Palladium-Catalyzed Cyanation of Propargylic Carbonates with Trimethylsilyl Cyanide

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SUPPORTING INFORMATION

Analytical Procedure. The NMR spectra of the sample in $CDCl_3$ were recorded on JEOL α-400 spectrometer: ^{1}H (400 MHz), ^{13}C (100 MHz), and ^{29}Si (79.4 MHz). The mass (GCMS) spectra were measured with Shimadzu QP-1000 equipped with a PAC 1100S computer system. The GC analysis was made on a Shimadzu GC-8APF with a column (3 mm i.d. × 3 m) packed with Silicon OV-17 (2% on Uniport HP, 60/80 mesh) or Apiezon Grease L (5% on Uniport HP, 60/80 mesh). Elemental analysis was performed at the Microanalytical Center of Kyoto University.

Cyanation of propargylic carbonate (1) with 1 equiv of trimethylsilyl cyanide (2) (eq 1 and Table 1). A typical procedure is described for the cyanation of **1a** (entry 1). A mixture of **1a** (226 mg, 1.0 mmol), **2** (99 mg, 1.0 mmol), $Pd(PPh_3)_4$ (58 mg, 0.050 mmol), and THF (4.0 mL) was placed under argon atmosphere in a 20 mL flask equipped with a three-way stopcock. The reaction was carried out under reflux for 1 h. After the reaction, the resulting reaction mixture was passed through a short Florisil column (8 mm i.d. × 70 mm) to give a almost colorless (or slightly yellow) solution. Kugelrohr distillation (pot temp 90-100 ºC / 0.1 mmHg) provided **3a** (161 mg) in 91% yield as colorless liquid.

Cyanation of 1 with excess 2 (Table 2, eq 3, and eq 5). A typical procedure is as follows (entry 9): A 20 mL flask was charged with **1h** (212 mg, 1.0 mmol), **2** (595 mg, 6.0 mmol), $Pd(PPh_3)_4$ (58 mg, 0.050 mmol), and THF (4.0 mL) under argon atmosphere. The reaction was carried out under reflux for 20 h. After the reaction, the resulting reaction mixture was passed through a short Florisil column (8 mm i.d. × 70 mm) to afford a pale yellow solution. Kugelrohr distillation (pot temp 90 ºC / 0.04 mmHg) afforded (*Z*)-**7a** (199 mg) in 80% yield as colorless liquid.

Reaction of cyanoallene (3) with excess 2 (eq 4 and eq 6). The following reaction shows a typical procedure (eq 4). A mixture of **3g** (149 mg, 1.0 mmol), **2** (496 mg, 5.0 mmol), $Pd(PPh_3)_4$ (58 mg, 0.050 mmol), and THF (4.0 mL) was stirred under argon atmosphere at 70 ºC for 20 h. GC analysis of the reaction mixture with the internal standard method showed (*Z*)-**7a** was afforded in 93% yield.

3a: ^{1}H NMR δ 0.85 (t, J = 6.8 Hz, 3H), 1.19-1.34 (m, 6H), 1.45 (quin, J = 7.2 Hz, 2H), 1.73 (s, 6H), 2.09 (t, J = 7.2 Hz, 2H); ^{13}C NMR δ 13.89 (CH_3), 19.53 (CH_3), 22.44 (CH_2), 27.42 (CH_2), 28.08(CH_2), 31.33 (CH_2), 31.46 (CH_2), 79.62 (C), 101.60 (C), 116.52 (C), 209.11 (C); MS m/z = 177 (M^+).

3b: ^{1}H NMR δ 0.88 (d, J = 6.4 Hz, 6H), 1.30–1.47 (m, 1H), 1.58 (q, J = 7.1 Hz, 2H), 1.75 (s, 6H), 2.12 (t, J = 7.1 Hz, 2H); ^{13}C NMR δ 19.64 (CH_3), 22.26 (CH_3), 27.01 (CH_2), 29.57 (CH), 36.51 (CH_2), 79.78 (C), 101.76 (C), 117.90 (C), 209.01 (C). Anal. Calcd for $C_{11}H_{17}N$: C, 80.93; H, 10.50. Found: C, 81.14; H, 10.73.

3c: ^{1}H NMR δ 0.89 (t, J = 7.3 Hz, 3H), 1.00 (t, J = 7.4 Hz, 3H), 1.33 (sex, J = 7.3 Hz, 2H), 1.45 (quin, J = 7.3 Hz, 2H), 1.74 (s, 3H), 2.02 (q, J = 7.4 Hz, 2H), 2.12 (t, J = 7.3 Hz, 2H); ^{13}C NMR δ 11.78 (CH_3), 13.67 (CH_3), 18.15 (CH_2), 21.67 (CH_3), 21.68 (CH_2), 29.74 (CH_2), 31.32 (CH_2), 81.50 (C), 107.98 (C), 116.79 (C), 208.67 (C). Anal. Calcd for $C_{11}H_{17}N$: C, 80.93; H, 10.50. Found: C, 81.04; H, 10.68.

3d: ^{1}H NMR δ 0.85 (t, J = 7.0 Hz, 3H), 1.00 (t, J = 7.2 Hz, 3H), 1.20-1.34 (m, 6H), 1.46 (quin, J = 7.4 Hz, 2H), 1.73 (s, 3H), 2.02 (q, J = 7.2 Hz, 2H), 2.11 (t, J = 7.4 Hz, 2H); ^{13}C NMR δ 11.75 (CH_3), 13.93(CH_3), 18.11(CH_3), 22.47(CH_2), 26.71(CH_2), 27.60(CH_2), 28.21(CH_2), 31.38(CH_2), 31.60(CH_2), 81.55(C), 107.93(C), 116.72(C), 208.65(C). Anal. Calcd for $C_{13}H_{21}N$: C, 81.62; H, 11.06. Found: C, 81.48; H, 11.28.

3e: ^{1}H NMR δ 0.89 (d, J = 6.4 Hz, 6H), 1.73 (d, J = 2.8 Hz, 3H), 1.73 (m, 1H), 1.90 (dd, J = 7.2 Hz, 2.8 Hz, 2H), 5.06 (sex, J = 2.8 Hz, 1H); ^{13}C NMR δ 17.60 (CH_3), 22.20 (CH_3), 26.08 (CH), 42.27 (CH_2), 65.49 (CH), 105.12 (C), 114.22 (C), 213.64 (C). Anal. Calcd for $C_9H_{13}N$: C, 79.95; H, 9.69. Found: C, 80.24; H, 9.88.

3f: ^{1}H NMR δ 0.86 (t, *J* = 7.4 Hz, 3H), 1.24–1.52 (m, 8H), 1.73 (d, *J* = 7.6 Hz, 3H), 2.14 (td, *J* = 7.4 Hz, 2.5 Hz, 2H), 5.54 (qt, *J* = 7.6 Hz, 2.5 Hz, 1H); ^{13}C NMR δ 13.25 (CH_3), 13.99 (CH_3), 22.50 (CH_2), 27.47 (CH_2), 28.19 (CH_2), 31.23 (CH_2), 31.38 (CH_2), 81.52 (C), 91.49 (CH), 116.10 (C), 211.75 (C); MS *m/z* = 163 (M^+).

3g: ^{1}H NMR δ 0.86 (t, *J* = 7.0 Hz, 3H), 1.21–1.38 (m, 6H), 1.51 (quin, *J* = 7.4 Hz, 2H), 2.17 (tt, *J* = 7.4 Hz, 2.9 Hz, 2H), 5.18 (t, *J* = 2.9 Hz, 2H); ^{13}C NMR δ 13.96 (CH_3), 22.46 (CH_2), 27.41 (CH_2), 28.21 (CH_2), 30.72 (CH_2), 31.33 (CH_2), 80.23 (CH_2), 82.08 (C), 115.33 (C), 214.82 (C); MS m/z = 134 (M^+–Me).

7a: (*Z*)-isomer: ^{1}H NMR δ 0.14 (s, 9H), 0.86 (t, *J* = 6.8 Hz, 3H), 1.25–1.36 (m, 6H), 1.57 (quin, *J* = 7.4 Hz, 2H), 2.08 (s, 2H), 2.49 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR δ –1.67 (CH_3), 13.82 (CH_3), 22.31 (CH_2), 26.65 (CH_2), 28.01(CH_2), 28.13 (CH_2), 31.14 (CH_2), 33.42 (CH_2), 116.13 (C), 116.23 (C), 124.59 (C), 127.38 (C); MS m/z = 248 (M^+). Anal. Calcd for $C_{14}H_{24}N_2Si$: C, 67.68; H, 9.74. Found: C, 67.95; H, 9.82. (*E*)-isomer: ^{1}H NMR δ 0.15 (s, 9H), 1.90 (s, 2H), 2.20 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR δ –1.48 (CH_3), 17.03 (CH_2); MS m/z = 248 (M^+). These (*Z*) and (*E*) assignments are confirmed with NOESY and HMQC spectra.

7b: ^{1}H NMR δ 0.13 (s, 9H), 0.77 (t, *J* = 7.6 Hz, 3H), 1.21 (sex, *J* = 7.6 Hz, 2H), 1.42 (quin, *J* = 7.6 Hz, 2H), 1.94 (s, 2H), 2.35 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR δ –1.51 (CH_3), 13.64 (CH_3), 21.82 (CH_2), 26.83 (CH_2), 30.28 (CH_2), 33.31 (CH_2), 116.32 (C), 116.39 (C), 124.72 (C), 127.56 (C); MS *m/z* = 220 (M^+). Anal. Calcd for $C_{12}H_{20}N_2Si$: C, 65.40; H, 9.15. Found: C, 65.21; H, 9.32. NOESY spectrum showed the product is the (*Z*)-isomer.

8: ^{1}H NMR δ 0.85 (t, *J* = 6.8 Hz, 3H), 1.20–1.51 (m, 8H), 1.69–1.78 (m, 1H), 1.87–1.97 (m, 1H), 1.92 (s, 3H), 2.12 (s, 3H), 3.48 (t, *J* = 7.9 Hz, 1H); ^{13}C NMR δ 13.86 (CH_3), 20.66 (CH_3), 22.35 (CH_2), 25.05 (CH_3), 26.75 (CH_2), 28.35 (CH_2), 30.96 (CH), 31.28 (CH_2), 31.81 (CH_2), 105.71 (C), 115.77 (C), 118.23 (C), 157.15 (C); MS m/z = 204 (M^+). Anal. Calcd for $C_{13}H_{20}N_2$: C, 76.42; H, 9.87, Found: C, 76.30; H, 10.11.