

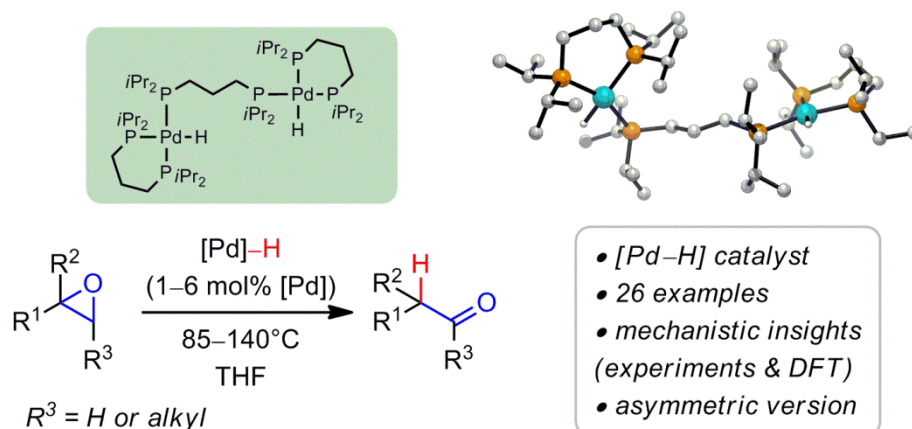
Isomerization of Epoxides by a [Pd–H] Catalyst: a Combined Experimental and Theoretical Mechanistic Study

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The isomerization of epoxides into the corresponding carbonyl derivatives is a reaction that bears substantial synthetic potential.^{1,2} Starting from readily accessible substrates, it provides a straightforward access to either ketones or aldehydes – arguably two of the most valuable and prevalent functions in synthesis. Surprisingly, this seemingly simple isomerization still belongs to the repertoire of promising chemical reactions for which the potentialities have yet to be fully revealed.

Herein, we report on the preparation of a well-defined palladium hydride complex which catalyzes the isomerization of a variety of terminal and internal epoxides with perfect regioselectivity, broad functional group tolerance and in practical yields. Experimental and theoretical investigations point to an unprecedented hydride-type mechanism. Preliminary observations revealed two distinct enantio-determining steps for the kinetic resolution of terminal epoxides. These results hold promise for the development of an enantioselective variant of the reaction.³



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