

Use of ^{13}C NMR in a Dehydration Experiment for Organic Chemistry

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Abstract: An experiment for the undergraduate organic laboratory has been developed that incorporates NMR spectroscopy early in the academic year. A series of cycloalkanols are given to the students as unknowns. These are dehydrated to the corresponding alkenes, and the unknowns are then identified by ^{13}C NMR and boiling point.

Introduction

During the first half of the typical two-semester undergraduate organic chemistry laboratory, there remains a need to learn basic laboratory techniques and explore concrete examples of reactions that the students are learning in lecture. An increasing number of experiments also incorporate the use of NMR, although most apply to “second-semester” reactions [1–7]. To this end, the experiment presented here includes running a simple reaction on an unknown, isolation of the product, and identification by ^{13}C NMR spectroscopy. The dehydration of cyclohexanol is carried out in many first-semester organic chemistry laboratories, incorporating important techniques such as distillation, extraction, and yield calculation [8, 9]. This classic experiment is modified here as the basis for the introduction of ^{13}C NMR spectroscopy. In this version of the experiment the students are given four cyclic alcohols to choose from. They are given the four possible structures, but don't know the identity of their particular sample. Dehydration of the alcohol provides an alkene, which is isolated and distilled. The starting alcohol is then identified by both boiling point and ^{13}C NMR of the alkene product.

Implementation and Discussion

The four alcohols used in the experiment have been chosen so that some of the alkene products are symmetrical and some are not. The alcohols used are cyclopentanol, 1-methylcyclopentanol, cyclohexanol, and 1-methylcyclohexanol (Table 1). These were chosen due to commercial availability and boiling point of the resulting alkene. The alcohols are labeled A, B, C, and D, and the students may choose any sample. The sample is weighed out, and dehydrated by heating with aqueous sulfuric acid. After extraction of the crude alkene, the product is distilled and the students acquire a ^{13}C NMR spectrum. One of the basic concepts that students need to learn from ^{13}C NMR is the idea of the chemical equivalence of carbons in order to decide how many signals should be observed in a spectrum. Because two of the possible alkenes have a plane of symmetry and exhibit only three signals, students can narrow down their possibilities based solely on the number of signals in the spectrum. Differences in boiling point of the alkenes allow confirmation of their assignment. As expected, E1 elimination of 1-methylcyclohexanol and 1-methylcyclohexanol afford only the

more highly substituted endocyclic alkenes and none of the exocyclic alkenes are observed [10].

Experimental Section

Preliminary Remarks. The experimental procedure has been developed with the assumption that the students have had one year of a general chemistry laboratory and that they have been introduced to distillation and liquid/liquid extraction procedures.

Safety. The students should wear gloves and safety goggles during the experiment. No flames are permitted in the laboratory. The alcohols are irritants and should be used in a hood or well-ventilated area. Chloroform is carcinogenic and should be handled in a hood or well-ventilated area. The products should be disposed of in an organic-waste-disposal container.

Semi-Microscale Procedure [11]. A sample of the alcohol (2 g) is weighed into a 10-ml distillation flask and 0.3 ml of water, 5 drops of concentrated sulfuric acid, and a boiling chip are added. The flask is fitted with a distillation head and then heated to reflux on a sand bath for 45 min taking care not to allow any material to distill over during this time. After 45 min., the temperature is raised and the sample is distilled. The distillate is collected in a small, ice-cooled, Erlenmeyer flask. Approximately 2 ml of saturated aqueous sodium chloride is then added to the distillate; the layers are mixed vigorously and allowed to separate. The organic layer is transferred to a small Erlenmeyer flask and calcium chloride pellets are added to remove excess water as well as unreacted alcohol. The organic layer is then transferred to a clean, dry 10-ml distillation flask. A boiling chip is added, the distillation head with fractionating column is attached, and the crude alkene is distilled to afford the pure product. The collection vial (with cap) should be tared, and must be ice-cooled during collection. As some of the alkenes are volatile, the vial should be capped and weighed immediately after completion of the distillation in order to avoid loss of material. Students may either run their own ^{13}C NMR spectra of the product or use spectra supplied to them by the instructor. All of the spectra included in the supporting material were obtained by students. Analysis of the ^{13}C NMR spectrum, combined with the observed boiling points during distillation allows assignment of the correct structure to their alkene product and hence their starting alcohol.

For this particular experiment, we used four different cycloalkanols: cyclohexanol [108-93-0], cyclopentanol [96-41-3], 1-methylcyclohexanol [590-67-0], and 1-methylcyclopentanol [1462-03-9]. Two of the alkene products, cyclohexene and cyclopentene, have a plane of symmetry and give three signals in the ^{13}C NMR and 1-methylcyclopentene and 1-methylcyclohexene give six and seven signals, respectively. The ^{13}C -NMR (CHCl_3 , 300MHz) data is as follows: cyclohexene (^{13}C , δ) 126.3, 24.2, 21.7; cyclopentene (^{13}C , δ) 129.7, 31.4, 21.8; methylcyclohexene (^{13}C , δ) 133.0, 120.1, 29.1,

Table 1. Structures of alcohols and alkene products









Alcohol	Alkene	Plane of symmetry	number of signals
		yes	3
		yes	3
		no	7
		no	6

Table 2. Data from Five Laboratory Sections (102 students)

alkene	Cyclohexene	Cyclopentene	1-methylcyclohexene	1-methylcyclopentene
b.p. (°C)	83	44	110	72
No. of NMR signals	3	3	7	6
% correct ^a (48 students)	90	50	100	67
% correct ^b (54 students)	68	40	52	40

^aStudents reporting b.p. within 10 °C of literature value. ^bStudents reporting b.p. varying more than 10° from literature value.

24.3, 22.9, 22.0, 21.4; methylcyclopentene (13C, δ) 139.4, 123.3, 35.9, 31.7, 22.7, 15.6

Results and Discussion

We have collected data from five different laboratory sections with an average of twenty students in each. Table 2 summarizes data from the five laboratories including the alkene boiling point, the NMR data, and the percent of students correctly assigning the structures.

Because all the students had access to the ¹³C NMR data, the main variable in their data is the boiling point of the alkene. The boiling point is obtained from their fractional distillation. Technical ability varies greatly from student to student, and we grouped them into those reporting a b.p. within 10 °C of the literature value and those reporting a b.p. outside that range. Those with an incorrect boiling point were, on average, 31% more likely to assign their structure incorrectly. Perhaps this is an illustration of the old saying "You can lead a

horse to water, but you can't make them drink." Although they had access to the NMR data, some students preferred to rely on their observed boiling points, which were not necessarily correct.

The value of this experiment lies in the combination of a number of experimental techniques and in the early use of NMR spectroscopy in the laboratory. For our students, this is only their second exposure to both liquid/liquid extraction and distillation, so it reinforces those techniques. Also, it allows the introduction of NMR with only a rudimentary understanding of spectral interpretation. They need only to understand the concept that each chemically unique carbon will give one signal, without needing to have mastered interpretation of splitting patterns that they will observe later with ¹H NMR.

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Supporting Materials. Copies of all ¹³C NMR spectra used in this experiment are available in a Zip file (<http://dx.doi.org/10.1333/s00897061084a>). All spectra were run in chloroform using no-D technology and show one signal at δ 76.3 for chloroform. NMR spectra were run on a 300-MHz JEOL EC-X NMR spectrometer.

References and Notes

- Feist, P. L. *J. Chem. Educ.* **2004**, *81*, 109–110.
- Crouch, R. D.; Holden, M. S. *J. Chem. Educ.* **2002**, *79*, 477–478.
- Clavier, J. W.; Fievet, J.; Geisler, V. *Chem. Educator* **2000**, *5*, 64–66; DOI .
- Reeves, P. C.; Chaney, C. P. *J. Chem. Educ.* **1998**, *75*, 1006–1007.
- Branz, S. E. *J. Chem. Educ.* **1985**, *62*, 899–900.
- Branz, S. E.; Miele, R. G.; Okuda, R. K.; Straus, D. A. *J. Chem. Educ.* **1995**, *72*, 659–661.
- Blankespoor, R. L.; Piers, K. *J. Chem. Educ.* **1991**, *68*, 693–695.
- Williamson, K. L. *Macroscale and Microscale Organic Experiments*, 2nd ed.; D. C. Heath and Co.: Boston, 1994.
- Campbell, B. N.; Ali, M. M. *Organic Chemistry Experiments, Microscale and Semi-Microscale*; Brooks/Cole: Monterey, CA, 1994.
- Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry, Part A: Structure and Mechanisms*, 4th ed.; Kluwer Academic: New York, 2000.
- Dunlap, N. K.; Friedli, A.; Kline, P. F. *Organic Odyssey I: A Laboratory Manual for Chem. 3010*; MTSU: Murfreesboro, TN, 2005.