Supporting Information

Nickel-Catalyzed Reactions of Silacyclobutanes with Aldehydes: Ring Cleavage and Ring Expansion Reaction

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Instrumentation and Materials

^1H NMR (500 MHz), ^{13}C NMR (125.7 MHz), and ^{19}F NMR (282 MHz) spectra were taken on Varian UNITY INOVA 500 and Mercury 300 spectrometers. ^1H NMR and ^{13}C NMR spectra were obtained in C_6D_6 and CDCl_3 with tetramethylsilane as an internal standard. ^{19}F NMR spectra were obtained in C_6D_6 and CDCl_3 with fluorotrichloromethane as an external standard. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel 60F₂₅₄. Silica gel (Wakogel 200 mesh) was used for column chromatography. The analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Toluene was dried over slices of sodium. Bis(1,5-cyclooctadiene)nickel and diphenylmethylphosphine were purchased from Strem. Tri(n-butyl)phosphine was obtained from TCI. 1,1-Dimethylsilacyclobutane and 1,1-dichlorosilacyclobutane were available from Shinetsu Silicone Chemicals.

1,1-Diphenylsilacyclobutane¹ and 2,3-benzo-1,1-dimethylsilacyclobutene² were prepared according to the reported procedures. 1,1-Diphenyl-2-methylsilacyclobutane³ was prepared from the corresponding dichloride.

Experimental Section

Procedure for Ring Cleavage of 1,1-Dimethylsilacyclobutane (1a) with Benzaldehyde (2a)

With a glovebox filled with argon, Ni(cod)₂ (13.8 mg, 0.050 mmol) was placed in a reaction flask. Toluene (5 mL) and PPh₂Me (0.25 M hexane solution, 0.40 mL, 0.10 mmol) were added dropwise. The solution was stirred for 10 min at 0 °C. Benzaldehyde (**2a**, 64 mg, 0.60 mmol) and 1,1-dimethylsilacyclobutane (**1a**, 50 mg, 0.50 mmol) were then added and the resulting solution was heated at 100 °C. After being stirred for 20 h at the same temperature, the mixture was cooled to room temperature and concentrated. Purification by silica gel column afforded allylbenzyloxydimethylsilane (**3a**, 93 mg, 0.44 mmol) in 88% yield.

Procedure for Ring Expansion of 2,3-Benzo-1,1-dimethylsilacyclobutene (1e) with Benzaldehyde (2a)

With a glovebox filled with argon, Ni(cod)₂ (13.8 mg, 0.050 mmol) was placed in a reaction flask. Toluene (3 mL) and PPh₂Me (0.25 M hexane solution, 0.40 mL, 0.10 mmol) were added dropwise. The solution was stirred for 10 min at 0 °C. Benzaldehyde (**2a**, 64 mg, 0.60 mmol) and a solution of 2,3-benzo-1,1-dimethylsilacyclobutene (**1e**, 74 mg, 0.50 mmol) in toluene (2 mL) were then added and the resulting solution was heated at 100 °C. After being stirred for 20 h at the same temperature, the mixture was cooled to room temperature and concentrated. The crude product was purified by column

chromatography to provide 4,5-benzo-1,1-dimethyl-2-oxa-3-phenyl-1-silacyclohexene (**9a**, 85 mg, 0.33 mmol) in 65% yield.

Procedure for Tamao-Fleming Oxidation of 4,5-Benzo-1,1-dimethyl-2-oxa-3-phenyl-1-silacyclohexene (9a)

A solution of 4,5-benzo-1,1-dimethyl-2-oxa-3-phenyl-1-silacyclohexene (**9a**, 25 mg, 0.10 mmol) in THF (1 mL) was added to a suspension of KF (12 mg, 0.20 mmol) and KHCO₃ (20 mg, 0.20 mmol) in MeOH (1 mL). Finally, aq. H₂O₂ (30–35%, 0.2 mL, 2.0 mmol) was added dropwise. After being stirred for 24 h at room temperature, the resulting mixture was poured into aqueous sodium thiosulfate. Extraction with Et₂O followed by silica gel column purification furnished (2-hydroxymethylphenyl)phenylmethanol (**10a**, 19 mg, 0.091 mmol) in 91% yield.

2

Characterization Data.

Spectral data for some compounds (**3a**⁴, **10a**⁵, and **10b**⁶) were found in the literature. ¹H NMR spectral charts for **3a**, **9a**, and **10a–10d** were shown in the last part.

Allyldimethyl(2-methylbenzyloxy)silane (3b): IR (neat) 3076, 2959, 2876, 1632, 1493, 1464, 1375, 1254, 1219, 1184, 1159, 1124, 1082, 1049, 991, 931, 895, 837 cm⁻¹; ¹H NMR (C₆D₆) δ 7.48 (d, *J* = 7.5 Hz, 1H), 7.14 (td, *J* = 7.5, 1.0 Hz, 1H), 7.09 (td, *J* = 7.5, 1.5 Hz, 1H), 7.00 (d, *J* = 7.0 Hz, 1H), 5.75–5.84 (m, 1H), 4.91–4.95 (m, 2H), 4.58 (s, 2H), 2.11 (s, 3H), 1.58 (dt, *J* = 8.0, 1.0 Hz, 2H), 0.09 (s, 6H); ¹³C NMR (C₆D₆) δ -2.44, 18.57, 24.66, 63.47, 113.93, 126.14, 127.31, 127.50, 130.21, 134.22, 135.71, 139.06. Found: C, 70.73; H, 8.89%. Calcd for C₁₃H₂₀OSi: C, 70.85; H, 9.15%.

Allyldimethyl(4-methoxybenzyloxy)silane (3c): IR (neat) 2957, 2872, 2835, 1630, 1614, 1514, 1466, 1302, 1250, 1302, 1171, 1159, 1086, 1038, 895, 835 cm^{-1} ; ^1H NMR (C_6D_6) δ 7.23 (d, J = 8.5 Hz, 2H), 6.81 (d, J = 8.5 Hz, 2H), 5.78–5.86 (m, 1H), 4.93–4.97 (m, 2H), 4.56 (s, 2H), 3.29 (s, 3H), 1.59 (d, J = 8.0 Hz, 2H), 0.10 (s, 6H); ^{13}C NMR (C_6D_6) δ -2.31, 24.74, 54.71, 64.79, 113.90, 113.99, 128.10, 128.25, 134.30, 159.43. Found: C, 65.79; H, 8.62%. Calcd for $\text{C}_{13}\text{H}_{20}\text{O}_2\text{Si}$: C, 66.05; H, 8.53%.

Allyldimethyl(4-trifluoromethylbenzyloxy)silane (3d): IR (neat) 2961, 2882, 1622, 1421, 1377, 1327, 1258, 1209, 1067, 1018, 993, 932, 824, 750, 719 cm^{-1} ; ^1H NMR (C_6D_6) δ 7.36 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 5.72–5.81 (m, 1H), 4.91–4.95 (m, 2H), 4.37 (s, 2H), 1.53 (dt, J = 8.0, 1.0 Hz, 2H), 0.04 (s, 6H); ^{13}C NMR (C_6D_6) δ -2.57, 24.42, 63.97, 114.20, 123.97, 125.31, 125.34, 125.37, 125.40, 126.13, 126.46, 129.23, 129.49, 133.84, 145.38 (The ^{13}C spectrum was very complex due to C-F coupling. All the signals observed were shown.); ^{19}F NMR (C_6D_6) δ -62.59. Found: C, 57.10; H, 6.35%. Calcd for $\text{C}_{13}\text{H}_{17}\text{F}_3\text{OSi}$: C, 56.91; H, 6.25%.

Allyldimethyl(4-methoxycarbonylbenzyloxy)silane (3e): IR (neat) 2954, 2883, 1722, 1631, 1613, 1436, 1419, 1280, 1257, 1192, 1174, 1160, 1089, 1019, 932, 897, 839, 811 cm^{-1} ; ^1H NMR (C_6D_6) δ 8.18 (d, J = 8.5 Hz, 2H), 7.22 (d, J = 8.5 Hz, 2H), 5.72–5.81 (m, 1H), 4.90–4.94 (m, 2H), 4.45 (s, 2H), 3.48 (s, 3H), 1.54 (dt, J = 8.0, 1.0 Hz, 2H), 0.05 (s, 6H); ^{13}C NMR (C_6D_6) δ -2.53, 24.47, 51.52, 64.29, 114.12, 126.19, 129.65, 129.95, 133.94, 146.49, 166.59. Found: C, 63.34; H, 7.45%. Calcd for $\text{C}_{14}\text{H}_{20}\text{O}_3\text{Si}$: C, 63.60; H, 7.62%.

Allyldimethyl(3-phenylpropoxy)silane (3f): IR (neat) 3063, 3028, 2918, 2864, 1632,

1497, 1454, 1387, 1254, 1157, 1101, 1040, 964, 895, 835, 806 cm^{-1} ; ^1H NMR (C_6D_6) δ 7.05–7.17 (m, 5H), 5.78–5.86 (m, 1H), 4.93–4.97 (m, 2H), 3.45 (t, $J = 6.3$ Hz, 2H), 2.61 (t, $J = 7.8$ Hz, 2H), 1.73–1.79 (m, 2H), 1.57 (dt, $J = 8.0, 1.0$ Hz, 2H), 0.08 (s, 6H); ^{13}C NMR (C_6D_6) δ –2.44, 24.65, 32.36, 34.63, 61.94, 113.80, 126.06, 128.61, 128.79, 134.37, 142.33. Found: C, 71.91; H, 9.52%. Calcd for $\text{C}_{14}\text{H}_{22}\text{OSi}$: C, 71.73; H, 9.46%.

Allyl(cyclohexylmethoxy)dimethylsilane (3g): IR (neat) 2924, 2854, 1632, 1450, 1253, 1157, 1115, 1083, 1070, 1056, 1029, 932, 897, 836, 806 cm^{-1} ; ^1H NMR (C_6D_6) δ 5.81–5.89 (m, 1H), 4.94–4.99 (m, 2H), 3.33 (d, $J = 6.5$ Hz, 2H), 1.74–1.79 (m, 2H), 1.66–1.70 (m, 2H), 1.58–1.63 (m, 1H), 1.60 (dt, $J = 8.0, 1.0$ Hz, 2H), 1.43–1.51 (m, 1H), 1.06–1.22 (m, 3H), 0.85–0.93 (m, 2H), 0.10 (s, 6H); ^{13}C NMR (C_6D_6) δ –2.45, 24.68, 26.27, 26.99, 29.99, 40.70, 68.63, 113.74, 134.47. Found: C, 67.80; H, 11.12%. Calcd for $\text{C}_{12}\text{H}_{24}\text{OSi}$: C, 67.86; H, 11.39%.

(E)-Allyl(cinnamyloxy)dimethylsilane (3h): IR (neat) 3061, 3026, 2959, 2855, 1632, 1497, 1448, 1379, 1254, 1157, 1124, 1061, 966, 932, 839, 731, 692 cm^{-1} ; ^1H NMR (C_6D_6) δ 7.26 (d, $J = 7.5$ Hz, 2H), 7.11 (t, $J = 7.5$ Hz, 2H), 7.03 (t, $J = 7.5$ Hz, 1H), 6.61 (dt, $J = 15.5, 1.5$ Hz, 1H), 6.18 (dt, $J = 16.0, 5.0$ Hz, 1H), 5.80–5.88 (m, 1H), 4.94–4.99 (m, 2H), 4.15 (dd, $J = 5.0, 1.5$ Hz, 2H), 1.61 (dt, $J = 8.0, 1.0$ Hz, 2H), 0.12 (s, 6H); ^{13}C NMR (C_6D_6) δ –2.30, 24.73, 63.63, 113.97, 126.71, 127.60, 128.82, 129.20, 129.94, 134.24, 137.48. Found: C, 72.10; H, 8.79%. Calcd for $\text{C}_{14}\text{H}_{20}\text{OSi}$: C, 72.36; H, 8.67%.

Allyl(benzyloxy)diphenylsilane (3i): IR (neat) 2866, 2341, 1630, 1589, 1497, 1454, 1429, 1379, 1159, 1069, 1028, 997, 901, 833, 735, 698, 679 cm^{-1} ; ^1H NMR (C_6D_6) δ 7.64–7.67 (m, 4H), 7.30 (d, $J = 7.0$ Hz, 2H), 7.16–7.18 (m, 8H), 7.08 (t, $J = 7.5$ Hz, 1H),

5.83–5.52 (m, 1H), 4.89–4.97 (m, 2H), 4.74 (s, 2H), 2.14 (dt, $J = 8.0, 1.3$ Hz, 2H); ^{13}C NMR (C_6D_6) δ 22.16, 65.61, 115.35, 126.62, 127.34, 127.91, 128.50, 130.26, 133.13, 134.74, 135.17, 141.00. Found: C, 80.25; H, 6.78%. Calcd for $\text{C}_{22}\text{H}_{22}\text{OSi}$: C, 79.95; H, 6.71%.

Allyldiphenyl(3-phenylpropoxyl)silane (3j): IR (neat) 2868, 2341, 1630, 1589, 1497, 1454, 1429, 1387, 1097, 1040, 966, 899, 735, 698, 675 cm^{-1} ; ^1H NMR (C_6D_6) δ 7.65–7.67 (m, 4H), 7.11–7.21 (m, 8H), 7.03–7.07 (m, 3H), 5.85–5.94 (m, 1H), 4.91–4.99 (m, 2H), 3.63 (t, $J = 6.0$ Hz, 2H), 2.61 (t, $J = 7.5$ Hz, 2H), 2.13 (dt, $J = 7.5, 1.5$ Hz, 2H), 1.76–1.81 (m, 2H); ^{13}C NMR (C_6D_6) δ 22.12, 32.30, 34.50, 62.85, 115.18, 126.01, 128.13, 128.58, 128.79, 130.18, 133.33, 135.11, 135.17, 142.24. Found: C, 80.16; H, 7.25%. Calcd for $\text{C}_{24}\text{H}_{26}\text{OSi}$: C, 80.39; H, 7.31%.

Benzyloxydiphenyl(1-methylpropenyl)silane (3k) and (E)-Benzyloxycrotyldiphenylsilane (3k'): IR (neat) 3001, 2867, 1497, 1453, 1428, 1378, 1207, 1161, 1069, 1027, 998, 964, 900, 800 cm^{-1} ; ^1H NMR (C_6D_6) For **3k** δ 7.67–7.72 (m, 4H), 7.29–7.33 (m, 2H), 7.17–7.20 (m, 8H), 7.06–7.09 (m, 1H), 6.13 (ddd, $J = 17.5, 10.5, 7.0$ Hz, 1H), 4.92–4.99 (m, 2H), 4.73 (d, $J = 4.0$ Hz, 2H), 2.38–2.45 (m, 1H), 1.25 (d, $J = 7.5$ Hz, 3H). For **3k'** δ 7.67–7.72 (m, 4H), 7.29–7.33 (m, 2H), 7.17–7.20 (m, 8H), 7.06–7.09 (m, 1H), 5.50–5.57 (m, 1H), 5.27–5.34 (m, 1H), 4.76 (s, 2H), 2.13 (dt, $J = 7.5, 1.5$ Hz, 2H), 1.48 (dq, $J = 6.5, 1.5$ Hz, 3H); ^{13}C NMR (C_6D_6) For **3k** and **3k'** δ 12.98, 18.19, 20.25, 26.34, 65.60, 65.71, 112.60, 125.06, 125.83, 126.48, 126.61, 127.29, 127.91, 128.12, 128.48, 128.49, 130.19, 130.26, 133.43, 133.68, 135.11, 135.18, 135.62, 135.69, 139.89, 141.08. Found: C, 80.40; H, 6.99%. Calcd for $\text{C}_{23}\text{H}_{24}\text{OSi}$: C, 80.18; H, 7.02%.

4,5-Benzo-1,1-dimethyl-2-oxa-3-phenyl-1-silacyclohexene (9a): IR (neat) 3063, 2959, 1493, 1481, 1452, 1252, 1175, 1026, 843, 812, 748, 723 cm^{-1} ; ^1H NMR (C_6D_6) δ 7.38–7.40 (m, 2H), 7.13–7.17 (m, 2H), 7.06–7.11 (m, 2H), 7.02–7.04 (m, 1H), 6.93–6.96 (m, 1H), 6.82–6.84 (m, 1H), 5.98 (s, 1H), 1.82 (d, $J = 15.5$ Hz, 1H), 1.76 (d, $J = 15.5$ Hz, 1H), 0.10 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (C_6D_6) δ –0.54, 0.06, 20.22, 78.20, 125.23, 127.23, 127.37, 127.91, 128.12, 128.36, 131.09, 136.47, 141.24, 143.47.

4,5-Benzo-1,1-dimethyl-3-(2-methylphenyl)-2-oxa-1-silacyclohexene (9b): IR (neat) 3019, 2957, 1478, 1454, 1251, 1031, 878, 842, 808, 772, 739, 632, 610 cm^{-1} ; ^1H NMR (C_6D_6) δ 7.47–7.49 (m, 1H), 7.07–7.12 (m, 5H), 6.85–6.88 (m, 1H), 6.70 (d, $J = 7.5$ Hz, 1H), 6.08 (s, 1H), 2.22 (s, 3H), 1.98 (s, 2H), 0.14 (s, 3H), –0.07 (s, 3H); ^{13}C NMR (C_6D_6) δ –0.50, –0.45, 19.55, 20.48, 74.96, 125.45, 126.29, 127.02, 127.74, 127.95, 128.11, 130.59, 130.86, 136.73, 137.26, 140.39, 141.05. Found: C, 76.07; H, 7.54%. Calcd for $\text{C}_{17}\text{H}_{20}\text{OSi}$: C, 76.07; H, 7.51%.

4,5-Benzo-1,1-dimethyl-2-oxa-1-sila-3-(4-trifluoromethylphenyl)cyclohexene (9c): IR (neat) 2882, 1619, 1602, 1484, 1454, 1411, 1326, 1253, 1110, 1068, 1036, 1017, 813, 778, 744 cm^{-1} ; ^1H NMR (C_6D_6) δ 7.32 (d, $J = 8.0$ Hz, 2H), 7.20–7.22 (m, 2H), 7.09 (td, $J = 7.5, 1.5$ Hz, 1H), 7.00 (d, $J = 7.5$ Hz, 1H), 6.94 (td, $J = 7.5, 1.5$ Hz, 1H), 6.68 (d, $J = 7.0$ Hz, 1H), 5.80 (s, 1H), 1.71 (d, $J = 15.0$ Hz, 1H), 1.66 (d, $J = 15.0$ Hz, 1H), 0.06 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (C_6D_6) δ –0.71, –0.14, 20.10, 77.57, 125.25, 125.28, 125.35, 127.43, 127.91, 128.10, 128.45, 131.17, 136.30, 140.27, 147.40 (The ^{13}C spectrum was very complex due to C-F coupling. All the signals observed were shown.); ^{19}F NMR (C_6D_6) δ –62.62. Found: C, 63.14; H, 5.39%. Calcd for $\text{C}_{17}\text{H}_{17}\text{F}_3\text{OSi}$: C, 63.33; H, 5.31%.

4,5-Benzo-1,1-dimethyl-2-oxa-3-(2-phenylethyl)-1-silacyclohexene (9d): IR (neat) 3026, 2860, 1603, 1485, 1454, 1252, 1194, 1074, 1036, 955, 841, 812 cm^{-1} ; ^1H NMR (C_6D_6) δ 7.13–7.18 (m, 4H), 7.06–7.10 (m, 2H), 7.03 (d, $J = 7.0$ Hz, 1H), 6.98 (t, $J = 7.5$ Hz, 1H), 6.83 (d, $J = 7.5$ Hz, 1H), 4.80 (dd, $J = 9.0, 4.5$ Hz, 1H), 2.89 (ddd, $J = 14.0, 1.0, 4.5$ Hz, 1H), 2.74 (ddd, $J = 14.0, 10.0, 7.0$ Hz, 1H), 2.03–2.10 (m, 1H), 1.90–1.97 (m, 1H), 1.95 (d, $J = 16.0$ Hz, 1H), 1.76 (d, $J = 16.0$ Hz, 1H), 0.15 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (C_6D_6) δ –0.51, 0.57, 19.60, 32.72, 40.01, 76.13, 125.39, 126.08, 126.55, 127.59, 128.66, 128.92, 131.61, 135.42, 141.79, 142.39. Found: C, 76.36; H, 7.89%. Calcd for $\text{C}_{18}\text{H}_{22}\text{OSi}$: C, 76.54; H, 7.85%.

(2-Hydroxymethylphenyl)(4-trifluoromethylphenyl)methanol (10c): IR (neat) 3289, 2892, 1619, 1414, 1327, 1112, 1068, 1016, 951, 861, 799, 757, 726, 668 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.61 (d, $J = 8.5$ Hz, 2H), 7.52 (d, $J = 8.5$ Hz, 2H), 7.32–7.35 (m, 3H), 7.18–7.20 (m, 1H), 6.12 (s, 1H), 4.71 (d, $J = 12.5$ Hz, 1H), 4.53 (d, $J = 12.5$, 1H), 2.50 (bs, 2H); ^{13}C NMR (CDCl_3) δ 64.22, 73.95, 123.06, 125.22 (q, $J = 3.8$ Hz), 126.64, 128.63, 128.84, 129.26, 129.62, 130.44, 138.14, 142.00, 146.67; ^{19}F NMR (CDCl_3) δ –62.98.

1-(2-Hydroxymethylphenyl)-3-phenyl-1-propanol (10d): IR (nujol) 3235, 2924, 2854, 1456, 1377, 1366, 1189, 1053, 1011, 922, 764, 749, 744 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.47 (d, $J = 7.5$ Hz, 1H), 7.28–7.37 (m, 5H), 7.20–7.23 (m, 3H), 4.96 (dd, $J = 8.5, 5.0$ Hz, 1H), 4.72 (d, $J = 12.5$ Hz, 1H), 4.65 (d, $J = 12.5$ Hz, 1H), 2.87 (ddd, $J = 14.0, 9.5, 5.5$ Hz, 1H), 2.74 (ddd, $J = 14.0, 9.5, 7.0$ Hz, 1H), 2.50 (bs, 2H), 2.23–2.30 (m, 1H), 2.10–2.17 (m, 1H); ^{13}C NMR (CDCl_3) δ 32.56, 38.44, 63.80, 70.63, 125.95, 126.42, 127.90, 128.43, 128.44, 128.59, 129.79, 137.97, 141.63, 142.40. m.p. 73–74 °C.

References and Notes

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^1H NMR in CDCl_3