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Alkylation Methodology for the Synthesis of 1,4-Disilacyclohexanes Using α,α'-Dilithiated Silanes

Masaki Shimizu,* Masayuki Iwakubo, Yasushi Nishihara, and Tamejiro Hiyama

Research Laboratory of Resources Utilization, Tokyo Institute of Technology
4259 Nagatsuta, Midori-ku, Yokohama, Kanagawa 226-8503, JAPAN

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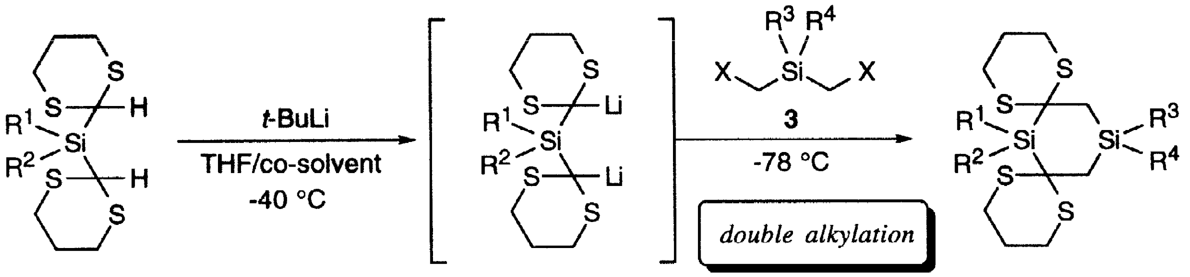
Abstract: The double alkylation of bis[2-(2-lithio-1,3-dithian)-yl]diorganosilane with bis(bromomethyl)diorganosilanes proceeds smoothly in good yields in a mixture of THF-hexamethylphosphoric triamide (HMPA) or THF-1,1,3,3-tetramethylurea (TMU) to give 1,4-disilacyclohexanes whose conformation was shown to be a twist-boat on the basis of X-ray analysis. © 1998 Elsevier Science Ltd. All rights reserved.

In the preceding paper, we have shown that the sulfur-stabilized α,α'-dilithiated silane is a useful reagent for dianionic ring-closure strategy toward various types of polysilacarbacycles. However, electrophiles employed in the reactions of α,α'-dilithiated silanes were limited to such reactive ones as chlorosilane and chlorogermane including our foregoing results.[1] To further extend the synthetic utility of the sulfur-stabilized dianions, we considered double *alkylation* using a bis(halomethyl)silane which seems to be a relatively reactive alkylating reagent due to the silicon accelerating effect for the nucleophilic substitution at the α-carbon.[2] In this paper, we present the first examples of the alkylation of α,α'-dilithiated silanes, giving rise to 1,4-disilacyclohexanes[3] (Scheme 1), and the unique structure of 1,3-dithianyl-substituted 1,4-disilacyclohexane characterized by X-ray diffraction analysis.



1 **2** **4**

Scheme 1

When bis[bis(methylthio)lithiomethyl]dimethylsilane[4] was treated with bis(bromomethyl)diphenylsilane

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(**3c**) in THF or THF/HMPA, alkylation did not take place with bis[bis(methylthio)methyl]dimethylsilane being recovered.[5] Starting with bis(2-(1,3-dithian)-yl)silane **1**,[6] the alkylation was again examined, because 2-lithio-2-triorganosilyl-1,3-dithianes could undergo alkylation in good yields.[7] To a solution of **1** (1.0 mmol) in THF (2 mL)/co-solvent (4 mmol) was added *t*-BuLi (1.51M in pentane, 1.46 mL, 2.2 mmol) at -40 °C. After 3 h, the reaction mixture was cooled to -78 °C and treated with a solution of **3** (1.2 mmol) in THF (1.2 mL). The whole was allowed to warm up to room temperature before quenching with sat. aq. NH_4Cl solution. Workup and purification by silica gel chromatography gave cyclized product **4**. The results are shown in Table 1. As can be seen from entries 1-4, the presence of such an aprotic polar co-solvent of THF as 1,3-dimethylpropyleneurea (DMPU), 1,1,3,3-tetramethylurea (TMU), and hexamethylphosphoric triamide (HMPA) is essential to obtain the product **4d**. Noteworthy is that no alkylation and no proton abstraction from **1a** occurred in THF only (entry 1)[8] in contrast to 2-lithio-2-silyl-1,3-dithiane which can be usually alkylated in THF only.[5] This result shows that the reactivity of **2** is lower than that of 2-lithio-2-silyl-1,3-dithiane. Judging from the fact that the addition of an electron donor solvent often enhances the carbanionic character of alkyllithiums by changing the degree of association,[9] the lower reactivity of **2** may be attributed to some structural features of **2** that are not clear at present.[10] As for alkylating reagent **3**, bromine is the best leaving group (entries 4-7). Under the optimized conditions, 1,4-disilacyclohexanes **4e-i** having various substituents on silicon could be prepared as white solids in 42-76% yields (entries 8-12). These are the first examples of the alkylation of α,α'-dilithiated silanes.

Table 1. Synthesis of 1,4-disilacyclohexane **4** via double alkylation of **1**

Entry	1	R^1	R^2	Co-solvent	3	R^3	R^4	X	4	Yield [%]
1	**1a**	Me	Me	none	**3c**	Ph	Ph	Br	**4d**	0
2	**1a**	Me	Me	DMPU	**3c**	Ph	Ph	Br	**4d**	34
3	**1a**	Me	Me	TMU	**3c**	Ph	Ph	Br	**4d**	69
4	**1a**	Me	Me	HMPA	**3c**	Ph	Ph	Br	**4d**	52
5	**1a**	Me	Me	HMPA	**3c**	Ph	Ph	Cl	**4d**	20
6	**1a**	Me	Me	HMPA	**3c**	Ph	Ph	I	**4d**	0
7	**1a**	Me	Me	HMPA	**3c**	Ph	Ph	OMs	**4d**	0
8	**1a**	Me	Me	TMU	**3b**	Ph	Me	Br	**4e**	76
9	**1b**	Me	Me	TMU	**3a**	Me	Me	Br	**4f**	68
10	**1b**	Ph	Me	TMU	**3c**	Ph	Ph	Br	**4g**	48
11	**1b**	Ph	Me	TMU	**3b**	Ph	Me	Br	**4h**	42
12	**1b**	Ph	Me	TMU	**3a**	Me	Me	Br	**4i**	70

The molecular structure of **4d** is shown in Figure 1.[11] Two 1,3-dithianyl rings adopted strain-free chair conformation, whereas the conformation of the 1,4-disilacyclohexane ring was twist-boat form with silicon-carbon bond lengths of Si(2)-C(2) and Si(2)-C(4) being 1.929(2) and 1.926(2) Å, respectively, somewhat longer than the normal silicon-carbon bond length (1.89 Å).[12] Another characteristic feature is the arrangement of S(2), Si(2), and S(4) atoms. To our surprise, these three atoms are aligned almost linearly ($\angle$S(2)-Si(2)-S(4) = 174.7°) and the atomic distances of Si(2)-S(2) and Si(2)-S(4), being 3.002 and 2.963 Å, respectively, are

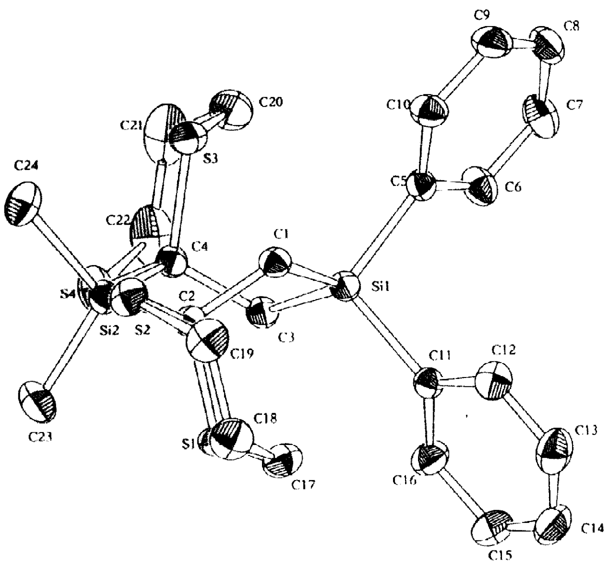
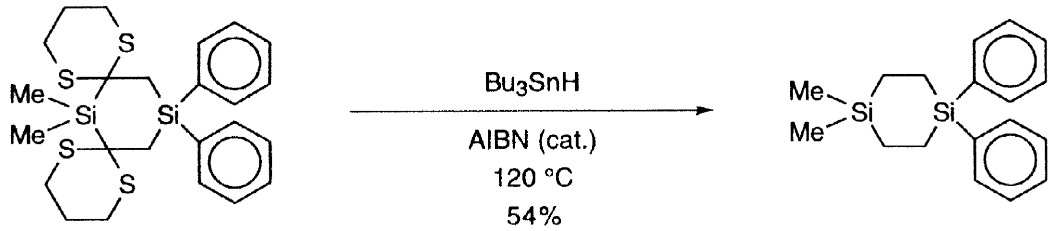


Figure 1. Molecular structure of **4d**

longer than the Si-S bond of H_3SiSH (2.14 Å)[13] but shorter than the sum of the van der Waals radii of Si (2.10 Å) and sulfur (1.80 Å).[14] The twist form may be attributable to the steric repulsion between the C(4)-S(3) and the C(2)-S(2) bonds, but the interaction between the silicon and two sulfur atoms should be considered also.

1,3-Dithianyl-substituted 1,4-disilacyclohexane **4d** was transformed into the parent silane **5** by reduction of the sulfenyl groups with tributyltin hydride (eq.1).[15]



4d **5** (1)

In conclusion, bis[2-(2-lithio-1,3-dithian)-yl)diorganosilane could be efficiently double-alkylated with bis(halomethyl)diorganosilanes in a solvent system consisting of THF and an aprotic polar solvent (HMPA or TMU) to give the 1,4-disilacyclohexanes. The present results are the first cases of the alkylation of α,α'-dilithiated silanes. The produced 1,3-dithianyl-substituted 1,4-disilacyclohexanes are shown to adopt twist-boat conformation by X-ray analysis and to be readily converted into the parent silane by Bu_3SnH reduction. Transformation of the 1,4-disilacyclohexanes to functional materials and extension of the concept to various alkylating reagents and reaction types are being studied in our laboratories.

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REFERENCES AND NOTES

1. a) Seyferth, D.; Rochow, E. G. *J. Am. Chem. Soc.* **1955**, *77*, 907-908; b) Seyferth, D.; Attridge, C. J. *J. Organomet. Chem.* **1970**, *21*, 103-106; c) Sakurai, H.; Umino, H. *J. Organomet. Chem.* **1977**, *142*, C49-C51; d) Akkerman, O. S.; Bickelhaupt, F. *J. Organomet. Chem.* **1988**, *338*, 159-168; e) Strohmann, C.; Lüdtke, S.; Wack, E. *Chem. Ber.* **1996**, *129*, 799-805; see also f) Strohmann, C.; Lüdtke, S. In *Organosilicon Chemistry II. From Molecules to Materials*; N. Auner and J. Weis, Ed.; VCH: Weinheim, 1996; pp 499-504.
2. a) Fleming, I. In *Comprehensive Organic Chemistry*; ed.; D. Barton and W. D. Ollis, Ed.; Pergamon Press: Oxford, 1979; Vol. 3; pp 541-686; b) Bassindale, A. R.; Taylor, P. G. In *The Chemistry of Organic Silicon Compounds*; ed.; S. Patai and Z. Rappoport, Ed.; John Wiley & Sons, Inc.: New York, 1989; Vol. 2; pp 893-963. Also see, Shimizu, M.; Hata, T.; Hiyama, T. *Tetrahedron Lett.* **1997**, *38*, 4591-4594.
3. 1,1,4,4-Tetrafluoro-1,4-disilacyclohexane was very recently utilized in the study of fluoride ion donor-acceptor system. a) Hoshi, T.; Takahashi, M.; Kira, M. *Chem. Lett.* **1996**, 683-684. 1,4-Disilacyclohexanes with no substituent on the ring carbons were often obtained as minor products (~30%) in the polymerization of diorganovinylsilane via hydrosilylation. b) Curry, J. W. *J. Am. Chem. Soc.* **1956**, *78*, 1686-1689; c) Curry, J. W. *J. Org. Chem.* **1961**, *26*, 1308-1309; d) Boury, B.; Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Planeix, J.-M.; Vioux, A. *Organometallics* **1991**, *10*, 1457-1461; e) Fry, B. E.; Neckers, D. C. *Macromolecules* **1996**, *29*, 5306-5312.
4. See the preceding paper.
5. As **3c** was consumed completely to give unidentified products, the 1,3-dianion **2** appears to act not as a nucleophile but as a base to cause deprotonation at the bromine-attached carbons.
6. Bis(2-(1,3-dithian)-yl)dimethylsilane (**1**) was prepared by silylation of 2-lithio-1,3-dithiane with dichlorodimethylsilane in THF at -78 °C in 67% yield.
7. For examples, see a) Brook, A. G.; Duff, J. M.; Jones, P. F.; Davis, N. R. *J. Am. Chem. Soc.* **1967**, *89*, 431-434; b) Corey, E. J.; Seebach, D.; Freedman, R. *J. Am. Chem. Soc.* **1967**, *89*, 434-436; c) Salzmann, T. N.; Ratcliffe, R. W.; Christensen, B. G.; Bouffard, F. A. *J. Am. Chem. Soc.* **1980**, *102*, 6161-6163; d) Chuang, T.-H.; Fang, J.-M.; Jiaang, W.-T.; Tsai, Y.-M. *J. Org. Chem.* **1996**, *61*, 1794-1805.
8. The generation of 1,3-dianion **2** in THF was confirmed by quenching with D_2O to obtain the deutrated **1** in 81% yield (98% *d*).
9. Wakefield, B. J. *Organolithium Methods*; Academic Press: London, 1988; Chapter 2, pp. 2-3.
10. The structural formula of **2** does not express the real structure in view of the aggregation and the solvation.
11. Crystals of **4d** suitable for X-ray structure determination were obtained as colorless prisms by recrystallization from dichloromethane/hexane (1 : 1). Crystal data for **4d**: $C_{24}H_{32}Si_2S_4$, $M = 504.93$, triclinic, space group P1 (#2), $a = 10.505(2)$, $b = 14.898(2)$, $c = 10.077(2)$ Å, $\alpha = 102.35(1)$, $\beta = 116.88(1)$, $\gamma = 69.65(1)°$, $V = 1315.9(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.274$ g cm^{-3}, $F(000) = 536.00$, $2\theta_{max} = 55.0°$, MoKα ($\lambda = 0.71069$ Å), μ(MoKα) = 4.62 cm^{-1}, $T = 296$ K; Of the 6363 reflections which were collected, 6032 were unique ($R_{int} = 0.012$). The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques. 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 4272 observed reflections $\{I > 3.00\sigma(I)\}$ and 271 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.038$ and $R_w = 0.034$. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100558.
12. The twist-boat conformation was also observed in case of **4f** as well as **4i**.
13. Herman, A.; Wojnowski, W. *Structural Chemistry* **1992**, *3*, 239-244.
14. Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441-451.
15. Reduction with Raney-Ni (W2) resulted in affording a complex mixture.