

CHEMISTRY

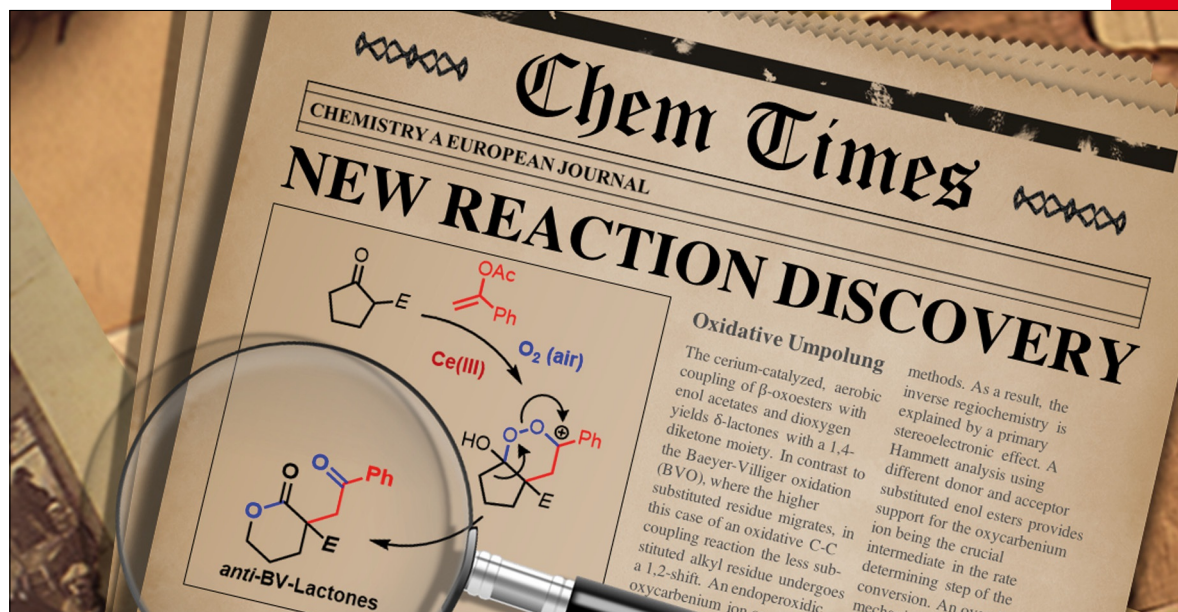
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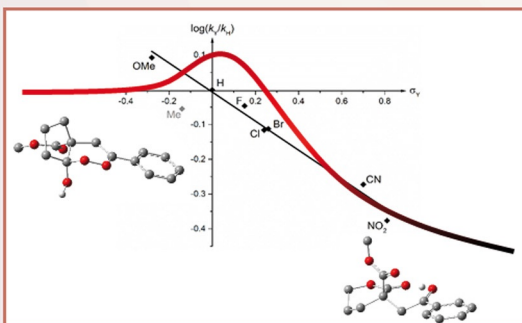


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Mechanistic Investigations

WOW NEWS



Reaction kinetics (Hammett analysis) supported by computational methods indicate an endoperoxidic oxycarbenium ion to be the reaction intermediate for the cerium-catalyzed coupling of β -oxoesters, enol acetates and dioxygen.

δ -Valerolactone derivatives with an 1,4-diketone moiety are formed by aerobic, cerium-catalyzed coupling of β -oxoester, enol acetates and dioxygen. This transformation can be regarded as an Umpolung reaction, since the normally nucleophilic α -carbon atom of the β -oxoester becomes an electrophilic radical center reacting with the electron rich olefin.

The existence of an oxycarbenium ion as intermediate is strongly supported by the kinetics of the reaction of several donor and acceptor substituted enol acetates. Donor substituents accelerate the reaction, whereas acceptor substituents slow it down. An analysis of the first order kinetics resulted in rate constants k , which

were linearly correlated with the para-substituent constants σ in a Hammett plot. The negative slope provides evidence for the existence of the benzyl cation, which could be considered as an analog to the Criegee intermediate of the BVO. Furthermore, the relative energies and optimized conformations of three possible stereoisomers were obtained by DFT calculations.

A conformational analysis of the two relevant isomers explains the regiochemistry of the rearrangement reaction by a primary stereoelectronic effect. In contrast to the BVO, where the higher substituted residue is migrating, the primary alkyl residue of the oxycarbenium intermediate undergoes a 1,2-alkyl shift and forms the δ -valerolactone

Cover Picture:

J. Christoffers et al.

Formation of δ -Lactones with anti-Baeyer-Villiger Regiochemistry: Investigations into the Mechanism of the Cerium-Catalyzed Aerobic Coupling of β -Oxoesters with Enol Acetates

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