Direct Cyclopropanations of Olefins with Methylene Compounds via Organoelectrocatalysis

Significance: Xu and co-workers disclose a direct intramolecular cyclopropanation of alkenes with active methylene compounds to furnish the corresponding cyclopropanes with moderate to excellent yields. The electrocatalytic method involves the use of a phenothiazine organocatalyst and proceeds through a radical–polar crossover process. The method tolerates a wide range of functional groups, displays excellent scalability, and provides access to a plethora of cyclopropane-fused scaffolds. Only catalytic amounts of electrolyte are required, and the electrochemical approach obviates the use of stoichiometric chemical oxidants.

Comment: The direct access of cyclopropanes from nonfunctionalized active methylene compounds and alkenes is highly desirable as it avoids the use of prefunctionalized precursors or potentially hazardous carbene precursors, such as α-di-azocarbonyls. The authors report an elegant and efficient organoelectrocatalytic strategy to address this challenge. Mechanistic studies suggest that the reaction proceeds in a stepwise manner through a kinetically favored exo-trig cyclization and a covalent sulfonium species. A nucleophilic substitution resembling the substitution step in the Corey–Chaykovsky reaction furnishes the cyclopropane product.