Push-Pull-Allenes: The Influences of Substituents on the Activation of Allenes by Biomimetic Zinc Complexes

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Dedicated to Professor Rolf W. Saalfrank on the occasion of his 70\textsuperscript{th} birthday

The influence of substituents at the allene skeleton on the rate-determining step of the reaction with nucleophiles catalyzed by biomimetic zinc complexes was investigated with quantum chemical (especially DFT) methods. Additional examinations were applied to derivatives of the zinc hydroxide complex modeled in analogy to the catalytic center of carbonic anhydrase. Especially suitable substituents in the allene moiety can lead to a significant lowering of the activation barrier. Further we demonstrate that by the application of this principle of a bioanalogous enhancement of reactivity other nucleophiles instead of the biological substrate can also be reactants in completely closed catalytic reaction cycles.

\textit{Key words:} Allenes, Substitution Effects, Carbonic Anhydrase, Cumulene Activation