Student Name: Quoc-Huy Pham

Student Number: 8623625

Partner's Name and Student #:
John Reilly (7664342)

Demonstrator's Name: Craig Yu

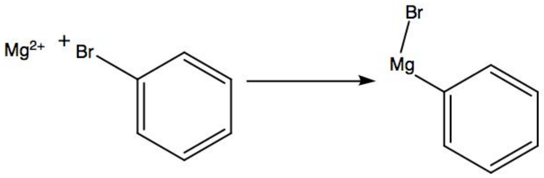
Lab Day (T/W/Th/F): W
Lab Week (even/odd): even
Lab time: 10:00

Experiment 5.
Preparation of Benzoic Acid using a Grignard Reagent

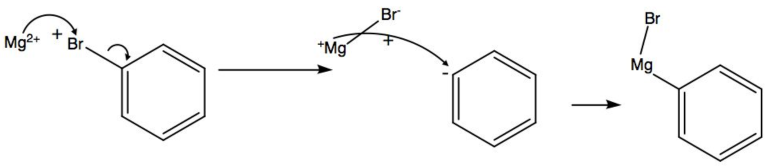
Initials: H.P.

Introduction:

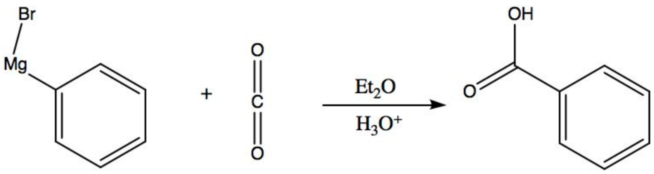
For the preparation of Grignard reagent, where:



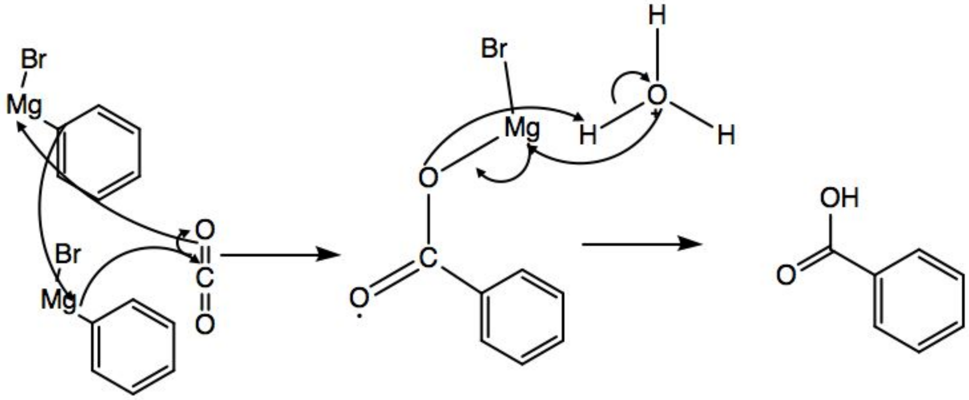
The mechanism proceeds as follows:



For the isolation of benzoic acid, where:



The mechanism proceeds as follows:



Part A: The Preparation of Grignard Reagent

Table of Reagents

Compound	Mol. Wt (g/mol)	Amount	Density (g/mL)	mmol
Magnesium	24.31	0.81 g		33.32
Iodine	126.9	N/A		N/A
Bromobenzene	157.01	3 mL	1.5[1]	28.66
Anhydrous diethyl ether	74.12	20 mL	0.71	

Procedure:

- The glassware were dried and heated in an oven for approximately 20 minutes
- The apparatus was quickly set up
- 0.81 g of Mg was measured and obtained and placed into the 50-mL round bottom flask
- A small crystal of iodine was obtained and placed into the 50-mL round bottom flask. There was a magenta colour in the flask that gradually faded into a brown and a pungent odour.
- Half of 3 mL of bromobenzene in 20 mL of anhydrous diethyl ether was slowly poured into the flask. Gas and heat were produced.
- The rest of the ether mixture was slowly poured into the flask. The mixture was boiling.
- After the boiling stopped, the reflux was activated to heat the mixture. The mixture was boiled for 25 minutes. The final mixture was brown and clear.

---

[1] "BROMOBENZENE." *National Center for Biotechnology Information. PubChem Compound Database*. U.S. National Library of Medicine. Web. 23 Mar. 2017.

Part B: Isolation of Benzoic Acid

Table of Reagents

Compound	Mol. Wt (g/mol)	Amount	Density (g/mL)	mmol
Phenylmagnesium bromide	181.31			28.66
Carbon dioxide (*s*)	44.01	N/A		Excess
Water	18.01	20 mL	1	
Hydrochloric acid	36.46	5 mL		
Sodium hydroxide	40	30 mL	2.13[2]	
Diethyl ether	74.12	45 mL	0.71[3]	

- A dry 200 mL beaker was filled approximately ⅔ full of DRY ICE.
- The mixture was slowly poured onto the dry ice. Gas was produced.
- Four ice cubes, 20 mL of water, 5 mL concentrated HCl and 15 mL ordinary diethyl ether were added to the beaker
- The mixture was transferred to a separatory flask
- The beaker was rinsed the beaker with 15 mL of ordinary diethyl ether and added to the flask.
- The contents were shaken and separated into two different containers (two 200-mL beakers). The organic phase had a bold yellow colour while the aqueous phase had a paler yellow colour and was more transparent.
- The aqueous phase was re-extracted with another 15 mL of ether.
- A TLC was taken of the organic phase with EtOAc:Hexanes 1:9 as the solvent system and the starting material as the reference.
- The organic phases were combined and extracted twice with separate intervals of 15 mL of NaOH. The organic phase was a and the aqueous phase was
- Concentrated HCl was added to the aqueous phase of the prior step until the solution was acidic
- The mixture was subjected to an ice bath
- A tube was attached to the nozzle of the water sink and to a suction flask

---

[2] "SODIUM HYDROXIDE." *National Center for Biotechnology Information. PubChem Compound Database*. U.S. National Library of Medicine. Web. 23 Mar. 2017.

[3] "DIETHYL ETHER." *National Center for Biotechnology Information. PubChem Compound Database*. U.S. National Library of Medicine. Web. 23 Mar. 2017.

- A Buchner funnel was attached to the top of the suction flask with filter paper placed on it
- The mixture was poured onto the funnel.
- A TLC was taken of the final product with EtOAc:Hexanes 1:9 as the solvent system and the starting material as the reference.
- The crystals was collected, dried and weighed. 0.44 g of crystal was obtained. 122.4 °C (Literature[4][5])

Data:

Table 1: Experimental data of TLC of first organic phase

Measurement (cm)	Displacement
Solvent front (R_s)	5.1
Displacement of Reference	2.6
Displacement of Co-spot	2.6/4.45
Displacement of Reaction Mixture	2.7/4.45

---

[4] "Benzoic Acid (HMDB01870)." *Human Metabolome Database*. The Metabolomics Innovation Centre (TMIC) Web. 28 Mar. 2017.

[5] Somasundaran, P., ed. *Encyclopedia of Surface and Colloid Science*. CRC Press, 2006. Web. 28 Mar. 2017.

Figure 1. TLC plate of first extracted organic phase compared with original reference

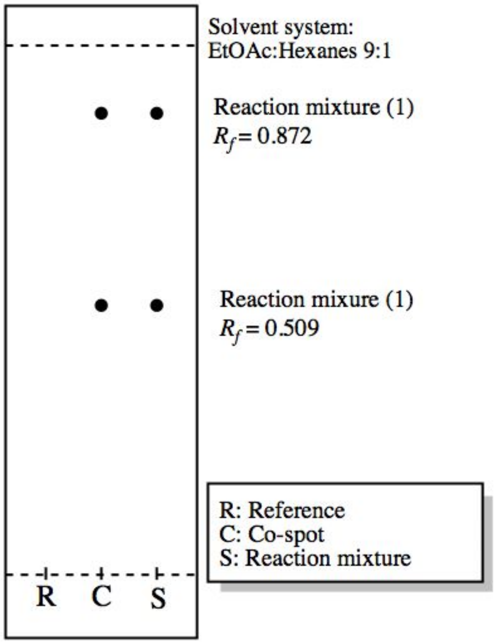
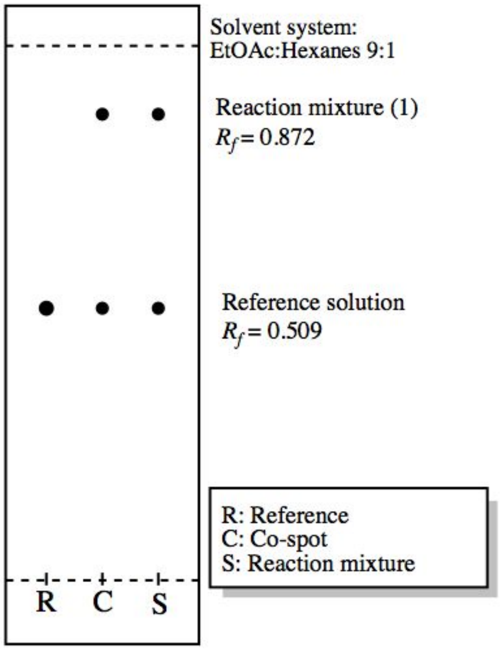


Table 2: Experimental data of TLC of final product

Measurement (cm)	**Displacement**
Solvent front (R_s)	4.5
Displacement of Reference	1.6
Displacement of Co-spot	1.6/3.5
Displacement of Reaction Mixture	1.6/3.5

Figure 2. TLC plate of final product compared with original reference



Calculation:

Retention Factor:

TLC 1

Retention factor of Reference

$$R_f = \frac{\textit{Displacement of Substance}}{\textit{Displacement of solvent front}} = \frac{2.6\ cm}{5.1\ cm} = 0.509$$

Retention factor of Co-spot (1)

$$R_f = \frac{\textit{Displacement of Substance}}{\textit{Displacement of solvent front}} = 0.509$$

Retention factor of Co-spot (2)

$$R_f = \frac{\textit{Displacement of Substance}}{\textit{Displacement of solvent front}} = 0.872$$

Retention factor of Reaction Mixture (1)

$$R_f = \frac{\textit{Displacement of Substance}}{\textit{Displacement of solvent front}} = 0.529$$

Retention factor of Reaction Mixture (2)

$$R_f = \frac{\textit{Displacement of Substance}}{\textit{Displacement of solvent front}} = 0.872$$

TLC 2

Retention factor of Reference

$$R_f = \frac{Displacement\ of\ Substance}{Displacement\ of\ solvent\ front} = \frac{1.6\ cm}{4.5\ cm} = 0.356$$

Retention factor of Co-spot (1)

$$R_f = \frac{Displacement\ of\ Substance}{Displacement\ of\ solvent\ front} = 0.356$$

Retention factor of Co-spot (2)

$$R_f = \frac{Displacement\ of\ Substance}{Displacement\ of\ solvent\ front} = 0.778$$

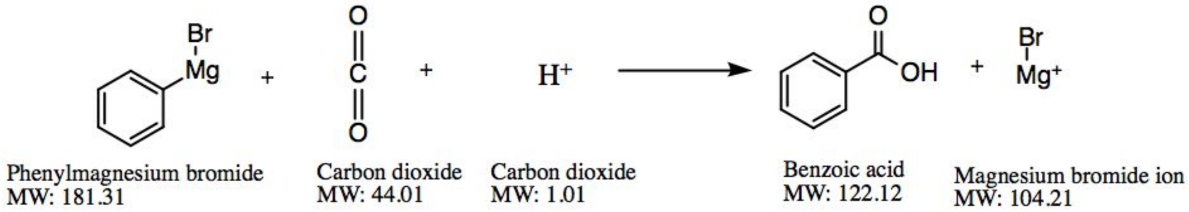
Retention factor of Reaction Mixture (1)

$$R_f = \frac{Displacement\ of\ Substance}{Displacement\ of\ solvent\ front} = 0.356$$

Retention factor of Reaction Mixture (2)

$$R_f = \frac{Displacement\ of\ Substance}{Displacement\ of\ solvent\ front} = 0.778$$

Percent Yield



Since the solid carbon dioxide is in excess, the phenylmagnesium bromide is the limiting reagent. Assuming a 100% yield for the creation of phenylmagnesium bromide, there is an initial 28.66 mmol of phenylmagnesium bromide. Since one mole of phenylmagnesium bromide produces one mole of benzoic acid, 2.66 mmol of benzoic acid is produced.

Theoretical yield (mass) = moles of benzoic acid × molar mass of benzoic acid
= 0.00266 moles of hydrobenzoin × 122.12 g/mol = 0.324 g of hydrobenzoin

Mass of benzoic acid obtained: 0.44 g of benzoic acid

$$\text{Percent Yield} = \frac{Experimental\ Yield}{Theoretical\ Yield} \times 100\%$$

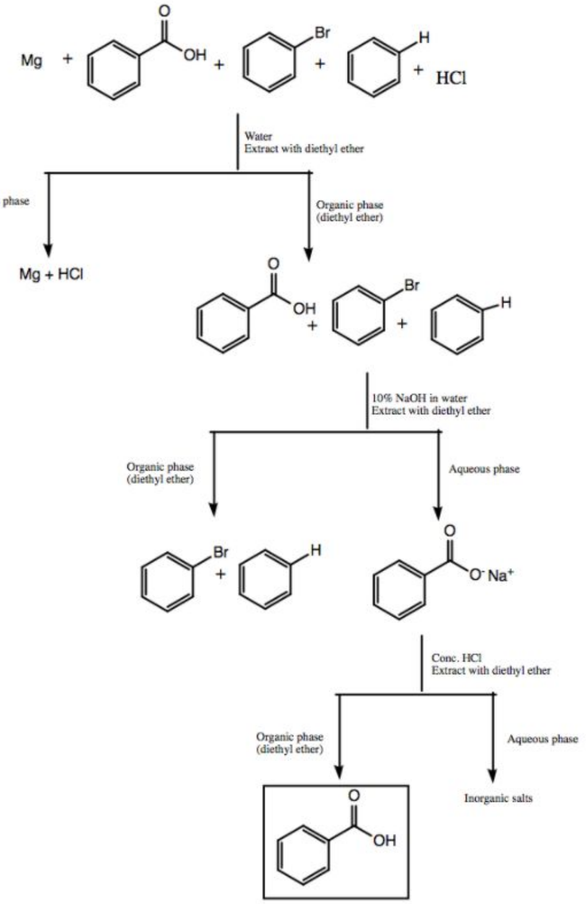
$$= \frac{0.44\ g\ of\ hydrobenzoin}{0.324\ g\ of\ hydrobenzoin} \times 100\% = 136\%$$

Discussion:

In order to produce the Grignard reagents, the magnesium first is exposed the iodine crystal to activate the reaction. When the anhydrous ether is added to the flask, the magnesium

attack the bromide group of bromobenzene, forming a benzene ring with a negatively charged carbon atom. This negatively charged carbon then forms a bond with the magnesium ion, forming phenylmagnesium bromide. If water was introduced, then there will be interference with the reaction through the protonation of the reagent (a strong base) by water, causing the phenyl group to be detached from the reagent prior to the introduction of carbonyl compound. When the carbon dioxide of the dry ice is introduced to the reagent, the phenyl group attacks the ketone carbon of the carbon dioxide, forming a bond with the carbon of the phenyl group and the carbon of the carbon dioxide. This nucleophilic attack causes a shift in the electron orbital space of one of double bonds towards the attached oxygen atoms. This results in oxygen being negatively charged, which allows for the formation of a bond with the negatively charged oxygen atom and another phenylmagnesium bromide. This causes the phenyl group of that molecule to be transferred in order to replenish the first magnesium ion. Finally, the introduction of a hydronium ion (result of the protonation of water molecules by hydrochloric acid) allows for the acidic proton to attack the singly-bonded oxygen atom. This produces an oxygen that is positively charged and is relatively unstable.
In order to increase stability, one of the bonds must be broken, which would be the bond between the oxygen and the magnesium ion as a result of that ion being a good leaving group for oxygen. This results in the expulsion of magnesium bromide from the oxygen and the formation of an alcohol group.

Figure 3. Extraction of benzoic acid



The resulting benzoic acid is present along with impurities such as excess magnesium and benzene. In order to isolate the benzoic acid, the mixture is placed into a separatory funnel along with separate intervals of 15 mL of diethyl ether. This forms an organic phase a bold yellow colour and an aqueous phase with a faint yellow colour. The molecules with an aromatic ring (benzene, bromobenzene and benzoic acid) migrates towards the organic phase while the magnesium and HCl migrate towards the aqueous phase. The organic phase is then extracted, leaving a solution of benzoic acid, bromobenzene and benzene. In order to separate the benzoic acid from the other aromatic compounds, the organic phase is placed into the separatory funnel along with 10% sodium hydroxide. The sodium hydroxide reacts with the benzoic acid to form benzoate ions, which are soluble in water. This results in the migration of benzoate ions towards the aqueous phase and the other aromatic compounds migrating towards the organic layer. The aqueous layer is extracted but the benzoate ions are dissociated in the water. The solution is subjected to the introduced of concentrated HCl, which reacts with the benzoate ions and sodium ions to form benzoic acid and sodium chloride respectively. Since the NaCl is more soluble in water than benzoic acid, the benzoic acid precipitates into solid extracts that can be captured through suction filtration.

From the results of the first TLC plate, which is developed using the organic phase of the first intervals of extraction, the lane for the sample mixture displayed two separated spots, indicating that the sample mixture contains two solutes. The lane for the reference solution displayed a spot which has a similar retention factor to one of the spots of the sample lane, so the sample mixture contains some of the starting material. As for the final TLC plate, the lane of the sample mixture displayed two separate spots, one of which possessing a retention factor that is equal to the retention factor of the reference lane. This means that the final mixture contains the component found in the reference mixture. As for the other spot, considering the greater value in the retention value, the second component of the final mixture is likely to be less polar than the reference component.

The percent yield obtained is beyond 100%, which may be a result of additional impurities (presumably solid sodium chloride) being collected during the suction filtration,

One source of error is the adhesion of solid crystals to the flask during the pouring of the final mixture for suction filtration. Through this adhesion, less crystals would be collected on filter paper, resulting in a decreased experimental mass and hence, a decreased percent yield. This issue can be mitigated through the further use of the solvent (by which the crystal is not soluble to) in order to limit the adhesion of the crystals and hence, those crystals may be collected.

Questions:

1. Anhydrous ether was used because as a result of its anhydrous property, it lacks any water. This aids the reaction as there is no source of interference with the Grignard reagents through the protonation of reagents.
2. In order to heat the reaction, a hot water bath would be used due to how this method of heating keeps the separation of the contents of the bath and the contents of reaction flask, preventing water from interfering with the reaction while the reaction is heated. By

heating the reaction flask, the reaction to produce Grignard reagents will be accelerated according to Arrhenius' equation by allowing the reagents to surpass the activation energy in less time and hence, more reagents can be made in a shorter span of time.

3. Dry ice refers to solid carbon dioxide, which has a -78.46°C. In addition, in the current atmospheric pressure, carbon dioxide lacks a liquid phase, resulting in sublimation of dry ice into gaseous carbon dioxide.
4. It is important that the dry ice was freshly obtained because if the dry ice was exposed to the laboratory conditions for too long, the dry ice may sublimate into the air as a result of the relatively low sublimation point of carbon dioxide. Also, the cold temperature of the dry ice (far below 0°C) may cause droplets of water in the surrounding air to freeze on the surface of the dry ice, forming a layer of frozen water on top of the solid carbon dioxide. If the Grignard reagent may added to that ice, the reagent will react with the layer of water and not carbon dioxide, causing a deviation in terms of the reaction that occurs through the product of benzene as a byproduct.

Works Cited

"Benzoic Acid (HMDB01870)." *Human Metabolome Database*. The Metabolomics Innovation Centre (TMIC) Web. 28 Mar. 2017.

"BROMOBENZENE." *National Center for Biotechnology Information. PubChem Compound Database*. U.S. National Library of Medicine. Web. 23 Mar. 2017.

"DIETHYL ETHER." *National Center for Biotechnology Information. PubChem Compound Database*. U.S. National Library of Medicine. Web. 23 Mar. 2017.

"SODIUM HYDROXIDE." *National Center for Biotechnology Information. PubChem Compound Database*. U.S. National Library of Medicine. Web. 23 Mar. 2017.

Somasundaran, P., ed. *Encyclopedia of Surface and Colloid Science*. CRC Press, 2006. Web. 28 Mar. 2017.

Mg: 0.81 g

(4)

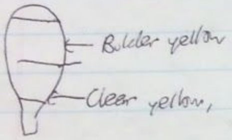
20 mL of wate
5 mL of conc HCl
~~20~~ · 15 mL of diethyl ethe
20 mL of · 10% NaOH (125 mL flask)

Flask → colour: bright pink/magenta
brownish
Boiling

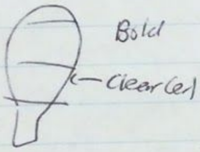
Pungent odour

Mixture
↳ Yellow, clear (ish), cold

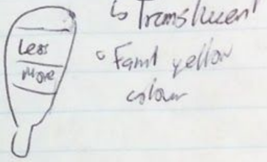
Ex. 1



Ex. 2



Ex. 3

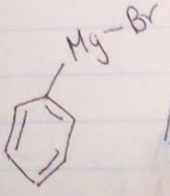


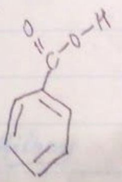
m = 0.44 g of NaCl

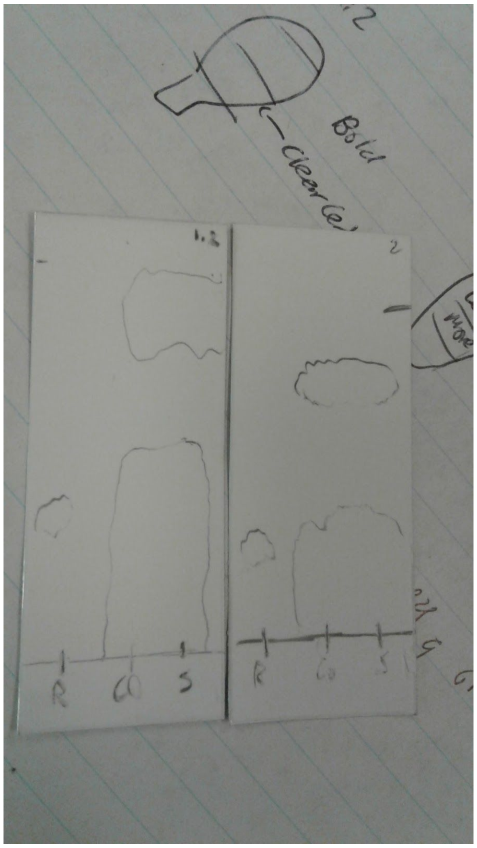
TLC Plate

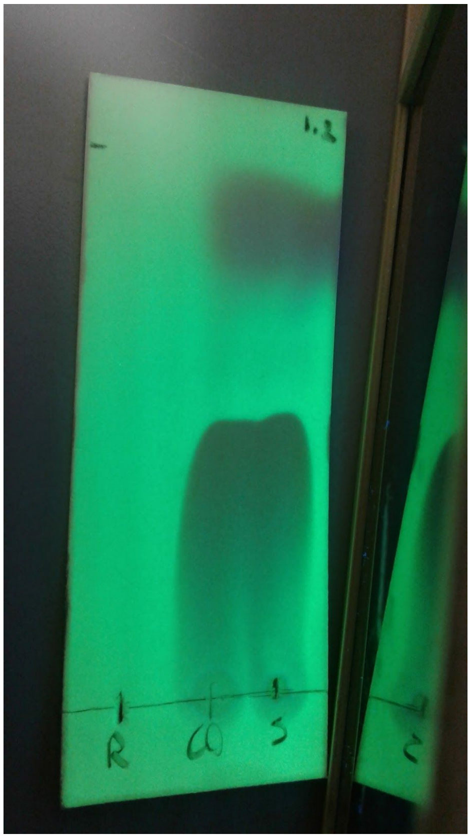
1) Solvent front: 5.1 cm ← R. 2.6
Co. 2.6 / 3.8 – 5.1
S 2.7 / 3.9 – 5.0

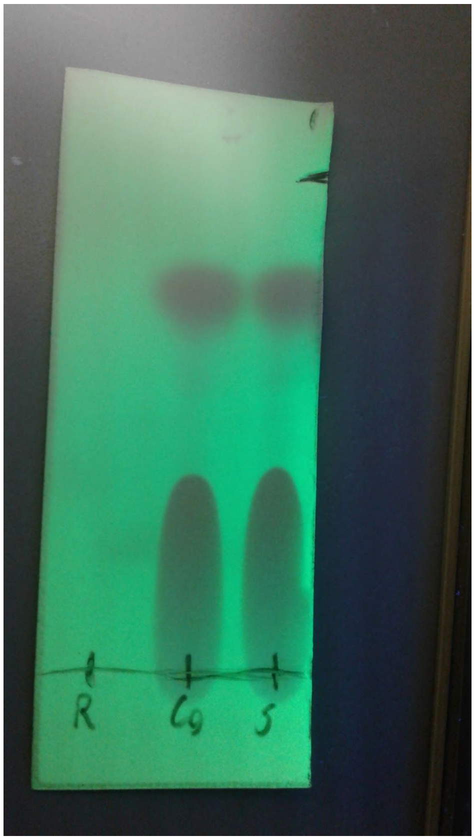
2) Solvent : 4.5 cm
R: 4.6 cm
S: | /3.5
Co: ↓ ↓






Bold
clear (e)
1.2
2
R
Co
S
R
Co
S


1.2
R
Co
S
2


R
Co
S