Acid Catalyzed Radical Reactions Via Alkenyl Peroxides

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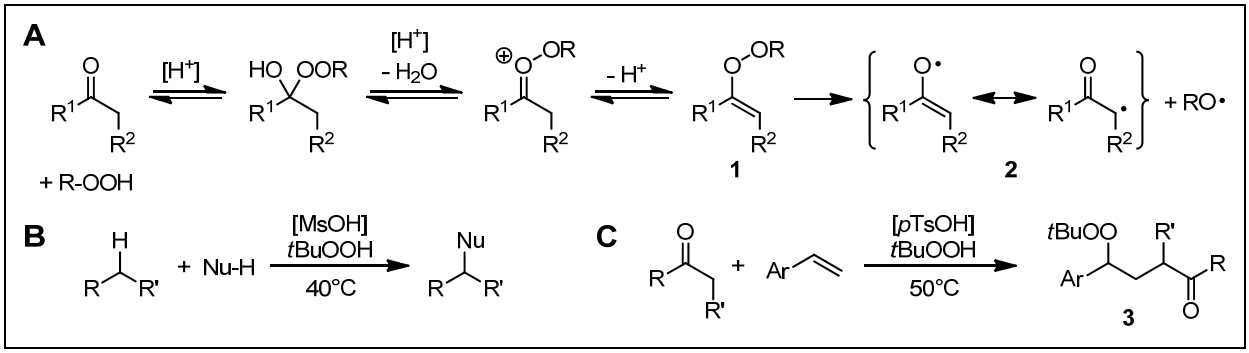
The combination of hydroperoxides, ketones and acid catalysis generates radicals. Mechanistic studies indicate that these reactions proceed via alkenyl peroxides **1**, formed in equilibrium by condensation, which decay by homolytic O-O bond cleavage into a stabilized ketone radical **2** and an oxyl radical (Scheme A).

Previously, alkenyl peroxide chemistry was essentially restricted to theoretical studies of atmospheric chemistry. From mechanistic studies, we realized that they can easily be formed in solution, which also allows to utilize them for various synthetic purposes.[1] For example, the radicals can mediate oxidative C-H functionalization reactions (Scheme B)[2] and they can be used to functionalize olefins (Scheme C).[1] The resulting γ-peroxyketones **3** are valuable products that can be converted to homoaldol products, 1,4-diketones or heterocycles.

An overview of alkenyl peroxide chemistry in solution will be given, including mechanistic studies and how they enable synthetic applications.



1. Schweitzer-Chaput, B.; Demaerel, J.; Engler, H.; Klussmann, M. *Angew. Chem. Int. Ed*. **2014**, *53*, 8737.
2. Schweitzer-Chaput, B.; Sud, A.; Pinter, Á.; Dehn, S.; Schulze, P.; Klussmann, M. *Angew. Chem. Int. Ed*. **2013**, *52*, 13228.