Vita

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Universities Attended:

University of New Brunswick (2021)
Bachelor of Science

University of New Brunswick (2022)
Masters of Science

Toward an Unsubstituted Pyridinium Methylide

UNIVERSITY OF NEW BRUNSWICK

THESIS DEFENCE AND EXAMINATION

in Partial Fulfillment

of the Requirement for the Degree of
Master of Science

by

Peter L. Fox

in the Department of Chemistry

U.N.B., Fredericton, N.B.

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via MS TEAMS

Examining Committee

Dr. Adam C. Dyker	Supervisor
Dr. Andreas Decken	Internal Examiner
Dr. David Keighley	Int-Ext Examiner
Dr. Gilles Villemure	Chair of Oral Examination

Abstract

Pyridinium ylides are useful tools in a wide range of synthetic applications due to their facile preparation, high reactivity, and excellent stability. The superior stability of pyridinium ylides can be attributed to electron-withdrawing substituents on the carbanionic moiety, which stabilize the lone pair through electron delocalization. Without these electron-withdrawing groups conjugation is lost, pyridinium ylides are not stable, and have never been reported in the literature.

One of the main focuses of the Dyker group is exploring the effects of substituents on the reduction potential of neutral organic reducing agents. Specifically, large exocyclic substituents known as iminophosphorano groups are employed to functionalize bipyridine scaffolds, ultimately leading to the formation of electron-donating molecules known as bispyridinylidenes.

Recently, while synthesizing a new tetrasubstituted bispyridinylidene, a long-lived intermediate has been detected by NMR spectroscopy. We believe this intermediate is a pyridinium ylide without electron-withdrawing groups, which would make it the first-ever example of an unsubstituted pyridinium methylide. To confirm the identity of this intermediate, several electrophiles including iodomethane, copper-(I) bromide, and silver triflate were tested as trapping agents under a wide range of experimental conditions in attempts to isolate stable products which support the involvement of this novel ylide intermediate. To complement these trapping studies, attempts to more thoroughly characterize the intermediate itself have been investigated. These include low temperature NMR studies and the preparation of a protected derivative designed to eliminate the expected decomposition mechanism and extend the lifetime of the ylide.