

LAB 5: Preparation of Benzoic Acid using a Grignard Reagent

Submitted by:

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uOttawa

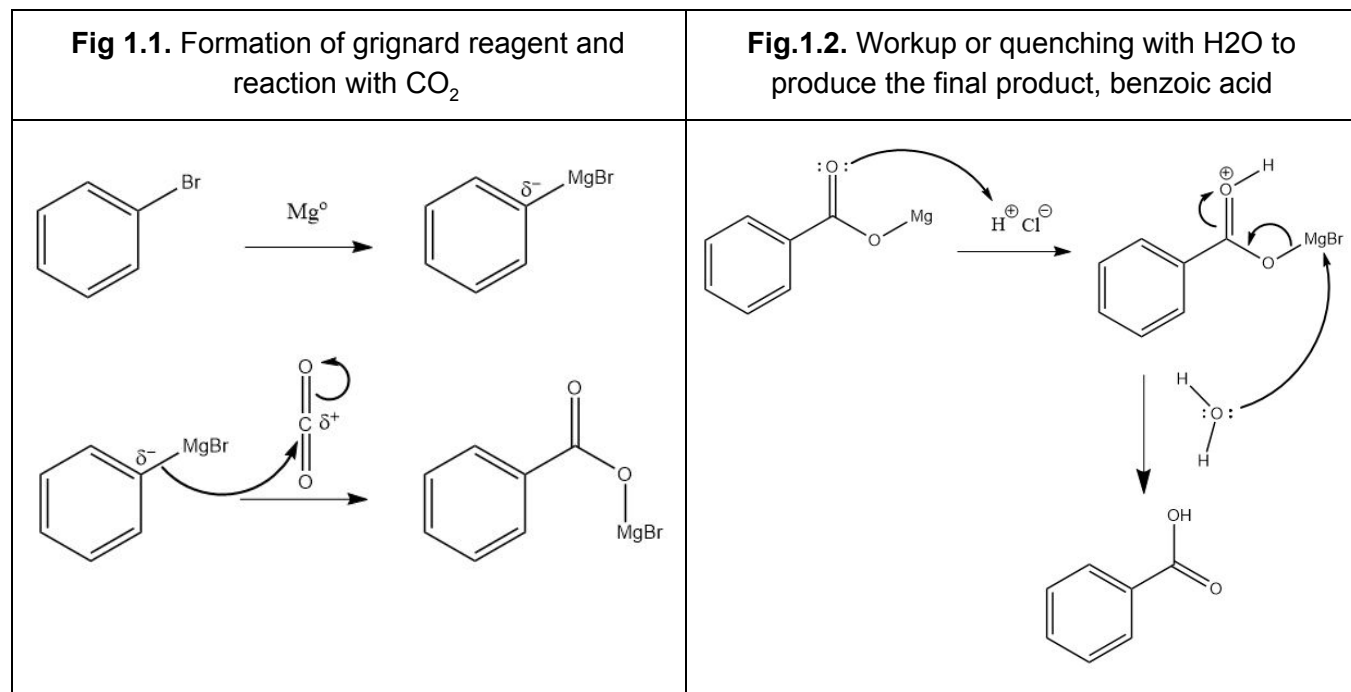
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Mechanism



Procedure

See lab manual [Experiment 5: Preparation of Benzoic Acid using a Grignard Reagent](#) (pg 1-6)*

* Step 12 of the procedure was modified. Instead of using the amount of dry ice suggested ($\frac{2}{3}$ full of a 150 ml beaker), 3-4 pellets of the dry ice was used.

Qualitative Observations

- Dry, hot glassware was used to set up the reflux apparatus.
- The magnesium turnings were silver in colour and the iodine was a very deep almost black-blue colour.
- The diethyl ether and bromobenzene mix was a clear transparent solution.
- When the reagents were mixed into the round flask, the clear once clear solution became red coloured. This red colour disappeared gradually over the course of a few minutes by turning orange then yellow then the solution cleared.
- A little after the solution cleared up bubbles started to form in the round flask. This showed that the reaction had started. The reaction was very vigorous and exothermic as vigorous bubbling was seen. The solution turned a dark brown colour, although it was still clear.
- Once the bubbling had subsided the resulting mixture was added to dry ice. Upon contact with the dry ice some wisps of smoke formed and there was bubbling.
- While mixing with the teflon rod, the mixture became almost like it was "sticky".

- The addition of HCl and diethyl ether causes the solution to become milky white and eventually a yellowish layer forms on the top.
- During this mixing process some white precipitate was also seen and became dissolved upon stirring the mixture.
- This mixture was then extracted with more diethyl ether. After shaking the separatory funnel and waiting for the layers to separate a clear yellow layer formed at the top and a clear layer formed on the bottom.
- Extraction was done multiple time with the same results.
- The final collected aqueous layer had some white precipitate already in it.
- Once extraction was finally complete with the addition of clear 10% NaOH, the collected aqueous layer was acidified with the addition of clear 12 M HCl. This caused the precipitation of white crystals. Once cooled in an ice bath, more crystals formed.
- The crystals were then collected by gravitational and suction filtration.
- The final crystal product was observed to be white and almost fluffy. The crystals formed clumps, as well.

Quantitative Observations and Results

Table 1.0. Reagents involved in the reaction

Reagent	Amount (g or ml)	Molecular Weight (g/mole)*	Moles (mmol)	Density (g/ml)	Equivalence
Bromobenzene	3.0 ml	157.01	28	1.49	1
Magnesium	0.80 g	24.305	33	-	1.2
Iodine	Few crystals	253.809	-	-	-
Anhydrous diethyl ether	20.0 ml	74.123	192	0.713	6.8
CO ₂ (dry ice)	3-4 pellets	44.009	-	-	-

*Molecular weights for reagents from (National Center for Biotechnology Information. PubChem Compound Database; CID=7961, CID=5462224, CID=807, CID=3283, CID=280)

TLCs

Figure 2.1. First TLC of organic phase and bromobenzene as the sample (reference)

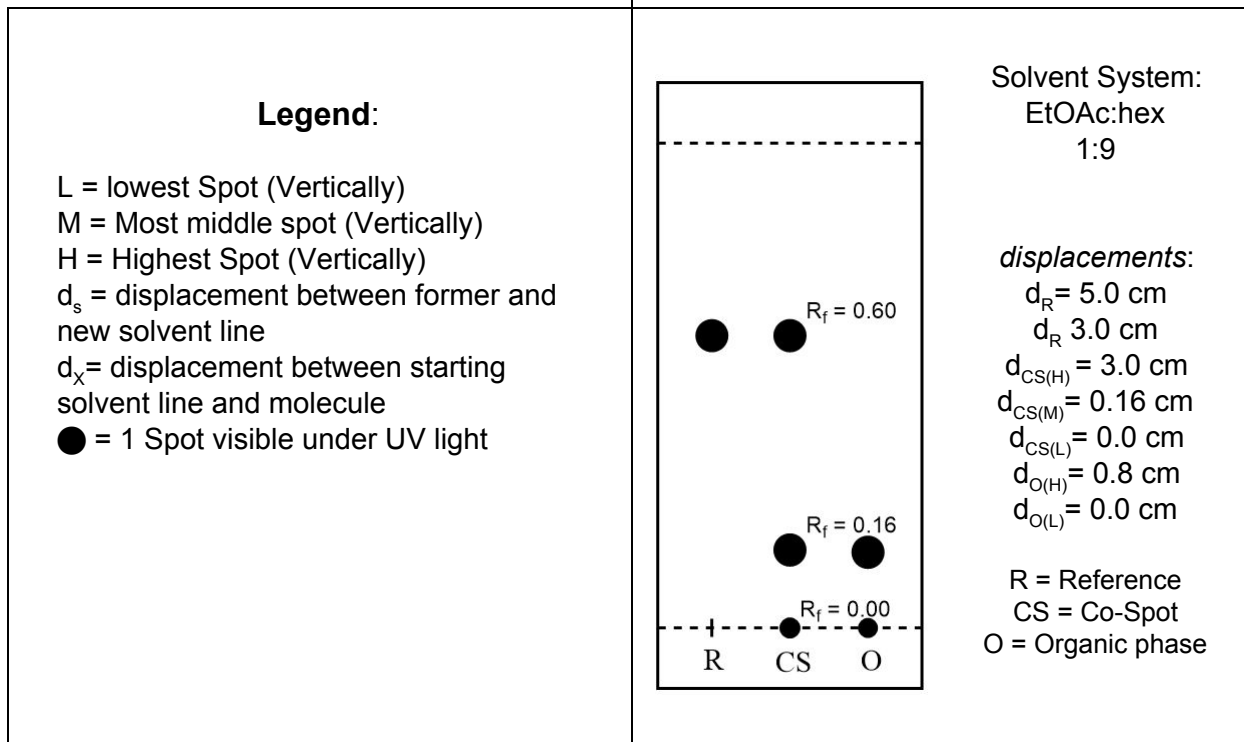


Figure 2.2. (1/2) final TLC of pure product with bromobenzene as the reference

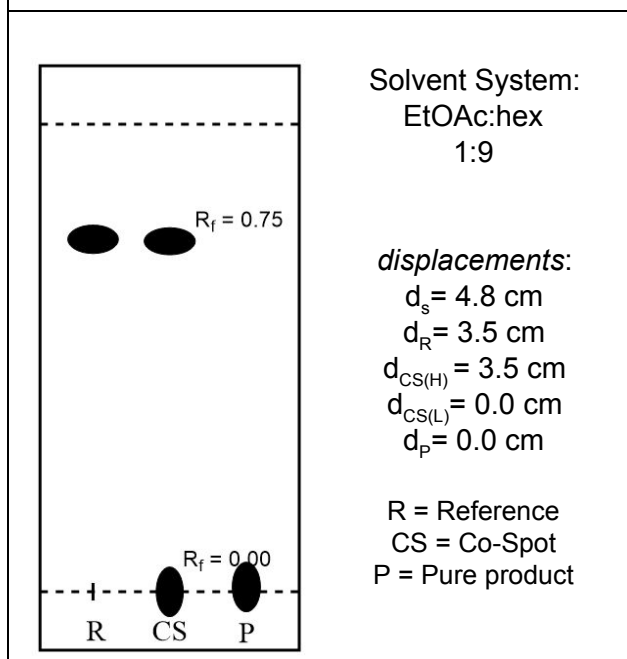


Figure 2.3. (2/2) Final TLC of pure product with bromobenzene as the reference

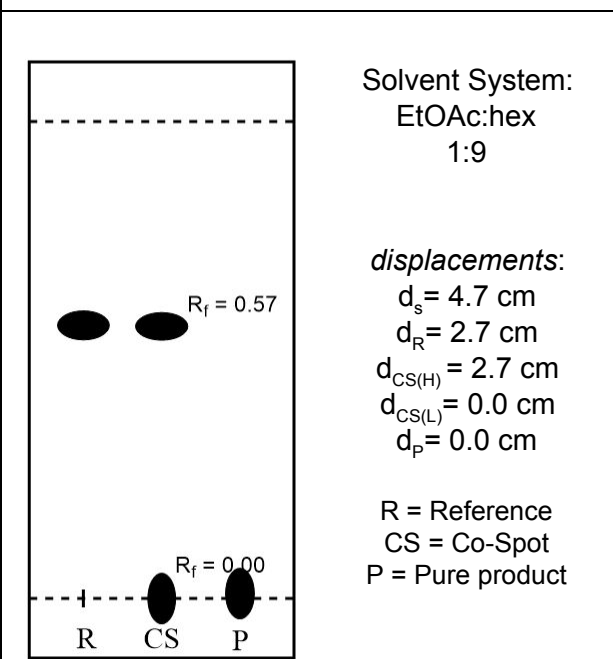


Table 2.0. Results regarding the final product of the grignard reaction, benzoic acid

Product	Amount (g or ml)	Molecular Weight (g/mole)*	Moles (mmol)	% Yield	Actual melting point* (°C)	Experimental melting point (°C)
Benzoic Acid	3.30 g	122.123	27	96	121 - 123	98.4 - 105.1

* Molecular weights for reagents from (National Center for Biotechnology Information. PubChem Compound Database; CID=243)

Calculations

Sample Rf Calculation from Part A, Figure 2.2

<i>Given:</i>	<i>Calculation:</i>
$d_s = 4.8 \text{ cm}$ $d_R = 3.5 \text{ cm}$ $d_{CS(H)} = 3.5 \text{ cm}$ $d_{CS(L)} = 0 \text{ cm}$ $d_p = 0 \text{ cm}$	$Rf = d_x/d_s$ $Rf_{S, CS(H)} = 3.5 \text{ cm} / 4.8 \text{ cm} = 0.75$ $Rf_{rm, CS(L)} = 0 \text{ cm} / 0 \text{ cm} = 0$

Calculation of the percent yield of benzoic acid product

Because stoichiometrically all of the bromobenzene becomes benzoic acid as bromobenzene is the limiting reagent the ratio of reactants to products is 1:1. Therefore, the amount of benzoic acid that should have been obtained theoretically in millimoles is 28 mmol.

$$\% \text{ Yield} = \frac{\text{actual yield (in mmol)}}{\text{theoretical yield (in mmol)}} \times 100$$

$$\% \text{ Yield} = \frac{\# \text{ of mol of product}}{\# \text{ of mol of starting material}} \times 100$$

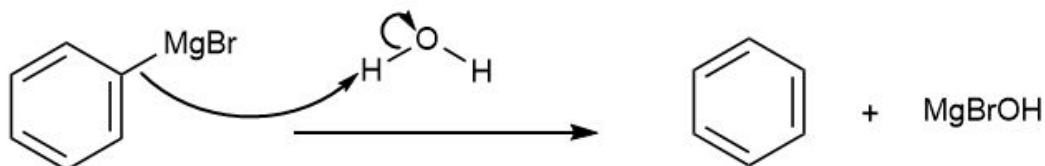
$$\% \text{ Yield} = \frac{27 \text{ mmol}}{28 \text{ mmol}} \times 100$$

$$\% \text{ Yield} = 96\%$$

Discussion

The reaction in this lab was conducted using anhydrous diethyl ether and making absolutely sure that water was not present in the reaction. This is because grignards react with water (H₂O) immediately and once this reaction has taken place it is not reversible. Thus, this ends up “killing” the grignard reagent (“Experiment 5 :Preparation of Benzoic Acid using a Grignard Reagent,” 2014).

Figure 3.1.: Mechanism depicting the formation of benzene



When our grignard reagent reacts with water, benzene is formed and MgBrOH (fig 3.1). The products of this reaction is much more stable i.e. benzene is more stable than phenylmagnesium bromide. Thus, making the reaction irreversible as most reactions favour the direction of the most stable compounds. Furthermore, anhydrous diethyl ether was used because if not anhydrous diethyl ether has the ability to dissolve trace amounts of water. It is this trace amount that has the potential to destroy the grignard at which point the reaction to get benzoic acid is not possible. Additionally water was prevented from entering the reaction by using completely dry glassware that had been heated in an oven beforehand and also by using a drying tube which absorbed any water from the atmosphere and prevented it from entering the apparatus (“Experiment 5 :Preparation of Benzoic Acid using a Grignard Reagent,” 2014).

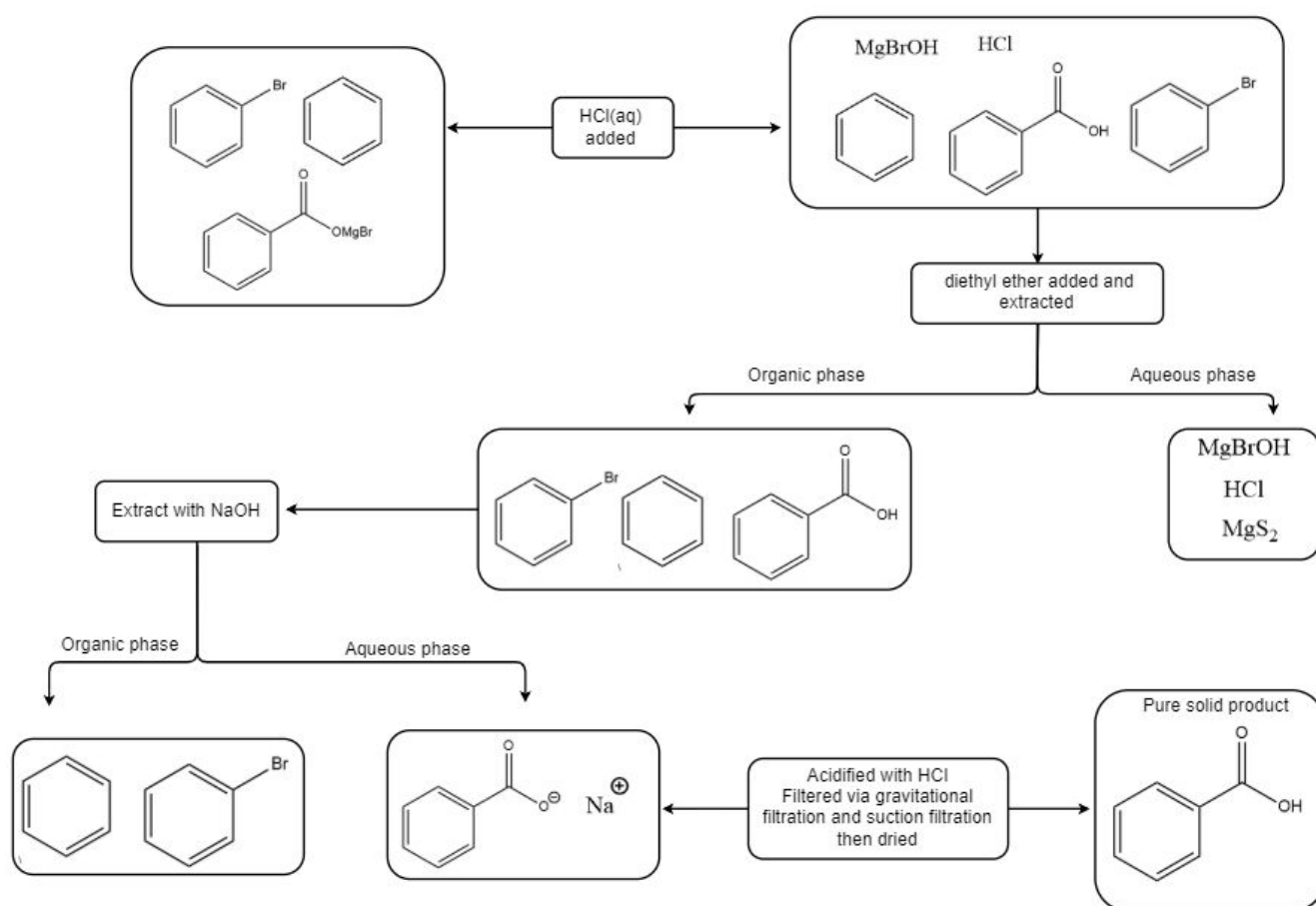
The next substance used for the reaction was iodine. Iodine was used in a catalytic amount. This means that only a small amount of iodine was used just to kick-start the reaction. Magnesium metal really wants to react and give away its electrons. Therefore, when this metal is left exposed to the atmosphere reacts quickly with O₂ to produce a more stable compound called magnesium oxide. So, the magnesium turnings used actually had a coating of magnesium oxide as this was the part exposed to the O₂ and under the coating was the pure magnesium metal required for the reaction. In order to get to the magnesium metal on the inside iodine was added to activate and “strip” away the magnesium oxide coating. This would expose the inner part of the metal turning which was the pure magnesium in order for the reaction to occur.

The next reactant added dry ice (CO₂) was essential because it is a strong electrophile. The grignard produced from the reaction in the reflux apparatus, on the other hand, is a strong nucleophile and really wants to give away electrons and react. This can be seen in fig 1.1. As the Carbon attached to the MgBr in the grignard has a partial negative charge and the carbon in the CO₂ had a partially positive charge (due to the O groups which are more electronegative

and have more pull on the electrons). Therefore, these two substances react readily in a fast exothermic process.

This final phase was conducted in order to isolate and purify the desired product, benzoic acid (fig 1.2) ("Experiment 5 :Preparation of Benzoic Acid using a Grignard Reagent," 2014). In this phase of the experiment, the reaction mixture containing the product formed from the grignard and CO₂ is reacted with 2.5 M HCl (aq) and ice (H₂O). This allowed for the quenching or workup of the previous product in order to obtain benzoic acid and some other byproducts. This mixture was then purified via extraction and is depicted in the flowchart below (Fig 3.2)

Figure 3.2. Flowchart depicting the steps taken to make solid benzoic acid



The thin layer chromatography was performed at first to check the products of the extraction in the organic phase. In the flowchart (fig 3.2) it is seen the benzoic acid some benzene and bromobenzene would be in the organic layer. The organic layer was only showing two spots, none of which matched with the reference bromobenzene which could mean it was fully reacted in the reaction that was performed before the extraction. The spot with the lowest *r_f* was most likely benzoic acid as it is more polar and binds to silica quicker and the other spot must have

been benzene, but it isn't polar at all and should have a high R_f. Perhaps there was some contamination as benzene should have had a much higher R_f than everything else. Overall the extraction mustn't have been done very well due to the discrepancies in the TLC. Some of the aqueous layer might have still been present in the organic layer and polar materials have a lower R_f. A second extraction was also conducted, but a TLC of the organic layer was not performed as per procedure. This might have yielded a TLC without any contamination.

The final TLC was performed with the pure solid benzoic acid co spotted with bromobenzene. No similarities were found, it was clear that the two things tested had very different polarities and the product is pure since it does not have more than 1 spot in its lane. It makes sense the benzoic acid also tested have a lower R_f as it is more polar and binds to the silica lining quicker than the relatively non polar bromobenzene.

The percent yield of benzoic acid obtained for this lab was 96%. This demonstrates that the amount of bromobenzene that got converted to benzoic acid was very high although there was a very tiny amount of water that must have reacted with the bromobenzene which produced the byproduct benzene which took away from the percent yield of benzoic acid.

The melting point of the product was found to be within the range 98.4 - 105.1°C. Compared to the actual melting point (121-123°C), this is quite low. While the range is fairly small, this could indicate that the final product had some contamination or there was too much water present as the suction filtration was unable to completely dry off the crystals. This is further supported by the fact that instead of being powdery, the crystals were more clumped together and fluffy which indicates that there was excess water.

Sources of Error

An unavoidable source of error was that the reactants always had a small trace amount of water. For example, the magnesium turnings were left out in the atmosphere and not dried which would allow water vapours to settle on its surface. This is the same for iodine. The beaker that was used to obtain the diethyl ether and bromobenzene mixture was also left out in the atmosphere for a while in order to cool. This would allow water vapour in the atmosphere to settle on it as well and some might get dissolved in the diethyl ether as well.

After the final extraction of the aqueous layer it was noticed that precipitate was present without acidification. Although once the HCl was added more of the substances precipitated out of the solution. This "premature" precipitation might have been the result of using a beaker that was not clean enough. Perhaps, there were remnants of HCl or some other acidic substances in the beaker that reacted with the aqueous layer upon contact and formed the precipitate. Another source of error was that a lot of the precipitate slipped through the buchner funnel and into the erlenmeyer flask. This also occurred during the suction filtration and decreases the percent yield of our product.

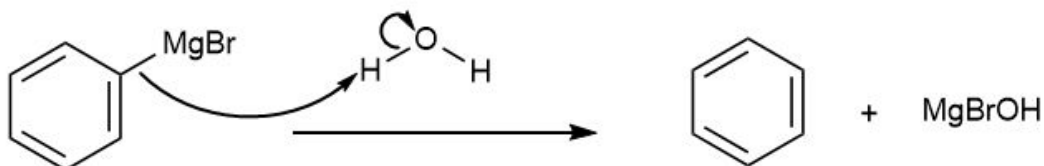
Conclusion

The percent yield of the final product, benzoic acid was determined to be 96% and the experimental melting point was determined to be between 98.4 - 105.1°C.

Questions

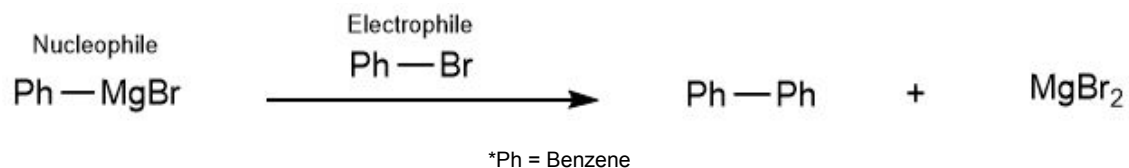
1. Benzene was formed in the reaction mixture by a side reaction with the grignard reagent and water.

Figure.4.1. Mechanism depicting the formation of benzene



2. The mechanism regarding the formation of biphenyl in the reaction mixture is not well known; however, what can be said is that the grignard reagent, being a nucleophile and whatever is left of the bromobenzene, being an electrophile would react together to form something more stable. This is biphenyl. The reaction can be attributed to nucleophiles and electrophiles coming together because one wants to donate electrons and one wants to receive them.

Figure 4.2: Hypothetical mechanism of the formation of biphenyl



3. Since 1 molecule of water will react with 1 molecule of the grignard (phenylmagnesium bromide), the number of moles of water present must be the same as the number of moles of the grignard reagent in order to kill the grignard reagent. As calculated above, the number of millimoles of the bromobenzene is 28 mM. This means that the number of moles of the grignard reagent should also be 28 mM. This is because bromobenzene was the limiting reactant during the reaction with magnesium in order to create the grignard reagent and every 1 molecule of the bromobenzene produced 1 molecule of the grignard reagent. Thus, the millimoles of water will also have to be 28 mM.

From moles we can calculate the mass of water and finally the volume.

$$28\text{mmol} = 0.028 \text{ mol}$$

$$\text{MM H}_2\text{O} = 18.01528 \text{ g/mol}$$

$$\begin{aligned} \text{mass H}_2\text{O} &= 0.028 \text{ mol} \times 18.01528 \text{ g/mol} \\ &= 0.50 \text{ g} \end{aligned}$$

$$\text{Density H}_2\text{O} = 1 \text{ g/ml}$$

$$\begin{aligned} \text{Volume H}_2\text{O} &= 0.50 \text{ g} \times 1 \text{ ml/g} \\ &= 0.50 \text{ ml} \end{aligned}$$

Therefore, the amount of water required to destroy the grignard reagent in this lab is 0.50g or 0.50ml.

- The reaction with bromobenzene and magnesium is very exothermic. This means that the reaction is very vigorous as proven by the vigorous bubbling in the flask. Furthermore, bromobenzene has a low boiling point which produces more bubbles. If all of the bromobenzene was added at once the reaction would be too vigorous and bubble out of the reflux apparatus. There is a possibility of serious harm when this happens. Thus, the addition of bromobenzene in two parts is a safety precaution.
- Before adding the dry ice, the grignard reagent would be present in the reaction mixture. When this mixture is applied to the TLC plate it will react with it. TLC plates are made up of silica gel which has a lot of OH groups and is weakly acidic. Since the grignard is a strong base these substances react to neutralise one another. These OH groups can react with the grignard reagent by protonating it and form benzene (fig.4.4). Thus, in addition to the spot for the grignard reagent another spot for benzene should also be seen in the reaction lane. While the actual R_f values cannot be determined, it can be said that the spot for benzene should appear higher than for the grignard reagent because the grignard reagent is more polar than benzene (see fig 4.3).

Figure 4.3. TLC of grignard before the addition of dry ice

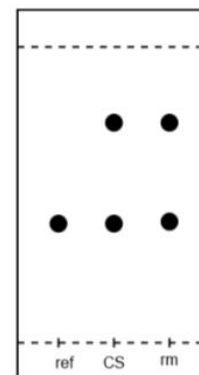
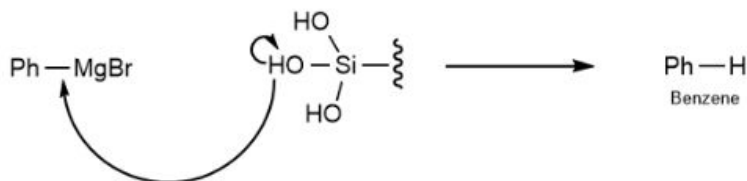


Fig 4.4. Mechanism depicting the formation of benzene on the TLC plate



References

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National Center for Biotechnology Information. PubChem Database. Ether, CID=3283, <https://pubchem.ncbi.nlm.nih.gov/compound/3283> (accessed on Mar. 20, 2019)

National Center for Biotechnology Information. PubChem Database. Carbon dioxide, CID=280, <https://pubchem.ncbi.nlm.nih.gov/compound/280> (accessed on Mar. 20, 2019)

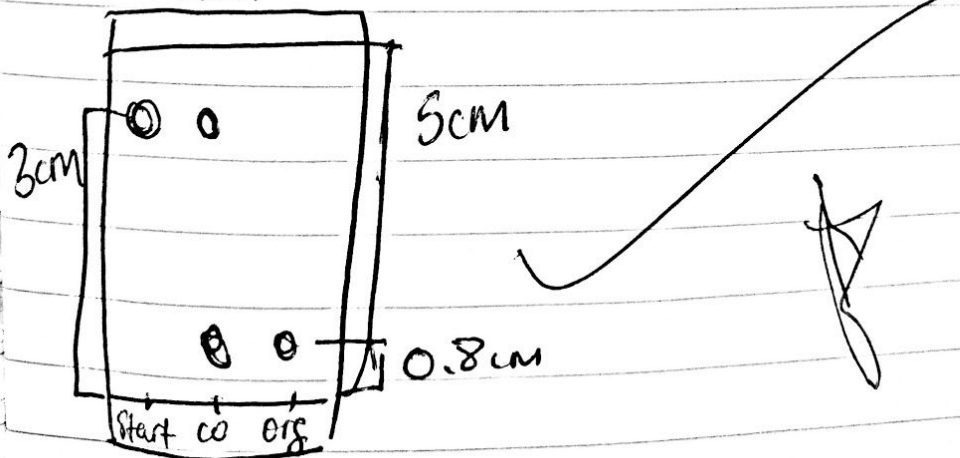
CAB 5

0.8g Mg

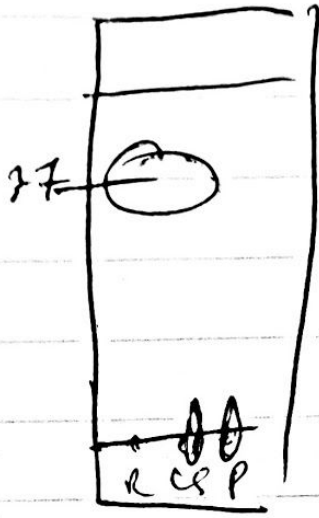
$0\frac{17}{17}$ g I_2

Adding Mg I_2 + solvent \rightarrow led/brown
then swirled & colour went away
bubbles formed & it started to boil
 $\frac{1}{2}$ was added & it boiled more
looks brown.

The w/ starting mix as ref & organic
layer from extraction as sample
1:9 Hex



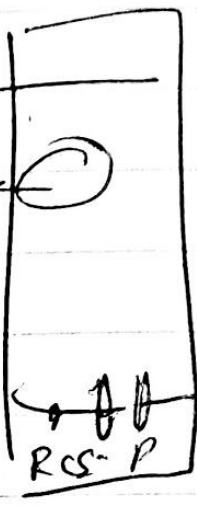
Final waste.



9.7

4.8

3.5



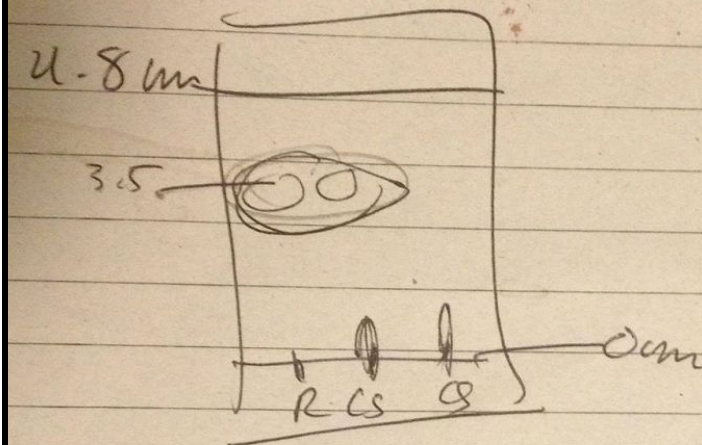
Product

Final weight : 3.30g

Temp \rightarrow ~~98.4~~

98.4 - 105.1°C

✓
for



② Product TLC

[Handwritten signature]