Supporting Information
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Supporting information for

**An effective catalytic epoxidation of terpenes with hydrogen peroxide under organic solvent-free conditions**

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**Instrumentation and Chemicals**

$^1$H (400 MHz) and $^{13}$C NMR (100 MHz) spectra were recorded on a JEOL ECX-400P spectrometer using CDCl$_3$ as solvent. Chemical shifts (δ) are reported in parts per million relative to internal tetramethylsilane at 0.00 ppm for $^1$H and relative to residual CHCl$_3$ at 77.0 ppm for $^{13}$C. Gas chromatographic (GC) analyses were performed on a Shimadzu GC-17A instrument using a TC-1 column (0.25 mm × 30 m, GL Sciences Inc.).

α-Pinene, 1-metyl-1-cyclohexene, 3-carene, α-terpineol, limonene, β-caryophyllene, and PhP(O)(OH)$_2$ were obtained from Tokyo Chemical Industry Co., Ltd. β-Myrcene were obtained from Wako Pure Chemicals Ind., Ltd. Na$_2$WO$_4$·2H$_2$O and H$_3$PO$_4$ were obtained from Kanto Chemical Co., Inc. NH$_2$CH$_2$P(O)(OH)$_2$, MeP(O)(OH)$_2$, EtP(O)(OH)$_2$, n-PrP(O)(OH)$_2$, and t-BuP(O)(OH)$_2$ were obtained from Aldrich Chemical Co. Aqueous hydrogen peroxide (60%) was obtained from Mitsubishi Gas Chemical. All materials were used as received except for β-myrcene which was distilled prior to use. [CH$_3$](n-C$_8$H$_{17}$)$_3$N]HSO$_4$ was prepared from [CH$_3$](n-C$_8$H$_{17}$)$_3$N]Cl (Tokyo Chemical Industry) and aqueous H$_2$SO$_4$.

**Experimental Procedure**

**Typical procedure for epoxidation of α-pinene**

A test tube equipped with a magnetic stirring bar was charged with α-pinene (409 mg, 3.00 mmol), 60% H$_2$O$_2$ (221 mg, 3.9 mmol), Na$_2$WO$_4$·2H$_2$O (79.1 mg, 0.24 mmol), [CH$_3$](n-C$_8$H$_{17}$)$_3$N]HSO$_4$ (112 mg, 0.24 mmol), PhP(O)(OH)$_2$ (19.0 mg, 0.12 mmol), and 3 M aqueous NaOH (60 μL, 0.18 mmol). The mixture was vigorously stirred at 25 °C for 12 h and extracted with toluene. The conversion and yield were determined by GC analysis of the toluene solution with ca. 0.2 mmol of biphenyl as internal standard.

**Hectogram-scale epoxidation of 3-carene**
To 60% H₂O₂ (54.1 g, 0.953 mol) in a 1-L round-bottomed flask cooled in an ice water bath was slowly added Na₂WO₄·2H₂O (9.69 g, 29.4 mmol), PhP(O)(OH)₂ (2.32 g, 14.7 mmol), [CH₃(n-C₈H₁₇)₃N]HSO₄ (13.7 g, 29.4 mmol), and NaOH (1.17 g, 29.4 mmol). While the mixture was cooled at 0 °C, 3-carene (100 g, 0.734 mol) was added dropwise. The mixture was gradually warmed to 25 °C with vigorous stirring. After 12 h, the two phases were separated, and the organic phase was washed with 10% aqueous sodium thiosulfate. Distillation of the organic phase under reduced pressure gave 3-carene oxide as a colorless oil, yield 97.6 g (87%).

Epoxidation of α-pinene under pH-controlled conditions

To 60% H₂O₂ (5.41 g, 95.3 mmol) in a test tube equipped with a magnetic stirring bar was added Na₂WO₄·2H₂O (1.94 g, 5.88 mmol), PhP(O)(OH)₂ (464 mg, 2.94 mmol) or NH₂CH₂P(O)(OH)₂ (326 mg, 2.94 mmol), and 3 M NaOH (1.47 mmol, 4.41 mmol). The pH of the solution was adjusted to 7.0 with additional aqueous NaOH. Then [CH₃(n-C₈H₁₇)₃N]HSO₄ (2.74 g, 5.88 mmol) and α-pinene (10.0 g, 73.4 mmol) were added. Then the procedure followed the above. Conversion and yield were determined by GC analyses (with biphenyl as internal standard) instead of an isolation of the product.

Characterization Data for Compounds

α-Pinene oxide:¹ ¹H NMR δ 0.94 (s, 3H), 1.29 (s, 3H), 1.34 (s, 3H), 1.62 (d, J = 9.6 Hz, 1H), 1.70–1.75 (br m, 1H), 1.87–2.03 (m, 4H), 3.07 (dd, J = 4.1, 1.4 Hz); ¹³C NMR δ 20.2, 22.4, 25.9, 26.7, 27.6, 39.7, 40.5, 45.1, 56.9, 60.3.

1,2-Epoxy-1-methylcyclohexane:² ¹H NMR δ 1.13–1.28 (m, 2H), 1.30 (s, 3H), 1.36–1.47 (m, 2H), 1.63–1.70 (m, 1H), 1.80–1.93 (m, 3H), 2.95 (d, J = 3.2 Hz, 1H); ¹³C NMR δ 19.6, 20.0, 24.0, 24.7, 29.9, 57.5, 59.5.

3,4-Epoxycarane:³ bp 35 °C/4.5 mmHg; ¹H NMR δ 0.44 (td, J = 9.1, 2.3 Hz, 1H), 0.52 (td, J = 9.1, 2.3 Hz, 1H), 0.72 (s, 3H), 1.00 (s, 3H), 1.25 (s, 3H), 1.48 (dd, J = 16.5, 2.3 Hz, 1H), 1.63 (dt, J = 16.5, 2.3 Hz, 1H), 2.13 (dd, J = 16.5, 9.2 Hz, 1H), 2.29 (dd, J = 16.5, 9.2, 1.8 Hz, 1H), 2.82 (s, 1H); ¹³C NMR δ 13.8, 14.6, 16.0 (2C), 19.2, 23.1, 23.3, 27.7, 55.9, 58.2.

α-Terpinol epoxide:⁴ 1:1 mixture of cis- and trans-epoxides; ¹H NMR δ 1.01 (qd, J = 12.3, 6.9 Hz, 1H), 1.13 (s, 3H), 1.141 (s, 3H), 1.144 (s, 3H), 1.16 (s, 3H), 1.313 (s, 3H), 1.315 (s, 3H), 1.43–1.54 (m, 3H), 1.58–1.69 (m, 3H), 1.79–1.94 (m, 2H), 2.00–2.08 (m, 2H), 2.19–2.24 (m, 1H), 3.00 (d, J = 5.5 Hz, 1H), 3.07 (br s, 1H); ¹³C NMR δ 20.1, 22.8, 22.9, 24.4, 25.9, 26.2, 26.6, 27.18, 27.22, 27.4, 29.5, 30.8, 40.2, 44.1, 57.5, 57.7, 59.2, 61.2, 72.2, 72.4.

β-Myrcene 6,7-epoxide:⁵ ¹H NMR δ 1.26 (s, 3H), 1.31 (s, 3H), 1.71–1.76 (m, 2H), 2.28–2.36 (m, 1H), 2.40–2.48 (m, 1H), 2.76 (t, 1H, J = 6.2 Hz), 5.02 (s, 1H), 5.05 (s, 1H), 5.08 (d, 1H, J = 11.0 Hz), 5.24 (d, 1H, J = 17.5 Hz), 6.38 (dd, 1H, J = 17.5, 11.0 Hz); ¹³C NMR δ 18.8, 24.8, 27.6, 28.1, 58.4, 64.0, 113.4, 116.1, 138.5, 145.5.

Limonene 2,3-epoxide:⁶ ¹H NMR δ 1.13–2.27 (m, 7H), 1.29 (s, 3H), 1.71 (s, 3H), 3.02 (t, 1H, J = 5.5 Hz), 4.75 (s, 2H); ¹³C NMR δ 20.2, 22.1, 25.8, 28.5, 30.7, 40.7, 57.3, 59.2, 109.0, 148.8.

β-Caryophyllene epoxide:⁷ ¹H NMR δ 0.98 (s, 3H), 1.01 (s, 3H), 1.20 (m, 3H), 1.28–1.52 (m, 3H), 1.58–1.71 (m, 3H), 1.76 (t, 1H, J = 9.8 Hz), 2.06–2.14 (m, 2H), 2.21–2.28 (m, 1H), 2.31–2.37
(m, 1H), 2.61 (q, 1H, J = 9.5 Hz), 2.87 (dd, 1H, J = 10.5, 4.1 Hz), 4.85 (s, 1H), 4.97 (s, 1H); $^{13}$C NMR δ 17.0, 21.6, 27.2, 29.8, 29.9, 30.2, 34.0, 39.1, 39.8, 48.7, 50.7, 59.8, 63.7, 112.7, 151.8.

References