

Direct Cyclopropanations of Olefins with Methylene Compounds via Organoelectrocatalysis

Category

Organo- and Biocatalysis

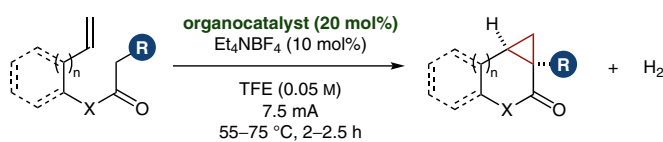
Key words

organoelectrocatalysis

cyclopropanation

radical–polar crossover

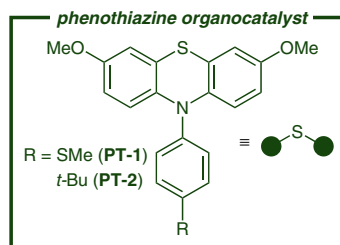
Corey–Chaykovsky reactions

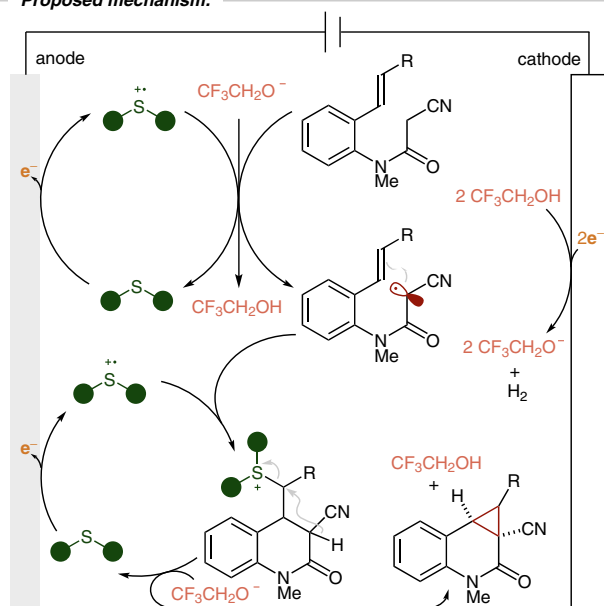
n = 0, 1

X = N-Alk, N-alkenyl, N-(Het)Ar, NH, O, CH₂R = CN, COMe, CO₂Me

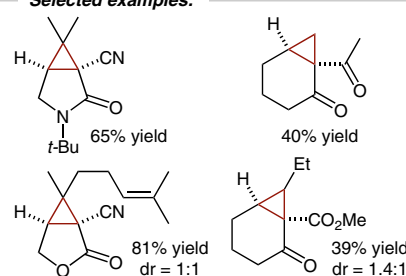
TFE = 2,2,2-trifluoroethan-1-ol



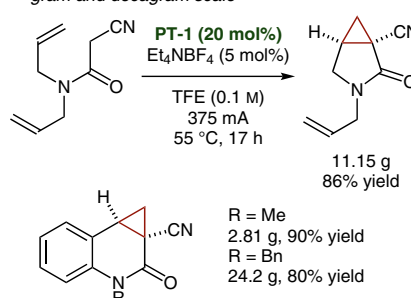
Proposed mechanism:



Selected examples:



gram and decagram scale



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 -diazocarbonyls. 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.