Silicon–Carbon Unsaturated Compounds. 34. Formation of Bis(trimethylsilyl)silenes from Acyltris(trimethylsilyl)silanes via a Peterson-Type Reaction

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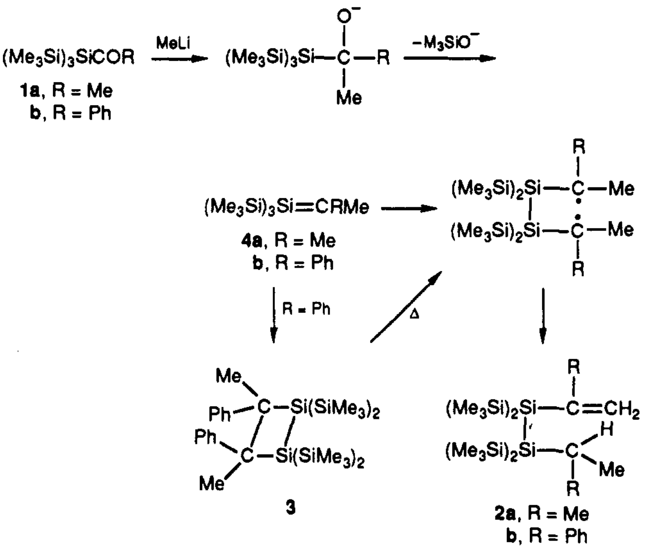
Summary: Reaction of acetyltris(trimethylsilyl)silane with methyllithium at −80 °C gave 1-isopropyl-2-(2-propenyl)tetrakis(trimethylsilyl)disilane, which can be best explained by head-to-head dimerization of a silene intermediate arising from the Peterson-type reaction. Benzoyltris(trimethylsilyl)silane also reacted with methyllithium to give 1-(1-phenylethenyl)-2-(1-phenylethyl)-1,1,2,2-tetrakis(trimethylsilyl)disilane and (*E*)-3,4-dimethyl-3,4-diphenyl-1,1,2,2-tetrakis(trimethylsilyl)-1,2-disilacyclobutane. The reaction of pivaloyltris(trimethylsilyl)silane with methyllithium afforded products arising from the cleavage of an acyl–silicon bond.

A considerable interest has been focused on the chemistry of silenes. Many papers concerning the synthesis and reactions of the silenes have been published to date. Various methods such as the photolysis, thermolysis, and salt elimination can be used for the synthesis of these compounds.[1] Especially, the photolysis of π-electron system substituted polysilanes offers a convenient route to the silenes. We have found that the photolysis of aryl-, alkenyl-, and alkynylpolysilanes readily produces the respective silenes.[2] Brook and his co-workers have also reported that the photolysis of acylpolysilanes can be used as a convenient method for the preparation of the silenes.[3] We now wish to report that the products that can be best understood in terms of head-to-head dimerization of silene intermediates can be obtained by the reaction of acylpolysilanes with methyllithium, via a Peterson-type reaction.

Results and Discussion

First, we investigated the reaction of acetyltris(trimethylsilyl)silane (**1a**) with methyllithium. Thus, when **1a** was treated with 1.2 equiv of methyllithium in diethyl ether at −80 °C, 1-isopropenyl-2-isopropyl-1,1,2,2-tetrakis(trimethylsilyl)disilane (**2a**) was obtained in 76% yield as the sole volatile product, in addition to 9% of the starting **1a**. The structure of **2a** was verified by spectroscopic analysis (see Experimental Section). Similar reaction of benzoyltris(trimethylsilyl)silane (**1b**) with methyllithium afforded 1-(1-phenylethenyl)-2-(1-phenylethyl)-1,1,2,2-tetrakis(trimethylsilyl)disilane (**2b**), analogous to compound **2a**, in 41% yield. In this reaction, (*E*)-3,4-dimethyl-3,4-diphenyl-1,1,2,2-tetrakis(trimethylsilyl)-1,2-disilacyclobutane (**3**) was also obtained in 19% yield. No other isomers of **3** were detected by either GLC or spectroscopic analysis. The structures of the products **2b** and **3** were confirmed by spectrometric analysis, as well as by elemental analysis (see Experimental Section). The proton NMR of **3** shows the presence of two different trimethylsilyl groups and a methylphenyl-substituted carbon unit. Furthermore, saturation of the trimethylsilyl protons at δ 0.25 ppm of **3** performed in NOE-FID difference experiments at 270 MHz caused a positive NOE of the methyl protons on the ring carbons, while saturation of the other trimethylsilyl protons at δ 0.38 ppm led to the enhancement of phenyl ring protons. Irradiation of methyl protons on the ring carbons resulted in the strong enhancement of trimethylsilyl protons at 0.25 ppm and the weak enhancement of trimethylsilyl protons at 0.38 ppm. The NNE (no nuclear Overhauser effect) ^{29}Si NMR spectrum reveals three resonances at δ −36.7, −11.8, and −12.2 ppm with equal intensities due to two kinds of trimethylsilyl groups and ring silicon atoms. Moreover, chemical shift of the ring silicon atoms of **3** appears in almost the same range as that of the ring silicon atoms of the dimer formed from head-to-head cycloaddition of 2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)silene.[4,5] When **3** was heated at 250 °C for 4 h in a sealed glass tube, compound **3** completely isomerized to give **2b**. These results are wholly consistent with the proposed structure. Similar isomerization of octamethyl-1,2-disilacyclobutane at 582–653 K has been reported by Davidson et al.[6]

Scheme I



Scheme I illustrates a possible mechanistic interpretation for the formation of **2a**, **2b**, and **3**. The mechanism involves addition of methyllithium across the carbon–oxygen double bond of **1a** and **1b**, followed by elimination of lithium trimethylsiloxide, leading to the formation of dimethylbis(trimethylsilyl)silene (**4a**) and methylphenylbis(trimethylsilyl)silene (**4b**). The silenes **4a** and **4b** thus

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[1] Raabe, G.; Michl, J. *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Ed.; Wiley: New York, 1989; Part 2, Chapter 17.

[2] (a) Ishikawa, M.; Kumada, M. *Adv. Organomet. Chem.* **1981**, *19*, 51. (b) Ishikawa, M.; Sakamoto, H.; Kanetani, F. *Organometallics* **1989**, *8*, 2767.

[3] Brook, A. G.; Harris, J. W.; Lennon, J.; Sheikh, M. E. *J. Am. Chem. Soc.* **1979**, *101*, 83.

[4] Baines, K.; Brook, A. G. *Organometallics* **1987**, *6*, 692.

[5] Brook, A. G.; Krishna, R.; Kallury, M.; Poon, Y. C. *Organometallics* **1982**, *1*, 987.

[6] Davidson, I. M. T.; Ostar, N. A.; Seyferth, D.; Duncan, D., P. *J. Organomet. Chem.* **1980**, *187*, 297.

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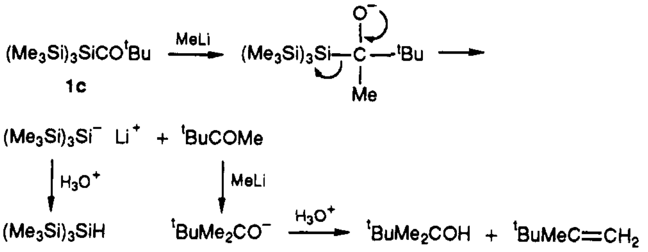
Scheme II



formed dimerize to give **2a**, **2b**, and **3** in a head-to-head fashion. In fact, trimethylsilanol (61%) and hexamethyldisiloxane (8%) were detected by GLC and GC–mass spectrometric analysis after hydrolysis of the mixture obtained from the reaction of **1b** with methyllithium. Brook and his co-workers have reported that 2-methyl-2-(trimethylsiloxy)bis(trimethylsilyl)silene generated photochemically from **1a** undergoes head-to-head dimerization to give the product, similar to **2a**.[4] The thermal isomerization of **3** to **2b** would involve the homolytic scission of a carbon–carbon bond in the four-membered ring of **3** to give a diradical intermediate.

Unfortunately, all attempt to trap the silenes **4a** and **4b** were unsuccessful. For example, when the reaction of **1a** with methyllithium was carried out in the presence of a large excess of 2,3-dimethylbutadiene, only the dimer **2a** was obtained in 30% yield. No addition products with 2,3-dimethylbutadiene were detected in the reaction mixture.

In an effort to stabilize the silene, we prepared a compound bearing a bulky substituent on the carbonyl carbon, pivaloyltris(trimethylsilyl)silane (**1c**), and carried out a similar reaction with methyllithium. However, the reaction of **1c** with methyllithium, followed by hydrolysis, gave no products derived from 2-*tert*-butyl-2-methyl-1,1-bis(trimethylsilyl)silene. The products formed from cleavage of an acyl–Si bond, tris(trimethylsilyl)silane, *tert*-butyl methyl ketone, *tert*-butyldimethylcarbinol, and 2,3,3-trimethyl-1-butene were obtained in 50, 15, 11, and 8% yields, respectively (Scheme II). Although, appreciable amounts of polymeric substances were detected after distillation of the resulting reaction mixture, no evidence for the formation of the silene was obtained by either GLC analysis or spectroscopic analysis.

Experimental Section

General. All reactions were carried out under an atmosphere of purified argon. NMR spectra were recorded on a JEOL Model EX 270 spectrometer using tetramethylsilane as an internal standard. Mass spectra were measured on a Shimadzu Model QP-1000 spectrometer and a JEOL Model JMS-D300 spectrometer equipped with a JMA-2000 data processing system.

Materials. Acylsilanes **1a–c** were prepared as reported in the literature.[3] Diethyl ether used as a solvent was dried over lithium aluminum hydride and distilled just before use.

Reaction of 1a with Methyllithium. In a 50-mL flask fitted with a dropping funnel was placed 0.602 g (2.08 mmol) of **1a** in 15 mL of diethyl ether, and the flask was cooled to −80 °C. To this was added dropwise 1.66 mL of 1.5 M methyllithium–ether solution (2.49 mmol) through the dropping funnel. The solution was allowed to warm to room temperature and then stand overnight. After hydrolysis of the mixture with water, the organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and dried over potassium carbonate. The solvent was evaporated. To the residue was added 93.8 mg (0.369 *m*mol) of octadecane as an internal standard and the mixture was analyzed by GLC as **2a** (76% yield) and **1a** (9%). Compound **2a** was isolated by MPLC on silica gel eluting with hexane: mp 107.6 °C; MS, *m/e* 432 (M^+); ^{1}H NMR (δ in $CDCl_3$) 0.22 (s, 18 H, Me_3Si), 0.24 (s, 18 H, Me_3Si), 1.16 (d, 6 H, *J* = 7.25 Hz, MeCH), 1.45 (sept, 1 H, *J* = 7.25 Hz, HCMe), 1.93 (dd, 3 H, *J* = 1.65, 0.99 Hz, $Me_2C{=}C$), 5.32 (dq, 1 H, *J* = 2.97, 0.99 Hz, HC=C), 5.60 (dq, 1 H, *J* = 2.97, 1.65 Hz, HC=C); ^{13}C NMR (δ in $CDCl_3$) 2.59, 2.97 (MeSi), 13.66 (MeCH), 23.94 (CHMe), 28.95 (MeC=C), 128.72, 144.13 (C=C). Exact MS calcd for $C_{18}H_{48}Si_6$: 432.2370. Found: 432.2343.

Reaction of 1b with Methyllithium. To a mixture of 0.817 g (2.32 mmol) of **1b** in 20 mL of ether was added dropwise 1.54 mL (2.32 mmol) of 1.5 M methyllithium–ether solution at −80 °C. The resulting mixture was allowed to stand overnight at room temperature. After workup as usual, The reaction mixture was analyzed by GLC using 95.4 mg (0.672 mmol) of decane and 29.3 mg (0.0945 mmol) of docosane as internal standards as **2b** (41%), **3** (19%), trimethylsilanol (61% yield), and hexamethyldisiloxane (8% yield). GLC retention times and mass spectra for trimethylsilanol and hexamethyldisiloxane were consistent with those of authentic samples. Compounds **2b** and **3** were isolated by MPLC on silica gel eluting with hexane. For **2b**: mp 75.5–75.7 °C; MS, *m/e* 556 (M^+); ^{1}H NMR (δ in $CDCl_3$) −0.07 (s, 9 H, Me_3Si), 0.21 (s, 18 H, Me_3Si), 0.38 (s, 9 H, Me_3Si), 1.60 (d, 3 H, *J* = 7.47 Hz, MeCH), 2.95 (q, 1 H, *J* = 7.69 Hz, HCMe), 5.79 (d, 1 H, *J* = 2.86 Hz, HC=C), 5.82 (d, 1 H, *J* = 2.86 Hz, HC=C), 7.19 (br s, 10 H, Ph); ^{13}C NMR (δ in $CDCl_3$) 2.62, 2.73, 4.19 (MeSi), 23.31 (MeCH), 28.19 (CHMe), 125.05, 126.24, 127.38, 127.92, 128.09, 128.36, 132.31, 148.13, 148.24, 150.14 (sp^2 carbons). Anal. Calcd for $C_{28}H_{52}Si_6$: C, 60.35; H, 9.41. Found: C, 60.18; H, 9.33. For **3**: mp 194–194.6 °C (dec); MS, *m/e* 556 (M^+); ^{1}H NMR (δ in $CDCl_3$) 0.25 (s, 18 H, Me_3Si), 0.38 (s, 18 H, Me_3Si), 1.68 (s, 6 H, MeC), 7.10–7.25 (m, 10 H, Ph); ^{13}C NMR (δ in $CDCl_3$) 3.1 ($4Me_3Si$), 31.0 (MeC), 52.8 (CPh), 125.1, 127.2, 129.8, 148.0 (sp^2 carbons); ^{29}Si NMR (δ in $CDCl_3$) −36.7 (ring silicon), −12.2, −11.8 (SiMe). Anal. Calcd for $C_{28}H_{52}Si_6$: C, 60.35; H, 9.41. Found: C, 60.07; H, 9.36.

Thermolysis of 3 at 250 °C. Compound **3** (2.7 mg, 0.0049 mmol) was heated at 250 °C for 4 h in a sealed degassed glass tube. GLC analysis and GC–mass and ^{1}H NMR spectra of the resulting mixture showed that all of the starting **3** was completely converted to compound **2b**.

Reaction of 1a with Methyllithium in the Presence of 2,3-Dimethylbutadiene. In a 50-mL flask fitted with a dropping funnel was placed 0.853 g (2.94 mmol) of **1a** and 0.80 mL (2.4 equiv) of 2,3-dimethylbutadiene in 15 mL of diethyl ether, and then the flask was cooled to −80 °C. To this was added dropwise 2.35 mL of a 1.5 M methyllithium–ether solution (3.52 mmol) through the dropping funnel. The solution was allowed to warm to room temperature and then to stand over night. After workup as usual, the resulting mixture was analyzed by GLC using 91.1 mg (0.358 mmol) of octadecane as an internal standard as **2a** (30% yield).

Reaction of 1c with Methyllithium. To a solution of 0.351 g (1.057 mmol) of **1c** in 10 mL of ether was added dropwise 0.85 mL (1.2 eq) of a 1.5 M methyllithium–ether solution at −80 °C. The resulting mixture was allowed to stand overnight at room temperature. After workup as usual, the resulting mixture was analyzed by GLC using 68.5 mg (0.242 mmol) of eicosane as an internal standard as tris(trimethylsilyl)silane (50% yield), *tert*-butyl methyl ketone (15% yield), *tert*-butyldimethylcarbinol (11% yield), and 2,3,3-trimethyl-1-butene (8% yield). All spectral data obtained for these products were identical with those of authentic samples.

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Registry No. 1a, 60154-96-3; **1b**, 60154-95-2; **1c**, 69397-47-3; **2a**, 135710-25-7; **2b**, 135710-26-8; **3**, 135710-27-9; methyllithium, 917-54-4; trimethylsilanol, 1066-40-6; hexmethyldisiloxane, 107-46-0; 2,3-dimethylbutadiene, 513-81-5; tris(trimethylsilyl)silane, 1873-77-4; *tert*-butyl methyl ketone, 75-97-8; *tert*-butyldimethylcarbinol, 594-83-2; 2,3,3-trimethyl-1-butene, 594-56-9.