



Supporting Information

© Wiley-VCH 2005

69451 Weinheim, Germany

Convenient and Efficient Palladium-Catalyzed Regioselective Oxyfunctionalization of Terminal Olefins Using Molecular Oxygen as Sole Reoxidant

Takato Mitsudome, Takuya Umetani, Naoya Nosaka, Kohsuke Mori, Tomoo Mizugaki, Kohki Ebitani, and Kiyotomi Kaneda*

*Department of Materials Engineering Science, Graduate School of Engineering Science,
Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan
Phone and Fax: +81-6-6850-6260, E-mail: kaneda@cheng.es.osaka-u.ac.jp*

General

Pd compounds were obtained from N. E. Chemcat Co. Ltd. Olefins as substrate and solvents were purchased from Tokyo Kasei and Aldrich, and purified by the standard procedures prior to experiments. All of the oxidation products are well known compounds, which identities were confirmed by NMR and MS spectra comparison with the literature data.

Experimental Section

A typical example for Wacker oxidation: Into a reaction vessel equipped with a reflux condenser and a rubber balloon were placed PdCl₂ (5×10^{-3} mmol), DMA (5 mL), and H₂O (0.3 mL). This mixture was heated at 80 °C under atmospheric O₂ pressure for 4 h. After addition of 1-decene (0.5 mmol), the mixture was vigorously stirred at 80 °C for 6

h. GC analysis of the solution using naphthalene as an internal standard showed an 84 % yield of 2-decanone as the sole product.

A typical example for Wacker-type intramolecular cyclization: Into a 100 mL stainless steel autoclave were placed PdCl₂ (5×10^{-3} mmol), 2-allylphenol (1 mmol), DMA (3 mL), and sodium acetate (0.1 mmol). The mixture was then pressurized to 6 atm with O₂ and the reaction mixture was vigorously stirred at 80 °C for 4 h. GC analysis of the solution using naphthalene as an internal standard showed a 95 % yield of 2-methylbenzofuran as the sole product.

A typical example for acetoxylation: Into a 100 mL stainless steel autoclave were placed PdCl₂ (1×10^{-2} mmol), 1-decene (1 mmol), acetic acid (0.2 mL), DMA (5 mL), sodium acetate (0.2 mmol), and 4Å molecular sieves (0.2 g), and the mixture was pressurized to 6 atm with O₂. The reaction mixture was vigorously stirred at 80 °C for 40 h. GC analysis of the solution using naphthalene as an internal standard showed an 80 % yield, with 93 % selectivity, of acetic acid 2-decenyl ester.

After the above reactions, the products were extracted using a 1:1 diethylether/water mixture (2 x 30 mL). The diethylether layers containing the products were dried over MgSO₄, filtrated and concentrated under reduced pressure. The resultant crude mixture was purified by column chromatography (silica gel), using an 1:4 EtOAc/hexane mixture as eluent, to obtain the pure oxidized products.

NMR data for Table 2

Entry 5: 2-hexadecanone

¹H NMR (400 MHz, CDCl₃) δ 2.41 (t, *J*=7.4 Hz, 2H), 2.13 (s, 3H), 1.55-1.59 (m, 2H), 1.26-1.41(br, 22H), 0.88 (t, *J*=6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 43.9, 32.0,

29.8, 29.7, 29.7, 29.7, 29.6, 29.5, 29.4, 29.3, 24.0, 22.8, 14.2.

Entry 6: 2-eicosanone

^1H NMR (400 MHz, CDCl_3) δ 2.41 (t, $J=7.4$ Hz, 2H), 2.13 (s, 3H), 1.53-1.59 (m, 2H), 1.26 (br, 30H), 0.88 (t, $J=6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 43.9, 32.0, 29.8, 29.7, 29.6, 24.0, 22.3, 14.2.

Entry 7: 2,7-octan-dione

^1H NMR (400 MHz, CDCl_3) δ 2.41-2.48 (m, 4H), 2.14 (s, 6H), 1.51-1.57 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.3, 43.4, 29.9, 23.2.

Entry 8: 10-oxo-undecanoic acid methyl ester

^1H NMR (400 MHz, CDCl_3) δ 3.66 (s, 3H), 2.41 (t, $J=7.6$ Hz, 2H), 2.29 (t, $J=7.6$ Hz, 2H), 2.13 (s, 3H), 1.54-1.61 (m, 4H), 1.23-1.30 (m, 8H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.7, 173.9, 51.3, 43.6, 34.0, 29.7, 29.1, 29.0, 29.0, 28.9, 24.9, 23.8.

Entry 9: 5-oxo-hexanenitrile

^1H NMR (400 MHz, CDCl_3) δ 2.64 (t, $J=6.9$ Hz, 2H), 2.42 (t, $J=6.9$ Hz, 2H), 2.17 (s, 3H), 1.91 (t, $J=6.8$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 206.3, 119.0, 41.2, 30.0, 19.3, 16.4.

Entry 10: 10-hydroxy-2-Decanone

^1H NMR (400 MHz, CDCl_3) δ 3.61 (t, $J=6.6$ Hz, 2H), 2.55 (br, 1H), 2.42 (t, $J=7.3$ Hz, 2H), 2.13 (s, 3H), 1.54-1.64 (br, 4H), 1.31 (br, 8H); ^{13}C NMR (100 MHz, CDCl_3) δ

209.1, 62.6, 43.7, 32.6, 29.7, 29.2, 29.1, 29.0, 25.6, 23.8.

Entry 12: 2-(2-oxopropyl)-cyclohexanone

^1H NMR (400 MHz, CDCl_3) δ 2.89-3.02 (m, 2H), 2.34-2.40 (m, 2H), 2.20 (s, 3H), 2.05-2.14 (m, 2H), 1.61-1.90 (m, 3H) 1.34-1.39 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 211.1, 207.0, 46.4, 43.2, 41.8, 34.0, 30.4, 27.9, 25.3.

Entry 13: 1-phenyl-2-propanone

^1H NMR (400 MHz, CDCl_3) δ 7.18-7.46 (m, 5H), 3.69 (s, 2H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 206.2, 134.2, 129.3, 129.0, 128.7, 128.4, 127.0, 51.1, 29.3.

NMR data for Table 3

Entry 2: 2-eicosen-1-ol acetate

^1H NMR (400 MHz, CDCl_3) δ 5.72-5.78 (m, 1H), 5.52-5.58 (m, 1H) 4.50 (d, $J=6.3$ Hz, 2H), 2.00-2.05 (m, 3H), 1.20-1.30 (m, 30H), 0.88 (t, $J=6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 136.5, 123.8, 65.2, 32.3, 32.0, 29.8, 29.7, .29.7, 29.7, 29.5, 29.4, 29.2, 29.0, 22.7, 21.0, 14.1.

Entry 3: 2,7-Octadien-1-ol acetate

^1H NMR (400 MHz, CDCl_3) δ 5.73-5.82 (m, 2H), 5.55-5.60 (m, 1H), 4.94-5.02 (m, 2H), 4.50 (d, $J = 6.3$ Hz, 2H), 2.02-2.14 (m, 8H), 1.45-1.50 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.7, 138.4, 136.0, 124.1, 114.6, 65.2, 33.1, 31.6, 28.1, 21.0.

2,6-Octadiene-1,8-diol diacetate

^1H NMR (400 MHz, CDCl_3) δ 5.72-5.78 (m, 2H), 5.21-5.61 (m, 2H), 4.50 (d, $J = 6.3$

Hz, 4H), 2.01-2.20 (m, 14H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.6, 134.9, 124.5, 65.0, 31.5, 21.0

Entry 4

11-(acetyloxy)-9-undecenoic acid methyl ester

^1H NMR (400 MHz, CDCl_3) δ 5.71-5.79 (m, 1H), 5.52-5.60 (m, 1H), 4.50 (d, $J=6.3$ Hz, 2H), 3.66 (s, 3H), 2.30(t, $J=7.4$ Hz, 2H), 2.05 (s, 3H), 2.04 (s, 2H), 1.61 (t, $J=7.3$ Hz, 2H), 1.25-1.37 (m, 10H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.3, 174.1, 136.4, 123.7, 65.3, 51.4, 34.1, 32.2, 29.1, 29.1, 29.1, 29.0, 28.8, 25.0, 21.1.

Entry 5

5-cyano-2-penten-1-ol acetate

^1H NMR (400 MHz, CDCl_3) δ 5.70-5.80 (m, 2H), 4.55 (d, $J=4.9$ Hz, 2H), 2.38-2.47 (m, 4H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.5, 130.5, 127.3, 118.8, 64.2, 28.0, 20.9, 17.0.

Entry 6

2-cyclohexylidene-ethanol acetate

^1H NMR (400 MHz, CDCl_3) δ 5.28 (t, $J=7.2$ Hz, 1H), 4.58 (t, $J=7.2$ Hz, 2H), 2.05 (s, 3H), 1.55-1.80 (m, 8H), 1.20-1.31 (m, 2H).

1-cyclohexene-1-ethanol acetate

^1H NMR (400 MHz, CDCl_3) δ 5.65 (m, 1H), 4.10-4.57 (m, 2H), 2.20-2.22 (m, 2H), 2.10-2.14 (m, 2H), 2.04 (s, 3H), 1.97 (m, 2H), 1.55-1.80 (m, 4H).

Entry 7

3-(1,4-dioxaspiro[4.5]dec-6-yl)-2-Propen-1-ol acetate

^1H NMR (400 MHz, CDCl_3) δ 5.80 (dd, $J = 15.6, 7.6$ Hz, 1H), 5.61 (dt, $J = 15.6, 6.2$ Hz, 1H), 4.52 (d, $J = 6.3$ Hz, 2H), 3.85-3.95 (m, 4H), 2.29-2.34 (m, 1H), 2.05 (s, 3H), 1.23-1.76 (m, 8H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.6, 135.0, 125.1, 109.8, 65.2, 65.1, 64.8, 48.2, 35.2, 30.0, 24.3, 23.8, 21.0.

General procedure for Wacker oxidation by Pd sponge: Preparation of Pd sponge is as follows. A mixture of PdCl_2 and 0.082 M of HCl aqueous solution (100 mL) was allowed to stir at room temperature until it became homogeneous, at which time the mixture was heated to 60 °C, followed by addition of sodium formate (3.3 g). The obtained solid was filtered, washed with deionized hot water (50 mL \times 4), and dried under vacuum to give Pd sponge.^[1] Into a reaction vessel equipped with a reflux condenser and balloon were placed Pd sponge (5×10^{-3} mmol), DMA (5 mL), and 0.033 M of HCl aqueous solution (0.3 mL). The mixture was heated to 80 °C under atmospheric O_2 pressure for 4 h. After addition of 1-decene (0.5 mmol), the reaction mixture was vigorously stirred at 80 °C for 8 h. GC analysis of the solution using naphthalene as an internal standard showed a 76 % yield of 2-decanone as the sole product.

X-ray absorption fine structure (XAFS) measurements: Pd K-edge X-ray absorption spectra were recorded at room temperature using a fluorescence-yield collection technique at the beam line 01B1 station attached with Si (311) monochromator (2004B0260-NXa-np). The yield was collected using the 19-element solid-state detector.

Details of data analysis are referred to the reported procedure, see: T. Yamamoto, T. Tanaka, S. Takenaka, S. Yoshida, T. Onari, Y. Takahashi, T. Kosaka, S. Hasegawa, and M. Kudo, *J. Phys. Chem. B*, **1999**, *103*, 2385.

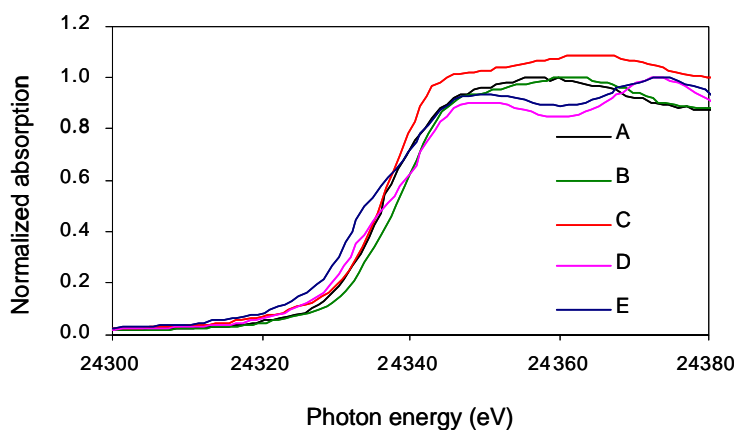


Figure 1S. Pd K-edge XANES spectra of (A) PdCl₂ after Wacker oxidation under the standard conditions, (B) Pd sponge after treatment with DMA in the presence of two equivalents of HCl at 80 °C under atmospheric O₂ for 4 h, (C) PdCl₂, (D) the fresh Pd sponge, and (E) Pd foil.

To gain insight into the oxidation states and structures of the Pd species in the catalytic solutions, the Pd K-edge XANES/EXAFS analyses were performed. Figure 1S shows the XANES spectra for (A) PdCl₂ after Wacker oxidation under the standard conditions and (B) Pd sponge after treatment with DMA in the presence of two equivalents of HCl at 80 °C under atmospheric O₂ for 4h, together with (C) PdCl₂, (D) the fresh Pd sponge, and (E) Pd foil as reference samples. The shapes of the XANES spectra and the edge positions in A and B were identical to those of C but differed from those of D and E, which reveals that all Pd species for A and B are in 2+ oxidation state. The Fourier transforms (FT) of k^3 -weighted EXAFS data are depicted in Figure 2S. No peaks due to Pd-Pd bond and Pd-O-Pd bonds were observed for A and B, which shows that monomeric Pd(II) species were formed in DMA.

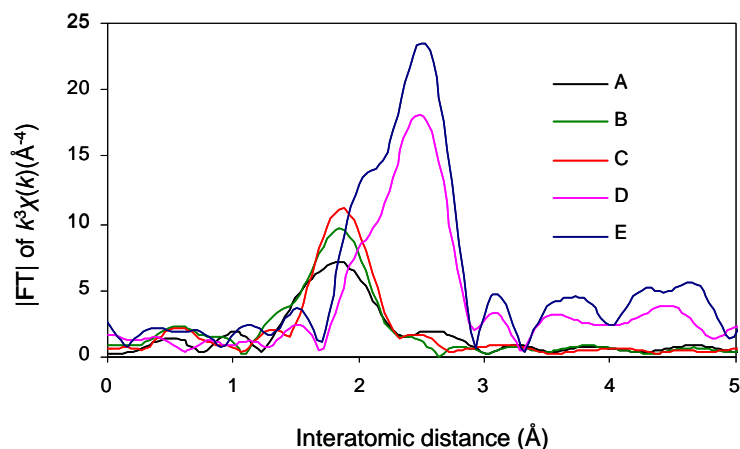


Figure 2S. Fourier transforms of k^3 -weighted Pd K-edge EXAFS experimental data for (A) PdCl₂ after Wacker oxidation under the standard conditions, (B) Pd sponge after treatment with DMA in the presence of two equivalents of HCl at 80 °C under atmospheric O₂ for 4 h, (C) PdCl₂, (D) the fresh Pd sponge, and (E) Pd foil.

Recycling experiments for the Wacker oxidation: Fresh reaction using 1-decene (0.5 mmol), DMA (5 mL), H₂O (0.3 mL) and PdCl₂ (5×10^{-3} mmol) were carried out at 80 °C under atmospheric O₂ pressure. After 6 h, the reaction mixture was cooled to a room temperature, and washed with *n*-heptane (5mL \times 2). The *n*-heptane phase was decanted, and another portion of 1-decene (1 mmol) was successively added into the Pd-DMA phase, followed by stirring under identical reaction conditions.

Kinetic study for the Wacker oxidation in DMA solvent: A typical procedure is as follows: Into a 100 mL of stainless steel autoclave were placed PdCl₂ (5×10^{-3} mmol), 1-decene (2 mmol), H₂O (0.5 mL), and DMA (5 mL), and the mixture was pressurized to 6 atm with O₂. The reaction mixture was vigorously stirred at 80 °C.

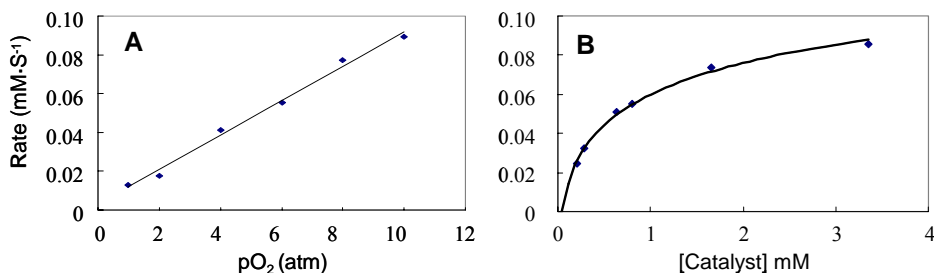
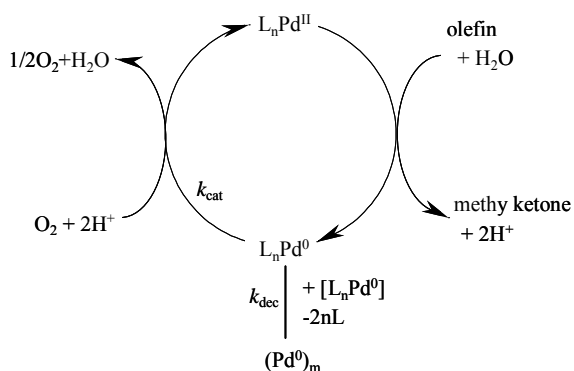


Figure 3S. Initial rate dependence on (A) initial O₂ pressure, and (B) catalyst concentrations.

The initial oxidation rate of 1-decene (R_0) was proportional to O₂ pressure and independent on 1-decene, H₂O, and H⁺ concentrations. The R_0 is also dependent on the concentrations of PdCl₂, but is asymptotic at high concentrations (Figure 3S). From these observations, we adopted

Scheme 1S. Proposed catalytic cycle



the following reaction mechanism proposed by Stahl et al. for Pd-catalyzed aerobic oxidations (Scheme 1S). Initially, a L_nPd^{II} reacts with an olefin and H₂O to afford the corresponding methyl ketone and a reduced L_nPd^0 species. The oxidation of the L_nPd^0 by O₂ regenerates the L_nPd^{II} along with the formation of H₂O. In the present catalytic cycle, the reoxidation step of L_nPd^0 (k_{cat}) competes with its decomposition step into inactive Pd⁰ metal (k_{dec}). The oxidation of L_nPd^0 species by O₂ may afford H₂O₂, which is easily decomposed into H₂O and O₂.^[2]

In a separate experiment, the stoichiometric Wacker oxidation of 1-decene by PdCl₂ took place within seconds under an Ar atmosphere, i.e., much faster than the initial catalytic turnover rates, which is consistent with the lack of rate dependence on both 1-decene, H₂O and H⁺ concentrations. Therefore, the oxidation of the L_nPd^0 is a

rate-determining step. Based on the above results, the following kinetic equations could be obtained.

$$R_0 = k_{\text{cat}} p\text{O}_2 \cdot [\text{Pd}]_t$$

$$[\text{Pd}]_0 = [\text{Pd}]_t + [(\text{Pd}^0)_m]$$

$$d[(\text{Pd}^0)_m]/dt = k_{\text{dec}}([\text{Pd}]_t)^2$$

The R_0 for the Wacker oxidation of 1-decene then could be expressed as

$$R_0 = k_{\text{cat}} p\text{O}_2 \cdot [\text{Pd}]_0 / (1 + [\text{Pd}]_0 k_{\text{dec}} \cdot t)$$

A linear plot of $p\text{O}_2/R_0$ versus $1/[\text{Pd}]_0$ showed that the values of k_{cat} and k_{dec} at 80 °C in DMA were determined to be $0.02 \text{ M}^{-1}\text{sec}^{-1}$ and $1.81 \text{ M}^{-1}\text{sec}^{-1}$, respectively. On the other hand, the values of k_{cat} and k_{dec} at 80 °C in DMF were determined to be $0.0033 \text{ M}^{-1}\text{sec}^{-1}$ and $0.69 \text{ M}^{-1}\text{sec}^{-1}$, respectively.

Cyclic voltammetry measurement: Cyclic voltammetry of palladium (10 mM) in various solvents (containing 0.3 M *n*-Bu₄NBF₄) were recorded with a potentiostat, NPOT-2501, and a wave-form generator (Figure 4S). Experiments were carried out in a three-electrode cell connected to a Schlenk line. The cyclic voltammetry was performed at a platinum wire of ca. 1 cm² apparent surface area with a scan rate of 0.2 Vs⁻¹. The counter electrode was also platinum wire; the reference was a saturated calomel electrode separated from the solution by a bridge (12 mL) filled with a saturated aqueous KCl solution.

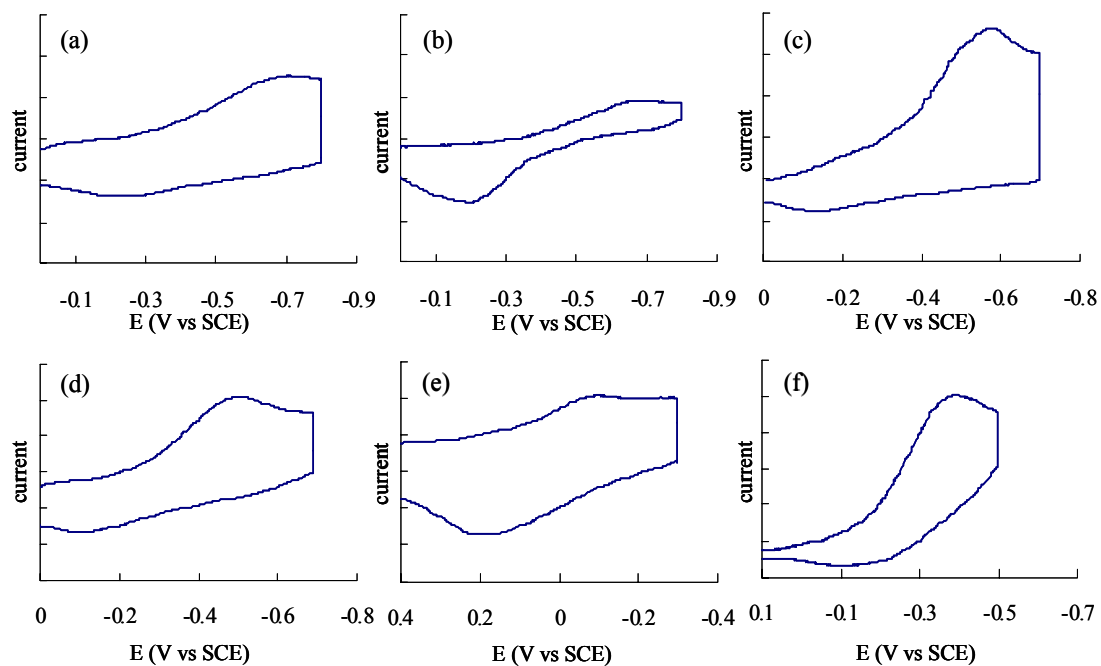


Figure 4S. Cyclic voltammetry of palladium in various solvents. (a) DMA, (b) NMP, (c) DMPA, (d) DMF, (e) EtOH, (f) MeCN.

References

- [1] T. Hosokawa, S. Miyagi, S-I, Murahashi, A. Sonoda, *J. Org. Chem.* **1978**, *43*, 2752.
- [2] B. A. Steinhoff, S. R. Fix, S. S. Stahl, *J. Am. Chem. Soc.* **2002**, *124*, 766.