Preparation of Silole Derivatives and Their Reactions with Dimethyl Acetylenedicarboxylate

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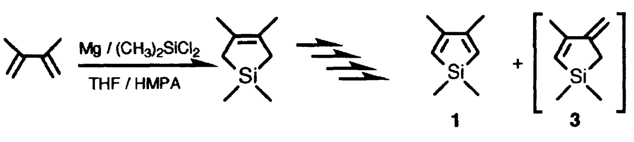
Reaction of silole derivatives such as 1,1,3,4-tetramethylsilole (**1**)[1)] and 2,3-dimethyl-5-silaspiro[4.4]nona-1,3-diene (**2**) with dimethyl acetylenedicarboxylate (DMADC) were investigated. It was found that the reactions of **1** and **2** with DMADC in toluene gave 7-membered ring compounds; trimethyl 7-methoxy-3,3,3′,4′-tetramethyl-6-oxa-3-sila-1,2-benzocyclohepta-1,4-diene-4,5,6′-tricarboxylate and trimethyl 5-methoxy- 8,9-dimethylspiro[5*H*-4,1-benzoxasilepin-1,1′-silacyclopentane]-2,3,6-tricarboxylate, respectively.

There has been considerable attention on the preparation and reaction of 7-silanorbornadiene derivatives. However, only a few 7-silanorbornadiene derivatives, which have bulky phenyl substituents on the ring, were isolated,[2,3)] because of their instability due to the highly strained structure. It is known that Diels–Alder adducts of siloles with DMADC rearrange easily to give a ketene acetal derivative,[2b)] and to give phthalic acid derivative in CH_2Cl_2 via formal extrusion of dimethylsilylene at 25 °C.[2a)]

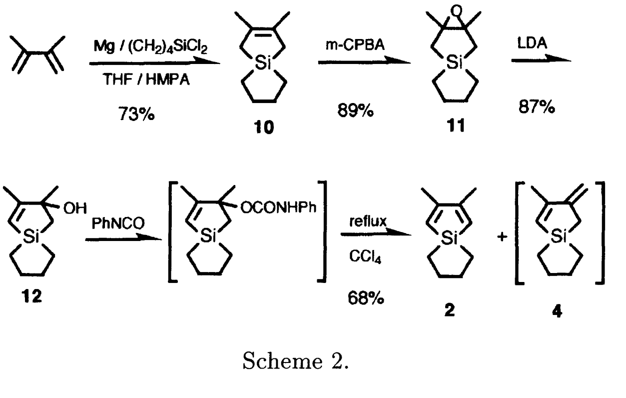
In this report, we are going to describe the preparation of a new silole derivative **2**, and the reactions of **1** and **2** with DMADC.

Results and Discussion

Preparation of Siloles. Silole **1** was prepared following the method of Dubac et al.[1b)] (Scheme 1), and **2** was obtained in a similar manner to the method described in the literature using 1,1-dichloro-1-silacyclopentane as a starting material instead of dichlorodimethylsilane (Scheme 2). The NMR spectrum of siloles **1** and **2** we prepared showed that both of them were contaminated with isomers; 1,1,3-trimethyl-4-methylene-1-silacyclopent-2-ene (**3**),[1a)] and 2-methyl-3-methylene-5-silaspiro[4.4]non-1-ene (**4**), respectively. The reactions of **1** and **2** with DMADC were carried out using them without further purification.



Scheme 1.



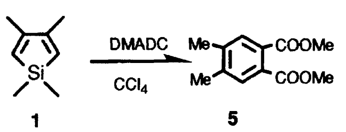
Scheme 2.

The reaction of silole **1** with DMADC in CCl_4 at room temperature gave dimethyl 4,5-dimethylphthalate (**5**) in 24% yield (Scheme 3). However, when the reaction was carried out using toluene as a solvent at room temperature, trimethyl 7-methoxy-3,3,3′,4′-tetramethyl-6-oxa-3-sila-1,2-benzocyclohepta-1,4-diene-4,5,6′-tricarboxylate (**6**) was isolated in 21% yield. Furthermore, GC-MS analysis and NMR spectrum showed the presence of a 5-membered ring compound; 7-methoxycarbonyl-3,3,4,5-tetramethyl-3-silaphthalide (**7**), in the reaction mixture, although all the attempts to isolate **7** in a pure form were unsuccessful.

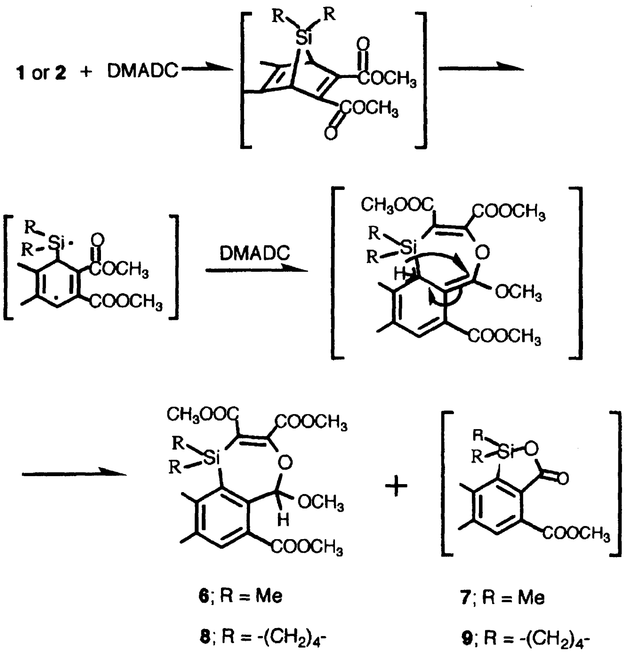
On the other hand, the reaction of **2** and DMADC was carried out in toluene at room temperature, the 7-membered ring product trimethyl 5-methoxy-8,9-dimethylspiro[5*H*-4,1-benzoxasilepin-1,1′-silacyclopentane]-2,3,6-tricarboxylate (**8**) was isolated in 17% yield. Compound **5** and a 5-membered ring compound; 7′-methoxycarbonyl-4′,5′-dimethylspiro[silacyclopentane-1,3′-silaphthalide] (**9**) were also found in the reaction mixture.

A plausible mechanism for yielding **6** and **8** is shown in Scheme 4.

There have been a lot of discussions on the degradation reaction mechanism of 7-silanorbornadiene derivatives.[2,3)] It is suggested that the reactions of **1** and **2** with DMADC contain radical species, because immediate disappearance of the purple color of 2,2-diphenyl-



Scheme 3.



Scheme 4.

1-picrylhydrazyl (DPPH) was observed when the reaction was carried out in the presence of a small amount of DPPH.

Experimental

The melting points are uncorrected. The NMR spectra were recorded on a JEOL 60Si (60 MHz), and a Bruker AM400 (400 MHz) spectrometer in $CDCl_3$ using TMS as an internal standard. The mass spectra were measured with a JEOL DX 303 mass spectrometer. All the reactions were carried out under a dry-nitrogen atmosphere. Silole **1** was prepared following the procedure described in the literature,[1] in 43% yield starting from 1,1,3,4-tetramethyl-1-silacyclopent-3-ene.

Preparation of 2,3-Dimethyl-5-silaspiro[4.4]nona-1,3-diene (2). A solution of 2,3-dimethylbutadiene (6.2 g, 74.9 mmol), 1,1-dichloro-1-silacyclopentane (11.6 g, 74.8 mmol) in a mixed solvent of tetrahydrofuran (THF) (20 ml) and hexamethylphosphoric triamide (HMPA) (9 ml) was added to a mixture of magnesium (2.7 g, 112 mmol) in THF (20 ml). The reaction mixture was refluxed for 15 h with stirring. Saturated aqueous NH_4Cl (25 ml) was added to the reaction mixture at 0 °C. The reaction mixture was extracted with hexane (20 ml×3). The combined extracts were dried (Na_2SO_4). Evaporation and distillation gave 2,3-dimethyl-5-silaspiro[4.4]non-2-ene (**10**) in 73% (9.0 g) yield. Bp 120 °C/35 Torr (1 Toor=133.322 Pa). ^{1}H NMR ($CDCl_3$) δ=0.6—0.7 (4H, m, $SiCH_2C$), 1.43 (4H, s, $SiCH_2C$=), 1.5—1.6 (4H, m, $SiCCH_2$), 1.70 (6H, s, CH_3). ^{13}C NMR ($CDCl_3$) δ=11.8 (Si–CH_2), 19.2 ($SiCH_2C$=), 24.2 ($SiCCH_2$), 27.3 (CH_3), 131.0 (C=). EI-MS m/z (rel intensity) 166 (M^+ 72), 108 (100). HR-MS Found: m/z 166.1182 [M^+]. Calcd for $C_{10}H_{18}Si$: M^+, 166.1178.

A solution of m-chloroperbenzoic acid (13.3 g, 77 mmol) in $CHCl_3$ (700 ml) was added dropwise to a solution of **10** (8.5 g, 51 mmol) in $CHCl_3$ (100 ml) with cooling. The reaction mixture was left in a refrigerator for 2 d. The mixture was extracted with aqueous 1 M NaOH (1 M=1 mol dm^{-3}) solution (200 ml), washed with water (100 ml), and then dried (Na_2SO_4). Evaporation and distillation gave 2,3-epoxy-2,3-dimethyl-5-silaspiro[4.4]nonane (**11**) in 89% (8.3 g) yield. Bp 80 °C/5 Toor. ^{1}H NMR ($CDCl_3$) δ=0.55—0.65 (4H, m, $SiCH_2$), 1.11 (2H, d, J=15.8 Hz, $SiCH_2CO$), 1.32 (2H, d, J=15.8 Hz, $SiCH_2CO$), 1.39 (6H, s, CH_3), 1.45—1.55 (4H, m, $SiCCH_2$). ^{13}C NMR ($CDCl_3$) δ=10.4, 12.6 ($SiCH_2$), 20.1 ($SiCH_2CO$), 22.4 (CH_3), 26.7, 27.1 ($SiCCH_2$), 66.6 (C–O). EI-MS m/z (rel intensity) 182 (M^+ 3), 126 (100). HR-MS Found: m/z 182.1132 [M^+]. Calcd for $C_{10}H_{18}OSi$: M^+, 182.1127.

A solution of **11** (8.3 g, 46 mmol) in dry ether (50 ml) was added to a solution of lithium diisopropylamide (LDA) prepared from diisopropylamine (13.8 g, 137 mmol) in pentane (60 ml) and n-BuLi (72 ml of 1.6 M solution in hexane, 114 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 4 h. The mixture was washed with an aqueous saturated NaCl solution (50 ml), then water (50 ml), and dried (Na_2SO_4). Evaporation and distillation gave 2,3-dimethyl-5-silaspiro[4.4]non-3-ene-2-ol (**12**) in 87% (7.2 g) yield. Bp 82 °C/0.3 Torr. ^{1}H NMR ($CDCl_3$) δ=0.61—0.74 (4H, m, $SiCH_2$), 1.13 (1H, d, J=14.9 Hz, SiCHCO), 1.32 (1H, d, 14.9 Hz, SiCHCO), 1.34 (3H, s, $SiCCCH_3$), 1.5—1.6 (4H, m, $SiCCH_2$), 1.83 (1H, broad s, OH), 1.93 (3H, d, J=1.1 Hz, SiC=CCH_3), 5.53 (1H, d, J=1.2 Hz, Si–CCH=). ^{13}C NMR ($CDCl_3$) δ=10.8, 11.3 ($SiCH_2$), 17.8 ($SiCH_2CO$), 27.0, 27.2, ($SiCCH_2$), 29.5, 29.7 (CH_3), 81.9 (COH), 124.3 (SiCH=), 168.3 (SiC=C). EI-MS m/z (rel intensity) 182 (M^+ 26), 127 (100). HR-MS Found: m/z 182.1122 [M^+]. Calcd for $C_{10}H_{18}OSi$: M^+, 182.1127.

A solution of phenylisocyanate (7.1 g, 60 mmol) in dry ether (40 ml) was added to a solution of **12** (7.2 g, 40 mmol) in dry ether (30 ml) in the presence of a catalytic amount of tin 2-ethylhexanoate at room temperature. After the reaction mixture was refluxed for 4 h with stirring, the solvent was evaporated. Carbon tetrachloride (200 ml) was added to the residue, and the mixture was refluxed for 24 h with stirring. The mixture was extracted with 1 M HCl (100 ml), washed with water (100 ml), and then dried (Na_2SO_4). Evaporation and distillation gave **2** in 68% (4.4 g) yield. Bp 70 °C/2 Torr. Proton NMR of the product showed that it contained about 16% of an isomer; 2-methyl-3-methylene-5-silaspiro[4.4]non-2-ene (**4**). Compound **2** was used for the next reaction with DMADC without further purification

2: ^{1}H NMR ($CDCl_3$) δ=0.75—0.78 (4H, m, Si–CH_2), 1.64—1.68 (4H, m, Si–C–CH_2), 2.02 (6H, s, CH_3), 5.62 (1H, s, =C–H). ^{13}C NMR ($CDCl_3$) δ=7.57 (Si–CH_2), 27.63 (Si–C–CH_2), 20.74 (CH_3), 124.17 (Si–C=), 158.35 (=C–C). EI-MS m/z (rel intensity) 164 (M^+ 82), 108 (100). HR-MS Found: m/z 164.1018 [M^+]. Calcd for $C_{10}H_{16}Si$: M^+ 164.1022.

4: ^{1}H NMR ($CDCl_3$) δ=0.63—0.70 (4H, m, Si–CH_2), 1.59—1.63 (4H, m, Si–C–CH_2), 1.73 (2H, s, Si–CH_2–C=), 2.00 (3H, s, CH_3), 5.02 (1H, s, =CH), 5.12 (1H, s, =CH), 5.92 (1H, s, =CH–Si). ^{13}C NMR ($CDCl_3$) δ=11.26 (Si–C), 17.60 (Si–C–C=), 27.20 (Si–C–C), 19.41 (CH_3), 109.07 (=CH_2), 132.51 (Si–C=), 151.37 (CH_2=C), 160.07 (CH_3–C=). EI-MS m/z (rel intensity) 164 (M^+ 68), 108 (100).

Reaction of 1 with DMADC. A solution of DMADC (170 mg, 1.2 mmol) in toluene (0.75 ml) was added to a solution of **1** (81 mg, 0.6 mmol) in toluene (0.25 ml) at 0 °C. The mixture was stirred for 24 h at room temperature. Evaporation and purification by preparative TLC (hexane : ethyl acetate=5 : 2) gave **6** in 21% (52 mg) (26% based on **1**) yield.

6: ^{1}H NMR ($CDCl_3$) δ=0.47, 0.49 (6H, two s, Si–Me), 2.33, 2.36 (6H, two s, CCH_3), 3.02 (3H, s, OCH_3), 3.71, 3.75, 3.81 (9H, three s, $COOCH_3$), 5.91 (1H, s, CH), 7.51 (1H, aromatic H), ^{13}C NMR ($CDCl_3$) δ=−0.3, −0.1 (SiMe), 19.2, 20.5 (CCH_3), 50.1 (OCH_3), 51.7, 52.0, 52.2, ($COOCH_3$), 106.9 (SiC=), 119.0 (O–C–O), 127.5 (=CO), 133.8, 137.7, 140.0, 141.6, 142.6, 151.9 (Aromatic), 165.4, 166.2, 167.9 (COO). EI-MS m/z (rel intensity) 422 (M^+ 93), 391 (100). HR-MS Found: m/z 422.1390 [M^+]. Calcd for $C_{20}H_{26}O_8Si$: M^+, 422.1397.

7: ^{1}H NMR ($CDCl_3$) δ=0.59 (6H, s, $SiCH_3$), 2.37, 2.39 (6H, two s, CH_3), 3.97 (3H, s, $COOCH_3$), 7.38 (1H, s, Aromatic). ^{13}C NMR ($CDCl_3$) δ=19.7, 20.3 ($SiCH_3$), 52.5 (OCH_3), 131.3, 131.6, 131.8, 142.0, 142.3, 142.4 (Aromatic), 165.6 (COOMe), 168.9 (COOSi). EI-MS m/z (rel intensity) 264 (M^+ 80), 233 (100). HR-MS Found: m/z 264.0799 [M^+]. Calcd for $C_{13}H_{16}O_4Si$: M^+, 264.0818.

A reaction of **2** (300 mg, 1.8 mmol) with DMADC (650 mg, 4.6 mmol) in toluene (6 ml) was carried out in a manner similar to that described above. Preparative silica-gel chromatography (hexane : ethyl acetate=7 : 2) gave **8** in 17% (139 mg) (24% based on **2**) yield.

8: ^{1}H NMR ($CDCl_3$) δ=0.92—0.94 (4H, m, Si–CH_2), 1.82—1.84 (4H, m, $SiCCH_2$), 2.33 (6H, s, CH_3), 3.00 (3H, s, OCH_3), 3.65, 3.71, 3.80 (9H, three s, $COOCH_3$), 6.18 (1H, s, OCHO), 7.58 (1H, s, Aromatic). ^{13}C NMR ($CDCl_3$) δ=11.3, 11.6 (Si–CH_2), 19.2, 20.8 (CH_3), 25.8, 25.9 ($SiCCH_2$), 49.9 (OCH_3), 51.9, 52.1, 52.1 ($COOCH_3$), 106.4 (SiC=), 119.4 (OCO), 127.6 (=CO), 134.2, 137.9, 138.0, 142.4, 143.3, 150.6 (Aromatic), 165.8, 166.2, 168.0 (COO). EI-MS m/z (rel intensity) 448 (M^+ 96), 433 (100). HR-MS Found: m/z 448.1542 [M^+]. Calcd for $C_{22}H_{28}O_8Si$: M^+, 448.1553.

9: EI-MS m/z (rel intensity) 290 (M^+ 80), 259 (100). HR-MS Found: m/z 290.0969 [M^+]. Calcd for $C_{15}H_{18}O_4Si$: M^+, 290.0974.

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