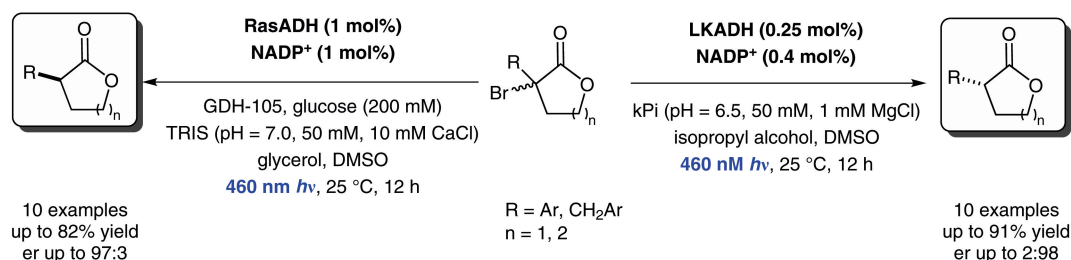
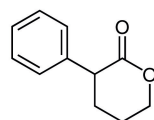


Nonnatural Reactivity of Cofactor-Dependent Enzymes upon Light Irradiation

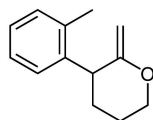


Selected examples:



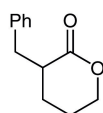
RasADH: 51% yield
er = 92.5:7.5

LKADH: 81% yield
er = 2:98



RasADH: 81% yield
er = 81:19

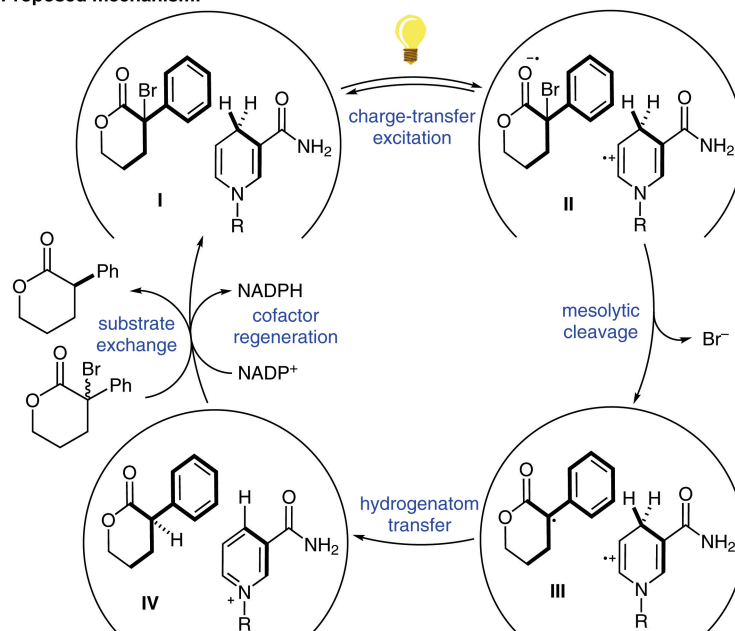
LKADH: 80% yield
er = 6:94



RasADH: 29% yield
er = 80:20

LKADH: 80% yield
er = 4:96

Proposed mechanism:



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 kefir* (LKADH) or *Ralstonia* (RasADH), NADP⁺, and blue LED light furnished the desired lactones in high yields ($\leq 91\%$) and good to excellent enantioselectivities ($er \leq 98:2$).

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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.