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Oxidation of Allylic Alcohols to α,β -Unsaturated Carbonyl Compounds with Aqueous Hydrogen Peroxide under Organic Solvent-Free Conditions

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1. Instrumentation and Chemicals

^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on JEOL winLambda-500 NMR spectrometers. Chemical shifts (δ) are in parts per million relative to tetramethylsilane at 0.00 ppm for ^1H and relative to residual CHCl_3 at 77.0 ppm for ^{13}C unless otherwise noted. Gas chromatographic (GC) analyses were performed on a Shimadzu GC-17A using an TC-FFAP column (0.25 mm x 30 m, GL Sciences Inc.).

All materials were used as received. Cinnamyl alcohol, *trans*-2-hexen-1-ol, *trans*-2-octen-1-ol, *trans*-2-decen-1-ol, *cis*-2-hexen-1-ol, 3-methyl-2-buten-1-ol, geraniol, *trans*-3-octen-2-ol, benzyl alcohol, 1-hexen-3-ol, 1-octen-4-ol, 2-hexanol, 2-octanol were obtained from Tokyo Chemical Industry Co., Ltd. 2-Butanol and cyclohexanol were obtained

from Wako Pure Chemicals Ind., Ltd. 30% Hydrogen peroxide was obtained from Kanto Chemical Co., Inc. 6-Methyl-5-hepten-2-ol was obtained from Aldrich Chemical Co. Platinum black was obtained from N. E. CHEMCAT Co.

2. Experimental Procedure

Typical procedure (hectogram-scale oxidation of cinnamyl alcohol)

A 1-liter round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser was slowly charged with 100 g (0.745 mol) of cinnamyl alcohol and 1.45 g (7.45 mmol) of Pt black. After the mixture was vigorously stirred at 90 °C for 10 min, 558 g (0.820 mol) of aqueous 5% H₂O₂ was added dropwise. The mixture was heated at 90 °C for 3 h, and then cooled to room temperature. The organic phase was separated and washed with 50 mL of saturated aqueous Na₂S₂O₃. After distillation, 92.6 g (0.701 mol, 94% yield) of cinnamaldehyde was obtained as a colorless liquid.

General Procedure for oxidation of allylic alcohol

A 30-mL round bottomed flask equipped with a magnetic stirring bar and a reflux condenser was charged with 10.0 mmol of allylic alcohol and 19.5 mg (0.100 mmol) of Pt black. After the mixture was vigorously stirred at 90 °C for 10 min, 7.48 g (11.0 mmol) of aqueous 5% H₂O₂ was added dropwise over the course of 1 h. The mixture was heated at 90 °C for 2 h, and then cooled to room temperature. The organic phase was separated and washed with 2.5 mL of saturated aqueous Na₂S₂O₃. The conversion and yield were determined by running the reaction with 4 mmol of internal standard, typically biphenyl.

3. Characterization Data for Compounds

Cinnamaldehyde¹: b.p. 104 °C/7 mmHg; ¹H NMR (CDCl₃): δ 6.52 (dd, 1H, *J* = 15.9, *J* = 7.6 Hz), 7.21–7.26 (m, 4H), 7.34–7.37 (m, 2H); 9.51 (d, 1H, *J* = 7.6 Hz); ¹³C NMR (CDCl₃) δ 128.4, 129.2, 131.1, 133.9, 152.8, 193.5.

trans-2-Hexenal²: ¹H NMR (CDCl₃): δ 0.96 (t, 3H, *J* = 8.8 Hz), 1.49–1.57 (m, 2H), 2.27–2.34 (m, 2H), 6.11 (ddt, 1H, *J* = 1.4, *J* = 7.9, *J* = 15.6 Hz), 6.84 (dt, 1H, *J* = 6.7, *J* = 15.6 Hz), 9.50 (d,

1H, $J = 7.9$ Hz); ^{13}C NMR (CDCl_3) δ 13.6, 21.1, 34.6, 133.0, 158.5, 193.9.

trans-2-Octenal³: ^1H NMR (CDCl_3): δ 0.91 (t, 3H, $J = 7.8$ Hz), 1.29–1.37 (m, 4H), 1.47–1.55 (m, 2H), 2.30–2.37 (m, 2H), 6.12 (ddt, 1H, $J = 1.4$, $J = 6.9$, $J = 15.4$ Hz), 6.86 (dt, 1H, $J = 6.7$, $J = 15.4$ Hz), 9.51 (d, 1H, $J = 6.9$ Hz); ^{13}C NMR (CDCl_3) δ 13.9, 22.3, 27.5, 31.3, 32.6, 132.9, 158.8, 193.9.

trans-2-Decenal⁴: ^1H NMR (CDCl_3): δ 0.89 (t, 3H, $J = 6.7$ Hz), 1.25–1.35 (m, 8H), 1.45–1.53 (m, 2H), 2.30–2.37 (m, 2H), 6.12 (dd, 1H, $J = 7.9$, $J = 15.6$ Hz), 6.86 (dt, 1H, $J = 6.9$, $J = 15.6$ Hz), 9.51 (d, 1H, $J = 7.9$ Hz); ^{13}C NMR (CDCl_3) δ 14.0, 22.6, 27.9, 29.0, 29.1, 31.7, 32.7, 132.9, 158.7, 193.8.

cis-2-Hexenal⁵: ^1H NMR (CDCl_3): δ 0.94 (t, 3H, $J = 6.2$ Hz), 1.46–1.58 (m, 2H), 2.18–2.23 (m, 2H), 5.90–6.05 (m, 1H), 6.60 (dt, 1H, $J = 6.7$, $J = 15.4$ Hz), 10.05 (d, 1H, $J = 7.9$ Hz); ^{13}C NMR (CDCl_3) δ 13.6, 21.0, 34.6, 130.0, 153.0, 191.1.

3-Methyl-2-butenal⁶: ^1H NMR (CDCl_3): δ 1.99 (s, 3H), 2.18 (s, 3H), 5.89 (dq, 1H, $J = 6.7$, $J = 2.4$ Hz), 9.96 (d, 1H, $J = 6.7$ Hz); ^{13}C NMR (CDCl_3) δ 18.9, 28.1, 128.1, 160.3, 190.8.

3,7-Dimethylocta-2E,6-dienal (Geranial)⁷: ^1H NMR (CDCl_3): δ 1.61 (s, 3H), 1.69 (s, 3H), 2.17 (s, 3H), 2.17–2.26 (m, 4H), 5.00–5.10 (m, 1H), 5.88 (d, 1H, $J = 8.5$ Hz), 10.00 (d, 1H, $J = 8.5$ Hz); ^{13}C NMR (CDCl_3) δ 17.7, 17.8, 25.7, 25.8, 40.6, 122.5, 127.4, 132.9, 163.9, 191.3.

trans-3-Octen-2-one⁸: ^1H NMR (CDCl_3): δ 0.91 (t, 3H, $J = 7.0$ Hz), 1.35 (tq, 2H, $J = 7.0$, $J = 7.2$ Hz), 1.43–1.47 (m, 2H), 2.10–2.25 (m, 5H), 6.07 (dt, 1H, $J = 1.5$, $J = 15.8$ Hz), 6.80 (dt, 1H, $J = 6.7$, $J = 15.8$ Hz); ^{13}C NMR (CDCl_3) δ 13.8, 22.2, 26.7, 30.2, 32.1, 131.3, 148.5, 198.6.

Benzaldehyde⁹: ^1H NMR (CDCl_3): δ 7.53 (dd, 2H, $J = 7.5$, $J = 7.8$ Hz), 7.63 (dt, 1H, $J = 1.5$, $J = 7.5$ Hz), 7.88 (dd, 2H, $J = 1.5$, $J = 7.8$ Hz), 10.03 (s, 1H); ^{13}C NMR (CDCl_3) δ 128.9, 129.7, 134.4, 136.4, 192.3.

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