

Preparation of Silole Derivatives and Their Reactions with Dimethyl Acetylenedicarboxylate

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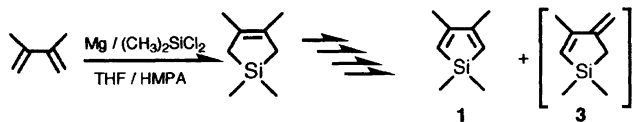
Reaction of silole derivatives such as 1,1,3,4-tetramethylsilole (**1**)¹⁾ and 2,3-dimethyl-5-silaspiro[4.4]nona-1,3-diene (**2**) with dimethyl acetylenedicarboxylate (DMADC) were investigated. It was found that the reactions of **1** and **2** with DMADC in toluene gave 7-membered ring compounds; trimethyl 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[5H-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 CH₂Cl₂ via formal extrusion of dimethylsilylene at 25 °C.^{2a)}

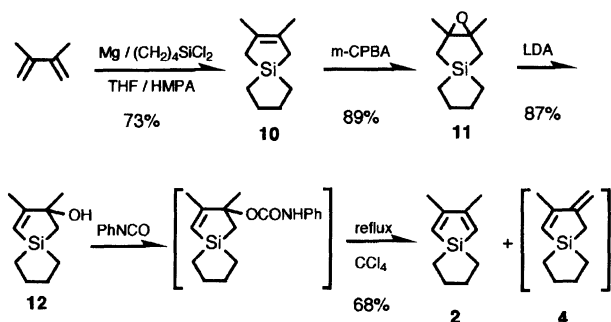
In this report, we are going to describe the preparation of a new silole derivative **2**, and the reactions of **1** and **2** with DMADC.

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



Scheme 1.



Scheme 2.

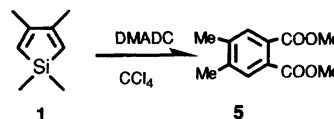
1 and **2** we prepared showed that both of them were contaminated with isomers; 1,1,3-trimethyl-4-methylene-1-silacyclopent-2-ene (**3**),^{1a)} and 2-methyl-3-methylene-5-silaspiro[4.4]non-1-ene (**4**), respectively. The reactions of **1** and **2** with DMADC were carried out using them without further purification.

The reaction of silole **1** with DMADC in CCl₄ 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.

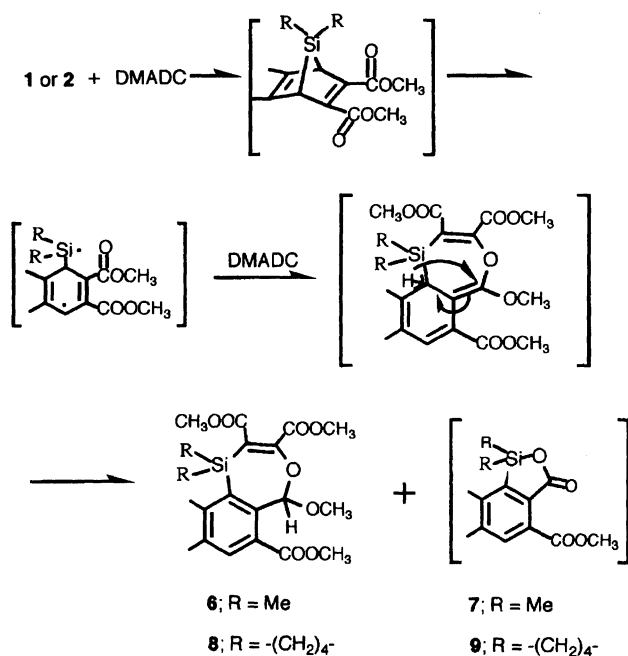
On the other hand, the reaction of **2** and DMADC was carried out in toluene at room temperature, the 7-membered ring product trimethyl 5-methoxy-8,9-dimethylspiro[5H-4,1-benzoxasilepin-1,1'-silacyclopentane]-2,3,6-tricarboxylate (**8**) was isolated in 17% yield. Compound **5** and a 5-membered ring 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 CDCl₃ 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 NH₄Cl (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 (Na₂SO₄). 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 Torr=133.322 Pa). ¹H NMR (CDCl₃) δ=0.6–0.7 (4H, m, SiCH₂C), 1.43 (4H, s, SiCH₂C=), 1.5–1.6 (4H, m, SiCCH₂), 1.70 (6H, s, CH₃). ¹³C NMR (CDCl₃) δ=11.8 (Si-CH₂), 19.2 (SiCH₂C=), 24.2 (SiCCH₂), 27.3 (CH₃), 131.0 (C=). EI-MS *m/z* (rel intensity) 166 (*M*⁺ 72), 108 (100). HR-MS Found: *m/z* 166.1182 [*M*⁺]. Calcd for C₁₀H₁₈Si: *M*⁺, 166.1178.

A solution of *m*-chloroperbenzoic acid (13.3 g, 77 mmol) in CHCl₃ (700 ml) was added dropwise to a solution of 10 (8.5 g, 51 mmol) in CHCl₃ (100 ml) with cooling. The reac-

tion 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 (Na₂SO₄). 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 Torr. ¹H NMR (CDCl₃) δ=0.55–0.65 (4H, m, SiCH₂), 1.11 (2H, d, *J*=15.8 Hz, SiCH₂CO), 1.32 (2H, d, *J*=15.8 Hz, SiCH₂CO), 1.39 (6H, s, CH₃), 1.45–1.55 (4H, m, SiCCH₂). ¹³C NMR (CDCl₃) δ=10.4, 12.6 (SiCH₂), 20.1 (SiCH₂CO), 22.4 (CH₃), 26.7, 27.1 (SiCCH₂), 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 C₁₀H₁₈O₂Si: *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 (Na₂SO₄). 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. ¹H NMR (CDCl₃) δ=0.61–0.74 (4H, m, SiCH₂), 1.13 (1H, d, *J*=14.9 Hz, SiCHCO), 1.32 (1H, d, 14.9 Hz, SiCHCO), 1.34 (3H, s, SiCCCH₃), 1.5–1.6 (4H, m, SiCCH₂), 1.83 (1H, broad s, OH), 1.93 (3H, d, *J*=1.1 Hz, SiC=CCH₃), 5.53 (1H, d, *J*=1.2 Hz, Si-CCH=). ¹³C NMR (CDCl₃) δ=10.8, 11.3 (SiCH₂), 17.8 (SiCH₂CO), 27.0, 27.2, (SiCCH₂), 29.5, 29.7 (CH₃), 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 C₁₀H₁₈O₂Si: *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 (Na₂SO₄). 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: ¹H NMR (CDCl₃) δ=0.75–0.78 (4H, m, Si-CH₂), 1.64–1.68 (4H, m, Si-C-CH₂), 2.02 (6H, s, CH₃), 5.62 (1H, s, =C-H). ¹³C NMR (CDCl₃) δ=7.57 (Si-CH₂), 27.63 (Si-C-CH₂), 20.74 (CH₃), 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 C₁₀H₁₆Si: *M*⁺ 164.1022.

4: ¹H NMR (CDCl₃) δ=0.63–0.70 (4H, m, Si-CH₂), 1.59–1.63 (4H, m, Si-C-CH₂), 1.73 (2H, s, Si-CH₂-C=), 2.00 (3H, s, CH₃), 5.02 (1H, s, =CH), 5.12 (1H, s, =CH), 5.92 (1H, s, =CH-Si). ¹³C NMR (CDCl₃) δ=11.26 (Si-C), 17.60 (Si-C-C=), 27.20 (Si-C-C), 19.41 (CH₃), 109.07 (=CH₂), 132.51 (Si-C=), 151.37 (CH₂=C), 160.07 (CH₃-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: $^1\text{H NMR}$ (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), $^{13}\text{C NMR}$ (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 $\text{C}_{20}\text{H}_{26}\text{O}_8\text{Si}$: M^+ , 422.1397.

7: $^1\text{H NMR}$ (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). $^{13}\text{C NMR}$ (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 $\text{C}_{13}\text{H}_{16}\text{O}_4\text{Si}$: 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: $^1\text{H NMR}$ (CDCl_3) δ =0.92-0.94 (4H, m, Si- CH_2), 1.82-1.84 (4H, m, SiC CH_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). $^{13}\text{C NMR}$ (CDCl_3) δ =11.3, 11.6 (Si- CH_2), 19.2, 20.8 (CH_3), 25.8, 25.9 (SiC CH_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 $\text{C}_{22}\text{H}_{28}\text{O}_8\text{Si}$: 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 $\text{C}_{15}\text{H}_{18}\text{O}_4\text{Si}$: M^+ , 290.0974.

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