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.

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