Supporting Information for:

Pd(OH)₂/C-Mediated Selective Oxidation of Silyl Enol Ethers by *tert*-Butylhydroperoxide, a Useful Method for the Conversion of Ketones to α,β -Enones or β -Silyloxy- α,β -enones

Jin-Quan Yu,^{†‡} Hai-Chen Wu,[‡] and E. J. Corey*

**Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138, USA*

[†]Department of Chemistry, Brandeis University, Waltham, Massachusetts 02454-9110, USA

*[‡]Department of Chemistry, Cambridge University, Cambridge CB2 1EW, UK
corey@chemistry.harvard.edu*

General methods. Dry solvents were obtained from Fluka (stored over molecular sieves) or were dried by standard methods prior to use and stored under nitrogen over 4Å molecular sieves. Degassed solvents were obtained by the freeze-thaw-freeze circle. Solvents were removed by evaporation on a Buchi rotary evaporator, with vacuum provided by a controlled Teflon-membrane pump. All products were dried at oil-pump vacuum (approximately 1.0 mm Hg) for at least 10min before spectroscopic characterization. Thin layer chromatography (TLC) analysis was performed using Merck 60 PF254 (Merck) 0.2 mM plates (glass backed) and were visualized by UV. Flash chromatography was performed using Merck 9385 Kieselgel 60 silica gel.

NMR spectra were obtained on CDCl₃ solution at 25°C using Bruker Avance DPX 400 MHz (400 MHz for ¹H NMR, 100 MHz for ¹³C and 160 MHz for ³¹P) and Bruker Avance 500 MHz Broadband (500 MHz for ¹H, 125 MHz for ¹³C and 202 MHz for ³¹P) unless stated otherwise. Chemical shifts were reported in δ ppm referenced to the residual solvent peak (δ 7.24 for ¹H and δ 77.0 for ¹³C). IR spectra were recorded using Perkin-Elmer Spectrum One FT-IR with ATR universal sampling accessory as neat liquids or solids. Wavelengths were quoted in cm⁻¹. Mass spectra were recorded on Perkin Elmer TurboMass GC-MS (LRMS) and Micromass Q-TOF (HRMS). The parent ion and significant fragments were quoted.

General procedure for the preparation of silyl enol ethers.¹ Triisopropylsilyl triflate (1.84 g, 6.0 mmol) was added to a solution of the ketone (5.0 mmol) and triethylamine (0.91 g, 9.0 mmol) in dichloromethane (15 mL). The progress of the reaction was monitored by TLC and

when complete, diluted with dichloromethane and washed with cold sodium bicarbonate. After the organic layer was dried over anhydrous sodium sulphate and concentrated on a rotavap, the residue was taken up in dry ether and separated from the insoluble triethylammonium triflate. The ether solution was then concentrated and chromatographed on basic alumina (pH 9.0-9.5) using pure hexane as eluent to give the pure product.

1-(triisopropylsiloxy)cyclopentene. Reaction time: 10 min. Yield: 99%. ^1H NMR: δ 4.65 (m, 1H), 2.28 (m, 4H), 1.87 (m, 2H), 1.18 (m, 3H), 1.09 (d, $J = 7$ Hz, 18H). ^{13}C NMR: δ 155.5, 102.2, 33.6, 28.7, 21.5, 17.9, 12.5. FT-IR: ν 2944, 2867, 1646, 1464, 1339, 1248, 1183, 996, 921, 882, 806 cm^{-1} . HRMS (70eV), calcd [M] for $\text{C}_{14}\text{H}_{28}\text{OSi}$: 240.1909; found: 240.1918.

2-Methyl-1-(triisopropylsiloxy)cyclopentene. Reaction time: 10 min. Yield: 99%. ^1H NMR: δ 2.32 (m, 2H), 2.17 (m, 2H), 1.78 (m, 2H), 1.57 (m, 3H), 1.13 (m, 3H), 1.09 (d, $J = 5$ Hz, 18H). ^{13}C NMR: δ 146.2, 111.6, 33.4, 32.9, 19.3, 17.4, 12.3, 11.4. FT-IR: ν 2944, 2867, 1689, 1464, 1381, 1332, 1248, 1218, 1079, 996, 882, 858 cm^{-1} . HRMS (70eV), calcd [M+H] for $\text{C}_{15}\text{H}_{31}\text{OSi}$: 255.2144; found: 255.2139.

1-(triisopropylsiloxy)cyclohexene. Reaction time: 10 min. Yield: 99%. ^1H NMR: δ 4.87 (m, 1H), 2.04 (m, 2H), 1.99 (m, 2H), 1.65 (m, 2H), 1.50 (m, 2H), 1.14 (m, 3H), 1.07 (d, $J = 5$ Hz, 18H). ^{13}C NMR: δ 151.3, 104.2, 30.6, 24.5, 23.9, 23.0, 18.6, 13.3. FT-IR: ν 2928, 2866, 1668, 1463, 1366, 1266, 1192, 987, 883, 826, 743 cm^{-1} . HRMS (70eV), calcd [M] for $\text{C}_{15}\text{H}_{30}\text{OSi}$: 254.2066; found: 254.2060.

4-Methyl-1-(triisopropylsiloxy)cyclohexene. Reaction time: 30 min. Yield: 99%. ^1H NMR: δ 4.86 (m, 1H), 2.19 (m, 1H), 2.08 (m, 2H), 1.75-1.64 (m, 3H), 1.35 (m, 1H), 1.17 (m, 3H), 1.12 (d, $J = 5$ Hz, 18H). ^{13}C NMR: δ 150.4, 102.9, 32.4, 31.4, 29.7, 28.4, 21.4, 18.0, 12.7. FT-IR: ν 2945, 2867, 1670, 1463, 1370, 1191, 881, 863 cm^{-1} . HRMS (70eV), calcd [M] for $\text{C}_{16}\text{H}_{32}\text{OSi}$: 268.2222; found: 268.2212.

4-*t*-Butyl-1-(triisopropylsiloxy)cyclohexene. Reaction time: 30 min. Yield: 95%. ^1H NMR: δ 4.88 (m, 1H), 2.11 (m, 1H), 2.06 (m, 2H), 1.84 (m, 2H), 1.17 (m, 3H), 1.11 (d, $J = 6$ Hz, 18H), 0.90 (s, 9H). ^{13}C NMR: δ 150.6, 103.2, 44.1, 32.1, 31.0, 27.4, 25.1, 24.5, 23.0, 18.0, 12.9. FT-IR: ν 2944, 2866, 1673, 1465, 1365, 1194, 881, 862 cm^{-1} . HRMS (70eV), calcd [M] for $\text{C}_{19}\text{H}_{38}\text{OSi}$: 310.2681; found: 310.2691.

1-(Triisopropylsiloxy)cycloheptene. Reaction time: 10 min. Yield: 99%. ^1H NMR: δ 5.01 (t, $J = 6.5$ Hz, 1H), 2.30 (m, 2H), 1.99 (m, 2H), 1.70 (m, 2H), 1.61 (m, 2H), 1.56 (m, 2H), 1.16 (m, 3H), 1.10 (d, $J = 6.4$ Hz, 18H). ^{13}C NMR: δ 156.4, 107.1, 35.6, 31.4, 27.8, 25.4, 25.2, 18.05, 12.6. FT-IR: ν 2922, 2866, 1660, 1463, 1367, 1229, 1170, 1130, 880 cm^{-1} . HRMS (70eV), calcd [M] for $\text{C}_{16}\text{H}_{32}\text{OSi}$: 268.2222; found: 268.2221.

Nopinone

(1R)-6,6-Dimethyl-2-(triisopropylsiloxy)bicyclo[3.1.1]hept-2-ene. Reaction time: 60 min. Yield: 78%. ^1H NMR: δ 4.52 (m, 1H), 2.42 (dt, $J = 8.5$ Hz, $J = 5.6$ Hz, 1H), 2.25-2.20 (m, 1H), 2.17-2.12 (m, 1H), 2.11-2.05 (m, 2H), 1.33 (m, 1H), 1.32 (s, 3H), 1.19 (m, 3H), 1.11 (m, 18H), 0.96 (s, 3H). ^{13}C NMR: δ 159.0, 94.6, 48.2, 41.4, 38.5, 27.9, 26.0, 22.6, 18.9, 12.6. FT-IR: ν 2944, 2867, 1650, 1464, 1340, 1221, 1187, 1129, 1050, 881, 854 cm^{-1} . HRMS (70eV), calcd [M] for $\text{C}_{18}\text{H}_{34}\text{OSi}$: 294.2379; found: 294.2390.

2-(Triisopropylsiloxy)bicyclo[3.2.1]oct-2-ene. Reaction time: 60 min. Yield: 93%. ^1H NMR: δ 4.44 (m, 1H), 2.34-2.25 (m, 3H), 2.04-1.99 (m, 1H), 1.88-1.81 (m, 1H), 1.77-1.69 (m, 3H), 1.52-1.47 (m, 1H), 1.46-1.40 (m, 1H), 1.15 (m, 3H), 1.11-1.09 (m, 18H). ^{13}C NMR: δ 157.0, 96.9, 41.5, 35.8, 34.7, 34.0, 33.0, 30.3, 18.1, 12.9. FT-IR: ν 2943, 2866, 1657, 1464, 1365, 1197, 998, 881, 840 cm^{-1} . HRMS (70eV), calcd [M+H] for $\text{C}_{17}\text{H}_{33}\text{OSi}$: 281.2304; found: 281.2295.

2-(Triisopropylsiloxy)bicyclo[4.1.0]hept-2-ene. Reaction time: 70 min. Yield: 82%. ^1H NMR: δ 4.58 (dt, $J = 7.2$ Hz, $J = 2$ Hz, 1H), 1.95-1.81 (m, 2H), 1.78-1.68 (m, 1H), 1.56-1.48 (m, 1H), 1.36 (m, 1H), 1.21-1.14 (m, 4H), 1.12 (m, 18H), 0.76-0.68 (m, 2H). ^{13}C NMR: δ 154.1, 98.2, 20.0, 19.9, 18.9, 15.8, 15.1, 13.5, 9.5. FT-IR: ν 2925, 2866, 1655, 1464, 1393, 1199, 1183, 1012, 883, 814 cm^{-1} . HRMS (70eV), calcd [M+H] for $\text{C}_{16}\text{H}_{31}\text{OSi}$: 267.2144; found: 267.2140.

2-(Triisopropylsiloxy)-3,4-dihydronaphthalene. Reaction time: 60 min. Yield: 95%. ^1H NMR: δ 7.13-7.09 (m, 2H), 7.02 (dt, $J = 1$ Hz, $J = 7.4$ Hz, 1H), 6.92 (d, $J = 7.5$ Hz, 1H), 5.75 (s, 1H), 2.95 (t, $J = 8.2$ Hz, 2H), 2.46 (t, $J = 8.2$ Hz, 2H), 1.33-1.26 (m, 3H), 1.18-1.16 (m, 18H). ^{13}C NMR: δ 155.9, 134.1, 131.9, 128.4, 127.0, 125.9, 124.5, 105.4, 29.1, 29.0, 18.1, 13.1. FT-IR: ν 2943, 2866, 1637, 1463, 1259, 1175, 998, 882, 814 cm^{-1} . HRMS (70eV), calcd $[\text{M}+\text{H}]$ for $\text{C}_{19}\text{H}_{30}\text{OSi}$: 302.2066; found: 302.2060.

General procedure for the synthesis of β -silyloxy- α,β -enones.² A 25 mL round-bottom flask equipped with a stir bar was charged under air with $\text{Pd}(\text{OH})_2/\text{C}$ (20% Pd) (8.5 mg, 0.016 mmol), Cs_2CO_3 (104 mg, 0.32 mmol), CH_2Cl_2 (1 mL) and silyl enol ether (0.32 mmol). The mixture was cooled to 4°C with ice bath and *t*-butylhydroperoxide (TBHP) (160 μL , 1.6 mmol) was added with vigorous stirring. The flask was purged with pure oxygen gas and kept under oxygen atmosphere with a balloon. The mixture was stirred at 4°C for the time indicated below (reaction complete by TLC analysis). The reaction mixture was then filtered through a short pad of silica gel and washed with CH_2Cl_2 . After removal of the solvent by rota evaporation at 24°C, the crude product was purified by flash column chromatography (ether / hexane, 1:1) to provide the analytically pure sample as a clear oil.

3-Oxo-1-(triisopropylsiloxy)cyclohexene. Reaction time: 38 h. Yield: 75% (68 mg). ^1H NMR: δ 5.41 (s, 1H), 2.39 (t, $J = 6.4$ Hz, 2H), 2.31 (t, $J = 6.8$ Hz, 2H), 1.97 (m, 2H), 1.24 (m, 3H), 1.07 (m, 18H). ^{13}C NMR: δ 202.9, 177.0, 110.4, 36.8, 31.4, 21.7, 18.2, 18.1, 12.9, 12.7. FT-IR: ν 2945, 2867, 1658, 1601, 1464, 1373, 1219, 1184, 92, 883, 781, 741 cm^{-1} . HRMS (70eV), calcd $[\text{M}]$ for $\text{C}_{15}\text{H}_{28}\text{O}_2\text{Si}$: 268.1859; found: 268.1856.

4-Methyl-3-oxo-1-(triisopropylsiloxy)cyclohexene. Reaction time: 36 h. Yield: 65% (90 mg). ^1H NMR: δ 5.38 (d, J = 1.6 Hz, 1H), 2.46-2.34 (m, 2H), 2.29-2.23 (m, 1H), 2.06-1.99 (m, 1H), 1.73-1.64 (m, 1H), 1.26-1.16 (m, 3H), 1.13 (d, J = 6.8 Hz, 3H), 1.07-1.03 (m, 18H). ^{13}C NMR: δ 203.0, 175.8, 109.8, 40.2, 30.8, 29.7, 18.2, 18.1, 17.5, 12.9, 12.7. FT-IR: ν 2943, 2866, 1646, 1602, 1463, 1372, 1191, 881, 852, 771 cm^{-1} . HRMS (70eV), calcd [M] for $\text{C}_{16}\text{H}_{30}\text{O}_2\text{Si}$: 282.2015; found: 282.2027.

3-Oxo-1-(triisopropylsiloxy)cycloheptene. Reaction time: 32 h. Yield: 62% (90 mg). ^1H NMR: δ 5.50 (s, 1H), 2.57 (m, 4H), 1.82 (m, 4H), 1.16 (m, 3H), 1.06 (m, 18H). ^{13}C NMR: δ 202.8, 174.5, 114.3, 42.8, 36.1, 24.5, 22.1, 18.3, 18.1, 12.9, 12.7. FT-IR: ν 2943, 2867, 1603, 1464, 1369, 1190, 881, 682 cm^{-1} . HRMS (70eV), calcd [M] for $\text{C}_{16}\text{H}_{30}\text{O}_2\text{Si}$: 282.2015; found: 282.2026.

(1R)-6-Dimethyl-4-oxo-2-(triisopropylsiloxy)bicyclo[3.1.1]hept-2-ene. Reaction time: 48 h. Yield: 70% (103 mg). ^1H NMR: δ 5.41 (d, J = 1.2 Hz, 1H), 2.53-2.47 (m, 1H), 2.44-2.38 (m, 1H), 2.35-2.30 (m, 1H), 2.11-2.04 (m, 1H), 1.76-1.68 (m, 1H), 1.61 (br, 2H), 1.32-1.22 (m, 3H), 1.16 (d, J = 6.9 Hz, 3H), 1.11-1.07 (m, 18H). ^{13}C NMR: δ 202.6, 175.4, 109.4, 39.8, 30.4, 29.3, 17.8, 17.7, 15.3, 12.5, 12.3. FT-IR: ν 2945, 2867, 1659, 1583, 1465, 1352, 1229, 1199, 882 cm^{-1} . HRMS (70eV), calcd [M] for $\text{C}_{18}\text{H}_{32}\text{O}_2\text{Si}$: 308.2172; found: 308.2179.

4-Oxo-2-(triisopropylsiloxy)bicyclo[3.2.1]oct-2-ene. Reaction time: 48 h. Yield: 76% (99 mg). ^1H NMR: δ 5.11 (m, 1H), 2.88 (m, 1H), 2.79 (m, 1H), 2.13-2.01 (m, 3H), 1.87-1.83 (m, 1H), 1.70-1.65 (m, 1H), 1.33-1.25 (m, 3H), 1.12-1.10 (m, 18H). ^{13}C NMR: δ 208.8, 182.9, 105.3, 49.4, 44.4, 38.7, 29.6, 26.2, 17.8, 12.5. FT-IR: ν 2947, 2868, 1665, 1593, 1465, 1373, 1255, 1211, 1167, 1124, 883, 843 cm^{-1} . HRMS (70eV), calcd $[\text{M}+\text{H}]$ for $\text{C}_{17}\text{H}_{30}\text{OSi}$: 295.2093; found: 295.2097.

General procedure for the synthesis of α,β -enones.² A 50 mL round-bottom flask equipped with a stir bar was charged under air with $\text{Pd}(\text{OH})_2/\text{C}$ (20% Pd) (17 mg, 0.032 mmol), Na_2HPO_4 (9.0 mg, 0.064 mmol), CH_2Cl_2 (2 mL) and silyl enol ether (0.64 mmol). The flask was purged with pure oxygen gas and kept under oxygen atmosphere with a balloon. To this mixture *t*-butylhydroperoxide (TBHP) (40 μL , 0.40 mmol) was added in 4 portions every 2 hours with vigorous stirring. The mixture was stirred at 24°C for the time indicated below (reaction complete by TLC analysis). The reaction mixture was then filtered through a short pad of silica gel and washed with CH_2Cl_2 . After removal of the solvent by rota evaporation at 24°C, the crude product was purified by flash column chromatography (ether / hexane, 1:1) to provide the analytically pure sample as a clear oil.

Cyclopent-2-enone. Reaction time: 42 h. Yield: 88% (23 mg). All the analytical data are identical with literature.

2-Methylcyclopent-2-enone. Reaction time: 48 h. Yield: 72% (22 mg). All the analytical data are identical with literature.

Cyclohex-2-enone. Reaction time: 42 h. Yield: 73% (22 mg). All the analytical data are identical with literature.

4-*t*-Butylcyclohex-2-enone. Reaction time: 48 h. Yield: 86% (42 mg). All the analytical data are identical with literature.³

Cyclohept-2-enone. Reaction time: 44 h. Yield: 74% (26 mg). All the analytical data are identical with literature.

Bicyclo[4.1.0]hept-3-en-2-one. 10 Equivalent Et₃N was used in this reaction as base. Reaction time: 72 h. Yield: 70 %. ¹H NMR: δ 6.51-6.47 (m, 1H), 5.90-5.88 (m, 1H), 2.77-2.64 (m, 2H), 1.90-1.86 (m, 1H), 1.78-1.72 (m, 1H), 1.34-1.28 (m, 2H). ¹³C NMR: δ 197.7, 143.3, 127.0, 51.1, 25.4, 21.9, 12.3. FT-IR: ν 2923, 1704, 1664, 1362, 1258, 864 cm⁻¹. HRMS (70eV), calcd [M+1] for C₇H₉O: 109.0653; found: 109.0658.

Synthesis of 2-(triisopropylsiloxy)naphthalene. A 25 mL round-bottom flask equipped with a stir bar was charged under air with Pd(OH)₂/C (20% Pd) (8.5 mg, 0.016 mmol), Cs₂CO₃ (104 mg, 0.32 mmol), CH₂Cl₂ (1 mL) and 2-(Triisopropylsiloxy)-3,4-dihydronaphthalene (97mg, 0.32 mmol). The mixture was cooled to 4°C with ice bath and *t*-butylhydroperoxide (TBHP) (160 μL, 1.6 mmol) was added with vigorous stirring. The flask was purged with pure oxygen gas and kept under oxygen atmosphere with a balloon. The mixture was stirred at 4°C for 36 h (reaction complete by

TLC analysis). The reaction mixture was then filtered through a short pad of silica gel and washed with CH₂Cl₂. After removal of the solvent by rota evaporation at 24°C, the crude product was purified by flash column chromatography (ether / hexane, 1:1) to provide the analytically pure sample as a clear oil. Yield: 80% (77 mg). ¹H NMR: δ 7.77-7.68 (m, 3H), 7.41 (m, 1H), 7.32 (m, 1H), 7.23 (d, *J* = 2.4 Hz, 1H), 7.13 (dd, *J* = 9.2 Hz, *J* = 2.8 Hz, 1H), 1.37-1.27 (m, 3H) 1.14 (d, *J* = 6.8 Hz, 18H). ¹³C NMR: δ 154.3, 135.1, 129.6, 129.5, 128.0, 127.3, 127.0, 124.9, 122.4, 114.9, 18.4, 13.1. FT-IR: ν 2944, 2867, 1630, 1599, 1466, 1270, 1258, 1221, 1174, 970, 928, 881, 850, 810, 745 cm⁻¹. HRMS (70eV), calcd [M] for C₁₉H₂₈OSi: 300.1909; found: 300.1905.

Reference

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