Palladium-Catalyzed Dehydrogenative Double Silylation of Acetylenes with Bis- and Tris(dichlorosilyl)methanes : One Step Synthesis of 1,1,3,3-Tetrachloro-1,3-disilacyclopent-4-ene Compounds

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Reactions of acetylenes with bis- and tris(dichlorosilyl)methanes in the presence of tetrakis(triphenylphosphine)palladium as catalyst gave dehydrogenative double silylation products, 1,1,3,3-tetrachloro-1,3-disilacyclopent-4-enes, in fair to excellent yields depending upon the molecular structures of two reactants. Tris(dichlorosilyl)methanes gave better yield than bis(dichlorosilyl)methanes. As bulky substituents were introduced to acetylene, the reactions proceeded more slowly and the product yields decreased.

Supporting Information

Experimental Section

All reactions and manipulations were carried out with flame-dried glassware under nitrogen. All air sensitive liquids were transferred by standard syringe or double tipped needle techniques.¹ All starting silane compounds such as bis(dichlorosilyl)methane, tris(silyl)methanes used for hydrosilylation reaction with alkynes were prepared through the modified direct synthesis method previously described.^{2, 3} Acetylene gas was commercially available and purified by passing it through a dry acetone trap and then a calcium chloride drying tube. Solvents were dried according to standard procedures.⁴ All other chemicals were purchased from Aldrich Chemical Co. and used as received unless otherwise noted. The progresses of reaction were monitored and product yields were determined by GLC using a packed column (10% OV-101 on 80-100 mesh Chromosorb W/AW, 1/8 in. x 1.5 m) or a capillary column (HP-1, 0.11 μm, ID 0.2 mm x 25 m) with a Varian

¹ Shriver, D.F.; Drezdon, M.A. *Manipulation of Air-Sensitive Compounds*, 2nd Ed; Willey, New York, 1986.

² Seung Ho Yeon, Joon Soo Han, Bok Ryul Yoo, and Il Nam Jung *J. Organomet. Chem.* **1996**, 516, 91

³ Chang Yeob Lee, Joon Soo Han, Hyung Sik Oh, Bok Ryul Yoo, and Il Nam Jung *Bull. Korean Chem. Soc.* **2000**, 21, 1020

⁴ *Purification of laboratory chemicals*, Perrin, D.D., Armarego W.L.F., Pergamon Press **1988**, New York, USA.

3300 gas chromatograph equipped with a thermal conductivity detector unless otherwise noted. NMR spectra were recorded on a Bruker Avance 300 spectrometer (300 MHz for ^1H ; 75 MHz for ^{13}C) using CDCl_3 as a solvent. The chemical shifts are given in ppm relative to the residual proton signal of the solvent: CDCl_3 7.25 ppm (1H) and 77.0 ppm (13C). Melting points (uncorrected) were measured with a Mel-Temp II melting point apparatus using sealed capillary tubes. GC-MS data were obtained with a HP6890/5973 system (70 eV, EI). Elemental analyses were performed by the Advanced Analysis Center of the Korea Institute of Science and Technology.

Procedure for the dehydrogenative double silylation reaction of **1a** with **2a**

To a 100 mL, two necked, flame dried, round bottom flask equipped with a magnetic stirrer bar, condenser/ N_2 inlet were charged with 0.087 g of $\text{Pd}[\text{PPh}_3]_4$, 4.91 g (15 mmol) of **1a** and 75 mL of dried benzene. The reaction flask was heated up to refluxing temperature for 8 hrs. The **2a** through gas inlet adapter was bubbled into the solution at a rate of 50 mL/min for 8 hrs. The reaction products were vacuum distilled at 0.5 torr to give **3aa** (4.88 g) in 92.7% isolated yield. Data for 2-methyldichlorosilyl-1,1,3,3-tetrachloro-1,3-disilacyclopent-4-ene (**3aa**) (white solid, bp: 55-57 $^\circ\text{C}$ / 0.5 torr, mp: 48-50 $^\circ\text{C}$): ^1H NMR δ 1.06 (s, 3H, SiCH_3), 1.30 (s, 1H, SiCHSi), 7.38 (s, 2H, CH=CH); ^{13}C NMR δ 8.34 (s, 1C, SiCH_3), 18.98 (SiCHSi), 153.67 (CH=CH); MS (70 eV, EI) m/z (relative intensity): 335 (100, $[\text{M}^+-\text{CH}_3]$), 315 (5), 299 (6), 226 (6), 211 (11), 189 (8), 139 (5), 113 (5), 63 (23).); HRMS (EI) m/z calcd for $\text{C}_3\text{H}_3\text{Cl}_6\text{Si}_3$ $[\text{M}^+-\text{CH}_3]$ 332.7674, found 332.7674; Anal calcd for $\text{C}_4\text{H}_6\text{Cl}_6\text{Si}_3$: C, 13.68; H, 1.72, found: C, 13.50; H, 1.80.

Procedure for the dehydrogenative double silylation reaction of **1a** with **2b**

A 100 mL, round-bottomed, flame dried, two-necked flask equipped with a magnetic stir bar, condenser/ N_2 inlet were charged with **1a** (4.91 g, 15 mmol), 0.087g of $\text{Pd}[\text{PPh}_3]_4$ and 75 ml of dried benzene. The flask was then heated up to refluxing temperature. **2b** (2.30 g, 22.5 mmol) was added at 0.02 mL/min to the flask using a syringe pump. After maintaining at refluxing temperature for a total of 3 hours, the reaction products were distilled off under vacuum to give 5.34 g of **3ab** in 83.3% isolated yield. Data for 2-methyldichlorosilyl-1,1,3,3-tetrachloro-4-phenyl-1,3-disilacyclopent-4-ene (**3ab**) (white solid, mp: 97-99 $^\circ\text{C}$): ^1H NMR δ 1.12 (s, 3H, SiCH_3), 1.57 (s, 1H, SiCHSi), 7.36 (s, 1H, CHCPh), 7.42-7.70 (m, 5H, ArH); ^{13}C NMR δ 8.00 (SiCH_3), 20.36 (SiCHSi), 127.43, 129.05, 130.31, 135.76, (phenyl-C), 143.16 (SiCHCPh), 163.66 (CHCPh); MS (70 eV, EI) m/z (relative intensity): 424 (22, M^+), 411 (100, $[\text{M}^+-\text{CH}_3]$), 226 (11), 211 (22), 191 (17), 178 (9), 115 (30), 102 (21), 63 (43); Anal calcd for $\text{C}_{10}\text{H}_{10}\text{Cl}_6\text{Si}_3$: C, 28.12; H, 2.36, found: C, 28.67; H, 2.38.

Reaction of 1a with 2c: Into the same apparatus as described previously was charged with **1a** (4.91 g, 15 mmol), 0.087 g of Pd[PPh₃]₄ and 75 ml of dried benzene. The flask was then heated up to refluxing temperature. 1.86 g (22.5 mmol) of **2c** was fed dropwise into flask by syringe pump. After maintaining at refluxing temperature for a total of 2 hours, the reaction products were distilled off under vacuum to give 5.04 g mixture of **3ac** (GC 86.4%) and 4-methyldichlorosilyl-3,3,5,5-tetrachloro-2,6-dibutyl-3,5-disilahepta-1,6-diene (GC 13.6 %). Data for 2-methyldichlorosilyl-1,1,3,3-tetrachloro-4-butyl-1,3-disilacyclopent-4-ene (**3ac**) (bp: 82-84 °C / 0.5 torr): ¹H NMR δ 0.94 (t, 3H, CH₂CH₃, *J* = 7.16 Hz), 1.05 (s, 3H, SiCH₃), [1.31-1.43](#) (m, [3H](#), CH₂CH₂CH₃ and SiCHSi), [1.54-1.64](#) (m, [2H](#), CH₂CH₂CH₂), 2.50 (t, 2H, CCH₂CH₂, *J* = 6.78 Hz), 6.86 (s, 1H, CH=CBu); ¹³C NMR δ 7.89 (SiCHSi), 13.85 (SiCH₃), 19.65 (CH₂CH₃), 22.31 (CH₂CH₂CH₃), 29.54 (CCH₂CH₂), 33.65 (CH₂CH₂CH₂), 143.89 (SiCHCBu), 169.74 (CHCBu); MS (70 eV, EI) *m/z* (relative intensity): 406 (10), 404 (5, M⁺), 377 (39), 364 (100, [M⁺-C₃H₇]), 349 (62), 325 (58), 211 (32), 191 (33), 115 (34), 63 (48); Anal calcd for C₈H₁₄Cl₆Si₃: C, 23.60; H, 3.47, found: C, 23.62; H, 3.50.

Reaction of 1b with 2a: Into the same apparatus as described previously were placed 3.21 g (15 mmol) of **1b**, 0.087 g of Pd(PPh₃)₄ and 75 mL of dried benzene. **2a** was bubbled into the flask at 50 ml / min for 5 hours. The products were vacuum distilled off to yield a mixture comprising 1.48 g of 1,1,3,3-tetrachloro-1,3-disilacyclopent-4-ene (**3ba**) (GC 93.9%); 1,1,3,3-tetrachloro-1,3-disilacyclopentane (**4ba**) (GC 4.6%); 3,3,5,5-tetrachloro-3,5-disilahepta-1,6-diene (GC 1.5%). Data for **3ba** (bp: 48-50 °C / 20 torr): ¹H NMR δ 1.13 (s, 2H, SiCH₂Si), 7.34 (s, 2H, CH=CH); ¹³C NMR δ 7.61 (SiCH₂Si), 153.83 (CH=CH); MS (70 eV, EI) *m/z* (relative intensity): 236 (46, M⁺), 212 (100, [M⁺-CH=CH]), 138 (22), 112 (13), 103 (46), 63 (73); Anal calcd for C₃H₄Cl₄Si₂: C, 15.14; H, 1.69, found: C, 15.16; H, 2.00.

Reaction of 1b with 2b: Into the same apparatus as described previously were added 3.21 g (15 mmol) of **1b**, 0.087 g of Pd(PPh₃)₄ and 75 ml of dried benzene. The flask content was heated to reflux and 3.06 g of **2b** was added dropwise for 2 hours. The products were vacuum distilled off to give a mixture comprising 1.68 g of 1,1,3,3-tetrachloro-4-phenyl-1,3-disilacyclopent-4-ene (**3bb**) (GC 91.7%), 1,1,3,3-tetrachloro-4-phenyl-1,3-disilacyclopentane (**4bb**) (GC 4.1%) and 3,3,5,5-tetrachloro-1-phenyl-3,5-disilapenta-1-ene (GC 2.7%). Data for **3bb** (bp: 116-118 °C / 0.5 torr): ¹H NMR δ 1.36 (s, 2H, SiCH₂Si), 7.34 (s, 1H, CHCPh), 7.41-7.69 (m, 5H, ArH); ¹³C NMR δ 9.75 (SiCH₂Si), 127.43, 128.96, 130.00, 136.33 (phenyl-C), 144.00 (SiCHCPh), 164.26 (CHCPh); MS (70 eV, EI) *m/z* (relative intensity): 314 (100, M), 214 (38, [M⁺-CH=CHPh]), 179 (38), 165 (24), 115 (32), 102 (28), 63 (68); Anal calcd for C₉H₈Cl₄Si₂: C, 34.41; H, 2.57, found: C, 34.50; H, 2.76.

Reaction of 1c with 2a. Into the same apparatus as described previously were placed 5.21 g (15 mmol) of **1c**, 0.087 g of Pd(PPh₃)₄ and 75 mL of dried benzene. **2a** was bubbled into the flask at 50 ml / min for 5 hours. The products were vacuum distilled off to yield a mixture comprising 2.88 g of 2-trichlorosilyl-1,1,3,3-tetrachloro-1,3-disilacyclopent-4-ene (**3ca**) (GC 87.6%), 4-trichlorosilyl-3,3,5,5-tetrachloro-3,5-disilapenta-1-ene (GC 0.8%) and 4-trichlorosilyl-3,3,5,5-tetrachloro-3,5-disilahepta-1,6-diene (GC 1.6%). Data for **3ca** (bp: 79-81 °C / 0.5 torr): ¹H NMR δ 1.51 (s, 1H, SiCHSi), 7.38 (s, 2H, CH=CH); ¹³C NMR δ: 20.94 (SiCHSi), 152.88 (CH=CH); MS (70 eV, EI) *m/z* (relative intensity): 368 (22, M⁺), 346(70), 335 (20), 272 (27), 237 (100, [M⁺-SiCl₃]), 211 (53), 175(11), 135 (12), 63 (85). Because of the sticky gel highly air sensitive properties of **3ca**, the elemental analyze data was unavailable. We switched to get methylated compound from **3ca** by using Grignard reagent.

Methylation of **3ca** was carried as followings: To a solution of **3ca** (0.76g, 2.05 mmol) in THF (15 mL) at 0 °C was added a 3 M solution of methylmagnesiumchloride in THF (5 mL, 15 mmol) for 10 min. The reaction mixture was stirred at ambient temperature for 1 h and raised up to 70 °C for 3h, quenched with water and extracted with ether. The extract was dried over anhydrous MgSO₄. Solvent was distilled off to give 2-trimethylsilyl-1,1,3,3-tetramethyl-1,3-disilacyclopent-4-ene in 81% yield: ¹H NMR δ 0.07 (s, 9H, Si(CH₃)₃), [0.14 \(s, 6H, Si\(CH₃\)₂\)](#), [0.16 \(s, 6H, Si\(CH₃\)₂\)](#), 0.19 (s, 1H, CH), 7.04 (s, 2H, CH=CH); ¹³C NMR δ 0.71 (SiCHSi), 1.53 (Si(CH₃)₃), 2.33 (Si(CH₃)₂), 155.80 (CH=CH); MS (70 eV, EI) *m/z* (relative intensity): 228 (1, M⁺), 213 (100, [M⁺-CH₃]), 197 (5), 129 (7), 125 (8), 99 (4), 73 (17), 59 (7). Anal calcd for C₁₀H₂₄Si₃: C: 52.55; H: 10.58, found: C: 52.80; H: 10.15.

Reaction of 1d with 2a: Into the same apparatus as described previously were placed 4.70 g (15 mmol) of **1d**, 0.087 g of Pd(PPh₃)₄ and 75 mL of dried benzene. **2a** was bubbled into the flask at 50 ml / min for 4 hours. The products were vacuum distilled off to yield a mixture comprising 2.76 g of 2-dichlorosilyl-1,1,3,3-tetrachloro-1,3-disilacyclopent-4-ene (**3da**) (GC 87.5%) and 4-dichlorosilyl-3,3,5,5-tetrachloro-3,5-disilahepta-1,6-diene (GC 7.6%). Data for **3da** (bp: 75-77 °C / 0.5 torr): ¹H NMR δ 1.29 (d, 1H, SiCHSi, *J*= 3.77 Hz), 5.70 (d, 1H, SiH, *J*= 3.77 Hz), 7.40 (s, 2H, CH=CH); ¹³C NMR δ 16.44 (SiCHSi), 153.30 (CH=CH); MS (70 eV, EI) *m/z* (relative intensity): 335 (100, M⁺), 300 (38), 238 (11, [M⁺-SiHCl₂]), 211 (17), 203 (34), 175 (16), 139 (15), 103 (15), 63(62); Anal calcd for C₃H₄Cl₆Si₃: C, 10.69; H, 1.20, found C: 10.84; H: 1.48.

Reaction of 1d with 2b: Into the same apparatus as described previously were added 4.69 g (15 mmol) of **1d**, 0.087 g of Pd(PPh₃)₄ and 75 mL of dried benzene. The flask content was heated to reflux and 3.06 g of **2b** was added dropwise for 2 hours. The products were vacuum distilled off to give 4.50g of 2-dichlorosilyl-1,1,3,3-tetrachloro-4-phenyl-1,3-disilacyclopent-4-ene (**3db**). Data for

3db (white solid, mp: 65-67 °C): ^1H NMR δ 1.54 (d, 1H, SiCHSi , $J = 4.14$ Hz), 5.78 (d, 1H, SiH , $J = 3.77$ Hz), 7.37 (s, 1H, CHCPh), 7.44-7.69 (m, 5H, ArH); ^{13}C NMR δ 18.15 (SiCHSi), 127.42, 129.11, 130.41, 135.68 (phenyl-C), 143.04 (SiCHCPh), 163.92 (CHCPh); MS (70 eV, EI) m/z (%): 410 (45, M^+), 376 (17), 314 (22), 279 (100, $[\text{M}^+ - \text{SiCl}_3]$), 211 (36), 179 (35), 165 (85), 115 (50), 102 (40), 63 (90); Anal calcd for $\text{C}_9\text{H}_8\text{Cl}_6\text{Si}_3$: C, 26.17; H, 1.95, found: C: 26.36; H: 2.13.

Reaction of 1b with 1-hexene. Into the same apparatus as described previously were added 725 μl of 0.1 M $\text{H}_2\text{PtCl}_6/\text{IPA}$ under dry nitrogen atmospheric pressure. After removing isopropyl alcohol under vacuum, 3.21 g (15 mmol) of **1b** and 75 ml of dried toluene were added. After 10 minutes of mixing, 2.25 mL (18 mmol) of 1-hexene was added into the flask for 30 min at room temperature. The reaction flask was then maintained at room temperature for an additional 1.5 hours. The reaction products were vacuum distilled at 0.5 torr to give 4.08 g mixture of 1,1,3,3-tetrachloro-1,3-disilanonane (GC 70.5%) and 7,7,9,9-tetrachloro-7,9-disilapentadecane (GC 14.4%). Data for 1,1,3,3-tetrachloro-1,3-disilanonane: ^1H NMR δ 0.89 (t, 3H, CH_3 , $J = 6.60\text{Hz}$), 1.18-1.55 (m, 10H, CH_2), 1.28 (d, 2H, SiCH_2Si , $J = 2.26\text{Hz}$), 5.67 (t, 1H, SiH , $J = 2.45\text{Hz}$); ^{13}C NMR δ 14.04 (SiCH_2Si), 14.60, 22.42, 31.23, 31.93 (CH_2 , n -hexyl), 22.19 (CH_3); MS (70 eV, EI) m/z (relative intensity): 296 (1, M^+), 213 (100, $[\text{M}^+ - \text{C}_6\text{H}_{13}]$), 177 (8), 141(4), 63(12); Anal calcd for $\text{C}_7\text{H}_{16}\text{Cl}_4\text{Si}_2$: C, 28.20; H, 5.41, found: C, 28.38; H, 5.50.

Reaction of 1b with 2-methylbuta-1,3-diene: Into the same apparatus as described previously were added 3.21 g (15 mmol) of **1b**, 0.087 g of $\text{Pd}(\text{PPh}_3)_4$ and 75 mL of dried benzene. The flask content was then heated to refluxing temperature and 3.0 mL of 2-methylbuta-1,3-diene was added dropwise for 1 hour. The reaction products were vacuum distilled at 0.5 torr to give 4.52 g mixture of 1,1,3,3-tetrachloro-5-methyl-1,3-disilahept-5-ene (GC 40.0%) and 5,5,7,7-tetrachloro-3,9-dimethyl-5,7-disilaundeca-2,9-diene (GC 49.8%).

Data for 1,1,3,3-tetrachloro-5-methyl-1,3-disilahept-5-ene: ^1H NMR δ 1.28 (d, 2H, SiCH_2Si , $J = 2.26\text{Hz}$), 1.57 (d, 3H, CH_3 , $J_{\text{cis}} = 6.78\text{Hz}$), 1.80 (d, 3H, CH_3 , $J_{\text{trans}} = 1.13\text{Hz}$), 2.21 (s, 2H, SiCH_2), 5.33-5.40 (m, 1H, CH_2CH), 5.68 (t, 1H, SiH , $J = 2.26\text{Hz}$); ^{13}C NMR δ 14.39 (SiCH_2Si), 14.60 (SiCH_2), 25.82, 27.98 (CH_3), 121.50 ($\text{CH}_2\text{C}=\text{CH}$), 127.83 ($\text{CH}_2\text{C}=\text{CH}$); MS (70 eV, EI) m/z (relative intensity): 280 (8, M^+), 240 (8), 213(100, $\text{CH}_2(\text{SiHCl}_2)_2$), 177 (12), 113 (4), 63 (24); Anal calcd for $\text{C}_6\text{H}_{12}\text{Cl}_4\text{Si}_2$: C, 25.54; H, 4.29, found: C, 25.37; H, 4.34.

Data for: 5,5,7,7-tetrachloro-3,9-dimethyl-5,7-disilaundeca-2,9-diene: ^1H NMR δ 1.22 (s, 2H, SiCH_2Si), 1.57 (d, 6H, CH_3 , $J_{\text{cis}} = 6.78\text{Hz}$), 1.80 (d, 6H, CH_3 , $J_{\text{trans}} = 0.75\text{Hz}$), 2.22 (s, 4H, SiCH_2), 5.32-5.39 (m, 2H, $\text{C}=\text{CH}$); ^{13}C NMR δ 14.38 (SiCH_2Si), 14.73 (SiCH_2), 25.82, 27.91 (CH_3), 121.24 ($\text{CH}_2\text{C}=\text{CH}$), 128.14 ($\text{CH}_2\text{C}=\text{CH}$); MS (70eV, EI) m/z (relative intensity): 348 (5, M^+), 281 (86,

$M^+ - C_5H_9$), 253 (41), 243 (57), 227(29), 213 (100, $CH_2(SiHCl_2)_2$), 177 (13), 131 (21), 63 (26); Anal calcd for $C_{11}H_{20}Cl_4Si_2$: C, 37.72; H, 5.76, found: C, 37.88; H, 5.83.