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Esterification, Purification and Identification of Cinnamic Acid Esters

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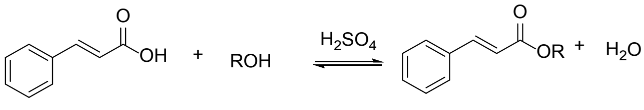
Abstract Fisher esterification is a topic covered in most second semester undergraduate organic chemistry courses. This article outlines the synthesis of several esters produced via Fisher esterification of *trans*-cinnamic acid and various alcohols. The esters are purified using column chromatography, a separation technique typically introduced in the first semester. The products are characterized using Nuclear Magnetic Resonance (NMR) spectroscopy. Based on the identification of the esters produced, students determine the unknown starting alcohol and write the correct mechanism of the reaction. This laboratory project was successfully carried out with second semester organic chemistry laboratory students.

Keywords Fisher esterification, Column chromatography, Nuclear Magnetic Resonance spectroscopy

1. Introduction

Most organic chemistry laboratory manuals include esterification experiments [1-4]. Fischer esterification is an organic chemistry reaction that is taught in lecture and often carried out in the organic chemistry laboratory. Typically students start with a known acid and known alcohol and produce a pleasant-smelling ester, that is considered to be the unknown [5-8] In this undergraduate lab, students carry out a Fisher esterification synthesis with cinnamic acid and one of multiple simple alcohols, such as ethanol, propanol, butanol, *iso*-butanol, hexanol. All students work with the same acid, *trans*- cinnamic acid, but are given different alcohols (ROH) in the presence of sulphuric acid as the catalyst (equation 1). The students are not only identifying what the "unknown ester" produced, but they are also determining which alcohol was used to synthesise this ester based on knowledge of the mechanism, as well as NMR interpretation of the ester.



Equation 1. Esterification reaction of cinnamic acid with unknown alcohols

This experiment takes two laboratory periods to complete. By completing this experiment, students will learn and reinforce prior knowledge of a variety of techniques used in organic chemistry laboratory, including reflux, liquid-liquid extraction, thin layer chromatography, and column chromatography. Student will also delve deeper into spectral interpretation using nuclear magnetic resonance (NMR) spectroscopy. They use standard ^{1}H-NMR and ^{13}C-NMR spectra, but they will also use Distortionless Enhancement by Polarization Transfer (DEPT). The DEPT spectral method identifies what type of carbon is represented in the ^{13}C spectra: R-CH_3, R_2-CH_2, R_3-CH, or C-R_4. This method is often left out of the undergraduate curriculum or barely mentioned.

Students use ^{13}C-NMR, DEPT 135 and DEPT 90 to identify all types of carbons in the compound. The ^{13}C-NMR spectra shows positive phase signals (peaks pointing up) for all carbons in the sample and is used for an overlay with the DEPT spectra. The DEPT 135 and DEPT 90 are used in conjunction with the ^{13}C-NMR to identify each carbon as a primary, secondary, tertiary, or quaternary carbon (R-CH_3, R_2-CH_2, R_3-CH, R_4-C). In both DEPT 90 and 135, the quaternary carbons are not observed, thus are easily identified in the ^{13}C-NMR spectra. The DEPT 135 spectra identifies all carbons that have hydrogen attached. Carbons with an odd number of hydrogens can be distinguished from carbons with an even number of hydrogens by the phase of the signals. Typically, the carbons attached to an odd number of hydrogens, R-CH_3 and R_3-CH, have a positive phase (peaks pointing up). The carbons attached to an even number of hydrogens, R_2-CH_2, have a negative phase (peaks pointing down). The phases of the signals in the DEPT 135 may be reversed in compounds that have long chains of R_2-CH_2. This is easily determined by several ways, but for this experiment, students can look at the tertiary aromatic ring

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carbons (R_3-CH) and see which direction the signals are and they can use the DEPT 90 spectra. The DEPT 90 shows the tertiary carbons (R_3-CH) only with positive phase signals. No other carbons will be present. Using all these types of NMR's students can identify all types of carbons present in the ester. For example, the overlay of ^{13}C-NMR, DEPT 90 and DEPT 135 for ethyl cinnamate is shown in Figure 1.

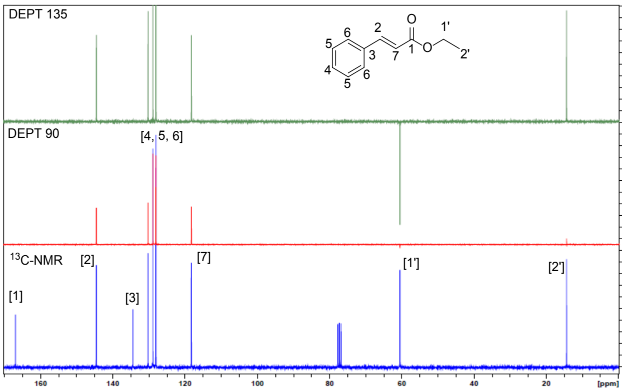

Figure 1. Overlay of ^{13}C-NMR, DEPT 90 and DEPT 135 of ethyl cinnamate from bottom to top

There are nine peaks in the ^{13}C-NMR, which represent all types of carbon atoms in the ethyl cinnamate. The DEPT 90 and DEPT 135 overlay do not show C-R_4 carbons, C-1 and C-3. The DEPT 90 overlay shows only R-CH carbons, C-2, C-4, C-5, C-6 and C-7. According to DEPT 135 C-1' is R-CH_2 with a negative signal and C-2' is a R-CH_3 carbon with a positive signal.

2. Method

Students typically work in pairs, but this experiment is suited for individuals as well. During the first laboratory session, students are assigned an unknown alcohol and all are given the same acid, *trans*-cinnamic acid as shown in Figure 2. The esterification reaction is carried out in the presence of sulfuric acid as describe in the procedure provided in the supplementary materials. The work-up removes most of the unreacted acids and alcohol, but further purification is used the following lab period.

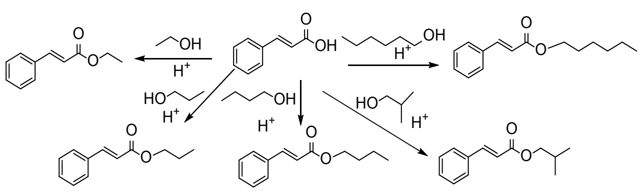

Figure 2. *Trans*-cinnamic acid with different types of alcohols

During the second laboratory period, students use column chromatography to purify the ester from any unreacted acid and alcohols. During this step, students see the usefulness of TLC in organic chemistry and their prior knowledge of TLC with the column chromatography is reinforced. Using ^{1}H-NMR, ^{13}C-NMR, DEPT 135, and DEPT 90, students identify the ester formed. Students are also given these spectra for their starting material, *trans*-cinnamic acid to aid in the identification of the ester. Based on the identity of the ester, students determine the unknown alcohol they started with at the beginning of the synthesis.

3. Conclusions

This lab was successfully carried out in second semester undergraduate laboratory section with 22 students at Austin Peay State University. The students seemed to enjoy discovering the unknown esters using new spectroscopy techniques. This lab is more in-depth than the general verification lab. Not only do students identify the unknown ester produced, but they have to identify the starting alcohol as well. For future work, we would like to partner with area community colleges, where the students do not have access to the instrumentation, to see if student engagement increases and if there is a shift in attitude toward the lab in general.

ACKNOWLEDGEMENTS

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Supporting Information

Student's handout and PDF Document: "*all NMRs*" available as supplementary information.

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