Supporting Information

Hydrosilylation of Alkynes with a Cationic Rhodium Species Formed in Anionic Micellar System

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Instrumentation and Materials

^1H NMR (300 MHz) and ^{13}C NMR (75.3 MHz) spectra were taken on Varian Mercury 300 and Unity 500 spectrometers. ^1H NMR and ^{13}C NMR spectra were obtained in CDCl_3 with the solvent residual peak (CDCl_3 : ^1H = 7.27 ppm, ^{13}C = 77 ppm) as internal reference. IR spectra were recorded on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra were determined on a JEOL Mstation 700 spectrometer. Silica gel (Wakogel 200 mesh) was used for column chromatography. The analyses were carried out at the Elemental Analysis Center of Kyoto University. Pure water was obtained with Millipore Direct-Q system and was degassed by bubbling of N_2 with sonication for 30 min before use. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

General Procedure

Hydrosilylation of Alkynes

In a 20-mL flask, $[\text{RhCl}(\text{nbd})_2]$ (2.3 mg, 0.005 mmol), dppp (5.4 mg, 0.013 mmol) and sodium dodecyl sulfate (144 mg, 0.5 mmol) were placed under argon atmosphere. Pure water (2.5 mL) was introduced, and the mixture was stirred at room temperature for 10 min. A yellow clear solution was obtained. To the mixture was added 1-octyne (0.15 mg, 1.0 mmol) and triethylsilane (0.18 mg, 1.1 mmol) were added via syringes. After stirring vigorously for 3 hours at room temperature, the mixture was extracted with ethyl acetate. The organic extracts were dried through a short pad of silica gel on Na_2SO_3 layer. Concentration followed by purification of the residual oil afforded (*E*)-1-triethylsilyl-1-octene ((*E*)-**1**, 174.3 mg, 0.77 mmol) in 77% yield, accompanying with 2-triethylsilyl-1-octene (**2**, 6.8 mg, 0.03 mmol) in 3% yield.

Hydrosilylation of Alkynes in the Presence of NaI (Preparation of (Z)-alkenylsilanes)

In a 20-mL flask, $[\text{RhCl}(\text{nbd})_2]$ (2.3 mg, 0.005 mmol), dppp (4.1 mg, 0.01 mmol), sodium dodecyl sulfate (144 mg, 0.5 mmol) and NaI (150 mg, 1.0 mmol) were placed under argon atmosphere. Pure water (2.5 mL) was introduced, and the mixture was stirred at room temperature for 10 min. A yellow clear solution was obtained. To the mixture was added 1-octyne (0.15 mg, 1.0 mmol) and triethyl silane (0.18 mg, 1.1 mmol) were added via syringes. After stirring vigorously for 3 hours at room temperature, the mixture was extracted with ethyl acetate. The organic extracts were dried through a short pad of silica gel on Na_2SO_3 layer. Concentration followed by purification of the residual oil afforded (Z)-1-triethylsilyl-1-octene ((Z)-**1**, 158 mg, 0.70 mmol) in 70% yield, along with (E)-1-triethylsilyl-1-octene ((E)-**1**, 11.2 mg, 0.05 mmol) in 5% yield and 2-triethylsilyl-1-octene (**2**, 2.7 mg, 0.012 mmol) in 1.2% yield.

Compound Data

(E)-5-Benzyloxy-1-triethylsilylpent-1-ene

IR (neat) 696, 733, 783, 1016, 1105, 1238, 1364, 1454, 1616, 2874, 2951, 3030, 3065 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.59 (q, $J = 8.0$ Hz, 6H), 0.97 (t, $J = 8.0$ Hz, 9H), 1.78 (tt, $J = 6.6$ Hz, 6.6 Hz, 2H), 2.27 (dt, $J = 6.6$ Hz, 6.6 Hz, 2H), 3.52 (t, $J = 6.6$ Hz, 2H), 4.54 (s, 2H), 5.62 (d, $J = 18.8$ Hz, 1H), 6.09 (dt, $J = 18.8$ Hz, 6.6 Hz, 1H), 7.28–7.45 (m, 5H); ^{13}C NMR (CDCl_3) δ 3.63, 7.49, 28.92, 33.50, 69.65, 72.84, 126.10, 127.30, 127.42, 128.15, 138.44, 147.50. Found: C, 73.94; H, 10.43%. Calcd for $\text{C}_{18}\text{H}_{30}\text{OSi}$: C, 74.42; H, 10.41%.

(Z)-5-Benzyloxy-1-triethylsilylpent-1-ene

IR (neat) 696, 731, 1016, 1105, 1236, 1364, 1454, 1605, 2874, 3030, 3065 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.66 (q, $J = 7.8$ Hz, 6H), 0.99 (t, $J = 7.8$ Hz, 9H), 1.75 (tt, $J = 7.0$ Hz, 7.0 Hz, 2H), 2.25 (dt, $J = 7.0$ Hz, 7.0 Hz, 2H), 3.53 (t, $J = 6.6$ Hz, 2H), 4.54 (s, 2H), 5.47 (d, $J = 14.3$ Hz, 1H), 6.42 (dt, $J = 14.3$ Hz, 7.0 Hz, 1H), 7.28–7.45 (m, 5H); ^{13}C NMR (CDCl_3) δ 4.80, 7.67, 29.94, 30.77, 69.87, 72.82, 125.59, 127.30, 127.39, 128.15, 138.44, 149.15. Found: C, 74.59; H, 10.29%. Calcd for $\text{C}_{18}\text{H}_{30}\text{OSi}$: C, 74.42; H, 10.41%.

Ethyl (E)-9-Triethylsilylnon-8-enoate

IR (neat) 719, 785, 1016, 1180, 1373, 1464, 1616, 1740, 2932 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.53 (q, $J = 8.0$ Hz, 6H), 0.92 (t, $J = 8.0$ Hz, 9H), 1.25 (t, $J = 7.1$ Hz, 3H), 1.25–1.40 (m, 6H), 1.55–1.68 (m, 2H), 2.10 (dt, $J = 6.6$ Hz, 6.6 Hz, 2H), 2.28 (t, $J = 7.7$ Hz, 2H), 4.12 (q, $J = 7.1$ Hz, 2H), 5.52 (d, $J = 18.8$ Hz, 1H), 6.01 (dt, $J = 18.8$ Hz, 6.6 Hz, 1H); ^{13}C NMR (CDCl_3) δ 3.63, 7.46, 14.33, 24.99, 28.63, 28.77, 29.04, 34.40, 36.97, 60.13, 125.56, 148.38, 173.63. Found: C, 68.63; H, 11.24%. Calcd for $\text{C}_{17}\text{H}_{34}\text{O}_2\text{Si}$: C, 68.39; H, 11.48%.

Ethyl (Z)-9-Triethylsilylnon-8-enoate

IR (neat) 733, 1016, 1180, 1238, 1373, 1464, 1605, 1740, 2874, 2934 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.60 (q, $J = 7.9$ Hz, 6H), 0.94 (t, $J = 7.9$ Hz, 9H), 1.26 (t, $J = 7.1$ Hz, 3H), 1.27–1.46 (m, 6H), 1.55–1.70 (m, 2H), 2.10 (dt, $J = 7.0$ Hz, 7.0 Hz, 2H), 2.29 (t, $J = 7.5$ Hz, 2H), 4.12 (q, $J = 7.1$ Hz, 2H), 5.39 (d, $J = 14.1$ Hz, 1H), 6.36 (dt, $J = 14.1$ Hz, 7.0 Hz, 1H); ^{13}C NMR (CDCl_3) δ 4.82, 7.63, 14.34, 25.00, 29.10, 29.15, 29.65, 34.05, 34.40, 60.17, 125.00, 149.95, 173.64. Found: C, 68.43; H, 11.23%. Calcd for $\text{C}_{17}\text{H}_{34}\text{O}_2\text{Si}$: C, 68.39; H, 11.48%.

(*E*)-9-Triethylsilylnon-8-enoic Acid

IR (neat) 719, 785, 1016, 1236, 1414, 1458, 1618, 1709, 2934, 3600–2400 (br) cm^{-1} ; ^1H NMR (CDCl_3) δ 0.55 (q, $J = 7.9$ Hz, 6H), 0.93 (t, $J = 7.9$ Hz, 9H), 1.25–1.47 (m, 6H), 1.55–1.70 (m, 2H), 2.12 (dt, $J = 6.5$ Hz, 6.5 Hz, 2H), 2.35 (t, $J = 7.4$ Hz, 2H), 5.54 (d, $J = 18.8$ Hz, 1H), 6.02 (dt, $J = 18.8$ Hz, 6.5 Hz, 1H), 10.00–12.00 (br, 1H); ^{13}C NMR (CDCl_3) δ 3.64, 7.49, 24.69, 28.62, 28.75, 28.96, 34.14, 36.97, 125.65, 148.34, 180.25. Found: C, 66.31; H, 11.10%. Calcd for $\text{C}_{15}\text{H}_{30}\text{O}_2\text{Si}$: C, 66.61; H, 11.18%.

(*E*)-5-*tert*-Butyldimethylsiloxy-1-triethylsilylpent-1-ene

IR (neat) 719, 775, 837, 1007, 1105, 1256, 1462, 1618, 2858, 2955 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.05 (s, 6H), 0.55 (q, $J = 8.0$ Hz, 6H), 0.90 (s, 9H), 0.93 (t, $J = 8.0$ Hz, 9H), 1.63 (tt, $J = 7.0$ Hz, 7.0 Hz, 2H), 2.18 (dt, $J = 7.0$ Hz, 7.0 Hz, 2H), 3.61 (t, $J = 7.0$ Hz, 2H), 5.57 (dt, $J = 18.6$ Hz, 1.5 Hz, 1H), 6.04 (dt, $J = 18.6$ Hz, 6.3 Hz, 1H); ^{13}C NMR (CDCl_3) δ -5.15, 3.64, 7.50, 18.48, 26.07, 31.95, 33.23, 62.59, 125.95, 147.86. Found: C, 64.62; H, 12.40%. Calcd for $\text{C}_{17}\text{H}_{38}\text{OSi}_2$: C, 64.89; H, 12.17%.

(Z)-5-*tert*-Butyldimethylsiloxy-1-triethylsilylpent-1-ene

IR (neat) 731, 775, 837, 1013, 1105, 1256, 1464, 1607, 2858, 2955 cm⁻¹; ¹H NMR (CDCl₃) δ 0.05 (s, 6H), 0.61 (q, *J* = 7.8 Hz, 6H), 0.90 (s, 9H), 0.95 (t, *J* = 7.8 Hz, 9H), 1.55–1.65 (m, 2H), 2.16 (dt, *J* = 7.2 Hz, 7.2 Hz, 2H), 3.62 (t, *J* = 2.2 Hz, 2H), 5.41 (d, *J* = 14.0 Hz, 1H), 6.38 (dt, *J* = 14.0 Hz, 7.2 Hz, 1H); ¹³C NMR (CDCl₃) δ -5.16, 4.79, 7.65, 18.45, 26.04, 30.67, 33.08, 62.89, 125.33, 149.45. Found: C, 64.61; H, 12.41%. Calcd for C₁₇H₃₈OSi₂: C, 64.89; H, 12.17%.