Photocatalytic Anti-Markovnikov Hydroetherification

**Significance:** A direct photocatalytic anti-Markovnikov hydroetherification has been described by the Nicewicz group. The reported procedure is promoted by the commercially available sensitizer 9-mesityl-10-methylacridinium perchlorate (A) and the H-atom donor 2-phenylmalonitrile (B). The authors suggest that the methodology is based on two different redox cycles. A primary one, which initiates the reaction by a single-electron transfer (SET) and a supporting one, which simultaneously facilitates the hydrogen exchange and serves as an electron-redox mediator.

**Comment:** The study of catalytic anti-Markovnikov additions of nucleophiles to olefins has gained great interest in the last decades since it had been described as one of the “top ten challenges for catalysis” [J. Haggin Chem. Eng. News 1993, 71(22), 23]. In this work, the authors describe the addition of alcohols to alkenes via a newly developed two-component organic photoredox catalytic system. The reaction affords a wide range of cyclic ethers with complete selectivity, which reflects the thermodynamic equilibrium between the three radical intermediates I, II, and III.

**Proposed catalytic cycle:**

1. Reaction initiation by a single-electron transfer (SET) to form intermediate I.
2. Supporting redox cycle involving H-atom donor B and sensitizer A.
3. Hydrogen exchange facilitated by the supporting redox cycle, leading to the formation of intermediate II.
4. Completion of the catalytic cycle via reformation of the sensitizer A and H-atom donor B.

**Key words:** photocatalysis, hydroetherification, anti-Markovnikov selectivity.