Oxidative Coupling of Lithium Silenolates: First Synthesis of Bis(acyl)-Substituted Polysilanes

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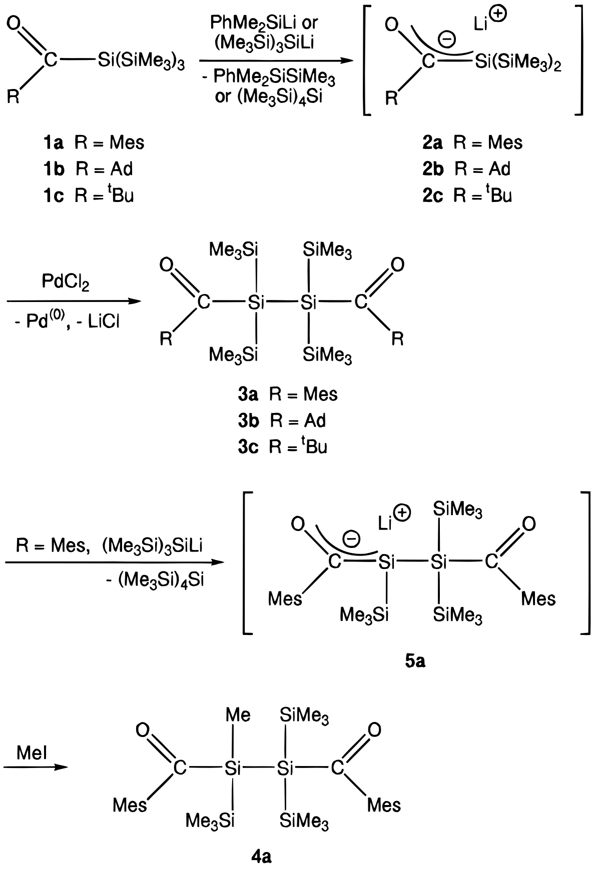
*Summary: Treatment of lithium 2-mesityl-, adamantyl-, and tert-butyl-1,1-bis(trimethylsilyl)-1-silen-2-olate with 0.5 equiv of palladium dichloride afforded the corresponding coupling products, 1,2-bis(acyl)tetrakis(trimethylsilyl)disilanes (**3a−c**), in high yields. The molecular structure of compound **3b** was established by single-crystal X-ray diffraction study.*

Acylpolysilanes are useful precursors for the synthesis of silenes. The photolysis[1] and thermolysis[2] of acyltris(trimethylsilyl)silanes cleanly produce various silenes, including stable ones, via a 1,3-trimethylsilyl shift from the tris(trimethylsilyl)silyl unit to the carbonyl oxygen. However, acylpolysilanes reported so far involve only one acyl−Si bond, and no acylpolysilanes bearing more than two acyl−Si bonds have been reported.

In the course of our studies concerning the chemical behavior of acylpolysilanes toward organolithium reagents,[3] we have demonstrated that the reactions of acyltris(trimethylsilyl)silanes with silyllithium reagents cleanly proceed to give the corresponding lithium silenolates by elimination of a trimethylsilyl group, if the acylpolysilanes have no enolizable protons and involve a sterically bulky group on the carbonyl carbon.[4] Lithium silenolates are silicon analogs of lithium enolates and react readily with several electrophiles, such as alkyl halides and triethylchlorosilane, to give the coupling products. In an effort to explore further scope of lithium silenolates as the synthetic tools for organosilicon compounds, we found that the reactions of lithium silenolates with palladium dichloride afford bis(acyl)polysilanes which have two acyl groups linked by a polysilane bridge.

When lithium 2-mesitylbis(trimethylsilyl)-1-silen-2-olate (**2a**) prepared from the reaction of mesitoyltris(trimethylsilyl)silane (**1a**) with 1 equiv of (dimethylphenylsilyl)lithium was treated with 0.5 equiv of palladium dichloride in THF at −80 °C, 1,2-dimesitoyltetrakis(trimethylsilyl)disilane (**3a**) was obtained in 41% isolated yield from **1a**, as shown in Scheme 1.[5] The structure of compound **3a** was verified by spectrometric analysis and elemental analysis. The IR spectrum of **3a** shows an absorption band at 1610 cm^{-1} characteristic of the stretching frequencies of silyl-substituted carbonyl bonds. Its ^{13}C NMR spectrum reveals a signal at 245.4 ppm due to the carbonyl carbon atoms in addition to signals attributed to the mesityl and tri-

Scheme 1



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(1) Brook, A. G. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Part 2, Chapter 15.

(2) (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. (c) Ishikawa, M.; Matsui, S.; Naka, A.; Ohshita, J. *Main Group Chem.*, in press.

(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.

(4) (a) Ohshita, J.; Masaoka, Y.; Masaoka, S.; Ishikawa, M.; Tachibana, A.; Yano, T.; Yamabe, T. *J. Organomet. Chem.* **1994**, *473*, 15. (b) Ohshita, J.; Masaoka, S.; Masaoka, Y.; Hasebe, H.; Ishikawa, M.; Tachibana, A.; Yano, T.; Yamabe, T. Submitted for publication in *Organometallics.*

(5) To a suspension of 0.487 g (2.74 mmol) of palladium dichloride in 7 mL of THF was added dropwise a solution of **2a** prepared from 2.147 g (5.44 mmol) of **1a** and an equimolar amount of (dimethylphenylsilyl)lithium in 16 mL of THF, at −80 °C. The resulting mixture was allowed to warm to room temperature over a period of 12 h. After hydrolysis of the mixture, 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. The solvent was evaporated, and the residue was chromatographed on a florisil column eluting with benzene to give crude **3a**. The crude product was recrystallized from hexane to give 0.712 g (41% yield) of analytically pure **3a** as yellow crystals: mp 93.5−94.5 °C; MS *m*/*z* 642 (M$^+$); ^{1}H NMR (δ in C_6D_6) 0.43 (s, 36H, Me$_3$Si), 2.09 (s, 6H, *p*-Me), 2.37 (s, 12H, *o*-Me), 6.63 (s, 4H, ring protons); ^{13}C NMR (δ in C_6D_6) 3.0 (Me$_3$Si), 20.9 (*p*-Me), 21.0 (*o*-Me), 129.3, 132.9, 138.4, 146.3 (ring carbons), 245.4 (C=O); ^{29}Si NMR (δ in C_6D_6) −61.2, −9.9; IR $\nu_{C=O}$ 1610 cm^{-1}. Anal. Calcd for $C_{32}H_{58}O_2Si_6$: C, 59.74; H, 9.09. Found: 59.72; H, 9.01.

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methylsilyl groups. The ^{29}Si NMR spectrum shows only two signals at −61.2 and −9.9 ppm. The UV spectrum of **3a** in THF shows absorptions at 218 (ϵ = 44 300) and 278 nm (3400), which are red-shifted relative to those of **1a** (214 (ϵ = 36 000), 244 (shoulder, 8270), and 263 nm (shoulder, 6610)), while in an n−π* absorption band for **3a** (392 nm (ϵ = 370)), slight blue shifs were observed relative to **1a** (373 (ϵ =159), 391 (243), and 404 nm (224)). All other spectra obtained for **3a** are also consistent with the proposed structure.[5] Similar treatment of lithium 2-adamantyl- (**2b**) and 2-*tert*-butylbis(trimethylsilyl)-1-silen-2-olate (**2c**) with palladium dichloride gave 1,2-diadamantoyltetrakis(trimethylsilyl)disilane (**3b**) and 1,2-dipivaloyltetrakis(trimethylsilyl)disilane (**3c**) in 66% and 52% isolated yields, respectively (Scheme 1). The structures of **3b**[6] and **3c**[7] were also confirmed by spectrometric and elemental analysis. In contrast to **3a**, no obvious red shifts in UV spectra for **3b** (214 (ϵ = 18 900), 378 nm (34)) and **3c** (215 (ϵ = 20 500, 368 nm (35)) in THF are observed, compared with those for acylpolysilanes **1b** (210 (ϵ = 18 100), 222 (17 500), 253 (shoulder, 2800), and 369 nm (150)) and **1c** (212 (ϵ = 16 900), 246 (shoulder, 2990), 352 (86), 363 (107), and 374 nm (94)).

The rather low isolated yields of products **3a**−**c** may be ascribed to decomposition of the products during workup, especially on treating them with florisil column chromatography. In fact, when the reactions of lithium silenolates **2a**−**c** with palladium dichloride were monitored by ^{1}H, ^{13}C, and ^{29}Si NMR spectrometry, almost all of the starting **2a**−**c** were consumed, immediately after addition of palladium dichloride to **2a**−**c**, and coupling products **3a**−**c** were formed in more than 80% yields at this stage. In these spectra, unidentified signals with low intensities were also observed.

The crystal structure of compound **3b**[8] was determined by single-crystal X-ray diffraction studies. Figure 1 depicts an ORTEP view of compound **3b**, showing the location of the acyl groups in an anti fashion with respect to the central Si−Si bond. All Si−Si bonds, especially the central one (2.407(3) Å), are slightly longer than normal values for strain-free disilanes (2.33−2.37 Å[9]). Since no crystal structures of acylpolysilanes have been reported to date, the electronic effect of a neighboring carbonyl group on the polysilane structure is unknown. However, it seems likely that the steric repulsion between substituents is the reason for the long Si−Si bonds. The larger Si(central)−Si(central)−SiMe$_3$ angles (112.4° (av)) than Si(central)−Si(central)−C(carbonyl) angles (101.72° (av)) would also result from the steric repulsion between trimethylsilyl groups. All bond lengths and angles in the adamantyl group are normal values. There are no intermolecular contacts less than the van der Waals distances.

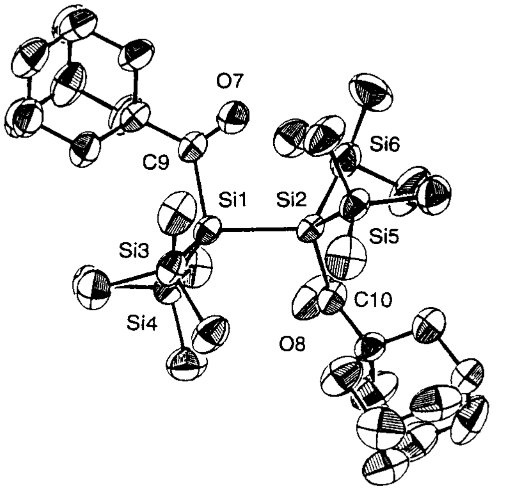

Figure 1. Molecular structure of **3b** with atomic labeling scheme. Selected bond lengths (Å) and bond angles (deg): Si1−Si2 = 2.399(1), Si1−Si3 = 2.378(1), Si1−Si4 = 2.385(1), Si1−C9 = 1.967(5), Si2−Si5 = 2.385(1), Si2−Si6 = 2.380(1), Si2−C10 = 1.967(5), O7−C9 = 1.208(3), O8−C10 = 1.214(4), C9−C11 = 1.546(6), Si2−Si1−Si3 = 111.68(5), Si2−Si1−Si4 = 113.13(6), Si2−Si1−C9 = 99.38(9), Si3−Si1−Si4 = 106.52(4), Si3−Si1−C9 = 107.2(1), Si4−Si1−C9 = 118.8(1), Si1−Si2−Si5 = 115.94(5), Si1−Si2−Si6 = 110.91(5), Si1−Si2−C10 = 104.05(9), Si5−Si2−Si6 = 105.54(4), Si5−Si2−C10 = 121.2(1), Si6−Si2−C10 = 97.6(1), Si1−C9−O7 = 114.9(3), Si1−C9−C11 = 126.9(2), O7−C9−C11 = 118.2(4), Si2−C10−O8 = 111.9.

Next, we examined the reactions of **3a**−**c** with a silyllithium. Thus, when **3a** was treated with 1 equiv of tris(trimethylsilyl)silyllithium in THF at −80 °C, followed by methyl iodide, 1,2-dimesitoylmethyltris(trimethylsilyl)disilane (**4a**)[10] and tetrakis(trimethylsilyl)silane were obtained quantitatively, indicating the formation of lithium silenolate (**5a**) as shown in Scheme 1. In contrast, **3b** and **3c** did not react with the silyllithium reagent even at room temperature. In these reactions, the starting compounds **3b**,**c** were recovered

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[6] Data for **3b**: colorless crystal; mp 183.0−184.5 °C; MS *m/z* 674 (M$^+$); ^{1}H NMR (δ in C$_6$D$_6$) 0.54 (s, 36H, Me$_3$Si), 1.65 (br t, 12H, Ad, *J* = 14.0 Hz), 1.96 (br s, 12H, Ad), 1.98 (br s, 6H, Ad); ^{13}C NMR (δ in C$_6$D$_6$) 3.5 (Me$_3$Si), 28.5, 36.9, 38.1, 52.3 (Ad), 248.7 (C=O); ^{29}Si NMR (δ in C$_6$D$_6$) −61.7, −10.6; IR $\nu_{C=O}$ 1616 cm^{-1}. Anal. Calcd for C$_{34}$H$_{66}$O$_2$Si$_6$: C, 60.46; H, 9.85. Found: 60.30; H, 9.84.

[7] Data for **3c**: colorless crystal; mp 145.0−145.5 °C; MS *m/z* 518 (M$^+$); ^{1}H NMR (δ in C$_6$D$_6$) 0.45 (s, 36H, Me$_3$Si), 1.11 (s, 18H, *tert*-Bu); ^{13}C NMR (δ in C$_6$D$_6$) 3.3 (Me$_3$Si), 25.9, 49.7 (*tert*-Bu), 247.9 (C=O); ^{29}Si NMR (δ in C$_6$D$_6$) −61.4, −10.4; IR $\nu_{C=O}$ 1622 cm^{-1}. Anal. Calcd for C$_{22}$H$_{54}$O$_2$Si$_6$: C, 50.90; H, 10.48. Found: 50.90; H, 10.36.

[8] Crystal structure analysis for **3b**: space group $P\bar{1}$, a = 13.259(4) Å, b = 15.928(3) Å, c = 12.059(4) Å, α = 90.41(2)°, β = 124.29(2)°, γ = 104.76(2)°, V = 1998(1) Å^3, Z = 2, μ(Cu Kα) = 2.02 mm^{-1}, 6416 unique reflections measured, 5936 reflections with $I \geq 3\sigma(I)$ used for calculation, R = 0.057, R_w = 0.066 where weighting scheme is $(\sigma(F_o)^2 + 0.0004|F_o|^2)^{-1}$. All unique diffraction maxima with $0 < 2\theta < 126.0°$ were recorded on a Rigaku AFC-6C automated four-circle diffractometer using graphite-monochromated Cu Kα radiation (λ = 1.5418 Å). The structures were solved by Monte-Carlo direct methods (Furusaki, A. *Acta Crystallogr., Sect. A* **1979**, *35*, 220) using the MULTAN 78 program system (Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declarcq, J.-P.; Woolfson, M. MULTAN78, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data, Univ. of York, England, and Louvain, Belgium, 1978) and refined by the full-matrix least-squares program (Katayama, C.; Sakabe, N.; Sakabe, K. *Acta Crystallogr., Sect. A* **1972**, *28*, S207). Atomic scattering factors were taken from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. 4. Anisotropic temperature factors were used for refinement of non-hydrogen atoms. All computations were performed on the HITAC M-680/180E system at the Information Processing Center of Hiroshima University using the CRYSTAN program system (Katayama, C.; Honda, M. CRYSTAN, The Computer Center of Nagoya University Library Program).

[9] Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; Part 1, Chapter 3.

[10] Data for **4a**: viscous yellow oil; MS *m/z* 584 (M$^+$); ^{1}H NMR (δ in C$_6$D$_6$) 0.30 (s, 9H, Me$_3$Si), 0.41 (s, 9H, Me$_3$Si), 0.48 (s, 9H, Me$_3$Si), 0.68 (s, 3H, MeSi), 2.10 (br s, 6H, *p*-Me), 2.27 (s, 6H, *o*-Me), 2.33 (s, 6H, o-Me), 6.64 (s, 2H, ring protons), 6.66 (s, 2H, ring protons); ^{13}C NMR (δ in C$_6$D$_6$) −2.7 (MeSi), −0.2, 2.2, 2.3 (Me$_3$Si), 20.3, 20.4 (*o*-Me), 20.9, 21.0 (*p*-Me), 129.2, 129.3, 132.1, 132.9, 138.0, 138.3, 144.4, 146.8 (ring carbons), 246.8, 248.1 (C=O); ^{29}Si NMR (δ in C$_6$D$_6$) −66.9, −33.3, −11.2, −9.9, −9.7; IR $\nu_{C=O}$ 1609 cm^{-1}. Anal. Calcd for C$_{30}$H$_{52}$O$_2$Si$_5$: C, 61.58; H, 8.96. Found: 61.65; H, 8.91.

unchanged. Further studies concerning the chemical behavior of **3a**−**c** are in progress and will be reported elsewhere.

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Supporting Information Available: An ORTEP view with a full atomic numbering scheme and tables of crystal data, experimental conditions, and a summary of structure refinement, full bond lengths and angles, atomic coordinates and equivalent isotropic thermal parameters, and anisotropic thermal parameters for **3b** (7 pages). Ordering information is given on any current masthead page.

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