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Asymmetric Bioreduction of Activated Alkenes Using Cloned 12-Oxophytodienoate Reductase Isoenzymes OPR-1 and OPR-3 from *Lycopersicon esculentum* (Tomato): A Striking Change of Stereoselectivity
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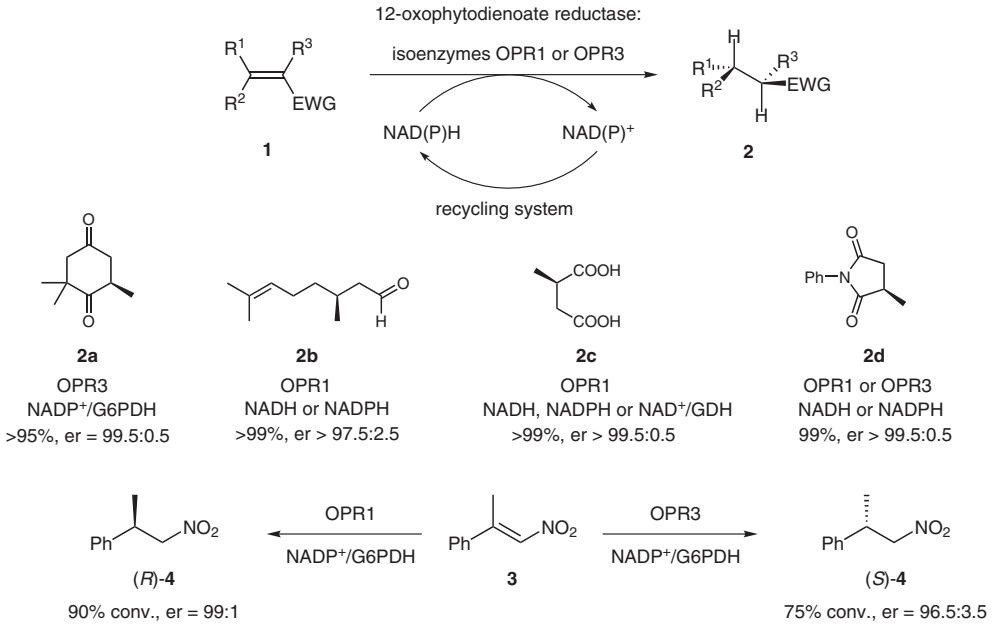
Enantioselective Reduction of Activated Olefins Using 'Old Yellow Enzymes'



Significance: A biocatalytic asymmetric reduction of olefins **1**, which bear an electron-withdrawing group (EWG) has been developed. Isoenzymes OPR1 and OPR3 of 12-oxophytodienoate reductase (OPR) from *Lycopersicon esculentum* (tomato) mediate chemoselective hydrogenations of α,β-unsaturated aldehydes, (di)ketones, dicarboxylic acids, and imides in high conversions and enantioselectivities. NADH or NADPH is used as cofactor, either in stoichiometric amounts or in combination with different recycling systems. Furthermore, both isoenzymes reduce nitroalkenes **3** to the corresponding nitroalkanes **4** in a stereochemically complementary manner.

Comment: Enoate reductases are also called 'old yellow enzymes' and mediate the *anti*-selective hydrogenation of activated olefins using a flavin cofactor. Although their mode of action has been elucidated thoroughly, the application of these enzymes on a preparative scale still remains in its infancy. Instead, whole-cell catalysts have dominated the field. Since an enoate reductase has previously been shown to reduce cyclohexenones to optically active cyclohexanones (J. D. Stewart et al. *J. Mol. Catal. B* **2006**, *42*, 52-54), its scope has now been expanded to a variety of electron-poor alkenes (**1**). Industrially relevant compounds such as ketoisophorone (**1a**) or citral (**1b**) are among them. While the use of whole-cell catalysts often suffers from the undesired reduction of C=O bonds, the present method is chemoselective for C=C bonds.

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