

Experiment 22

FISCHER ESTERIFICATION

Fig. 22-1



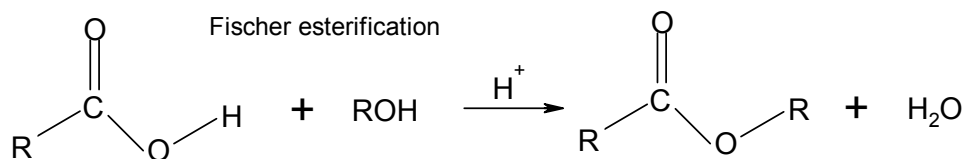
Emil Fischer (see Expt. 27)

Text Topics

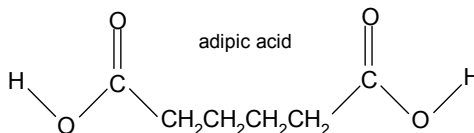
Fischer esterification.

Discussion and Techniques

In another part of this course, you will study some of the elegant research performed by Emil Fischer that elucidated the structures of sugars. You will probably also recognize his name for the projections used in stereochemistry called Fischer projections. In addition, Fischer's name is used for esterifications that involve an acid catalyzed reaction of a carboxylic acid with an alcohol to form an ester.



While most potential chemical reactions either do not go or go essentially all the way to products, Fischer esterifications are unusual in that at equilibrium, there are usually substantial amounts of both reactants and products. To obtain reasonable yields, the position of equilibrium is usually shifted towards the right by either removal of the water as it is formed or by use of an excess of the lower priced reagent (usually the alcohol). Today, you will attempt to esterify adipic acid. Because it is a dicarboxylic acid, it is possible that the esterification could yield the mono ester or the diester. Use of H-nmr should enable you to distinguish between these options.



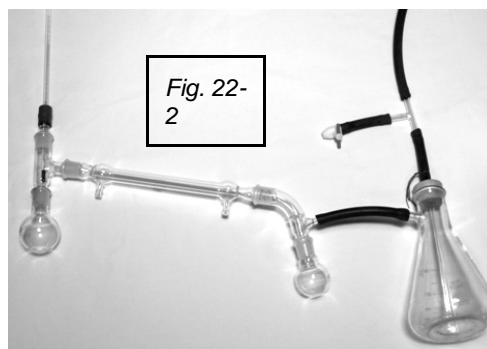
Both possible products of the reaction, the mono ethyl ester of adipic acid and diethyl adipate, have boiling points considerably above 200°C. As discussed in **Experiment 11**, many organic compounds have a tendency to decompose at high temperatures. For compounds that boil above 200°C, distillations are commonly performed at reduced pressure to lower the boiling point. Please refer to the discussion of vacuum distillation in **Experiment 11** before proceeding.

Procedure

Fischer esterification and a vacuum distillation. Set up a simple distillation apparatus with a 100 mL flask containing a magnetic stirring bar mounted in a heating mantle on top of a magnetic stirring device. Add 7.5 g of adipic acid, 20 mL of absolute ethanol, 7.5 mL of toluene and 2 drops of concentrated (18 M) sulfuric acid to the flask and start the stirrer and condenser water. Distill at atmospheric pressure until the temperature reaches about 78°C. Keep the boiling pot with its contents and the distillation apparatus in place.

The distillate should be an azeotrope containing ethanol, water and toluene. Add 10 g of potassium carbonate to the distillate and shake for several minutes. Decant the dried distillate back into the distilling flask being sure not to transfer any potassium carbonate into the flask. Because of the equilibrium issue associated with Fischer esterifications, removal of the water moves the position of equilibrium to the right and more product should be obtained. Distill again until the temperature reaches about 111°C. The product which boils above 200°C should still be in the distilling flask. Do not discard the liquid in the distilling flask but you can now properly dispose of the distillate.

Using the same distillation apparatus, attach a vacuum hose connected via a trap to an aspirator to the receiver adapter. Attach a clean and dry receiver flask. Very lightly grease all the joints and make sure the stirrer and water are on. Always establish a vacuum and have the instructor check the setup before turning on the heating mantle. At water aspirator pressure (about 18 mm), the product should distill in the mid 130°C's. Record the temperature at which you collect distillate and stop the distillation when there is still a small amount of liquid in the distilling flask.



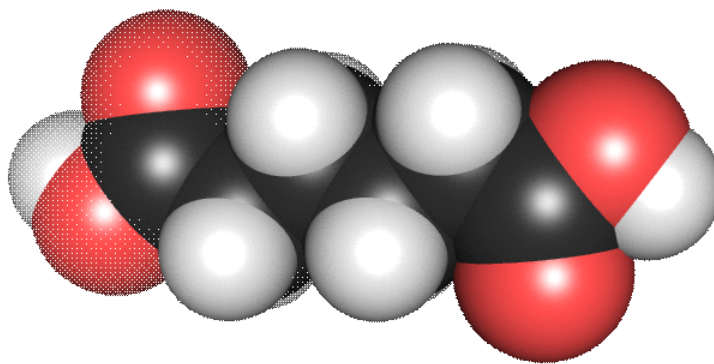
Run the ir and nmr spectra (^1H and ^{13}C if available) and compare the spectra to those on the NIMC and Aldrich sites. [go to: http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi?lang=eng and <http://www.sigmaaldrich.com> - find the compound of interest and then select *Safety and Documentation*]

Reference

MacKenzie, Charles, *Experimental Organic Chemistry*, Prentice-Hall, **1971**, 209-214.

For additional esterifications that lead to observations about odor as a function of structure, please see: Epstein, J. L.; Castaldi, M.; Patel, G.; Telidecki, P.; Karakkatt, K. *J. Chem. Educ.*, **2015**, 92, 954-957.

Fig. 22-3
space filling model
of adipic acid



Prelaboratory Preparation - *Experiment 22*

First, be sure to list all the goals of the experiment. Based on the general reaction for esterification, write the reactions for formation of the mono and diethyl esters. Prepare a table for insertion of useful and observed data such as molecular mass, mass, moles, melting points and percent yields and recoveries for starting materials and both possible products. Predict what the ^1H -nmr and ^{13}C -nmr spectra should look like for the diethyl adipate and the monoethyl ester of adipic acid. Describe how you will use nmr to distinguish between the two most probable products. Could it be used to distinguish between the two most probable products? Locate this type of reaction on the *Reaction-Map of Organic Chemistry* in **Appendix C** and include the reaction number in your report. For applications and information on dialkyladipates, see:

<http://chem.sis.nlm.nih.gov/chemidplus/>
<http://www.epa.gov/safewater/pdfs/factsheets/soc/adipate.pdf>
<http://www.inchem.org/documents/iarc/vol77/77-02.html>
<http://www.plasticisers.org/plasticisers/specialty-plasticisers>

Observations

Report all relevant observations including boiling points and spectra.

Conclusions

This section should include the following:

1. Were the goals of the experiment achieved? Explain your answer.
2. What was the identity of your product and was it one of the two predicted possibilities? Explain your answer. Is it possible the product is a mixture of the mono and diethyl esters.
3. Use the observed reduced pressure boiling point and the equation in **Experiment 11** to calculate the atmospheric pressure boiling point of the product. Compare this value to the literature value for the boiling point of the product. Comment on the accuracy of the equation.
4. How could the percent yield and recoveries have been improved?
5. Evaluate the usefulness of vacuum distillations. Comment on when a vacuum distillation should be used (e.g., size of sample, boiling point of sample, etc.)

