Oxidation of allylic alcohols to α,β-unsaturated carbonyl compounds with aqueous hydrogen peroxide under organic solvent-free conditions†

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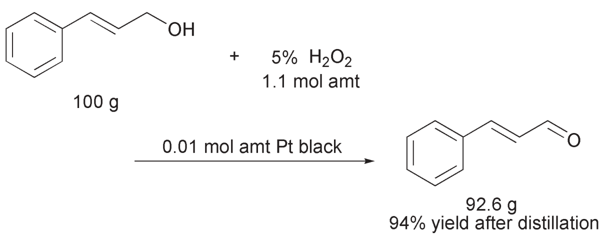
Allylic alcohols are chemoselectively oxidized to α,β-unsaturated carbonyl compounds in high yield with aqueous H_2O_2 in the presence of Pt black catalyst under organic solvent-free conditions. The catalyst is easily recyclable and effective for at least 7 cycles.

Oxidation of alcohols is one of the most frequently used synthetic reactions in the laboratory[1] and in chemical manufacturing.[2] Chemoselective oxidation is important in fine organic syntheses, as well as regio- and stereo-selective oxidation.[3] One of the central issues in chemoselective oxidation is the discrimination between olefinic double bonds and hydroxy groups. In particular, oxidation of allylic alcohols to α,β-unsaturated carbonyl compounds has long been of interest. Various oxidants with high chemoselectivity such as MnO_2 and CrO_3 have been developed, and they are frequently used in organic synthesis.[4] However, the atom efficiency of these oxidants is low, and they form equimolar amounts of the deoxygenated compounds as waste.[5,6] Moreover, use of organic solvents and toxic compounds should be decreased for environment conscious chemical processes. Hydrogen peroxide (H_2O_2) is an ideal oxidant, because the atom efficiency is excellent and water is theoretically the sole co-product.[7] Therefore, we have developed various oxidation reactions with aqueous H_2O_2 under organic solvent-free conditions.[8] The completely chemoselective alcohol oxidation of allylic alcohols with H_2O_2 to generate carbonyl compounds has been little reported, as far as we know.[9] In general, epoxidation of allylic alcohols easily proceeds with H_2O_2.[10] We here report a practical method for the synthesis of α,β-unsaturated carbonyl compounds from the selective oxidation of allylic alcohols using aqueous H_2O_2 catalyzed by easily reusable Pt^0 under organic solvent-free conditions with high yield and selectivity. Although H_2O_2 is generally decomposed in the presence of trace transition metals,[1b] Pt black works surprisingly well as a catalyst in the present method.

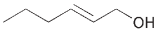
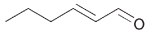
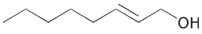
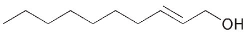
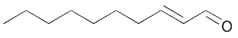
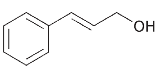
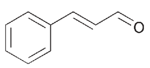
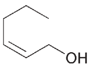
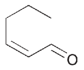
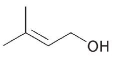
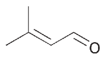
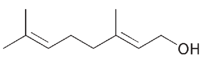
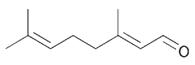
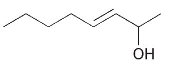
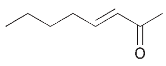
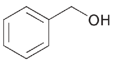
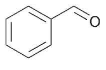
The operation is very simple, even on a hectogram-scale synthesis as shown in Scheme 1. Cinnamyl alcohol (100 g) and a 0.01 molar amount of Pt black were stirred in open air at 90 °C for 10 min, and then a 1.1 molar amount of aqueous 5% H_2O_2 was slowly added dropwise. The mixture was stirred at 90 °C for 3 h to give cinnamaldehyde in a 94% yield (92.6 g). Epoxidation of cinnamyl alcohol was not observed. Without the use of H_2O_2 (under an air atmosphere), cinnamaldehyde was obtained in only <10% yield.[11,12]



Scheme 1 Hectogram-scale oxidation of cinnamyl alcohol.

This chemoselective oxidation system is applicable to various allylic alcohols to yield α,β-unsaturated carbonyl compounds. These results are shown in Table 1. Primary allylic alcohols were chemoselectively oxidized to form the corresponding α,β-unsaturated aldehydes (Entries 1–8). Secondary allylic alcohol also underwent oxidation by H_2O_2 to give the corresponding

Table 1 Oxidation of allylic and benzyl alcohols with aqueous H_2O_2[a]

Entry	Alcohol	Carbonyl compound	Yield (%)[b]
1			81
2			93
3			90
4[c]			94[d]
5			92
6[e]			84
7			91
8[f]			97
9[f,g]			97
10[g]			>99

[a] Unless otherwise stated, reaction was run using alcohol (10 mmol), 5% H_2O_2, and Pt black in a 100 : 110 : 1 molar ratio at 90 °C for 3 h. [b] Determined by GC analysis. Based on alcohol charged. [c] Reaction was run using 100 g of alcohol (0.745 mol). [d] Isolated yield after distillation. [e] Alcohol : H_2O_2 :Pt = 33 : 100 : 1. [f] Alcohol : H_2O_2 : Pt = 33 : 67 : 1. [g] 30% H_2O_2 was used.

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† Electronic supplementary information (ESI) available: experimental procedure and characterization data for compounds. See DOI: 10.1039/b708612a

Table 2 Oxidation of cinnamyl alcohol with H_2O_2 catalyzed by Pt black[a]

Reused number	1	2	3	4	5	6	7
%Yield of cinnamaldehyde[b]	96	92	90	90	91	97	97

[a] Reaction was run using cinnamyl alcohol (10 mmol), 5% H_2O_2, and Pt black in a 30 : 33 : 1 molar ratio at 90 °C for 5 h. [b] Determined by GC analysis. Based on alcohol charged.

α,β-unsaturated ketone (Entry 9). Benzyl alcohol was easily oxidized in this catalytic system (Entry 10). Interestingly, the alcohol oxidation of allylic alcohols having a terminal double bond, like 1-hexen-3-ol, did not proceed at all, nor did epoxidation. While the oxidation of *trans*-2-hexen-1-ol with H_2O_2 catalyzed by Pt black resulted in the formation of *trans*-2-hexenal in a 81% yield (Table 1, Entry 1), the addition of 1-hexen-3-ol or 1-hexene retarded this oxidation of *trans*-2-hexen-1-ol (*trans*-2-hexenal in 43% yield with 1-hexen-3-ol and in 26% yield with 1-hexene). This result indicates that the strong coordination of terminal olefin to Pt^0 largely retards the alcohol oxidation of allylic alcohols.[13] The oxidation of cinnamyl alcohol was completely stopped by the removal of Pt black from the reaction solution. This result indicates that any Pt species that may have leached into the reaction solution were not active homogeneous catalysts.

Pt black catalyst was easily reused in the oxidation of cinnamyl alcohol.[9] After the first alcohol oxidation, the catalyst was filtrated and washed with water, then reused for the second reaction. Seven cycles of oxidation could be catalyzed by reused Pt black without decrease of its catalytic activity. Yields of each reaction were mostly over 90%, as shown in Table 2.

This catalytic chemoselective oxidation of allylic alcohols to form α,β-unsaturated carbonyl compounds is a green method under organic solvent-free conditions. The catalyst is easily reusable with simple manipulation. This green route is straightforward, effective, and environmentally conscious, meeting with the requirements of modern organic synthesis.

Notes and references

1 (*a*) R. A. Sheldon and J. K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, 1981, pp. 350–357; (*b*) M. Hudlicky, *Oxidation in Organic Chemistry*, ACS Monograph Ser. 186, American Chemical Society, Washington, DC, 1990, pp. 114–163; (*c*) G. Procter, in *Comprehensive Organic Synthesis*, ed. B. M. Trost, I. Fleming and S. V. Ley, Academic Press, Oxford, 1st edn., 1991, vol. 7, pp. 251–289, 305–327; (*d*) J. March, *Advanced Organic Chemistry,*, John Wiley & Sons, Inc., New York, 4th edn., 1992; (*e*) R. C. Larock, *Comprehensive Organic Transformations*, John Wiley & Sons, Inc., New York, 2nd edn., 1999, pp. 1646–1650.

2 (*a*) G. Franz and R. A. Sheldon, in *Ullmann's Encyclopedia of Industrial Chemistry*, ed. B. Elvers, S. Hawkins and G. Schulz, VCH, Weinheim, 5th edn., 1991, vol. A18, pp. 261–311; (*b*) S. Caron, R. W. Dugger, S. G. Ruggeri, J. A. Ragan and D. H. B. Ripin, *Chem. Rev.*, 2006, **106**, 2943.

3 R. A. Sheldon, *CHEMTECH*, 1991, 566.

4 For review of alcohol oxidation with MnO_2, see: (*a*) A. J. Fatiadi, *Synthesis*, 1976, 65. Oxidation of allylic alcohol with CrO_2Cl_2, see: (*b*) K. B. Sharpless and K. Akashi, *J. Am. Chem. Soc.*, 1975, **97**, 5927. Oxidation with DMSO–trifluoroacetic acid anhydride, see: (*c*) K. Omura, A. K. Sharma and D. Swern, *J. Org. Chem.*, 1976, **41**, 957. Oxidation with $(C_5H_5NH)_2Cr_2O_7$, see: (*d*) E. J. Corey and G. Schmidt, *Tetrahedron Lett.*, 1979, 399.

5 (*a*) B. M. Trost, *Science*, 1991, **254**, 1471; (*b*) R. A. Sheldon, *Chem. Ind.*, 1992, 903.

6 (*a*) J. O. Metzger, *Angew. Chem., Int. Ed.*, 1998, **37**, 2975; (*b*) P. T. Anastas and J. C. Warner, *Green Chemistry, Theory and Practice*, Oxford University Press, New York, 1998; (*c*) W. M. Nelson, in *Green Chemical Syntheses and Processes*, ed. P. T. Anastas, L. G. Heine and T. C. Williamson, American Chemical Society, Washington, DC, 2000, pp. 313–328; (*d*) M. Eissen, J. O. Metzger, E. Schmidt and U. Schneidewind, *Angew. Chem., Int. Ed.*, 2002, **41**, 414.

7 (*a*) G. Strukul, *Catalytic Oxidations with Hydrogen Peroxide as Oxidant*, Kluwer Academic Publishers, Netherlands, 1992; (*b*) R. Noyori, M. Aoki and K. Sato, *Chem. Commun.*, 2003, 1977.

8 (*a*) K. Sato, M. Aoki, M. Ogawa, T. Hashimoto and R. Noyori, *J. Org. Chem.*, 1996, **61**, 8310; (*b*) K. Sato, M. Aoki, J. Takagi and R. Noyori, *J. Am. Chem. Soc.*, 1997, **119**, 12386; (*c*) K. Sato, M. Aoki, M. Ogawa, T. Hashimoto, D. Penyella and R. Noyori, *Bull. Chem. Soc. Jpn.*, 1997, **70**, 905; (*d*) K. Sato, M. Aoki and R. Noyori, *Science*, 1998, **281**, 1646; (*e*) K. Sato, J. Takagi, M. Aoki and R. Noyori, *Tetrahedron Lett.*, 1998, **39**, 7549; (*f*) K. Sato, M. Aoki, J. Takagi, K. Zimmermann and R. Noyori, *Bull. Chem. Soc. Jpn.*, 1999, **72**, 2287; (*g*) K. Sato, M. Hyodo, J. Takagi, M. Aoki and R. Noyori, *Tetrahedron Lett.*, 2000, 1439; (*h*) K. Sato, M. Hyodo, M. Aoki, X.-Q. Zheng and R. Noyori, *Tetrahedron*, 2001, **57**, 2469; (*i*) Y. Usui and K. Sato, *Green Chem.*, 2003, **5**, 373; (*j*) Y. Usui, K. Sato and M. Tanaka, *Angew. Chem., Int. Ed.*, 2003, **42**, 5623.

9 R. Anderson, K. Griffin, P. Johnston and P. L. Alsters, *Adv. Synth. Catal.*, 2003, **345**, 517.

10 (*a*) T. Hori and K. B. Sharpless, *J. Org. Chem.*, 1978, **43**, 1689; (*b*) C. Venturello and M. Gambaro, *J. Org. Chem.*, 1991, **56**, 5924; (*c*) P. Kumar, R. Kumar and B. Pandey, *Synlett*, 1995, 289; (*d*) I. W. C. E. Arends, R. A. Sheldon, M. Wallau and U. Schuchardt, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1144; (*e*) T. Tatsumi, K. A. Koyano and N. Igarashi, *Chem. Commun.*, 1998, 325; (*f*) I. W. C. E. Arends and R. A. Sheldon, *Top. Catal.*, 2002, **19**, 133.

11 A complex mixture containing benzaldehyde, benzoic acid, and other carboxylic acids was formed.

12 Although the oxidation of cinnamyl alcohol to cinnamaldehyde with O_2 (or air) has been reported, organic solvents and/or base are necessary to achieve high yield and selectivity:(*a*) T. Mallat and A. Baiker, *Chem. Rev.*, 2004, **104**, 3037; (*b*) M. Matsumoto and N. Watanabe, *J. Org. Chem.*, 1984, **49**, 3435; (*c*) J.-E. Bäckvall, R. L. Chowdhury and U. Karlsson, *J. Chem. Soc., Chem. Commun.*, 1991, 473; (*d*) K. Kaneda, M. Fujii and K. Morioka, *J. Org. Chem.*, 1996, **61**, 4502; (*e*) I. E. Markó, P. R. Giles, M. Tsukazaki, S. M. Brown and C. J. Urch, *Science*, 1996, **274**, 2044; (*f*) G.-J. ten Brink, I. W. C. E. Arends and R. A. Sheldon, *Science*, 2000, **287**, 1636; (*g*) A. F. Lee, J. J. Gee and H. J. Theyers, *Green Chem.*, 2000, **2**, 279; (*h*) K. Yamaguchi and N. Mizuno, *Angew. Chem., Int. Ed.*, 2002, **41**, 4538; (*i*) K. Mori, K. Yamaguchi, T. Hara, T. Mizugaki, K. Ebitani and K. Kaneda, *J. Am. Chem. Soc.*, 2002, **124**, 11572; (*j*) A. Abad, P. Concepción, A. Corma and H. García, *Angew. Chem., Int. Ed.*, 2005, **44**, 4066; (*k*) D. I. Enache, J. K. Edwards, P. Landon, B. S. -Espriu, A. F. Carley, A. A. Herzing, M. Watanabe, C. J. Kiely, D. W. Knight and G. J. Hutchings, *Science*, 2006, **311**, 362; (*l*) G. An, M. Lim, K.-S. Chun and H. Rhee, *Synlett*, 2007, 95.

13 Coordination ability of terminal double bond to Ni^0 complex, see: C. A. Tolman, *J. Am. Chem. Soc.*, 1974, **96**, 2780.