

# Oxonium Ions, Total Synthesis and Structure Determination

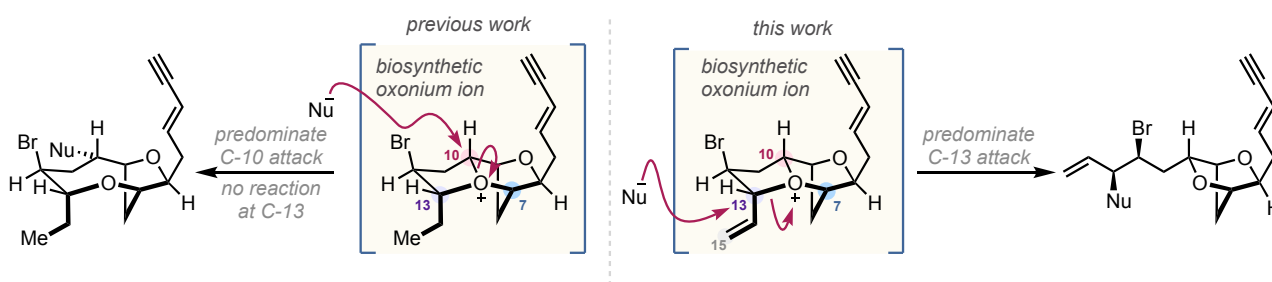
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The primary focus of this presentation will be the chemistry of oxonium ions; additionally, the total synthesis of numerous natural products along with the structure reassignment of a number of natural products will be presented.

Trialkyl oxonium ions have been proposed as intermediates in the biosynthesis of numerous C<sub>15</sub>-halogenated natural products from *Laurencia* species.<sup>1,2</sup> Previously we have reported the synthesis and characterization (low T NMR) of four of these trialkyl oxonium ions, and demonstrated their reaction with a range of nucleophiles, at two of the three electrophilic sites (C-10 and C-7), to yield numerous natural products; notably the reaction of nucleophiles at C-13 was not observed (**Figure 1**).<sup>3,4</sup>

In this presentation we report the synthesis, characterization (low T NMR) and reactivity of a proposed biosynthetic allyldialkyl oxonium ion. This oxonium ion reacts with nucleophiles primarily at the allylic position (C-13) leading to a plausible biosynthetic route to four dioxabicyclo[2.2.1]heptane *Laurencia* natural products.



**Figure 1.** Site selectivity in the reaction of related oxonium ions with nucleophiles,

1 A. Fukuzawa, M. Aye, M. Nakamura, M. Tamura, A. Murai, *Tetrahedron Lett.* **1990**, 31, 4895.

2 H. Kikuchi, T. Suzuki, E. Kurosawa, M. Suzuki, *Bull. Chem. Soc. Jpn.* **1991**, 64, 1763.

3 H. S. S. Chan, Q. N. N. Nguyen, R. S. Paton, J. W. Burton, *J. Am. Chem. Soc.* **2019**, 141, 15951.

4 H. S. S. Chan, A. L. Thompson, K. E. Christensen, J. W. Burton, *Chem. Sci.* **2020**, 11, 11592.