Experiment 5:

Preparation of Benzoic Acid using Grignard Reagent

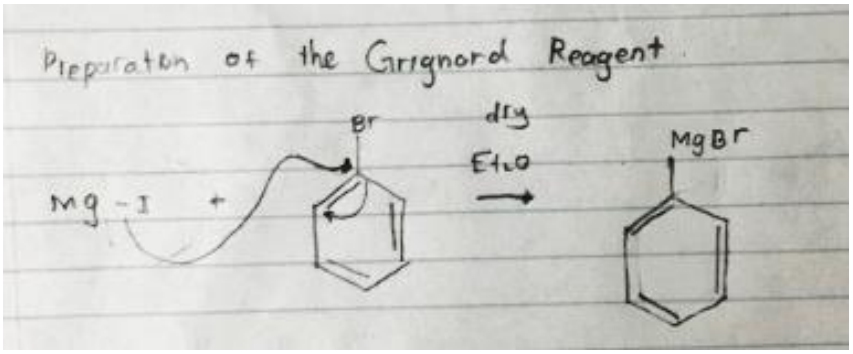
Balance Chemical Equation

- $Mg + + C_6H_5Br \xrightarrow[Et_2O\ dry]{} C_6H_5MgBr$
- $C_6H_5MgBr + CO_2 \longrightarrow C_6H_5COO^- + MgBr^+$
- $C_6H_5COO^- + H_2O \longrightarrow C_6H_5COOH + OH^-$
- $C_6H_5COOH + H_2O \longrightarrow C_6H_5COO^- + H_3O^+$
- $NaOH + C_6H_5OH \longrightarrow C_6H_5COONa + H_2O$
- $C_6H_5COONa + HCl \longrightarrow C_6H_5COOH + NaCl$

Mechanism

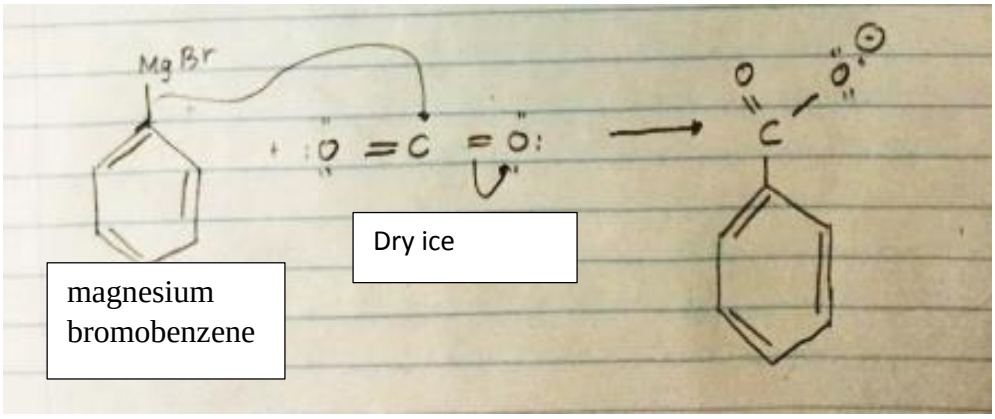
- Preparation of Grignard Reagent

- Reaction of MgI with Bromobenzene

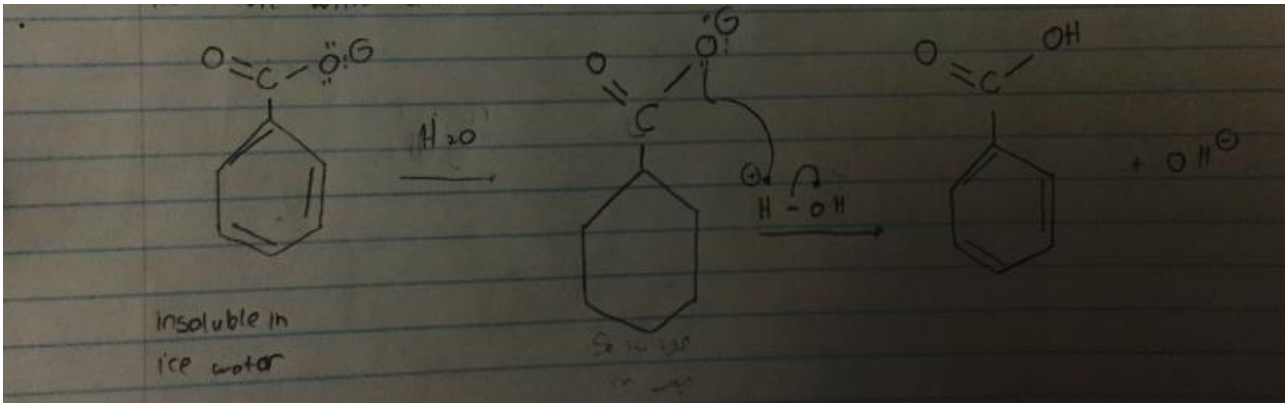


Mechanism

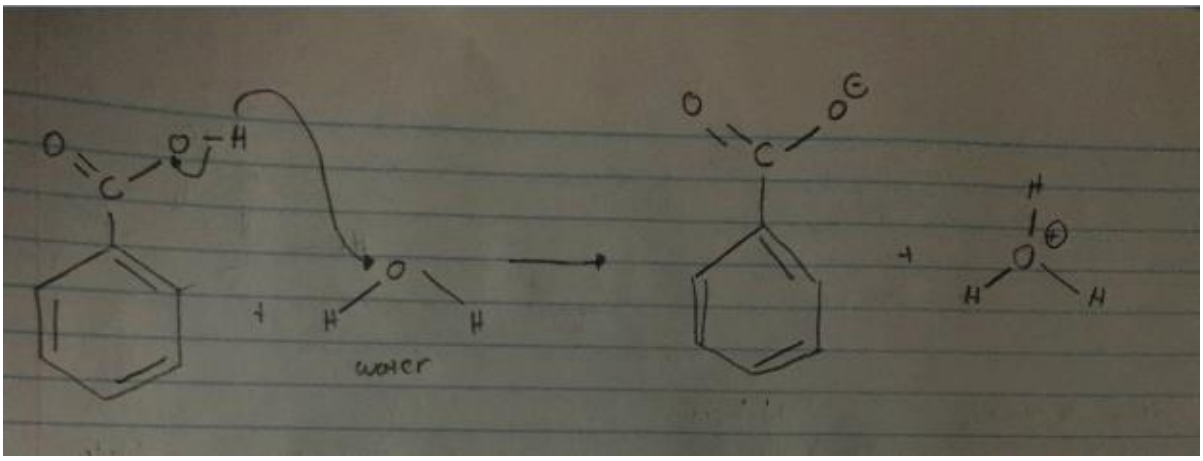
- Reaction of magnesium bromobenzene with dry ice



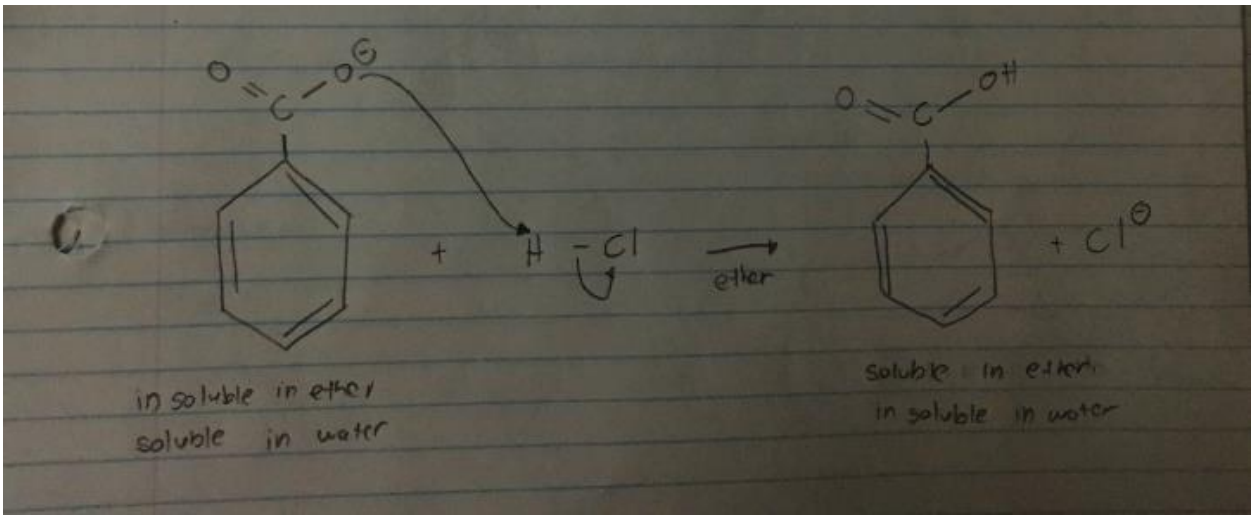
- Reaction with ice water



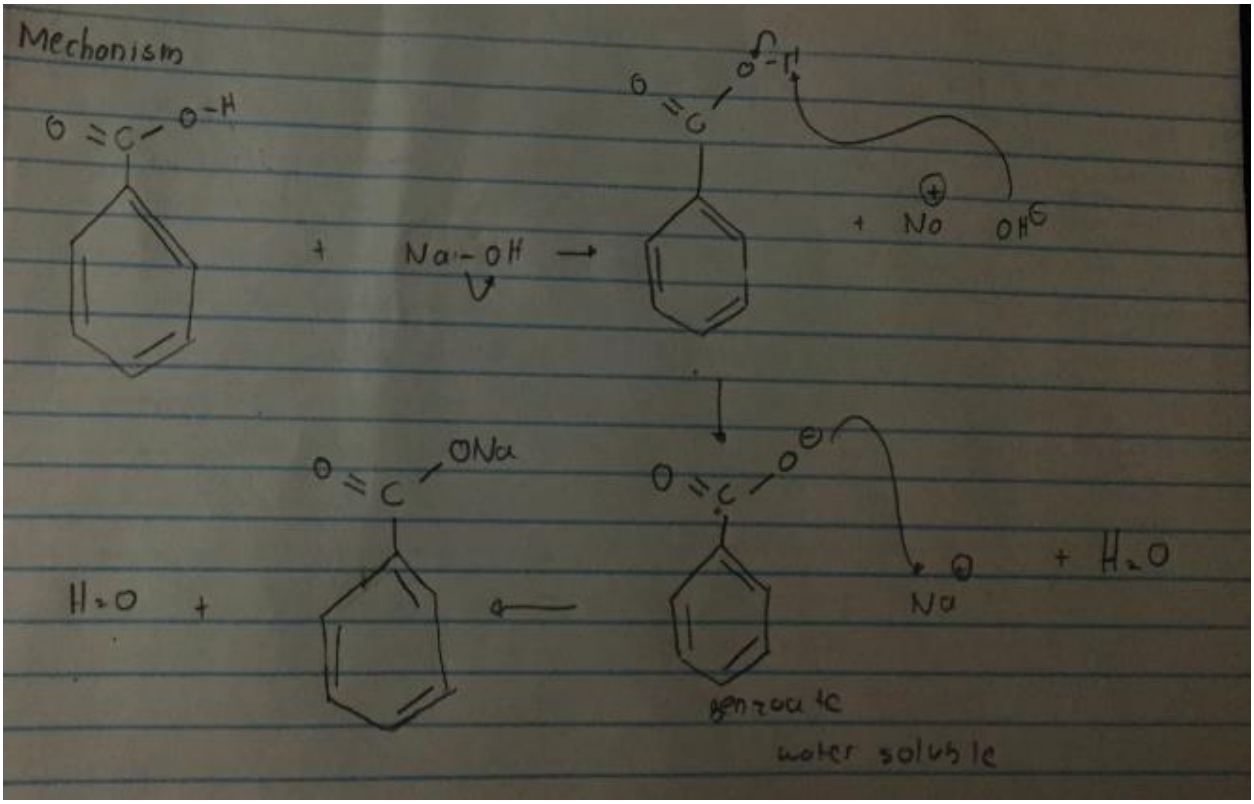
- Reaction with water



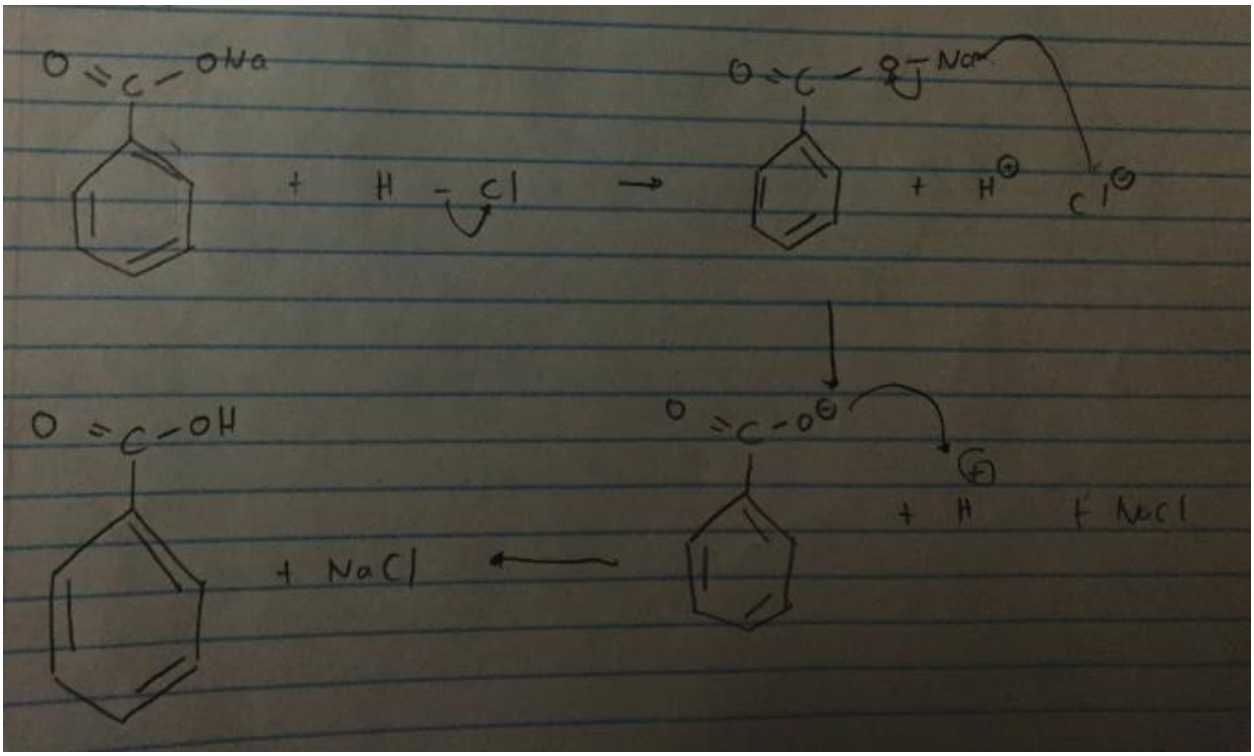
- Reaction with 5 ml of HCL



- Reaction with NaOH



- Reaction sodium benzoate with Concentrated HCl

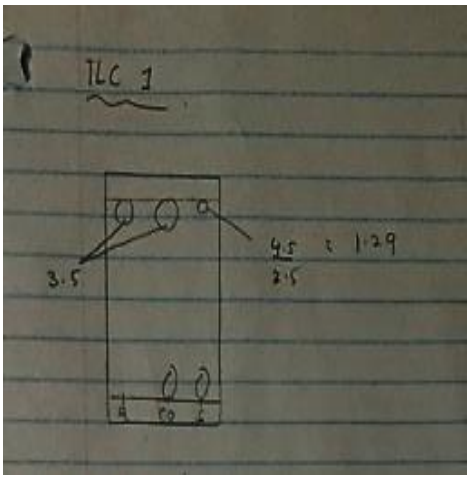


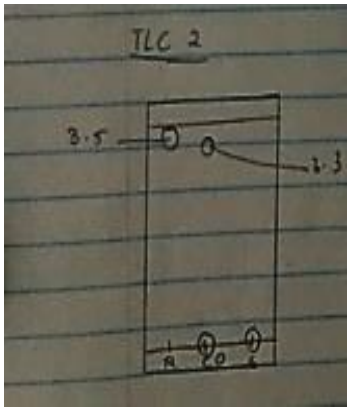
Observation

Table 1: Sample of reagent for procedure

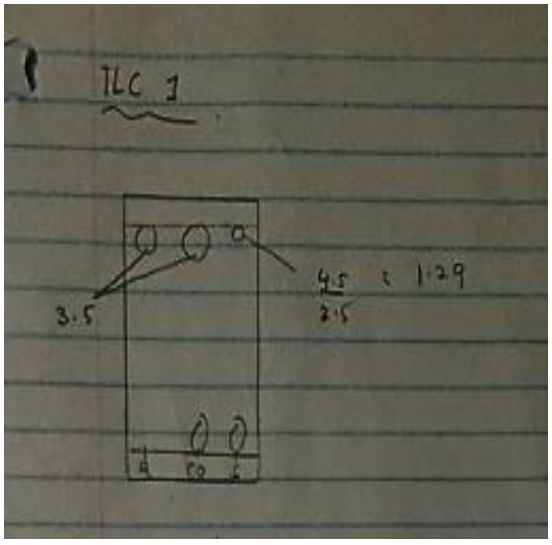
Compound	Molecular formula	Mol(g mol^{-1})	Amount	Density
Anhydrous diethyl ether	$C_4H_{10}O$	74.1216 g/mol	20 ml	713 kg/m^3
Bromobenzene	C_6H_5Br	157.0079 g/mol	3 ml	1.5 g/cm^3
1:9 Etoac Hexane	$C_4H_8O_2$	88.10512 g/mol	10 ml	897 kg/m^3
Diethyl ether	$C_4H_{10}O$	74.1216 g/mol	30 ml	713 kg/m^3
Dry ice	CO_2	44.0095 g/mol	2/3 of 100 ml	1.6 g/cm^3
12 mol Hydrochloric acid	HCl	36.46094 g/mol	5 ml	1.49 g/cm^3
Iodine	I_2	253.80894 g/mol	1 / 2small crystal	4.933 g/cm^3
Magensium	Mg	24.305 g/mol	0.8 g	1.74 g/cm^3
Sodium hydroxide	NaOH	39.997109 g/mol	40 ml	2.13 g/cm^3
Water	H_2O	18.01528 g/mol	20 ml	1000 kg/m^3

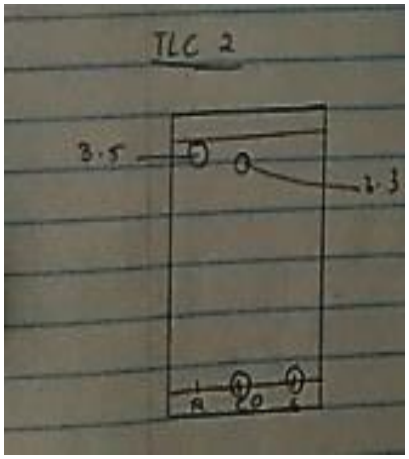
Table 2: Observation

Subject	Observation
Preparation Grignard reagent	The solution changes from dark red to light brown
TLC 1  Reference- bromobenzene Co-spot – bromoenzene + organic layer Sample spot – organic layer Solvent: 1:9 Etoac Hexane Rf Reference- 3.5 Co-spot – 3.5 Sample spot –1.29	• The Rf of the bromobenzene is the highest. • The Rf of bromobenzene and bromoenzene + organic layer is 3.5. • The Rf of the organic layer is the smallest. • The Rf is 1.29. • There are one spot for the reference • There are two spots for both the co-spot and sample spot.

TLC 2  Reference- bromobenzene Co-spot – bromoenzene + product and ether Sample spot –product and ether Solvent: 1:9 Etoac Hexane Rf Reference- 3.5 Co-spot –0.733 Sample spot –0	• The Rf of the bromobenzene is the highest. • The Rf of bromobenzene is 3.5. • The Rf of the product and layer is the smallest. • The Rf is 0. • The Rf of the co – spot is 0.733 • There are one spot for the reference and sample spot • There are two spots for the co-spot
Product produced	• 1.4 g of product produced • Pinkish solid was produced

<u>Results</u>

Subject	Observation
TLC 1  Reference- bromobenzene Co-spot – bromoenzene + organic layer Sample spot – organic layer Solvent: 1:9 Etoac Hexane	• The Rf of the bromobenzene is the highest. • Thus, bromobenzene is the most polar substance • The Rf of bromobenzene and bromoenzene + organic layer is 3.5. • The Rf of the organic layer is the smallest. • Thus, the organic layer is the least polar substance

Rf Reference- 3.5 Co-spot – 3.5 Sample spot –1.29	• The Rf is 1.29. • There are one spot for the reference • Thus the bromobenzene is pure • There are two spots for both the co-spot and sample spot • Thus, there might be some impurities in the co-spot and sample spot
TLC 2  Reference- bromobenzene Co-spot – bromoenzene + product and ether Sample spot –product and ether Solvent: 1:9 Etoac Hexane Rf Reference- 3.5 Co-spot –0.733 Sample spot –0	• The Rf of the bromobenzene is the highest. • The Rf of bromobenzene is 3.5. • Bromobenzene is the most polar substance • The Rf of the product is the smallest. • The Rf is 0. • Thus the product is the least polar substance. • The Rf of the co – spot is 0.733 • There are one spot for the reference and sample spot • There are two spots for the co-spot

Product produced	• 1.4 g of product produced • Pinkish solid was produced • The pinkish color produced due to excess HCl reacting with the litmus paper

Flow chart

Preparation of Benzoic acid

0.8 g of magnesium and small amount of Iodine react with 3 ml of bromobenzene in 20 ml of anhydrous ether.

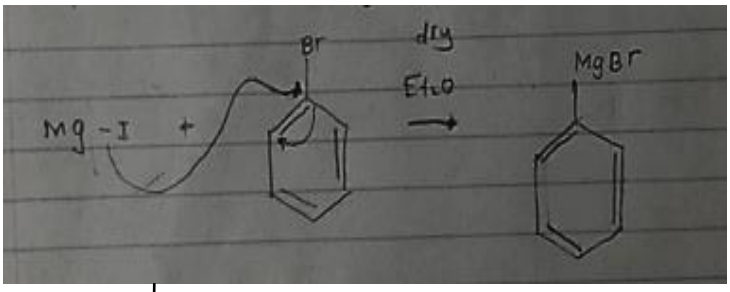
In a 50 ml round bottom flask.

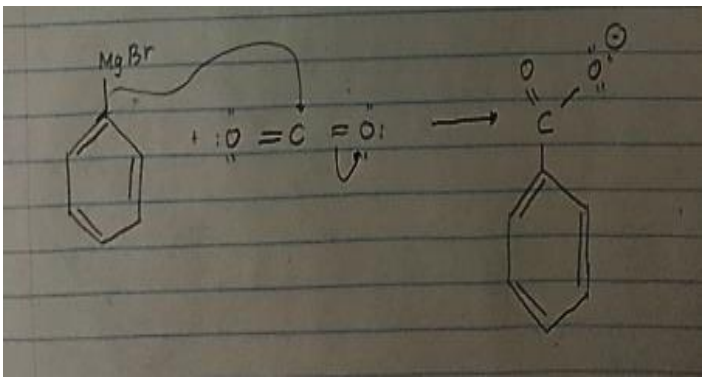
The mixture was boil by using a water bath.

The solution was left to boil for 20-30 minute.

Water bath was used to avoid the solution to be contaminated with water.

The solution was a light cloudy brown solution.





Magnesium bromobenzene was reacted with 2/3 of 100 ml dry ice.

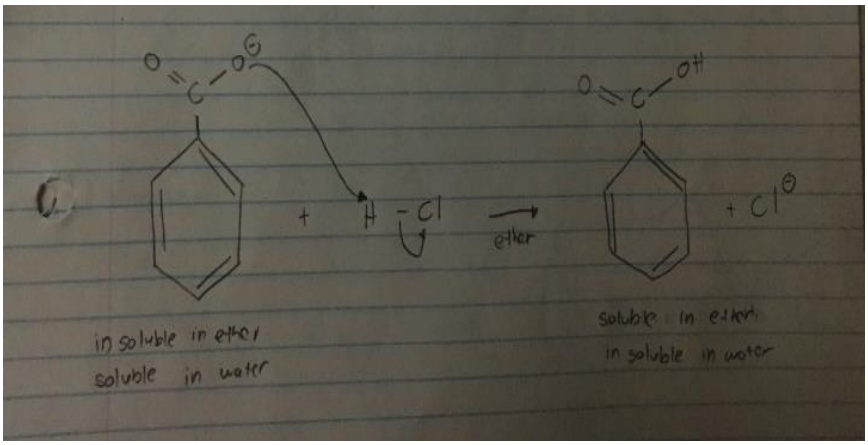
The solution was stir carefully using a Teflon rod.

The product of this reaction is a benzoate

Isolation of benzoic acid

20- 30 g of ice water and 20 ml of water was added into the sticky solution.

- 5 ml of HCl and 15 ml of diethyl ether was added into the mixture.
- The ether acts as a solvent for the reaction of benzoate and HCl.



Workup phase

- Benzoic acid
- 15 ml of ether
- Separatory funnel (shake gently) 3 times
- Done twice

<u>Aqueous phase</u>

Benzoic acid

Biphenyl

<u>Organic phase</u>

inorganic salt (discard)

Add 15 ml of ether

<u>Aqueous phase</u>

Benzoic acid

Biphenyl

<u>Organic phase</u>

inorganic salt (discard)

- Both organic layer was added
- 20 ml 10 % NaOH solution was added
- Separatory funnel (shake gently) 3 times
- The reaction was done twice

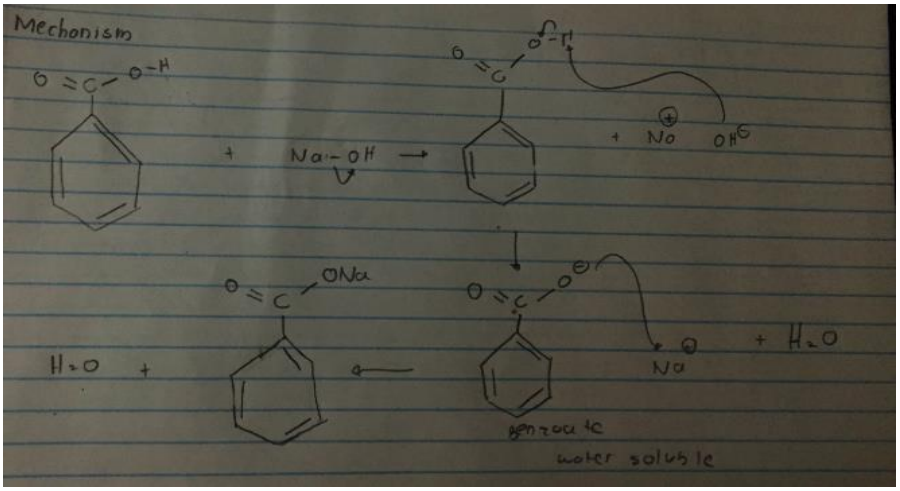
Aqueous phase

Soluble Benzoic acid salt/ sodium benzoate

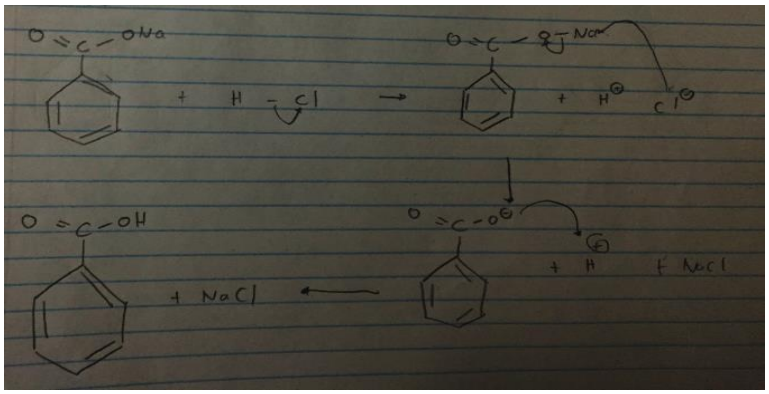
Organic phase

Biphenyl

(discard)



- Concentrated HCl was added until the litmus paper changes from blue to red
- The solution was cool in an ice bath
- The solid products was collect by suction filtration
- The product was put on a watch glass and was left to dry
- 1.4 g of product was gain from the reaction.



Discussion

The purpose of the experiment is to produce benzoic acid by using a Grignard Reagent. Grignard reagent does not react well with alkyl halides such as bromobenzene. Thus to produce a Grignard reagent we have to isolate our desired product from the bromine. This is achieve by mixing 0.8 g of magnesium and small amount of crystal iodine in a 50 ml round bottom flask. Then 3 ml of bromobenzene and 20 ml anhydrous diethyl ether was added into the flask. Anhydrous ether was used because any presence of water would kill and protonate the Grignard reagent.

2/3 of 100 ml of dry ice were used to react the Grignard reagent with carbon dioxide. This produce a sticky like mass of benzoate ion. Benzoate ion was produce due to the collapsed of MgBr from the benzene. Thus forming a carbonyl ion with the carbon dioxide molecule.

The sticky like mass was then reacted with 20-30 g of ice water, 20 ml of water, 5 ml of concentrated HCl and 15 ml of diethyl ether. From these mixture, it helps to produce a benzoic acid. The ether acts as a solvent for the reaction of benzoate ion and HCl.

There are two workup phase for this reaction. First mixture of benzoic acid and1 5 ml of ordinary ether was put into a separatory funnel. The mixture was shake gently 3 times. The aqueous phase from the extraction was mix with another 15 ml of diethyl ether. Both organic phase from the extraction was mixed. A TLC of the organic layer was done.1:9 EtoAc hexane was used as the solvent.

The TLC analysis reveal there were a single spot for the bromobenzene (reference spot). Thus, we could consider the bromobenzene to be pure. However, there were two spots for both the co and sample spot. There might be some impurities for both the mixture of bromobenzene and organic layer spot (co-spot) and the organic layer spot (sample spot). Besides, the bromobenzene have the highest Rf from all of the spots. Thus, this shows that the bromobenzene is more polar than the other two. The organic layer spot (co-spot) and the organic layer spot (sample spot) have an Rf of 1.29. Moreover, the highest height for the co-spot and sample spot is the same as the bromobenzene. This shows that there are small amount of bromobenzene present in the organic layer (sample spot) and the mixture of organic layer and bromobenzene (co-spot).

For the second workup phase the mix organic phase was reacted with 20 ml of 10% NaOH. This extraction was done twice by using the aqueous phase from the second workup phase. Sodium benzoate was produce from the aqueous phase of the reaction. Then the sodium benzoate was reacted with concentrated HCl. This reaction produces benzoic acid and a small amount of sodium chloride. The mixture of benzoic acid and sodium chloride were cooled in an ice bath. Then the solid product was collected by suction filtration. Another A TLC of the solid product was done. 1:9 EtoAc hexane was used as the solvent.

The TLC analysis reveal there were a single spot for the bromobenzene (reference spot) and the product dissolve in ether (sample spot). Thus we could consider that both the bromoenzene and product is pure. However, there were two spots on the mixture of bromobenzene and product dissolve in ether. Hence, there might be some impurities in the mixture bromobenzene and product dissolve in ether. Moreover, bromobenzene have the highest Rf while the product have the lowest Rf. Thus, this shows that the bromobenzene is the most polar while the product is the least polar. This is due to the distance travel by the substance on the TLC. However, for the Rf of the co-spot is 0.733. From the co-spot also we could see that there were excess product produce. This because one of the spot is the same height as the spot on the sample. We could also conclude that the mixture is less polar than the bromobenzene but more polar than the product.

From the suction filtration we gain 1.4 g of product. The percentage yield of the experiment is 23%. Since the yield was less than 100%, we could conclude that some of the product was lost during the reaction. This might occur because too much HCl was added into the sodium benzoate mixture. This, had cause some of the mixture to precipitate into NaCl. Moreover, the product gain was pink in color. The product should be a white solid. This pink color might be produced due to the excess HCl reacting with the litmus paper. Thus causing the product to be pinkish in color.

Questions

1) Anhydrous ether was used because to avoid killing and protonation of the Grignard reagent. This because there are presence of OH in normal ether, does this would kill and protonate the Grignard reagent.
2) A water bath was used to heat the reaction because the boiling point of diethyl ether is 37C which is extremely dangerous if to be heated directly on the flask.
3) Dry ice is produced from solid carbon dioxide.
4) It is important to used freshly obtained dry ice because dry ice is easily condensed. When dry ice condensed it would produce water due to the properties of carbon dioxide. Thus, it would accidently kill and protonate the Grignard reagent.

Calculation

$NaOH + C_6H_5OH \longrightarrow C_6H_5COONa + H_2O$

(10 g NaOH x 1.00 NaOH)/ 40.0g Na OH = 0.25 mol NaOH

0.25 mol NaOH/ 0.1 L = 2.5 M NaOH

MV = mol

Mol NaOH = 2.5 M NaOH x 0.02 L NaOH

= 0.05 mol NaOH

0.05 mol NaOH = 0.05 mol C_6H_5COONa

$C_6H_5COONa + HCl \longrightarrow C_6H_5OH + NaCl$

0.05 mol C_6H_5COONa = 0.05 mol C_6H_5COOH

0.05 mol C_6H_5COOH x 122.12 g/mol = theoretical mass C_6H_5COOH

= 6.106 g C_6H_5COOH

% yield = (amount obtained (g) /theoretical amount possible (g)) x 100 %

= (1.4 g/ 6.106 g)x 100 %

= 23%

Reference

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