Trends in Chemistry | **Mechanism of the Month**

Electrocatalytic Diazidation of Alkenes

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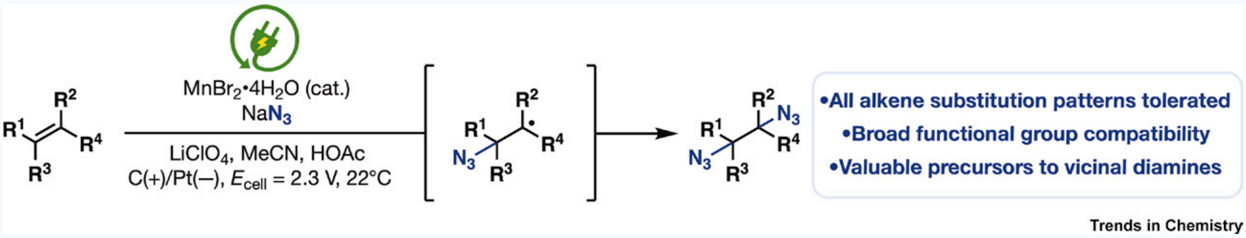


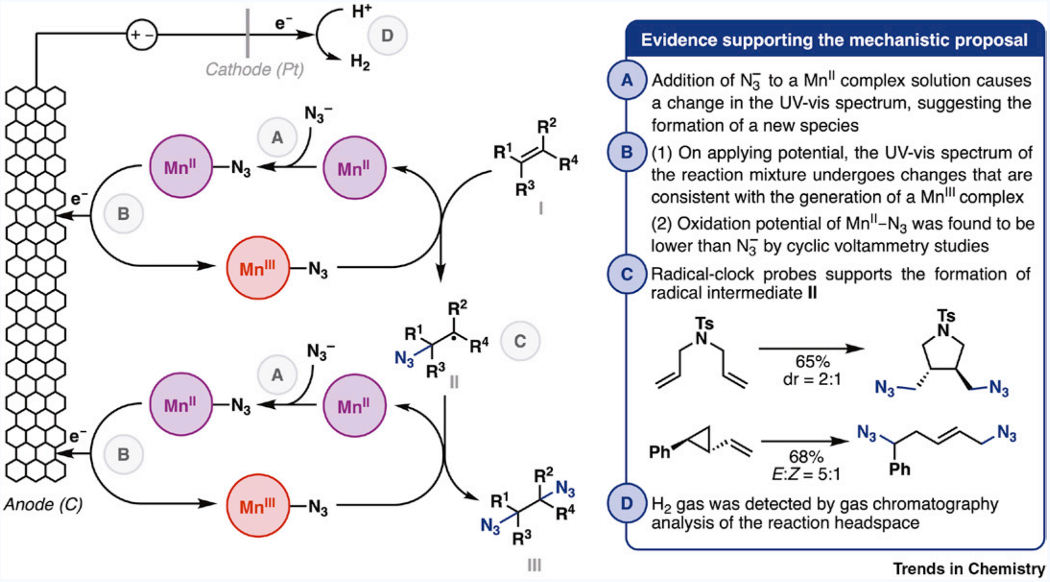
- All alkene substitution patterns tolerated
- Broad functional group compatibility
- Valuable precursors to vicinal diamines

ORIGIN

Vicinal diamines are common structures in numerous biologically relevant molecules and useful ligands in asymmetric catalysis. However, a general synthetic approach to access vicinal diamines with high efficiency and broad substrate generality remains a challenge in organic chemistry. Recently, our group developed an electrocatalytic strategy to convert simple alkenes and sodium azide into 1,2-diazides, which can then be readily reduced to vicinal diamines.

REACTION MECHANISM

The difunctionalization of alkenes, in which two functional groups are added across a C=C double bond, can adopt nucleophilic, electrophilic, or radical mechanisms. The electrocatalytic diazidation developed by our group undergoes a radical pathway mediated by a redox-active transition-metal catalyst and is relatively insensitive to the structure and electronic property of the alkene. Cyclic voltammetry and spectrometry data support the proposed catalytic cycle shown below. The Mn^{II} catalyst first participates in ligand exchange with the azide anion to generate a $[Mn^{II}]–N_3$ complex (A). This intermediate is oxidized on the carbon anode to the corresponding Mn^{III} species (B), which subsequently transfers an azidyl group to the alkene (I) to generate radical intermediate II (C). The catalytic cycle is repeated and $[Mn^{III}]–N_3$ is also responsible for delivering the second equivalent of azidyl to intermediate II to complete diazidation. The anodic generation of the $[Mn^{III}]–N_3$ complex is a key feature of this mechanism, as this catalytic species plays several key roles in the reaction. $[Mn^{III}]–N_3$ can be produced at a lower potential than the free azidyl radical ($N_3^{\bullet}$) and it preserves a radical nature that induces homolysis of the π bond of the alkene. In addition, carbon-centered radical II is a transient radical and can undergo various side reactions such as dimerization and overoxidation. However, $[Mn^{III}]–N_3$ captures II efficiently to ensure high reaction selectivity. On the reductive side of the electrochemical reaction, protons from acetic acid are reduced on the platinum cathode surface to generate hydrogen gas (D).



Evidence supporting the mechanistic proposal

A. Addition of N_3^- to a Mn^{II} complex solution causes a change in the UV-vis spectrum, suggesting the formation of a new species

B. (1) On applying potential, the UV-vis spectrum of the reaction mixture undergoes changes that are consistent with the generation of a Mn^{III} complex
(2) Oxidation potential of $Mn^{II}–N_3$ was found to be lower than N_3^- by cyclic voltammetry studies

C. Radical-clock probes supports the formation of radical intermediate **II**

D. H_2 gas was detected by gas chromatography analysis of the reaction headspace

IMPORTANCE

Electrocatalysis promotes the generation of reactive radical intermediates in a controlled manner and regulates their downstream reactivity. The present mechanism uses electricity as a formal oxidizing agent to generate azidyl radical equivalents, which in combination with redox-metal catalysis enables the diazidation of alkenes in a milder and more sustainable fashion with a broader substrate scope than conventional chemical approaches.

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