Preparation of Benzoic Acid using a Grignard Reagent

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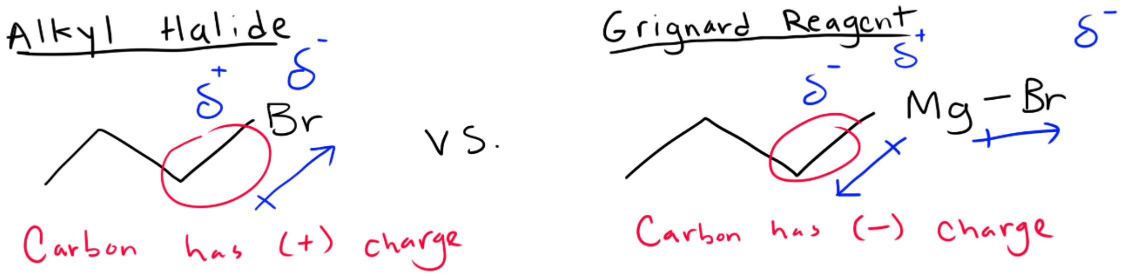
INTRODUCTION:

Synthesis of chemicals using a Grignard reagent is a commonly used technique to be able to easily form new carbon to carbon bonds within organic molecules. In this lab experiment, it is possible by turning a typical alkyl halide into a Grignard reagent through the addition of a magnesium atom. This magnesium is less electronegative than both the carbon and the halogen that it forms bonds with, causing the polarity of the carbon to invert. This is shown in the sketches below:



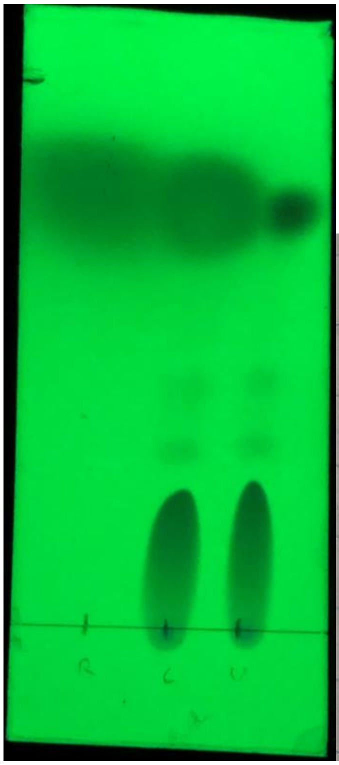
In this lab experiment, the Grignard reagent is used to form benzoic acid. This is possible because of the polarity on the terminal carbon of the Grignard reagent becoming negatively charged, which is uncommon for organic molecules. This makes Grignard reagents very practical to use to form larger carbon chain and to form carbon to carbon bonds easily.

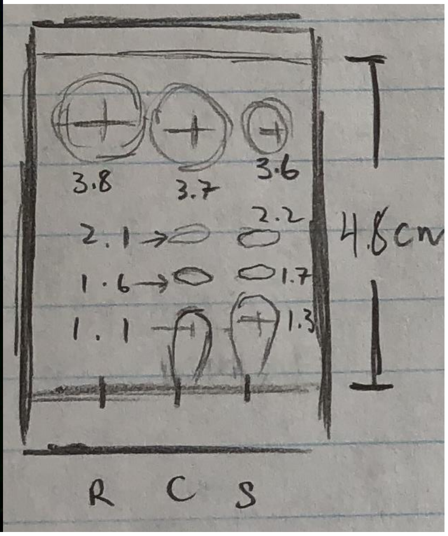
PROCEDURE & MATERIALS: As described in the lab manual (Experiment 5: Preparation of Benzoic Acid using a Grignard Reagent, University of Ottawa, 2008, p. 4-5).

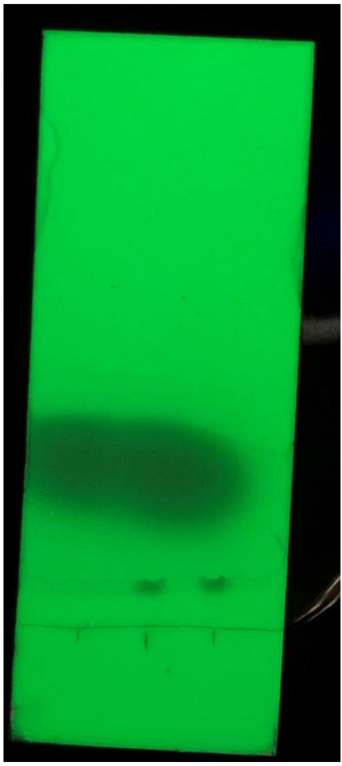
OBSERVATIONS:

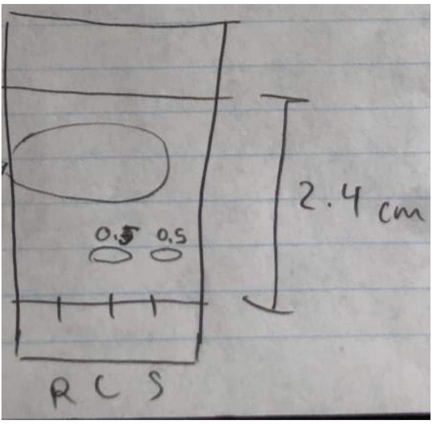
- Bromobenzene (3mL) is a clear liquid
- Magnesium was in the form of small metallic crystals or chunks (0.8g)
- 32.16g of non-dry ice used for reaction
- Large amounts of metallic precipitate stuck to the walls of the 50mL flask during reflux
- 20 minutes of boiling the solution in the 50mL flask caused the solution to turn to a dark brown colour, with some translucency
- When adding the cooled solution to dry ice, bubbling and sizzling noises are observed
  - This bubbling and sizzling slowed down as the solution began to freeze
  - Stirring and agitating the mixture continued the once stalled reaction to completion
- TLC plates use Silicon Dioxide (SiO_2) as stationary solid phase
- EtOAc:Hexanes 1:9 is used as the eluent

TLC PLATES:





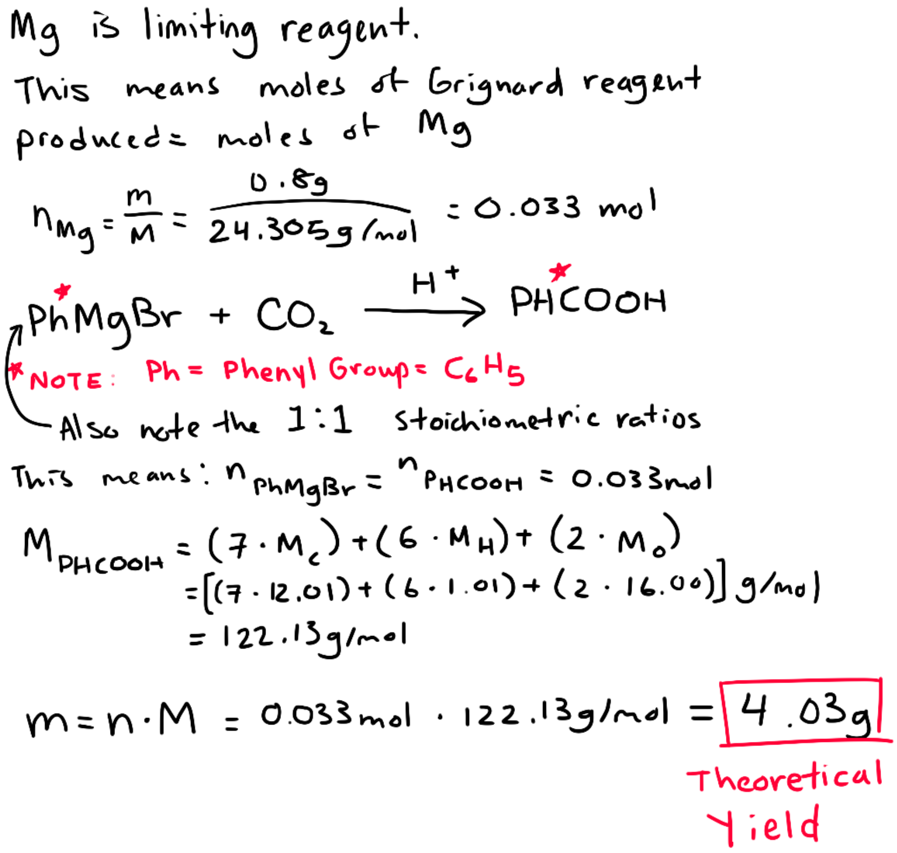




Note: TLC plates are spotted in the order of Reference, Co-spot, Sample.

CALCULATIONS:

The calculation for theoretical yield is displayed below:



Mg is limiting reagent.

This means moles of Grignard reagent produced = moles of Mg

$$n_{Mg} = \frac{m}{M} = \frac{0.8g}{24.305g/mol} = 0.033 \text{ mol}$$

$$\overset{*}{Ph}MgBr + CO_2 \xrightarrow{H^+} P\overset{*}{H}COOH$$

*NOTE: Ph = Phenyl Group = C_6H_5

Also note the 1:1 stoichiometric ratios

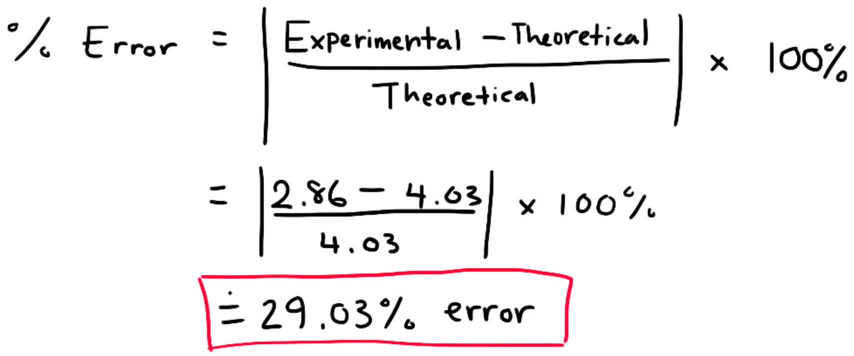
This means: $n_{PhMgBr} = n_{PHCOOH} = 0.033mol$

$$M_{PHCOOH} = (7 \cdot M_C) + (6 \cdot M_H) + (2 \cdot M_O)$$
$$= [(7 \cdot 12.01) + (6 \cdot 1.01) + (2 \cdot 16.00)] \text{ g/mol}$$
$$= 122.13 \text{ g/mol}$$

$$m = n \cdot M = 0.033 \text{mol} \cdot 122.13 \text{g/mol} = \boxed{4.03g}$$

Theoretical Yield

The calculation for percentage error is displayed below:



$$\% \text{ Error} = \left| \frac{\text{Experimental} - \text{Theoretical}}{\text{Theoretical}} \right| \times 100\%$$

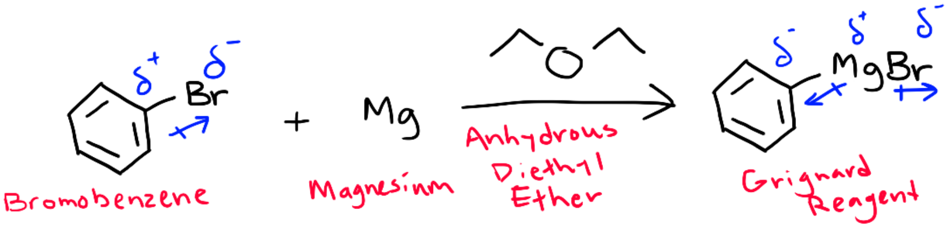
$$= \left| \frac{2.86 - 4.03}{4.03} \right| \times 100\%$$

$$\boxed{\doteq 29.03\% \text{ error}}$$

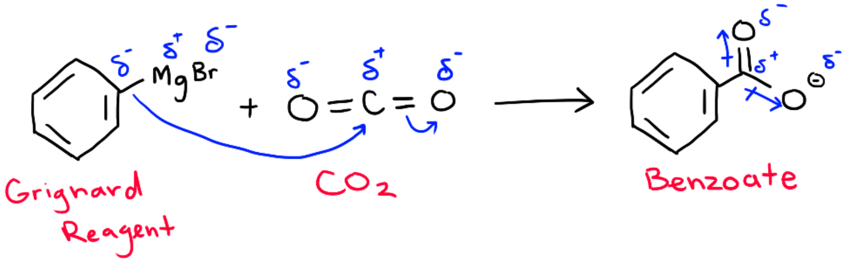
DISCUSSION:

In this lab experiment, two important products are formed. The first is the Grignard reagent, and the second is benzoic acid. The formation of the Grignard reagent is crucial to the subsequent formation of the benzoic acid, as the Grignard reagent is used in the reaction which produces the benzoic acid.

To form the Grignard reagent, we are given bromobenzene and solid magnesium as reactants. When suspended in a nonpolar solution (in this case it is anhydrous diethyl ether), the bromobenzene reacts with the solid magnesium to form the Grignard reagent. This is displayed in the sketch below:

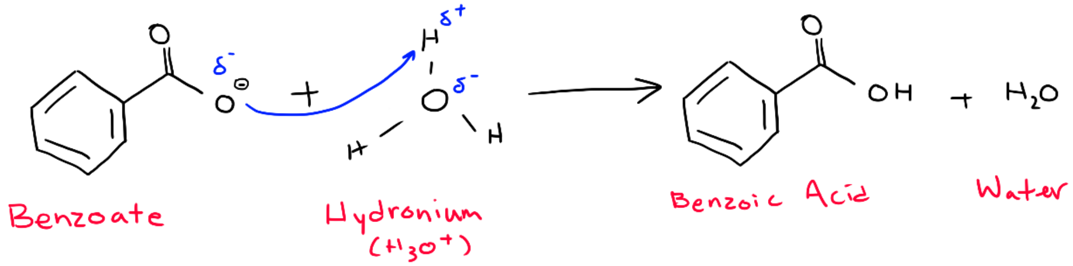


The synthesis of benzoic acid is the next part of the experiment. This is possible by first introducing carbon dioxide (CO_2) to the Grignard reagent and allowing it to react, forming benzoate. In the reaction, the partially negative carbon from the Grignard reagent reacts with the partially positive carbon from the CO_2, forming benzoate. The formation of benzoate is displayed in the sketch below:



In this stage of the experiment, benzoate is the precursor to our desired benzoic acid. To form the benzoic acid, it is necessary to introduce positively charged hydrogen to the benzoate. The hydrogen will bond the negatively charged oxygen on the benzoate, thus yielding benzoic acid. To achieve this, we introduce hydrochloric acid (HCl) to the benzoate solution, allowing the HCl to fully dissociate its hydrogen ions (H^+). These dissociated hydrogen ions form hydronium

(H_3O^+) in the presence of water, which will subsequently react with benzoate to form benzoic acid. This reaction is displayed below in the following sketch:



After the protonation of benzoate into benzoic acid, we isolate the benzoic acid from any unwanted by-products, such as biphenyl. This is achieved through extraction via a separatory funnel. Rinsing the benzoic acid in the funnel with NaOH causes benzoic acid to deprotonate back into benzoate, which is polar, allowing it dissolve into the aqueous layer. The unwanted by-products, such as biphenyl however, are nonpolar, meaning it will dissolve into the organic layer. This allows us to isolate the desired product into the aqueous layer.

After this separation, we are able to protonate the benzoate into benzoic acid using HCl. It is then possible to subject the product to gravity filtration, and subsequently suction filtration. The final yield of benzoic acid was 2.86g. Theoretically, the yield should have been 4.03g, which is greater than our yield, with a percentage error of 29.03%. This is likely due to experimental error, which occurred during this experiment when the filter paper broke during our filtration process. The broken paper made it extremely difficult to obtain the maximum possible yield, due to the loss of product during filtration.

The melting point of our obtained product was 113.6°C, which is less than that of the literature value of between 122°C-124°C, according to the PubChem online chemical database. Due to observational error and time restraints, the range of values associated with our melting point was not recorded/observed. This difference of nearly 10°C could be explained by impurities due to ineffective filtration, and possibly any traces of broken filter paper in our product.

The first TLC plate in this lab experiment shows that there was a large quantity of bromobenzene which had gone unreacted. This is observed by a spot on both the co-spot lane and the sample lane of the TLC plate which reaches near where the reference spot (bromobenzene) had ended at, indicating the presence of bromobenzene.

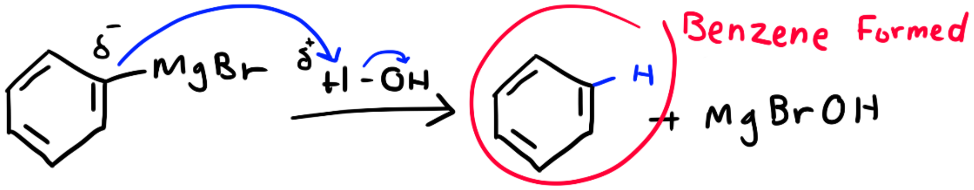
However, there are three other spots on the C and S lanes of the TLC plate respectively. This is indicative of the presence of by-products, as well as the desired product. The tear shaped spot at the bottom of both of the C and S lanes is most likely indicative of benzoate, as it is the most polar molecule which is produced in the reaction. The spots in between the bromobenzene and benzoate spots are likely caused by traces of by-products, such as biphenyl and benzene.

The final TLC plate developed very poorly in our lab experiment. This was due to our first attempt at this TLC plate not absorbing the eluent properly, leading us to encounter an issue with time for our second attempt at this plate. The TLC plate appears to have a large spot encompassing all three lanes, likely caused by a spot in each lane (with extremely close R_f values) bleeding into each other, giving the appearance of one large spot.

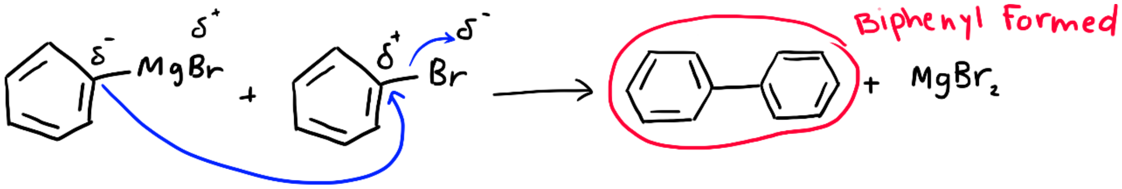
However, we still observed a small spot near the bottom of the TLC plate, in both the C and S lanes. This is likely indicative of benzoic acid, as it is a very polar molecule, which would bind well to the stationary phase of the plate, and prevent any significant movement up the plate via the mobile liquid phase.

QUESTIONS:

1. Grignard reagents (phenylmagnesium bromide in this lab experiment) react readily with water. This is to say that when the phenylmagnesium bromide is in contact with water, the R group of the phenylmagnesium bromide is “released” (in this case it is the benzene ring). The bond between the magnesium (and bromine) and the benzene ring is broken, being replaced with a hydrogen atom from the water present. This is the reaction mechanism which forms benzene, and is possible because the hydrogen from the water is partially negative, while the carbon from the broken magnesium bond is partially positive.



2. In this reaction, biphenyl is formed when the bromobenzene, or phenyl bromide (makes the mechanism easier to understand) reacts with the phenylmagnesium bromide. This reaction forms biphenyl and $MgBr_2$, magnesium bromide. This reaction is possible because of a partially negative carbon atom on the Grignard reagent and a partially positive one on the bromobenzene.



3.

Mg is the limiting reagent.
This means moles of Grignard reagent produced = moles of Mg

$$n_{Mg} = \frac{m}{M} = \frac{0.8g}{24.305\ g/mol} = 0.033\ mol$$

$$\overset{*}{Ph}MgBr + H_2O \longrightarrow MgBrOH + \overset{*}{Ph}\text{-}H$$

* Note: Ph = phenyl group = C_6H_5

Also note the 1:1 stoichiometry throughout the reaction

∴ H_2O required to destroy 0.033 mol of PhMgBr is also 0.033 mol.

$$m_{H_2O} = n \cdot M = 0.033\,mol \cdot 18.02\,g/mol \doteq 0.59g$$

4. The bromobenzene is added to the flask in two portions, as the formation of the Grignard reagent is exothermic, meaning once the reaction is initiated, it will likely cause the solution to reflux. To prevent a violent reflux, which could negatively affect the experiment and yield, the bromobenzene is added in two portions.

There is also the concern that biphenyl will be produced in a side reaction, consuming bromobenzene in the process. The consumption of bromobenzene could possibly negatively affect yield, therefore excess bromobenzene is added to solution (the two part addition of bromobenzene).

5. Before the addition of the CO_2 to the phenylmagnesium bromide, the Grignard reagent is polar where the Mg bond is located. This polarity is caused by the difference in electronegativity between the magnesium and the carbon and bromine. The magnesium is partially positive, while the carbon and bromine are partially negative. This polarity causes the phenylmagnesium bromide to bind to the stationary phase of the TLC plate, which makes it difficult to be eluted by the mobile liquid phase, and thus the TLC spot should stay relatively low, with a low R_f value.

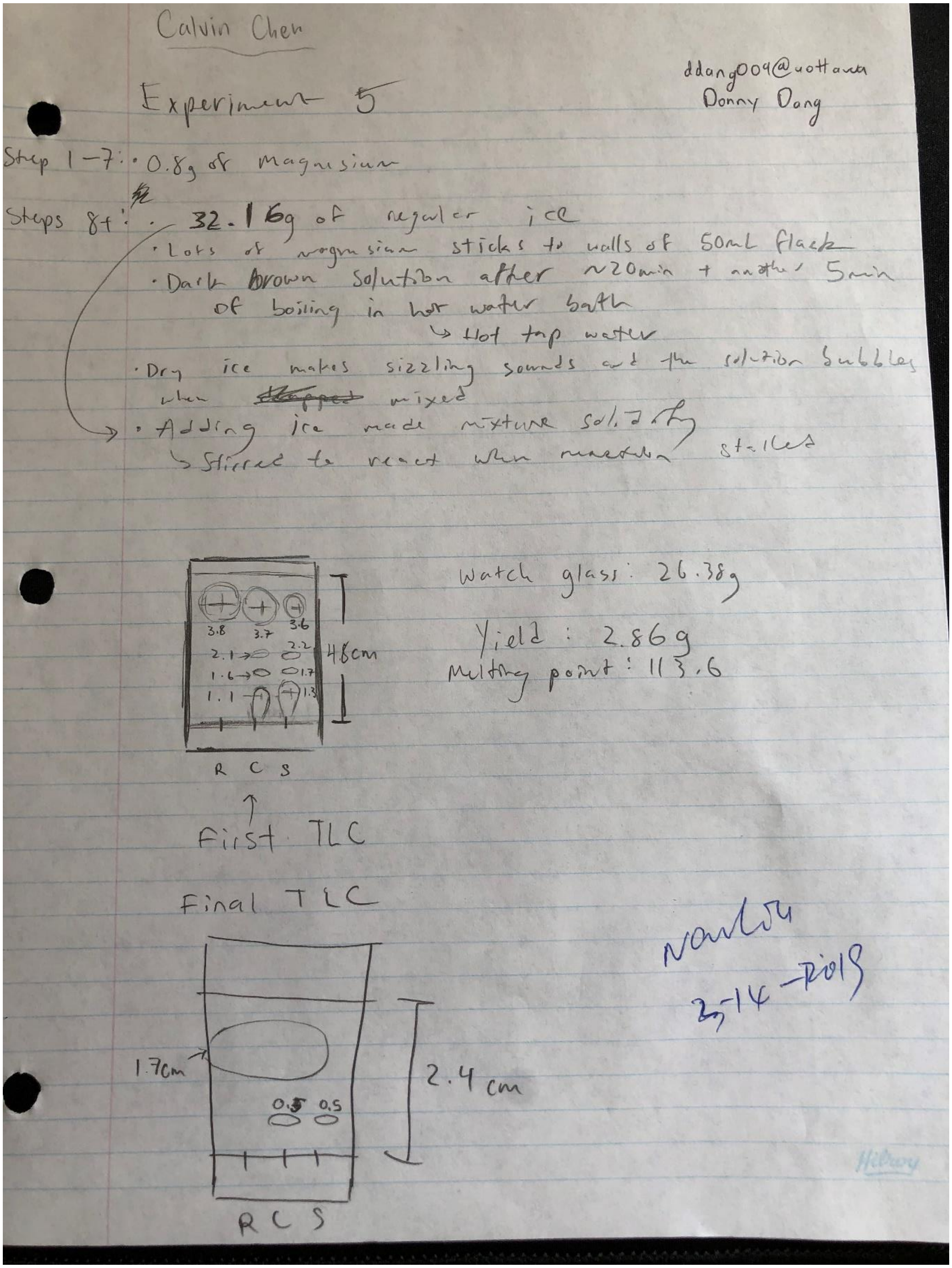
CONCLUSION:

Through the completion of this lab experiment, we are able to fully comprehend the importance and practical use of Grignard reagents. We also are able to develop the important habit of keeping the reaction dry, as there an unwanted reaction would have occurred in the presence of water. The charges associated with the Grignard reagent is also explored through later analysis of the reaction mechanisms, and lab results, allowing us to truly grasp the concept of Grignard reagents.

WORKS CITED:

National Center for Biotechnology Information. PubChem Database. Benzoic acid, CID=243, https://pubchem.ncbi.nlm.nih.gov/compound/243 (accessed on Mar. 20, 2019)

RAW DATA:



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Experiment 5

Step 1–7: • 0.8g of magnesium

Steps 8+: • 32.16g of regular ice
- Lots of magnesium sticks to walls of 50mL flask
- Dark brown solution after ~20min + another 5min of boiling in hot water bath
  - ↳ Hot tap water
- Dry ice makes sizzling sounds and the solution bubbles when ~~stopped~~ mixed
- Adding ice made mixture solidify
  - ↳ Stirred to react when magnesium stalled

Watch glass: 26.38g

Yield: 2.86g

Melting point: 113.6

First TLC

Final TLC

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