Pyrolysis of 1,1-Dialkoxy-1-Ethyl-2,2,2-Trimethyldisilane

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Intramolecular C-H insertion of alkylsilylenes, giving silacyclopropane intermediates, is well known.[1] Seyferth reported that hexamethylsilacyclopropane decomposes by thermal extrusion of dimethylsilylene.[2] Kumada and Ishikawa reported that photolysis of tris(trimethylsilyl)phenylsilane in the presence of carbonyl compounds resulted in the formation of disilanyl enol ethers.[3] The authors suggested a possible mechanism involving initial formation of an ylide and an oxasilacyclopropane intermediate. Ando and Sekiguchi reported that pyrolysis of 1,2-dimethoxy-1,1,2,2-tetramethyldisilane in the presence of alkyl ketones afforded the respective silyl enol ethers and occurred through a mechanism involving initial formation of oxasilacyclopropane intermediate.[4] The same authors reported that dimesitylsilanediyl was generated from photolysis and pyrolysis of the stable oxasilacyclopropane *via* a [3→2+1] cycloelimination reaction.[5] Seyferth reported that reactions of hexamethylsilacyclopropane with carbonyl compounds in the presence of tertiary phosphines were found to proceed through an oxasilacyclopropane intermediacy.[6]

In a previous paper we reported that 2-phenyloxasilacyclopropane intermediate might be formed from the intramolecular silylene insertion into a C-H bond of the methoxy group in methoxyphenylsilylene which produced from the conventional α-elimination of methoxytrimethylsilane from the 1,1-dimethoxy-1-phenyl-2,2,2-trimethyldisilane under thermal condition.[7a] Here, we report a competitive intramolecular silylene insertion into a C-H bond of the alkoxy and ethyl group of alkoxyethylsilylene which is generated from the vacuum pyrolysis of 1,1-dialkoxy-1-ethyl-2,2,2-trimethyldisilane (alkoxy group; methoxy, methoxy-d_3 and ethoxy).

Experimental

The progress of pyrolysis[10] was followed by gas chromatography with a flame ionization detector (FID) using a Hewlett-Packard 5890 instrument on a HP-1 capillary column (cross-linked 5% methyl phenyl silicone, 25 m). Product yields were determined by GC (FID) with cyclohexane as an internal standard on the basis of the quantity of 1,1-dialkoxy-1-ethyl-2,2,2-trimethyldisilane (alkoxy; OMe, OMe-d_3 and OEt) decomposed. Separation of the products was performed on a Varian Model 920 GC with a thermal conductivity (TCD) using 20% OV-17 column (Chromosorb W 80/100 1/4 in × 13 ft). The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Hitachi R1200 60 MHz and Bruker AM-300 NMR Spectrophotometer in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. Mass spectra were obtained on a Hewlett Packard 5890 Series II GC coupled to a 5970 Series mass selective dectector. High resolution mass spectra were obtained by using a Jeol SX-102A double focusing mass spectrometer.

Preparation of 1,1-dichloro-1-ethyl-2,2,2-trimethyldisilane (1). For the preparation of 1-ethyl-1,1-diphenyl-2,2,2-trimethyldisilane, to a suspension of 0.42 g (0.06 g atm) of lithium metal in 50 mL of dry THF was slowly added 9.8 g (40 mmol) of chlorodiphenylethylsilane in 10 mL of dry THF at ice-water temperature. After being stirred for an additional 4h at room temperature, 5.2 g (48 mmol) of chlorotrimethylsilane was placed in the dropping funnel, and added dropwise to the well stirred mixture at ice-water temperature. The reaction was exothermic and the mixture was stirred vigorously. After addition was complete, the mixture was stirred overnight followed by filtration of Li metal and salt. The organic layer was washed with water, and dried over anhydrous calcium chloride. Preparative GC on the 4ft OV-17 column afforded 10 g (35 mmol, 88%) of 1-ethyl-1,1-diphenyl-2,2,2-trimethyldisilane. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.16 (s, 9H, $Si(CH_3)_3$), 1.05 (t, 3H, $SiCH_2CH_3$, J=7.5 Hz), 1.18 (q, 2H, $SiCH_2CH_3$, J=7.5 Hz), 7.32 (m, 6H, SiPh), 7.47 (m, 4H, SiPh). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 1.13, 4.57, 8.43, 127.84, 128.36, 128.71, 135.31. MS m/z (rel. intensity): 284 (M^+, 28), 269 (3), 255 (14), 211 (43), 197 (17), 183 (100), 149 (8), 135 (16), 121 (7), 105 (18), 73 (8). For the preparation of 1,1-dichloro-1-ethyl-2,2,2-trimethyldisilane (**1**),[7a,11,12] a mixture of 6.0 g (21 mmol) of 1-ethyl-1,1-diphenyl-2,2,2-trimethyldisilane and 0.5 g (3.8 mmol) of sublimed aluminium chloride in 40 mL of dry benzene was placed in a three-necked flask fitted with a stirrer, condenser and inlet tube for hydrogen chloride gas. Dry hydrogen chloride was passed into the stirred solution at room temperature. The complete consumption of the starting material was identified with GC analysis. A small amount of acetone (0.5 mL) was added to the mixture in order to deactivate the catalyst and then solvent was evaporated. Separation of 1,1-dichloro-1-ethyl-2,2,2-trimethyldisilane by the preparative GC on the same OV-17 column afforded 3.6 g (18 mmol, 86%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.60 (s, 9H, $Si(CH_3)_3$), 0.87 (q, 2H, $SiCH_2CH_3$, J= 8.0 Hz), 1.27 (t, 3H, $SiCH_2CH_3$, J=8.0 Hz). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 1.74, 6.28, 13.95. MS m/z (rel. intensity): 204 (M^++4, 4), 202 (M^++2, 19), 200 (M^+, 27), 189 (2), 187 (10), 185 (13), 173 (5), 171 (8), 167 (2), 165 (7), 161 (2), 159 (11), 157 (16), 129(3), 127 (5), 95 (15), 93 (40), 73 (100), 63 (64), 59 (49).

Preparation of 1-ethyl-1,1-dimethoxy-2,2,2-trimethyldisilane (2). In a dry 100 mL flask equipped with a condenser, a magnetic stirring bar and a $CaCl_2$ drying tubing, were placed 8 g (75 mmol) of trimethyl orthoformate and 5 g (25 mmol) of 1,1-dichloro-1-ethyl-2,2,2-trimethyldisilane.[7a,13] The mixture was refluxed for 12h. Preparative GC on a 1/4 in × 13 ft 20% OV-17 column (detector temp. 220 °C, injector temp. 200°C, oven temp. 150 °C and flow rate 50 mL/ min) afforded 4 g (21 mmol, 84%) of **2**.

Compound **2**: ^{1}H NMR ($CDCl_3$, 300 MHz,): δ 0.59 (s, 9H, $Si(CH_3)_3$, 1.09 (q, 2H, $SiCH_2CH_3$, J=7.8 Hz), 1.42 (t, 3H, $SiCH_2CH_3$, J=7.8 Hz), 3.94 (s, 6H, $Si(OCH_3)_2$). ^{13}C NMR ($CDCl_3$, 300 MHz): δ-1.31, 6.17, 7.10, 50.26. MS m/z (rel. intensity): 192 (M^+, 7), 177 (44), 163 (25), 149 (29), 147 (13), 133 (10), 119 (41), 103 (7), 91 (15), 89 (18), 87 (6), 73 (26), 59 (100).

Preparation of 1-ethyl-1,1-dimethoxy-d_6-2,2,2-trimethyldisilane (2-d_6). For the synthesis of **2-d_6**, 2 g (10 mmol) of 1,1-dichloro-1-ethyl-2,2,2-trimethyldisilane was added dropwise to well stirred solution of 1.1 g (30 mmol) of methyl-d_3 alcohol-d and 3.0 g (30 mmol) of triethylamine in 4 mL of dry benzene at ice-water temperature. After addition was complete, the reaction mixutre was stirred overnight at room temperature. Bulb-to-bulb distillation of the mixture followed by preparative GC on the same OV-17 column afforded 1.5 g (7.6 mmol, 76 %) of **2-d_6**.

Compound **2-d_6**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.32 (s, 9H, $Si(CH_3)_3$), 0.83 (q, 2H, $SiCH_2CH_3$, J=7.8 Hz), 1.14 (t, 3H, $SiCH_2CH_3$, J=7.8 Hz). ^{13}C NMR ($CDCl_3$, 300 MHz): δ −1.22, 6.11, 6.99, 46.39. MS m/z (rel. intensity): 198 (M^+, 5), 180 (36), 169 (24), 152 (26), 148 (10), 137 (5), 125 (22), 121 (19), 105 (3), 97 (19), 92 (12), 87 (6), 73 (30), 62 (100).

Preparation of 1,1-diethoxy-1-ethyl-2,2,2-trimethyldisilane (8). For the synthesis of **8**, 2 g (10 mmol) of 1,1-dichloro-1-ethyl-2,2,2-trimethyldisilane was added dropwise to the well stirred solution of 1.4 g (30 mmol) of ethyl alcohol and 3.0 g (30 mmol) of triethylamine in 4 mL of dry benzene at ice-water temperature. After the addition was complete, the mixture was stirred overnight at room temperature. Bulb-to-bulb distillation of the mixture followed by preparative GC on the same OV-17 column afforded 1.6 g (7.3 mmol, 73%) of 1,1-diethoxy-1-ethyl-2,2,2-trimethyldisilane (**8**).

Compound **8**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.50 (s, 9H, $Si(CH_3)_3$), 1.00 (q, 2H, $SiCH_2CH_3$, J=7.8 Hz), 1.34 (t, 3H, $SiCH_2CH_3$, J=7.8 Hz), 1.56 (t, 6H, $Si(OCH_2CH_3)_2$, J=6.9 Hz), 4.12 (q, 4H, $Si(OCH_2CH_3)_2$, J=6.9 Hz). ^{13}C NMR ($CDCl_3$, 300 MHz): δ −1.19, 6.38, 7.72, 18.74, 58.57. MS m/z (rel. intensity): 220 (M^+, 0.6), 205 (9), 191 (64), 175 (5), 163 (56), 147 (93), 135 (41), 119 (100), 103 (55), 91 (16), 73 (96), 63 (33), 59 (17).

Pyrolysis of 1-ethyl-1,1-dimethoxy-2,2,2-trimethyldisilane (2) in the presence of 2,3-dimethyl-1,3-butadiene. The mixture of 0.2 g (1.0 mmol) of **2** and 1.2 g (15 mmol) of 2,3-dimethyl-1,3-butadiene as a trapping agent was injected into the rubber septum at the inlet of the vertical quartz tube, which is connected to a vacuum line,[10] using a gas tight syringe over a period of 3h. The vacuum pyrolysis of the mixture at 400-500 °C and 10^{-3} torr afforded quantitative recovery of the starting material **2**. The pyrolysate was collected in a trap cooled with a liquid nitrogen and separated by a preparative GC on the same OV-17 column. The observed major products were 1-ethyl-1-methoxy- (**3**), 1-ethyl- (**4**) and 1-methoxy-3,4-dimethyl-1-silacyclopent-3-ene (**5**) along with methoxytrimethylsilane. The spectral properties of these products given below.

Compound **3**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.83 (q, 2H, $SiCH_2CH_3$, J=8.1 Hz), 1.09 (t, 3H, $SiCH_2CH_3$, J=8.1 Hz), 1.43 (m, 4H, $(SiCH_2)_2$), 1.80 (s, 6H, $(CCH_3)_2$), 3.52 (s, 3H, $SiOCH_3$). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 5.69, 6.76, 19.12, 21.42, 50.73, 130.36. MS m/z (rel. intensity): 170 (M^+, 73), 155 (0.2), 141 (89), 138 (45), 127 (2), 119 (6), 113 (16), 111 (11), 109 (16), 105 (7), 99 (5), 95 (5), 75 (6), 67 (7), 61 (9), 59 (100), 55 (5), 53 (5). HRMS calcd for $C_9H_{18}SiO$ 170.1127, found 170.1131.

Compound **4**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.70 (dq, 2H, $SiCH_2CH_3$, J=7.2 Hz, J=3.0 Hz), 1.01 (t, 3H, $SiCH_2CH_3$, J=7.2 Hz), 1.53 (m, 4H, $Si(CH_2)_2$), 1.73 (s, 6H, $(CCH_3)_2$), 4.07 (septet, 1H, SiH, J=3.0 Hz). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 4.11, 7.93, 19.14, 20.98, 130.80. MS m/z (rel. intensity): 140 (M^+, 51), 139 (5), 125 (5), 111 (100), 110 (7), 109 (27), 105 (0.4), 97 (15), 95 (12), 85 (9), 83 (23), 69 (14), 67 (9), 55 (11), 53 (8). HRMS calcd for $C_8H_{16}Si$ 140.1022, found 140.1022.

Compound **5**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.53 (m, 4H, $Si(CH_2)_2$), 1.80 (s, 6H, $(CCH_3)_2$), 3.55 (s, 3H, $SiOCH_3$), 4.97 (quintet, 1H, SiH, J=1.5 Hz). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 19.07, 22.69, 51.83, 130.08. MS m/z (rel. intensity): 142 (M^+, 32), 141 (15), 127 (17), 112 (6), 110 (26), 108 (6), 105 (9), 100 (6), 95 (9), 67 (9), 61 (9), 59 (100), 55 (4), 53 (5). HRMS calcd for $C_7H_{14}SiO$ 142.0814, found 142.0815. The formed methoxytrimethylsilane was identified and compared with authentic sample. A trace of 3,4-dimethyl-1-silacyclopent-3-ene (**6**) and 1,2-dimethylcyclohexene (**7**) in the reaction mixture was identified with GC/MS only and compared with the MS of authentic samples. Compound **6**: MS m/z (rel. intensity): 112 (M^+, 80), 111 (41), 110 (13), 109 (14), 97 (100), 95 (43), 84 (32), 83 (29), 71 (24), 70 (38), 69 (31), 67 (24), 58 (9), 55 (29), 53 (16). Compound **7**: MS m/z (rel. intensity): 110 (M^+, 31), 95 (55), 93 (26), 91 (22), 82 (35), 81 (26), 79 (20), 77 (22), 68 (33), 67 (100), 65 (13), 55 (27), 53 (27), 51 (11).

Pyrolysis of 1-ethyl-1,1-dimethoxy-d_6-2,2,2-trimethyldisilane (2-d_6) in the presence of 2,3-dimethyl-1,3-butadiene. The vacuum copyrolysis of 0.2 g (1.0 mmol) of 1,1-dimethoxy-d_6-1-ethyl-2,2,2-trimethyldisilane (**2-d_6**) and 1.2 g (15 mmol) of the trapping agent at 450 °C was performed in the same procedure as describeved above. The observed major products were 1-ethyl-1-methoxy-d_3-(**3-d_3**, 8%), 1-deuterio-1-ethyl-(**4-d**, 3%) and 1-methoxy-d_3-3,4-dimethyl-1-silacyclopent-3-ene (**5-d_3**, 21%) along with methoxy-d_3-trimethylsilane.

Compound **3-d_3**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.84 (q, 2H, $SiCH_2CH_3$, J=8.2 Hz), 1.10 (t, 3H, $SiCH_2CH_3$, J=8.2 Hz), 1.44 (m, 4H, $Si(CH_2)_2$), 1.82 (s, 6H, $(CCH_3)_2$). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 6.08, 7.19, 19.56, 21.82, 51.13, 130.79. MS m/z (rel. intensity): 173 (M^+, 27), 158 (0.4), 144 (42), 138 (23), 119 (2), 112 (6), 109 (8), 91 (3), 78 (4), 67 (4), 64 (9), 62 (100). HRMS calcd for $C_9H_{15}D_3SiO$ 173.1316, found 173.1310.

Compound **4-d**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.72 (q, 2H, $SiCH_2CH_3$, J=7.7 Hz), 1.04 (t, 3H, $SiCH_2CH_3$, J=7.7 Hz), 1.55 (m, 4H, $Si(CH_2)_2$), 1.75 (s, 6H, $(CCH_3)_2$). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 4.15, 8.04, 19.25, 21.02, 130.62. MS m/z (rel. intensity): 141 (M^+, 51), 126 (5), 112 (100). HRMS calcd for $C_8H_{15}DSi$ 141.1085, found 141.1085.

Compound **5-d_3**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.55 (m, 4H, $Si(CH_2)_2$), 1.81 (s, 6H, $(CCH_3)_2$), 4.95 (quintet, 1H, SiH, J=1.5 Hz). ^{13}C NMR ($CDCl_3$, 300 MHz): μ 19.51, 23.09, 52.23, 130.51. MS m/z (rel. intensity): 145 (M^+, 38), 130 (16), 110 (29), 103 (7), 95 (7), 67 (5), 64 (8), 62 (100), 55

(2), 53 (3). HRMS calcd for $C_7H_{11}D_3SiO$ 145.1002, found 145.0996. The formation of methoxy-d_3-trimethylsilane was identified and compared with the MS of an authentic sample. A trace of 1-deuterio-3,4-dimethyl-1-silacyclopent-3-ene (**6-*d***) and 1,2-dimethylcyclohexene (**7**) in the reaction mixture was also observed and identified with GC/MS only. Compound (**6-*d***): MS m/z (rel. intensity): 113 (M^+, 78), 112 (38), 111 (18), 110 (22), 98 (100), 85 (58), 84 (48), 72 (59), 71 (67), 70 (29), 55 (49).

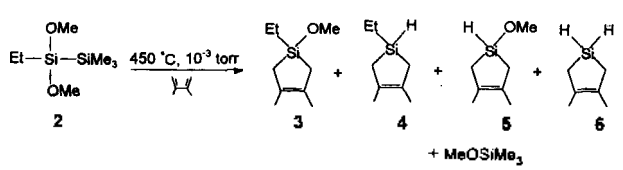
Pyrolysis of 1,1-diethoxy-1-ethyl-2,2,2-trimethyldisilane (8) in the presence of 2,3-dimethyl-1,3-butadiene. The mixture of 0.22 g (1.0 mmol) of 1,1-diethoxy-1-ethyl-2,2,2-trimethyldisilane (**8**) and 1.2 g (15 mmol) of the trapping agent was copyrolyzed at 450 °C. The observed major products were 1-ethoxy-1-ethyl-(**9**, 11%), 1-ethyl-(**4**, 3%) and 1-ethoxy-3,4-dimethyl-1-silacyclopent-3-ene (**10**, 29%) along with ethoxytrimethylsilane.

Compound **9**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.79 (q, 2H, $SiCH_2CH_3$, J=8.1 Hz), 1.05 (t, 3H, $SiCH_2CH_3$, J=8.1 Hz), 1.25 (t, 3H, $SiOCH_2CH_3$, J=6.9 Hz), 1.39 (m, 4H, Si(CH_2)$_2$), 1.77 (s, 6H, (CCH_3)$_2$), 3.73 (q, 2H, $SiOCH_2CH_3$, J=6.9 Hz). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 6.03, 6.85, 18.43, 19.19, 22.01, 58.95, 130.35. MS m/z (rel. intensity): 184 (M^+, 68), 169 (0.4), 155 (100), 138 (18), 127 (5), 119 (7), 113 (12), 111 (59), 73 (90), 71 (6), 69 (5), 67 (9), 61 (7), 55 (5), 53 (2). HRMS calcd for $C_{10}H_{20}SiO$ 184.1284, found 184.1290.

Compound **10**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.26 (t, 3H, $SiOCH_2CH_3$, J=6.9 Hz), 1.55 (m, 4H, Si(CH_2)$_2$), 1.78 (s, 6H, (CCH_3)$_2$), 3.73 (q, 2H, $SiOCH_2CH_3$, J=6.9 Hz), 4.76 (m, 1H, SiH). MS m/z (rel. intensity): 156 (M^+, 88), 141 (29), 127 (57), 114 (15), 113 (13), 111 (33), 110 (35), 99 (16), 95 (17), 83 (26), 73 (100), 71 (10), 69 (11), 67 (15), 61 (12), 55 (12), 53 (9). HRMS calcd for $C_8H_{16}SiO$ 156.0971, found 156.0968. The formation of ethoxytrimethylsilane was observed and confirmed with the MS of an authentic sample. A trace of 3,4-dimethyl-1-silacyclopent-3-ene (**6**) and 1,2-dimethylcyclohexene (**7**) in the reaction mixture was also observed and confirmed with MS of the authentic samples. From the neat pyrolysis of **8** at 450 °C, the formation of a trace of silyl enol ether ($EtH_2SiOCH{=}CH_2$) was observed and identified with GC/MS only. MS m/z (rel. intensity): 102 (M^+, 55), 101 (55), 87 (11), 75 (16), 74 (9), 73 (100), 61 (6), 59 (11), 57 (17), 55 (6).

Results and Discussion

Vacuum pyrolysis of 1-ethyl-1,1-dimethoxy-2,2,2-trimethyldisilane (**2**) in the presence of an excess of 2,3-dimethyl-1,3-butadiene as a good silylene trapping agent at 400-500 °C gives three major products, 1-ethyl-1-methoxy-1-silacyclopent-3-ene (**3**), 1-ethyl-1-silacyclopent-3-ene (**4**), 1-methoxy-3,4-dimethyl-1-silacyclopent-3-ene (**5**), and a trace of 3,4-dimethyl-1-silacyclopent-3-ene (**6**) along with methoxytrimethylsilane.



2 3 4 5 6

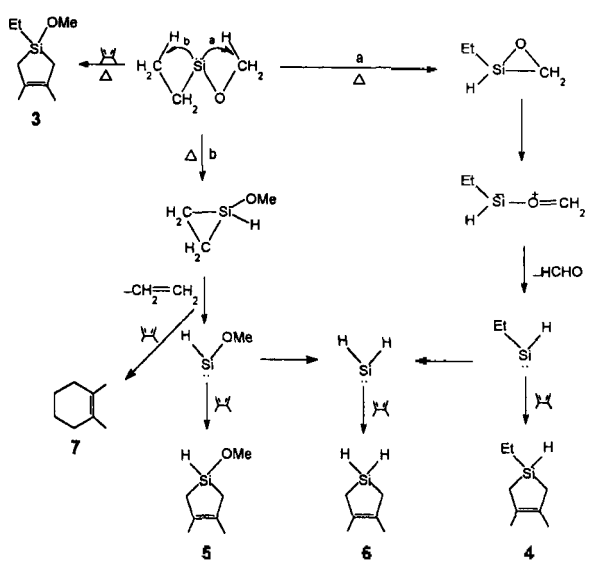
The pyrolysis of **2** is initiated by a conventional α-elimination[8] of methoxytrimethylsilane forming ethylmethoxysilylene which is believed to be a primary intermediate. The observed products **4** and **5** can arise from the addition of ethylsilylene and methoxysilylene into 2,3-dimethyl-1,3-butadiene, respectively. The ethylsilylene might be formed from a [3→2+1] cycloelimination reaction of the 2-ethyloxasilacyclopropane intermediate which can arise from an intramolecular silylene insertion into a C-H bond of the methoxy group in ethylmethoxysilylene,[4a,5a,7] as suggested in Scheme 1.

The methoxysilylene might be formed from dissociation of 1-methoxy-1-silacyclopropane intermediate which derived from an intramolecular silylene insertion into a C-H bond of the ethyl group of ethylmethoxysilylene.[1] The trapped adduct **6** (trace), which was compared with MS of an authentic sample, might be produced from the addition of silylene (H-S̈i-H) to the trapping agent. Extrusion of ethylene from 1-methoxy-1-silacyclopropane intermediate was confirmed from the observation of a trace of 1,2-dimethyl-cyclohexene (**7**), which was compared with MS of an authentic sample.

A labelling experiment employing 1-ethyl-1,1-dimethoxy-d_6-2,2,2-trimethyldisilane (**2-*d*$_6$**) may help identification of the reaction methanism for generation of ethylsilylene and methoxysilylene intermediate. Vacuum pyrolysis of **2-*d*$_6$** in the presence of an excess of the same trapping agent at 450°C resulted in formation of 1-ethyl-1-methoxy-d_3-(**3-*d*$_3$**), 1-deuterio-1-ethyl-(**4-*d***), 1-methoxy-d_3-(**5-*d*$_3$**), and 1-deuterio-3,4-dimethyl-1-silacyclopent-3-ene (**6-*d***, trace) along with methoxy-d_3-trimethylsilane. Formation of **4-*d*** and **5-*d*$_3$** in the trapping reaction implys that deuterioethylsilylene and methoxy-d_3-silylene might be generated from the dissociation of ethylmethoxy-d_3-silylene, as suggested in Scheme 1.

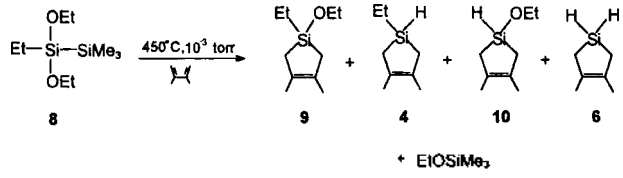
The trapping adduct **6-*d***(trace) might be also formed from the addition of deuteriosilylene, derived from the dissociation of deuterioethylsilylene and methoxy-d_3-silylene, to the same trapping agent.

Intermediacy to ethylsilylene of the oxasilacyclopropane in the dissociation of ethylmethoxysilylene is suppored by



Scheme 1.

the observation that the vacuum pyrolysis of **8** in the presence of the same trapping agent produces three major products, 1-ethoxy-1-ethyl-1-silacyclopent-3-ene (**9**), 1-ethyl-1-silacyclopent-3-ene (**4**), and 1-ethoxy-3,4-dimethyl-1-silacyclopent-3-ene (**10**) along with ethoxytrimethylsilane.



Formation of **4** from the pyrolysis of **8** in the trapping reaction can be explained by the [3→2+1] cycloelimination reaction of the 2-ethyl-3-methyloxasilacyclopropane (EtH Si-O-CHCH$_3$) which can arise from the intramolecular silylene insertion into methylene C-H bond of the ethoxy group of Et-Si-OCH$_2$CH$_3$. The product **10** is produced from the reaction of ethoxysilylene, which may be generated from the decomposition of 1-ethoxy-1-silacyclopropane (HEtOSiCH-CH$_2$), with the trapping agent. We could observe the formation of a trace of silyl enol ether (EtH$_2$SiOCH=CH$_2$) in the reaction mixture from the neat pyrolysis of **8**. The silyl enol ether, however, was not observd in the vacuum pyrolysis of **8** with the trapping agent.[7a] It seems to us that the dissociation of 2-ethyl-3-methyloxasilacyclopropane to ethylsilylene is more rapid than the isomerization of the oxasilacyclopropane into the silyl enol ether. Formation of the silyl enol ether can be explained by the reaction pathway involving prior formation of 2-ethyl-3-methyloxasilacyclopropane followed by conserted rearrangement of an ylide or by γ-hydrogen abstraction of silyl radical through the homolytic cleavage of silicon-carbon ring bond.[3-5] Temperature dependence on distribution of trapped adducts from the pyrolysis of **2** is listed in Table 1.

In previous work it was found that direct addition of methoxyphenylsilylene to the same diene trapping agent was more favorable than intramolecular C-H insertion of the silylene at 500-700 °C,[7a] since direct addition of methoxyphenylsilylene to the diene may involve a sufficently low energy barrier compared with intramolecular insertion into a C-H bond of the methoxy group of the silylene. It appears, however, that ethyl subtitution at silicon atom of alkoxysilylenes (alkoxy group: OMe, OMe-d_3 and OEt) leads more predominantly to intramolecular insertion into a C-H bond of the ethyl group of alkoxyethylsilylenes than to direct addition between the silylenes and the trapping agent. This different behavior may be explained in terms of electronic factor of ethyl and phenyl group of the silylene intermediates. As the reaction temperature increases, the product ratios of **4** to **3** and **5** to **3** increase.[7a,9] This implies the increasing importance of the dissociation of Et-Si-OMe into Et-Si-H and H-Si-OMe respectively at higher temperature relative to the direct addition of Et-Si-OMe to the trapping agent. Competition experiments indicate intramolecular C-H insertion product is formed more easily from the ethyl group than the methoxy group of ethylmethoxysilylene. The C-H insertion to ethyl group of ethylmethoxysilylene may involve a sufficently small energy barrier compared with the C-H insertion to methoxy group of the silylene. Increasing reaction temperature also favors formation of the trapping adduct **4** over **5**. Since the activation barrier for dissociation of ethylmethoxysilylene into ethylsilylene, which may be an activated process, is higher than that of ethylmethoxysilylene into methoxysilylene.

Table 1. Temperature dependence on the product ratios from vacuum pyrolysis of Et(MeO)$_2$SiSiMe$_3$(**2**) and 2,3-dimethyl-1,3-butadiene

Temp (°C)	Yields of product (%)			Product ratio		
	3	**4**	**5**	**4/3**	**5/3**	**5/4**
400	4	2	13	0.5	3.3	6.5
450	4	6	18	1.5	4.5	3.0
500	4	11	27	2.8	6.8	2.5

Summary

It was found that 1-ethyl-1,1-dimethoxy-2,2,2-trimethyldisilane was a good precursor for generation of ethylmethoxysilylene from α-elimination of methoxytrimethylsilane and intramolecular insertion into a C-H bond of the ethyl group of the silylene was more favorable than direct addition of ethylmethoxysilylene to the diene trapping agent. Increasing reaction temperature favors the dissociation of ethylmethoxysilylene into ethylsilylene and methoxysilylene over the direct addition of ethylmethoxysilylene to the diene trapping agent. Competition experiments indicate intramolecular C-H insertion product is formed more easily from the ethyl group than the methoxy group of ethylmethoxysilylene.

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Syntheses of Porphyrin-Isoflavonoid Conjugates and Octa-Substituted Porphyrins as a Building Blocks for 3-Dimensional Array of Porphyrins

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Porphyrins which is one of the most widely studied macrocycles could be a good carrier of drugs.[1a] The meso-substituted porphyrins are especially versatile compounds with regard that meso-position is convenient for functionalization and controlling the substituent geometry.[1b] Moreover wealth of available substituents make meso-substituted porphyrins ideally suited for various purposes. Flavonoid compounds such have been shown to possess various biological activities including antibacterial, anti viral, anti cancer, anti-inflammatory and immuno regulatory activities.[2] Due to the reduced side effects compared to nonsteroidal acidic drug or steroidal anti-inflammatory drug, much interests have been focused on the anti-inflammatory activities of flavonoids. The structure-activity relationship for the simple alkylated biochanin-A derivatives have been reported recently and the results indicates that flavonoids possess some improved activities *in vivo*.[3]

The porphyrins are well known as photosensitizing activities also.[4] The coupling of flavonoids and porphyrins may show compensating activities against inflammation and tumor. The convenience of the synthesis and their unique structural characteristic led us to synthesize various octa-substituted porphyrins including biochin A-porphyrin conjugates as potential anti-inflammatory compounds. A three dimensional array of porphyrins with two connecting bridges has been synthesized.[5] But multi-porphyrin array with four connecting straps are not synthesized. These compounds will have restricted coplanar geometry and thus it might be useful in studying geometry dependence of electronic excitation[6] electron transfer or energy transfer.[7] A specific order of porphyrins are found in many biological substructures including light harvesting complexes and cytochromes.[8] One of the key question would be the extent of interaction between porphyrins with such close contact. With these regards, we report the synthesis of porphyrins coupled with biochinin-A or salicylaldehyde with facial encumbrance.

The synthetic work is summarized in Scheme 1 and Scheme 2. α-Bromomethylbenzaldehyde **2** is easily synthesized by reduction of p-(α-Bromomethyl)benzonitrile **1**.[9] The dipyrromethane **3** is synthesized by treatment of aldehyde **2** with excess pyrrole in the presence of borontrifluoride etherate. Simple base wash followed by removal of residual pyrrole usually gave high yield of **3**.[10] The condensation of dipyrromethane **3** with mesityl aldehyde was performed at 0.01 M using BF_3 catalyst in chloroform at room temperature. Oxidation of the resulting porphyrinogen with DDQ afforded the porphyrin **5**. The porphyrin **5** was purified by column chromatography on silica gel in 21% yield. The similar reaction of aldehyde **2** with pyrrole gave porphyrin **4** in 22% yield. The synthesis of the conjugates **10** and **11** was carried out by dissolving proper amount of biochinin-A and **4** or **5** in N,N-dimethylformamide in the presence of K_2CO_3. The coupling reaction did not result any appreciable side reaction. But due to the limited solubility of **10** in organic solvent, the isolated yields was quite low.

Since one of the our objectives is to develop a method that can give a multiporphyrin array and related porphyrin system. we attempted to synthesize a building blocks for