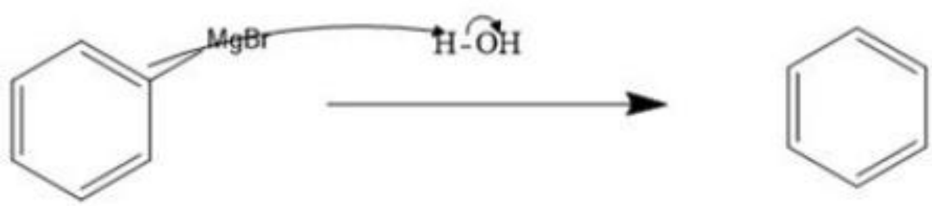
Therefore, a mass of 0.51 ml of water is required to destroy this experiment.

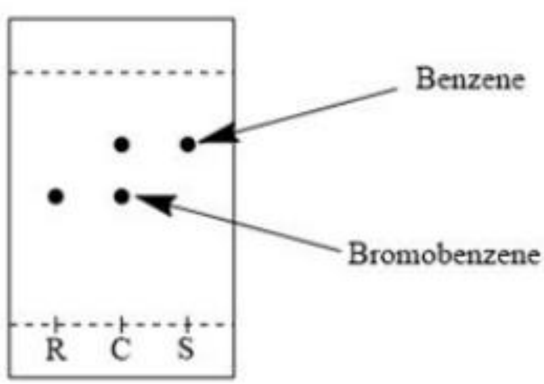
4. Why is the bromobenzene added to your flask in two portions rather than one?

The bromobenzene is added to the flask in two portions rather than one to minimize the amount of bromobenzene in the solution at any given time. Should there be too much bromobenzene in the solution at one point, this will frequently react with the Grignard reagent and this will result in the production of large amounts of biphenyl which will in turn reduce the yield of benzoic acid. Additionally, because of the highly exothermic nature of the reaction, if it is added all at once, the reaction would cause a loss of product due to violent splashing.

5. If you were to take a TLC of your Grignard solution before you add it to the dry ice, what would your TLC look like?

The TLC of phenylmagnesium bromide will only show benzene as the phenylmagnesium bromide will get smothered by the moisture present in the atmosphere. The following reaction would happen spontaneously, where *R* represents the starting material, *C* represents the co-spot, and *S* represents the system:





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