Supporting Information

Reaction of Silyldihalomethylolithiums with Nitriles. Formation of α -Keto Acylsilanes via Azirines and 1,3-Rearrangement of Silyl Group from C to N (JA047708O)

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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 tetramethylsilane as an internal standard. IR spectra were recorded on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra were determined on a JEOL Mstation 700 spectrometer. X-ray data were taken on a Bruker Smart APEX X-Ray diffractometer equipped with a large area CCD detector. The structures were solved with the program system SHELXS-97¹ and refined with SHELXL-97² package from Bruker. Silica gel (Wakogel 200 mesh) was used for column chromatography. The analyses were carried out at the Elemental Analysis Center of Kyoto University. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl before use. All reactions were carried out under an argon atmosphere. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

General Procedure

Synthesis of α -Keto Acylsilanes

A solution of *tert*-butyldibromomethyldimethylsilane (288.1 mg, 1.0 mmol) in THF (1.5 mL) was added to a solution of LDA (1.5 mmol) in THF (3 mL) at $-78\text{ }^\circ\text{C}$. The mixture was stirred for 1 h at $-78\text{ }^\circ\text{C}$ to provide a yellow solution of **1a**. To the resulting mixture, benzonitrile (0.25 mL, 2.4 mmol) was added at $-78\text{ }^\circ\text{C}$. After stirred for 1 h at $-78\text{ }^\circ\text{C}$, the reaction was quenched with HCl aq. (5 mL, 1.0 M), and the organic phase turned red during this period. The mixture was extracted with

¹ Sheldrick, G. M. SHELXS 97 program for the solution of crystal structures. University of Göttingen, Germany, 1997.

² Sheldrick, G. M. SHELXL 97 program for the refinement of crystal structures. University of Göttingen, Germany, 1997

hexane/ethyl acetate (10/1, 20 mL $\times$ 3). The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated in vacuo. Purification by chromatography on a silica gel column afforded 1-(*t*-butyldimethylsilyl)-2-phenylethane-1,2-dione (**8a**, 183.8 mg, 0.74 mmol) as crimson oil in 74 % yield.

C→N Homo-Brook Silyl Rearrangement

To a solution of LDA (0.75 mmol) in THF (3 mL), a solution of *tert*-butyldichloromethyldimethylsilane (99.4 mg, 0.50 mmol) in THF (1.5 mL) was added at $-78\text{ }^{\circ}\text{C}$, and the mixture was stirred for 10 min at $-78\text{ }^{\circ}\text{C}$ to give a light yellow solution of **1c**. To the resulting mixture, *p*-methoxybenzonitrile (79.5 mg, 0.60 mmol) was added at $-78\text{ }^{\circ}\text{C}$. After stirred for 1 h at $-78\text{ }^{\circ}\text{C}$, benzaldehyde (0.060 mL, 0.60 mmol) was added to the reaction mixture at $-78\text{ }^{\circ}\text{C}$. After the mixture was stirred for 10 min, trimethylsilyl chloride (0.080 mL, 0.60 mmol) was added to the solution at $-78\text{ }^{\circ}\text{C}$, and the mixture was stirred for 30 min at room temperature. After the quenching the reaction with water, the mixture was extracted with hexane/ethyl acetate (10/1, 20 mL $\times$ 3). The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated in vacuo. Purification by chromatography on a neutral silica gel column afforded 1-(*t*-butyldimethylsilylimino)-2,2-dichloro-1-(4-methoxyphenyl)-3-phenyl-3-trimethylsiloxypropane (**13b**, 225.1 mg, 0.44 mmol) in 88 % yield.

Compound Data

1-(*t*-Butyldimethylsilyl)-2-phenylethane-1,2-dione (**8a**)

IR (neat) 2929, 2860, 1666, 1633, 1596, 1463, 1450, 1253, 840, 785, 765, 705 cm⁻¹; ¹H NMR (CDCl₃) δ 0.28 (s, 6H), 0.99 (s, 9H), 7.43–7.50 (m, 2H), 7.57–7.63 (m, 1H), 7.89–7.98 (m, 2H); ¹³C

NMR (CDCl₃) δ -6.51, 17.24, 26.63, 129.85, 131.23, 134.13, 195.25, 240.92. Found: C, 67.67; H, 8.23%. Calcd for C₁₄H₂₀O₂Si: C, 67.69; H, 8.12%.

1-(*t*-Butyldimethylsilyl)-2-(4-methoxyphenyl)ethane-1,2-dione (8b)

IR (neat) 2932, 2860, 1599, 1574, 1510, 1464, 1423, 1315, 1259, 1172, 1028, 839, 808, 785 cm⁻¹; ¹H NMR (CDCl₃) δ 0.25 (s, 6H), 0.97 (s, 9H), 3.86 (s, 3H), 6.91–6.97 (m, 2H), 7.86–7.92 (m, 2H); ¹³C NMR (CDCl₃) δ -6.43, 17.25, 26.67, 55.57, 114.16, 124.10, 132.30, 264.36, 194.08, 240.24. Found: C, 64.65; H, 8.06%. Calcd for C₁₅H₂₂O₃Si: C, 64.71; H, 7.96%.

1-(*t*-Butyldimethylsilyl)-2-(4-bromophenyl)ethane-1,2-dione (8c)

IR (neat) 2929, 2858, 1668, 1585, 1469, 1398, 1251, 1072, 1010, 839, 781 cm⁻¹; ¹H NMR (CDCl₃) δ 0.28 (s, 6H), 0.99 (s, 9H), 7.61–7.66 (m, 2H), 7.77–7.83 (m, 2H); ¹³C NMR (CDCl₃) δ -6.45, 17.28, 26.67, 129.79, 130.01, 131.32, 132.10, 193.61, 240.30. HRMS Found: 326.0327. Calcd for C₁₄H₁₉BrO₂Si: 326.0338.

1-(*t*-Butyldimethylsilyl)-2-(2-methylphenyl)ethane-1,2-dione (8d)

IR (neat) 2929, 2860, 1666, 1633, 1600, 1463, 1249, 840, 812, 781, 744 cm⁻¹; ¹H NMR (CDCl₃) δ 0.26 (s, 6H), 0.99 (s, 9H), 2.55 (s, 3H), 7.22–7.30 (m, 2H), 7.44 (ddd, *J* = 1.5 Hz, 7.5 Hz, 7.5 Hz, 1H), 7.53 (dd, *J* = 1.5 Hz, 7.5 Hz, 1H); ¹³C NMR (CDCl₃) δ -6.31, 17.29, 21.82, 26.67, 125.48, 130.50, 131.94, 132.21, 132.93, 140.79, 198.65, 240.25. Found: C, 68.36; H, 8.60%. Calcd for C₁₅H₂₂O₂Si: C, 68.65; H, 8.45%.

1-(*t*-Butyldimethylsilyl)-2-(4-triisopropylsiloxypheyl)ethane-1,2-dione (8e)

IR (neat) 2868, 1633, 1595, 1506, 1276, 1166, 997, 842, 783, 667 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.27 (s, 6H), 0.99 (s, 9H), 1.10 (d, $J = 4.2$ Hz, 18H), 1.27 (sept, $J = 4.2$ Hz, 3H), 6.93 (d, $J = 5.4$ Hz, 2H), 7.84 (d, $J = 5.4$ Hz, 2H); ^{13}C NMR (CDCl_3) δ -6.68, 12.68, 17.12, 17.82, 26.55, 120.24, 124.50, 132.47, 162.02, 194.49, 241.85. HRMS Found: 421.2596. Calcd for MH^+ , $\text{C}_{23}\text{H}_{41}\text{O}_3\text{Si}_2$: 421.2594.

1-(*t*-Butyldimethylsilyl)-2-(4-phenylethynylphenyl)ethane-1,2-dione (8f)

IR (neat) 2858, 2218, 1662, 1600, 1255, 1180, 840, 756 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.31 (s, 6H), 1.01 (s, 9H), 7.36–7.40 (m, 3H), 7.53–7.58 (m, 2H), 7.63 (d, $J = 8.2$ Hz, 2H), 7.93 (d, $J = 8.2$ Hz, 2H); ^{13}C NMR (CDCl_3) δ -6.50, 17.26, 26.65, 88.47, 93.69, 122.31, 128.28, 128.80, 129.39, 129.81, 130.29, 131.61, 131.71, 194.18, 240.73. HRMS Found: 349.1625. Calcd for MH^+ , $\text{C}_{22}\text{H}_{25}\text{O}_2\text{Si}$: 349.1624.

1-(4-Methoxyphenyl)-2-(triisopropylsilyl)ethane-1,2-dione (8g)

IR (neat) 2945, 2868, 1657, 1597, 1574, 1510, 1464, 1261, 1173 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.12 (d, $J = 7.5$ Hz, 18H), 1.43 (septet, $J = 7.5$ Hz, 3H), 3.88 (s, 3H), 6.96 (d, $J = 9.0$ Hz, 2H), 7.93 (d, $J = 9.0$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 11.25, 18.70, 55.58, 114.20, 123.99, 132.42, 164.35, 193.96, 241.83. Found: C, 67.26; H, 8.64%. Calcd for $\text{C}_{18}\text{H}_{28}\text{O}_3\text{Si}$: C, 67.46; H, 8.81%.

2,3-Diallyl-2-(*t*-butyldimethylsilyl)-3-(4-methoxyphenyl)aziridine (10a)

IR (neat) 3076, 2870, 2850, 1639, 1612, 1514, 1248, 1178, 1050, 912, 826, 772 cm^{-1} ; ^1H NMR (CDCl_3) δ -0.85 (s, 3H), -0.20 (s, 3H), 0.91 (s, 9H), 1.00–1.40 (bs, 1H), 2.30–2.41 (m, 2H), 2.56 (dd, $J = 6.3$ Hz, 7.8 Hz, 1H), 2.90 (ddd, $J = 1.5$ Hz, 7.8 Hz, 16.5 Hz, 1H), 3.76 (s, 3H), 4.79–4.90 (m, 2H),

5.09–5.15 (m, 2H), 5.57–5.71 (m, 1H), 5.85–6.00 (m, 1H), 6.77 (d, $J = 7.5$ Hz, 2H), 7.11 (d, $J = 7.5$ Hz, 2H); ^{13}C NMR (CDCl_3) δ –5.51, –4.71, 18.53, 28.18, 37.84, 37.13, 41.48, 49.69, 55.13, 112.88, 116.90, 129.58, 134.62, 136.38, 158.13. Found: C, 73.46; H, 9.74%. Calcd for $\text{C}_{21}\text{H}_{33}\text{NO}_2\text{Si}$: C, 73.41; H, 9.68%.

2-(*t*-Butyldimethylsilyl)-3-(4-methoxyphenyl)aziridine (10b)

Mp 69 °C; IR (nujol) 3240, 1614, 1512, 1166, 1033, 906, 839, 826, 683 cm^{-1} ; ^1H NMR (CDCl_3) δ –0.48 (s, 3H), –0.36 (s, 3H), 0.89 (s, 9H), 1.41 (d, $J = 7.5$ Hz, 1H), 3.37 (d, $J = 7.5$ Hz, 1H), 3.78 (s, 3H), 6.80 (d, $J = 8.4$ Hz, 2H), 7.24 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (CDCl_3) δ –6.82, –6.76, 17.01, 25.09, 26.62, 36.28, 55.18, 113.10, 128.64, 131.50, 158.24. Found: C, 68.09; H, 9.61%. Calcd for $\text{C}_{15}\text{H}_{25}\text{NOSi}$: C, 68.38; H, 9.56%.

3-Allyl-2-(*t*-butyldimethylsilyl)-3-(4-methoxyphenyl)-2-phenylaziridine (10c)

IR (neat) 2923, 2856, 1612, 1514, 1247, 1037, 831, 769, 705 cm^{-1} ; ^1H NMR (CDCl_3) δ –0.86 (s, 3H), 0.12 (s, 3H), 0.53 (s, 9H), 1.50 (d, $J = 6.9$ Hz, 1H), 1.55 (d, $J = 6.9$ Hz, 1H), 2.02–2.20 (bs, 1H), 3.78 (s, 3H), 4.55 (dd, $J = 2.1$ Hz, 17.1 Hz, 1H), 4.76 (dd, $J = 2.1$ Hz, 10.2 Hz, 1H), 5.54 (dddd, $J = 6.9$ Hz, 6.9 Hz, 10.2 Hz, 17.1 Hz, 1H), 6.85 (d, $J = 9.0$ Hz, 2H), 7.16–7.39 (m, 6H), 7.42–7.58 (bs, 1H); ^{13}C NMR (CDCl_3) δ –6.29, –5.32, 18.59, 26.81, 43.36, 50.61, 55.10, 112.96, 116.68, 125.76, 127.15, 128.27, 128.53, 129.53, 133.78, 134.18, 142.34, 158.16. HRMS Found: 379.2332. Calcd for $\text{C}_{24}\text{H}_{33}\text{ONSi}$: 379.2331.

3-(*t*-Butyldimethylsilyl)-2-(4-methoxyphenyl)-3-phenylazirine (11a)

Mp 72 °C; IR (nujol) 1739, 1602, 1506, 1309, 1249, 1166, 1020, 839, 704 cm⁻¹; ¹H NMR (CDCl₃) δ -0.05 (s, 3H), 0.19 (s, 3H), 0.89 (s, 9H), 3.86 (s, 3H), 7.03 (d, *J* = 9.0 Hz, 2H), 7.11–7.17 (m, 1H), 7.21–7.26 (m, 2H), 7.35–7.39 (m, 2H), 7.83 (d, *J* = 9.0 Hz, 2H); ¹³C NMR (CDCl₃) δ -5.26, -4.12, 18.32, 27.29, 34.64, 55.53, 114.64, 117.94, 125.85, 127.39, 128.07, 131.19, 144.29, 162.99, 169.03. Found: C, 74.72; H, 7.84%. Calcd for C₂₁H₂₇NOSi: C, 74.73; H, 8.06%.

3-Butyl-3-(*t*-butyldimethylsilyl)-2-(4-methoxyphenyl)azirine (11b)

IR (neat) 2957, 2928, 2856, 1730, 1605, 1578, 1508, 1464, 1304, 1258, 1171, 1030, 833, 806, 770 cm⁻¹; ¹H NMR (CDCl₃) δ -0.09 (s, 3H), -0.04 (s, 3H), 0.79 (t, *J* = 7.5 Hz, 3H), 0.90–1.10 (m, 2H), 0.97 (s, 9H), 1.10–1.27 (m, 2H), 1.16 (ddd, *J* = 5.7 Hz, 11.0 Hz, 14.3 Hz, 1H), 1.83 (ddd, *J* = 5.7 Hz, 11.0 Hz, 14.3 Hz, 1H), 3.89 (s, 3H), 7.03 (d, *J* = 9.0 Hz, 2H), 7.76 (d, *J* = 9.0 Hz, 2H); ¹³C NMR (CDCl₃) δ -6.08, -5.77, 11.04, 17.72, 22.93, 27.33, 28.96, 32.64, 34.82, 55.43, 114.49, 119.49, 130.71, 162.56, 170.19. HRMS Found: 317.2184. Calcd for C₁₉H₃₁ONSi: 317.2175.

1-(*t*-Butyldimethylsilylimino)-2,2-dichloro-1-(4-methoxyphenyl)-3-phenyl-3-trimethylsiloxyp propane (13b)

IR (neat) 2854, 1683, 1606, 1506, 1174, 1107, 700, 600 cm⁻¹; ¹H NMR (CDCl₃) δ -0.22 (s, 3H), -0.17 (s, 3H), 0.04 (s, 9H), 0.98 (s, 9H), 3.80 (s, 3H), 5.83 (s, 1H), 6.80 (d, *J* = 8.9 Hz, 2H), 7.00 (d, *J* = 8.9 Hz, 2H), 7.28–7.35 (m, 3H), 7.51–7.57 (m, 2H); ¹³C NMR (CDCl₃) δ -4.82, -4.59, 0.48, 18.19, 26.20, 55.16, 79.24, 93.55, 112.68, 127.03, 128.09, 128.15, 130.04, 133.02, 138.50, 159.34, 174.69. Found: C, 58.88; H, 7.42%. Calcd for C₂₅H₃₇Cl₂NO₂Si₂: C, 58.80; H, 7.30%.

2,2-Dichloro-1-(4-methoxyphenyl)-3-phenylpropane-1,3-dione (13c)

IR (neat) 2936, 1683, 1573, 1220, 1174, 997, 848, 601 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.88 (s, 3H), 6.96 (d, $J = 8.7$ Hz, 2H), 7.26–7.43 (m, 2H), 7.47–7.53 (m, 3H), 7.96 (d, $J = 8.7$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 55.59, 88.07, 113.89, 123.83, 128.46, 130.26, 131.38, 132.86, 133.97, 164.06, 183.44, 185.00. Found: C, 59.69; H, 3.75%. Calcd for $\text{C}_{16}\text{H}_{12}\text{Cl}_2\text{O}_3$: C, 59.47; H, 3.74%.

1-(*N*-Allylimino)-2-(*t*-butyldimethylsilyl)-2,2-dichloro-1-(4-methoxyphenyl)ethane (12d)

IR (neat) 2858, 1609, 1510, 1298, 1249, 1174, 1035, 921, 833 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.15 (s, 6H), 0.94 (s, 9H), 3.40–3.55 (m, 2H), 3.83 (s, 3H), 5.00–5.10 (m, 2H), 5.80 (ddt, $J = 10.5, 16.8, 6.3$ Hz, 1H), 6.86 (d, $J = 9.0$ Hz, 2H), 7.28 (d, $J = 9.0$ Hz, 2H); ^{13}C NMR (CDCl_3) δ -4.37, 20.31, 27.75, 50.83, 55.20, 113.18, 113.73, 116.46, 129.91, 131.23, 136.65, 144.01, 159.49. Found: C, 57.77; H, 7.12%. Calcd for $\text{C}_{18}\text{H}_{27}\text{Cl}_2\text{NOSi}$: C, 58.05; H, 7.31%

2,2-Dichloro-1-(4-methoxyphenyl)-pent-4-en-1-one (13d)

IR (neat) 2841, 1681, 1600, 1510, 1259, 1178, 1031, 846, 642 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.23 (d, $J = 6.9$ Hz, 2H), 3.89 (s, 3H), 5.27–5.34 (m, 2H), 6.03 (ddt, $J = 10.5, 16.5, 6.9$ Hz, 1H), 6.65 (d, $J = 9.3$ Hz, 2H), 8.32 (d, $J = 9.3$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 48.71, 55.52, 85.46, 113.24, 120.89, 130.99, 133.52, 163.59, 186.34. Found: C, 55.73; H, 4.72%. Calcd for $\text{C}_{12}\text{H}_{12}\text{Cl}_2\text{O}_2$: C, 55.62; H, 4.67%