Nonnatural Reactivity of Cofactor-Dependent Enzymes upon Light Irradiation

**Significance:** An asymmetric light-mediated reductive debromination of racemic α-bromolactones is reported by the Hyster group. The combination of a ketoreductase derived from either *Lactobacillus kefiri* (LKADH) or *Ralstonia* (RasADH), NADP⁺, and blue LED light furnished the desired lactones in high yields (≥91%) and good to excellent enantioselectivities (er ≤ 98:2).

**Comment:** A great challenge in biocatalysis is the discovery and development of novel reaction pathways and catalytic functions. The authors demonstrate that a nicotinamide-dependent ketoreductase can change its natural function from carbonyl reduction to that of a radical initiator and chiral source of hydrogen, simply by irradiation of the cofactor with light. This strategy leads to novel and selective radical-mediated reactions.

**Key words:** ketoreductase, photoexcitation, nicotinamide-dependent enzymes, debromination, lactones