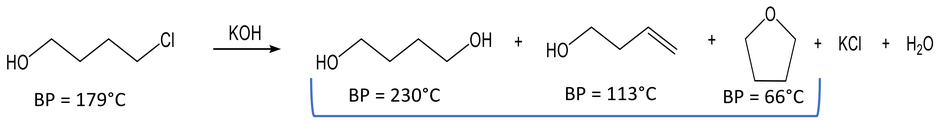
Reaction of hydroxide with 4-chloro-1-butanol: Characterization of products for the development of an undergraduate organic chemistry laboratory experiment

Duy Le and Christopher Gulgas* - Chemistry Department, University of Cincinnati Blue Ash College, Cincinnati, OH 45236

Introduction

Classroom theory should be reinforced in the laboratory as students predict the results of reactions and use data to verify their predictions. Several reactions have numerous plausible outcomes that require students to use critical thinking in making their predictions.[1] This project seeks to develop a procedure for carrying out one such reaction and determine methods to analyze the results in the design of a future undergraduate laboratory experiment. The goals of this project were (1) predict all possible products (2) design and customize the reaction between 4-chlorobutan-1-ol and potassium hydroxide and (3) characterize the product mixture by using infrared spectroscopy (IR), gas chromatography (GC) and nuclear magnetic resonance (NMR). Ultimately, the reaction was successful to produce an intramolecular nucleophilic substitution product – tetrahydrofuran (THF)

Reaction

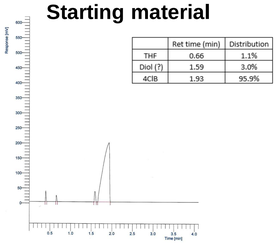


Possible products

Gas Chromatography (GC)

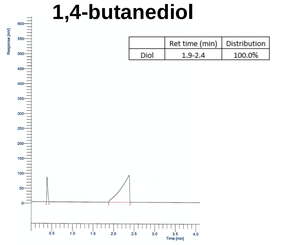
Starting material

	Ret time (min)	Distribution
THF	0.66	1.1%
Diol (?)	1.59	3.0%
4ClB	1.93	95.9%



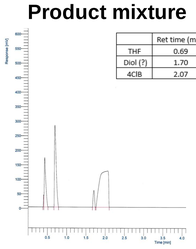
1,4-butanediol

	Ret time (min)	Distribution
Diol	1.9-2.4	100.0%



Product mixture

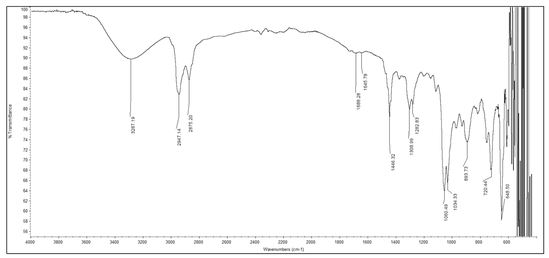
	Ret time (min)	Distribution
THF	0.69	29.0%
Diol (?)	1.70	4.9%
4ClB	2.07	66.1%



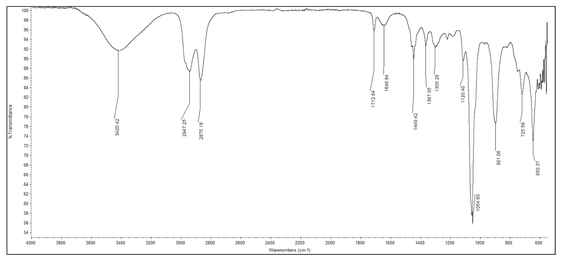
GC was used to analyze the starting materials and each reaction product mixture. The starting material is contaminated with THF and HCl due to the unstable nature of the haloalcohol. The behavior of the haloalcohol and the 1,4-butanediol product was inconsistent and identification was not possible using GC alone. However, analysis of the reaction product mixture shows increased production of THF. Ethanol is used to clean the syringe and appears as the first peak in each spectrum. The alkene product is not observed in the GC.

Infrared Spectroscopy (IR)

Starting material



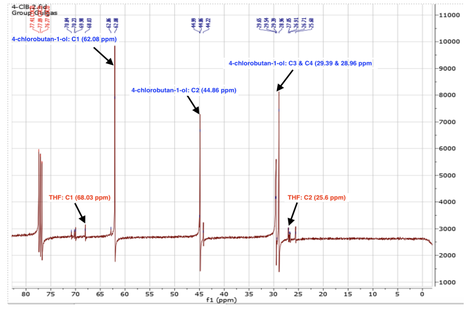
Reaction product mixture



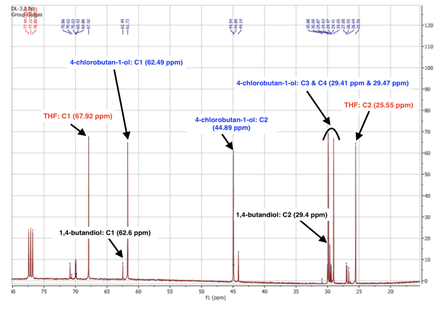
IR data indicated that no alkene product was formed through elimination in this reaction due to the lack of a signal in the 1600-1680 cm^{-1} range. Otherwise, O-H bonds (3200-3400 cm^{-1}), sp^3 C-H bonds (2900-3000 cm^{-1}), C-O bonds (1060 cm^{-1}) and C-Cl bonds (650 cm^{-1}) were observed in these spectra. The product mixture spectrum is consistent with an incomplete reaction, where the presence of THF is not conclusively observed.

^{13}C Nuclear Magnetic Resonance Spectroscopy (^{13}C NMR)

Starting material

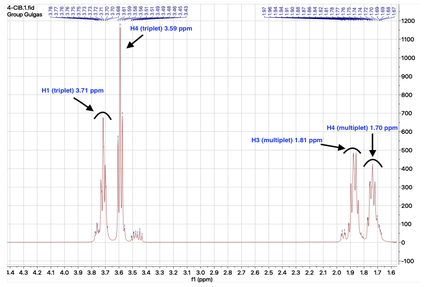


Reaction product mixture

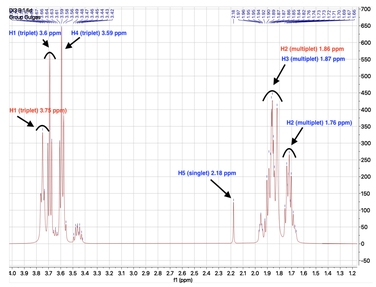


The starting material contains 4-chlorobutan-1-ol (~85%) and THF (~15%). The carbons for each molecule are labeled in the above spectrum. There are other small unidentified impurities present. The product data showed the amount of THF increasing significantly and a small amount of 1,4-butanediol is also observed. No alkene product is observed. However, it is clear the starting haloalcohol is still present in large amounts, and the reaction was incomplete.

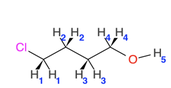
^{1}H Nuclear Magnetic Resonance Spectroscopy (^{1}H NMR)



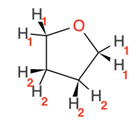
Starting material



Reaction product mixture



4-chlorobutan-1-ol



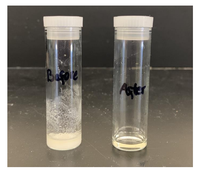
Tetrahydrofuran (THF)

^{1}H-NMR data confirms what was observed in the ^{13}C-NMR experiments. The amount of THF relative to the starting material has increased significantly with no other signals appearing due to other potential products in a measurable fashion. Resonances due to the 1,4-diol may be covered by larger signals, but again the alkene product is clearly not observed, with no signals appearing between 4.5-6.5 ppm.

Undergraduate Experiment Design and Future Work

This work has shown that the reaction of 4-chlorobutan-1-ol with hydroxide is a good candidate for an undergraduate organic lab experiment - utilizing GC, IR, and NMR methods for data analysis. Although work is ongoing, the major product appears to be the intramolecular substitution product (THF). Students will be asked to predict the major product of the reaction before carrying it out and analysing the result in lab. Future work involves heating the reaction to drive it towards completion and developing conditions that may produce significant quantities of the 1,4-diol product. These results will be used to fine tune the experimental design to be incorporated into the organic laboratory curriculum.

Experimental set-up



Reaction work-up

Acknowledgement

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(1) Lieber, L. Graulich, N. "Thinking in alternatives – A task design for challenging students' problem-solving approaches in organic chemistry" *J. Chem. Educ. 97*, **2020**, 3731-3738.