Facile Thermal Elimination of LiOR (R = Me, Ph) in the Reaction of [*o*-(*N*,*N*-Dimethylaminomethyl)phenyl]-organoxymethylvinylsilane with *t*-BuLi

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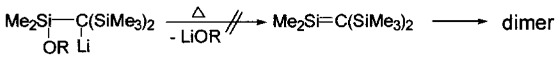
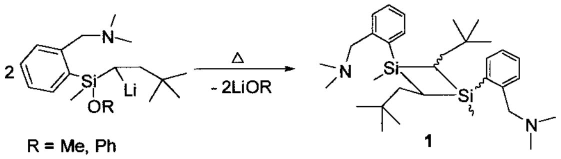
Summary: Intramolecular coordination by an amino group enhanced the thermolability of α-lithiated organoxysilane, from which elimination of LiOR (R = Me, Ph) is facile under mild conditions, giving 1,3-disilacyclobutanes, ***1****.*

Introduction

The generation of a silene[1] (Si=C) by the salt (M^+X^-) elimination method requires a starting organosilicon compound in which silicon is bonded to an electronegative substituent X (usually halogen) and to a carbon atom bearing an electropositive metal M (usually an alkali metal). Wiberg and Preiner reported the generation of a silene by the elimination of LiOR (R = Ph_2PO, (PhO)PhPO, $(PhO)_2PO$, *p*-tolylSO_2) under mild conditions.[2] However, α-lithiated organoxysilanes, where R = Me, Ph, were stable at least to 220 °C (eq 1). We report here the remarkably enhanced LiOR elimination of α-lithiated [*o*-(*N*,*N*-dimethylaminomethyl)phenyl]organoxysilanes due to an intramolecular, neutral donor atom[3] (eq 2).



$$\underset{\mathrm{OR}\ \ \mathrm{Li}}{\mathrm{Me_2Si{-}C(SiMe_3)_2}} \overset{\Delta}{\underset{-\,\mathrm{LiOR}}{\not\longrightarrow}} \mathrm{Me_2Si{=}C(SiMe_3)_2} \longrightarrow \text{dimer} \qquad (1)^2$$



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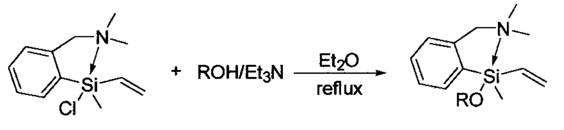
(2)

Results and Discussion

We synthesized the silene precursors, [*o*-(*N*,*N*-dimethylaminomethyl)phenyl]methoxymethylvinylsilane, **2**,[4] and [*o*-(*N*,*N*-dimethylaminomethyl)phenyl]methylphenoxyvinylsilane, **3**, in high yields as shown in Scheme 1.

Scheme 1



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2 : R = Me 78%
3 : R = Ph 72%

The reaction of **2** with *t*-BuLi at −78 °C in heptane was carried out in order to investigate the possibility of generating a silene[5] through the elimination of LiOMe. When the reaction mixture was allowed to warm slowly to room temperature, the α-lithiated methoxysilane was still observed to be present; no elimination of LiOMe occurred.[6] However, when the solution in *n*-heptane was stirred at reflux temperature (ca. 98 °C) for 12 h, *β*-elimination of LiOMe did occur to yield five isomeric 1,3-disilacyclobutanes, **1**, as a yellow oil.[7] In the presence of an excess of 2,3-dimethyl-1,3-butadiene and ethoxytrimethylsilane, the corresponding silene-derived products, **5** and **6**, respectively, were obtained (Scheme 2).

In similar manner, the reaction of compound **3** with *t*-BuLi in *n*-hexane also was carried out.[8] Interestingly the reaction gave **1** at room temperature. However, in attempted trapping experiments, we could obtain only **1**. None of the expected silene-trapping products were formed (Scheme 2). This result is in agreement with our recent report on the reaction of [*o*-(*N*,*N*-dimethylaminomethyl)phenyl]chloromethylvinylsilane, **4**, with *t*-

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[6] Following the hydrolysis of the α-lithiated methoxysilane, 2-*o*-(dimethylaminomethyl)phenyl-2-methoxy-5,5-dimethyl-2-silahexane was identified by GC−MS. MS: *m*/*z* (relative intensity) 293 (M^+, 13.3), 278 (20.9), 246 (61.4), 236 (100), 58 (45.1).

[7] The mixture of dimers was separated by chromatography (silica gel, petroleum ether/ethyl acetate) and then by preparative GC with TCD; see: Lee, M. E.; Cho, H. M.; Lee, S. H.; Kim C. H. *Bull. Korean Chem. Soc.* **2001**, *22*, 593.

[8] Following the hydrolysis of the α-lithiated phenoxysilane, 2-*o*-(dimethylaminomethyl)-phenyl-2-phenoxy-5,5-dimethyl-2-silahexane was identified by GC−MS. MS: *m*/*z* (relative intensity) 355 (M^+, 0.63), 340 (3.2), 298 (12.7), 262 (100), 135 (15.1), 58 (12.2).

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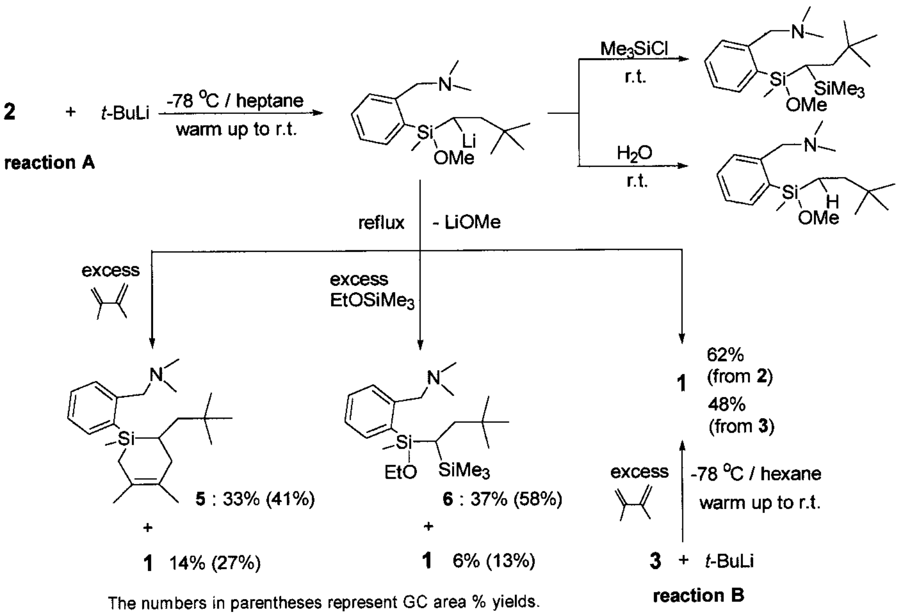
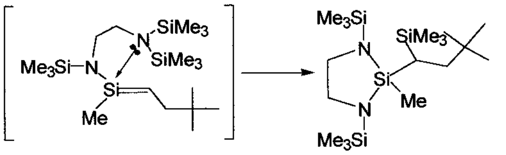
Scheme 2



The numbers in parentheses represent GC area % yields.

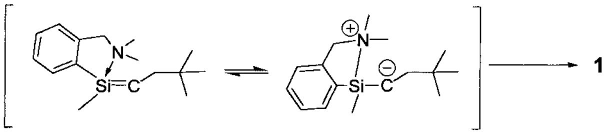
BuLi in hexane in the presence of numerous trapping agents, which gave only **1** but no silene-trapping products at low temperature.[7]

Generally, the formation of dimers, **1**, does not require the intermediacy of a silene, since the dimer can be formed not only *via* a silene but also by a bimolecular organometallic process involving the α-lithiosilane.[1d,2b,9] However, the results of reaction B (Scheme 2) were different from the results of silene/trapping agent as well as α-lithiosilane/trapping agent.[5] This fact might imply the existence of zwitterionic species (N^+-Si-C^-),[10] as an important intermediate in reaction B. In 1992, Auner et al. reported that the reaction of an amino-substituted chlorovinylsilane with *t*-BuLi gave a diazasilacyclopentane involving N−Si bond formation by way of zwitterionic species (eq 3).[3a,11] Additionally in 2001, Oehme and co-workers reported that the stable 1-(aminonaphthyl)-1,2,2-tris(trimethylsilyl)silene did not react with 2,3-dimethyl-1,3-butadiene, due to the ylide-like nature of the donor-stabilized silene.[12]



(3)[3a,11]

In phenoxy-substituted system **3**, the increased intramolecular N→Si coordination at low temperature[13] also might give a zwitterionic species which would dimerize promptly.



In contrast to reaction B, the reaction A (Scheme 2) showed general silene behavior toward trapping agents.[5] This different reactivity in the reaction A seems to be a result of the salt-eliminating temperature conditions. When the elimination of LiOMe occurred at 98 °C, the silene should be generated because of the weak N→Si coordination. Several facts, (1) that the stable α-lithiated methoxysilane did not react with 2,3-dimethyl-1,3-butadiene even at room temperature, (2) that the corresponding silene-trapping products were obtained in the presence of ethoxytrimethylsilane as well as 1,3-dimethyl-2,3-butadiene at 98 °C,[5a,14] and (3) that an acyclic compound, $[(CH_3)_2NCH_2C_6H_4](CH_3)(OMe)Si(t\text{-}BuCH_2)CH[(CH_3)_2NCH_2C_6H_4](CH_3)Si(t\text{-}BuCH_2)CLi$, which is an intermolecular elimination product, was not observed,[15] indicate strongly the existence of a silene intermediate.

In conclusion, intramolecular coordination by the amino group enhanced the thermolability of α-lithiated organoxysilane, so that the elimination of LiOR occurred under mild conditions, to give 1,3-disilacyclobutanes. Methoxysilane, **2**, could be a useful precursor for the generation of a silene. We also suggest that an intramolecular donor atom might result in formation of a charge-separated zwitterionic species, which could form dimers rapidly at low temperature.

Experimental Section

In all reactions where air-sensitive chemicals were used, the reagents and solvents were dried prior to use. Ether, hexane,

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and heptane were distilled from Na/Ph_2CO. Other starting materials were purchased in reagent grade and used without further purification. Glassware was flame-dried under nitrogen or argon flushing prior to use. Experiments were performed under a nitrogen or argon atmosphere. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 250 FT-NMR spectrometer and Bruker AMX 500 NMR spectrometer and referenced to residual protons of the solvent with chemical shifts being reported as δ ppm. Analyses of product mixtures were accomplished using a HP 5890 II with FID (HP-1, 15 m column) and with TCD (Thermal Conductivity Detector, OV-1, 1/8 in. 6 ft column). Mass spectra were recorded on a low-resolution Shimadzu GC/MS QP-2000A mass spectrometer and a high-resolution VG ANALITICLA 70-VSEQ mass spectrometer. The data for **1** and **2** were communicated previously.[4,7]

Syntheses of 2 and 3. To dichloromethylvinylsilane[16] (13.0 mL, 0.10 mol) at 0 °C was added slowly 2-(*N*,*N*-dimethylaminomethyl)phenyllithium (14.1 g, 0.10 mol) in 200 mL of ether. The reaction mixture was stirred for about 12 h at room temperature. The precipitated LiCl was removed by filtration, and volatiles were distilled under vacuum. The residue was distilled to yield **4** in 70% yield. A mixture of MeOH (1.5 mL, 0.037 mol) and Et_3N (6.0 mL, 0.043 mol) was slowly added to 8.5 g (0.036 mol) of **4** in 100 mL of diethyl ether at 0 °C. After addition was completed, the mixture was heated at reflux for 6 h. The reaction mixture was cooled, the precipitated $Et_3N^+HCl^-$ was removed by filtration, and volatiles were distilled from the filtrate under vacuum. The residue was distilled off to afford **2** in 78% yield (6.6 g). In similar manner, compound **3** was obtained in 72% yield (7.7 g). **2**: ^{29}Si NMR ($CDCl_3$, 60 MHz): δ −6.78. Anal. Calcd for $C_{13}H_{21}NOSi$: C, 66.03; H, 8.99; N, 5.95. Found: C, 65.90; H, 8.92; N, 5.87. **3**: bp: 98−102 °C (0.25 Torr). MS: *m*/*z* (relative intensity) 297 (M^+, 0.3), 254 (16.8), 204 (100), 188 (25.2), 161 (28.7), 91 (25.3), 58 (78.6). ^1H NMR ($CDCl_3$, 250 MHz): δ 0.55 (s, 3H), 2.13 (s, 6H), 3.44−3.60 (dd, $J = 13.1$ Hz, 2H), 5.79−6.47 (m, 3H), 6.87−7.94 (m, 9H). ^{13}C NMR ($CDCl_3$, 63 MHz): δ −2.28 (CH_3Si), 45.27 ($N(CH_3)_2$), 64.60 (CH_2N), 120.25−156.08 (aryl and vinyl). Anal. Calcd for $C_{18}H_{23}NOSi$: C, 72.68; H, 7.79; N, 4.71. Found: C, 72.60; H, 7.73; N, 4.57. HRMS: $C_{18}H_{23}NOSi$ 297.1549 (calcd), 297.1547 (found).

Reaction of 2 with *t*-BuLi. To a stirred solution of 2.00 g (8.5 mmol) of **2** in 80 mL of *n*-heptane cooled to −78 °C was added dropwise 5.0 mL (8.5 mmol) of *t*-BuLi diluted to 1.7 M in pentane. The reaction mixture was allowed to warm slowly to room temperature and then stirred for 1 h at room temperature. After the mixture had been heated at reflux for 12 h, **1** was obtained as a yellow oil in 62% yield (1.4 g). The isomer distribution ratio of **1** was 1:2:12:5 (GC area ratio; two of five isomers, **1**, were not separated by GC). **1**: Anal. Calcd for $C_{32}H_{54}N_2Si_2$: C, 73.49; H, 10.41; N, 5.36. Found: C, 73.29; H, 10.44; N, 5.32.

Reaction of 2 with *t*-BuLi in the Presence of an Excess of 2,3-Dimethyl-1,3-butadiene. To a stirred solution of 5.3 g (22 mmol) of **2** and 29.0 mL (251 mmol) of 2,3-dimethyl-1,3-butadiene in 150 mL of *n*-heptane cooled to −78 °C was added dropwise 13.2 mL (22 mmol) of *t*-BuLi diluted to 1.7 M in pentane. The reaction mixture was allowed to warm slowly to room temperature. After the mixture was heated at reflux for 12 h, the corresponding silene-trapping adduct **5** was obtained in 33% yield (2.5 g) and **1** in 14% yield (0.80 g). The isomer distribution ratio of **1** was 2:1:8:3 (GC area ratio). **5**: bp: 126−128 °C (0.25 Torr). MS: *m*/*z* (relative intensity) 343 (M^+, 14.0), 328 (11.0), 286 (23.2), 258 (12.7), 204 (100.0), 162 (13.5), 135 (10.4), 58 (8.5), 57 (10.0). ^1H NMR ($CDCl_3$, 250 MHz): δ 0.32 (s, 3H), 0.90 (s, 9H), 0.80−1.54 (m, 7H), 1.70 (s, 3H), 1.80 (s, 3H) 2.22 (s, 6H) 3.42, 3.48, 3.52, 3.57 (dd, $J = 13.3$ Hz, 2H) 7.19−7.53 (m, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ −4.46 ($SiCH_3$), 18.01 ($SiCH_2$), 21.05 ($SiCH$), 21.71 ($SiCH_2CCH_3$), 23.38 ($SiCH_2C{=}CCH_3$), 30.12 ($C(CH_3)_3$), 32.31 ($C(CH_3)_3$), 39.69 (CH_2t-Bu), 44.21 ($CHCH_2C{=}C$), 45.53 ($N(CH_3)_2$), 64.90 (CH_2N), 125.63−137.72 (olefin, aryl). Anal. Calcd for $C_{22}H_{37}NSi$: C, 76.90; H, 10.85; N, 4.08. Found: C, 76.73; H, 10.84; N, 3.98. HRMS: $C_{22}H_{37}NSi$ 343.2695 (calcd), 343.2695 (found).

Reaction of 2 with *t*-BuLi in the Presence of an Excess of Ethoxytrimethylsilane. To a stirred solution of 4.3 g (18 mmol) of **2** and 33.0 mL (211 mmol) of ethoxytrimethylsilane in 120 mL of *n*-heptane cooled to −78 °C was added dropwise 10.5 mL (17.9 mmol) of *t*-BuLi diluted to 1.7 M in pentane. In a similar manner as described above, we obtained the corresponding silene-trapping adduct **6** in 36% (2.5 g) yield and **1** in 6% yield (0.28 g). **6**: bp: 129−136 °C (0.25 Torr). MS: *m*/*z* (relative intensity) 364 ($M^+ - 15$, 14.9), 294 (74.7), 245 (100.0), 193 (10.1), 131 (36.6), 58 (39.0). ^1H NMR ($CDCl_3$, 500 MHz): δ 0.18 (s, 9H), 0.59 (s, 3H), 0.46−0.99 (m, 3H), 1.04 (s, 9H), 1.36 (t, 3H), 2.42 (s, 6H) 3.71 (s, 2H) 3.78 (q, 2H) 7.39−7.70 (m, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 2.70 ($Si(CH_3)_3$), 3.83 ($SiCH_3$), 9.27 ($SiCH$), 23.16 (OCH_2CH_3), 32.53 ($C(CH_3)_3$), 34.79 ($C(CH_3)$), 41.70 (CH_2t-Bu), 49.18 ($N(CH_3)_2$), 61.55 ($SiOCH_2$), 68.00 (CH_2N) 129.75−149.76 (aryl). Anal. Calcd for $C_{20}H_{38}NOSi_2$: C, 66.42; H, 10.88; N, 3.69. Found: C, 66.03; H, 10.22; N, 3.58. HRMS: $C_{20}H_{38}NOSi_2$ 364.2492 ($M^+{-}15$ calcd), 364.2498 (found).

Reaction of 3 with *t*-BuLi in the Presence of an Excess of 2,3-Dimethyl-1,3-butadiene. To a stirred solution of 1.05 g (3.5 mmol) of **3** and 4.1 mL (35 mmol) of 2,3-dimethyl-1,3-butadiene in 80 mL of *n*-hexane cooled to −78 °C was added dropwise 2.1 mL (3.5 mmol) of *t*-BuLi diluted to 1.7 M in pentane. The reaction mixture was allowed to warm slowly to room temperature and then stirred for 12 h at room temperature. We obtained only **1** in 48% yield (0.44 g). The isomer distribution ratio of dimers was 8:16:23:1 (GC area ratio).

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