

## Experiment VI. Part a: Fischer Esterification Of A Carboxylic Acid And Identification of The Product By GC, Micro-Boiling Point and IR spectroscopy.

**Reading assignment:** Review the mechanism of Fischer esterification. See, for example, KPC Vollhardt and NE Schore, *Organic Chemistry*, 5<sup>th</sup> or 6<sup>th</sup> ed, Ch 19-9 or any introductory organic chemistry text.

*Techniques in Organic Chemistry* pages: 56-58, 60-61, 33. IR: 225-240, 243-266.  
3<sup>rd</sup> ed pages 58-63, 24,-25, 277-288, 291-307.

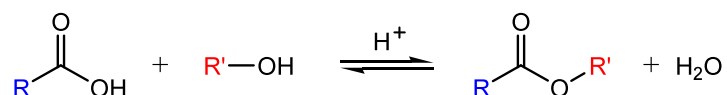
**Watch the video! It will help you in setting the experiment correctly.**

### Topics and Techniques

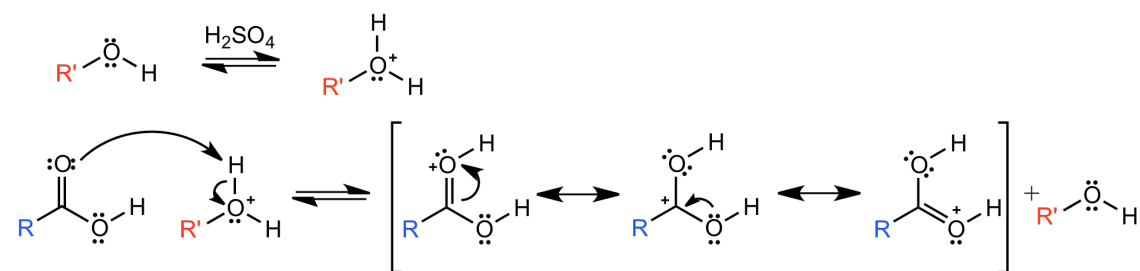
i) reaction mechanisms and reaction conditions, ii) reaction work-up, product isolation and purification, iii) infrared spectroscopy, iv) micro-boiling point determination of unknowns

### Introduction

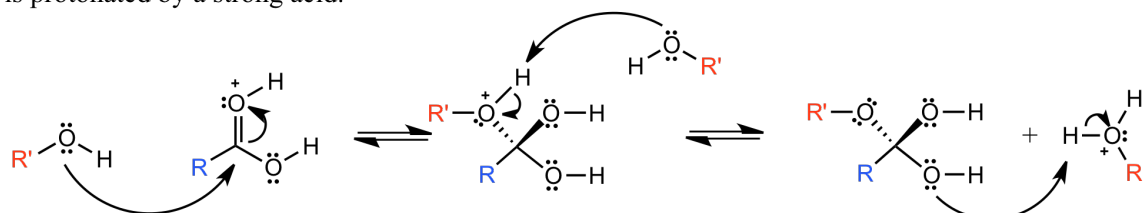
In a Fischer esterification reaction, a carboxylic acid is exposed to an alcohol and a strong acid catalyst that in turn yields an ester and water as the reaction products. The reaction is reversible and the composition of the reaction mixture or position of equilibrium is determined by thermodynamics.



The reaction mechanism for formation of the ester is given below. There are a number of ways to obtain good yields of the product ester. Generally these methods involve the removal (or complexation) of water or the use a large excess of one of the reactants in order to favor the formation of the ester. Both procedures for obtaining good yields of ester exploit Le Chatelier's principle in that the removal of water or the addition of an excess of one of the reactants drives the reaction towards formation of the ester. In this experiment, an excess of carboxylic acid will be used. In this respect, the presence or addition of water is of some concern since, water will shift the composition of the reaction mixture away from formation of the ester and toward the formation of carboxylic acid, so use dry glassware.

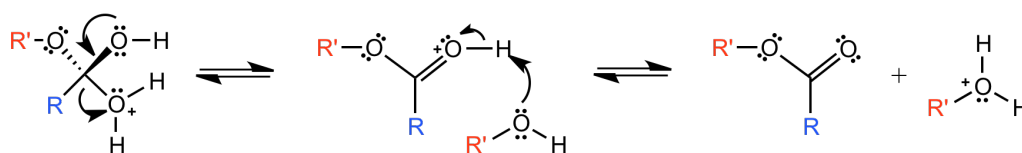


A carboxylic acid is protonated by a strong acid.



The alcohol attacks the protonated carbonyl

tetrahedral intermediate



### The Experiment (overview)

In this experiment you will be given an "unknown alcohol" to react with acetic acid in an esterification reaction. You will isolate, purify, and identify your ester product by performing a microboiling point determination, GC and IR spectroscopy. Your product ester will be one of the esters below:

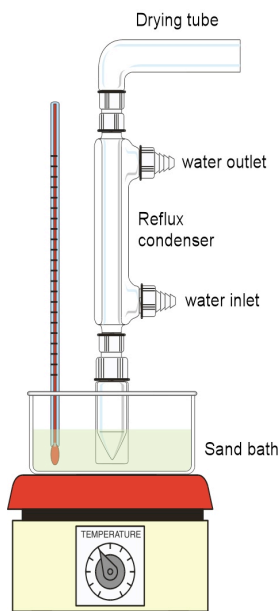
- n-propyl acetate
- isobutyl acetate
- isopentyl acetate
- hexyl acetate
- n-octyl acetate
- benzyl acetate

#### Part A: Procedure, reaction conditions, isolation and purification of the ester

Transfer 0.50 mL of your "unknown alcohol" into a dry 5.0 mL conical vial. Place a magnetic spin vane in the conical vial and add 1.5 mL of glacial acetic acid. Next, have your TA add one drop of concentrated sulfuric acid to the conical vial. Connect a reflux condenser equipped with a calcium chloride drying tube to the conical vial. Connect the condenser to the water. Which direction should the water be flowing through the condenser? Place the vial inside a sand bath. Turn-on both stirring and heating and heat the sand to about 160-180 °C. Note: you should observe refluxing of the alcohol in the condenser. Heating the sand bath to 160 - 180°C will assure you that the reaction

contents in the vial will be brought to a state of reflux, which should be noticeable upon careful inspection of the condenser.

Following a 1 hour reflux, very carefully remove the sand bath, clamp the conical vial 1.5 inches above the magnetic stir plate and allow the conical vial and contents to cool (you may want to use a room temperature water bath to cool your reaction vial and contents more quickly).



**Figure 4.a** Microscale reflux with stirring under anhydrous conditions

When the conical vial and contents have approached room temperature continue rigorous stirring and add 1.5 mL of an aqueous 10% sodium carbonate solution to the reaction mixture. Make sure that the reaction contents have been mixed well. Following this, add 1.0 mL of MTBE to the neutralized reaction mixture with thorough mixing, but do not shake too vigorously. Allow the aqueous and organic phases of the reaction contents to separate. Which layer is the organic layer and which the aqueous layer? Which layer is your product in? Carefully remove the aqueous layer from the reaction vial with a pipette. Wash the organic layer 2 more times with 1.5 mL of aqueous 10% sodium carbonate. The last aqueous sodium carbonate wash should be basic to litmus. If not, wash the organic layer an additional time or more until the aqueous layer is basic to litmus. Why is the organic layer washed with additional 10% aqueous sodium carbonate? **Do not discard the aqueous washes until you have isolated and characterized your product.** Dry the organic phase for 15 minutes over anhydrous sodium sulfate.

Construct a small chromatography column by filling a dry filter Pasteur pipet with a small plug of cotton followed by approximately 1 mm of sea sand, 5 cm of silica gel, and 2-3 mm of sea sand sequentially. Tare a 10.0 mL Erlenmeyer flask containing a boiling chip and place this below the silica gel filled filter pipet to act as a receiver. Apply 1.0 mL of methylene chloride to the column. Use a Pasteur pipette to add the crude product ester to the top of the column. Rinse the reaction vial twice with 0.5 mL portion of methylene chloride and add the methylene chloride rinse to the top of the column. Add an

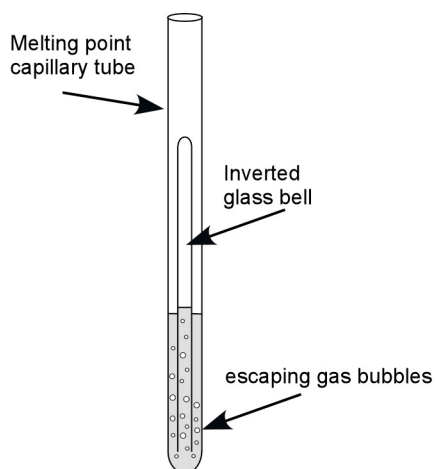
additional 2.5 mL of methylene chloride to the column to ensure complete elution of the product. Evaporate the MTBE-methylene chloride solvent mixture from your product ester **completely** by gently warming the contents of the flask using a sand bath with a temperature of 80 - 100 °C. If the evaporation of solvent is not complete and solvent is present, what effect would this have on the percent yield? What effect would this have on the micro-boiling point? What effect would this have on the IR spectra?

Remember use a fume hood whenever possible. Weigh the ester and calculate the experimental yield of the reaction. Your product ester should be sufficiently pure as isolated to allow the calculation of an experimental yield and characterization.

### **Part B: Boiling Point Determination by the “Ultramicro Boiling-Point” Method.**

A common way to determine a boiling point of a liquid, is to use the Mel-Temp. Measuring the boiling point of a compound using a Mel-Temp apparatus is similar to taking the melting point of a solid. Thus, the higher limit for taking the boiling point determination is the range of the thermometer or the decomposition temperature of the oil. **The TA will prepare the boiling point bells for all students and demo the correct procedure for obtaining micro boiling points using the Mel-Temp instrument.** Practice your technique of obtaining micro boiling points using a "known liquid" that will be made available for you.

Use a TLC capillary tube to add your liquid product to a melting-point capillary tube. The volume of your liquid product in the melting-point capillary tube should not exceed one-half of an inch. Centrifuge the liquid in the melting-point capillary tube so that the liquid ends up at the bottom of the capillary tube.



**Fig 4b.** Ultramicro boiling-point determination

Insert a “glass bell” into the melting point capillary tube, with the **open end of the bell pointing down**. **Your TA will provide the bells**. Push or shake the glass bell down so that it rests near or on the bottom of the melting point capillary tube, with the open end of the glass bell submerged **below** the surface of the liquid. Air should be trapped inside the inverted glass bell at this stage. Place the loaded melting point capillary tube in the Uni-Melt melting point apparatus. Raise the temperature gradually until a steady stream of

bubbles exits the glass bell (approximately one bubble exiting every one or two seconds). As the temperature begins to rise, the trapped air will expand. Some of this air will exit the bell and bubble out through the liquid sample. As the temperature continues to rise, sample vapors will enter the glass bell and displace the air. Eventually, no air will remain in the glass bell; only sample vapors fill the bell. At this stage, the bubbles escaping the glass bell are due only to the sample and will begin to escape more rapidly. When the escaping bubbles are coming out of the inverted tube in a rate that you cannot count them or tell them apart from one another, turn off the heat and allow the temperature to drop. When the last bubble exits the glass bell, the vapor pressure of the sample is equal to the atmospheric pressure. This is the boiling point of the sample. With a minuscule amount of additional cooling, the temperature falls below the boiling point of the sample (condensation point). As a consequence, sample vapors inside the glass bell condenses to liquid, a vacuum forms, and sample liquid is pulled **very rapidly** into the bell. If upon cooling, your liquid sample slowly enters the inverted tube, this is **NOT** the boiling/condensation point. This is simply the shrinking of the gas inside the bell due to the cooling of the sample. You need to heat the sample up again to a higher temperature. Once you have gotten your first reading of the boiling point, it is sometimes possible to heat the sample again and get a second or third reading, but be careful because they tend not to be as accurate as the first time. This way it is possible to confirm your boiling point with a second reading.

Since the ultramicro boiling-point method is hard to master, you will also identify your product by GC. Inject a sample of your product and compare its retention time to the provided standards as you did in the previous experiment. Since the GC will give you an accurate identification, at this time you can evaluate your boiling point determination technique. It is important that you will be able to measure an accurate boiling point for the next experiment.

### **Part C: Characterization of the Product by IR Spectroscopy.**

Obtain an IR spectrum of the product using the capillary film technique. A summary of sample preparation and the operation of the IR are provided below. Be sure to mark the peaks of strong and medium intensity on the IR spectra. **Your TA will demonstrate the technique used for sample preparation and more importantly the use of the IR instrument.**

Report the name of the ester you prepared and include the percent yield for your synthesis, the boiling point of your product, comparisons with literature values, the IR spectrum of your product, and an analysis of the spectrum in your report. Compare the IR spectra of your product with the IR spectra of reactants and products that are available on line.

#### **IR Spectrum of a Liquid Sample**

A liquid sample is placed between two salt plates (NaCl or KBr) and then an FT-IR spectrometer is used to obtain the IR spectrum.

- 1) make sure the sample is dry, no water. Water will dissolve the plate.
- 2) use capillary tube (mp capillary tube with two sides open, cut top of close side) to place a drop of liquid sample on the center of one NaCl plate. Cover the drop with another plate and slide it to spread the liquid into a film. The sample should be spread out to cover the entire plate.
- 3) place the NaCl plates vertically on an IR sample holder.
- 4) run the IR.

*Note 1: Sodium Chloride plate is water soluble, no water should touch the plate. The plates must be kept in a desiccator to prevent exposure to atmospheric humidity.*

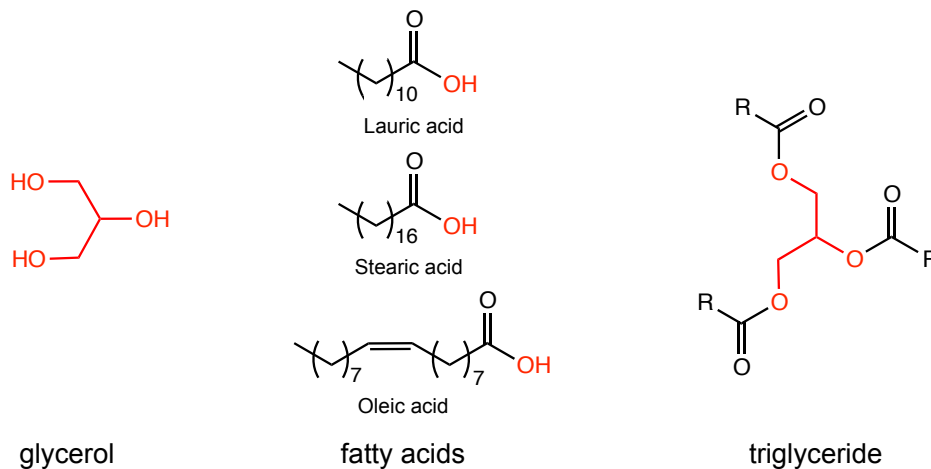
*Note2: After running the IR the liquid sample should be removed from the salt plates by Kimwipe. Then the plates are placed in a special funnel and rinsed with methylene chloride and dried with Kimwipe.*

## Exp 6-Part 2: Synthesis of Biodiesel

### Introduction

Biodiesel is an alternative fuel to petroleum-based diesel. It is derived from renewable sources such as vegetable oils and fats. Diesel fuel is used to operate internal combustion diesel engines, which are the most thermal-efficient engines. In contrast to petrol engines where a spark ignites the fuel, diesel engines relies on the heat of compression to initiate ignition. Therefore diesel fuel has different chemical characteristics than gasoline. In recent years biodiesel is gaining popularity as an alternative “clean” fuel. Pure biodiesel emissions have decreased levels of toxic emissions such as polycyclic aromatic hydrocarbons and nitrated aromatics. Biodiesel is usually used as a mixture with petro-based diesel.

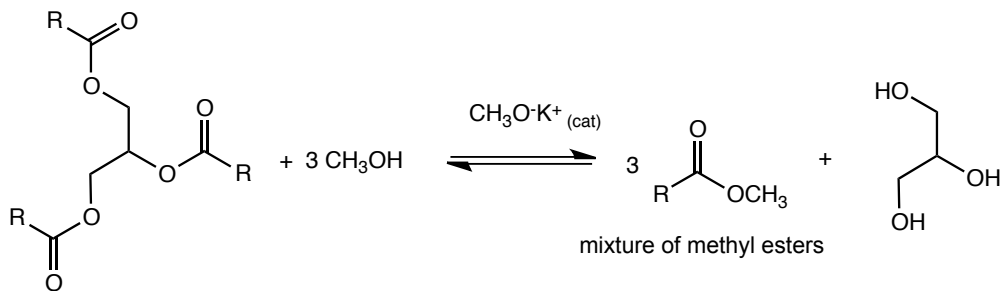
Biodiesel, also known as FAME (fatty-acid methyl ester) is produced by transesterification of oils or fats. Chemically speaking, oil is a tri-ester (triglyceride) derived from glycerol and three long-chain carboxylic acids (fatty acids). The three fatty acids usually differ in their chain length, the number of double bonds, the location of the double bonds along the chain and their geometry (cis or trans).



**Figure 1.** The chemical structure of oil

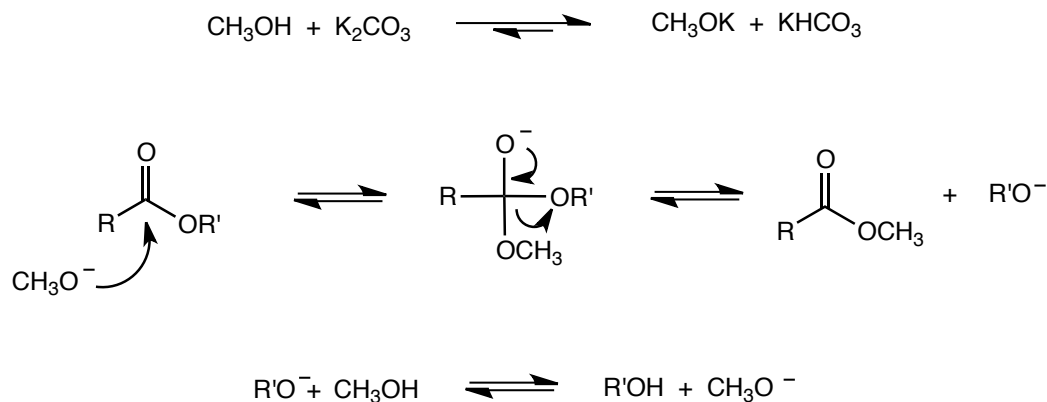
Trans-esterification is a reaction in which the alcohol residue of an ester is replaced by another alcohol. In biodiesel synthesis, a triglyceride is reacted with methanol to form fatty-acid methyl esters and glycerol. The result mixture of methyl esters has chemical characteristics suitable for operating diesel engines.

Trans-esterification can be catalyzed by acid or base. Acid catalysis is essentially a reversed Fisher esterification, and requires a very large excess of alcohol. Base catalysis is much faster and more efficient.



**Figure 2.** Base catalyzed trans-esterification of triglyceride

The mechanism for the reaction is presented below. The first step is a reaction of the base with the alcohol, producing a methoxide catalyst. The nucleophilic attack of the methoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate. The intermediate restores the carbonyl double bond to form an alkyl ester while the corresponding anion of the diglyceride acts as a leaving group. The latter deprotonates another molecule of methanol to continue the reaction.



**Figure 3.** Mechanism of base catalyzed trans-esterification.

### Can biodiesel replace petroleum?

It looks very simple: all you need to produce oil for production of biofuel is sunlight, carbon dioxide and water. The reality is that it is actually much more complex. The biofuel comes from plant matter it is limited by the amount of agricultural land available. This land is already required for food production. Algae is being explored as an alternative source for oil production, but the process is not economical. Genetic engineering is currently explored as another method of producing biofuel.

### The experiment

Note: vegetable oil contains a mixture of triglycerides and therefore it is not possible to calculate accurately the number of moles in a reaction. Based on the typical composition of oil we will assume an average molecular weight of 880 g/mol. Efficient transesterification requires 2 fold molar excess of alcohol for each ester group. Calculate how many milliliters of methanol are required for transesterification of 2 g of vegetable oil.

### Caution!

To avoid slippery floors, any oil or biodiesel spill should be wiped immediately and cleaned with hexane.



### Procedure

Add 2 g (2.2 mL) of vegetable oil into 5.0 mL conical vial. Place a magnetic spin vane in the conical vial and then add methanol according to your calculation. Next add potassium carbonate (0.12 g) and connect a water-cooled reflux condenser to the conical vial. Heat the conical vial using a hot sand bath (the thermometer should be well positioned in the sand bath with a reading of about 70 °C). Note: you should observe in the condenser a refluxing of the alcohol. Reflux the solution for 20 minutes. Note changes in the reaction mixture during the reaction.

Carefully remove the vial from the sand bath, and allow the conical vial and contents to cool (you may want to use a room temperature water bath to cool your reaction vial and contents more quickly). Continue vigorous stirring and add 2 mL of an aqueous acetic acid solution (Vinegar) to the reaction mixture. Make sure that the reaction contents have been mixed well. If done correctly, CO<sub>2</sub> bubbles will escape. Check that the pH of the solution is neutral.

Transfer the solution mixture to a centrifuge tube. Centrifuge for 1-2 minutes and let the two layers separate. Discard the bottom aqueous layer and keep the top biodiesel layer. Add anhydrous sodium sulfate to dry the biodiesel. Filter the product through a filtering pipette into a tarred 10 mL Erlenmeyer. Weigh the product. Take IR of the product.

### TLC analysis:

Obtain a small TLC plate and a filter paper. Dissolve a drop of the biodiesel in few drops of 5% tBME in Hexanes. Place a drop of the solution on the TLC plate. Dissolve a drop of the starting oil in few drops of 5% tBME in Hexanes. Place a drop on the oil solution on the TLC plate. Develop the TLC in 5% tBME in Hexanes. Inspect the plate under UV light and then in Iodine.

Calculate and compare the R<sub>f</sub> of both the starting material and the product. Was all the starting material consumed?

### Viscosity determination using calibrated Pasteur pipette:

Relative flow rate through a glass pipette will be used to estimate the the viscosity of biodiesel and the vegetable oil

Mark a 5 3/4' glass pipette with two calibration marks at 3 cm and 6 cm up from the tip.

While holding a finger against the tip, fill the pipette with the biodiesel sample slightly above the top calibration mark. Remove the finger and measure the time required for the sample to travel between both marks.

Using the same glass pipette above, measure the time for a vegetable oil sample.

Calculate the relative viscosity: Oil time / Biodiesel time

Postlab question:

If the excess methanol is not properly separated after the reaction is completed, the biodiesel product often has a lower flash point than the required specification. Aside from being a safety concern, off-spec biodiesel fuel may have adverse effects on engine wear and performance. How will you prove that your sample is methanol-free?

Reference:

*J. Chem. Educ.*, **2011**, 88 (9), pp 1290–1292