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Aerobic Palladium-Catalyzed Dioxygenation of Alkenes Enabled by Catalytic Nitrite. — Catalytic nitrite is found to enable carbon-oxygen bond-forming reductive elimination from unstable alkyl palladium intermediates, providing dioxygenated products from alkenes. A variety of functional groups are tolerated, and high yields are observed with many substrates, also for a multigram-scale reaction. Nitrogen dioxide, which could form from nitrite under the reaction conditions, is demonstrated to be a potential intermediate in the catalytic cycle. Furthermore, the reductive elimination event is probed with ¹⁸O-labeling experiments, which demonstrate that both oxygen atoms in the difunctionalized products are derived from one molecule of acetic acid. — (WICKENS, Z. K.; GUZMAN, P. E.; GRUBBS*, R. H.; Angew. Chem., Int. Ed. 54 (2015) 1, 236-240, http://dx.doi.org/10.1002/anie.201408650; Div. Chem. Chem. Eng., Calif. Inst. Technol., Pasadena, CA 91125, USA; Eng.) — U. Scheffler

$$\begin{array}{c} \text{excess Ac-O-Ac (II), 1 atm O}_2 & \text{a R}^1 : -(\text{CH}_2)_9 - \text{Me} & 83\% \\ \text{PdCl}_2(\text{NC-Ph})_2/\text{CuCl}_2 \cdot 2\text{H}_2\text{O}/\text{AgNO}_2 \text{ (cat.)} \\ \text{I} \\ \\ \text{I} \\ \end{array} \begin{array}{c} \text{AcOH/MeNO}_2 \text{ (10:3), 35°C, [dark]} \\ \text{III} \\ \end{array} \begin{array}{c} \text{a R}^1 : -(\text{CH}_2)_8 - \text{CO-DH} & 74\% \\ \text{b R}^1 : -(\text{CH}_2)_8 - \text{CO-O-Et} & 91\% \\ \text{d R}^1 : -(\text{CH}_2)_8 - \text{Br} \\ \text{d R}^1 : -(\text{CH}_2)_8 - \text{Br} \\ \text{d R}^1 : -(\text{CH}_2)_8 - \text{Br} \\ \text{f R}^1 : -(\text{CH}_2)_8 - \text{CO-DH} \\ \text{f R}^2 : -(\text{CH}_2)_8 - \text{CO-$$