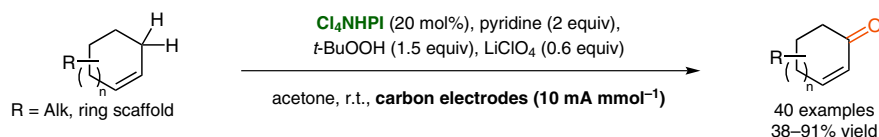
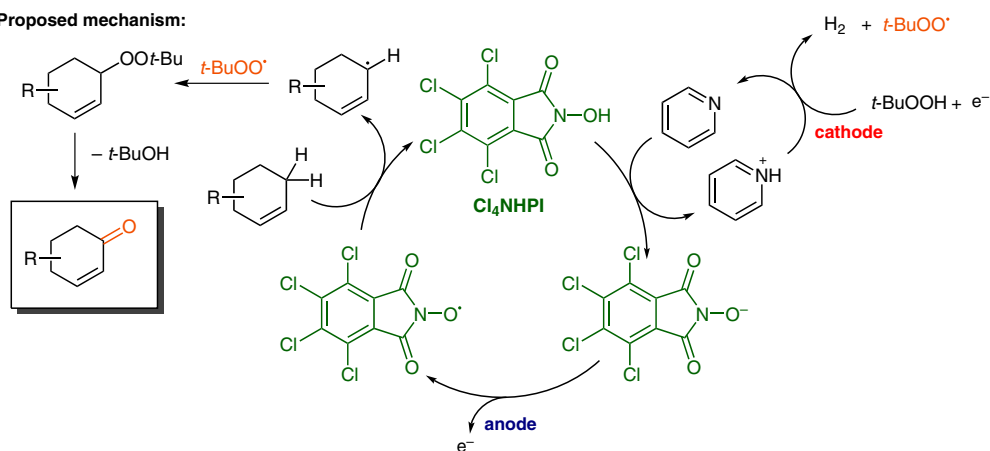


E. J. HORN, B. R. ROSEN, Y. CHEN, J. TANG, K. CHEN, M. D. EASTGATE, P. S. BARAN* (THE SCRIPPS RESEARCH INSTITUTE, LA JOLLA AND BRISTOL-MYERS SQUIBB, NEW BRUNSWICK, USA; ASYMCHM LIFE SCIENCE (TIANJIN), P. R. OF CHINA)
 Scalable and Sustainable Electrochemical Allylic C–H Oxidation
Nature **2016**, *533*, 77–81.

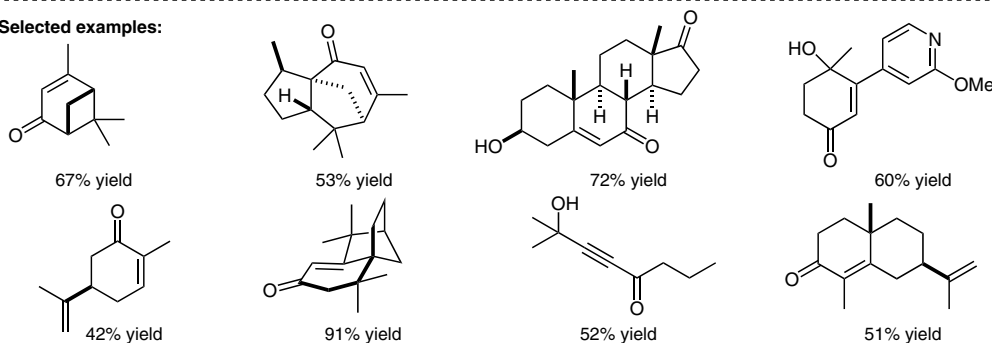
N-Hydroxyphthalimide-Catalyzed Electrochemical Allylic Oxidation



Proposed mechanism:



Selected examples:



Significance: The Baran group reports an electrochemical oxidation of allylic methylene groups to give unsaturated ketones with *t*-BuOOH as the terminal oxidant. Anodic oxidation of the *N*-hydroxyphthalimide catalyst (**Cl₄NHPI**) is proposed to give an oxyl radical species. Upon abstraction of a hydrogen atom from the substrate, the resulting allylic radical is suggested to further react with a *tert*-butyl peroxy radical to give the product after elimination of *t*-BuOH.

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Comment: Atom-economical and sustainable methods for allylic oxidations on an industrial scale are rare and cumbersome. This report suggests a catalyst-controlled electrochemical approach and aims for a simple and chemoselective solution. Although the isolated yields remain moderate in some cases, the broad scope as well as the low cost and toxicity of the materials render this methodology an auspicious alternative for large-scale applications.

Category

Organo- and Biocatalysis

Key words

electrochemistry

allylic oxidation

cyclohexenones

hydroxysuccinimides

hydroxyphthalimide

Synfact
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