

Experiment 5: Preparation of Benzoic Acid Using a Grignard Reagent



March 21, 2018

**CHM 1321
Organic Chemistry Lab
University of Ottawa**

Procedure:

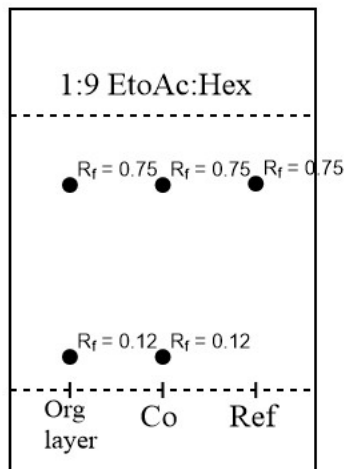
- Refer to the CHM 1321 Organic Chemistry Laboratory manual (Experiment 5: Preparation of the Benzoic acid using a Grignard Reagent). Procedure pages are (46-47)
 - Changes were done during the experiment for the following steps:
 - Step 12: 150 mL beaker was filled about $\frac{1}{4}$ with ice rather than $\frac{2}{3}$.
 - Step 14: Only 25 mL of 2.5 M HCl and 10 mL of ether were added.

Observations:

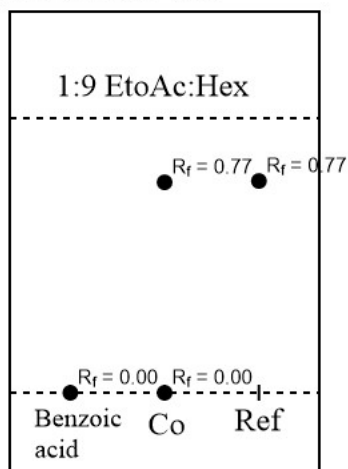
- During the addition of Magnesium and Iodine together in the round bottom flask, a cloud of purple gas appeared.
- The solution turned dark brown when Bromobenzene was mixed with Anhydrous ether as they were added top of the Grignard reagent.
- During the process of boiling ether in the round bottom flask, the solution turns cloudy white, with the formation of white foam. After, it turns back to dark brown.
- Adding Dry ice to the solution causes an aggressive reaction with the production of smoke.
- The addition of 25 mL of 2.5 M HCl on top of the solution, production of smoke and bubbling. Then the solution turns its colour to milky white as it slowly forms two layers with the colour of yellow on top and milky white on bottom.
- A clear yellow layer was on top and white layer on the bottom was produced after the solution was added into a separatory funnel. Shaking the funnel vigorously caused to produce a clear layer on the bottom, and clear yellow on top.
- After washing with NaOH, the addition of HCl was added as drops. The HCl caused the solution to form white solid crystals and heating up the beaker.
- Placing the beaker on an ice bath causing more crystals to form.
- 4.36 grams of crystals were obtained after suction filtration.
- First TLC paper was made for organic layer before being washed up. It resulted into two dots on the organic layer lane which one has the same R_f value of the Bromobenzene, and the other was indicating formation of Benzoic acid.
- Second TLC paper was done of the crystals Benzoic acid after it was washed with NaOH that showed no dots matching Bromobenzene lane, that indicates separation of Bromobenzene from Benzoic acid.

TLC Analysis:

TLC 1: Organic layer and Bromobenzene



TLC 2: Bromobenzene and benzoic acid



Tables:

Table of Reagents :

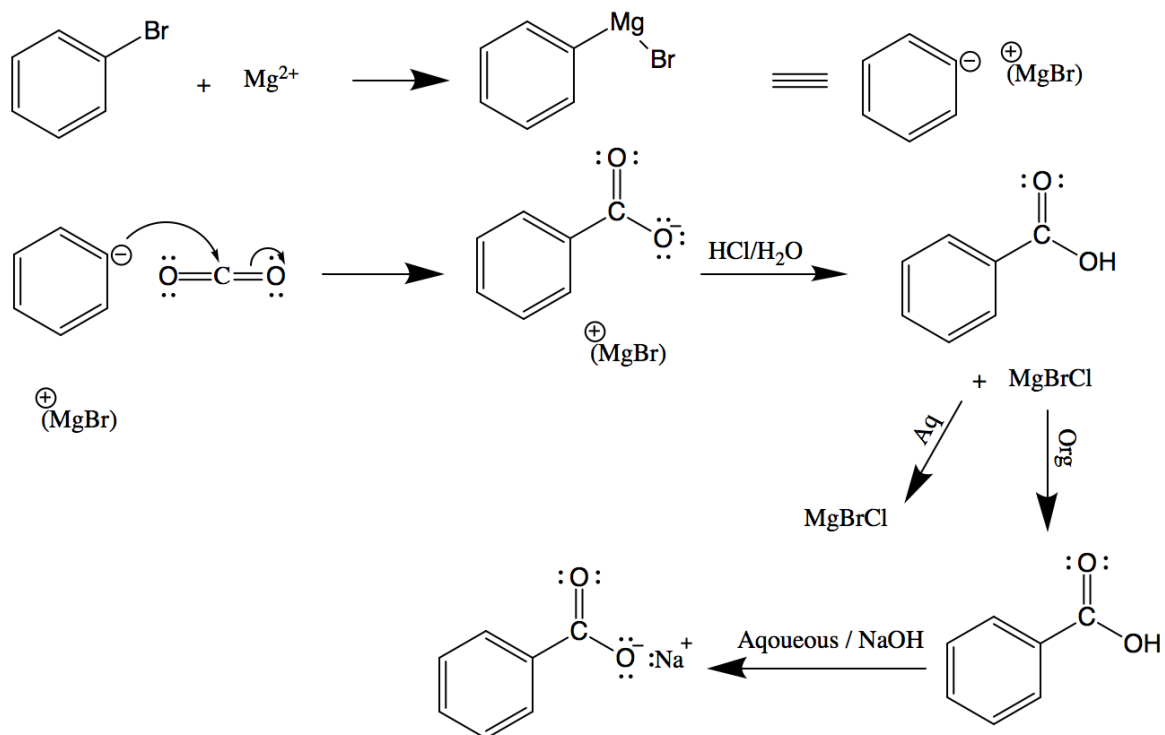
Reagent	Amount (g / mL)	Molecular Weight (g/mol)	# Mol
Bromobenzene	0.80 g	157	0.00509
Anhydrous ether	20 mL	-	-
Magnesium	0.30 g	24.3	0.012
Dry ice (Carbon Dioxide)	40 g	44	0.91

Table of Products:

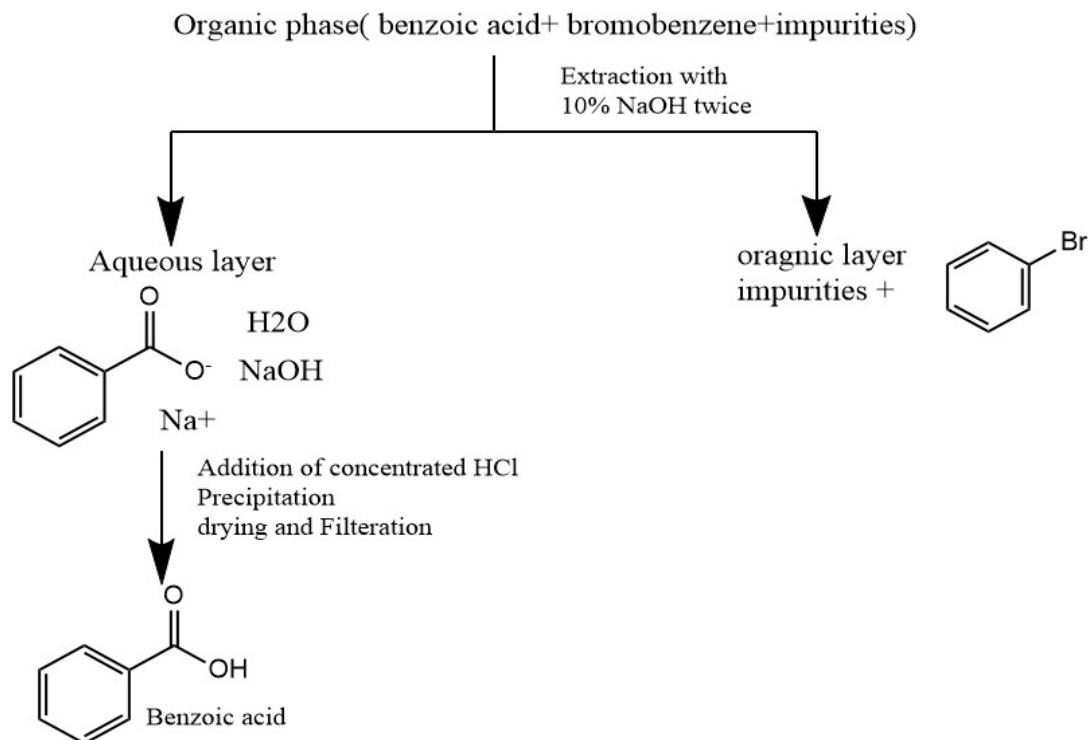
Product	Amount (g)	Molecular Weight (g/mol)	# Mol	Melting point (°C)	Percentage Yield
Benzoic acid	4.36	122.12	0.036	145	

Flowchart :

- Mechanism of the reaction:



- Washing with NaOH



Calculations:

dI : The distance of the dot from the starting line

ds : The distance from the starting line to the solvent line

- Calculating Rf values for TLC papers:
 - TLC 1: Bromobenzene and First Organic layer:
 - Bromobenzene lane
 - $R_f(\text{Bromobenzene}) = dI/ds$
 - 1.8/2.4
 - 0.75
 - Organic layer lane
 - $R_f(\text{Organic layer}) = dI/ds$
 - 1st dot = 0.75
 - 2nd dot = 0.12
 - TLC 2: Benzoic acid and Bromobenzene
 - Bromobenzene lane
 - $R_f = 0.77$
 - Benzoic acid
 - $R_f = 0$

- Calculating percent yield
 - Theoretical Moles of Benzoic acid = 0.0051 moles
 - Mass obtained of Benzoic acid : 4.36 g
 - Moles: $4.36 \text{ g} / 122.12 \text{ g/mol} = 0.036 \text{ moles}$
 - Percent Yield = (actual yield / theoretical yield) * 100
 - $(0.036 / 0.051) * 100$
 - % yield = 706.5 %

Discussion:

In the beginning of the experiment, it was warned that if the reaction made any contact with water, it will result in failure, and the reaction will not proceed as planned. This was prevented by placing all glassware equipment in the oven overnight to evaporate all the water and moisture. Also, Calcium chloride was added in the drying tube to help absorb most of the water in the atmosphere and prevent any leaking into the reaction. When Magnesium was added to Iodine in the round bottom flask, it produced a purple cloud that indicates the beginning of the reaction. A Grignard reagent is known to carry a formula of R-Mg-X. R is known to be a chain of organic group such as alkyl, where X is just a halogen connected to Magnesium. First, the reaction occurs as organo-halide reaction that produces Bromobenzene. Furthermore, the Bromobenzene in anhydrous ether was added to the round flask that had Magnesium in it. This caused the reaction between Bromobenzene and Magnesium to produce Phenylmagnesium bromide.

When Magnesium and Bromine leave the Benzene ring, the carbon in the ring becomes negative and the Magnesium with Bromine becomes positively charged. Dry ice was introduced as in Carbon dioxide, and the double bond changed move electrons to one of the Oxygen atoms making it negatively charged, and the carbon is now positive charged. This positively charged Carbon is attractive to the negatively charged Carbon on the benzene. The electrons on the Carbon in the Benzene compound is able to form a bond to the positively charged Carbon. Addition of HCl, it helps to protonate the negatively charged Oxygen, making the whole compound out of Benzene and carboxylic acid, known as Benzoic acid. The Chloride ion from HCl will bind to positive MgBr, and making MgBrCl, that is able to move to the aqueous layer.

The next step was to end up solid formation of Benzoic acid, so a separatory funnel was prepared and the mixture that had Benzoic acid was added and washed with 10 mL of ether to create two distinguishable layers. A yellow organic layer at the top and clear almost transparent aqueous layer at the bottom. The organic layer was separated from the aqueous layer, and a TLC paper was done using Bromobenzene as reference. TLC paper had the organic layer lane, and the reference lane that a drop of Bromobenzene was added to it. The Organic layer showed two spots, and the reference lane had one spot. One spot from the organic lane matched same Rf value with the spot that reference had. This indicates that the organic layer had Benzoic acid and Bromobenzene in it, as the second lower spot with lower Rf value indicate the stronger polarity of Benzoic acid.

Furthermore, the organic layer was washed twice with 10% NaOH. Organic layer had Benzoic acid in it, and when NaOH was introduced, it reacted and deprotonated it. When Carboxyl group was deprotonated, it left charged species that is no longer soluble in organic layer, and transfers to the aqueous layer. After the separation, the aqueous layer now contains a deprotonated Benzoic acid with Na⁺ and NaOH, then concentrated HCl was added to protonate the carboxyl group again and make Benzoic acid neutral again. Benzoic acid now is insoluble in the aqueous layer, and it starts to form crystals, with NaCl as well. To help crystallization, the beaker was placed in an ice bath to form more crystals. After filtering the beaker, it was measured to have approximately 4.36 grams of Benzoic acid crystals. At the end, last TLC paper was made that had Bromobenzene as reference, and Benzoic acid dissolved in Dichloromethane. The Benzoic acid lane showed one spot with 0 Rf value. This means that the separation of Benzoic acid and Bromobenzene is successful. Moreover, the crystals that were weighted had high percentage yield that was 706.5%. This is due to the fact that the crystals did not only have Benzoic acid in them, but also had NaCl, and water, which increased the mass, and resulted in a high percentage yield.

The melting point of the crystals were tested, and it was found to be approximately 145 degrees. This value for melting point of Benzoic acid is higher than the expected value which is approximately 122 degrees [1]. The higher value was due to having the salt NaCl in the filtered crystals, and it is known that NaCl has approximately 801 degrees melting point [3]. NaCl melting point value influenced the overall crystal melting point that was found during the experiment.

Questions:

1- Why is anhydrous ether used in this reaction?

- Anhydrous ether is used because it does not contain any traces of regular water, for example, regular ether. Water can cause the reaction to not proceed, and that's because of the water's capability of protonating the grignard reagent, which will prevent the formation of magnesium intermediate, to help form Benzoic acid. [2]

2- Why is a water bath used to heat the reaction?

- Water bath was used to help with the reaction of magnesium and bromobenzene to proceed. This is by heating up the flask and boiling ether so the reaction can continue.

3- What is dry ice?

- Dry ice is carbon dioxide in a solid form, that was used in the experiment, when the molecule was bonded to benzene, and help with the formation of Benzoic acid.

4- In this experiment, why is it important to use freshly obtained dry ice?

- It is important to have freshly obtained dry ice, because it can prevent moisture condensation on it. Having water can interfere with the reaction and cause the percent yield to reduce, also can affect the results at the end of the experiment.

References:

[1]- Benzoic acid. (n.d.). Retrieved March 27, 2018, from https://pubchem.ncbi.nlm.nih.gov/compound/benzoic_acid

[2]- CHM 1321 Organic Chemistry Lab Manual 2018, (Experiment 5: Preparation of Benzoic Acid using a Grignard Reagent , Sep. 2013)

[3]- Sodium chloride. (n.d.). Retrieved March 27, 2018, from https://pubchem.ncbi.nlm.nih.gov/compound/sodium_chloride

Raw Data:

Lab 5. Preparation of Benzoic acid using a Grignard Reagent.

→ 0.3g magnesium + crystals of iodine. (cloud of purple gas = iodine reaction.)

→ 3.0ml bromobenzene + Anhydrous ether

poured over magnesium + iodine → turns reddish brown, gets darker

ether boils, bubbling, turns ^{cloudy} white, but then as boils and foams turn slowly to brown, more white foam, darker brown

turns dark brown, less foam.

• when adding it to dry ice, violent reaction lots of smoke. crush it with stirring rod.

add 25ml of 2.5 mol HCl, lots of smoke. boils, then turn milky white.

two layers yellow on top, white on bottom clear.

put in separatory funnel, bottom turn clear, yellow clear on top, wash with 10ml ordinary ether, some left in beaker.

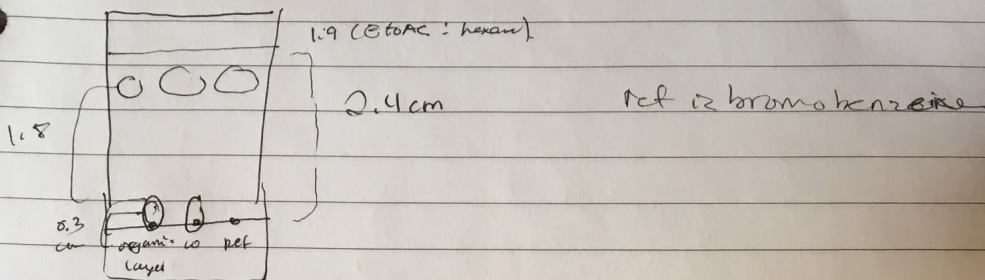
• ~~top~~ bottom aqueous layer. ~~bottom~~ clear

• shake separatory funnel; makes clear bottom layer, clear yellow top layer.

rewash aqueous phase

Lab 5.

TLC 1



becomes charge sol aqueous layer
benzoic acid reacts with NaOH, but brom benzene
does not, so separated

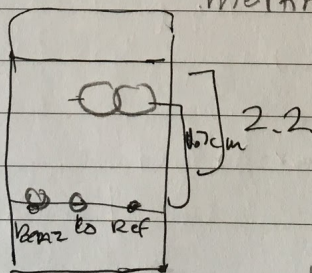
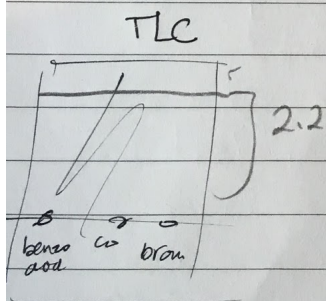
- separate organic layer with NaOH, charges acid
make it go to aqueous phase

aqueous layer = bottom

rewash organic layer

- acidify aqueous layer with HCl; solid started
to form to get benzoic acid, beaker warmer
put in ice bath the filter through suction filtration
weigh the solid, = 4.36 g benzoic acid.

melting point 145°
why high.



we got 4.36 g
c2 impurity \rightarrow NaCl
which increases
melting point.