Green Chemistry

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

Yoko Usui, Kazuhiko Sato,* and Masato Tanaka

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.^[1] 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.^[2] The *syn* dihydroxylation of olefins is most commonly performed in the presence of metal oxides, including KMnO₄^[3] and OsO₄,^[4] and *t*-C₄H₉OOH with a catalytic amount of OsO₄.^[5] The *anti* dihydroxylation can be achieved with CH₃CO₃H^[6] and *m*-ClC₆H₄CO₃H^[7] in water. However, the atom efficiency of these oxidants is low, and they form equimolar amounts of the deoxygenated compounds as waste.^[8,9] Hydrogen peroxide is

[*]	Dr. K. Sato, Dr. Y. Usui, Prof. Dr. M. Tanaka ⁺			
	Research Institute for Green Technology			
	National Institute of Advanced Industrial Science			
	and Technology (AIST)			
	Tsukuba Central 5, Tsukuba, Ibaraki, 305-8565 (Japan)			
	Fax: (+81) 29-861-4852			
	E-mail: k.sato@aist.go.jp			
[+]	Present address:			
	Chemical Resources Laboratory			
	Tokyo Institute of Technology			
	4259 Nagatsuda, Midori-ku, Yokohama 226-8503 (Japan)			

[**] This work was supported in part by the New Energy and Industrial Technology Development Organization (NEDO)–Research Institute of Innovative Technology for the Earth (RITE) and the Japan Science and Technology Corporation (JST)–Core Research for Evolutional Science and Technology (CREST) program. an ideal oxidant, because the atom efficiency is excellent and water is theoretically the sole by-product. However, H₂O₂ can be a clean oxidant only if it is used in a controlled manner without organic solvents and other toxic compounds.^[10] In this context, we developed various oxidation reactions with aqueous H₂O₂ under organic-solvent-free conditions.^[11,12] Although mixtures of aqueous H₂O₂ and CH₃CO₂H or HCO₂H have been known as an effective reagents for the dihydroxylation of olefins,^[13] neutralization of the acid solvent with a strong alkali is necessary for isolation of the product. The dihydroxylation of olefins with H₂O₂ catalyzed by transition metal complexes has also been reported.^[14] However, the selectivity for 1,2-diols in these catalytic reactions is moderate, with formation of epoxides as byproducts 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,^[15] 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% H₂O₂ 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.

$$C = C + 30\% H_2O_2 \xrightarrow{\text{cat.} (P-SO_3H)} - C = C - C - C - (1)$$

The dihydroxylation of cyclohexene with 30 % H_2O_2 in the presence of nafion NR50^[16] beads (0.04 equiv, 0.8 mmol g⁻¹ of SO₃H group) at 70 °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 % H₂O₂ 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

Table 1: Dihydroxylation of cyclohexene with $30\% H_2O_2$ in the presence of recycled resin-supported sulfonic acid as catalyst.^[a]

Run	Yield [%] ^[b]	Run	Yield [%] ^[b]
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% $H_2O_2/$ nafion NR50 (25:50:1), 70 °C, 20 h. [b] Yield of isolated trans-1,2-cyclohexanediol.

Angew. Chem. Int. Ed. 2003, 42, 5623-5625

DOI: 10.1002/anie.200352568

Communications

 $\mbox{\it Table 2:}$ Dihydroxylation of olefins with 30% H_2O_2 in the presence of resin-supported sulfonic acid catalyst.^{[a]}



[a] Unless otherwise stated, the reactions were run with olefin (10 mmol), $30\% H_2O_2$, and nafion NR50 (25:50:1) at 70°C for 20 h. [b] Yield of isolated product. [c] Olefin/30% H_2O_2 /nafion SAC-13 (25:50:1). [d] Determined by GC analysis. Based on olefin charged. [e] Olefin/30% H_2O_2 /amberlyst 15 (25:50:1). [f] Olefin/30% H_2O_2 / 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 $15^{[17]}$ (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 CF₃SO₃H, 19% when using H₂SO₄, 11% when using C₆H₅SO₃H, and 0% when using CH₃CO₂H. Resin-supported carboxylic acid (amberlite IRC76^[17]) did not work as a catalyst.

This dihydroxylation of olefins proceeds through two steps (Scheme 1): 1) epoxidation of the olefin by H_2O_2 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.^[18,19] 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).^[20]

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_2O_2 (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 nation NR50 was removed by filtration, MnO₂ (ca. 10 mg) was added to the solution. The absence of H₂O₂ was examined by testing with starch-iodide paper. After filtration of MnO₂, the water was removed by evaporation to provide trans-1,2cyclohexanediol^[21] was obtained as a white powder (1.14 g, 98% yield). M.p. 101–102 °C. ¹H NMR (500 MHz, D₂O): $\delta = 1.38$ (br s, 2H), 1.80 (br s, 2H), 2.06 (br s, 1H), 3.50 ppm (br s, 1H); ¹³C NMR (125 MHz, D_2O): $\delta = 76.0$, 33.6, 24.4 ppm. The nation NR50 used above was washed with water $(5 \times 5 \text{ mL})$, and the same dihydroxylation reaction was carried out under the same conditions to give trans-1,2-cyclohexanediol (1.12 g, 96% yield).

Received: August 5, 2003 [Z52568]

Keywords: alkenes · dihydroxylation · green chemistry · hydrogen peroxide · oxidation

- a) Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 12, 4th ed. (Eds.: J. I. Kroscwitz, M. Howe-Grant), Wiley, New York, 1991; b) K. Kulkaand, J. W. Dittrick, Cosmet. Perfum. 1975, 90, 90-95.
- [2] a) M. Hudlicky, Oxidations in Organic Chemistry, American Chemical Society, Washington, DC, **1990**, pp. 174–184 (ACS Monograph Ser. 186); b) A. H. Haines in Comprehensive Organic Synthesis, Vol. 7., 1st ed. (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, **1991**, pp. 437–438; c) J. March, Advanced Organic Chemistry, 4th ed., Wiley, New York, **1992**, pp. 822– 825.
- [3] a) G. Wagner, Ber. Dtsch. Chem. Ges. 1888, 21, 1230-1240;
 b) G. Wagner, Ber. Dtsch. Chem. Ges. 1888, 21, 3347-3355; c) G. Wagner, Ber. Dtsch. Chem. Ges. 1890, 23, 2307-2319; d) A. J. Fatiadi, Synthesis 1989, 85-127.
- [4] a) R. Criegee, *Justus Liebigs Ann. Chem.* 1936, 522, 75–97; b) R. Criegee, B. Marchand, H. Wannowius, *Justus Liebigs Ann. Chem.* 1942, 550, 99–133; c) M. Schröder, *Chem. Rev.* 1980, 80, 187–213.
- [5] K. Akashi, R. E. Palermo, K. B. Sharpless, J. Org. Chem. 1978, 43, 2063–2066.
- [6] D. Swern, Chem. Rev. 1949, 49, 1–68.
- [7] F. Fringuelli, R. Germani, F. Pizzo, G. Savelli, Synth. Commun. 1989, 19, 1939–1943.
- [8] B. M. Trost, Angew. Chem. 1995, 107, 285–307; Angew. Chem. Int. Ed. Engl. 1995, 34, 259–281.
- [9] R. A. Sheldon, Chem. Ind. 1997, 12-15.
- [10] a) J. O. Metzger, Angew. Chem. 1998, 110, 3145-3148; Angew. Chem. Int. Ed. 1998, 37, 2975-2978; b) P. T. Anastas, J. C. Warner, Green Chemistry, Theory and Practice, Oxford University Press, New York, 1998.
- [11] a) K. Sato, M. Aoki, M. Ogawa, T. Hashimoto, R. Noyori, J. Org. Chem. 1996, 61, 8310-8311; b) K. Sato, M. Aoki, J. Takagi, R. Noyori, J. Am. Chem. Soc. 1997, 119, 12386-12387; c) K. Sato, M. Aoki, M. Ogawa, T. Hashimoto, D. Penyella, R. Noyori, Bull. Chem. Soc. Jpn. 1997, 70, 905-915; d) K. Sato, M. Aoki, R. Noyori, Science 1998, 281, 1646-1647; e) K. Sato, J. Takagi, M. Aoki, R. Noyori, Tetrahedron Lett. 1998, 39, 7549-7552; f) K. Sato, M. Aoki, J. Takagi, K. Zimmermann, R. Noyori, Bull. Chem. Soc. Jpn. 1999, 72, 2287-2306; g) K. Sato, M. Hyodo, J. Takagi, M. Aoki, R. Noyori, Tetrahedron Lett. 2000, 41, 1439-1442; h) K. Sato, M. Hyodo, M. Aoki, X.-Q. Zheng, R. Noyori, Tetrahedron 2001, 57, 2469-2476; i) Y. Usui, K. Sato, Green Chem. 2003, 5, 373-375.
- [12] R. Noyori, M. Aoki, K. Sato, Chem. Commun. 2003, 1977-1986.
- [13] For dihydroxylation with aqueous H₂O₂ in acetic acid, see: a) T. P. Hilditch, J. Chem. Soc. **1926**, 1828–1836; in formic acid, see: b) D. Swern, G. N. Billen, T. W. Findley, J. T. Scanlan, J. Am. Chem. Soc. **1945**, 67, 1786–1789; c) A. Roebuck, H. Adkins in Org. Synth. Coll. Vol., Vol. 3 (Ed.: E. C. Horning), Wiley, New York, **1962**, pp. 217–219.
- [14] For H₂WO₄-catalyzed dihydroxylation with H₂O₂, see: a) M. Mugdan, D. P. Young, J. Chem. Soc. 1949, 2988-3000; b) G. B. Payne, C. W. Smith, J. Org. Chem. 1957, 22, 1682-1685; c) V. Singh, P. T. Deota, Synth. Commun. 1988, 18, 617-624; d) T. Oguchi, T. Ura, Y. Ishii, M. Ogawa, Chem. Lett. 1989, 857-860; for the use of a heteropoly acid catalyst, see: e) M. Schwegler, M. Floor, H. van Bekkum, Tetrahedron Lett. 1988, 29, 823-826; f) C. Venturello, M. Gambaro, Synthesis 1989, 295-297; for the use of CH₃ReO₃ as catalyst, see: g) W. A. Herrmann, R. W. Fischer, D. W. Marz, Angew. Chem. 1991, 103, 1706-1708; Angew. Chem. Int. Ed. Engl. 1991, 30, 1638-1641.

Angew. Chem. Int. Ed. 2003, 42, 5623-5625

- [15] For dihydroxylation with H₂O₂ in the presence of (NH₄)₁₀W₁₂O₄₁/hydrotalcite catalyst, see: a) T. Tatsumi, K. Yamamoto, H. Tajima, H. Tominaga, *Chem. Lett.* **1992**, 815–818; For the use of Ti-beta zeolites as catalyst, see: b) A. Corma, M. A. Camblor, P. Esteve, A. Martínez, J. Pérez-Pariente, *J. Catal.* **1994**, 145, 151–158; for the use of Ti-MCM zeolites as catalysts, see: c) A. Corma, M. T. Navarro, J. Pérez-Pariente, *J. Chem. Soc. Chem. Commun.* **1994**, 147–148; d) T. Tatsumi, K. A. Koyano, N. Igarashi, *Chem. Commun.* **1998**, 325–326; for the use of Nb-MCM-41 zeolites as catalyst, see: e) J. Xin, J. Suo, X. Zhang, Z. Zhang, *New J. Chem.* **2000**, *24*, 569–570.
- [16] Nafion resins were first synthesized at DuPont; see: a) D. C. England, US Patent, 2852554, 1958 [*Chem. Abstr.* 1959, 53, 2253]; b) D. J. Conolly, W. F. Gresham, US Patent 3282875, 1966; for a review on the use of nafion for organic syntheses, see: c) G. A. Olah, P. S. Iyer, G. K. Surya Prakash, *Synthesis* 1986, 513–531.
- [17] Amberlyst and amberlite products are ion-exchange resins produced by the ORGANO Corporation.
- [18] S. Vayssié, H. Elias, Liebigs Ann. 1997, 2567-2572.
- [19] One of the referees for this Communication suggested the possibility that H₂O₂ is activated by the resin-supported sulfonic acid through hydrogen-bond formation; for example, see: a) M. C. A. van Vliet, I. W. C. E. Arends, R. A. Sheldon, *Synlett* 2001, 248–250; b) J. Wahlen, D. E. De Vos, P. A. Jacobs, *Org. Lett.* 2003, 5, 1777–1780.
- [20] a) D. Swern, Org. React. 1953, 7, 378-433; b) J. Rebek, Jr., L. Marshall, R. Wolak, J. Org. Chem. 1986, 51, 1649-1653.
- [21] W. D. Emmons, A. S. Pagano, J. P. Freeman, J. Am. Chem. Soc. 1954, 76, 3472–3474.