ORGANIC SEMINAR

Tuesday, February 27, 2024 4:30 PM, WTHR 104

"Oxidopyrylium-Based (5 + 2) Cycloadditions: Old Roads, New Pathways"



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Abstract:

We train next generation scientists by guiding them through important research questions in the realm of oxidopyrylium-based (5+2) cycloadditions. Initial efforts probed the mechanism of formation and cycloaddition of oxidopyrylium intermediates, which led to a (5+2) cycloaddition conjugate addition cascade (C3) sequence in which 3 new rings, 4 new bonds, and 6 new stereocenters were constructed with high diastereoselectivity. In collaboration with the Tantillo group, several experimental observations were corroborated via theoretical calculations including evidence for the RDS of deprotonation and Kinetic Isotope Effects that matched our ²H-labeling experiments. In addition, we have discovered a superior silyl transfer group (i.e. TBDPS) in silyloxypyronebased (5+2) cycloadditions that may proceed through a variety of mechanisms thus opening new cycloaddition pathways. We have also explored applications such as efforts toward the total synthesis of toxicodenane A in which we utilized an oxidopyrylium-based (5+2) cycloaddition of a silicon-tethered BOC-pyranone. Within this framework, next generation scientists are trained to ask important questions in the context of this fascinating discipline of organic synthesis.



Department of Chemistry