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A convenient synthesis of 1,3-disilacyclobutanes

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Abstract

Flash vacuum pyrolysis of bis(trimethylsilylmethyl)methoxysilanes was found to be an efficient route to 1,3-disilacyclobutanes. Flash vacuum pyrolysis of bis(trimethylsilylmethyl)dimethoxysilane or bis(trimethylsilylmethyl)chloromethoxysilane gave 1-methoxy-1,3,3-trimethyl-1,3-disilacyclobutane or 1-chloro-1,3,3-trimethyl-1,3-disilacyclobutane, respectively. The thermolysis is regarded as proceeding through initial β-elimination of trimethylmethoxysilane followed by intramolecular cyclization of the resulting 2-methoxy-4,4-dimethyl-2,4-disilapent-1-ene or 2-chloro-4,4-dimethyl-2,4-disilapent-1-ene to give the products.

Introduction

Polycarbosilanes have been regarded as important precursors for silicon carbide, which is one of the high performance fine ceramics [1]. 1,3-Disilacyclobutanes are strong candidates as starting material for polycarbosilanes, since 1,3-disilacyclobutanes can be polymerized to polycarbosilanes by simple ring-opening polymerization, catalyzed by platinum or other metals [2–4]. When these processes are properly developed, commercialization and utilization of silicon carbide would be quite simple and benefits enormous. However, the synthetic methods of 1,3-disilacyclobutanes need to be improved for the large scale preparation. Until now, 1,3-disilacyclobutanes have been mainly prepared by methods utilizing either Grignard reactions starting from chloromethylchlorosilanes [5–7] or thermolysis of monosilacyclobutanes [8–10], also prepared by Grignard methods. Grignard reactions are known to be expensive and difficult to carry out on a large scale.

It is well known that flash vacuum pyrolysis of monosilacyclobutanes give silene intermediates, and the intramolecular rearrangement of the silene formed gives the ring-closed products, 1,3-disilacyclobutanes, when a trimethylsilyl group is attached to α-carbon. The intramolecular rearrangement [9] is envisioned as

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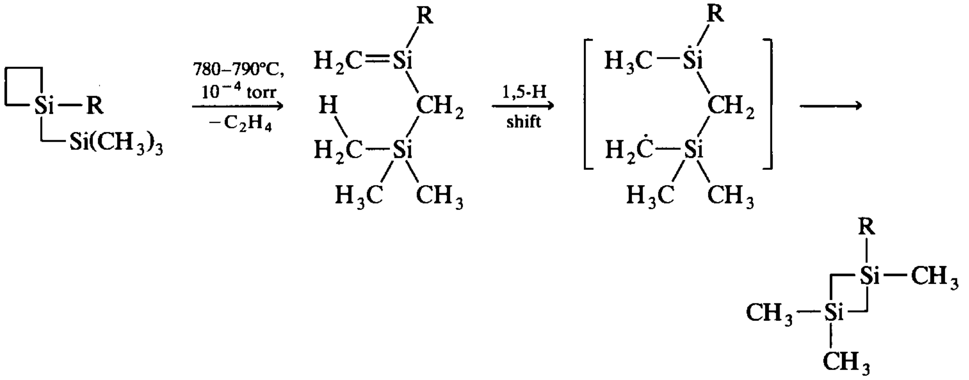
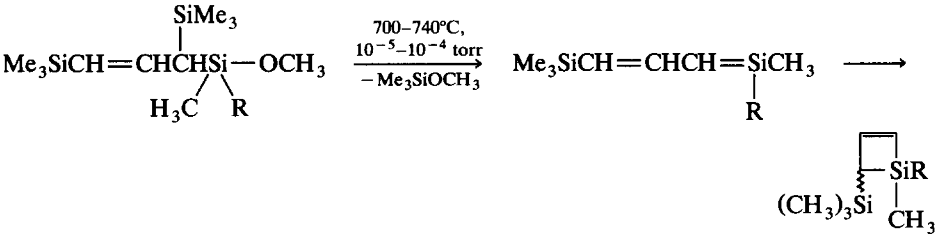
arising from hydrogen atom transfer from the methyl of trimethylsilyl group to the terminal methylene to yield a 1,4-biradical, which closes into 1,3-disilacyclobutane.



The success [11] in the generation of silenes through the β-elimination of trimethylmethoxysilane from the 2,2-dimethyl-6-methoxy-5-trimethylsilyl-2,6-disila-3-heptenes, followed by intramolecular ring closure to monosilacyclobutenes suggested that this method might be of use for the synthesis of 1,3-disilacyclobutanes.

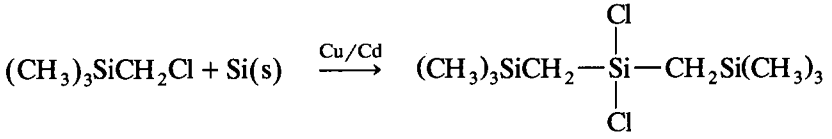


$(R = CH_3, OCH_3)$

Thus, we have attempted to design compounds that can give 1,3-disilacyclobutanes relatively easily, and can be prepared using relatively simple methods. We report here a novel convenient synthetic route for 1,3-disilacyclobutanes which employs readily available starting materials, utilizes mild reaction conditions, affords good yields, gives clean product mixtures separable by distillation, tolerates functionality on silicon, and can be produced in a large scale.

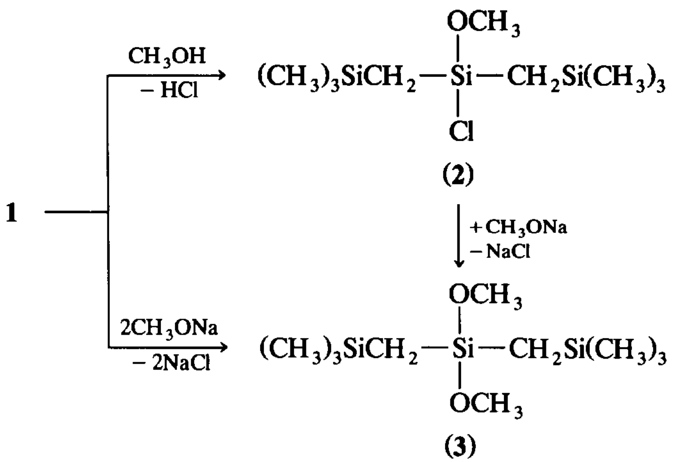
Results and discussion

Bis(trimethylsilylmethyl)chloromethoxysilane (**2**) was prepared in 84% yield by methanolysis of bis(trimethylsilylmethyl)dichlorosilane (**1**) which was in turn synthesized from the direct reaction [12] of chloromethyltrimethylsilane with metallic silicon in the presence of copper catalyst and cadmium cocatalyst at 300°C or above. Bis(trimethylsilylmethyl)dimethoxysilane (**3**) was prepared by treating **2** with sodium methoxide or directly from **1** with two equivalents of sodium methoxide in 94% yield.



$$(CH_3)_3SiCH_2Cl + Si(s) \xrightarrow{Cu/Cd} (CH_3)_3SiCH_2-\overset{Cl}{\underset{Cl}{Si}}-CH_2Si(CH_3)_3$$

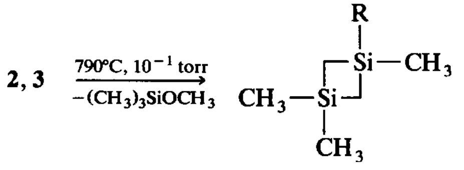
(**1**)



$$\mathbf{1} \xrightarrow[-\mathrm{HCl}]{\mathrm{CH_3OH}} (CH_3)_3SiCH_2-Si(OCH_3)(Cl)-CH_2Si(CH_3)_3\ (\mathbf{2})$$

$$\mathbf{2} \xrightarrow[-\mathrm{NaCl}]{+\mathrm{CH_3ONa}} \mathbf{3};\quad \mathbf{1} \xrightarrow[-2\mathrm{NaCl}]{2\mathrm{CH_3ONa}} (CH_3)_3SiCH_2-Si(OCH_3)_2-CH_2Si(CH_3)_3\ (\mathbf{3})$$

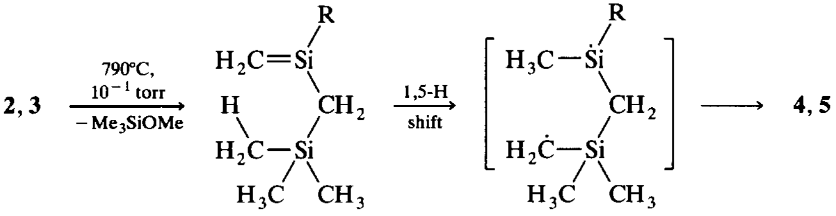
The structures of the bis(trimethylsilylmethyl)methoxysilanes **2** and **3** contain a methoxy group at the central silicon atom and trimethylsilyl group at the α-carbon, providing good conditions for β-elimination of trimethylmethoxysilane upon pyrolyzation. With this in mind and having the advantages of simple preparations of **1**, **2** and **3**, we presumed that preparation of 1,3-disilacyclobutanes might be possible in a large scale. In fact, FVP of **2** or **3** at 790°C gave 1-chloro-1,3,3-trimethyl-1,3-disilacyclobutane (**4**) and 1-methoxy-1,3,3-trimethyl-1,3-disilacyclobutane (**5**) respectively, as a colorless liquid after distillation. The mass recovery was 94% for FVP of **2** with 71% conversion and 93% for **3** with 83% conversion after the thermolyses. In addition to unreacted **2** and **3**, FVP gave a 30% isolated yield for **4** and a 44% isolated yield for **5** based on reacted **2** and **3** respectively, which were distilled from the reaction mixture and were identified from their spectral characteristics comparing with those of authentic samples.



4 R = Cl 30%
5 R = OCH_3 44%

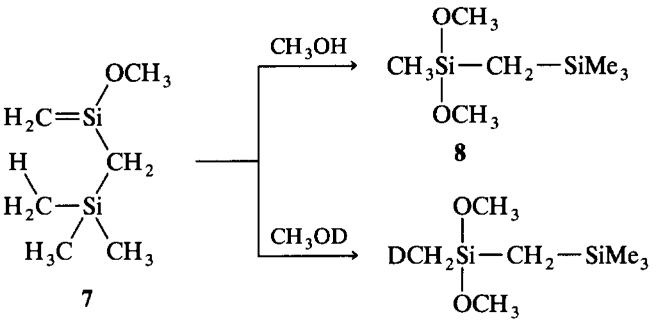
When **2** was thermolyzed, the reaction mixture contained not only the expected product **4**, but also **5** with a mixing ratio of about 2 to 1. FVP of **1** under the same reaction condition did not give trimethylchlorosilane elimination, indicating that trimethylchlorosilane came from the chlorine–methoxy exchange reaction between **4** and trimethylmethoxysilane. The exchange was confirmed by the detection of the same amount of trimethylchlorosilane produced in the reaction mixture. This is a rather unexpected result that should be noted.

We also regarded this reaction as proceeding by thermally induced β-elimination of trimethylmethoxysilane from **2** and **3** to give 4,4-dimethyl-2,4-disila-1-pentenes (**6** and **7**) followed by 1,5-hydrogen atom shift to give a 1,4-biradical which closes into **4** and **5**, as suggested by Barton *et al.* [11]. It is interesting to note that no [2 + 2] inter-molecular cyclized product was detected. This is probably caused by the favorable intra-molecular cyclization, that is faster than the inter-molecular reaction. The reaction pathways that are consistent with these results are illustrated in the following scheme.



6 R = Cl
7 R = OCH$_3$

In order to probe the β-elimination of trimethylmethoxysilane on generating the silenes, FVP of **3** was repeated with a large excess amount of methanol or CH$_3$OD vapor. The adducts, 2,2-dimethoxy-4,4-dimethyl-2,4-disilapentane (**8**), or 1-deutero-2,2-dimethoxy-4,4-dimethyl-2,4-disilapentane (**9**) were isolated as the sole product providing a positive evidence for the silenes. However, an attempt to trap the silene with 3,4-dimethylbutadiene failed.



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8

9

These results indicate that the methanol trapping reaction is faster than the intra-molecular cyclization or the inter-molecular dimerization reaction of the silene, whereas the butadiene trapping reaction is less favorable than the intra-molecular cyclization.

Experimental

All solvents were dried by distillation from sodium benzophenone ketyl under nitrogen, immediately prior to use. All reagents and solvents were transferred by standard syringe or cannula techniques. Reaction products were analyzed by GLC over a 12 m capillary column coated with SE-30 using a Varian 3300 gas chromatograph, flame ionization detector, and a Varian 4290 integrator. A Varian aerograph series 1400 gas chromatograph (with thermal conductivity detector) was used with a 3 m by 1/8 inch stainless steel column packed with 15% SE-30 on 60–80 mesh Chromosorb W. Proton and carbon NMR spectra were obtained on a Varian Gem 300 spectrometer using a CDCl$_3$ as the internal lock. Mass spectra were obtained using a Hewlett Packard 5970 GC/MS. Flash vacuum pyrolyses were conducted by slowly adding the precursor into a 20 cm (ID 15 mm) vertical quartz tube packed with quartz chips, and pyrolysate was collected in liquid nitrogen cooled traps.

Synthesis of 2

To a stirred solution of 21.25 g (77.72 mmol) of **1** 2.49 g (77.72 mmol) of methanol was added dropwise at room temperature for 90 min, then the solution was stirred for an additional 2 h at 40°C. Vacuum distillation at 64–65°C (1.5 torr) yielded 17.56 g (84%) of **2**.

For **2**: ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 18H, $SiMe_3$); 0.19 and 0.18 (s, 2H, $SiCH_2$); 3.50 (s, 3H, OMe); ^{13}C NMR ($CDCl_3$) δ 0.95 ($SiMe_3$), 7.56 ($SiCH_2$), 50.37 (OMe); HRMS (70 eV, EI), Calc.: 253.066 ($M^+ -$ Me). Found: 253.063.

Synthesis of 3

To a stirred sodium methoxide solution, obtained by addition of 1.67 g (72.6 mmol) of sodium to 30 ml of methanol in 150 ml of THF, 18.57 g (69.03 mmol) of **2** was added dropwise at room temperature for 100 min. Then the solution was stirred for an additional 30 min and solvents were removed by distillation. n-Hexane was added to the residue and the product was extracted from salt. The solvent was removed by distillation, and vacuum distillation at 67–67.5°C (1.5 torr) yielded 17.17 g (94%) of **3**.

For **3**: ^{1}H NMR ($CDCl_3$) δ -0.16 (s, 4H, $SiCH_2$); 0.06 (s, 18H, $SiMe_3$); 3.46 (s, 6H, OMe); ^{13}C NMR ($CDCl_3$) δ 1.06 ($SiMe_3$); 2.06 ($SiCH_2$); 49.92 (OMe); Anal. Found: C, 45.40; H, 10.80. $C_{10}H_{28}O_2Si_3$ calc.: C, 45.40; H, 10.67%.

Vacuum pyrolysis of 2

Vacuum pyrolysis of 15.26 g (56.73 mmol) of **2** was conducted at 790°C (10^{-1} torr) by slowly adding the precursor for 4 h. 14.36 g (94% mass recovery) of pyrolysate was collected and distillation at 72–73°C (66 torr) yielded 3.25 g (30% based on reacted **2**) of **4**.

For **4** [13]: ^{1}H NMR ($CDCl_3$) δ 0.29, 0.36 and 0.63 (s, 3H, SiMe); δ 0.51 and 0.60 (d, 2H, $J_{gem} = 15$ Hz, $SiCH_2$); ^{13}C NMR ($CDCl_3$) δ 1.44 and 1.64 (SiMe), 10.37 ($SiCH_2$).

Vacuum pyrolysis of 3

13.70 g (51.78 mmol) of **3** was pyrolysed for 70 min by the method described above. 12.74 g (93% mass recovery) of pyrolysate was collected and distillation at 71–72°C (67 torr) yielded 3.03 g (44% based on reacted **3**) of **5**.

For **5** [14]: ^{1}H NMR ($CDCl_3$) δ 0.24 (s, 3H, SiMe); 0.28 (s, 6H, $SiMe_2$); 0.18 and 0.33 (d, 2H, $J_{gem} = 17$ Hz, $SiCH_2$); 3.49 (s, 3H, OMe); ^{13}C NMR ($CDCl_3$) δ 1.06, 1.29 and 1.83 (SiMe); 5.93 ($SiCH_2$); 50.14 (OMe).

Vacuum pyrolysis of 3 in the presence of excess methanol

Vacuum pyrolysis of 1.75 g (6.61 mmol) of **3** was conducted in the presence of methanol flow (0.5 ml/min) at 790°C for 35 min. Other than methoxytrimethylsilane, **8** was a major product and separated by a preparative GC.

For **8** [15]: ^{1}H NMR ($CDCl_3$) δ -0.12 (s, 2H, $SiCH_2$); 0.06 (s, 9H, $SiMe_3$); 0.12 (s, 3H, SiMe); 3.49 (s, 6H, OMe); ^{13}C NMR ($CDCl_3$) δ -3.27 ($SiCH_2$); 0.92 ($SiMe_3$); 1.05 (SiMe); 49.96 (OMe).

If pyrolysis conducted in the presence of methanol-*d*, 1-deutero-2,2-dimethoxy-4,4-dimethyl-2,4-disilapentane (**9**) was isolated.

For **9**: ^1H NMR ($CDCl_3$) δ -0.12 (s, 2H, $SiCH_2$), 0.06 (s, 9H, $SiMe_3$), 0.12 (t, 2H, $J(HD) = 2.1$ Hz, CH_2D), 3.50 (s, 6H, OMe).

Acknowledgment

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