4-17-2024

Effect of Halide in Ammonium Salts in the Addition of Benzoic Acid to Styrene Oxide

Annalyse Gilmore
Pittsburg State University

Jeffrey Horinek
Pittsburg State University

Lindsay Pruett
Pittsburg State University

Ryn Sprague
Pittsburg State University

Tristian Stevens
Pittsburg State University

See next page for additional authors

Authors

Annalyse Gilmore, Jeffrey Horinek, Lindsay Pruett, Ryn Sprague, Tristian Stevens, Kelsie Tucker, and Charles J. Neef

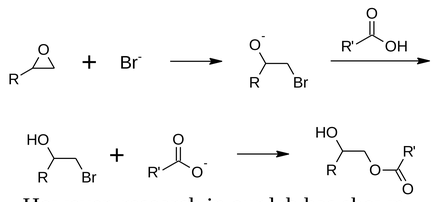
Effect of halide in ammonium salts in the addition of benzoic acid to styrene oxide

Annalyse Gilmore, Jeffrey Horinek, Lindsay Pruett, Ryn Sprague, Tristian Stevens, Kelsie Tucker & Charles J. Neef*

Chemistry Department, Pittsburg State University, Pittsburg, KS
cneef@pittstate.edu, 620-235-4494

Introduction

- Addition reactions to epoxides are an important and well studied class of reactions.
- The use of TBAB as a catalyst for the addition of, phenols[1], carboxylic acids[2],and thiols[3] has been reported.
- The proposed mechanism for the addition of carboxylic acids is shown below.[3]

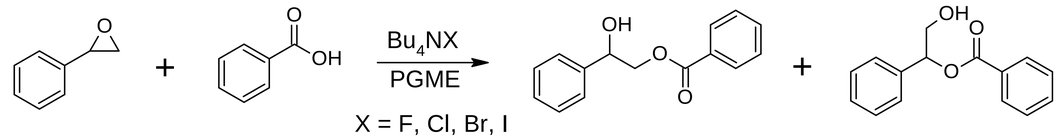


- However, research in our lab has shown that TBAF gives faster reaction times with phthalimide as the nucleophile.
- From the results with phthalimide, we were interested in reinvestigating the reaction of a carboxylic acid with an epoxide..

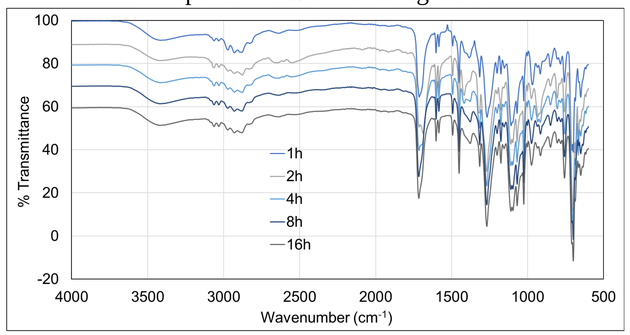
Experimental

- All materials were commercially available and used as received.
- To a round bottom flask was added benzoic acid, styrene oxide, ammonium salt (1 mol% of benzoic acid), and PGME. The reaction was then heated at reflux.
- Aliquots were removed at 1, 2, 4, 8, and 16 h for analysis by IR spectroscopy.

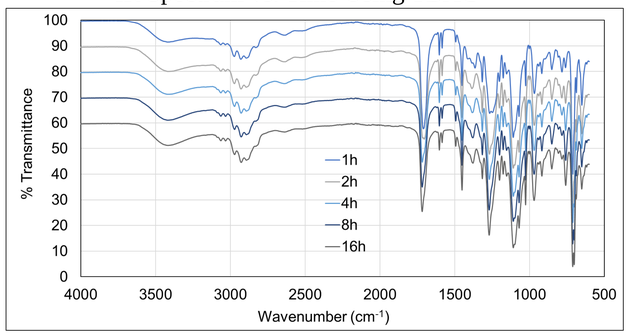
Results



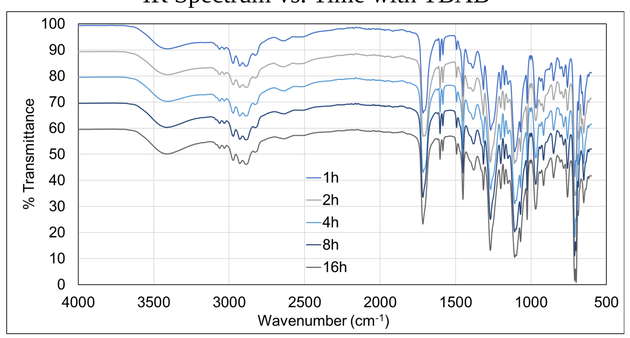
IR Spectrum vs. Time Using TBAF



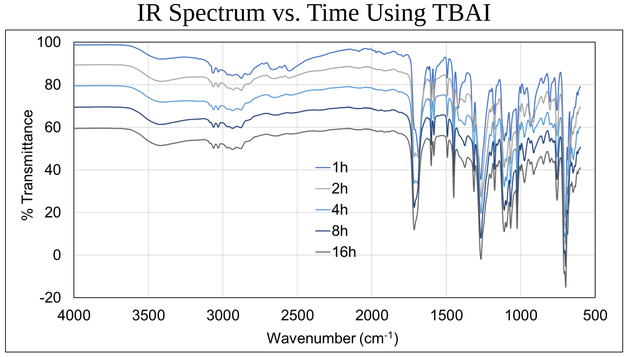
IR Spectrum vs. Time Using TBAC



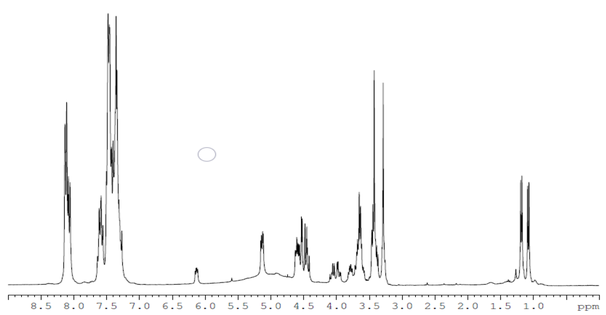
IR Spectrum vs. Time with TBAB



IR Spectrum vs. Time Using TBAI



H-NMR Spectrum of Products



Conclusion & Future Directions

- Ratio of products was near 3:1 for all catalyst and differed from the 1:1 product ratio with phthalimide.
- Significantly less catalyst (1%) was needed for benzoic acid compared to phthalimide (6%).
- Catalyst with fluoride or chloride seemed to show slightly faster reaction rates than bromide or iodide.
- Reaction mechanism does not seem to follow published mechanism.
- Future work will use phenyl glycidyl ether to determine the effect of catalyst with an epoxide that is more aliphatic.
- In addition, NMR studies will be performed to more accurately determine the effect of catalyst.

References

1. Han-Ting Chang and Jean M. J. Fre´chet, Proton-Transfer Polymerization: A New Approach to Hyperbranched Polymers, *J. Am. Chem. Soc.* 1999, 121, 2313-2314
2. Caiguo Gong and Jean M. J. Fre´chet, Proton Transfer Polymerization in the Preparation of Hyperbranched Polyesters with Epoxide Chain-Ends and Internal Hydroxyl Functionalities, *Macromolecules* 2000, 33, 4997-4999
3. Ikhlas Gadwal, Selmar Binder, Mihaiela C. Stuparu, and Anzar Khan, Dual-Reactive Hyperbranched Polymer Synthesis through Proton Transfer Polymerization of Thiol and Epoxide Groups, *Macromolecules* 2014, 47, 5070−5080

Acknowledgements

We would like to thank Pittsburg State University for support of this project.