

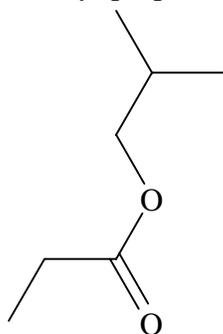
Preparation of 3-Methylbutylacetate (Banana Oil) in the Microwave Oven

Purpose: to prepare 3-methylbutylacetate (also known as isoamyl acetate) using microwave energy

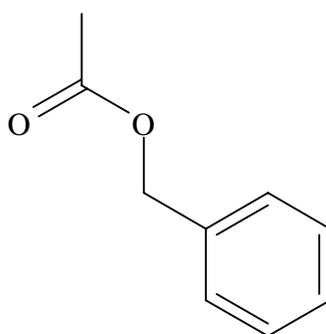
Introduction: What are esters?

Esters are a class of organic compounds with the general formula RCOOR'. Esters have pleasant odors and many of the characteristic flavors and fragrances of flowers and fruits are due to esters. Two examples are provided below:

Isobutyl propionate- rum



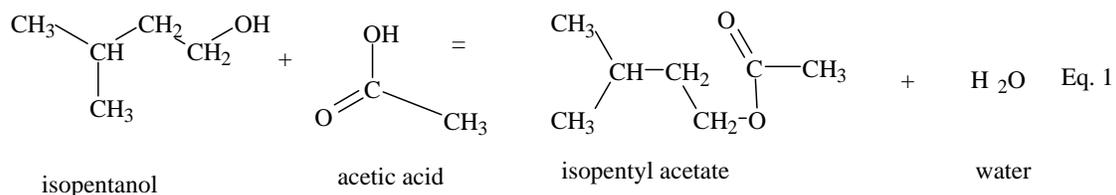
Benzyl acetate- peach



In this lab you will be synthesizing the ester 3-methylbutylacetate, banana oil. There are many routes for synthesizing this compound. Two of them will be described.

You may also be surprised to learn that 3-methylbutylacetate is a honeybee alarm pheromone. When a bee stings an intruder, 3-methylbutylacetate is secreted with the sting venom. The chemical causes aggressive attack on the intruder by other bees. Needless to say wash your hands before leaving the lab!

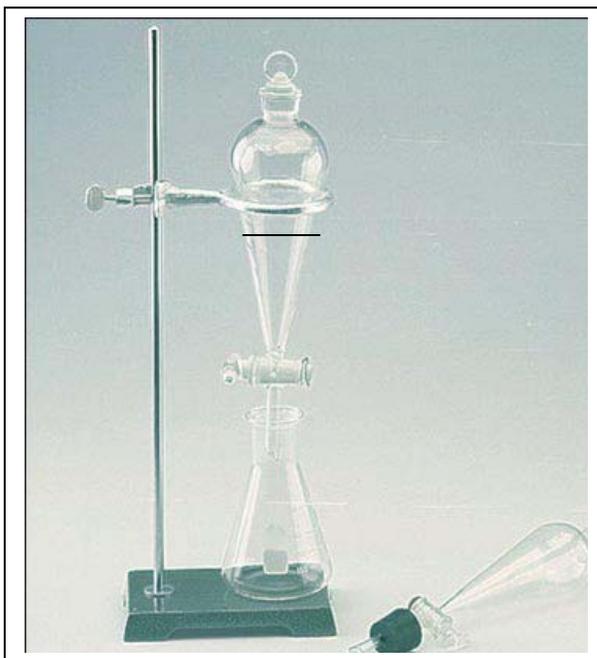
1. Reaction 1: The synthesis of 3-methylbutylacetate via Fisher esterification requires H_2SO_4 as the acid catalyst. The reaction follows:



Using traditional heating, the reaction requires about one hour of reflux to reach equilibrium. For the above reaction, $K_{\text{eq}} = 4.2$ which is not large. At equilibrium the yield is only about 67%. Aqueous potassium carbonate is often added at 0°C to neutralize the acids and stop any reverse reaction, producing potassium acetate and potassium sulfate. Carbon dioxide gas is emitted

2. Purification of 3-methylbutylacetate after Reaction 1 In order to purify the 3-methylbutylacetate, ethyl ether is added to extract the 3-methylbutylacetate. The ethyl ether is insoluble in water, so two phases form – an aqueous and an organic phase - just as oil and water don't mix and form two phases. Potassium acetate and potassium sulfate

remain in the aqueous phase. The 3-methylbutylacetate and unreacted 3-methylbutanol are present in the organic phase. This is shown below:



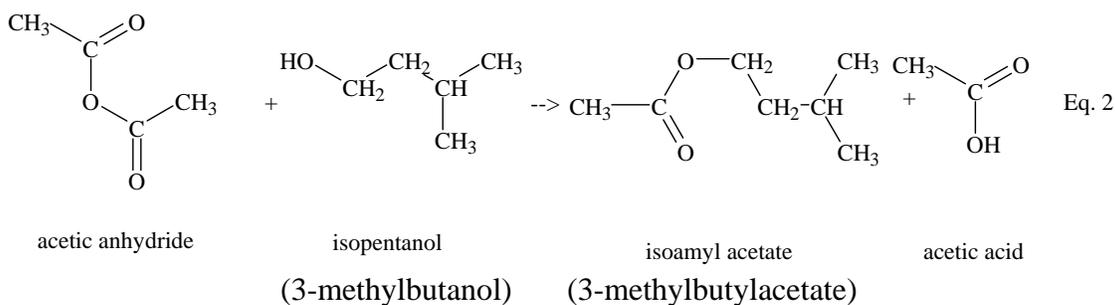
Organic phase – 3-methylbutylacetate,
unreacted 3-methylbutanol

Aqueous phase - water, potassium
acetate, potassium sulfate

The organic phase is separated from the aqueous phase. The 3-methylbutylacetate is then separated from the ether and 3-methylbutanol by fractional distillation. Note that fractional distillation is necessary because the boiling point of 3-methylbutanol and 3-methylbutylacetate are so close. The yield is determined by weighing the 3-methylbutylacetate. IUPAC names are given in parenthesis.

Compound	Boiling Point (C)
Acetic acid (ethanoic acid)	117.9
3-methylbutanol	131.1
3-methylbutylacetate (3-methyl-1-butanolacetate)	142.5
Ethyl ether (1, 1' oxybis-ethane)	34.5

3. Reaction 2: Another synthesis route for 3-methylbutylacetate is the reaction of acetic anhydride with 3-methylbutanol as shown below:



Higher yields are possible because the equilibrium constant is larger. The 3-methylbutylacetate is synthesized using Reaction 2 in this laboratory exercise. The expected yield is 80-90%.

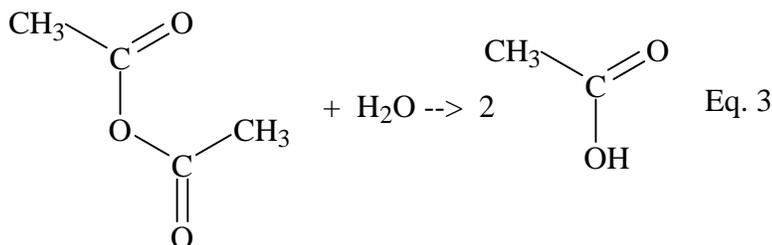
4. Microwave Heating: This lab introduces a new method for 3-methylbutylacetate synthesis using microwave heating. When dipole molecules such as 3-methylbutanol are exposed to an electric field, they align with the field. When the field oscillates the molecules realign over and over. This results in molecular friction, which produces heating. Because this heating occurs within the sample, the reactants experience rapid, uniform heating. In conventional heating, the reaction vessel is heated first, and the temperatures are greatest near the walls. Thus reactions occur more rapidly with microwave heating, and there are fewer side reactions, because there are fewer hot spots that might trigger them. Here with rapid, efficient microwave heating, sulfuric acid is not needed as a catalyst, as it is with conventional heating. In addition, reaction 2 proceeds to completion in a matter of minutes, compared to the hour of reflux required with conventional heating.

In a domestic microwave oven the frequency is 2450 MHz. This means there are 2.450×10^9 oscillations per second. The microwave you are using today is a laboratory model with fiber optic temperature control. It is significantly more expensive than a domestic microwave oven where the user controls the power level and cooking time, but not the power level. Care should always be taken using microwave heating. Some reactions may undergo dangerous runaway heating. It is advisable to start with small samples and short heating times.

5. Using Titration to Determine the Percentage Yield of 3-methylbutylacetate

With microwave heating no sulfuric acid catalyst is required so titration can be used to determine the yield.

Reaction 3. Water will react with acetic anhydride to produce acetic acid:



acetic anhydride water acetic acid

Reaction 4. Sodium hydroxide will react with acetic acid to produce sodium acetate and water as shown below:



acetic acid sodium hydroxide sodium acetate water

From Reaction 3 it can be seen that the maximum number of moles of acetic acid that can be produced is two times the moles of acetic anhydride reactant. From Reaction 2 it can be seen that producing one mole of 3-methylbutylacetate consumes one mole of acetic acid. Thus the moles of 3-methylbutylacetate produced can be determined by titration:

$$\begin{aligned} &\text{Moles 3-methylbutylacetate produced} \\ &= 2X \text{ initial moles of acetic anhydride} - \text{moles of acetic acid in product} \\ &= 2X \text{ initial moles of acetic anhydride} - \text{moles of NaOH to titrate product} \end{aligned} \quad \text{Eq. 5}$$

$$\% \text{ Yield} = \frac{\text{moles 3 - methylbutylacetate produced}}{\text{moles 3 - methylbutanol in feed}} 100\% \quad \text{Eq. 6}$$

One mole of sodium hydroxide reacts with one mole of acetic acid. This will also remove any acetic acid from the organic phase as sodium acetate is soluble in water but not 3-methylbutylacetate. The organic phase contains the product 3-methylbutylacetate and any unreacted 3-methylbutanol. The aqueous phase contains water and sodium acetate.

Example: Suppose 7.5 grams of acetic anhydride is mixed with 6.5 grams of 3-methylbutanol. The sample is placed in the microwave at a power level of 300 Watts. It takes 2 minutes for the sample to reach 90C then it is held at 90C for one minute. The reaction mixture is allowed to cool and is then titrated with 40.0 mL of 2.0M NaOH. Determine the % yield of 3-methylbutylacetate. Useful physical properties are presented below:

Substance	MW (g/mole)	Density (20C)	Volume (mL)
Acetic anhydride	102.09	1.078	7.0
3-methylbutanol	88.15	0.818	8.0

Solution:

Moles acetic anhydride in feed = 7.5 g (1mole/102 g) = 0.074 moles

Moles 3-methylbutanol in feed = 6.5 g (1 mole/88 g) = 0.074 moles

Moles NaOH added = moles acetic acid remaining in reaction vessel = (0.040L)(2.0M) = 0.080 moles

Moles 3-methylbutylacetate produced = 2X initial moles of acetic anhydride - moles of acetic acid in product =

$$\begin{aligned} &2(0.074) - 0.080 = 0.068 \text{ moles 3-methylbutylacetate produced} \\ \% \text{ Yield} &= \frac{\text{moles 3 - methylbutylacetate produced}}{\text{moles 3 - methylbutanol in feed}} 100\% = \frac{0.068}{0.074} 100\% = 92\% \end{aligned}$$

Materials: Acetic anhydride and 3-methylbutanol, 2 M sodium hydroxide solution, microwave reaction vessel HP 500, CEM MARS Microwave oven

Caution: 3-methylbutanol may be harmful by ingestion or inhalation. Acetic anhydride is corrosive. It causes burns to any area of contact, including the eyes and respiratory tract. It is harmful if swallowed or inhaled. It is water reactive. Liquid and vapor are flammable. Work in the hood in a well-ventilated area. Wear appropriate gloves, approved safety glasses, and a lab coat.

Procedure

- 1) Under the hood, mix 7.0 mL (7.5 g) of acetic anhydride with 8.0 mL (6.5 g) of 3-methylbutanol in the microwave reaction vessel provided by the instructor. Label with your name and submit the microwave reaction vessel to the instructor. The instructor will heat your sample in the microwave for 8 minutes at 100C and return it to you.
- 2) Under the hood, pour the products into a 100 mL beaker. Slowly add 25 mL of water. Titrate with 2 M NaOH. Record the exact concentration and the volume of NaOH added at the endpoint.
- 3) Decant off the top layer and carefully smell your product.

Analysis

Compute the number of moles of 3-methylbutylacetate produced and the percent yield. Show your work.

Discussion

1. Discuss the advantages and disadvantage of microwave synthesis. Could microwave heating be used with nonpolar reactants?
2. It has been said that microwave synthesis is an example of “green chemistry” – less energy and materials are used. Give specific examples of this in this experiment.
3. Suggest any improvements to this experiment.
4. What are some possible commercial applications of this type of synthesis?

References

1. http://www.cchem.berkeley.edu/~chem4a/fall2002/laboratory/labmanual/exp7_equilibrium Accessed 10/02/03
2. <http://chemistry.org/education/inchemistry.html> Accessed November, 2003