

Catalytic, Enantioselective, Intramolecular Carbosulfenylation of Olefins. Mechanistic Aspects: A Remarkable Case of Negative Catalysis

Hyung Min Chi and Scott E. Denmark

In the course of developing an enantioselective, Lewis base/Brønsted acid co-catalyzed carbosulfenylation of alkenes, a seemingly contradicting phenomenon of a catalyst inhibiting a stoichiometric reaction was observed. In the absence of catalyst, the background reaction rates were comparable to or greater than the catalyzed process, despite the observation of highly enantioenriched product when a chiral, nonracemic catalyst was employed. Detailed kinetic and spectroscopic studies revealed that the conversion of the Lewis base pre-catalyst to the catalytically active species was responsible for the observed comparable reactivity. Specifically, the equimolar formation of the byproducts of the catalyst activation, sulfonate ion and phthalimide, buffered the Brønsted acid, resulting in inhibition of the uncatalyzed racemic pathway. Therefore, the operating background reaction under catalytic conditions cannot be represented by simply omitting the catalyst.

