

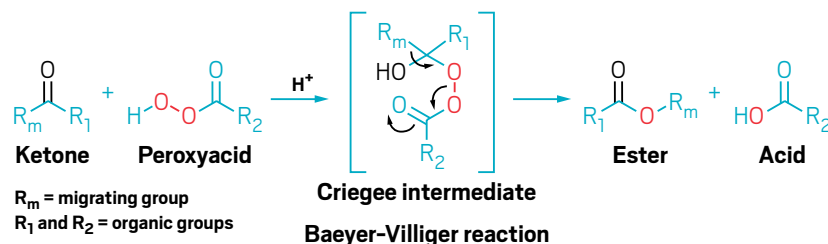
# Elusive reaction intermediate captured

Stabilized version of reactive species could aid study of Baeyer-Villiger reaction mechanism

In 1899, German chemists Adolf von Baeyer and Victor Villiger discovered a reaction of a ketone and peroxyacid to form an ester. The reaction is widely used in research and industrially—to produce the polymer precursor caprolactone, for example. But its mechanism, which includes a tricky alkyl group rearrangement, has

active that researchers created a stabilized version only once, in 1973, using a reaction involving harsh reagents—sulfuric acid and concentrated hydrogen peroxide.

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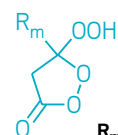


long been difficult to decipher, making it tough to optimize the reaction's efficiency.

The reaction mechanism was controversial historically, and in 1953 William von Eggers Doering and a coworker at Yale University used isotope labeling to nail down the correct one, proposed by German chemist Rudolf Criegee. The Criegee reaction intermediate is so fleeting and re-

State University, and coworkers have now produced a stabilized intermediate more easily, using a mild Lewis acid and dilute hydrogen peroxide, and they characterized it structurally and computationally (*Angew. Chem. Int. Ed.* 2018, DOI: 10.1002/anie.201712651).

They stabilized the intermediate by cyclizing it and turning a hydroxide group



$R_m$  = migrating group

**Cyclic Criegee intermediate**

into a hydroperoxide ( $-OOH$ ), modifications that disrupt key electron orbital interactions that normally make the reaction so fast. If the chemists convert the hydroperoxide back to a hydroxide, the cyclic intermediate remains fairly stable but can also react to form a Baeyer-Villiger ester product.

Sosale Chandrasekhar of the Indian Institute of Science critiques some of the study's details, noting, for example, that bond-angle strain may control the reaction's rearrangement kinetics more than orbital alignment does. But the study's structural and computational analyses of the intermediate "enrich our understanding of this fundamental reaction," he says.

The ability "to isolate a key derivative of the Criegee intermediate and then trigger its reaction" could advance the synthetic utility of the Baeyer-Villiger reaction, adds Cathleen Crudden of Queen's University.—STU BORMAN

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