

Synthesis of 1,1-Dialkoxy Derivatives of 2,5-Diphenylsilacyclopent-3-ene and 2,5-Diphenylsilacyclopentane

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(Received January 7, 1993)

The 1,1-dialkoxy derivatives of 2,5-diphenylsilacyclopent-3-ene were prepared by a one-pot reaction of magnesium with (*E,E*)-diphenyl-1,3-butadiene and dialkoxydichlorosilanes. The trans content in each silacyclopentene was higher than the cis content. Hydrogenation of these silacyclopentenes gave the corresponding silacyclopentanes in high yields.

Metallic magnesium is known to react with certain 1,3-dienes, yielding organomagnesium compounds. However, the reaction of magnesium with 1,3-dienes, such as 1,3-butadiene or isoprene, is usually accompanied by dimerization, trimerization, and oligomerization.¹⁾ Although the utilization of these organomagnesium compounds has been quite limited, several silacyclopentenes are being prepared by the reaction of 1,3-butadienes with dichlorosilanes by using magnesium.^{2–4)} Recently, substituted (2-butene-1,4-diyl)magnesium complexes are conveniently prepared through the reaction of activated magnesium with the corresponding 1,3-dienes, and dichlorodimethylsilane reacts with (1,4-diphenyl-2-butene-1,4-diyl)magnesium to give *cis*-1,1-dimethyl-2,5-diphenylsilacyclopent-3-ene.^{5,6)} Although the structure of the magnesium complex has been shown,⁷⁾ the reaction of dialkoxydichlorosilanes with the complex has not been reported.

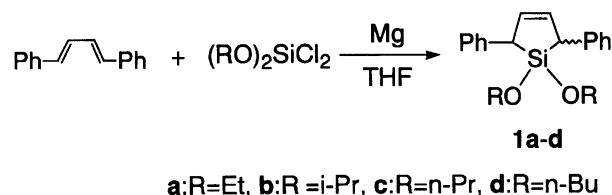
In this paper we report on the reaction of magnesium with (*E,E*)-1,4-diphenyl-1,3-butadiene and dialkoxydichlorosilanes by a one-pot reaction to give 1,1-dialkoxy-2,5-diphenylsilacyclopent-3-enes (**1a–d**). The hydrogenation of the silacyclopentenes is also described.

Results and Discussion

To a mixture of magnesium (Grignard reaction grade) and (*E,E*)-1,4-diphenyl-1,3-butadiene in THF were added dialkoxydichlorosilanes at room temperature. The mixture was stirred at 25–65 °C for 30–70 h and 1,1-dialkoxy-2,5-diphenylsilacyclopent-3-enes were obtained by distillation. The products were obtained as a mixture of *cis* and *trans* isomers (Table 1).

Reactions at 65 °C for 30 h yielded 1,1-dialkoxy-2,5-diphenylsilacyclopent-3-enes in good yields when alkyl = Et (78%), *i*-Pr (65%), *n*-Pr (79%) (Scheme 1). The *cis* and *trans* isomers in each 1,1-dialkoxy-2,5-diphenylsilacyclopent-3-ene were confirmed by ¹H NMR. The *trans* contents were higher in all of the alkoxy derivatives; the highest ratio (*trans/cis*) was 1.6 (R = *i*-Pr).

The mechanism of this reaction was postulated to be as shown in Scheme 2. During the initial step, the magnesium complex (**I**) is generated; then, **I** attacks the dialkoxydichlorosilane to give the intermediate (**II**), and a silicon–carbon bond is formed in **II** to give **1**. **I** was



Scheme 1.

confirmed to be *cis*.⁷⁾ Therefore, a possible explanation for the *trans*-rich products (**1**) in this reaction involves the greater ability of the alkoxy group to chelate with magnesium in intermediate **II** thereby, making it a stable *trans* conformation by disturbing its reaction to the *cis* conformation.

The reaction of 1,1-diethoxy-2,5-diphenylsilacyclopent-3-ene with neopentyl alcohol or *l*-menthol in hexane at 68 °C for 7 h in the presence of *p*-toluenesulfonic acid gave 1,1-bis(neopentyloxy)- or 1,1-bis(*l*-menthyloxy)-2,5-diphenylsilacyclopent-3-ene in 12% or 29% yields, respectively (Scheme 3).

Furthermore, the catalytic hydrogenation of 1,1-dialkoxy-2,5-diphenylsilacyclopentenes with 5% Pd–carbon gave the corresponding 1,1-dialkoxy-2,5-diphenylsilacyclopentanes in good yields (Table 2) (Scheme 4).

High yields of 1,1-dimethyl-2,5-diphenylsilacyclopentane were obtained by the reaction of styrene with dichlorodimethylsilane in the presence of lithium (Scheme 5).⁸⁾ However, the reaction of styrene with dichlorodiethoxysilane in the presence of lithium gave 1,1-diethoxy-2,5-diphenylsilacyclopentane only in low yield (11%) because of polymer formation.

Experimental

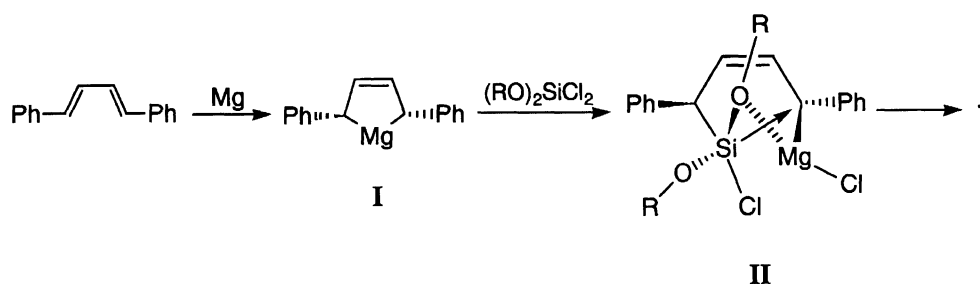
General. ¹H NMR (60 MHz) spectra and fully decoupled ¹³C NMR (22.5 MHz) spectra were recorded in CCl₄ or CDCl₃ solutions, respectively. All of the chemical shifts were reported in ppm (δ) downfield from internal tetramethylsilane. The mass spectra were taken at the Mass Spectrometry Center at the Science University of Tokyo. Elemental analyses were performed at the Analysis Center of the Nippon Mining Co., Ltd. and at the Instrument Center of the Science University of Tokyo.

All manipulations were carried out under an atmosphere of nitrogen. Unless otherwise noted, all materi-

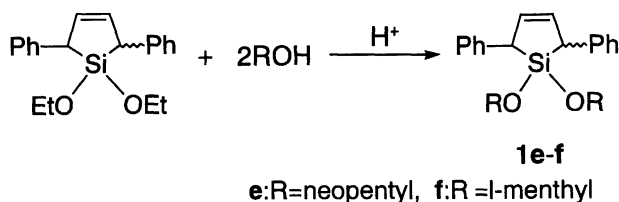
Table 1. Preparation of Silacyclopent-3-enes (**1a—d**)

R	Mole ratio ^{a)}	Temp/°C	Time/h	Yield/% ^{b)} of 1a—d	Isomer ratio ^{c)} trans/cis
Et	1 : 1 : 1	65	30	1a 78	1.4
<i>i</i> -Pr	1 : 1 : 2	62	30	1b 24	1.5
<i>i</i> -Pr	1 : 1 : 2	25	54	1b 31	1.3
<i>i</i> -Pr	1 : 1 : 1	65	30	1b 65	1.6
<i>i</i> -Pr	1 : 1 : 1	25	72	1b 13	1.3
<i>n</i> -Pr	1 : 1 : 1	65	30	1c 79	1.4 ^{d)}
<i>n</i> -Bu	1 : 1 : 1	65	30	1d 40	1.4 ^{d)}

a) (*E,E*)-1,4-Diphenyl-1,3-butadiene : Dialkoxydichlorosilane : Magnesium. b) Isolated yields by distillation; bp (°C/mmHg, 1 mmHg=133.322 Pa): **1a** 138.0—139.0/0.4, **1b** 150.2—152.0/0.3, **1c** 140.4—143.4/0.2, **1d** 158.0—160.0/0.2. The products were fully characterized by ¹H NMR, IR, and mass spectra. c) Isomer ratios were determined by ¹H NMR analysis of the products. d) Isomer ratios were determined by ¹H NMR analysis of the reaction products after the reaction with MeMgBr.



Scheme 2.



Scheme 3.

als were obtained commercially. Dichlorodiisopropoxysilane,⁹⁾ dichlorodipropoxysilane,¹⁰⁾ and dichlorodibutoxysilane¹⁰⁾ were prepared according to methods described in the literature. THF, benzene, and hexane were distilled from Na under an atmosphere of nitrogen before use.

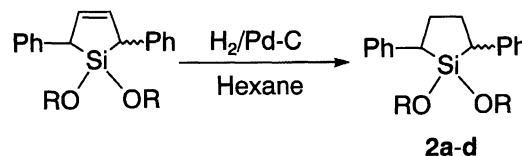
Preparation of 2,5-Diphenylsilacyclopent-3-enes 1a—d. General Procedure. In most examples, dialkoxydichlorosilanes (3.83 mmol) in THF (20 ml) were added to (*E,E*)-1,4-diphenyl-1,3-butadiene (3.83 mmol) and magnesium (for Grignard reactions 3.83 mmol) in THF (60 ml) at room temperature. The mixture was stirred at 25—65 °C for 30—72 h. After evaporation of THF from the reaction mixture, the residue was poured into either benzene or hexane, and the insoluble precipitate was removed by filtration, respectively. The filtrate was evaporated in order to remove the solvent, and the residue was distilled under reduced pressure to give **1a—d**.

1,1-Diethoxy-2,5-diphenylsilacyclopent-3-ene (1a): **1a** was obtained in 78% isolated yield by a reaction at 60 °C for 30 h; ¹H NMR (500 MHz, CDCl₃) δ=7.27—7.08 (10H, m,

Table 2. Hydrogenation of Silacyclopentenes (**1a—d**)

R	Time/h ^{a)}	Products and Yield/% ^{b)}
Et	48	2a 67
<i>i</i> -Pr	45	2b 67
<i>n</i> -Pr	45	2c 56
<i>n</i> -Bu	45	2d 82 ^{c)}

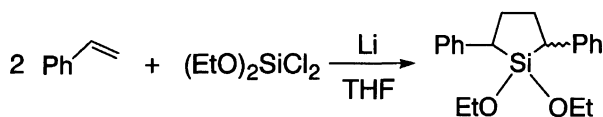
a) Reactions were carried out at room temperature in 1 atm hydrogen gas over 5% Pd-carbon. b) Isolated yields by distillation; bp (°C/mmHg): **2a** 130.5—133.5/0.04, **2b** 135.0—136.0/0.06, **2c** 139.0—142.2/0.05. c) Yield from NMR.



a:R=Et, b:R=i-Pr, c:R=n-Pr, d:R=n-Bu

Scheme 4.

Aromatic H), (6.23 (s, =CH for trans), 6.17 (s, =CH for cis) (2H)), (3.26 (s, CH for trans), 3.13 (s, CH for cis) (2H)), (3.95 (q, *J*=7.0 Hz, OCH₂ for cis), 3.31 (q, *J*=7.0 Hz, OCH₂ for trans), 2.96 (q, *J*=7.0 Hz, OCH₂ for cis) (4H)), and (1.32 (t, *J*=7.0 Hz, CH₃ for cis), 0.82 (t, *J*=7.0 Hz, 2×CH₃ for trans), 0.48 (t, *J*=7.0 Hz, CH₃ for cis) (6H)); ¹³C NMR (CDCl₃) δ for each pair of cis and trans=(141.5,



Scheme 5.

141.3), (135.1, 134.3), (128.4, 128.2), (127.3, 127.1), 124.7, (59.4, 59.1, 59.0), (35.5, 35.1), and (18.4, 17.7, 17.4); MS m/z 324 (M^+); Anal. Calcd for $C_{20}H_{24}O_2Si$: C, 74.0; H, 7.5%. Found: C, 74.4; H, 7.4%.

1,1-Diisopropoxy-2,5-diphenylsilacyclopent-3-ene (1b): Yield 65% in a reaction at 65 °C for 30 h; 1H NMR (500 MHz, $CDCl_3$) δ =7.29–7.08 (10H, m, Aromatic H), (6.25 (s, =CH for trans), 6.15 (s, =CH for cis) (2H)), (4.83 (sept, J =6.0 Hz, OCH for cis), 3.83 (sept, J =6.0 Hz, OCH for trans), 3.47 (sept, J =6.0 Hz, OCH for cis) (2H)), (3.24 (s, CH for trans), 3.10 (s, CH for cis) (2H)), and (1.32 (d, J =6.0 Hz, $2\times CH_3$ for cis), 0.84 (d, J =6.0 Hz, $2\times CH_3$ for trans), 0.82 (d, J =6.0 Hz, $2\times CH_3$ for trans), 0.43 (d, J =6.0 Hz, $2\times CH_3$ for cis) (12H)); ^{13}C NMR ($CDCl_3$) δ for each pair of cis and trans=(142.0, 141.7), (135.1, 134.3), (128.3, 128.1), (127.4, 127.1), 124.6, (66.3, 66.1), (36.2, 35.5), and (25.7, 25.1, 24.6); MS m/z 352 (M^+); Anal. Calcd for $C_{22}H_{28}O_2Si$: C, 75.0; H, 8.0%. Found: C, 75.2; H, 7.8%.

1,1-Dipropoxy-2,5-diphenylsilacyclopent-3-ene (1c): Yield 78% in a reaction at 65 °C for 30 h; 1H NMR (CCl_4) δ =7.13–6.83 (10H, m, Aromatic H), (5.98 (s, =CH for trans), 5.90 (s, =CH for cis) (2H)), (3.67 (t, J =6.0 Hz, OCH_2 for cis), 3.12 (t, J =6.0 Hz, OCH_2 for trans), 2.72 (t, J =6.0 Hz, OCH_2 for cis) (4H)), (3.08 (s, CH for trans), 2.93 (s, CH for cis) (2H)), and 1.83–0.35 (10H, m, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ for each pair of cis and trans=(141.6, 141.3), (135.1, 134.3), (128.3, 128.2), (127.3, 127.1), 124.6, (65.4, 65.1, 64.7), (35.4, 35.0), (25.8, 25.3, 24.9), and (10.3, 9.9, 9.6); MS m/z 352 (M^+); Anal. Calcd for $C_{22}H_{28}O_2Si$: C, 75.0; H, 8.0%. Found: C, 74.7; H, 7.7%.

1,1-Dibutoxy-2,5-diphenylsilacyclopent-3-ene (1d): Yield 40% in a reaction at 65 °C for 30 h; 1H NMR (CCl_4) δ =7.17–6.82 (10H, m, Aromatic H), (6.05 (s, =CH for trans), 5.98 (s, =CH for cis) (2H)), (3.77 (t, J =6.0 Hz, OCH_2 for cis), 3.20 (t, J =6.0 Hz, OCH_2 for trans), 2.83 (t, J =6.0 Hz, OCH_2 for cis) (4H)), (3.16 (s, CH for trans), 3.03 (s, CH for cis) (2H)), and 1.90–0.33 (14H, m, $CH_2CH_2CH_3$); ^{13}C NMR ($CDCl_3$) δ for each pair of cis and trans=(141.6, 141.4), (135.1, 134.4), (128.4, 128.2), (127.3, 127.1), (124.7, 124.6), (63.6, 63.3, 62.9), (35.1, 35.1), (34.7, 34.2, 33.8), (19.0, 18.7, 18.3), and (13.9, 13.7, 13.6); MS m/z 380 (M^+); Anal. Calcd for $C_{24}H_{32}O_2Si$: C, 75.7; H, 8.5%. Found: C, 76.1; H, 8.3%.

Preparation of 2,5-Diphenylsilacyclopent-3-ene (1e,f) from 1a. A solution of **1a** (0.40 mmol), neopentyl alcohol (2.42 mmol) and *p*-toluenesulfonic acid (0.080 mmol) in hexane (5 ml) was refluxed for 7 h. The resulting solution was evaporated in order to remove only hexane, and the residue was distilled under reduced pressure to give **1e**. The reaction of **1a** with *l*-menthol gave **1f** by a similar method.

1,1-Bis(neopentyloxy)-2,5-diphenylsilacyclopent-3-ene (1e): **1e** was obtained in 12% isolated yield; 1H NMR (CCl_4) δ =7.00–6.65 (10H, m, Aromatic H), (5.89 (s, =CH for trans), 5.80 (s, =CH for cis) (2H)), (3.40 (s, OCH_2 for cis), 2.83 (s, OCH_2 for trans), 2.40 (s, OCH_2 for

cis) (2H)), (3.05 (s, CH for trans), 2.93 (s, CH for cis) (2H)), and (0.94 (s, $3\times CH_3$ for cis), 0.65 (s, $6\times CH_3$ for trans), 0.33 (s, $3\times CH_3$ for cis) (18H)); ^{13}C NMR ($CDCl_3$) δ for each pair of cis and trans=141.4, (135.0, 134.4), (128.3, 128.2), (127.3, 127.1), (124.7, 124.6), (73.6, 73.1, 72.4), 59.2, (35.0, 34.6), and (26.3, 25.9, 25.5); MS m/z 408 (M^+); Calcd for $C_{26}H_{36}O_2Si$: C, 76.4; H, 8.9%. Found: C, 76.0; H, 8.9%.

1,1-Bis(*l*-menthyloxy)-2,5-diphenylsilacyclopent-3-ene (1f): Yield 29%; 1H NMR (CCl_4) δ =7.03–6.67 (10H, m, Aromatic H), (6.65 (s, =CH for trans), 5.89 (s, =CH for cis) (2H)), (3.07 (s, CH for trans), 2.93 (s, CH for cis) (2H)), 3.80–0.40 (38H, m, Menthyl H); ^{13}C NMR ($CDCl_3$) δ =142.0, 135.0, 128.3, 127.3, 124.6, 73.8, 49.7, 44.9, 37.0, 34.3, 31.4, 24.8, 22.9, 22.1, 21.2, 15.5; MS m/z 544 (M^+).

Preparation of 2,5-Diphenylsilacyclopentanes 2a–d. General Procedure. Palladium carbon (5% Pd–C, 0.20 g) and **1a** (0.28 mmol) in hexane (6 ml) were stirred under an atmosphere of hydrogen for 48 h at room temperature. After palladium carbon was removed by filtration, the solution was evaporated in order to remove the solvent, and the residue was distilled under reducing pressure to give **2a**. Other silacyclopentanes **2b–d** were obtained by the same procedure.

1,1-Diethoxy-2,5-diphenylsilacyclopentane (2a): **2a** was obtained in 67% isolated yield; 1H NMR (CCl_4) δ =7.03–6.67 (10H, m, Aromatic H), (3.71 (q, J =6.0 Hz, OCH_2 for cis), 3.27 (q, J =6.0 Hz, OCH_2 for trans), 3.19 (q, J =6.0 Hz, OCH_2 for trans), 2.93 (q, J =6.0 Hz, OCH_2 for cis) (4H)), 2.40–2.00 (6H, m, $CHCH_2$), and (1.19 (t, J =6.0 Hz, CH_3 for cis), 0.85 (t, J =6.0 Hz, $2\times CH_3$ for trans), 0.57 (t, J =6.0 Hz, CH_3 for cis) (6H)); ^{13}C NMR ($CDCl_3$) δ for each pair of cis and trans=(143.3, 142.6), 128.2, 127.3, (124.4, 124.3), (59.2, 58.9, 58.7), 34.1, (32.0, 31.3, 30.4), and (18.4, 17.9, 17.5); MS m/z 326 (M^+); Anal. Calcd for $C_{20}H_{26}O_2Si$: C, 73.6; H, 8.0%. Found: C, 73.7; H, 8.0%.

1,1-Diisopropoxy-2,5-diphenylsilacyclopentane (2b): Yield 67%; 1H NMR (CCl_4) δ =7.03–6.59 (10H, m, Aromatic H), (4.01 (sept, J =6.0 Hz, OCH for cis), 3.67 (sept, J =6.0 Hz, $2\times OCH$ for trans), 3.40 (sept, J =6.0 Hz, OCH for cis) (2H)), 2.40–1.90 (6H, m, $CHCH_2$), and (1.17 (d, J =6.0 Hz, $2\times CH_3$ for cis), 0.87 (d, J =6.0 Hz, $2\times CH_3$ for trans), 0.80 (d, J =6.0 Hz, $2\times CH_3$ for trans), 0.50 (d, J =6.0 Hz, $2\times CH_3$ for cis) (12H)); ^{13}C NMR ($CDCl_3$) δ for each pair of cis and trans=(143.8, 142.9), (128.1, 128.0), 127.3, (124.3, 124.1), (65.9, 65.7), 34.6, (32.7, 31.3, 30.1), and (25.7, 25.4, 25.2, 24.8); MS m/z 354 (M^+); Anal. Calcd for $C_{22}H_{30}O_2Si$: C, 74.5; H, 8.5%. Found: C, 74.7; H, 8.6%.

1,1-Dipropoxy-2,5-diphenylsilacyclopentane (2c): Yield 56%; 1H NMR (CCl_4) δ =7.07–6.83 (10H, m, Aromatic H), (3.60 (t, J =6.0 Hz, OCH_2 for cis), 3.17 (t, J =6.0 Hz, OCH_2 for trans), 3.10 (t, J =6.0 Hz, OCH_2 for trans), 2.80 (t, J =6.0 Hz, OCH_2 for cis) (4H)), 2.37–2.00 (6H, m, $CHCH_2$), and 1.80–0.30 (10H, m, CH_2CH_3); ^{13}C NMR ($CDCl_3$) δ for each pair of cis and trans=(143.4, 142.7), 128.1, 127.3, (124.4, 124.3), (65.2, 64.8, 64.5), 34.1 (32.0, 31.3, 30.4), (25.8, 25.5, 25.1), and (10.3, 10.0, 9.8); MS m/z 354 (M^+); Anal. Calcd for $C_{22}H_{30}O_2Si$: C, 74.5; H, 8.5%. Found: C, 74.6; H, 8.4%.

1,1-Dibutoxy-2,5-diphenylsilacyclopentane (2d): Yield 82%; 1H NMR (CCl_4) δ =7.03–6.77 (10H, m, Aromatic H), (3.61 (t, J =6.0 Hz, OCH_2 for cis), 3.17 (t, J =6.0

Hz, OCH₂ for trans), 3.10 (t, *J*=6.0 Hz, OCH₂ for trans), 2.83 (t, *J*=6.0 Hz, OCH₂ for cis) (4H), 2.38–2.07 (6H, m, CHCH₂), and 1.56–0.57 (14H, m, CH₂CH₂CH₃); ¹³C NMR (CDCl₃) δ for each pair of cis and trans=(143.4, 142.7), 128.1, 127.3, (124.2, 123.7), (63.3, 63.0, 62.6), 34.8, (34.4, 34.1, 34.0), (3.0, 31.3, 30.3), (18.7, 18.4), and (13.9, 13.7, 13.6); MS *m/z* 382 (M⁺); Anal. Calcd for C₂₄H₃₄O₂Si: C, 75.3; H, 9.0%. Found: C, 75.5; H, 9.0%.

Preparation of 1,1-Diethoxy-2,5-diphenyl-1-silacyclopentane (2a) from Styrene. A solution of 10.5 g (0.101 mol) of styrene and 8.1 g (0.042 mol) of dichlorodiethoxysilane in 20 ml of THF was added to 1.1 g (0.16 mol) of lithium (1 cm of wire) in 60 ml of THF at 5–10 °C with stirring. After the mixture was stirred for 26 h at room temp, unreacted lithium was removed and the mixture was evaporated in order to remove THF. The residue was poured into benzene and insoluble precipitate was removed by filtration. After the filtrate was evaporated to remove benzene, the residue was poured into hexane, and insoluble precipitate (polymer) was removed by filtration. The filtration was evaporated in order to remove hexane and the residue was distilled to give **2a** (1.5 g, 11%, trans/cis=1.7).

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