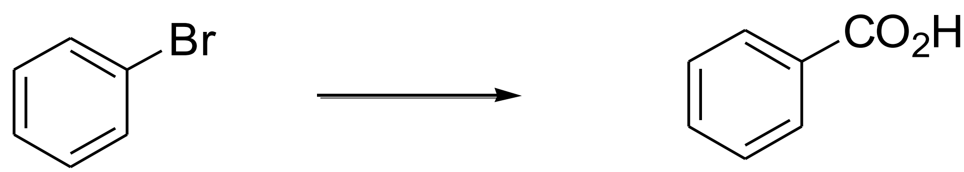
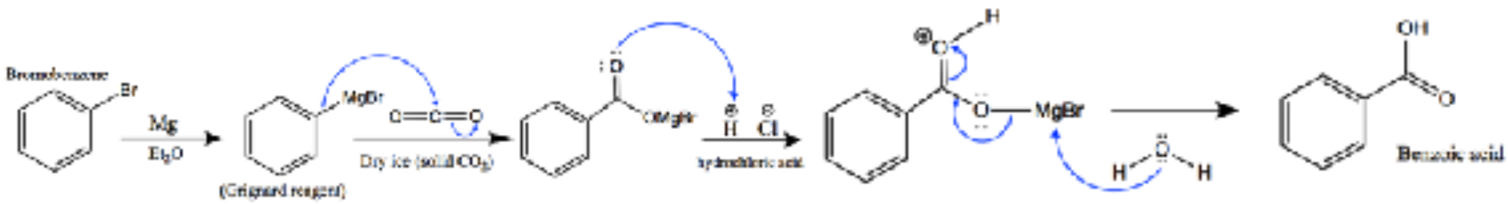
The Formation of Benzoic Acid using a Grignard Reagent



Introduction:

The mechanisms for the formation of solid benzoic acid using a Grignard reagent.



Procedure:

As described in the Organic Chemistry Laboratory Manual on pages 46 to 47.

Modifications:

In step 14, 25mL of concentrated HCl was added (instead of 5mL).

Data and Observations:

Magnesium turnings: Silver, thin, small pieces and different shapes, solid

$CaCl_2$: White, small, round/spherical solid

Iodine: Grey, small, square shaped solid pieces

Bromobenzene: Transparent, colourless solution with an odour

Anhydrous diethyl ether: Transparent, colourless solution with an odour

Ordinary diethyl ether: Transparent, colourless liquid with a faint odour

Dichloromethane: Transparent, colourless liquid with a faint odour

Dry ice (solid CO_2): white solid, cold, looks like snow when grouped together

HCl: Transparent, colourless solution with a strong odour

1:9 ethyl acetate and hexane (eluent): Transparent, colourless liquid with a mild odour that resembles nail polish remover

- The mixture was turning white so we added a hot water bath then it turned a dark reddish brown colour
- During the reaction, some magnesium pieces stayed at the bottom of the round bottom flask
- When the mixture was added to the beaker with dry ice, conc. HCl, H_2O, Et_2O and ice, it was very sticky, opaque, and brownish copper in colour
- When separating and extracting the different phases for the first time with diethyl ether, the organic phase was on top and it looked like oil. The aqueous phase was clear and below the organic layer however, both phases were transparent
- After NaOH was added to the organic phase, there was a transparent faint yellow solution on top and an opaque faint yellow solution on the bottom.

Table of Reagents

Reagent	Molecular Weight (g/mol)	Amount (Mass or Volume)	Moles (mol)	Density (g/mL)
Magnesium	24.31	0.80g	0.0329	—
Bromobenzene	157.01	3mL	0.0286	1.50
Anhydrous diethyl ether	74.12	20mL	0.1916	0.71
Iodine	126.9	—		—
Solid carbon dioxide	44.01	—	(excess)	—

TLC:

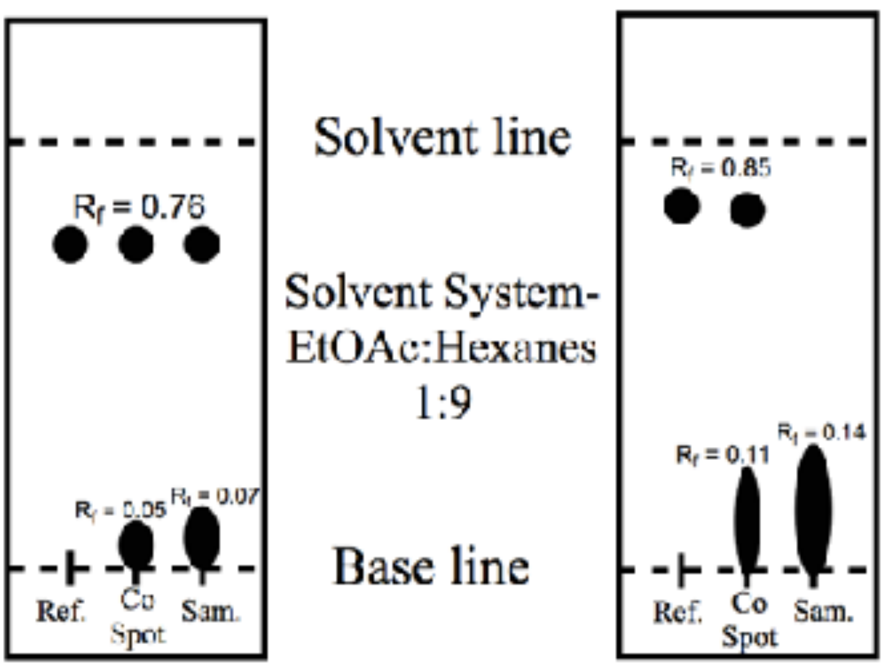


Figure 1:
The composition of the organic phase
Ref: reference - bromobenzene
Co spot: reference + sample
Sam: sample- organic layer

Figure 2:
TLC of the final product
Ref: reference - bromobenzene
Co spot: reference + sample
Sam: benzoic acid product dissolved in dichloromethane

Flow Chart: The extraction of benzoic acid

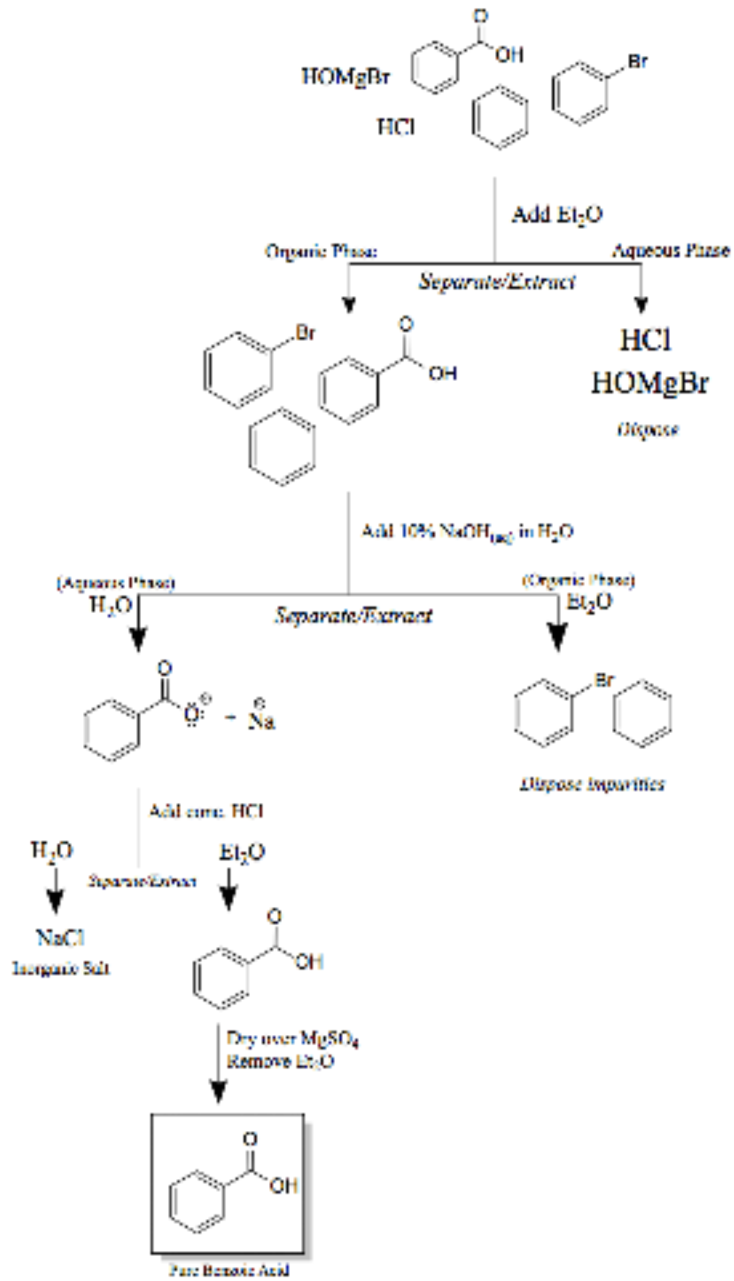


Table of Results

Table 1: Rf Values for Figure 1 and 2

Spot Number (left to right)	R_f values for Figure 1	R_f values for Figure 2
1	0.76	0.85
2	0.76	0.85
3	0.05	0.11
4	0.76	0.14
5	0.07	–

Table 2: Results for benzoic acid

Product	Amount	Molecular weight	Moles (mol)	Percent Yield	Melting point	Theoretical melting point
Benzoic acid	0.62g	122.12 g/mol	0.00508	17.8%	124 ℃	122 ℃

Calculations:

Percent Yield = (# mol of product) ÷ (# mol of starting material) x 100

= (# mol of benzoic acid) ÷ (# mol of bromobenzene) x 100

= (0.00508 ÷ 0.0286) x 100%

= 17.8%

Discussion:

In this experiment a Grignard reagent was used to prepare benzoic acid. Initially, all the glassware and equipment had to be clean and dried in the oven because any water molecules would interfere with the reaction. We also filled a drying tube with cotton and $CaCl_2$; this was important in ensuring that no moisture entered the reaction because the drying tube's function is to trap water. Two small pieces of iodine were added to the magnesium so that it could activate the surface of the metal and expose the reactive sites. Most of the magnesium attached itself in between the carbon and bromine bonds on the bromobenzene molecules. Water could not be present because it would protonate the reagent causing the phenyl group to detach before solid carbon dioxide could be introduced. The reaction is exothermic therefore, a condenser had to be used to ensure that the volume of solvent remained constant throughout the reaction. Also, due to the fact that we had to heat our reaction with a hot water bath, the condenser kept the solvent within the flask even when it evaporated. Once the reaction was complete we had to quickly obtain dry ice because it would sublime when exposed to atmospheric conditions. After hydrochloric acid and diethyl ether were added, the mixture needed to be separated to get benzoic acid on its own. The hydrochloric acid protonated the molecule to create a hydronium ion, which is rather unstable. The magnesium is a good leaving group, so the bond between oxygen and magnesium will be broken to create a molecule that is more stable. This process results in the formation of a carboxylic acid. Therefore, benzoic acid is present along with excess magnesium and benzene, which would be considered impurities. To isolate solely benzoic acid, a separatory funnel was used to separate the mixture several times. Aromatic molecules such as benzene, bromobenzene and benzoic acid would be found in the organic phase. Meanwhile, hydrochloric acid and magnesium will be found in the aqueous phase. Sodium hydroxide was used to separate benzoic acid from the other compounds in the organic layer, as well as deprotonate it, because the NaOH reacts with the benzoic acid to form benzoate ions. These ions are soluble in water so they move into the aqueous phase while benzene and bromobenzene stay in the organic phase. The drop wise addition of concentrated HCl was used to react with the benzoate ions so that the molecule could return back to benzoic acid, and NaCl would also be formed in the process. Due to the fact that NaCl is more soluble in water, the benzoic acid becomes the perpetrate product, which was obtained via suction filtration. In between and after the multiple extractions, two TLCs were taken. Figure 1 is the TLC of the organic layer after the first separation and extraction. There are 3 spots in a row which means that the organic layer definitely contained bromobenzene. However, the second spot in the sample column with an R_f value of 0.07 is the other component which is benzoic acid. The benzene ring is very non polar so bromobenzene travelled very far on the TLC and had an R_f of 0.76 whereas the carboxylic acid group on benzoic acid is polar therefore the molecule does not travel as far. Figure 2's TLC was taken after the benzoic acid had been extracted and filtered. The precipitate was dissolved in dichloromethane so that it could be spotted on the TLC. The results show that the product was only benzoic acid and contained no bromobenzene, which also means it does not contain a significant amount of impurities. The purity of the product was good however the percent yield was not because a large quantity of the aqueous phase was spilt before the final extraction took place. Due to the loss of the majority of our product, the percent yield was only 17.8%. The aqueous solution containing the benzoic acid was very acidic and had a pH of 1 according to the blue litmus paper. The melting point of 124 ℃ for benzoic acid was obtained using another group's data however, it is extremely close to the theoretical melting point which is 122 ℃. This means that the product obtained was very close to being pure benzoic acid and contained very little impurities.

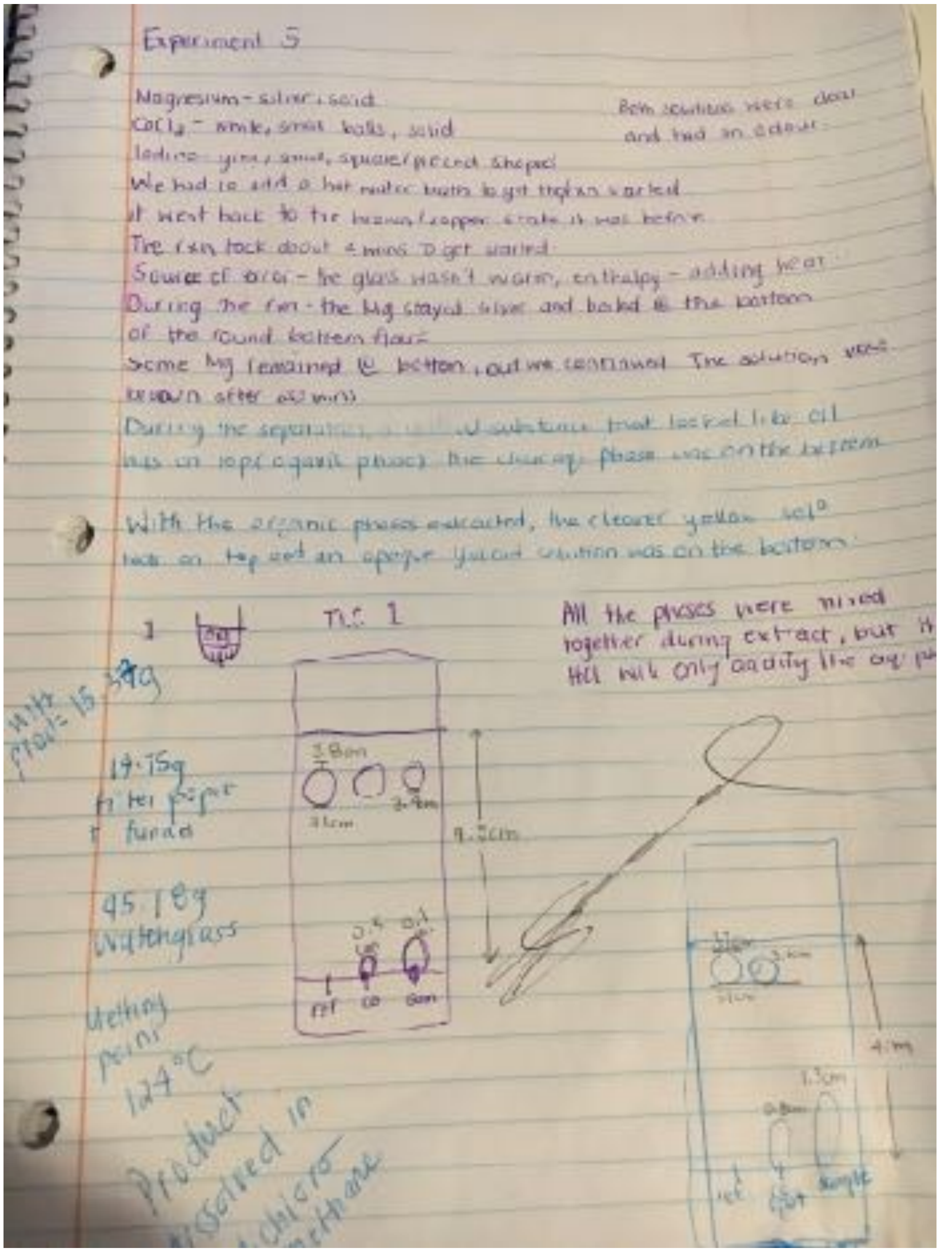
Sources of Error—

In this experiment, there were many chances for an error to occur, which would result in impurities in the final product. For instance, for the majority of the experiment, water could not be present whatsoever. If there was water on the glassware, or even if water from the atmosphere entered the mixture, or the dry ice, impurities would arise. Also, if the product was spilled, like in our case, you would get a very low percent yield. Therefore this experiment required a lot of precision.

Questions:

1. The reason we used anhydrous ether in this reaction was because it does not contain any water, which is also indicated by the anhydrous part of its name. If water were present, it would interfere with the Grignard reagent via protonation and lead to the formation of benzene.
2. Heating the reaction allows the reagents to overcome the activation energy faster than if you were to allow the reaction to proceed on its own. Also, the reaction is exothermic so heating it helps maintain its enthalpy.
3. Dry ice is simply solid carbon dioxide. It is extremely cold (-78°C) so touching it directly will give you frostbite. A interesting fact is that carbon dioxide does not exist in liquid form, so sublimation will occur which means the carbon dioxide will turn to gas when exposed to the atmosphere. It's chemical structure consists of a single carbon atom that is double bonded to two different oxygen atoms. (O=C=O)
4. It is very important to use freshly obtained dry ice because if it was exposed then water molecules found in the air could freeze on the surface of the dry ice. Once again the Grignard would react with the water and not the carbon dioxide.

Raw Data


Experiment 5
Magnesium - silver, solid
and had an odour
All the phases were mixed
together during extract, but
TLC 1
45.18g
watchglass
124°C
Product
dissolved in


HYDRION