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 prefuctionalized precursors or potentially hazardous carbene precursors, such as \( \alpha \)-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.