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NEWS OF THE WEEK

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IRON-CATALYZED OLEFIN OXIDATION

New iron catalysts use H₂O₂ to epoxidize or
dihydroxylate alkenes

STEPHEN STINSON

By emulating natural oxidations by certain enzymes that have iron at their active sites, two research groups have made significant progress toward environmentally friendly reactions that oxidize organic compounds using relatively nontoxic metal catalysts. The catalyst ligands used with the iron are inexpensive and simple to make, unlike the complex porphyrin ligands called hemes that are found in some enzymes. And the new reactions use hydrogen peroxide as the oxidizing agent, which results in harmless water as the by-product.

"The development of environmentally benign catalytic oxidations, in particular using hydrogen peroxide, is a major scientific challenge of great importance for the chemical industry," comments organic chemistry professor Ben L. Feringa of the University of Groningen, in the Netherlands. "Nonheme iron systems are among the most difficult, though attractive, targets for new catalysts."



QUE

In one of the new reports, organic and inorganic chemistry professor [Eric N. Jacobsen](#) of [Harvard University](#) describes a



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high-yielding conversion of olefins to racemic epoxides [*J. Am. Chem. Soc.*, **123**, 7194 (2001)]. The Harvard publication follows close on the communication of an enantioselective dihydroxylation of olefins by bioinorganic chemistry professor [Lawrence Que Jr.](#) of the University of Minnesota, Minneapolis [*J. Am. Chem. Soc.*, **123**, 6722 (2001)]. The catalyst ligands for each reaction type are similar, based on ethylenediamine units bonded to two pyridylmethyl groups.



JACOBSEN

Working with postdoctoral fellow M. Christina White and undergraduate student Abigail G. Doyle, Jacobsen uses *N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)-ethylenediamine. The Harvard group gets an 85% yield of epoxide from 1-decene.

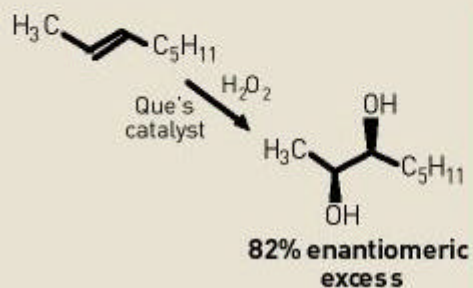
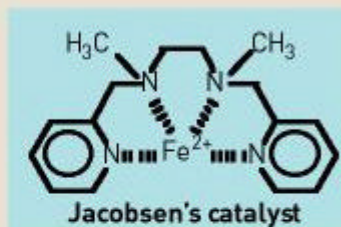
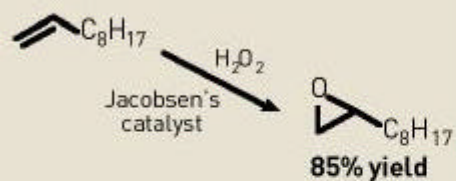
As Feringa says, "Jacobsen made significant progress by devising a catalytic system that brings epoxidation with iron using hydrogen peroxide within the realm of synthetic organic chemistry. The high epoxide yields and the apparently low hydrogen peroxide decomposition--the latter being a notorious problem with iron catalysts--are particularly noteworthy."

Que's work with postdoctoral fellows Miquel Costas, Adrienne K. Tipton, and Du-Hwan Jo and graduate student Kui Chen uses either enantiomer of *N,N'*-dimethyl-*N,N'*-bis(6-methyl-2-pyridylmethyl)-1,2-cyclohexanediamine. The Minnesota team gets, for example, a 38% yield of 2,3-octanediol in 82% enantiomeric excess from trans-2-octene.

"The finding by Que and coworkers of the first asymmetric iron-catalyzed dihydroxylation of olefins with high enantioselectivities is a rather spectacular one," Feringa says. "Although the yields of diols with these new chiral catalysts are still rather low, one easily recognizes the great potential of the system featuring a combination of iron salts, simple chiral amines as ligands, and hydrogen peroxide."

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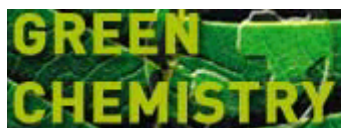
Iron catalyzes oxidations by H_2O_2



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Toward environmentally benign
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