CH 246
Exp 7: Cannizzaro Reaction

I pledge my honor that I have abided by the Stevens Honor System.
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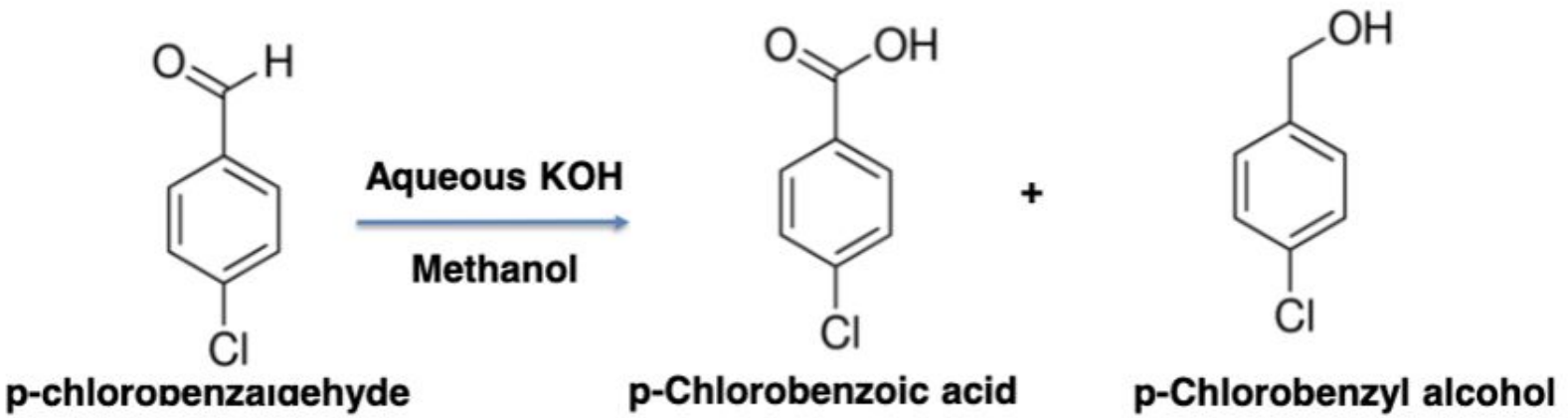
Purpose and Reaction

The objective of this experiment is to prepare p-chlorobenzoic acid and p-chlorobenzyl alcohol from benzaldehyde via the Cannizzaro Reaction.



Reagents

Name	**M.W.** (0.5 pts)	**Density** (0.5 pts)	**Amount (grams/mL)** (0.5 pts)	**Moles** (0.5 pts)	**Hazards/Precautions (MSDS data) and melting point or boiling point** (2 pts)	**Role of the reagent** (1 pts)*
p-chlorobenzaldehyde	140.567 g/mol	1.19 g/mL	2 g	0.01423 mol	Harmful if swallowed. Causes skin irritation. Causes serious eye irritation. May cause respiratory irritation. MP: 47.1C at 1atm	Reagent
p-chlorobenzoic acid	156.56 g/mol	1.57 g/mL	2.23 g	0.01423 mol	Harmful if swallowed. Causes skin irritation. Causes serious eye irritation. May cause respiratory irritation. MP: 243C at 1atm	Product
p-chlorobenzyl alcohol	142.58 g/mol	1.2 g/mL	2.03 g	0.01423 mol	Avoid inhalation. BP: 234C at 1atm MP: 69-72C at 1atm	Product
Potassium hydroxide	56.1056 g/mol	2.12 g/mL	3.2 g	0.057 mol	Corrosive, eye damage and harmful if swallowed BP: 1327C at 1atm MP: 360C at 1atm	Reactant
Methanol	32.04 g/mol	0.792 g/mL	4 mL	0.09888 mol	Flammable liquid and vapor. Toxic, both by ingestion and inhalation. May be fatal or cause blindness if swallowed. BP: 64.7C at 1atm MP: -97.6C at 1atm	Solvent
Dichloromethane	84.93 g/mol	1.33 g/mL	Two 20mL portions	Two portions of 0.3132 mol	Corrosive, eye damage, respiratory irritation, organ toxicity and cancer. BP: 39.6C at 1atm MP: -96.7C at 1atm	Solvent used work up process

Procedure

1. Dissolve 3.2 g of potassium hydroxide in 8 mL of water in an Erlenmeyer flask. Cool to room temperature.
2. Add slowly, with swirling, a solution of 2.0 g p-chlorobenzaldehyde in 4 mL of methanol. Swirl the flask gently during addition. Add a stir bar.
3. Warm to 55-60 0C in for at least 45 minutes while stirring (the mixture turns into a cloudy solution or slurry).
4. Cool the solution and extract with two 20 mL portions of dichloromethane. If the reaction mixture is still contains solid, add a little more (5-10 mL) dichloromethane. Combine the organic (dichloromethane) extracts.

SAVE THE AQUEOUS LAYER

5. Organic Phase: Wash the combined organic layer once with 10% sodium bicarbonate solution and then with 10 mL of water. Dry using ~ 1g magnesium sulphate.
6. Distill off the dichloromethane using distillation apparatus. Cool the residue remaining in boiling flask to room temperature and then in ice to induce crystallization.
7. Collect the crude p-chlorobenzyl alcohol, record yield and melting point.
8. Recrystallization from 5% acetone-hexane mixture (if necessary).
9. Aqueous Phase. Acidify the aqueous layer with conc. HCl (~ 8-10 mL may be required). Check the pH of the solution using a pH paper (should be ~ 1). A thick voluminous precipitate will be formed.
10. Collect the precipitate using suction filtration. Wash thoroughly with cold water. Dry and record crude yield and melting point of p-chlorobenzoic acid.
11. Recrystallize if necessary from methanol.
12. Take TLC of the three compounds (p-chlorobenzaldehyde, p-chlorobenzoic acid, p-chlorobenzoyl alcohol) with 20% ethyl acetate/hexane

Stepwise Procedure

1. Dissolve 3.2 g of potassium hydroxide in 8 mL of water in an Erlenmeyer flask. Cool to room temperature.
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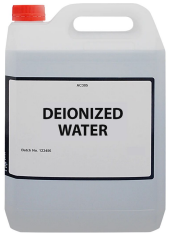


8 mL

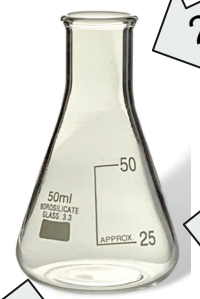
Potassium Hydroxide

3.2 g

Cool to room temperature

With swirling

Add contents

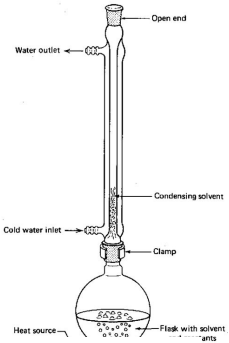


4 mL

2.0 g

p-chlorobenzaldehyde

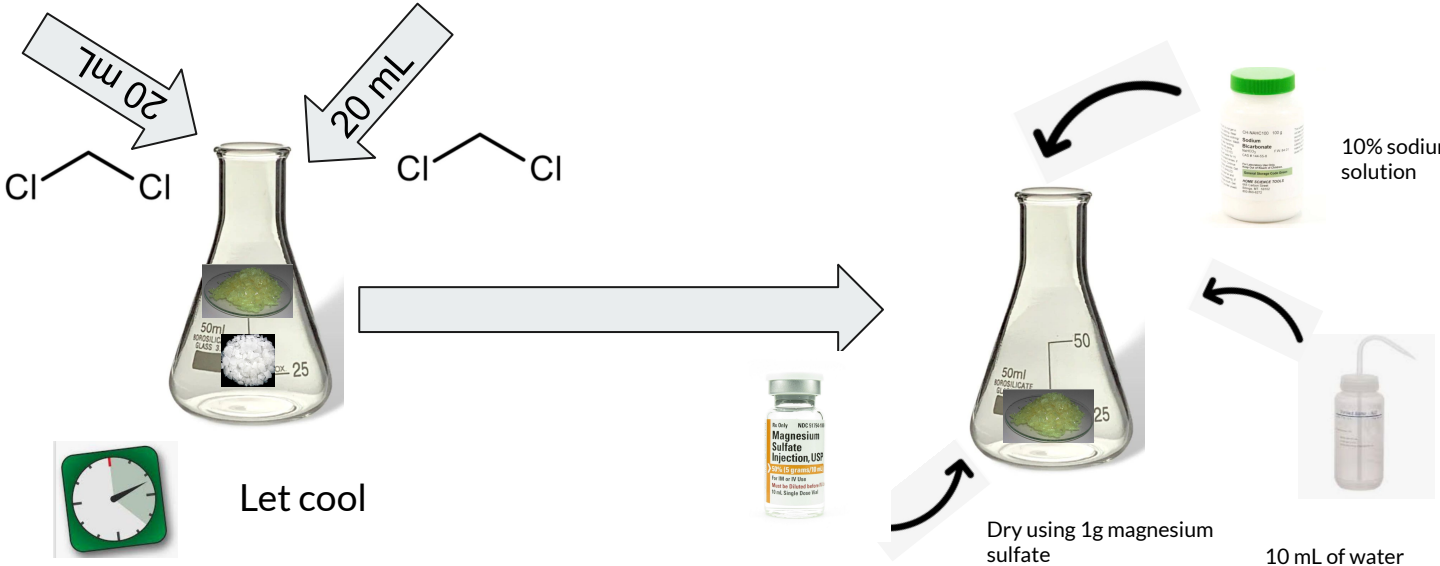
Reflux



55-60℃, 45 min

Stepwise Procedure

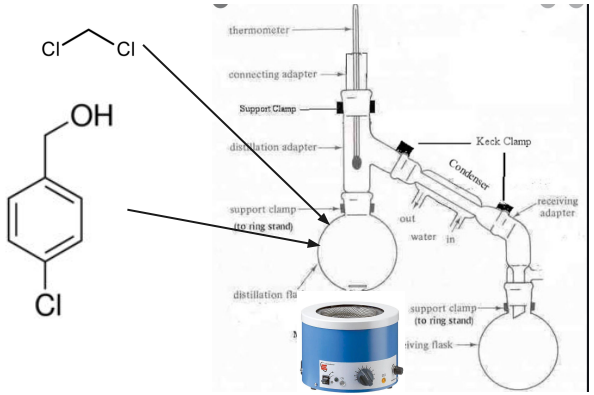
4. Cool the solution and extract with two 20 mL portions of dichloromethane. If the reaction mixture is still contains solid, add a little more (5-10 mL) dichloromethane. Combine the organic (dichloromethane) extracts. SAVE THE AQUEOUS LAYER
5. Organic Phase: Wash the combined organic layer once with 10% sodium bicarbonate solution and then with 10 mL of water. Dry using ~ 1g magnesium sulphate.



Stepwise Procedure

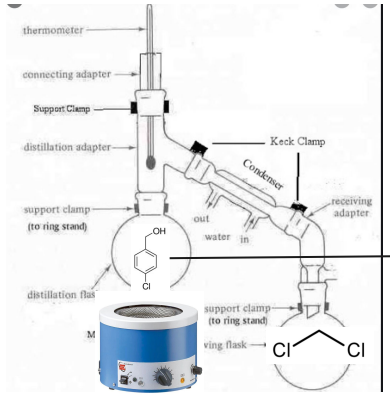
6. Distill off the dichloromethane using distillation apparatus. Cool the residue remaining in boiling flask to room temperature and then in ice to induce crystallization.

Distillation of dichloromethane from p-chlorobenzoyl alcohol



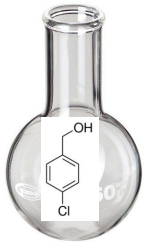
DCM and p-chlorobenzyl alcohol in left flask

Distill



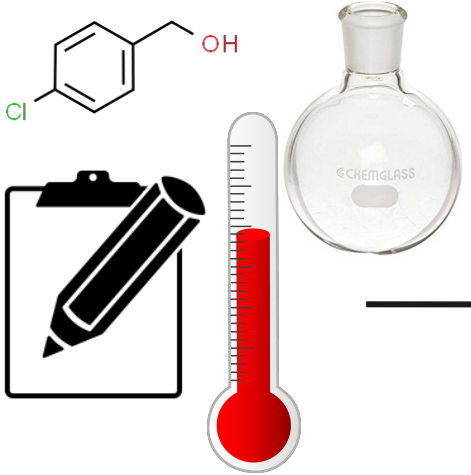
DCM in right flask and p-chlorobenzyl alcohol in left flask

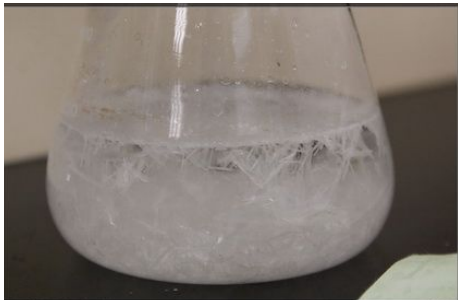
Cool to room temp then crystallize in ice bath

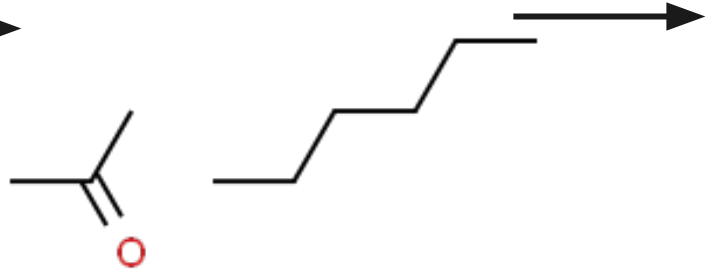


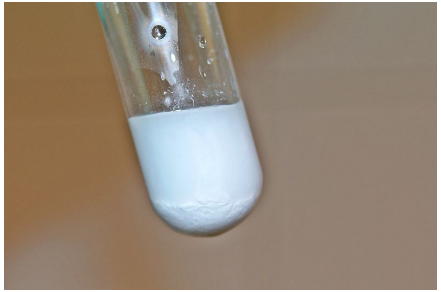
Stepwise Procedure

7. Collect the crude p-chlorobenzyl alcohol, record yield and melting point.
8. Recrystallization from 5% acetone-hexane mixture (if necessary).
9. Aqueous Phase. Acidify the aqueous layer with conc. HCl (~ 8-10 mL may be required). Check the pH of the solution using a pH paper (should be ~ 1). A thick voluminous precipitate will be formed.





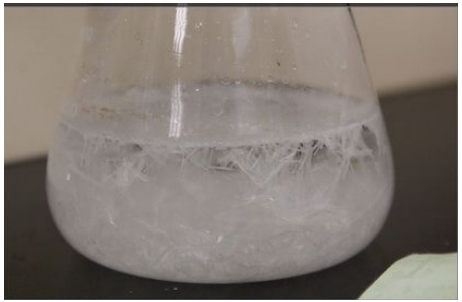


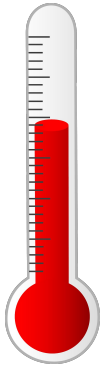


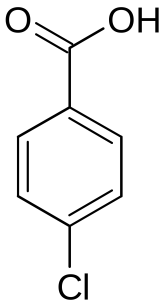
Stepwise Procedure

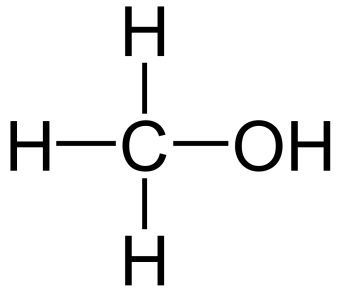
10. Collect the precipitate using suction filtration. Wash thoroughly with cold water. Dry and record crude yield and melting point of p-chlorobenzoic acid.
11. Recrystallize if necessary from methanol.

H_2O



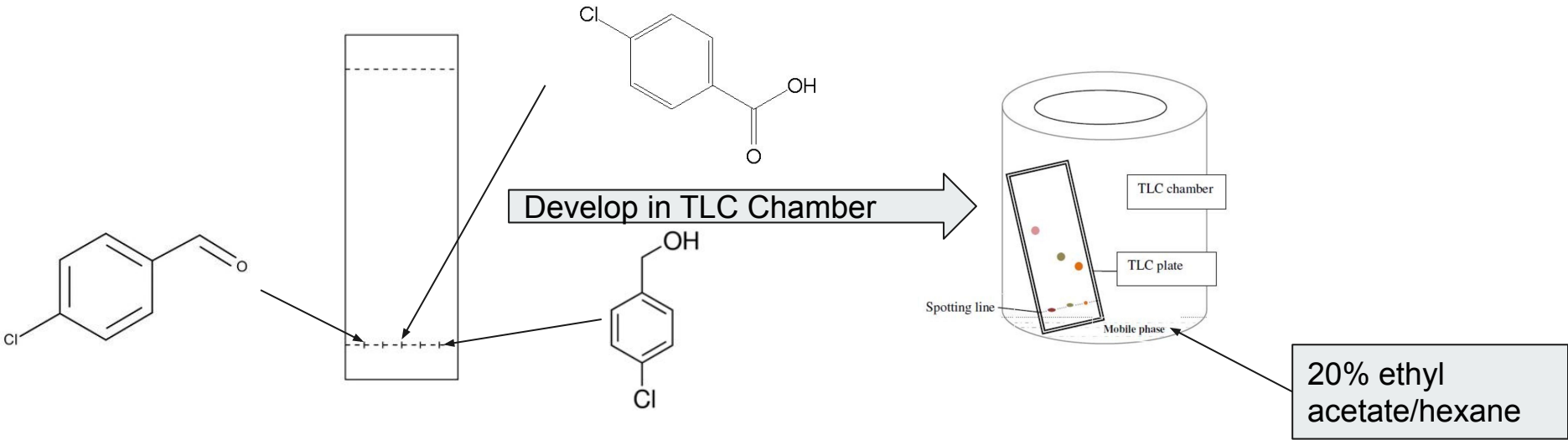






Stepwise Procedure

12. Take TLC of the three compounds (p-chlorobenzaldehyde, p-chlorobenzoic acid, p-chlorobenzoyl alcohol) with 20% ethyl acetate/hexane



Results

1) *% Yield of the p-chlorobenzyl alcohol and p-chlorobenzoic acid.*

P-chlorobenzyl alcohol: (0.68 g/2.03 g) x 100 = 33.50 %

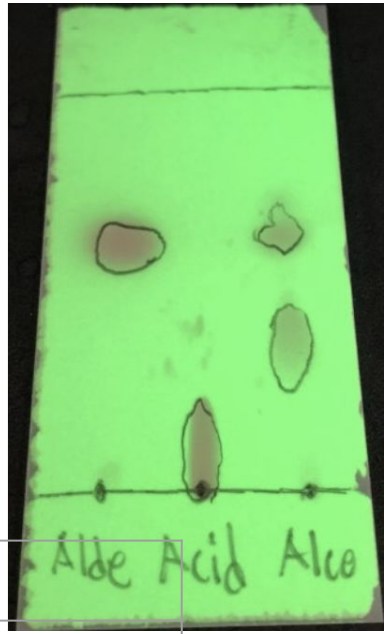
P-chlorobenzoic acid: (1.59 g/2.23 g) x 100 = 71.30 %

2) *Melting Point of the p-chlorobenzyl alcohol and p-chlorobenzoic acid.*

P-chlorobenzyl alcohol: 64 °C- 65 °C

P-chlorobenzoic acid: 240 °C - 241 °C

3) *TLC picture and Rf of p-chlorobenzaldehyde, p-chlorobenzyl alcohol and p-chlorobenzoic acid.*



	Solute Distance (cm)	Solvent Distance (cm)	Rf Value
p-chlorobenzaldehyde	2.9	4.0	0.725
p-chlorobenzyl alcohol	1.8 and 2.9	4.0 and 4.0	0.45 and 0.725
p-chlorobenzoic acid	1.0	4.0	0.25

Conclusion

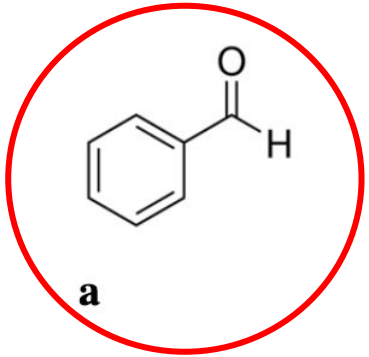
This lab demonstrated the preparation of p-chlorobenzoic acid and p-chlorobenzyl alcohol from benzaldehyde via the Cannizzaro Reaction. 1HNMR spectroscopy was conducted to view the spectra of the benzaldehyde, p-chlorobenzoic acid, and p-chlorobenzyl alcohol. The results of the experiment were seen using Thin Layer Chromatography, or TLC. As expected, it was observed that the acid product had the lower Rf value, and the aldehyde had the highest Rf value. This result makes sense because of the relative polarities of the three compounds. There were no issues during the experiment. There are no further recommendations, since the lab was conducted remotely. A practical application for the Cannizzaro reaction is to produce resins, varnish finishes, lubricants, and plasticizers.

Post-Lab Questions

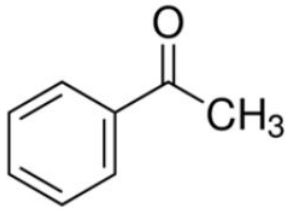
(1) **Which of the following three compounds can undergo Cannizzaro reaction. (2point)**

Only aldehydes that do NOT have a hydrogen on the alpha-carbon → a and c

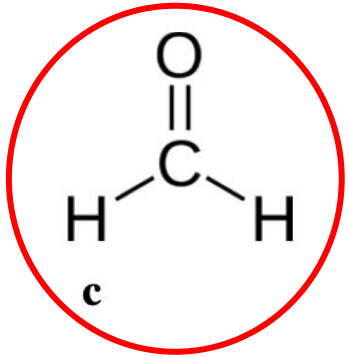
B and D undergo aldol reaction because they have a methyl group attached to the carbonyl (HAS alpha-proton)



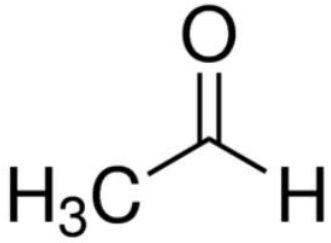
a



b



c



d

Post Lab Question

(2) Why did we wash the organic layer (dichloromethane layer) with 10% aqueous sodium bicarbonate solution during the work-up? (2point)

We washed with sodium bicarbonate in order to get rid of any leftover chlorobenzoic acid that might still remain in the organic layer and wash it out into the aqueous layer.