

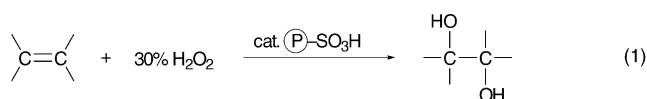
## Green Chemistry

## Catalytic Dihydroxylation of Olefins with Hydrogen Peroxide: An Organic-Solvent- and Metal-Free System\*\*

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1,2-Diols are widely used as intermediates in the perfume and fragrance industry, for the manufacture of cosmetics, for the synthesis of commercial products such as photographic materials and lubricants, and in drugs and foods.<sup>[1]</sup> Dihydroxylation of olefins is a straightforward method for the synthesis of 1,2-diols, and various oxidants are now used for this purpose both in the laboratory and in industry.<sup>[2]</sup> The *syn* dihydroxylation of olefins is most commonly performed in the presence of metal oxides, including  $\text{KMnO}_4$ <sup>[3]</sup> and  $\text{OsO}_4$ ,<sup>[4]</sup> and  $t\text{-C}_4\text{H}_9\text{OOH}$  with a catalytic amount of  $\text{OsO}_4$ ,<sup>[5]</sup> The *anti* dihydroxylation can be achieved with  $\text{CH}_3\text{CO}_3\text{H}$ <sup>[6]</sup> and  $m\text{-ClC}_6\text{H}_4\text{CO}_3\text{H}$ <sup>[7]</sup> in water. However, the atom efficiency of these oxidants is low, and they form equimolar amounts of the deoxygenated compounds as waste.<sup>[8,9]</sup> Hydrogen peroxide is

an ideal oxidant, because the atom efficiency is excellent and water is theoretically the sole by-product. However,  $\text{H}_2\text{O}_2$  can be a clean oxidant only if it is used in a controlled manner without organic solvents and other toxic compounds.<sup>[10]</sup> In this context, we developed various oxidation reactions with aqueous  $\text{H}_2\text{O}_2$  under organic-solvent-free conditions.<sup>[11,12]</sup> Although mixtures of aqueous  $\text{H}_2\text{O}_2$  and  $\text{CH}_3\text{CO}_2\text{H}$  or  $\text{HCO}_2\text{H}$  have been known as an effective reagents for the dihydroxylation of olefins,<sup>[13]</sup> neutralization of the acid solvent with a strong alkali is necessary for isolation of the product. The dihydroxylation of olefins with  $\text{H}_2\text{O}_2$  catalyzed by transition metal complexes has also been reported.<sup>[14]</sup> However, the selectivity for 1,2-diols in these catalytic reactions is moderate, with formation of epoxides as by-products or overoxidation involving C–C bond cleavage. Furthermore, all these methods require chlorohydrocarbons or other organic solvents. The use of zeolites as catalysts has allowed dihydroxylation without organic solvents,<sup>[15]</sup> but the selectivity for 1,2-diols was lower than 59 % as a result of the formation of epoxides, alcohols, ketones, and/or ethers along with the desired 1,2-diols. We report herein a procedure for the synthesis of 1,2-diols by the dihydroxylation of olefins with aqueous 30 %  $\text{H}_2\text{O}_2$  catalyzed by resin-supported sulfonic acid [Eq. (1)]. The present method satisfies the following conditions: 1) organic-solvent- and metal-free system; 2) high yield and selectivity for 1,2-diols; 3) the catalyst is easily recycled; and 4) simple and safe manipulation.



The dihydroxylation of cyclohexene with 30 %  $\text{H}_2\text{O}_2$  in the presence of nafion NR50<sup>[16]</sup> beads (0.04 equiv,  $0.8 \text{ mmol g}^{-1}$  of  $\text{SO}_3\text{H}$  group) at  $70^\circ\text{C}$  for 20 h produced *trans*-1,2-cyclohexanediol in 98 % yield. The catalyst was recycled very easily. After the first dihydroxylation, the catalyst was filtrated and washed with water, then reused for the second reaction. Ten cycles of dihydroxylation of cyclohexene could be catalyzed by the recycled resin-supported sulfonic acid without a decrease in the catalytic activity. The yield of each reaction was over 94 % (Table 1).

Some examples of the dihydroxylation of a range of substrates with 30 %  $\text{H}_2\text{O}_2$  are given in Table 2. The reactivity of internal olefins is higher than that of terminal olefins (Table 2, entry 1 vs. entries 2 and 3). The dihydroxylation of (*E*)- and (*Z*)-2-hexene proceeded stereospecifically to give

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**Table 1:** Dihydroxylation of cyclohexene with 30 %  $\text{H}_2\text{O}_2$  in the presence of recycled resin-supported sulfonic acid as catalyst.<sup>[a]</sup>

Run	Yield [%] <sup>[b]</sup>	Run	Yield [%] <sup>[b]</sup>
1	98	6	94
2	96	7	94
3	96	8	96
4	97	9	95
5	96	10	96

[a] Reaction conditions: cyclohexene (10 mmol)/30 %  $\text{H}_2\text{O}_2$ /nafion NR50 (25:50:1),  $70^\circ\text{C}$ , 20 h. [b] Yield of isolated *trans*-1,2-cyclohexanediol.

**Table 2:** Dihydroxylation of olefins with 30% H<sub>2</sub>O<sub>2</sub> in the presence of resin-supported sulfonic acid catalyst.<sup>[a]</sup>

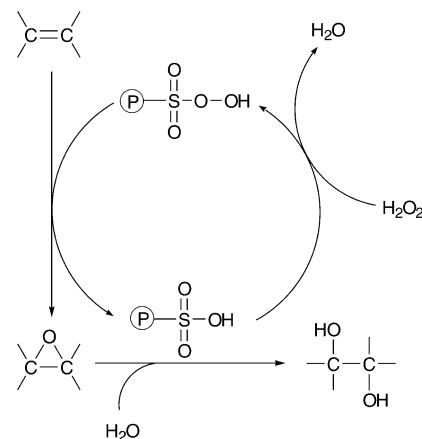
Entry	Olefin	Product	Yield [%] <sup>[b]</sup>
1 <sup>[c]</sup>			40 <sup>[d]</sup>
2 <sup>[c]</sup>			67
3 <sup>[c]</sup>			85
4			83 <sup>[d]</sup>
5			86
6			98
7 <sup>[c]</sup>			95
8 <sup>[e]</sup>			83
9			92 <sup>[d]</sup>
10			100
11			93
12 <sup>[f]</sup>			80

[a] Unless otherwise stated, the reactions were run with olefin (10 mmol), 30% H<sub>2</sub>O<sub>2</sub>, and nafion NR50 (25:50:1) at 70 °C for 20 h. [b] Yield of isolated product. [c] Olefin/30% H<sub>2</sub>O<sub>2</sub>/nafion SAC-13 (25:50:1). [d] Determined by GC analysis. Based on olefin charged. [e] Olefin/30% H<sub>2</sub>O<sub>2</sub>/amberlyst 15 (25:50:1). [f] Olefin/30% H<sub>2</sub>O<sub>2</sub>/nafion SAC-13 (8:32:1), 90 °C.

the corresponding *anti*- and *syn*-2,3-hexanediols, respectively (Table 2, entries 2 and 3). Functionalized olefins were also easily oxidized to produce the corresponding 1,2-diols without affecting alcohol and carboxylic acid groups present in the substrate (Table 2, entries 10–12). Nafion SAC-13 (powder, supported on silica) showed almost the same catalytic activity as nafion NR50 (Table 2, entries 6 and 7). The ion-exchange resin, amberlyst 15<sup>[17]</sup> (polystyrene-supported sulfonic acid) also proved to be a good catalyst for dihydroxylation, producing *trans*-1,2-cyclohexanediol from cyclohexene in 83% yield (Table 2, entry 8). Interestingly, the catalytic activity of resin-supported sulfonic acids is much higher than that of homogeneous acid catalysts. For example, the yields of *anti*-2,3-hexanediol from the dihydroxylation of (*E*)-2-hexene were 85% when using nafion SAC-13, 36% when

using CF<sub>3</sub>SO<sub>3</sub>H, 19% when using H<sub>2</sub>SO<sub>4</sub>, 11% when using C<sub>6</sub>H<sub>5</sub>SO<sub>3</sub>H, and 0% when using CH<sub>3</sub>CO<sub>2</sub>H. Resin-supported carboxylic acid (amberlite IRC76<sup>[17]</sup>) did not work as a catalyst.

This dihydroxylation of olefins proceeds through two steps (Scheme 1): 1) epoxidation of the olefin by H<sub>2</sub>O<sub>2</sub> and 2) hydration of the epoxide to form 1,2-diol. The rate-

**Scheme 1.** Proposed catalytic cycle for the dihydroxylation reaction.

determining step seems to be the epoxidation of olefins as epoxides could not be detected in the reaction mixtures. Indeed, under these reaction conditions, cyclohexene oxide produced *trans*-1,2-cyclohexanediol quantitatively within 10 min. The initial epoxidation is probably carried out by resin-supported peroxysulfonic acid formed in situ.<sup>[18,19]</sup> Competitive experiments showed the following relative reactivity: 1-hexene/(*Z*)-2-hexene/(*E*)-2-hexene/2-methyl-2-pentene = 1:24:46:153. These values are similar to the epoxidation ratio of these olefins with peroxycarboxylic acid (1:22:20:230).<sup>[20]</sup>

In summary, we have developed a clean and safe method for the dihydroxylation of alkenes under organic-solvent- and metal-free conditions. The resin-supported sulfonic acid catalyst is easily recycled.

## Experimental Section

Typical procedure: A 50-mL round-bottomed flask equipped with a magnetic stirring bar and reflux condenser was charged with nafion NR50 (501 mg) and aqueous H<sub>2</sub>O<sub>2</sub> (30%; 2.23 g, 20 mmol). The mixture was stirred at room temperature for 10 min, after which cyclohexene (821 mg, 10 mmol) was added. The triphasic mixture was heated at 70 °C with vigorous stirring for 20 h and then cooled to room temperature. After the nafion NR50 was removed by filtration, MnO<sub>2</sub> (ca. 10 mg) was added to the solution. The absence of H<sub>2</sub>O<sub>2</sub> was examined by testing with starch–iodide paper. After filtration of MnO<sub>2</sub>, the water was removed by evaporation to provide *trans*-1,2-cyclohexanediol<sup>[21]</sup> was obtained as a white powder (1.14 g, 98% yield). M.p. 101–102 °C. <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O): δ = 1.38 (br s, 2H), 1.80 (br s, 2H), 2.06 (br s, 1H), 3.50 ppm (br s, 1H); <sup>13</sup>C NMR (125 MHz, D<sub>2</sub>O): δ = 76.0, 33.6, 24.4 ppm. The nafion NR50 used above was washed with water (5 × 5 mL), and the same dihydroxylation reaction was carried out under the same conditions to give *trans*-1,2-cyclohexanediol (1.12 g, 96% yield).

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