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Scalable and Sustainable Electrochemical Allylic C–H Oxidation


**N-Hydroxyphthalimide-Catalyzed Electrochemical Allylic Oxidation**

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 peroxyl radical to give the product after elimination of t-BuOH.

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.

**Proposed mechanism:**

\[
\text{Cl}_4\text{NHPI} \quad \text{(20 mol%), pyridine (2 equiv),} \\
\text{t-BuOOH (1.5 equiv), LiClO}_4 \quad \text{(0.6 equiv)} \\
\text{acetone, r.t., carbon electrodes (10 mA mmol}^{-1})
\]

**Selected examples:**

- 67% yield
- 53% yield
- 72% yield
- 60% yield
- 42% yield
- 91% yield
- 52% yield
- 51% yield

**Key words**

electrochemistry
allylic oxidation
cyclohexenones
hydroxysuccinimides
hydroxyphthalimide

**Category**

Organo- and Biocatalysis

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