Synthesis of Polysilacage Compounds Containing a Trisilane Bridge

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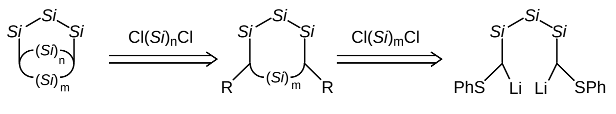
Abstract: Reductive lithiation of 1,1,5,5-tetrakis(phenylthio)-2,2,3,3,4,4-hexamethyl-2,3,4-trisilapentane or deprotonation of 1,5-bis(phenylthio)-2,2,3,3,4,4-hexamethyl-2,3,4-trisilapentane gave 1,5-bis(phenylthio)-1,5-dilithio-2,2,3,3,4,4-hexamethyl-2,3,4-trisilapentane which was silylated with dichlorodimethylsilane or 1,2-dichloro-1,1,2,2-tetramethyldisilane to give the corresponding tetrasilacyclohexane or pentasilacycloheptane, respectively. The tetrasilacyclohexane was transformed by reductive lithiation and sequential silylation to 2,2,3,3,4,4,6,6,7,7-decamethyl-2,3,4,6,7-pentasilabicyclo[3.1.1]heptane and 2,2,3,3,4,4,6,6,7,7,8,8-dodecamethyl-2,3,4,6,7,8-hexasilabicyclo-[3.2.1]octane.

Key words: silicon, lithium, dianion, trisilane, cyclizations

In view of the fact that σ-electrons of such acyclic linkage as -Si-Si-C- or -Si-Si-Si-Si-C- have recently been suggested to be delocalized along the acyclic framework (σ-conjugation),[1,2] cage compounds containing -(Si)$_n$- bridges connected via bridgehead carbons are an attractive subject of research. We very recently reported that λ_{max} of 1,2,4,5-tetrasilacyclohexane and 2,3,5,6,7,8-hexasilabicyclo[2.2.2]octane exhibited a bathochromic shift as compared with an acyclic standard. This observation suggests the possibility of three-dimensional σ-conjugation in the cage molecules with disilane moieties.[3] To gain further insight into the nature of σ-conjugation in polysilacycloalkanes, it is intriguing to synthesize bicyclic polysilacycloalkane **1** containing a trisilane bridge (Scheme 1). However, efficient synthetic methods for such compounds are rare,[4] and, hence, we felt it necessary to establish a convenient synthetic method for **1**.[5] We report here a facile solution for the synthesis of cyclic and cage compounds having a -Si-Si-Si- unit based on the silylation of 1,5-bis(phenylthio)-1,5-dilithio-2,3,4-trisilapentane.

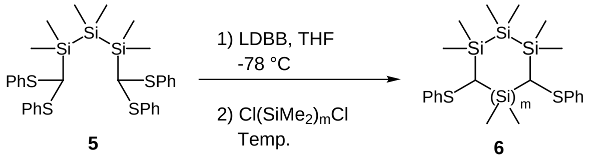
For the dianion reagent with a trisilane unit, we designed 1,5-bis(phenylthio)-1,5-dilithio-2,3,4-trisilapentane **4**, wherein a phenylthio group could facilitate its generation, stabilize **4**, and be easily reduced by lithium radical anions to afford requisite dianion reagent **2** via initial polysilacarbocycle **3**.



1 (*Si* = SiMe$_2$)   **2** (R = Li)   **3** (R = SPh)   **4**

Scheme 1

At first, bis(phenylthio)methyllithium was generated from bis(phenylthio)methane and silylated with 1,3-dichloro-1,1,2,2,3,3-hexamethyltrisilane to give trisilane **5** in 71% yield. Treatment of **5** with lithium 4,4'-di-*tert*-butylbiphenylide (LDBB) in THF at -78 °C and then with dichlorodimethylsilane gave 1,2,3,5-tetrasilacyclohexane **6a** as a diastereomeric mixture (*cis* : *trans* = 1 : 1) (run 1-3).[6] When silylation was effected at -98 or -78 °C, **6a** was produced in 47-50% yield (run 1 and 2); the yield decreased in the reaction at -30 °C (run 3). Although the yields are moderate, the results are of synthetic value considering the steric factors of octamethyltetrasilacyclohexane ring formation. Similarly, silylation of **4** with 1,2-dichloro-1,1,2,2-tetramethyldisilane at -78 °C yielded the corresponding 7-membered ring **6b** in 69% yield (run 4), whereas no cyclized product was obtained upon use of 1,3-dichloro-1,1,2,2,3,3-hexamethyltrisilane (run 5).

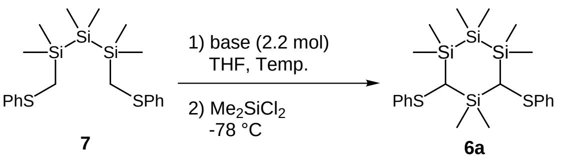


5   **6**

Table 1 Synthesis of **6** via reductive lithiation of **5**

Run	m	Temp/°C	**6**	Yield/%
1	1	-98	**6a**	47
2	1	-78	**6a**	50
3	1	-30	**6a**	27
4	2	-78	**6b**	69
5	3	-78	**6c**	0

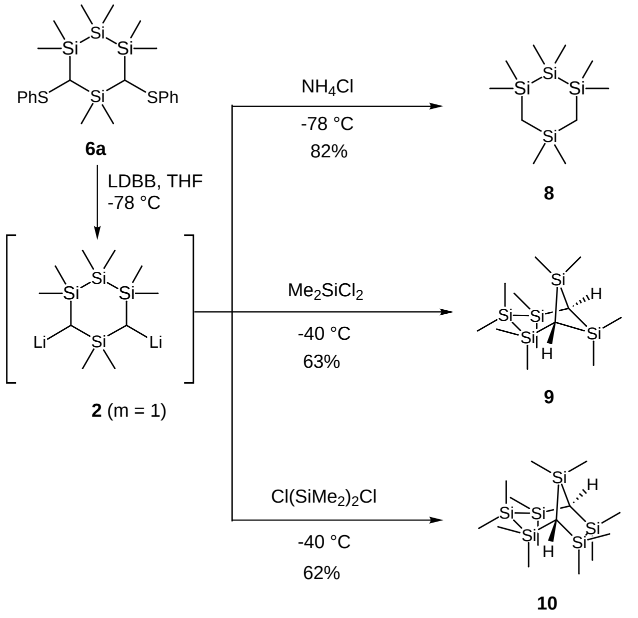
Since separation of the polysilacycloalkanes from the contaminants like benzenethiol entailed a tedious procedure, **4** was alternatively generated by deprotonation of **7** with a base. Trisilane **7** was prepared by treatment of phenylthiomethyllithium with 1,3-dichloro-1,1,2,2,3,3-hexamethyltrisilane in THF at -78 °C in 65% yield. Treatment of **7** (1 mol) with a base (2.2 mol) under various conditions was followed by silylation with dichlorodimethylsilane as shown in eq. 1.[7] The most effective was the use of *s*-BuLi at -30 °C, giving **6a** in 51% yield, comparable to the yield via the reductive lithiation protocol.



s-BuLi, -50 °C (38%); s-BuLi, -30 °C (51%); BuLi/t-BuOK, -78 °C (32%)

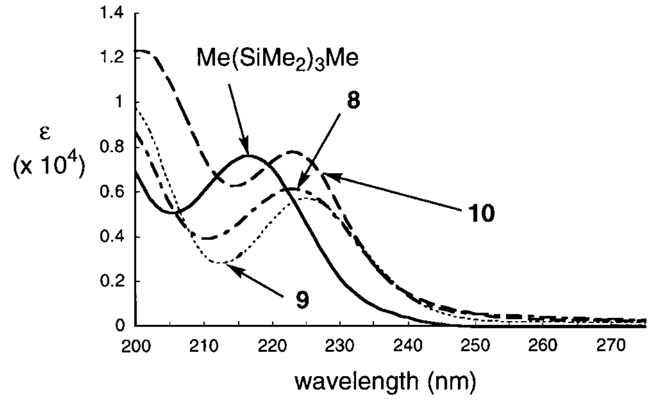
Equation 1

With **6a** in hand, we next studied the generation of a cyclic dianion reagent and its cyclization toward the cage compounds (Scheme 2). Treatment of **6a** with LDBB in THF at -78 °C effectively produced cyclic 1,3-dianion reagent **2** (m = 1) which, upon quenching with aq. NH_4Cl, gave 1,2,3,5-tetrasilacyclohexane **8** in 82% yield. Silylation of **2** (m = 1) with dichlorodimethylsilane or 1,2-dichloro-1,1,2,2-tetramethyldisilane at -40 °C proceeded successfully, giving rise to 2,3,4,6,7-pentasilabicyclo[3.1.1]heptane **9**[8] or 2,3,4,6,7,8-hexasilabicyclo[3.2.1]octane **10**[9] in 62% or 63% yields, respectively. Since **6a** was proved to be a 1 : 1 diastereomeric mixture, the fact that the yields of **9** and **10** were over 50% indicates that epimerization at the lithiated carbons was faster than the cyclization at -40 °C.



Scheme 2

The UV absorption spectra of octamethyltrisilane, **8**, **9**, and **10** were measured in cyclohexane ($1x10^{-4}$ M) at room temperature. As shown in Figure 1, λ_{max} originated from a trisilane linkage of octamethyltrisilane (217 nm, ε = 7590), **8** (223 nm, ε = 6130), **9** (225 nm, ε = 5720), and **10** (223 nm, ε = 7780) exhibited a bathochromic shift when the dimensions of the molecular structure increased.



UV spectra of octamethyltrisilane, **8**, **9**, and **10**

Figure 1

In summary, we have demonstrated that 1,5-bis(phenylthio)-1,5-dilithio-2,3,4-trisilapentane **4** is effective for the synthesis of such cyclic compounds as 1,2,3,5-tetrasilacyclohexane **6a** and 1,2,3,5,6-pentasilacycloheptane **6b**. In addition, the synthesis of the cage compounds 2,3,4,6,7-pentasilabicyclo[3.1.1]heptane **9** and 2,3,4,6,7,8-hexasilabicyclo[3.2.1]octane **10** was accomplished using **6a** as a common precursor. Further synthetic and spectroscopic studies on polysilacycloalkanes are in progress.

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(6) One isomer of the diastereomeric mixture was separable by recrystallization from hexane. **6a** (one isomer): mp 121-122 °C; ^{1}H NMR (200 MHz, CDCl$_3$) δ 0.06 (s, 3H), 0.19 (s, 6H), 0.20 (s, 3H), 0.21 (s, 3H), 0.23 (s, 3H), 0.25 (s, 3H), 1.62 (s, 6H), 7.10-7.38 (10H); ^{13}C NMR (50 MHz, CDCl$_3$) δ -6.9, -6.6, -3.5, -3.4, -2.5, -1.0, 19.6, 125.2, 128.0, 128.6, 140.1; MS (EI, 70 eV) *m/z* 481 (M$^+$+5, 0.1), 480 (M$^+$+4, 0.6), 479 (M$^+$+3, 1), 478 (M$^+$+2, 3), 477 (M$^+$+1, 4), 476 (M$^+$, 8), 399 (8), 367 (93), 309 (5), 257 (100), 73 (29); HRMS calcd for $C_{22}H_{36}S_2Si_4$ 476.1335; found 476.1322.

(7) All attempts at treating **5** with *t*-BuLi (THF, -78 °C), *s*-BuLi (THF, -78 °C), *s*-BuLi (Et$_2$O, -30 °C), BuLi (THF, 0 °C), or BuLi/*t*-BuOK (THF, -78 °C) followed by treatment with Me$_2$SiCl$_2$ turned out futile.

(8) **9**: mp 121-122 °C; ^{1}H NMR (200 MHz, CDCl$_3$) δ 0.03 (s, 2H), 0.10 (s, 12H), 0.21 (s, 6H), 0.27 (s, 6H), 0.28 (s, 6H); ^{13}C NMR (50 MHz, CDCl$_3$) δ -5.5, 1.7, 3.6, 5.1, 9.9; MS (EI, 70 eV) *m/z* 321 (M$^+$+5, 0.5), 320 (M$^+$+4, 2), 319 (M$^+$+3, 5), 318 (M$^+$+2, 16), 317 (M$^+$+1, 29), 316 (M$^+$, 76), 301 (100), 243 (85), 227 (38), 185 (17), 73 (36); HRMS calcd for $C_{12}H_{32}Si_5$ 316.1350; found 316.1334.

(9) **10**: mp 152-153°C; ^{1}H NMR (200 MHz, CDCl$_3$) δ -0.45 (s, 2H), 0.04 (s, 3H), 0.09 (s, 3H), 0.15 (s, 12H), 0.168 (s, 3H), 0.173 (s, 12H), 0.20 (s, 3H); ^{13}C NMR (50 MHz, CDCl$_3$) δ -6.0, -5.1, 1.3, 1.9, 2.7, 3.5, 4.6, 5.3, 6.2; MS (EI, 70 eV) *m/z* 379 (M$^+$+5, 1), 378 (M$^+$+4, 3), 377 (M$^+$+3, 10), 376 (M$^+$+2, 30), 375 (M$^+$+1, 45), 374 (M$^+$, 100), 301 (89), 243 (20), 227 (30), 73 (38); HRMS calcd for $C_{14}H_{38}Si_6$ 374.1589; found 374.1587.

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