

# Fischer Esterification

## Introduction:

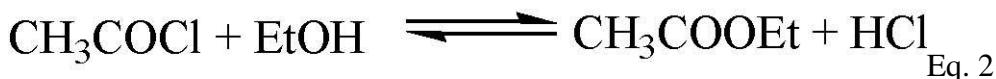
Esters are one of the most common derivatives of carboxylic acids and are widely distributed in both nature and industry. A typical procedure to synthesize esters is the Fischer esterification, wherein a carboxylic acid is treated with an alcohol in the presence of a mineral inorganic acid catalyst. In this experiment, lauric acid (dodecanoic acid) is converted to ethyl laureate. Lauric acid is representative of a class of molecules called fatty acids. These are long, straight chain carboxylic acids (C12-C40) found as ester derivatives in oils, fats, and waxes. For example, a component of carnuba wax is  $\text{CH}_3(\text{CH}_2)_{33}\text{CO}_2(\text{CH}_2)_{26}\text{CH}_3$ . Carnuba wax is found in finer automobile waxes and is exuded by leaves of Brazilian wax palm tree. Animal fats are fatty acids of 1,2,3-propanetriol, also known as glycerol. Thus, these fats are often referred to as triglycerides.

Objective: To synthesize ethyl laureate via Fischer esterification method.

Experiment Overview: With 1° alcohols, neither side of the equilibrium depicted in equation 1 is strongly favored. To drive the equilibrium to make more ester, excess alcohol is added following Le Chatelier's Principle.



In addition, an acid catalyst is needed. Its role is to facilitate the nucleophilic attack of the alcohol at the carbonyl carbon of the carboxylic acid. The tetrahedral intermediate formed by the attack of the alcohol can then isomerize by means of proton migration, to allow water to behave as a leaving group. Loss of water yields a carbocation stabilized by resonance, which need only lose a proton to give the desired ester, and regenerate the acid catalyst. In this experiment, the acid catalyst will be generated in-situ (during the reaction) using acetyl chloride ( $\text{CH}_3\text{COCl}$ ) treated with a small amount of the ethanol used in the reaction mix, producing HCl, which then will initiate the reaction (shown in equation 2 below).



## Waste Disposal:

The aqueous layer from ether extraction: let the solution sit in the hood to allow ether to evaporate. At the end of the experiment, you can dispose of it in the sink.

## Procedure:

1. Start with DRY glassware. Assemble a water jacketed condenser; the 5mL conical vial equipped with magnetic spin vane; and an aluminum heating block-equipped hot plate-stirrer. Make sure that the system to be heated is not a closed system!! Have everything at the correct height and ready to go when adding the samples. Do not attach the water lines and begin passing water through the condenser *until later*.
2. Once assembled, detach the 5mL conical vial and charge it with 70mg of lauric acid and 1.0mL of absolute (200 proof) ethanol. Lastly, add 30 $\mu$ L of acetyl chloride (using syringe) into the conical vial in the public hood then cap it tightly and return to your own hood. Remove the cap and immediately and rapidly reassemble the reaction apparatus. Acetyl

- chloride and moisture in the air react readily, so the acetyl chloride should be tightly capped when not in use.
3. Attach the water lines and begin passing water through the condenser. Heat the reaction mixture to a gentle reflux for 1 hour (block temperature of about 120°C). Remember to turn on the water so reflux can occur.
  4. Then discontinue heating and allow the mixture to cool. Once the reaction vial is comfortable to touch, take off the condenser and concentrate the reaction mixture by heating to an approximate volume of 0.3mL. This is done to prevent emulsions (if any, try adding small amount of NaCl solids, or using a centrifuge but be sure the vial is balanced) during the subsequent extractive isolation.
  5. Upon cooling of the conical vial, remove the spin vane (by using the spin vane remover), and add about 0.5mL (by counting drops) of diethyl ether (for simple extraction) and 0.5mL of 5% aqueous sodium bicarbonate solution (a strong base to react with acids). Gently agitate (no shaking, o/w when venting, you may lose some sample) the conical vial after having capped it (twisted in order to seal well). Make sure to vent the vial periodically (due to the production of CO<sub>2</sub>) by slightly lifting the cap. Remove the lower aqueous layer with a disposable pipette and set aside for combination with later aqueous extracts. Wash the ethereal layer with two more 0.5mL portions of sodium bicarbonate. Combine the aqueous extracts and set them aside to let ether evaporate. At the end of the experiment, you can dispose of them in the sink.
  6. Dry the ethereal product with addition of sodium sulfate, and then separate the dried solution from the wet drying agent matrix, and pass it through a cotton-plugged disposable pipette. Rinse the sodium sulfate matrix with a fresh 0.5mL portion of ether and pass it through the plug, adding it to the dried ethereal solution of the product. Add ether as quickly as possible. Otherwise, cotton would absorb the already small amount of the solution. After the filtration, you may want to pass some extra ether (a few drops) through the cotton to rinse off and collect any absorbed solution.
  7. In order to purify the product even further, assemble a chromatography column and then place sequentially a disc of sand, alumina (about 1 to 1.5 inches of the height, too much of the height will slow down the process dramatically), and another disc of sand. Pipette the dry solution through the micro-column. Wet the column with dichloromethane (about 0.5mL will be needed), then pass the product mixture, followed by another 2.0mL portion of fresh dichloromethane through the column in order to rinse off your product.
  8. Collect the solution as much as possible in a small, tared Erlenmeyer flask with a boiling stone (The mass of the boiling stone must be included in the tared mass. The reason is that as much as about 2/3 of the sample you collected in the flask could be stuck in the boiling stone). At this point you have purified ethyl laureate dissolved in ether and dichloromethane.
  9. To carry out the final stage of product concentration, place the flask on a hot plate and boil off the solvent. Determine the mass of the product. Obtain the IR spectrum of your product.

**For your report:**

1. Calculate the percent yield.
2. Analyze the IR spectrum, and compare your spectrum to that found in the literature.
3. Predict the <sup>1</sup>H-NMR spectrum for ethyl laureate.