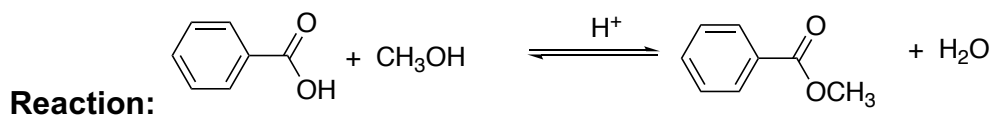


## SAMPLE LAB REPORT

**Date:** 15 July 2019

**Experiment:** The Synthesis of Methyl Benzoate

**Objective:** In this experiment the process of Fischer Esterification will be used to synthesize methyl benzoate from benzoic acid and methanol.

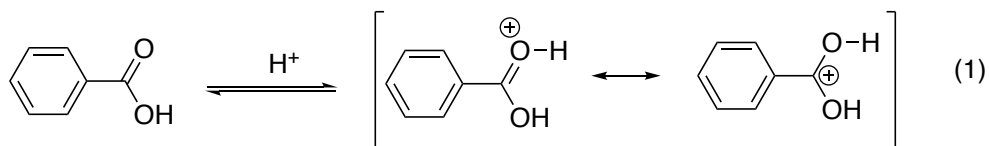


### References:

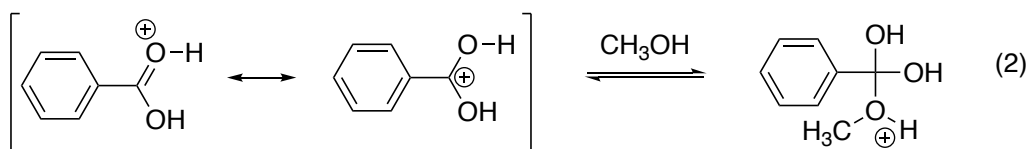
- (1) Organic Chemistry, T.W. Graham Solomons, Craig B. Fryhle, Wiley, New York, 2000, pp. 828 – 830.
- (2) Experimental Organic Chemistry, John A. Mangravite, Marc L. Durand, West Chester University, 2001, pp. 72 – 74.
- (3) “Physical Constants of Organic Compounds”, CRC Handbook of Chemistry and Physics, 58<sup>th</sup> Edition, 1977, CRC Press.

**Theory:** Fischer Esterification is an example of acyl nucleophilic substitution. The reaction is an acid catalyzed equilibrium in which an alcohol acts as a nucleophile, ultimately displacing water from a carboxyl group of a carboxylic acid. The mechanism is as follows:

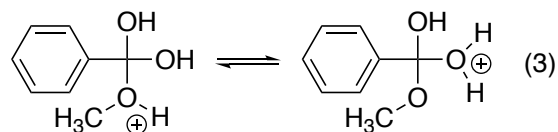
- 1) Protonation of a carboxylic acid increases the positive charge on the carboxyl carbon through resonance:



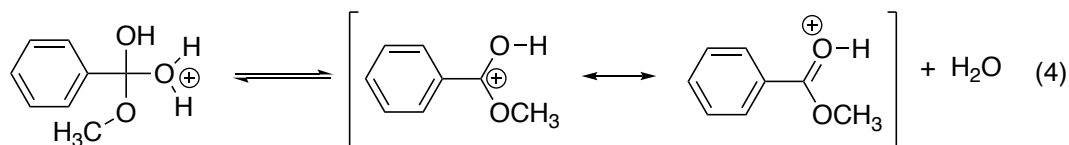
- 2) Methanol, acting as a nucleophile, attacks the carboxyl carbon:



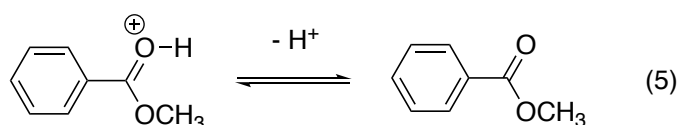
- 3) A proton transfer (probably solvent-mediated) creates the good leaving group (water); in this process the methanolic oxygen becomes neutral and the hydroxylic oxygen gains a plus charge:



- 4) Water leaves; the resulting carbocation is stabilized through resonance:



- 5) The proton leaves the carboxylic oxygen, regenerating the catalyst and yielding the product:



Proton catalysis occurs through the addition of a small amount of strong acid (sulfuric or phosphoric acid). The proton adds to the carbonyl oxygen, generating a resonance form with an increased positive charge on the carbonyl carbon. The activation energy to attack on the protonated carboxylic acid is lower than the activation energy to attack the non-protonated acid; thus, the reaction rate is increased by proton catalysis.

The spare pair electrons of the nucleophile (in this case, the oxygen of the alcohol is the nucleophilic atom) attacks the carbonyl carbon, forming a new covalent bond. The nucleophilic oxygen now has a formal charge of +1, as it is sharing electrons with three other atoms and has only one spare pair of electrons left.

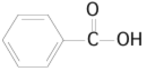
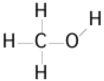
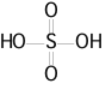
A proton transfer (probably solvent mediated) removes the positive charge from the methanolic oxygen, and by transferring a proton to a hydroxyl group creates a good leaving group (water). Once water leaves, taking the electron pair it shared in the covalent bond to the carbonyl carbon with it, deprotonation yields the final product and regenerates the proton catalyst.

The reaction is a series of steps in equilibrium. The equilibrium constants do not favor products. In order to shift the reaction towards the product

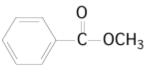

side of the equation, we apply the concepts of Le Chatelier's Principle: When a stress is placed on a system in equilibrium, the equilibrium will shift in the direction that attempts to remove the stress. We can "stress" this equilibrium in two ways:

- (1) add excess reactant (stress: too much reactant), or
- (2) remove product as it is formed (stress: not enough product). In the reaction to be performed a 2:1 molar ratio of methanol to benzoic acid will be used to shift the equilibrium towards the formation of methyl benzoate. Note that if the starting materials and the resultant ester are all high-boiling compounds it is often reasonable to distill off the water as it is formed, thus shifting the position of equilibrium toward products.

**Table I: Table of Reactants**

Name	Structure	Mol. Wt.	MP/BP <sup>1</sup>	Phys. Prop. <sup>1</sup>	Amt. Used	Moles	Hazards <sup>2</sup>
Benzoic Acid		122.13 g/mol	mp=122.4°C	White xtals	10.0 grams	0.082 mole	skin/eye irritation
Methanol		32.04 g/mol	bp =64.96°C	n <sub>d</sub> = 1.3288 d=0.7914 g/mL	25.0 mL = 19.79 g	0.618 mole	POISON! headache blindness
Sulfuric Acid		98.08 g/mol		18 M solution	3.0 mL	0.054 moles	Severe burns, ingestion fatal
Diethyl Ether	CH <sub>3</sub> CH <sub>2</sub> -O-CH <sub>2</sub> CH <sub>3</sub>		bp = 34.5°C		100 mL		anesthetic , produces stupor

**Table 2: Table of Products**

Name	Structure	Mol. Wt.	MP/BP <sup>1</sup>	Phys. Prop. <sup>1</sup>	Amt. Used	Moles	Hazards <sup>2</sup>
Methyl Benzoate		136.16 g/mol	bp=199.6 °C at 760 mm	$n_d = 1.5164$ <sup>20</sup> $d = 1.0888$	11.17 grams	0.082 mole (theoretical)	harmful if swallowed or inhaled.
Water		18.02 g/mol	bp =100.0°C	$d = 1.000$	1.48 grams	0.082 mole (theoretical)	

**Sources:**

<sup>1</sup> "Physical Constants of Organic Compounds", CRC Handbook of Chemistry and Physics, 58<sup>th</sup> Edition, 1977, CRC Press.

<sup>2</sup> <http://msds.ehs.cornell.edu/msdssrch.asp>, accessed 15 July 2004.

**Procedure and Observations:**

**23 August 2003**

**Procedure:**

Benzoic acid was charged into a 250 mL beaker. Fifteen mL of methanol was added to the beaker; the contents were stirred to completely dissolve the benzoic acid. The solution was transferred to a 100 mL one necked roundbottom flask using a short stem funnel. The beaker was washed with 10 mL more methanol, which was added to the contents of the roundbottom flask. Boiling chips were added to the flask. The reaction mixture was cooled to 10°C in an ice bath, then three mL of concentrated sulfuric acid were poured down the side of the flask into the reaction mixture with swirling.

The reaction apparatus was set up for reflux (Figure 1) with the condenser open to the

**Observations:**

Benzoic acid is a colorless crystalline solid.

Heat was evolved during this process and a very slight discoloration occurred, leaving a pale yellow color.

atmosphere. The reaction mixture was heated to reflux for one hour using a heating mantle and a voltage regulator (Variac).

A deepening of the yellow color occurred during this process.

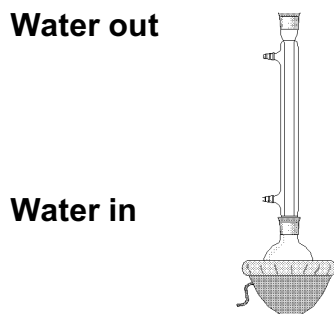


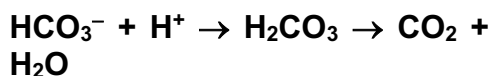
Figure 1: Apparatus for Reflux

After one hour of reflux the reaction mixture was cooled to room temperature and poured into a separatory funnel containing 50 mL of deionized water. The roundbottom flask was rinsed with 10 mL of ether; this was added to the separatory funnel. The reaction flask was washed again with 10 mL of ether and this ether was added to the separatory funnel. An additional 30 mL of ether was added to the separatory funnel for a total of 50 mL of ether, and the reaction mixture shaken to extract the organic material into the ether layer. After the layers separated, the aqueous layer (lower layer) was drained from the separatory funnel; the ether layer remaining in the separatory funnel was decanted from the top of the separatory funnel into a 250 mL Erlenmeyer flask. The extraction was then repeated with another 50 mL of fresh ether. The aqueous layer was drained from the separatory funnel; the ether layers were combined in the separatory

Two layers were seen; the ether layer is the upper layer. It is pale yellow in color.

funnel and washed first with water (30 mL), then with 5% aqueous sodium bicarbonate solution (50 mL) to neutralize excess sulfuric acid that may have been extracted into the ether layer and to extract unreacted benzoic acid. The layers were separated and the aqueous layer set aside for further analysis. The ether layer was washed with saturated NaCl solution (25 mL) to remove bulk water, then after removal of the NaCl solution from the bottom of the separatory funnel the ether layer was decanted from the top of the separatory funnel into a 125 mL Erlenmeyer flask. Anhydrous MgSO<sub>4</sub> was added to the ether solution to remove any remaining water and the flask was corked. The ether solution was dried over magnesium sulfate for ten minutes, gravity filtered into a clean, dry 100 mL one neck roundbottom flask. The ether was removed on the rotary evaporator. The roundbottom flask was then corked and the liquid residues in the flask stored in the lab drawer.

Bubbles evolved due to the reaction of the bicarbonate ion with excess acid:



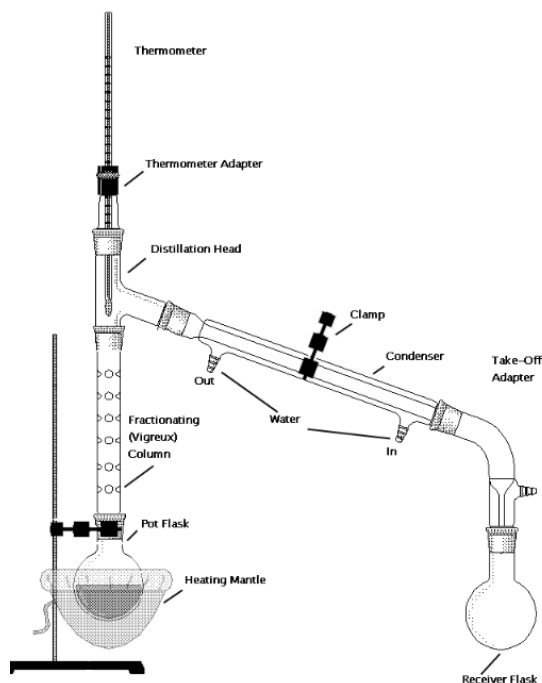
The liquid residues that remained were pale yellow.

[Signature and date here]

30 August 2003

Boiling chips were added to the solution in the roundbottom flask and the solution was distilled over a Vigreux fractionating column at atmospheric pressure (Figure 2).

The liquid in the pot flask was pale yellow.



**Figure 2: Apparatus for Fractional Distillation**

A small amount (2 mL) of residual ether was collected at 34 – 35°C. Once no more ether distilled over, the collection flask was replaced by a new flask and a small amount of methanol (3 mL) was collected at 64 – 65°C. The product was then distilled using an air-cooled condenser to yield product, boiling point 197 – 199°C/758 mm Hg.

While the product was distilling, the aqueous bicarbonate layer was made acidic to litmus by adding concentrated HCl in a dropwise manner with stirring.

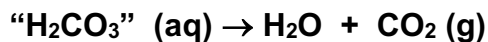
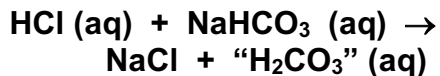
After bubbling ceased, continued addition of HCl precipitated a colorless solid. Addition of HCl ceased when the solution was acidic to litmus. The colorless solid was collected, dried, and weighed.

The distillate was clear and colorless.

The distillate was clear and colorless.

The distillate was clear and colorless.

On addition of HCl rapid bubbling was seen. This was due to the HCl reacting with excess bicarbonate:



Blue litmus turned red when the solution was acidic.

Gross Weight: 22.46 grams  
Tare Weight: 20.80 grams  
Net Weight: 1.66 grams

The melting point of the solid was 122°C, thus verifying the identity of the solid as unreacted benzoic acid.

### Results and Discussion:

The acid catalyzed esterification of benzoic acid with methanol was carried out using excess methanol to shift the equilibrium to favor product formation. Once the reaction was complete, water was used to dissolve much of the excess methanol. Extraction with ether recovered product along with some of the methanol. Fractional distillation was necessary to separate the desired product from excess starting material. The pure product was recovered in good yield by this method.

Gross Weight: 16.58 grams  
Tare Weight: 8.23 grams  
Net Weight: 8.35 grams

Analysis of the product provided the following data:

Boiling point: 197 – 199°C/758 mm Hg	Literature boiling point: 199.6°C/760 mm Hg
Refractive Index: $n_d = 1.5155^{25}$	Literature refractive Index = $1.5164^{20}$
Yield: 8.35 grams (0.061 mol)	
Theoretical Yield: 9.30 grams (0.068 mol) (based on benzoic acid used)	Benzoic acid used = 10.00 grams – 1.66 grams = 8.34 grams (0.068 mole)
% Yield: 89.8%	

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**Comments on this lab write up;**

1. Sources are given for the information in the table using superscripts that refer to footnotes. You may need to use a superscript for each item if you gathered the information from many sources.
2. The theory is thorough but not overly wordy (I hope).
3. The lab report is written in the impersonal passive voice, past tense.

**Examples:**

“Boiling chips were added to the solution in the roundbottom flask “ **NOT**  
“Added boiling chips to the solution in the roundbottom flask”

“Fifteen mL of methanol was added to the beaker” not “I added fifteen mL of methanol to the beaker”

4. Figures and tables are numbered and labeled; numbering is sequential, meaning that the first figure is Figure 1, the second is Figure 2, and so on throughout the lab report. Each figure also has a descriptive title. Tables are numbered and labeled in the same manner. (Graphs are treated as figures and are labeled as such).
5. As much data as possible are reported in tabular fashion.
6. Observations are frequent and descriptive – color changes, heat evolved, observed boiling behavior, etc.
7. “Clear” means that you can see through the sample. “Colorless” means that the sample has no color. **THESE ARE NOT SYNONYMOUS!** If a solid sample is white, it is described as “colorless”.
8. The weighing procedure (gross, tare, net) is done in this manner if you do not have a balance with a “tare” feature. If your balance has a “tare” feature, you may report the net weight.