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The Discovery-Oriented Approach to Organic Chemistry. 2. Selectivity in Alcohol Oxidation. An Exercise in ^1H NMR Spectroscopy for Sophomore Organic Laboratories

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The Discovery-Oriented Approach to Organic Chemistry

2. Selectivity in Alcohol Oxidation

An Exercise in ^1H NMR Spectroscopy for Sophomore Organic Laboratories

Steven R. Shadwick and Ram S. Mohan

The majority of the experiments involving oxidation of alcohols found in textbooks are of "cookbook" variety and do little to sustain student interest and enthusiasm. We have developed a simple oxidation experiment that presents the student with a puzzle and also illustrates the important concept of selectivity in organic synthesis. It has been reported that sodium hypochlorite in acetic acid solution selectively oxidizes secondary alcohols to ketones in the presence of primary alcohols (1). Oxidation of secondary alcohols using sodium hypochlorite solution has also been adapted as a lab experiment. However, these laboratory experiments involve either large quantities of bleach or time-consuming steam distillation and column chromatography (2). We wish to report the oxidation of a mixture of 1-heptanol and 2-heptanol using commercial swimming pool chlorine on a semi-microscale in an experiment that can be completed in less than two hours.

Discussion

Students are told that the possible products from 1-heptanol are heptanal and heptanoic acid and the possible product from 2-heptanol is 2-heptanone. The ^1H NMR spectrum of a 1:1 mixture of 1-heptanol and 2-heptanol is compared with the ^1H NMR spectrum of the product mixture to determine the selectivity exhibited by the reagent (Fig. 1). It has been reported that primary alcohols react slowly to give dimeric ester as a product. In this case, ^1H NMR analysis of the crude product showed 7% of an impurity that was consistent with *n*-heptyl heptanoate. This impurity is conveniently removed by simple distillation of the product mixture.

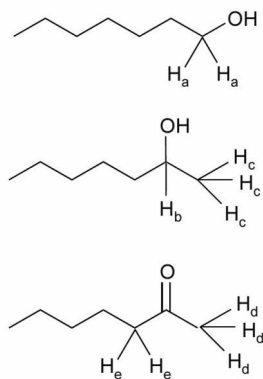


Figure 1. ^1H NMR data: δ H_a 3.62 (t), H_b 3.77 (m), H_c 1.16 (d), H_d 2.11 (s), H_e 2.39 (t).

Safety

CAUTION: Contact with swimming pool chlorine should be avoided. It is suggested that the experiment *not* be performed with a mixture of 1-hexanol and 2-hexanol because inhalation of 2-hexanone, the product of oxidation, is reported to cause peripheral neuropathy (3). Diethyl ether is highly flammable and hence no flames should be present in the lab during the course of this experiment.

Procedure

Swimming pool chlorine (10.6 g, 8.8 mL, 13.8 mmol) was added dropwise over 15 minutes from a separatory funnel to a well-stirred solution of 1-heptanol (1.0 g, 8.6 mmol) and 2-heptanol (1.0 g, 8.6 mmol) in glacial acetic acid (5 mL). The resulting solution was stirred for another 15 min and excess hypochlorite was destroyed by addition of 15 mL of 10% aq NaHSO_3 . The mixture was extracted with diethyl ether (25 mL) and the organic layer was washed with 10% aq Na_2CO_3 ($3 \times 15 \text{ mL}$)² and saturated aq NaCl (15 mL). The organic layer was dried (Na_2SO_4) and the solvent was removed by placing the flask in a warm (50 $^\circ\text{C}$) water bath. The residue was distilled using a microscale distillation apparatus and distillate in the range 155–78 $^\circ\text{C}$ was collected in a preweighed, ice-cooled vial (typically 1.5–1.6 g, 75–80%) and analyzed by ^1H NMR spectroscopy.³

Acknowledgments

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Notes

^WSupplementary materials for this article are available on JCE Online at <http://jchemed.chem.wisc.edu/Journal/issues/1999/Aug/abs1121.html>.

1. The concentration of swimming pool chlorine drops with time and hence it should be used within a week after titration.

2. The ether layer was washed until the aqueous layer was basic to litmus. Considerable effervescence occurs and so the funnel should be vented frequently.

3. ^{13}C NMR spectroscopy analysis of the pot residue from distillation clearly shows the presence of an ester carbonyl (δ 174.1); ^1H NMR δ 4.04 (t, COOCH_2), 2.27 (t, CH_2CO). We found GC analysis to be impractical, since even at 250 $^\circ\text{C}$ the ester has a retention time of ca. 25 min. Also, 2-heptanol and 2-heptanone have identical retention

Experimental Section

General

^1H NMR spectra were recorded on a JEOL NMR spectrometer at 270 MHz in CDCl_3 as the solvent. Swimming pool chlorine was purchased from a local pool supplies store and titrated iodometrically before use. It was found to contain 9.7% NaOCl by weight.¹

times on a packed column GC. The products of oxidation do not stain well with iodine or any TLC spray reagents.

Literature Cited

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