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Silicon−Carbon Unsaturated Compounds. 55. Synthesis and Reactions of Lithium Silenolates, Silicon Analogs of Lithium Enolates

Joji Ohshita,* Shin Masaoka, Yoshiteru Masaoka, Hidenobu Hasebe, and
Mitsuo Ishikawa*

Department of Applied Chemistry, Faculty of Engineering, Hiroshima University,
Higashi-Hiroshima 739, Japan

Akitomo Tachibana,* Tasuku Yano, and Tokio Yamabe

Division of Molecular Engineering, Faculty of Engineering, Kyoto University,
Kyoto 606-01, Japan

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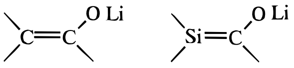
Chemical behavior of acylpolysilanes, (Me$_3$Si)$_3$SiCOR (**1a**, R = Mes; **1b**, R = *o*-Tol; **1c**, R = Ad; **1d**, R = *t*-Bu; **1g**, R = Ph; **1h**, R = Me), toward silyllithium reagents has been studied. Reactions of **1a**−**d** with [tris(trimethylsilyl)silyl]lithium gave the corresponding lithium silenolates, (Me$_3$Si)$_2$Si=CROLi (**5a**, R = Mes; **5b**, R = *o*-Tol; **5c**, R = Ad; **5d**, R = *t*-Bu), in high yield by removal of a trimethylsilyl group from the acylpolysilane. However, a similar reaction of **1g** gave an unstable lithium silenolate, which undergoes dimerization and then further reactions under the conditions used. Acetylpolysilane **1h** did not afford the lithium silenolate but gave lithium [tris(trimethylsilyl)silyl]ethenolate. Lithium silenolate **5a** was produced also by treating **1a** with (dimethylphenylsilyl)lithium. The reactions of **1b**,**c** with (dimethylphenylsilyl)lithium proceed in a different fashion from that of **1a** to afford products arising from addition of the silyllithium to the carbonyl bond as major products. Lithium silenolates **5a**,**c**,**d** are stable at low temperature in THF solution and can be characterized by NMR spectroscopy. Silenolates **5a**−**d** reacted with alkyl halides to afford Si-alkylated products in high yield. Treatment of **5a**,**b** with chlorotriethylsilane led to the formation of silenes arising from O-silylation of the lithium silenolates, almost quantitatively, while **5c**,**d** gave the corresponding acylpolysilanes by Si-silylation in high yield. Results of theoretical studies which were carried out using the reaction of (H$_3$Si)$_3$SiCOCH$_3$ with H$_3$SiLi as a model also are described.

Introduction

Lithium enolates have been found to be versatile reagents in organic synthesis. One of the most important reagents for the synthesis of organic compounds, silyl enol ethers, can be readily obtained from enolate anions, by reaction with chlorosilanes.[1] To date, the chemistry of the enolate anions has been investigated in detail, and many types of lithium enolates (**A**) (Chart 1) have been used as a convenient synthetic tool in organic chemistry.[2] In contrast, much less is known about the chemistry of silicon analogs of lithium enolates, lithium silenolates (**B**).

During the course of our studies concerning the chemical behavior of acylpolysilanes toward organolithium reagents,[3] we have found that the reaction of acylpolysilanes with silyllithium reagents affords stable lithium silenolates in solution. To our knowledge, two papers concerning the formation of lithium silenolates have been published thus far. Biltueva et al. have reported that the reactions of pivaloyl- and adamantoyltris(trimethylsilyl)silanes with (triethylgermyl)lithium afforded the respective lithium silenolates which were characterized by ^{29}Si NMR spectroscopy.[4] On the basis of the chemical shifts of the central silicon atoms of the lithium silenolates which appear in the same region as those for similarly substituted silyl silenol ethers, (Me$_3$Si)$_2$Si=C(OSiMe$_3$)R, reported by Brook et al.,[6] they concluded that the central Si−C bonds of the lithium silenolates have high double-bonding character and that the lithium silenolates can be understood as silenoxylithiums rather than (acylsilyl)lithiums. However, when we followed the same reaction, we could not

Chart 1



A **B**

[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1996.

(1) (a) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: London, 1988. (b) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: New York, 1983.

(2) For review, see: Caine, D. In *Comprehensive Organonic Synthesis*; Pergamon Press: Oxford, U.K., Vol. 3, Chapter 1.1, 1991.

(3) (a) Ohshita, J.; Masaoka, Y.; Ishikawa, M. *Organometallics* **1991**, *10*, 3775. (b) Ohshita, J.; Masaoka, Y.; Ishikawa, M.; Takeuchi, T. *Organometallics* **1993**, *12*, 876. For related work, see also ref 5.

(4) Biltueva, I. S.; Bravo-Zhivotovskii, D. A.; Kalikhman, I. D.; Vitkovskii, V. Yu; Shevchenko, S. G.; Vyazankin. N. S.; Voronkov, M. G. *J. Organomet. Chem.* **1989**, *368*, 163.

(5) (a) Brook, A. G.; Chiu, P.; McClenaghnan, J.; Lough, A. J. *Organometallics* **1991**, *10*, 3292. (b) Bravo-Zhivotovskii, D.; Braude, V.; Stanger, A.; Kapon, M.; Apeloig, Y. *Organometallics* **1992**, *11*, 2326. (c) Krempner, C.; Oehme, H. *J. Organomet. Chem.* **1994**, *464*, C7. (d) Krempner, C.; Reinke, H.; Oehme, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1615.

(6) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Krishna, R.; Kallury, M. R.; Poon, Y. C.; Chang, Y.-M.; Wong-Ng, W. *J. Am. Chem. Soc.* **1982**, *104*, 5667.

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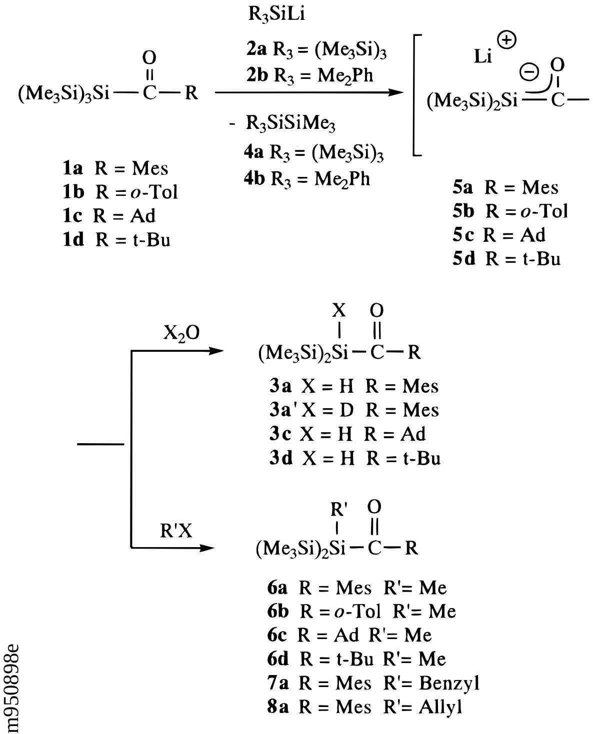
Scheme 1



observe ^{29}Si NMR signals reported by these authors.[7] Apeloig et al. reported that the similar reaction of adamantoyltris(trimethylsilyl)silane with (triethylgermyl)lithium affords a product that may be explained in terms of a lithium silenolate intermediate.[8]

In this paper, we report the synthesis and NMR spectroscopic analysis of the lithium silenolates in detail and some reactions of the silenolates with alkyl halides and chlorotriethylsilane. We also describe the results of molecular orbital calculations, which were performed on the reaction of acetyltrisilylsilane with silyl anion as a model.

Table 1. ^{29}Si NMR Shifts for the Central Silicons of Acylpolysilanes and Lithium Silenolates

R	acylpolysilane (ppm)[a]	lithium silenolate (ppm)[a]
Mes	-75.3	-59.9
Ad	-79.0	-70.5
t-Bu	-79.6	-70.3

[a] In 70% THF + 30% THF-d_8 at −40 °C.

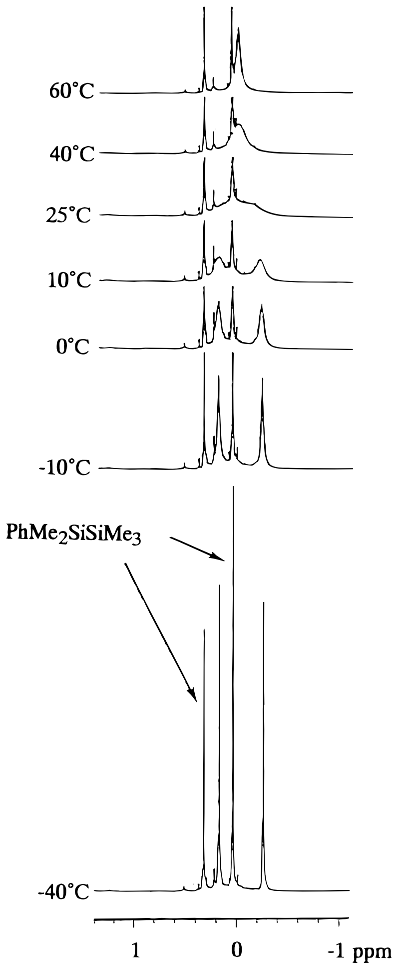


Figure 1. ^{1}H NMR spectra of lithium silenolate **5a** in 70% THF + 30% THF-d_8.

Results and Discussion

Synthesis and Reactions of Lithium Silenolates. The reaction of mesitoyltris(trimethylsilyl)silane (**1a**) with 1 equiv of [tris(trimethylsilyl)silyl]lithium (**2a**) in THF at −80 °C for 2 h, followed by hydrolysis of the resulting mixture with water, gave mesitoylbis(trimethylsilyl)silane (**3a**) in 91% yield, along with a quantitative yield of tetrakis(trimethylsilyl)silane (**4a**), indicating the formation of lithium mesitylbis(trimethylsilyl)silenolate (**5a**), as shown in Scheme 1. A similar reaction of **1a** with 1 equiv of (dimethylphenylsilyl)lithium (**2b**) under the same conditions also afforded **3a** in 76% yield, along with a 87% yield of pentamethylphenyldisilane (**4b**). When the resulting reaction mixture was hydrolyzed with D_2O, deuteriomesitoylbis(trimethylsilyl)silane (**3a′**) was obtained in 71% yield. Direct evidence for the formation of lithium silenolate **5a** was obtained by NMR spectroscopy. Thus, when the reaction of **1a** with 1 equiv of **2b** in a mixed solvent composed of THF and THF-d_8 in a ratio of 7:3 at −40 °C was monitored by ^{1}H NMR spectroscopy, all of **1a** was found to have been transformed into **5a**, immediately after addition of **2b** to **1a**. The ^{29}Si NMR spectrum of **5a** at −40 °C reveals a signal at −59.9 ppm due to the central silicon atom, which is shifted to lower field by 15.4 ppm relative to that of **1a**, indicating that the central silicon atom in silenolate **5a** must have sp^2 character (Table 1). In this spectrum, resonances of two trimethylsilyl groups appear separately at −12.8 and −10.6 ppm with equal intensities. ^{1}H and ^{13}C NMR spectra of **5a** also reveal two signals with equal intensities due to nonequivalent trimethylsilyl groups. The presence of the nonequivalent trimethylsilyl groups in **5a** may be ascribed to double-bond character for the central Si−C bond. On warming, two trimethylsilyl signals observed in the ^{1}H NMR spectrum at −40 °C are broadened and finally coalesced at 25 °C as shown in Figure 1. Similarly, the ^{13}C and ^{29}Si NMR spectra of **5a** at 25 °C showed a single resonance for the trimethylsilyl groups indicating that two trimethylsilyl groups become magnetically equivalent at this temperature. When this solution was again cooled to −40 °C, the two nonequivalent trimethylsilyl resonances were reproduced in these spectra, indicating that this process

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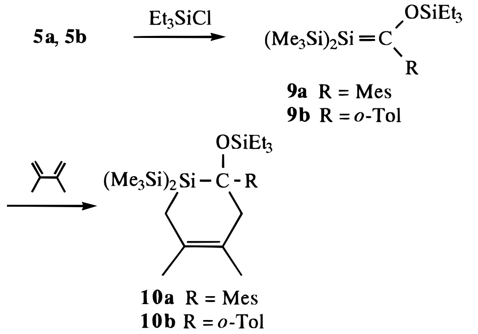
[7] Ohshita, J.; Masaoka, Y.; Masaoka, S.; Ishikawa, M.; Tachibana, A.; Yano, T.; Yamabe, T. *J. Organomet. Chem.* **1994**, *473*, 15.

[8] Bravo-Zhivotovskii, D.; Apeloig, Y.; Ovchinnikov, Y.; Igonin, V.; Struchkov, Y. T. *J. Organomet. Chem.* **1993**, *446*, 123.

Scheme 2



is reversible. The activation barrier for this change, which corresponds to the π-bond energy of the central silicon−carbon bond was calculated to be $\Delta G^{\ddagger}_{TC} = 14.3$ kcal/mol on the basis of the ^{1}H NMR spectroscopy.

Like lithium enolates, which react with alkylating agents to give the C-alkylated products,[2] lithium silenolate **5a** can be converted into acylpolysilanes by treatment with alkyl halides. Thus, the reaction of **1a** with **2b**, followed by quenching the reaction mixture with methyl iodide, gave mesitoylmethylbis(trimethylsilyl)silane (**6a**) in 91% yield. Lithium silenolate **5a** reacts also with benzyl and allyl bromide at the silicon center to give benzylmesitoylbis(trimethylsilyl)silane (**7a**) and allylmesitoylbis(trimethylsilyl)silane (**8a**) in 75% and 68% yields, respectively.

Lithium enolates are well-known to react with chlorosilanes to give silyl enol ethers.[1,2] When a THF solution of **5a** was treated with chlorotriethylsilane at −80 °C, 2-mesityl-2-(triethylsiloxy)-1,1-bis(trimethylsilyl)-1-silene (**9a**) was produced quantitatively, as indicated by the NMR spectroscopic analysis of the resulting mixture. ^{1}H, ^{13}C, and ^{29}Si NMR spectra of **9a** closely resemble those of 2-mesityl-2-(trimethylsiloxy)-1,1-bis(trimethylsilyl)silene reported by Brook et al.[9] As expected, the reaction of **5a** with a mixture of chlorotriethylsilane and 2,3-dimethylbutadiene gave 6-(mesityl)-3,4-dimethyl-6-(trimethylsiloxy)-1,1-bis(trimethylsilyl)-1-silacyclohex-3-ene (**10a**) in 88% yield based on **1a** (Scheme 2).

The reaction of (*o*-toluoyl)tris(trimethylsilyl)silane (**1b**) with **2a** also proceeded smoothly yielding lithium silenolate **5b** as evidenced by the quantitative formation of **4a**, as well as by the formation of an Si-methylated product, (*o*-toluoyl)methylbis(trimethylsilyl)silane (**6b**) in 70% yield on treatment of the reaction mixture with methyl iodide. However, **5b** is thermally unstable and all attempts to characterize it by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopic analysis were unsuccessful even when the NMR spectra were measured at −80 °C. Only unresolved, broad signals were observed in these spectra. Treatment of **1b** with **2a** at −80 °C, followed by addition of a mixture of chlorotriethylsilane and 2,3-dimethylbutadiene, gave a cycloadduct, 3,4-dimethyl-6-*o*-tolyl-6-(triethylsiloxy)-1,1-bis(trimethylsilyl)-1-silacyclohex-3-ene (**10b**) in 60% yield, indicating the formation of 2-*o*-tolyl-2-(triethylsiloxy)-1,1-bis(trimethylsilyl)-1-silene (**9b**), as in the case of **1a**. In this reaction, compound **4a** and (triethylsilyl)tris(trimethylsilyl)silane were also obtained in 67% and 27% yield, respectively.

Alkyl-substituted lithium silenolates were also prepared by the present procedure. Thus, the reaction of adamantoyltris(trimethylsilyl)silane (**1c**) with 1 equiv of **2a** in THF at −100 °C, followed by hydrolysis of the resulting mixture with water, gave adamantoylbis(trimethylsilyl)silane (**3c**) in 97% yield along with a quantitative yield of **4a**. Similar treatment of tris(trimethylsilyl)pivaloylsilane (**1d**) with **2a**, and then hydrolysis of the reaction mixture, gave bis(trimethylsilyl)pivaloylsilane (**3d**) and **4a** in 84% and 99% yield, respectively. These results clearly indicate the formation of lithium silenolates **5c**,**d** in these reactions. When **5c**,**d** were quenched with methyl iodide, the corresponding Si-methylated products, adamantoylmethylbis(trimethylsilyl)silane (**6c**) and methylbis(trimethylsilyl)pivaloylsilane (**6d**), were obtained in 78% and 87% yield, respectively, similar to the reactions of **5a**,**b**.

Lithium silenolates **5c**,**d** are thermally less stable than **5a**, but more stable than **5b**, and can be characterized by NMR spectroscopy. ^{1}H, ^{13}C, and ^{29}Si NMR spectra of the reaction mixtures obtained from **1c**,**d** with **2a** at −40 °C clearly show that all of the starting acylpolysilanes are transformed into the respective **5c**,**d**. In contrast to the NMR spectra for **5a**, in which two trimethylsilyl groups on the central silicon atom are magnetically nonequivalent, all of the ^{1}H, ^{13}C, and ^{29}Si NMR spectra for lithium silenolates **5c**,**d** show a single resonance for these two trimethylsilyl groups even at −80 °C. These results indicate the free rotation of the central Si−C bond. The signals of the central silicon atoms for **5c**,**d** in ^{29}Si NMR spectra appear at −70.5 and −70.3 ppm, lower field by 8.5 and 9.3 ppm than those of the respective starting compounds **1c**,**d** (Table 1). However, the degree of the low-field shifts observed for **5c**,**d** is much smaller than that for **5a**. These facts strongly suggest that sp^2-character of the central silicon atoms in these silenolates decreases in comparison with that of **5a**. The anion charge in **5c**,**d** seems to localize moderately on the central silicon atoms.

In disagreement with our present observation, Biltueva et al. have reported that the reactions of **1c**,**d** with (triethylgermyl)lithium in THF at room temperature produce the respective lithium silenolates whose ^{29}Si NMR signals of the central silicon atoms appear at 64.86 and 67.77 ppm, respectively.[4] When we followed the reaction of **1c** with (triethylgermyl)lithium and monitored the reaction by ^{29}Si NMR spectroscopy at −40 °C, only signals which were identical with those of **5c** were observed, along with those of (triethylgermyl)trimethylsilane and the starting compound **1c**. No other signals were observed. Furthermore, when a THF solution of **5c** was allowed to stand at room temperature for 7 h and then treated with methyl iodide, many decomposition products were produced in low yields. Only one product, 1-adamantoyl-1-adamantyl-1-methoxyethane (**11**) was isolated from the mixture in 30% yield. The formation of **11** suggests that dimerization of **5c** takes place during the decomposition as shown in Scheme 3. Recently, Apeloig et al. reported that the reaction of **1c** with 2 equiv of (triethylgermyl)lithium gives a product which may be explained by a series of reactions involving the formation of **5c** and its dimerization.[8]

Interestingly, the reactions of lithium silenolates **5c**,**d** which bear an alkyl substituent on the carbonyl carbon, with chlorotriethylsilane proceed in a quite different fashion from those of **5a**,**b** which have an aryl substituent on the carbonyl carbon atom (Scheme 4). Thus, treatment of a THF solution of **5c** with chlorotriethylsilane at −80 °C gave adamantoyl(triethylsilyl)bis-

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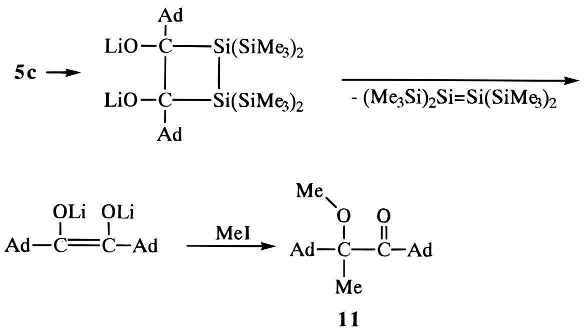
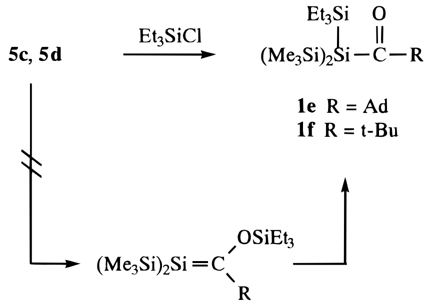
(9) Brook, A. G.; Wessely, H.-J. *Organometallics* **1985**, *4*, 1487.

Scheme 3



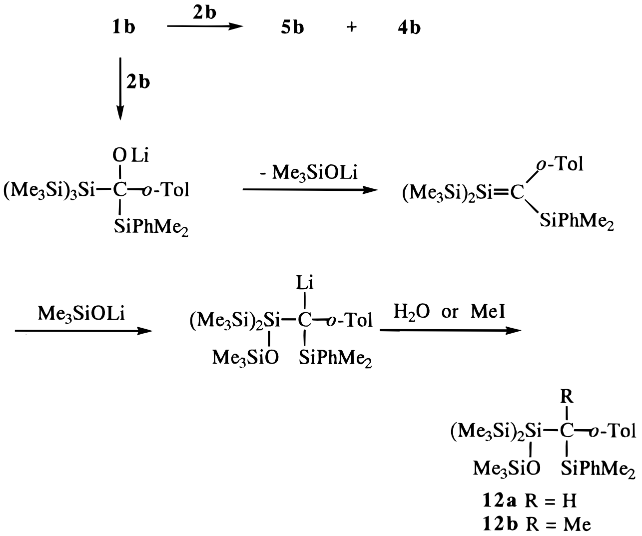
Scheme 4



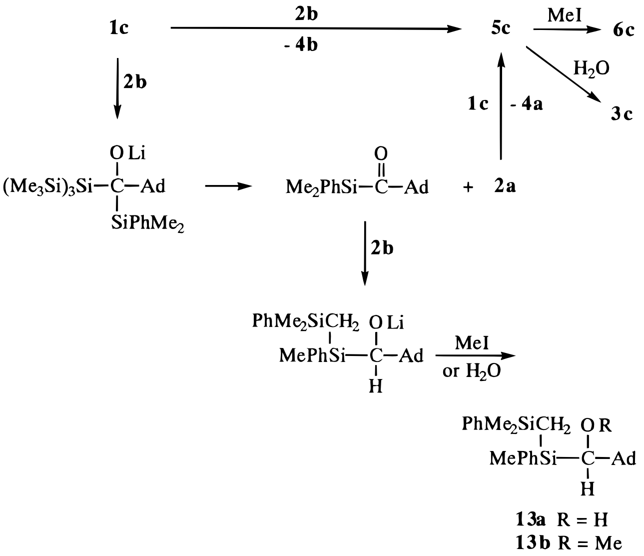
(trimethylsilyl)silane (**1e**) in 94% yield in which the triethylsilyl group is attached to the central silicon atom in **5c** but not the oxygen atom. The reaction of **5d** under the same conditions again afforded an Si-silylated product, pivaloyl(triethylsilyl)bis(trimethylsilyl)silane (**1f**) in 83% yield. For the formation of the Si-silylated products, one might consider the possibility that the reactions of **5c**,**d** with chlorotriethylsilane produce the respective silenes as in the case of **5a**,**b** and then the resulting silenes isomerize to **1e**,**f**.[10] However, when we carried out similar reactions of **5c**,**d** with chlorotriethylsilane in the presence of an excess of 2,3-dimethyl-1,3-butadiene as a silene trapping agent, again the products **1e**,**f** were obtained in 71% and 83% yield, respectively, as the sole volatile product. No [2 + 4] cycloadducts analogous to **10a**,**b** were detected by either GLC analysis or spectroscopic analysis of the reaction mixtures. The results indicate that **1e**,**f** are the initial products in the reactions of **5c**,**d** with chlorotriethylsilane but not the secondary products from isomerization of the silenes once formed. As indicated by NMR spectroscopic analysis, the anion charge in **5c**,**d** is moderately localized on the central silicon atoms, whereas in **5a**,**b** the anion charge is effectively delocalized over the silicon atoms and carbonyl groups. This may be the reason for the different chemical behavior of **5c**,**d** vs **5a**,**b** toward chlorotriethylsilane.

In contrast to the reaction of **1a** with **2b** in which lithium silenolate **5a** was produced in high yield, the reactions of **1b,c** with **2b** afforded the respective lithium silenolates **5b**,**c** only in low yield. Thus, when **1b** was treated with silyllithium **2b** under the same conditions and the resulting mixture was hydrolyzed with water, disilane **4b** was obtained in 14% yield. In this reaction, [(dimethylphenylsilyl)-*o*-tolylmethyl](trimethylsiloxy)-bis(trimethylsilyl)silane (**12a**) was also formed in 20% yield. Treatment of the mixture from the reaction of **1b** and **2b** with methyl iodide gave **4b** and [(dimethylphenylsilyl)methyl-*o*-tolylmethyl](trimethylsiloxy)bis-(trimethylsilyl)silane (**12b**) in 38% and 40% yield, respectively. In these reactions, small amounts of many products in less than 10% yield were detected by GLC analysis of the reaction mixtures. The formation of **12a**,**b** can be explained by a series of reactions involving addition of **2b** to the carbonyl bond of **1b**, a Peterson-type olefination giving a silene, and addition of trimethylsiloxylithium to the resulting silicon−carbon double bond, as observed for the reactions of aroyltris-(trimethylsilyl)silane with aryllithium reagents (Scheme 5).[3b] Similar Peterson-type olefinations yielding silenes have been reported by Brook et al.[5a] and Apeloig and his co-workers.[8]

Scheme 5



Scheme 6



Similarly, treatment of **1c** with **2b** followed by hydrolysis gave **4b** only in 17% yield, along with **4a**, **3c**, and (adamantylhydroxymethyl)[(dimethylphenylsilyl)-methyl]methylphenylsilane (**13a**) in 18%, 29%, and 15% yield, respectively. In this reaction, small amounts of many products were also produced in less than 10% yield, in addition to the 18% yield of the starting compound **1c**. When the mixture obtained from the reaction of **1c** and **2b** was treated with methyl iodide, **4b**, **4a**, **6c**, (adamantylmethoxymethyl)[(dimethyl-

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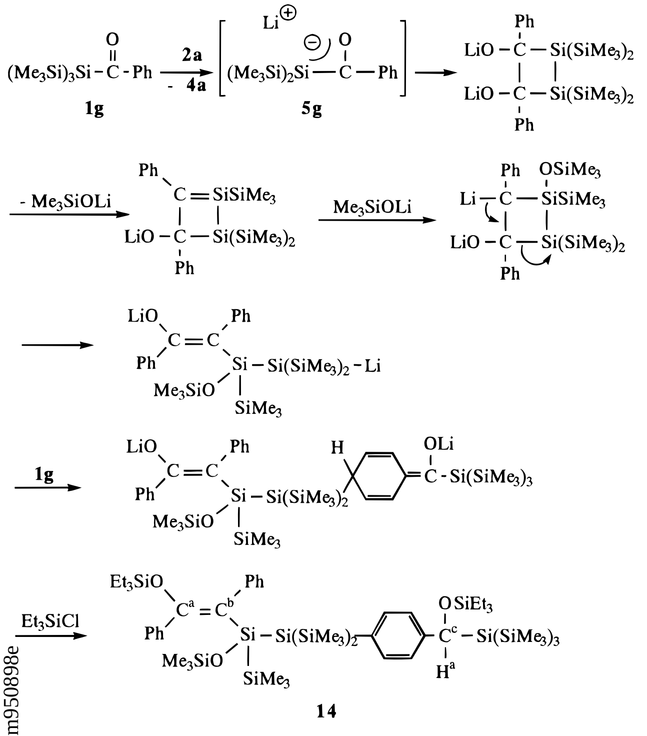
[10] Thermal equilibrium between acylpolysilanes and siloxysilenes has been reported previously. See: (a) Brook, A. G.; Harris, J. W.; Lennon, J.; El Sheikh, M.; *J. Am. Chem. Soc.* **1979**, *101*, 83. (b) Ohshita, J.; Hasebe, H.; Masaoka, Y. Ishikawa, M. *Organometallics* **1994**, *13*, 1064.

Scheme 7



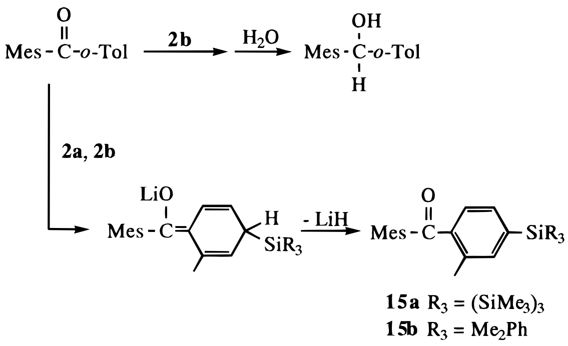
phenylsilyl)methyl]methylphenylsilane (**13b**) and the unchanged starting compound **1c** were obtained in 15%, 21%, 17%, 15%, and 17% yield, respectively. For the formation of **4a** and **13a,b**, it seems likely that **2b** adds across the carbonyl bond of **1c** giving {adamantyl[tris(trimethylsilyl)silyl](dimethylphenylsilyl)methoxy}lithium in the initial step. The (adamantylmethoxy)lithium thus formed would undergo elimination of [tris(trimethylsilyl)silyl]lithium (**2a**) to produce adamantoyldimethylphenylsilane. The silyllithium **2a** would react with **1c** to give lithium silenolate **5c** and **4a**, while the reaction of the resulting adamantoyldimethylphenylsilane with **2b**, followed by quenching with methyl iodide and water, would afford compounds **13a**,**b**. At present, any evidence for the formation of adamantoyldimethylphenylsilane in these reactions has not yet been obtained, and the pathway leading to the formation of **13** is still unknown. However, that the reaction of **1d** with methyllithium to give **2a** and *tert*-butyl methyl ketone has been reported, previously.[3a]

We also carried out the reactions of benzoyltris(trimethylsilyl)silane (**1g**) and acetyltris(trimethylsilyl)silane (**1h**) with **2a** in the hope of obtaining sterically less hindered lithium silenolates. However, all attempts to get evidence for the formation of lithium phenylbis(trimethylsilyl)silenolate (**5h**) from reaction of **1g** and 1 equiv of **2a** in THF by NMR spectroscopic analysis at low temperature and by quenching experiments with a variety of trapping agents, such as water, methyl iodide, and benzyl bromide, were unsuccessful. In all cases, tetrakis(trimethylsilyl)silane (**4a**) was obtained in 56–68% yield as the sole volatile product, together with nonvolatile products. When the reaction mixture was quenched with chlorotriethylsilane, product **14**, whose mass spectrum shows a parent ion peak at *m*/*z* 1140, was produced in 26% yield. Product **14** was isolated by preparative GPC, and the structure was verified by spectroscopic and elemental analysis (Scheme 7). Compound **14** consists of a pair of diastereomers in a ratio of 52:48. Assignment of the signals for each diastereomer in the ^{1}H and ^{13}C NMR spectra was performed by using ^{1}H–^{1}H and ^{13}C–^{1}H COSY experiments. The results show the presence of a $(Me_3Si)_3Si$ unit, four nonequivalent Me_3Si, two Et_3Si, one *p*-phenylene, two phenyl, and an alkoxymethyne (H^aC^cO) group for each diastereomer (see **14** in Scheme 7). The ^{13}C NMR spectrum of **14** exhibits signals at 121.1 and 133.5 ppm for the major diastereomer, and 120.5 and 133.5 ppm for the minor one, probably assignable to enol carbons, C^b and C^a, respectively. In the long-range ^{13}C–^{1}H COSY spectrum of **14**, the alkoxymethyne proton (H^a) couples with the phenylene carbon at 125.8 ppm of the major diastereomer and that at 125.7 ppm of the minor one, indicating the presence of an $H^aC^c(OR)(p\text{-}C_6H_4)$– moiety. Selective proton decoupling experiments in ^{13}C NMR spectroscopy are also consistent with the structure proposed for **14**. Thus, irradiation of signals due to protons at the ortho positions of phenyl rings at 7.60 and 7.75 ppm led to sharpening of both of the two enol carbons, indicating the presence of a $-C^bPh{=}C^aPh(OR)$ moiety. In the ^{29}Si NMR spectrum, signals of two trisilyl-substituted silicons at −64 to −70 ppm and three siloxy silicons at 8 to 22 ppm are observed in addition to four monosilyl-substituted and one disilyl-substituted silicons at −17 to −10 ppm for each diastereomer. On the basis of these results, product **14** was identified as 2-[(*E*)-1,2-diphenyl-2-(triethylsiloxy)ethenyl]-1-{4-[(triethylsiloxy)(tris(trimethylsilyl)silyl)methyl]phenyl}-2-(trimethylsiloxy)-1,1,2-tris(trimethylsilyl)disilane. Unfortunately, no evidence for the configuration of **14** was obtained even in the NOE-FID difference experiments. However, we tentatively identified **14** as the (*E*)-isomer, which seems to be sterically favorable geometry. In this reaction, no other regioisomers were detected by spectroscopic analysis.

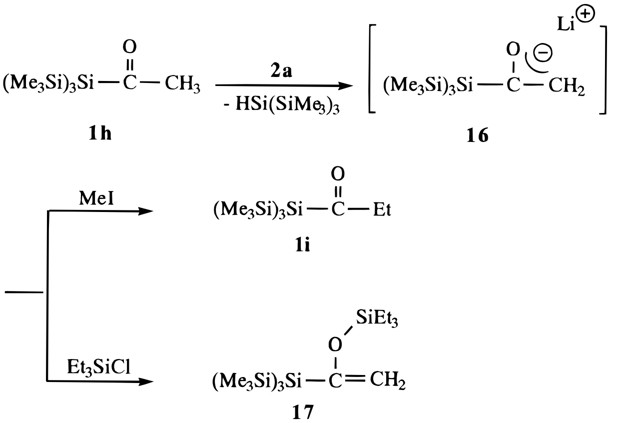
The possible mechanistic interpretation for the formation of **14** is presented in Scheme 7, which involves dimerization of lithium silenolate **5g** to produce a disilacyclobutane, similar to that which occurs with **5c**. Peterson-type olefination of the resulting disilacyclobutane intermediate, followed by addition of (trimethylsiloxy)lithium to the silicon–carbon double bond, and subsequent ring opening would produce a silyllithium. The silyllithium thus formed would react with **1g** to give an adduct bearing a 1,4-dihydrophenylene unit. Finally, the reaction of the resulting adduct with chlorotriethylsilane, involving an intramolecular 1,5-hydrogen shift to produce phenylene ring, would afford compound **14**.

Addition of the silyllithium at the para-position of the phenyl ring of **1g** is not unexpected. In fact, when the reaction of **2a** with a sterically hindered ketone, mesityl *o*-tolyl ketone, was carried out at −94 °C in THF and the resulting mixture was treated with chlorotrimethylsilane, a para-substituted product, mesityl {2-methyl-4-[tris(trimethylsilyl)silyl]phenyl} ketone (**15a**) was obtained in 22% yield, together with 53% of the starting ketone and a 15% yield of tetrakis(trimethylsilyl)silane (Scheme 8). In this reaction, a product whose mass spectrum shows the parent signal at *m*/*z* 558, corresponding to the product arising from the reaction of anionic intermediates derived from the reaction of the starting ketone and **2a** with chlorotrimethylsilane, was detected by GLC analysis in 6% yield. The product was stable toward hydrolytic workup but decomposed on attempted preparative GPC, and attempts to isolate the product were unsuccessful. The much lower yield of the adduct than that of **15a** seems to indicate that elimina-

Scheme 8



Scheme 9



tion of lithium hydride from an anionic intermediate for the formation of **15a** occurs before the addition of chlorotrimethylsilane, as illustrated in Scheme 8. Similar treatment of mesityl *o*-tolyl ketone with **2b** and then chlorotrimethylsilane gave mesityl [2-methyl-4-(dimethylphenylsilyl)phenyl] ketone (**15b**) and pentamethylphenyldisilane in 29% and 12% yield, respectively, along with 38% of the starting ketone. In this reaction, mesityl-*o*-tolylmethanol was also obtained in 35% yield. The GC−mass spectroscopic analysis of the reaction mixture revealed the presence of a product arising from the reaction of the anionic intermediate with chlorotrimethylsilane in 11% yield, as in the reaction of the ketone with **2a**, but the product again decomposed on attempted preparative GPC.

The reaction of **1h** with **2a** in THF did not afford the corresponding lithium silenolate but produced lithium 1-[tris(trimethylsilyl)silyl]ethenolate (**16**) arising from H−Li exchange between the acetyl group and silyllithium as shown in Scheme 9. Treatment of the resulting mixture with chlorotriethylsilane gave tris(trimethylsilyl)silane and triethylsilyl 1-[tris(trimethylsilyl)silyl]enol ether (**17**) in 81% and 80% yield, respectively. With methyl iodide, **16** afforded propionyltris(trimethylsilyl)silane (**1i**) in 93% yield, along with a 85% yield of tris(trimethylsilyl)silane.

Theoretical Studies. In order to learn more about the formation of lithium silenolates from the reactions of acylpolysilanes with silyllithium reagents, we carried out molecular orbital calculations using GAUSSIAN 92[11] on a model reaction of $(H_3Si)_3SiCOCH_3$ (**1j**) with the H_3Si anion (**2c**).[7] The geometries of all compounds were optimized at the HF/6-31G* level. For the optimized geometries, single point calculations were performed at CISD(FC)/6-31G* level. The reaction energetics were then calculated using the results obtained from the CISD(FC)/6-31G*.

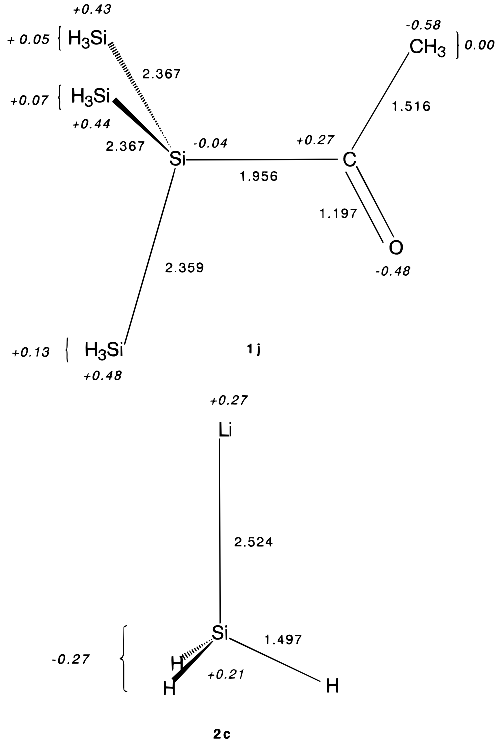


Figure 2. Optimized geometries of **1j** and **2c**. Lengths are given in Å, and Mulliken charges of heavy atoms and the SiH_3 and CH_3 groups are italicized style.

The optimized geometries of reactants **1j** and H_3SiLi (**2c**) are shown in Figure 2. Mulliken charges of heavy atoms and SiH_3 and CH_3 groups are shown in italic type. As shown in Figure 2, the Si atom adjacent to a $COCH_3$ group in **1j** is slightly negatively charged, −0.04. Other Si atoms in **1j** are positively charged. The SiH_3 group in **2c** is negatively charged, −0.27, and therefore, the silyl anion will attack either one silicon atom of the three SiH_3 groups (reaction A) or the carbonyl carbon (reaction B) in acylpolysilane **1j**.[12]

In reaction A, the silyl anion, H_3Si^-, in **2c** attacks the positively charged silicon atom to give disilane (**4c**). Hence, products **5j** and **4c** are expected to be formed from the reaction A.

In the case of reaction B, the silyl anion adds the positively charged carbonyl carbon to afford the anion $(H_3Si)_3SiC(SiH_3)(CH_3)O^-$ (**18**). Heterolytic bond scission of the central Si−C bond in **18** will lead to SiH_3COCH_3 (**19**) and $(SiH_3)_3Si^-$ (**20**) as shown in Scheme 10.

We have performed molecular orbital calculations for the reactions A and B in which the lithium cation is removed.[13] The optimized geometries and energy diagram are shown in Figures 3 and 4, respectively. Enthalpies of the reactions A and B are −30.0 and −34.0 kcal/mol, respectively. Each reaction is exothermic, but reaction B is more favorable by 4.0 kcal/mol than reaction A. Therefore, thermodynamically, acetylsilane

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(11) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1992.

(12) The preliminary results on the theoretical calculations at a lower level, using the HF/6-31G** method for single-point energy caluculations and MNDO for geometry optimization, also indicate that reaction A is exothermic but the enthalpy for reaction A is estimated to be −13.81 kcal/mol, smaller than that from the present studies.[7]

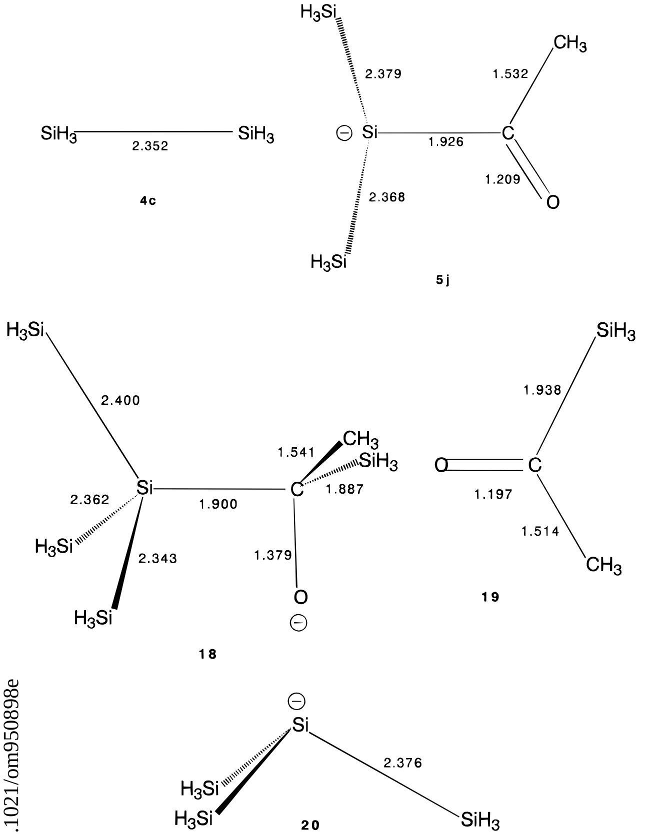


Figure 3. Optimized geometries of **5j**, **4c**, **18**, **19**, and **20**. Lengths are given in Å.

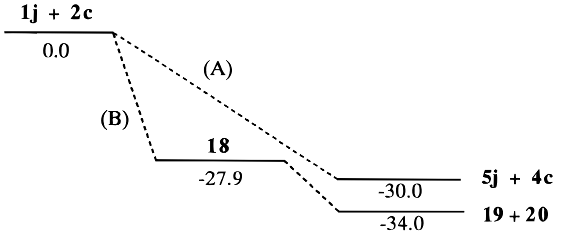
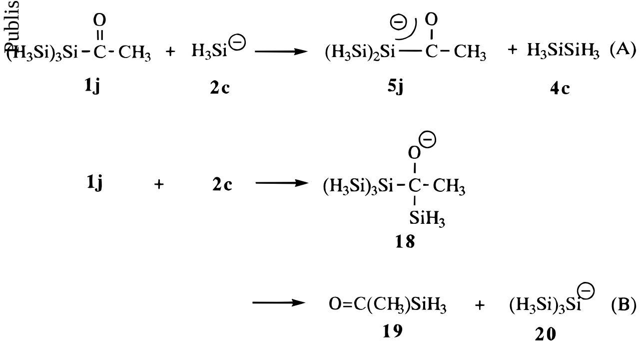


Figure 4. Energy diagram of reaction paths A and B. Relative energies are given in kcal/mol.

Scheme 10



$$(H_3Si)_3Si-C(=O)-CH_3 + H_3Si^{\ominus} \longrightarrow (H_3Si)_2Si^{\ominus}-C(=O)-CH_3 + H_3SiSiH_3 \quad (A)$$

$$\mathbf{1j} + \mathbf{2c} \longrightarrow (H_3Si)_3Si-C(O^{\ominus})(SiH_3)-CH_3\ (\mathbf{18}) \longrightarrow O{=}C(CH_3)SiH_3\ (\mathbf{19}) + (H_3Si)_3Si^{\ominus}\ (\mathbf{20}) \quad (B)$$

19 and tris(trimethylsilyl)silyl anion **20** can be expected to form as major products.

However, replacement of the methyl group in **1j** by a strong electron-donating substituent, such as a mesityl, *o*-tolyl, adamantyl, and *tert*-butyl, would decrease the positive charge on the carbonyl carbon in the acylpolysilane to reduce the reactivity for addition of the silyl anion to this carbonyl carbon. Moreover, the presence of a bulkier substituent on the carbonyl carbon would prevent reaction B. In contrast to this, reaction A would not be affected by replacing the CH_3 group with other substituents. With respect to probability, the number of reaction sites in reaction B is merely $^1/_3$ that in reaction A. Therefore, reaction of acylpolysilanes that have a mesityl, *o*-tolyl, adamantyl, and *tert*-butyl group on the carbonyl carbon with the silyl anion can be expected to form **4c** and **5j** as the major products.

Conclusion

The reactions of $(Me_3Si)_3SiCOR$ (**1a**–**d**; R = Mes, *o*-Tol, Ad, *t*-Bu) with [tris(trimethylsilyl)silyl]lithium or (dimethylphenylsilyl)lithium in THF gave the respective lithium silenolates **5a**–**d** in high yield, along with tetrakis(trimethylsilyl)silane or pentamethylphenyldisilane. Lithium silenolate **5a** formed in the reaction of **1a** (R = Mes) with silyllithium is thermally stable. The π-bond energy of **5a** was calculated to be 14.3 kcal/mol on the basis of the temperature-dependence experiments on ^1H NMR spectra in THF.

The chemical behavior of the lithium silenolates toward chlorosilane is significantly influenced by the nature of the substituent on the carbonyl carbon atom. The reaction of lithium silenolates **5a**,**b** with chlorotriethylsilane gave the O-silylated products, silene derivatives. Similar reactions of **5c**,**d** produced the Si-silylated products.

Benzoyltris(trimethylsilyl)silane reacted with silyllithium to afford unstable lithium silenolate. Acetyltris(trimethylsilyl)silane afforded a product arising from H–Li exchange between the acetyl group and silyllithium.

Theoretical studies showed that the reaction of $(H_3Si)_3SiCOCH_3$ (**1j**) with the silyl anion leading to disilane and silenolate anion **5j** is exothermic.

Experimental Section

General Methods. All reactions were carried out in the dark under an atmosphere of purified argon. NMR spectra were recorded on a JEOL EX-270 spectrometer using tetramethylsilane as an internal standard. IR spectra were measured on a Perkin-Elmer FT1600 spectrophotometer. Mass spectra were measured on a Shimadzu QP-1000 spectrometer. Exact mass spectra were measured on a Hitachi M-80B spectrometer.

Materials. THF was dried over sodium–potassium alloy and distilled just before use. Acylpolysilanes **1a**,[9] **1c**,[6] **1d**,[10a] **1g**,[10a] and **1h**[10a] and silyllithium reagents **2a**[14] and **2b**[15] were prepared as reported in the literature.

Preparation of 1b. In a 200 mL two-necked flask fitted with a dropping funnel was placed 6.12 mL (46.9 mmol) of *o*-toluoyl chloride and 50 mL of THF, and the flask was cooled at −80 °C. To this was added 31.3 mmol of [tris(trimethylsilyl)silyl]lithium (**2a**) in 100 mL of THF, and the resulting mixture was stirred overnight at room temperature. The resulting mixture was hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with

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(13) As reported in ref 7, we have carried out geometry optimization of the products containing a lithium cation by the semi-empirical calculation method and found that the final product obtained from reaction B is a lithium-bridged complex, $(H_3Si)_3Si-Li-O{=}C(CH_3)_2$, but not a pair of separated molecules, **19** and $(H_3Si)_3SiLi$. We have attempted to obtain optimized geometries of the products in the presence of the lithium cation, by using ab initio calculations, but have not yet succeeded. Therefore, we have omitted the lithium cation from the present calculations. Our attempts to find transition states of the reactions in the presence of the lithium cation by *ab initio* calculations have been also unsuccessful. They may be performed by using significantly more computing time and will be reported in the future.

(14) Brook, A. G.; Nyburg, S. C.; Abdesaben, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. M. R.; Poon, Y. C.; Chang, Y.-M.; Wong-Ng, W. *J. Am. Chem. Soc.* **1982**, *104*, 5667.

(15) Gutekunst, G.; Brook, A. G. *J. Organomet. Chem.* **1982**, *225*, 1.

ether. The organic layer and the extracts were combined and washed with water and then dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was chromatographed on a silica gel column eluting with hexane to give 7.40 g (65% yield) of **1b**: MS *m/z* 366 (M^+); ^{1}H NMR (δ in $CDCl_3$) 0.21 (s, 27H, Me_3Si), 2.32 (s, 3H, *o*-Me), 7.15−7.37 (m, 4H, ring protons); ^{13}C NMR (δ in C_6D_6) 1.3, 19.7, 125.1, 128.0, 129.7, 131.4, 133.1, 146.6, 243.5; IR $\nu_{C=O}$ 1605 cm^{-1}. Anal. Calcd for $C_{17}H_{34}OSi_4$: C, 55.67; H, 9.34. Found: C, 55.67; H, 9.30.

Reaction of 1a with 2a Followed by Hydrolysis. In a 30 mL two-necked flask was placed 0.515 g (1.308 mmol) of **1a** and 5 mL of THF, and the flask was cooled at −80 °C. To this was added dropwise 1.308 mmol of **2a** in 5 mL of THF. The resulting mixture was stirred for 2 h at this temperature and then hydrolyzed with water. The organic layer was separated, and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and washed with water and then dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was analyzed by GLC, using 65.5 mg (0.355 mmol) of tridecane as an internal standard, as containing **3a** (91% yield) and **4a** (99.8% yield). GLC retention time and the mass spectrum of **4a** are identical with those of an authentic sample prepared as reported in the literature.[16] Compound **3a** was isolated by MPLC on a silica gel column eluting with hexane: MS *m/z* 322 (M^+); ^{1}H NMR (δ in C_6D_6) 0.32 (s, 18H, Me_3Si), 2.14 (s, 3H, *p*-Me), 2.33 (s, 6H, *o*-Me), 4.21 (s, 1H, HSi), 6.70 (s, 2H, ring protons); ^{13}C NMR (δ in C_6D_6) 0.8, 20.3, 21.5, 129.8, 132.8, 138.9, 146.4, 245.7; IR ν_{Si-H} 2081 cm^{-1}, $\nu_{C=O}$ 1609 cm^{-1}; exact MS calcd for $C_{16}H_{30}OSi_3$ 322.1605, found 322.1695.

Reaction of 1a with 2b Followed by Hydrolysis. In a 30 mL two-necked flask was placed 0.374 mg (0.948 mmol) of **1a**, 67.0 mg (0.279 mmol) of heptadecane as an internal standard, and 5 mL of THF, and the flask was cooled at −80 °C. To this was added a solution of 0.948 mmol of **2b** in 2.6 mL of THF. The resulting mixture was stirred at this temperature for 2 h. At this stage, 87% of **4b** was found to be formed by a GLC analysis of the mixture. A half-volume of the mixture was hydrolyzed with water, and the other half was hydrolyzed with D_2O. Each of the resulting mixtures was analyzed by GLC as containing **3a** (76% yield) and **3a′** (71% yield), respectively. Compounds **3a** and **3a′** were isolated by MPLC on a silica gel column eluting with hexane. GLC retention time and mass spectrum of **4b** are identical with those of an authentic sample.[17] All spectral data obtained for **3a** are identical with those of an authentic sample. Data for **3a′**: MS *m/z* 323 (M^+); ^{1}H NMR (δ in C_6D_6) 0.32 (s, 18H, Me_3Si), 2.14 (s, 3H, *p*-Me), 2.33 (s, 6H, *o*-Me), 6.70 (s, 2H, ring protons); ^{13}C NMR (δ in C_6D_6) 0.8, 20.3, 21.5, 129.8, 132.8, 138.9, 146.4, 245.7; ^{2}H NMR (δ in C_6D_6) 4.19 (DSi); exact MS calcd for $C_{16}H_{29}DOSi_3$ 323.1668, found 323.1677.

Reaction of 5a with Methyl Iodide. To a solution of **5a** prepared from 0.325 g (0.824 mmol) of **1a** and an equimolar amount of **2b** in 6 mL of THF was added 0.10 mL (1.60 mmol) of methyl iodide at −80 °C. The resulting mixture was stirred overnight at room temperature. After hydrolysis of the mixture with water and the usual workup as above, the products were analyzed by GLC, using 52.0 mg (0.262 mmol) of tetradecane as an internal standard, as containing **6a** (91% yield from **1a**). Compound **6a** was isolated by MPLC on a silica gel column eluting with hexane: MS *m/z* 336 (M^+); ^{1}H NMR (δ in $CDCl_3$) 0.15 (s, 18H, Me_3Si), 0.28 (s, 3H, MeSi), 2.13 (s, 6H, *o*-Me), 2.25 (s, 3H, *p*-Me), 6.77 (s, 2H, ring protons); ^{13}C NMR (δ in C_6D_6) −8.3, −0.7, 19.2, 21.0, 128.6, 131.3, 137.7, 144.7, 252.1; ^{29}Si NMR (δ in $CDCl_3$) −46.9, −14.1; IR $\nu_{C=O}$ 1610 cm^{-1}. Anal. Calcd for $C_{17}H_{32}OSi_3$: C, 60.64; H, 9.58. Found: C, 60.44; H, 9.49.

Reaction of 5a with Benzyl Bromide. To a solution of **5a** prepared from 0.266 g (0.674 mmol) of **1a** and an equimolar amount of **2b** in 5 mL of THF was added 67 mg (0.71 mmol) of benzyl bromide at −80 °C. The resulting mixture was stirred overnight at room temperature. After hydrolysis of the mixture with water and usual work up as above, the products were analyzed by GLC, using 56.6 mg (0.285 mmol) of tetradecane as an internal standard, as containing **7a** (75% yield from **1a**). Compound **7a** was isolated by MPLC on a silica gel column eluting with hexane: MS *m/z* 412 (M^+); ^{1}H NMR (δ in $CDCl_3$) 0.10 (s, 18H, Me_3Si), 2.08 (s, 6H, *o*-Me), 2.28 (s, 3H, *p*-Me), 2.47 (s, 2H, CH_2), 6.79 (s, 2H, ring protons), 6.82−7.10 (m, 5H, Ph); ^{13}C NMR (δ in $CDCl_3$) 0.1, 19.4, 19.9, 21.0, 128.8, 131.6, 138.0, 144.7, 124.5, 128.3, 128.4, 140.4, 251.3; IR $\nu_{C=O}$ 1610 cm^{-1}. Anal. Calcd for $C_{23}H_{36}OSi_3$: C, 66.92; H, 8.79. Found: C, 66.77; H, 8.79.

Reaction of 5a with Allyl Bromide. To a solution of **5a** prepared from 0.321 g (0.815 mmol) of **1a** and an equimolar amount of **2b** in 5 mL of THF was added 0.14 mL (1.63 mmol) of allyl bromide at −80 °C. The resulting mixture was stirred overnight at room temperature. After hydrolysis of the mixture with water and usual workup as above, the products were analyzed by GLC, using 48.7 mg (0.245 mmol) of tetradecane as an internal standard, as containing **8a** (68% yield from **1a**). Compound **8a** was isolated by MPLC on a silica gel column eluting with hexane: MS *m/z* 362 (M^+); ^{1}H NMR (δ in $CDCl_3$) 0.18 (s, 18H, Me_3Si), 1.92 (d, 2H, CH_2), 2.13 (s, 6H, *o*-Me), 2.25 (s, 3H, *p*-Me), 2.32 (d, 2H, CH_2, $J = 8.4$ Hz), 4.76 (dd, 1H, $CH_2{=}C$, $J = 10.7, 1.3$ Hz), 4.80 (dd, 1H, $CH_2{=}C$, $J = 16.8, 1.7$ Hz), 5.63−5.78 (m, 1H, CH=C), 6.77 (s, 2H, ring protons); IR $\nu_{C=O}$ 1610 cm^{-1}. Anal. Calcd for $C_{19}H_{34}OSi_3$: C, 62.91; H, 9.45. Found: C, 62.92; H, 9.45.

Reaction of 5a with Chlorotriethylsilane. To a solution of **5a** prepared from 0.302 g (0.767 mmol) of **1a** and an equimolar amount of **2b** in 5 mL of THF was added 0.116 g (0.767 mmol) of chlorotriethylsilane at −80 °C. The mixture was allowed to warm to room temperature and stirred overnight. The NMR spectroscopic analysis of the resulting mixture showed that all of **5a** was transformed into silene **9a**, quantitatively. The mixture was then cooled at −80 °C. To this was added 0.26 mL (2.30 mmol) of 2,3-dimethyl-1,3-butadiene. After being stirred for 24 h, the resulting mixture was analyzed by GLC as containing **10a** (66% yield from **1a**). After hydrolysis of the mixture and the usual workup as above, compound **10a** was isolated by MPLC on a silica gel column eluting with hexane. Data for **9a**: ^{1}H NMR (δ in 70% THF + 30% THF-d_8 at −40 °C) −0.15 (s, 9H, Me_3Si), 0.34 (s, 9H, Me_3Si), 0.38 (q, 6H, $J = 7.92$ Hz, CH_2Si), 0.83 (t, 9H, $J = 7.92$ Hz, CH_3CH_2), 2.20 (s, 3H, *p*-Me), 2.39 (s, 6H, *o*-Me), 6.81 (br s, 2H, ring protons); ^{13}C NMR (δ in 70% THF + 30% THF-d_8 at −40 °C) 0.9, 1.7, 5.5, 7.1, 21.0 (2C), 128.8, 136.3, 137.1, 142.0, 197.7; ^{29}Si NMR (δ in 70% THF + 30% THF-d_8 at −40 °C) −13.2, 12.4, 16.6, 34.3. Data for **10a**: MS *m/z* 518 (M^+); ^{1}H NMR (δ in C_6D_6) −0.09 (s, 9H, Me_3Si), 0.40 (s, 9H, Me_3Si), 0.65 (q, 6H, $J = 8.12$ Hz, CH_2Si), 0.94 (t, 9H, $J = 8.12$ Hz, CH_3CH_2), 1.40 (d, 1H, $J = 15.18$ Hz, ring CH_2), 1.67 (br d, 1H, $J = 15.18$ Hz, ring CH_2), 1.91 (s, 3H, MeC=C), 1.93 (s, 3H, MeC=C), 2.09 (s, 3H, *p*-Me), 2.55 (br s, 3H, *o*-Me), 2.73 (br s, 3H, *o*-Me), 3.10 (br s, 2H, ring CH_2), 6.70 (br s, 2H, aromatic ring protons); ^{13}C NMR (δ in C_6D_6) 0.5, 2.3, 8.0, 8.4, 20.0, 20.9, 22.3, 27.3, 50.8, 84.4, 127.7, 128.6, 132.5, 133.4, 136.2, 143.8; IR ν_{Si-O} 1050 cm^{-1}. Anal. Calcd for $C_{28}H_{54}OSi_4$: C, 64.79; H, 10.49. Found: C, 64.75; H, 10.48.

Reaction of 5a with Chlorotriethylsilane and 2,3-Dimethylbutadiene. To a solution of **5a** prepared from 0.516 g (1.309 mmol) of **1a** and an equimolar amount of **2b** in 10 mL of THF was added a mixture of 0.197 g (1.307 mmol) of chlorotriethylsilane and 0.444 mL (3.928 mmol) of 2,3-dimethylbutadiene at −80 °C. The resulting mixture was stirred for 2 h at room temperature. After hydrolysis of the mixture with water and the usual workup, the products were analyzed by GLC, using 72.6 mg (0.302 mmol) of heptadecane as an internal standard, as containing **10a** (88% yield from **1a**). After hydrolysis and the usual workup as above, compound **10a** was

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(16) Gilman, H.; Lichtenwalter, G. D. *J. Am. Chem. Soc.* **1958**, *80*, 608.

(17) Gilman, H.; Smith, C. L. *J. Am. Chem. Soc.* **1964**, *86*, 1454.

isolated by preparative GPC eluting with benzene. All spectral data obtained for **10a** are identical with those of an authentic sample.

Preparation of 5b and the Reaction with Methyl Iodide. To a mixture of 0.541 g (1.476 mmol) of **1b** and 2.0 mL of THF was added 1.471 mmol of **2a** in 6.0 mL of THF at −86 °C, and the mixture was allowed to warm to −20 °C over a period of 5 h. To this was added 5.0 mL (80.32 mmol) of methyl iodide, and the resulting solution was stirred overnight at room temperature. After hydrolysis of the mixture and the usual work up as above, the products were analyzed by GLC, using 52.9 mg (0.243 mmol) of eicosane as an internal standard, as containing **6b** (70% yield) and **4a** (82% yield). GLC retention time and mass spectrum of **4a** are identical with those of an authentic sample. Compound **6b** was isolated by preparative GPC eluting with benzene: MS *m/z* 308 (M^+); ^1H NMR (δ in C_6D_6) 0.21 (s, 18H, Me_3Si), 0.45 (s, 3H, MeSi), 2.54 (s, 3H, *o*-Me), 6.97−7.64 (m, 4H, aromatic ring protons); ^{13}C NMR (δ in C_6D_6) −8.0, −0.6, 20.7, 125.4, 130.5, 130.7, 132.3, 135.4, 143.6, 240.3; ^{29}Si NMR (δ in C_6D_6) −52.6, −20.9; IR $\nu_{C=O}$ 1612 cm^{-1}. Anal. Calcd for $C_{15}H_{28}OSi_3$: C, 58.39; H, 9.15. Found: C, 58.18; H, 9.09.

Reaction of 5b with a Mixture of Chlorotriethylsilane and 2,3-Dimethylbutadiene. To a mixture of 0.947 g (2.587 mmol) of **1b** and 10 mL of THF was added 2.587 mmol of **2a** in 10 mL of THF at −80 °C, and the mixture was stirred for 2 h at this temperature. A mixture of 0.390 g (2.588 mmol) of chlorotriethylsilane and 0.877 mL (7.758 mmol) of 2,3-dimethylbutadiene was added to the resulting mixture at −80 °C, and the mixture was stirred overnight at room temperature. After hydrolysis of the mixture with water and the usual workup as above, the products were analyzed by GLC, using 135.6 mg (0.564 mmol) of heptadecane as an internal standard, as containing **4a** (67% yield), (triethylsilyl)tris(trimethylsilyl)silane (27% yield), and **10b** (60% yield). (Triethylsilyl)tris(trimethylsilyl)silane and **10b** were isolated by preparative GPC eluting with benzene. Data for (triethylsilyl)tris(trimethylsilyl)silane: MS *m/z* 362 (M^+); ^1H NMR (δ in C_6D_6) 0.21 (s, 27H, Me_3Si), 0.75 (q, 6H, CH_2Si, $J = 7.9$ Hz), 1.01 (t, 9H, CH_3CH_2, $J = 7.9$ Hz); ^{13}C NMR (δ in C_6D_6) 3.2, 7.1, 8.9. Anal. Calcd for $C_{15}H_{42}Si_5$: C, 49.64; H, 11.66. Found: C, 49.48; H, 11.55. Data for **10b**: MS *m/z* 490 (M^+); ^1H NMR (δ in C_6D_6) −0.01 (s, 9H, Me_3Si), 0.56 (s, 9H, Me_3Si), 0.71 (q, 6H, $J = 7.92$ Hz, CH_2Si), 1.05 (t, 9H, $J = 7.92$ Hz, CH_3CH_2), 1.56 (d, 1H, $J = 14.19$ Hz, ring CH_2), 1.91 (s, 3H, MeC═C), 2.07 (br d, 1H, $J = 14.19$ Hz, ring CH_2), 2.09 (s, 3H, MeC═C), 2.81 (s, 3H, *o*-Me), 3.05 (br d, 1H, $J = 13.86$ Hz, ring CH_2), 3.20 (br d, 1H, $J = 13.86$ Hz, ring CH_2), 7.19−7.42 (m, 4H, aromatic ring protons); ^{13}C NMR (δ in C_6D_6) 0.9, 1.6, 8.0 (2C), 18.9, 21.8, 22.5, 25.2, 50.8, 81.4, 125.0, 125.5, 126.1, 127.1, 131.7, 132.4, 138.0, 148.3; IR ν_{Si-O} 1029 cm^{-1}; exact MS calcd for $C_{26}H_{50}OSi_4$ 490.2936, found 490.2924.

Preparation of 5c and Hydrolysis. To a mixture of 0.403 g (0.981 mmol) of **1c** and 2 mL of THF was added 0.983 mmol of **2a** in 3.2 mL of THF at −100 °C. The mixture was allowed to warm to −20 °C over a period of 4 h. After hydrolysis of the mixture with water and the usual workup as above, the products were analyzed by GLC, using 18.7 mg (0.0943 mmol) of tetradecane as an internal standard, as containing **4a** (100% yield) and **3c** (97% yield). GLC retention time and mass spectrum of **4a** were identical with those of an authentic sample. Compound **3c** was isolated by preparative GPC eluting with benzene: MS *m/z* 338 (M^+); ^1H NMR (δ in C_6D_6) 0.30 (s, 18H, Me_3Si), 1.63 (br d, 6H, Ad, $J = 2.70$ Hz), 1.89 (br d, 6H, Ad, $J = 3.38$ Hz), 1.96 (br s, 3H, Ad), 4.28 (s, 1H, HSi); ^{13}C NMR (δ in C_6D_6) 0.3, 28.4, 37.0, 37.4, 52.3, 247.2; ^{29}Si NMR (δ in C_6D_6) −84.4, −12.6; IR ν_{Si-H} 2073, $\nu_{C=O}$ 1618 cm^{-1}; exact MS calcd for $C_{17}H_{34}OSi_3$ 338.1915, found 338.1901.

Reaction of 5c with Methyl Iodide. To a solution of **5c** prepared from 0.980 g (2.386 mmol) of **1c** and 2.383 mmol of **2a** in 12 mL of THF was added 0.8 mL (12.8 mmol) of methyl iodide at −91 °C, and the mixture was stirred overnight at room temperature. The resulting mixture was analyzed by GLC, using 15.3 mg (0.831 mmol) of tridecane as an internal standard, as containing **6c** (78% yield from **1c**). Compound **6c** was isolated by preparative GPC eluting with benzene: Mp 30.5−31.0 °C; MS *m/z* 337 ($M^+ - Me$); ^1H NMR (δ in C_6D_6) 0.22 (s, 3H, MeSi), 0.23 (s, 18H, Me_3Si), 1.64−1.96 (m, 15H, Ad); ^{13}C NMR (δ in C_6D_6) −5.7, −0.4, 28.4, 37.1, 37.2, 52.0, 247.3; ^{29}Si NMR (δ in C_6D_6) −50.2, −13.6; IR $\nu_{C=O}$ 1614 cm^{-1}. Anal. Calcd for $C_{18}H_{36}OSi_3$: C, 61.79; H, 10.29. Found: C, 61.50; H, 10.36.

Isolation of 11. A solution of **5c** prepared from 1.011 g (2.461 mmol) of **1c** and an equimolar amount of **2a** in 12 mL of THF was allowed to stand at room temperature for 7 h. To this was added 1.0 mL (16.1 mmol) of methyl iodide at −80 °C. The mixture was then allowed to warm to room temperature and stirred for 24 h. After hydrolysis of the mixture and the usual workup as above, the products were isolated by preparative GPC eluting with benzene to give 264 mg (30% yield from **1c**) of **11**: MS *m/z* 356 (M^+); ^1H NMR (δ in C_6D_6) 1.19 (s, 3H, Me), 1.69−2.12 (m, 30H, Ad), 3.09 (s, 3H, MeO); ^{13}C NMR (δ in C_6D_6) 16.5, 28.9, 29.1, 37.2, 37.28, 37.34, 38.4, 43.6, 49.2, 52.5, 92.1, 218.7; IR $\nu_{C=O}$ 1687 cm^{-1}. Anal. Calcd for $C_{24}H_{36}O_2$: C, 80.85; H, 10.18. Found: C, 80.73; H, 10.08.

Preparation of 5d and Hydrolysis. To a mixture of 0.311 g (0.933 mmol) of **1d** and 2 mL of THF was added 0.922 mmol of **2a** in 3 mL of THF at −100 °C. The mixture was allowed to warm to −10 °C over a period of 4 h. After hydrolysis of the mixture with water and the usual workup as above, the products were analyzed by GLC, using 25.1 mg (0.088 mmol) of eicosane as an internal standard, as containing **4a** (99% yield) and **3d** (84% yield). GLC retention time and the mass spectrum of **4a** are identical with those of an authentic sample. Compound **3d** was isolated by preparative GPC eluting with benzene: MS *m/z* 260 (M^+); ^1H NMR (δ in C_6D_6) 0.23 (s, 18H, Me_3Si), 1.06 (s, 9H, *t*-Bu), 4.12 (s, 1H, HSi); ^{13}C NMR (δ in C_6D_6) 0.3, 24.9, 49.6, 246.6; ^{29}Si NMR (δ in C_6D_6) −82.3, −12.6; IR ν_{Si-H} 2076, $\nu_{C=O}$ 1625 cm^{-1}; exact MS calcd for $C_{11}H_{28}OSi_3$ 260.1446, found 260.1380.

Reaction of 5d with Methyl Iodide. To a solution of **5d** prepared from 0.346 g (1.038 mmol) of **1d** and an equimoler amount of **2a** in 8 mL of THF was added 5.0 mL (80.3 mmol) of methyl iodide at −41 °C. The mixture was stirred overnight at room temperature. After hydrolysis of the mixture and the usual workup as above, the products were analyzed by GLC, using 124.5 mg (0.441 mmol) of eicosane as an internal standard, as containing **6d** (87% yield from **1d**). Compound **6d** was isolated by preparative GPC eluting with benzene: MS *m/z* 274 (M^+); ^1H NMR (δ in C_6D_6) 0.22 (s, 18H, Me_3Si), 0.42 (s, 3H, MeSi), 1.03 (s, 9H, *t*-Bu); ^{13}C NMR (δ in C_6D_6) −5.8, −0.6, 24.7, 49.2, 247.4; ^{29}Si NMR (δ in C_6D_6) −50.0, −13.6; IR $\nu_{C=O}$ 1625 cm^{-1}. Anal. Calcd for $C_{12}H_{30}OSi_3$: C, 52.48; H, 11.01. Found: C, 52.43; H, 10.92.

Reaction of 5c with Chlorotriethylsilane. To a solution of **5c** prepared from 0.417 g (1.014 mmol) of **1c** and an equimoler amount of **2a** in 12 mL of THF was added 0.233 g (1.547 mmol) of chlorotriethylsilane. The mixture was stirred overnight at room temperature. After hydrolysis and the usual workup as above, the resulting products were analyzed by GLC, using 183.4 mg (0.924 mmol) of tetradecane as an internal standard, as containing **1e** (94% yield from **1c**). Compound **1e** was isolated by preparative GPC eluting with benzene: MS *m/z* 437 ($M^+ - Me$); ^1H NMR (δ in C_6D_6) 0.39 (s, 18H, Me_3Si), 0.92 (q, 6H, CH_2Si, $J = 7.59$ Hz), 1.11 (t, 9H, CH_3CH_2Si, $J = 7.59$ Hz), 1.64 (br t, 6H, Ad, $J = 3.2$ Hz), 1.83 (br d, 6H, Ad, $J = 3.3$ Hz), 1.97 (br s, 3H, Ad); ^{13}C NMR (δ in C_6D_6) 2.6, 6.6, 9.0, 28.5, 37.0, 37.6, 52.0, 247.2; ^{29}Si NMR (δ in C_6D_6) −79.8, −11.7, 0.5; IR $\nu_{C=O}$ 1619 cm^{-1}. Anal. Calcd for $C_{23}H_{48}OSi_4$: C, 60.99; H, 10.68. Found: C, 60.72; H, 10.64.

Reaction of 5d with Chlorotriethylsilane. To a solution of **5d** prepared from 0.317 g (0.953 mmol) of **1d** and an equimolar amount of **2a** in 6 mL of THF was added 0.153 g (1.012 mmol) of chlorotriethylsilane at −87 °C, and the mixture was stirred overnight at room temperature. After hydrolysis and the usual workup as above, the products were analyzed by GLC, using 48.5 mg (0.156 mmol) of docosane as an internal standard, as containing **1f** (83% yield from **1d**). Compound **1f** was isolated by preparative GPC eluting with benzene: MS m/z 359 ($M^+ - Me$); ^1H NMR (δ in C_6D_6) 0.36 (s, 18H, Me_3Si), 0.90 (q, 6H, CH_2Si, $J = 7.9$ Hz), 1.06 (s, 9H, *t*-Bu), 1.09 (t, 9H, CH_3CH_2Si, $J = 8.3$ Hz); ^{13}C NMR (δ in C_6D_6) 2.3, 6.4, 8.9, 25.2, 49.4, 246.5; ^{29}Si NMR (δ in C_6D_6) −80.2, −13.2, −1.2; IR $\nu_{C=O}$ 1625 cm^{-1}. Anal. Calcd for $C_{17}H_{42}OSi_4$: C, 54.47; H, 11.29. Found: C, 54.35; H, 11.29.

NMR spectroscopic Analysis of Lithium Silenolates 5a,c,d. A solution of approximately 50 mmol of **5a** prepared from **1a** and an equimolar amount of **2b** was placed in a 5 mm i.d. NMR tube and analyzed at −40 °C: ^1H NMR (δ in 70% THF + 30% THF-d_8 at −40 °C) −0.26 (s, 9H, Me_3Si), 0.17 (s, 9H, Me_3Si), 2.15 (s, 3H, *p*-Me), 2.33 (s, 6H, *o*-Me), 6.64 (s, 2H, ring protons); ^{13}C NMR (δ in 70% THF + 30% THF-d_8 at −40 °C) 3.2, 3.9, 20.5, 20.9, 127.9, 132.2, 133.8, 151.2, 262.7; ^{29}Si NMR (δ in 70% THF + 30% THF-d_8 at −40 °C) −10.6, −12.8, −59.9. NMR spectra of **5c**,**d** were measured in a similar manner to **5a**. Data for **5c**: ^1H NMR (δ in 70% THF + 30% THF-d_8 at −40 °C) 0.16 (s, 18H, Me_3Si), signals due to adanantyl protons are overlapping with the solvent signals; ^{13}C NMR (δ in 70% THF + 30% THF-d_8 at −40 °C) 5.6, 26.6, 29.9, 40.9, 49.9, 274.1; ^{29}Si NMR (δ in 70% THF + 30% THF-d_8 at −40 °C) −11.3, −70.5. Data for **5d**: ^1H NMR (δ in 70% THF + 30% THF-d_8 at −40 °C) 0.17 (s, 18H, Me_3Si), 1.11 (s, 9H, *t*-Bu); ^{13}C NMR (δ in 70% THF + 30% THF-d_8 at −40 °C) 5.5, 29.4, 47.8, 274.3; ^{29}Si NMR (δ in 70% THF + 30% THF-d_8 at −40 °C) −70.3, −11.3.

Reaction of 1b with 2b and Hydrolysis. To a mixture of 0.819 g (2.232 mmol) of **1b** and 1.5 mL of THF was added dropwise 2.238 mmol of **2b** in 1.20 mL of THF at −81 °C. The resulting solution was warmed to −55 °C over a period of 7 h and then hydrolyzed with water. After the usual workup as above, the products were isolated by preparative GPC eluting with benzene to give 65 mg (14% yield) of **4b** and 225 mg (20% yield) of **12a**. All spectral data obtained for **4b** are identical with those of an authentic sample. Data for **12a**: MS m/z 502 (M^+); ^1H NMR (δ in C_6D_6) 0.10 (s, 9H, Me_3Si), 0.16 (s, 9H, Me_3Si), 0.26 (s, 9H, Me_3Si), 0.35 (s, 3H, MeSi), 0.66 (s, 3H, MeSi), 1.88 (s, 3H, *o*-Me), 2.42 (s, 1H, HC), 6.95−7.38 (m, 9H, aromatic ring protons); ^{13}C NMR (δ in C_6D_6) −1.0, 0.08, 0.13, 1.8, 2.3, 20.7, 25.7, 124.5, 126.1, 127.8, 129.1, 130.1, 130.7, 134.1, 135.2, 139.7, 141.5; ^{29}Si NMR (δ in C_6D_6) −19.8, −19.0, −12.7, −3.3, 2.5; IR ν_{Si-O} 1039 cm^{-1}. Anal. Calcd for $C_{25}H_{46}OSi_5$: C, 59.69; H, 9.22. Found: C, 59.67; H, 9.20.

Reaction of 1b with 2b Followed by Methyl Iodide. To a mixture of 0.471 g (1.284 mmol) of **1b** and 3.0 mL of THF was added dropwise 1.270 mmol of **2b** in 1.25 mL of THF at −96 °C. The resulting solution was warmed to −30 °C over a period of 6 h. To this was added 5 mL (80.3 mmol) of methyl iodide, and then the mixture was stirred overnight at room temperature. After hydrolysis with water and the usual workup as above, the products were analyzed by GLC using 181.7 mg (0.986 mmol) of tridecane as an internal standard, as containing **4b** (38% yield) and **12b** (40% yield). GLC retention time and the mass spectrum for **4b** are identical with those of authentic sample. Compound **12b** was isolated by preparative GPC eluting with benzene: MS m/z 516 (M^+); ^1H NMR (δ in $CDCl_3$) −0.12 (s, 9H, Me_3Si), 0.20 (s, 9H, Me_3Si), 0.24 (s, 9H, Me_3Si), 0.33 (s, 3H, MeSi), 0.45 (s, 3H, MeSi), 1.62 (s, 3H, Me), 1.68 (s, 3H, Me), 6.77−7.49 (m, 9H, aromatic ring protons); ^{13}C NMR (δ in $CDCl_3$) −3.6, −1.4, 0.8, 1.2, 2.8, 17.7, 23.3, 30.2, 124.1, 124.9, 127.1, 128.7, 131.2, 133.7, 134.7, 136.8, 137.8, 142.1; ^{29}Si NMR (δ in $CDCl_3$) −17.1, −1.2, −0.7, 6.6; IR ν_{Si-O} 1034 cm^{-1}. Anal. Calcd for $C_{26}H_{48}OSi_5$: C, 60.39; H, 9.36. Found: C, 60.24; H, 9.35.

Reaction of 1c with 2b Followed by Hydrolysis. To a mixture of 0.883 g (2.149 mmol) of **1c** and 5 mL of THF was added 2.141 mmol of **2b** in 1.8 mL of THF at −80 °C, and the mixture was allowed to warm to room temperature. After hydrolysis of the mixture and the usual workup as above, the products were analyzed by GLC, using 198.8 mg (1.002 mmol) of tetradecane as an internal standard, as containing **4a** (18% yield), **4b** (17% yield), **3c** (29% yield), **13a** (15% yield), and **1c** (18% yield). GLC retention times and the mass spectra of **4a**, **4b**, **3c**, and **1c** are identical with those of authentic samples. Compound **13a** was isolated as a 63:37 diastereomeric mixture by preparative GPC eluting with benzene: MS m/z 434 (M^+); IR ν_{O-H} 3456 cm^{-1}. Anal. Calcd for $C_{27}H_{38}OSi_2$: C, 74.59; H, 8.81. Found: C, 74.41; H, 8.80 (as a diastereomeric mixture). Data for the major isomer of **13a**: ^1H NMR (δ in C_6D_6) 0.23 (s, 3H, MeSi), 0.29 (s, 3H, MeSi), 0.46 (s, 3H, MeSi), 0.53 (s, 1H, CH_2), 0.57 (s, 1H, CH_2), 0.95 (br s, 1H, OH), 1.44−1.88 (m, 15H, Ad), 2.91 (s, 1H, HC), 7.22−7.27 (m, 6H, ring protons), 7.50−7.54 (m, 2H, ring protons), 7.56−7.60 (m, 2H, ring protons); ^{13}C NMR (δ in C_6D_6) −1.1, 0.4, 0.8, 1.2, 29.4, 37.9, 38.9, 40.8, 77.1, 128.4, 128.5, 129.5, 129.7, 134.2, 135.3, 139.8, 141.8; ^{29}Si NMR (δ in C_6D_6) −6.6, −3.7. Data for the minor isomer of **13a**: ^1H NMR (δ in C_6D_6) 0.20 (s, 3H, MeSi), 0.26 (s, 3H, MeSi), 0.50 (s, 3H, MeSi), 0.53 (s, 1H, CH_2), 0.57 (s, 1H, CH_2), 0.95 (br s, 1H, OH), 1.44−1.88 (m, 15H, Ad), 2.95 (s, 1H, HC), 7.22−7.27 (m, 6H, ring protons), 7.50−7.54 (m, 2H, ring protons), 7.56−7.60 (m, 2H, ring protons); ^{13}C NMR (δ in C_6D_6) −1.9, 0.4, 0.8, 0.9, 29.4, 37.9, 39.1, 40.7, 76.7, 128.5, 128.8, 129.4, 129.7, 134.2, 135.1, 140.3, 141.9; ^{29}Si NMR (δ in C_6D_6) −6.1, −3.5.

Reaction of 1c with 2b Followed by Methyl Iodide. To a mixture of 0.374 g (0.910 mmol) of **1c** and 3 mL of THF was added an equimoler amount of **2b** in 0.7 mL of THF at −80 °C, and the mixture was allowed to warm to room temperature. To this was added 4.0 mL (64.3 mmol) of methyl iodide, and the resulting mixture was stirred overnight. After hydrolysis of the mixture and the usual workup as above, the products were analyzed by GLC, using 67.7 mg (0.341 mmol) of tetradecane as an internal standard, as containing **4a** (21% yield), **4b** (15% yield), **6c** (17% yield), **13b** (15% yield), and **1c** (17% yield). GLC retention time and mass spectra of **4a**, **4b**, **6c**, and **1c** are identical with those of authentic samples. Compound **13b** was isolated as a 77:23 diastereomeric mixture by preparative GPC eluting with benzene: MS m/z 448 (M^+). Anal. Calcd for $C_{28}H_{40}OSi_2$: C, 74.94; H, 8.98. Found: C, 74.86; H, 8.93 (as a diastereomeric mixture). Data for the major isomer of **13b**: ^1H NMR (δ in C_6D_6) 0.20 (s, 3H, MeSi), 0.28 (s, 3H, MeSi), 0.48 (s, 3H, MeSi), 0.59 (s, 2H, CH_2Si), 1.65−1.91 (m, 15H, Ad), 2.44 (s, 1H, HC), 3.17 (s, 3H, MeO), 7.23−7.25 (m, 6H, ring protons), 7.51−7.54 (m, 2H, ring protons), 7.65−7.67 (m, 2H, ring protons); ^{13}C NMR (δ in $CDCl_3$) −2.1, −0.2, 0.0, 0.5, 28.5, 37.1, 39.5, 40.6, 63.4, 88.7, 127.3, 127.5, 128.5, 128.6, 133.2, 134.3, 139.4, 141.1; ^{29}Si NMR (δ in $CDCl_3$) −8.6, −3.8. Data for the minor isomer of **13b**: MS m/z 448 (M^+); ^1H NMR (δ in C_6D_6) 0.19 (s, 3H, MeSi), 0.26 (s, 3H, MeSi), 0.53 (s, 3H, MeSi), 0.61 (s, 2H, CH_2Si), 1.65−1.91 (m, 15H, Ad), 2.46 (s, 1H, HC), 3.26 (s, 3H, MeO), 7.23−7.25 (m, 6H, ring protons), 7.51−7.54 (m, 2H, ring protons), 7.58−7.61 (m, 2H, ring protons); ^{13}C NMR (δ in $CDCl_3$) −2.1, −0.5, −0.2, 0.0, 28.5, 37.1, 39.7, 40.6, 63.7, 88.6, 127.4, 127.5, 128.5, 128.6, 133.2, 134.2, 139.4, 141.1; ^{29}Si NMR (δ in $CDCl_3$) −7.8, −3.8.

Reaction of 1g with 2a. To a mixture of 0.760 g (2.154 mmol) of **1g** and 10 mL of THF was added 2.208 mmol of **2a** in 3 mL of THF at −83 °C. The mixture was allowed to warm to −41 °C over a period of 5 h. To this was added 0.493 g (3.273 mmol) of chlorotriethylsilane at −100 °C, and the resulting mixture was stirred at room temperature for 42 h. After hydrolysis of the mixture with water and the usual workup as above, the products were analyzed by GLC, using 21.7 mg (0.109 mmol) of tetradecane as an internal standard, as containing **4a** (56% yield) and (triethylsilyl)tris(trimethylsilyl)silane (12% yield). GLC retention times and mass spectra of **4a** and (triethylsilyl)tris(trimethylsilyl)silane are identical with those of authentic samples. Isolation of the products by preparative GPC eluting with benzene gave 0.631 g (26% yield) of **14** as a 52:48 diastereomeric mixture: mp 70.0−70.5 °C; MS m/z 1140 (M^+); IR ν_{Si-O} 1010 cm^{-1}. Anal. Calcd for $C_{54}H_{108}O_3Si_{12}$: C, 56.77; H, 9.53. Found: C, 56.84; H, 9.51

(as a diastereomeric mixture). Data for the major diastereomer of **14**: ^{1}H NMR (δ in C_6D_6) −0.17 (s, 9H, Me_3Si), −0.04 (s, 9H, Me_3Si), 0.29−0.36 (m, 6H, CH_2Si), 0.31 (s, 27H, $3Me_3Si$), 0.54 (s, 9H, Me_3Si), 0.605 (s, 9H, Me_3Si), 0.614 (q, 6H, CH_2Si, $J = 6.40$ Hz), 0.770 (t, 9H, CH_3CH_2, $J = 7.65$), 1.02 (t, 9H, CH_3CH_2, $J = 7.81$ Hz), 5.19 (s, 1H, HCO), 7.09−7.11 (m, 1H, *p*-Ph), 7.11−7.13 (m, 1H, *p*-Ph), 7.15−7.23 (m, 2H, *m*-Ph), 7.26−7.31 (m, 2H, *m*-Ph), 7.35 (d, 2H, phenylene, $J = 6.72$ Hz), 7.60 (d, 2H, *o*-Ph, $J = 7.77$), 7.75 (d, 2H, *o*-Ph, $J = 7.27$ Hz), 7.89 (d, 2H, phenylene, $J = 8.08$); ^{13}C NMR (δ in $CDCl_3$) 0.4, 1.8, 2.2, 2.55, 2.7, 5.1, 6.6, 70.7, 121.1, 125.7, 125.8, 127.8, 128.1, 128.5, 129.7, 130.9, 133.5, 137.8, 140.3, 142.0, 146.8, 155.1; ^{29}Si NMR (δ in C_6D_6) −70.0, −64.70, −16.2, −12.69, −11.01, −10.8, −4.5, 8.4, 19.3, 21.7. Data for the minor diastereomer of **14**: ^{1}H NMR (δ in C_6D_6) −0.16 (s, 9H, Me_3Si), −0.03 (s, 9H, Me_3Si), 0.29−0.36 (m, 6H, CH_2Si), 0.32 (s, 27H, $3Me_3Si$), 0.54 (s, 9H, Me_3Si), 0.614 (q, 6H, CH_2Si, $J = 6.40$ Hz), 0.62 (s, 9H, Me_3Si), 0.767 (t, 9H, CH_3CH_2, $J = 7.93$), 1.04 (t, 9H, CH_3CH_2, $J = 7.88$ Hz), 5.21 (s, 1H, HCO), 7.09−7.11 (m, 1H, *p*-Ph), 7.11−7.13 (m, 1H, *p*-Ph), 7.15−7.23 (m, 2H, *m*-Ph), 7.26−7.31 (m, 2H, *m*-Ph), 7.35 (d, 2H, phenylene, $J = 6.72$ Hz), 7.60 (d, 2H, *o*-Ph, $J = 7.77$), 7.75 (d, 2H, *o*-Ph, $J = 7.27$ Hz), 7.85 (d, 2H, phenylene, $J = 8.06$); ^{13}C NMR (δ in $CDCl_3$) 0.3, 1.8, 2.4, 2.63 (2C), 5.4, 7.2, 70.7, 120.5, 125.6, 125.7, 127.8, 128.0, 128.4, 129.6, 130.8, 133.5, 137.8, 140.3, 141.8, 146.7, 155.1; ^{29}Si NMR (δ in C_6D_6) −69.3, −64.66, −15.7, −12.74, −10.96, −10.9, −4.3, 8.1, 19.4, 21.6.

Preparation of Mesityl *o*-Tolyl Ketone. To a suspension of 2.7 g (20.25 mmol) of aluminum trichloride in 10 mL of dichloromethane was added 3.1 g (20.05 mmol) of *o*-toluoyl chloride at 0 °C. To the resulting red solution was added 2.8 g (23.30 mmol) of mesitylene, and the mixture was stirred for 14 h at room temperature. After hydrolysis, the organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the extracts were combined and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was recrystallized from ether to give 3.55 g (74% yield) of mesityl *o*-tolyl ketone: Mp 93.0−93.5 °C; MS *m*/*z* 238 (M^+); ^{1}H NMR (δ in C_6D_6) 2.09 (s, 6H, *o*-Me Mes), 2.15 (s, 3H, *p*-Me Mes), 2.81 (s, 3H, *o*-Me Tol), 6.70 (s, 2H, Mes ring protons), 6.85 (br t, 1H, Tol ring proton, $J = 7.4$ Hz), 7.04 (br d, 1H, Tol ring proton, $J = 6.6$ Hz), 7.07 (br t, 1H, Tol ring proton, $J = 7.3$ Hz), 7.45 (br d, 1H, Tol ring proton, $J = 7.6$ Hz); ^{13}C NMR (δ in C_6D_6) 19.5, 21.1, 22.1, 126.1, 128.8, 132.0, 132.1, 132.5, 134.6, 137.6, 138.3, 139.3, 140.1, 201.8; IR $\nu_{C=O}$ 1660 cm^{-1}. Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: 85.81; H, 7.61.

Reaction of Mesityl *o*-Tolyl Ketone with 2a. To a solution of 0.246 g (1.032 mmol) of mesityl *o*-tolyl ketone in 2 mL of THF was added 0.276 mmol of **2a** in 3.7 mL of THF at −94 °C. The mixture was allowed to warm to −40 °C and stirred at this temperature for 6 h, and then 1.00 mL (7.86 mmol) of chlorotrimethylsilane was added to the mixture. After hydrolysis and the usual workup as above, the mixture was analyzed by GLC, using 26.2 mg (0.184 mmol) of decane as an internal standard, as containing mesityl *o*-tolyl ketone (53%), tetrakis(trimethylsilyl)silane (15% yield), and **15a** (22% yield). The products were isolated by preparative GPC eluting with benzene. All spectral data obtained for mesityl *o*-tolyl ketone and tetrakis(trimethylsilyl)silane[16] are identical with those of the authentic samples. Data for **15a**: MS *m*/*z* 484 (M^+); ^{1}H NMR (δ in C_6D_6) 0.29 (s, 27H, Me_3Si), 2.08 (s, 6H, *o*-Me Mes), 2.16 (s, 3H, Me), 2.92 (s, 3H, Me), 6.70 (s, 2H, Mes ring protons), 7.37 (br d, 1H, Tol ring proton, $J = 7.8$ Hz), 7.48 (br d, 1H, Tol ring proton, $J = 7.7$ Hz), 7.67 (br s, 1H, Tol ring proton); ^{13}C NMR (δ in C_6D_6) 1.3, 19.5, 21.1, 22.4, 128.8, 131.1, 134.4, 134.6, 136.7, 138.2, 138.9, 139.3, 140.8, 142.8, 201.8; ^{29}Si NMR (δ in C_6D_6) −76.2, −12.5; IR $\nu_{C=O}$ 1666 cm^{-1}; HRMS calcd for $C_{26}H_{44}OSi_4$ 484.2466 (M^+), found 484.3437.

Reaction of Mesityl *o*-Tolyl Ketone with 2b. To a solution of 0.333 g (1.399 mmol) of mesityl *o*-tolyl ketone in 3 mL of THF was added 1.038 mmol of **2b** in 1.4 mL of THF at −92 °C. The mixture was allowed to warm to room temperature and stirred for 24 h, and then 1.00 mL (7.86 mmol) of chlorotrimethylsilane was added to the mixture. After hydrolysis and the usual workup as above, the mixture was analyzed by GLC, using 25.4 mg (0.179 mmol) of decane as an internal standard, as containing mesityl *o*-tolyl ketone (38%), mesityl-*o*-tolylmethanol (35% yield), pentamethylphenyldisilane (12% yield), and **15b** (29% yield). The products were isolated by preparative GPC eluting with benzene. All spectral data obtained for mesityl *o*-tolyl ketone and pentamethylphenyldisilane are identical with those of the authentic samples.[17] Data for mesityl-*o*-tolylmethanol: MS *m*/*z* 240 (M^+); ^{1}H NMR (δ in C_6D_6) 1.51 (s, 1H, OH), 2.11 (s, 3H, Me), 2.17 (s, 9H, Me), 6.08 (s, 1H, HCO), 6.75 (s, 2H, Mes ring protons), 7.06−7.11 (m, 3H, Tol ring protons), 7.60−7.64 (m 1H, Tol ring proton); ^{13}C NMR (δ in C_6D_6) 19.6, 20.8, 21.1, 70.9, 125.8, 127.3, 130.5, 130.8, 136.0, 136.8, 137.1, 141.2; IR ν_{O-H} 3314 cm^{-1}. Anal. Calcd for $C_{17}H_{20}O$: C, 84.96; H, 8.39. Found: C, 84.67; H, 8.33. Data for **15a**: Mp 74.5−75.5 °C; MS *m*/*z* 372 (M^+); ^{1}H NMR (δ in C_6D_6) 0.48 (s, 6H, MeSi), 2.10 (s, 6H, *o*-Me Mes), 2.17 (s, 3H, *p*-Me Mes), 2.83 (s, 3H, Me Tol), 6.73 (s, 2H, Mes ring protons), 7.22−7.25 (m, 4H, ring protons), 7.43 (d, 1H, ring proton, $J = 7.59$ Hz), 7.50−7.53 (m, 2H, ring protons), 7.54 (br s, 1H, ring proton); ^{13}C NMR (δ in C_6D_6) −2.6, 19.5, 21.1, 22.1, 128.2, 128.5, 128.7, 129.6, 131.2, 132.3, 134.46, 134.54, 137.5, 138.0, 138.3, 139.0, 139.3, 144.0, 202.1; ^{29}Si NMR (δ in C_6D_6) −7.7; IR $\nu_{C=O}$ 1667 cm^{-1}. Anal. Calcd for $C_{25}H_{28}OSi$: C, 80.59; H, 7.57. Found: C, 80.52; H, 7.43.

Reaction of 1h with 2a Followed by Methyl Iodide. To a mixture of 0.716 g (2.464 mmol) of **1h** and 7 mL of THF was added 2.470 mmol of **2a** in 5 mL of THF at −95 °C. The mixture was allowed to warm to −32 °C over a period of 5.5 h. To this was added 5.0 mL (80.3 mmol) of methyl iodide at −80 °C, and the resulting mixture was stirred at room temperature for 15 h. After hydrolysis of the mixture with water and the usual workup as above, the products were analyzed by GLC, using 31.0 mg (0.156 mmol) of tetradecane as an internal standard, as containing tris(trimethylsilyl)silane (85% yield) and **1i** (93% yield). GLC retention time and mass spectrum of tris(trimethylsilyl)silane are identical with those of an authentic sample prepared as reported in the literature.[18] Compound **1i** was isolated by preparative GPC eluting with benzene. All spectral data obtained for **1i** are identical with those reported in the literature.[19]

Reaction of 16 with Chlorotriethylsilane. To a solution of **16** prepared from mixture of 0.846 g (2.911 mmol) of **1g** and 2.933 mmol of **2a** in 13 mL of THF was added 0.664 g (4.404 mmol) of chlorotriethylsilane at −92 °C. The mixture was allowed to warm to room temperature and stirred for 15 h. After hydrolysis of the mixture with water and the usual workup as above, the products were analyzed by GLC, using 30.7 mg (0.155 mmol) of tetradecane as an internal standard, as containing tris(trimethylsilyl)silane (81% yield) and **17** (80% yield). GLC retention time and the mass spectrum of tris(trimethylsilyl)silane are identical with those of an authentic sample.[18] Compound **17** was isolated by preparative GPC eluting with benzene: MS *m*/*z* 404 (M^+); ^{1}H NMR (δ in C_6D_6) 0.36 (s, 27H, Me_3Si), 0.76 (q, 6H, CH_2CH_3, $J = 7.92$ Hz), 1.05 (t, 9H, CH_3CH_2, $J = 7.92$ Hz), 4.55 (s, 1H, $H_2C{=}$), 4.92 (s, 1H, $H_2C{=}$); ^{13}C NMR (δ in C_6D_6) 1.2, 5.6, 7.1, 104.5, 164.0; ^{29}Si NMR (δ in C_6D_6) −76.8, −12.7, 18.7; IR ν_{Si-O} 1071 cm^{-1}. Anal. Calcd for $C_{17}H_{44}OSi_5$: C, 50.42; H, 10.95. Found: 50.33; H, 10.92.

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