Facile Synthesis of the 1,3-Disilacyclohexane Ring

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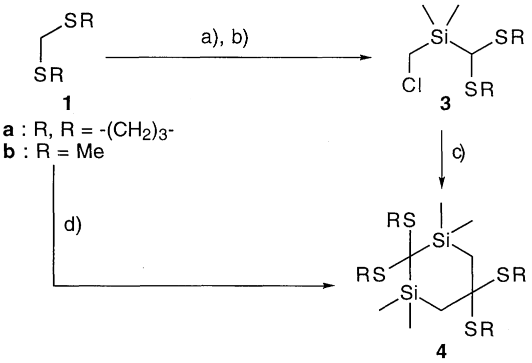
A new method for the synthesis of the 1,3-disilacyclohexane skeleton is established involving silylation of a dithioacetal followed by ring closure with a base. The spiro-fused disilacyclohexane ring is shown to be structurally strain-free, like cyclohexane, on the basis of its X-ray analysis. The reaction mechanism involving a silacyclopropane intermediate is proposed.

Organosilicon compounds have been attracting more attention than before in such fields as polymers, ceramics, and functional materials due to their unique physical and chemical properties.[1] Particularly, considerable interest is presently focused on carbacyclic silanes,[2] cyclic compounds containing at least one silicon atom in the ring system, as such molecules or as precursors of the target molecules. For example, silacyclohexanes are reportedly utilized as a part of liquid crystals.[3] However, disilacyclohexane derivatives are rarely applied to such functional materials, probably because the efficient synthesis of these compounds has been quite limited.[4] Thus, an effective synthetic method for the disilacyclohexane ring system has been sought.

We report a new method for the synthesis of the 1,3-disilacyclohexane skeleton through silylation of a dithioacetal followed by ring closure by means of a base as summarized in Scheme 1.[5]



Scheme 1. a) *n*-BuLi (1.0 mol), THF, -30 °C, 5 h; b) $ClCH_2Me_2SiCl$ (**2**, 1.0 mol), THF, -78 °C to r.t., 10 h, 46% of **3a**; c) LDA (1.2 mol), THF, -30 °C to r.t., 8.5 h, 52% of **4a**; d) *t*-BuLi (1.0 mol), THF, -42 °C to 0 °C, then **2** (0.5 mol), -78 °C, 1 h, 32% of **4a**, 73% of **4b**.

Silylation of 1,3-dithiane (**1a**) with chloro(chloromethyl) dimethylsilane (**2**) was carried out using butyllithium as the base and gave 2-{(chloromethyl)dimethylsilyl}-1,3-dithiane (**3a**) in 46% yield.[6] A THF (5 mL) solution of **3a** (224 mg, 0.99 mmol) was then treated with LDA (1.0 mL, 1.2 M in THF, 1.2 mmol) at -30 °C. The mixture was stirred at -30 °C for 2 h, and at room temperature for 6.5 h before quenching with sat. aq. NH_4Cl solution. Workup and chromatographic purification gave **4a** (99 mg, 52%) as a white solid, which was recrystallized from dichloromethane/hexane at room temperature to give colorless prisms (mp 170 °C). Disilacyclohexane **4a** could be prepared in 32% yield in one pot by treatment of **2** with 2 molar equivalents of 2-lithio-1,3-dithiane generated with *t*-butyllithium. In a similar manner, we carried out the reaction of bis(methylthio)methane (**1b**, 12 mmol) and *t*-butyllithium (5 mmol) at -42 °C to 0 °C to generate the corresponding carbanion, which was then silylated with **2** (2.5 mmol) at -78 °C. Workup and purification by silica gel chromatography gave **4b** (mp 79.5 ~ 80.5 °C) in 73% yield. Single crystals of **4b** suitable for X-ray structure determination were obtained as colorless prisms by recrystallization from hexane.

Figure 1 shows the X-ray data of **4a**.[7] The spiro-fused disilacyclohexane of **4a** is characterized as a chair form with silicon-carbon bond lengths of Si(1)-C(4) and Si(2)-C(4) being ca. 1.93 Å and 1.90 Å, respectively, approximately the same as the normal silicon-carbon bond length (1.89 Å).[8] The observed bond angles of the 1,3-disilacyclohexane ring **4a** also suggest that the frameworks are strain-free. Consequently, the conformation of the 1,3-disilacyclohexane ring is shown to be similar to that of cyclohexane.

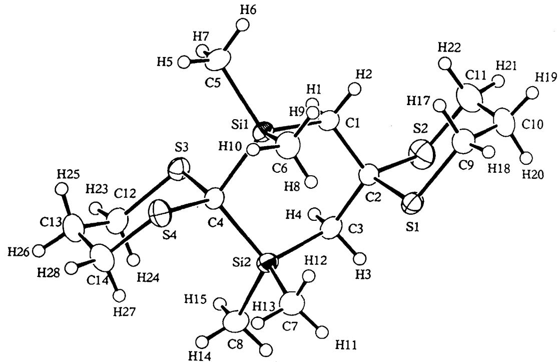
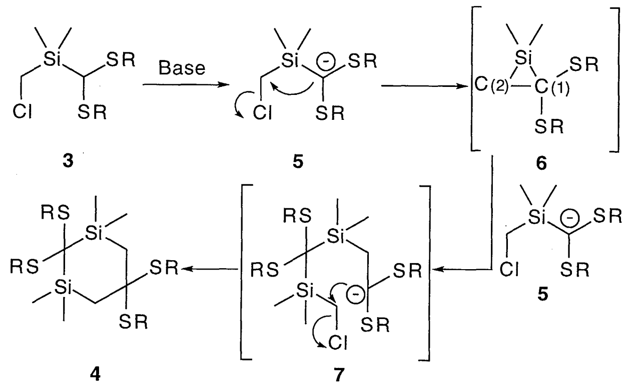


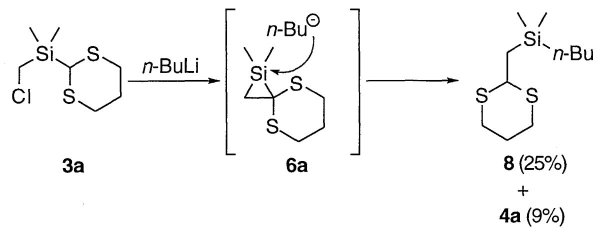
Figure 1. ORTEP drowing of **4a**. Selected bond lengths (Å) and angles (°): Si(1)-C(1) 1.817(3), Si(1)-C(4) 1.927(3), Si(2)-C(3) 1.883(3), Si(2)-C(4) 1.900(3), C(1)-C(2) 1.538(4), C(2)-C(3) 1.528(4), C(1)-Si(1)-C(4) 107.3(1), C(3)-Si(2)-C(4) 105.6(1), Si(1)-C(1)-C(2) 119.9(2), Si(2)-C(3)-C(2) 121.4(2), Si(1)-C(4)-Si(2) 108.4(1).

Formation of the 1,3-disilacyclohexane ring may be understood in terms of silacyclopropane intermediate **6** as illustrated in Scheme 2. The carbanion **5** formed by treatment of **3a** with LDA or **2** with 2 molar equivalents of bis(alkylthio)methyllithium should generate **6** by intramolecular alkylation reaction. Since **6** should be highly reactive due to the strain energy, this would be immediately attacked at the Si atom[9] by another carbanion **5**, thereupon it cleaves the Si-C(1) bond to produce **7**, which then undergoes cyclization to afford **4**.

The proposed mechanism is supported experimentally by the result in the reaction of **3a** with butyllithium. Thus, when butyllithium was employed in place of LDA, **8** was obtained in 25% yield along with **4a** (9%). Formation of **8** is definitely ascribed to the nucleophilic attack of the butyl anion at the Si atom



Scheme 2.



Scheme 3.

of **6a** (Scheme 3).

In addition, the high electrophilicity of the Si atom of silacyclopropane **6** is supported by the calculation study.[10] Thus, the lowest unoccupied molecular orbital (LUMO) of **6** (R = H) is localized largely on the Si atom, not on carbons. The charge distribution of the Si-C bonds also shows Si$^{\delta+}$-C$^{\delta-}$ illustrated in Figure 2. Therefore, assumed nucleophilic attack at the Si atom can be reasonably.

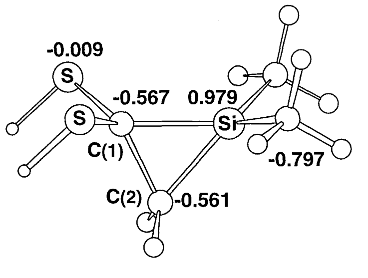


Figure 2. The charge distribution of **6** (R = H).

In conclusion, we have shown that the 1,3-disilacyclohexane ring is readily constructed in high yields through a silacyclopropane intermediate in which the Si atom exhibits high electrophilicity. We are studying further mechanistic details of this reaction sequence and synthetic transformations of the 1,3-disilacyclohexane ring obtained.

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3 a) T. Kinsho, T. Shimizu, T. Ogihara, T. Kaneko, and M. Nakashima, EP 682,031 (1995); *Chem. Abstr.*, **124**, 161201k (1996); b) T. Kinsho, T. Shimizu, T. Ogihara, R. Saito, K. Asakura, and M. Nakashima, EP 673,942 (1995); *Chem. Abstr.*, **124**, 72665x (1996); c) T. Ogihara, T. Shimizu, T. Kinsho, T. Kaneko, R. Saito, and H. Kurihara, EP 650,969, (1995); *Chem. Abstr.*, **123**, 270895q (1995).

4 Recent examples; 1,3-disilacyclohexane: S. Mansel, U. Rief, M.-H. Prosenc, R. Kirsten, and H.-H. Brintzinger, *J. Organomet. Chem.*, **512**, 225 (1996); 1,4-disilacyclohexane: T. Hoshi, M. Takahashi, and M. Kira, *Chem. Lett.*, 683 (1996).

5 Brook and Kucera reported that silylation of 2-lithio-1,3-dithiane with $R_2ClSi\text{-}(CH_2)_n\text{-}Br$ [R = Me, Ph; n = 3, 4, 5] followed by treatment with butyllithium gave the corresponding monosilacycloalkanes via intramolecular alkylation in moderate yields. See, A. G. Brook and H. W. Kucera, *J. Organomet. Chem.*, **87**, 263 (1975).

6 a) A. G. Brook, J. M. Duff, P. F. Jones, and N. R. Davis, *J. Am. Chem. Soc.*, **89**, 431 (1967); b) E. J. Corey, D. Seebach, and R. Freedman, *J. Am. Chem. Soc.*, **89**, 434 (1967).

7 Crystal data for **4a**: $C_{14}H_{28}Si_2S_4$, M = 380.79, monoclinic, space group $P2_1/c$, a = 13.542(2), b = 14.516(2), c = 9.985(2) Å, β = 92.34(1)°, V = 1961.1(9) Å^3, Z = 4, D_{calcd} = 1.290 g/cm^3, $F(000)$ = 816, T = 296 K, λ(Mo-Kα) = 0.71069 Å, $2\theta max$ = 50°; Of the 3809 reflections which were collected, 3593 were unique ($Rint$ = 0.029). No decay correction was applied. The data were corrected for Lorentz and polarization effects. The structure was solved by direct method with the program MITHRIL90 and expanded using Fourier technique. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 2540 observed reflections {I > 3.00σ(I)} and 181 variable parameters and converged with unweighted and weighted agreement factors of R = 0.034 and Rw = 0.038. All calculations were carried out by using the teXsan program system.

8 a) E. W. Colvin, "Silicon in Organic Synthesis," Butterworths, Boston (1981), p 4.; b) M. J. O. Anteunis and R. Dedeyne, *Org. Magn. Reson.*, **9**, 127 (1977).

9 A variety of nucleophiles (H_2O, ROH, NH_3, RNH_2, R_2NH, RSH, RR'C=O, RCO_2H, MeLi, $LiAlH_4$, etc.) are reported by Seyferth to attack at the Si atom of 7-siladispiro[2.0.2.1]heptane. D. Seyferth, *J. Organomet. Chem.*, **100**, 237 (1975). See also, M. Ishikawa, K.-I. Nakagawa, and M. Kumada, *J. Organomet. Chem.*, **178**, 105 (1979).

10 Geometry was fully optimized by *ab initio* caclulations without imposing any symmetry constraints at the restricted Hartree-Fock level by using gradient optimization techniques and 6-31G* basis set incorporated Mulliken implemented in a CAChe worksystem. Vibrational frequencies were further calculated for this conformer with the same basis set, which unambiguously showed the obtained conformer as a stationary point.