an NMR spectrum of the residue showed only the presence of V.

Reaction of IV with KF(tech). A solution of IV (1.41 g, 7.12 mmol) in acetonitrile was heated at reflux with KF(tech) (85% KF, 0.64 g, 9.4 mmol) for 22.5 h. After removal of the solvent, the residue was extracted with ether–water and the ether layer dried over Na_2SO_4. Removal of the ether resulted in the recovery of IV (1.36 g, 96%).

Reaction of V with KF(tech). A solution of V (1.82 g, 9.2 mmol) in acetonitrile (50 mL) was heated with KF(tech) (85% KF, 0.83 g, 12 mmol) at reflux for 22.5 h. After workup, V (1.79 g, 98%) was recovered.

Acknowledgment. V.H.T.C. wishes to thank Miles Laboratories for the use of their facilities for a portion of the investigation.

Registry No. Ia, 71445-87-9; Ib, 80532-94-1; II, 80532-95-2; III, 80532-96-3; IV, 19578-70-2; V, 57076-47-8; VI, 80532-97-4; VII, 80532-98-5; *o*-bromobenzyl *o*-bromophenyl ether, 5310-54-3; *o*-cresol, 95-48-7; α-bromotoluene, 100-39-0; phenol, 108-95-2; *o*-methylbenzyl bromide, 89-92-9.

Reaction of Secondary and Tertiary Alkyllithium Reagents with Vinyl Di- and Trisiloxanes. Synthesis of α-Silyl Silanols

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Department of Chemistry, University of Southern California, Los Angeles, California 90007

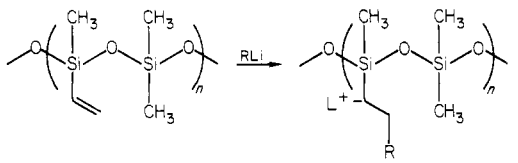
Received November 24, 1981

Secondary and tertiary alkyllithiuim reagents add to the carbon–carbon double bond of vinyl di- and trisiloxanes at low temperature (−78 °C) to yield α-lithioalkyl di- and trisiloxanes. If these are quenched with moist THF at low temperature alkyl di- and trisiloxanes are formed. However, if such α-lithioalkyl di- and trisiloxanes are warmed to 0 °C prior to quenching, α-silyl silanols are found. These products result from a 1,3 rearrangement of a silyl group from oxygen to the carbanion center. This converts the carbanion into an alkoxide anion. The scope and generality of these reactions have been explored.

We have been interested recently in developing methods to modify siloxane polymers. Despite previous reports that organolithium reagents easily cleave hexaorganodisiloxanes to yield tetraorganosilanes and lithium triorganosilanoates,[1] the possible addition of alkyllithium reagents to the

$$Ph_3SiOSiPh_3 + PhLi \rightarrow Ph_4Si + Ph_3SiO^-Li^+ \quad (1)$$

carbon–carbon double bond of vinyl methyl siloxanes seemed worthy of examination.



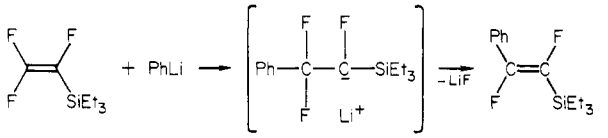
(2)

The addition of Grignard and organolithium reagents to vinylsilanes to yield α-silyl organometallics has been known for almost 30 years.[2–5]

$$Ph_3Si{-}CH{=}CH_2 + PhLi \rightarrow Ph_3Si{-}{}^-CH{-}CH_2{-}Ph \quad Li^+ \quad (3)$$

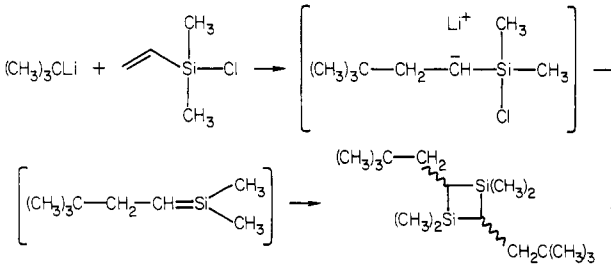
Such α-silyl organometallics have proved useful for the preparation of substituted alkenes via the Peterson olefination reaction.[6,7]

However, addition of organolithium reagents to (β-halovinyl)silanes or to vinylchlorosilanes yield α-silyl organometallics which may undergo elimination of the elements of lithium halide. This may result in the formation of a carbon–carbon double bond or reactive silicon–carbon doubly bonded intermediate. For example, addition of organolithium reagents to perfluorovinyltriethylsilane results in an α-silyl organolithium intermediate which undergoes loss of lithium fluoride to yield (β-organo-α,β-difluorovinyl)triethylsilanes (eq 4),[8,9] while addition of



(4)

tert-butyllithium to vinyldimethylchlorosilane gives substituted 1,3-disilacyclobutanes.[10–12] The formation of these compounds have been interpreted in terms of addition of the organolithium reagent to the vinylchlorosilane to yield an α-silyl organolithium reagents which undergoes loss of lithium chloride to yield a reactive intermediate possessing a silicon–carbon double bond. These dimerize in a head-to-tail manner to yield the products observed (eq 5).



(5)

(1) H. Gilman, H. N. Bendict, and H. Hartzfeld, *J. Org. Chem.* **19**, 419 (1954).
(2) L. F. Cason and H. G. Brooks, *J. Am. Chem. Soc.*, **74**, 4582 (1952).
(3) L. F. Cason and H. G. Brooks, *J. Org. Chem.*, **19**, 1278 (1954).
(4) J. F. Mulvaney and Z. G. Gardlund, *J. Org. Chem.*, **30**, 917 (1965).
(5) A. G. Brook, J. M. Duff, and D. G. Anderson, *Can. J. Chem.*, **48**, 561 (1970).
(6) D. J. Peterson, *J. Org. Chem.*, **33**, 780 (1968).
(7) For a review see: D. J. Peterson, *J. Organomet. Chem. Libr.*, **7**, 295 (1972).
(8) D. Seyferth, T. Wada, and G. Raab, *Tetrahedron Lett.*, 20 (1960).
(9) D. Seyferth and T. Wada, *Inorg. Chem.* **1**, 78 (1962).
(10) P. R. Jones and T. F. O. Lin, *J. Am. Chem. Soc.*, **99**, 2013 (1977).
(11) P. R. Jones and T. F. O. Lin, *J. Am. Chem. Soc.*, **99**, 8447 (1977).
(12) P. R. Jones, T. F. O. Lin, and R. A. Pierce, *J. Am. Chem. Soc.*, **102**, 4970 (1980).

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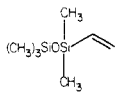
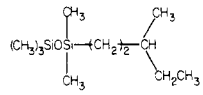
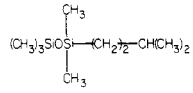
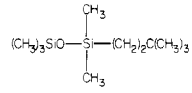
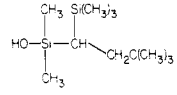
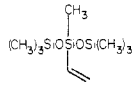
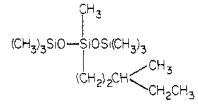
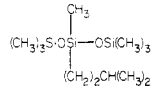
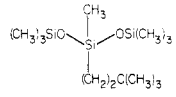
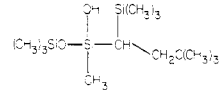
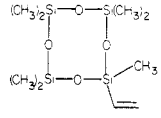
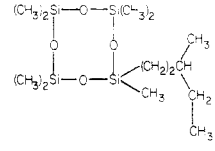
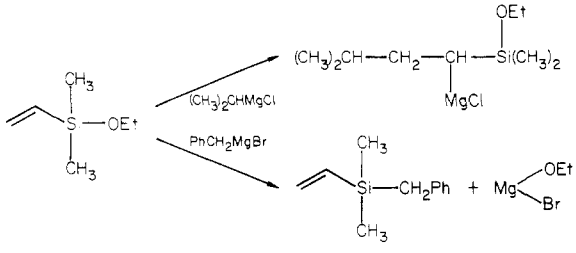
Table I. Reaction of Secondary and Tertiary Alkyllithium Reagents with Vinyl Siloxanes at Low Temperature

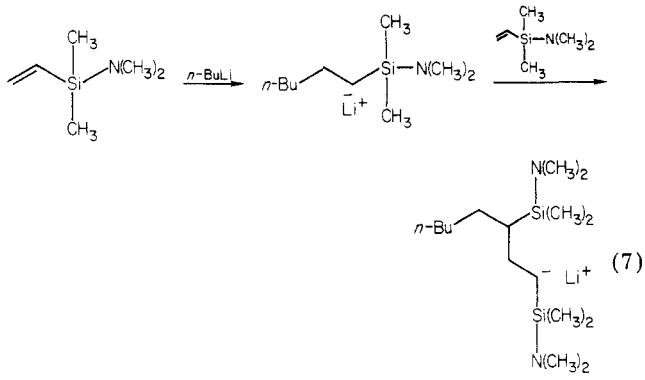
siloxane	alkyl-lithium	products	yield, %
 I	*s*-BuLi	 IV	90
I	*i*-PrLi	 VI	91
I	*t*-BuLi	 VIII	77
		 IX	23
 II	*s*-BuLi	 XI	95
II	*i*-PrLi	 XIII	91
II	*t*-BuLi	 XV	75
		 XVI	25
	*s*-BuLi	 XIX	90

On the other hand, addition of secondary and tertiary alkyl Grignard reagents to vinyl alkoxysilanes to yield α-silyl Grignard reagents has been observed (eq 6). With



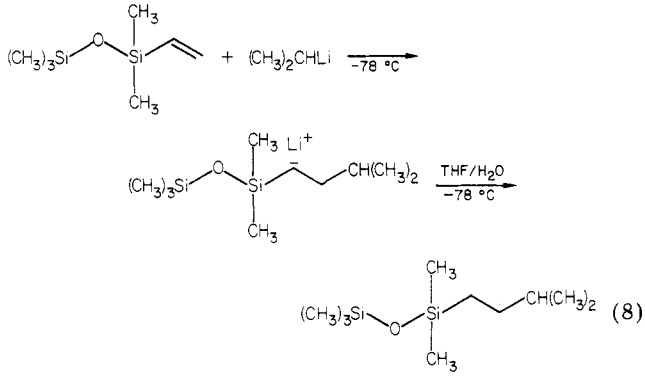
(6)

phenyl, benzyl, allyl, and methyl Grignard reagents displacement of the alkoxy group from silicon occurs.[13] Likewise, *n*-butyllithium has been found to initiate anionic polymerization of vinyldimethyl(dimethylamino)silane.[14] This polymerization involves an α-silyl organolithium species (eq 7).



(7)

We have studied the reaction of vinyl di- and trisiloxanes with alkyllithium reagents. We have found that secondary and tertiary alkyllithium reagents rapidly add in essentially quantitative yield to the carbon–carbon double bond of vinyl siloxanes at −78 °C to yield (α-lithioalkyl)disiloxanes or (α-lithioalkyl)trisiloxanes. The addition does not occur with primary alkyl- or aryllithium reagents under these low-temperature conditions. Secondary and tertiary alkyllithium reagents are frequently found to be more reactive than primary alkyl- or aryllithium reagents.[15] If these anions are quenched at low temperature (−78° C) by addition of moist THF, alkyl siloxanes are obtained. These reactions have been studied with *tert*-butyllithium, isopropyllithium, and *sec*-butyllithium in combination with vinylpentamethyldisiloxane (I), 3-vinylheptamethyltrisiloxane (II) and vinylheptamethylcyclotetrasiloxane (III)(eq 8). See Table I for data.



(8)

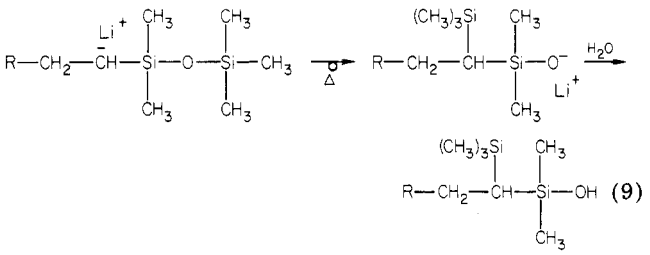
On the other hand, if such (α-lithioalkyl)disiloxanes or (α-lithioalkyl)trisiloxanes are permitted to warm to 0 °C prior to quenching a rearrangement occurs in which a silyl group migrates from oxygen to the carbanion center to yield an α-silyl silanoate. In this process, a carbanion is converted to an alkoxide anion. In the case of *tert*-butyllithium this rearrangement can not be completely suppressed (~20–25%) even at −95° C. After quenching, such reactions yield hindered dimethyl(α-trimethylsilyl)alkyl)silanols (eq 9). See Table II for data. Possibly due to steric hindrance these are quite stable to dehydration and do not readily form siloxanes.

There is only one previous report in the literature of this type of rearrangement. West observed that metalation of hexamethyldisiloxane with *tert*-butyllithium gave dimethyl(trimethylsilylmethyl)silanol after quenching with

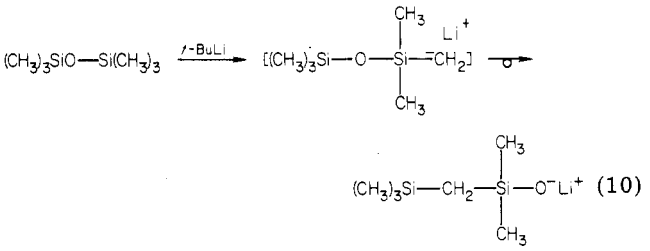
(13) G. R. Buell, R. Corriu, C. Guerin, and L. Spialter, *J. Am. Chem. Soc.*, **92**, 7424 (1970).

(14) M. R. Stober, K. W. Michaels, and J. L. Speier, *J. Org. Chem.*, **32**, 2740 (1967).

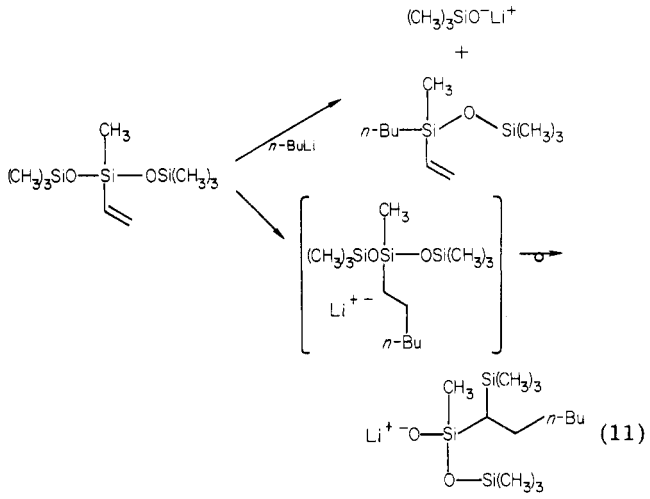
(15) P. D. Bartlett, S. J. Tauber, and W. P. Weber, *J. Am. Chem. Soc.*, **91**, 6362 (1969).



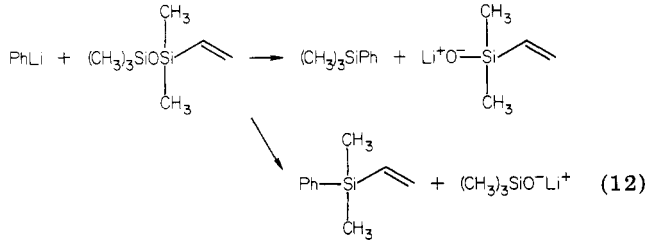
water[16] (eq 10). The rearrangement we have observed may also be related to the anionic rearrangements of cyclotrisilazanes to cyclodisilazanes[17] and of *N*-lithiocyclosiloxanes.[18]



Addition of primary alkyllithium reagents such as *n*-butyllithium to I does not occur at −78 °C but requires high temperature (0 °C). Under these conditions addition and rearrangement occur consecutively so that only rearranged dimethyl((α-trimethylsilyl)hexyl)silanol is obtained after workup. Reaction of *n*-butyllithium and II results in competitive addition rearrangement and substitution at silicon (eq 11). Reaction of I with methyllithium did not ooccur in ether. In THF at reflux only substitution occurs.

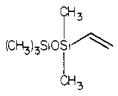
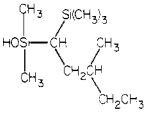
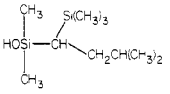
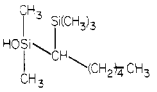
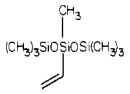
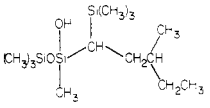
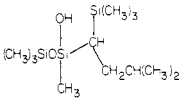
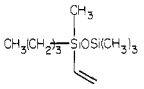
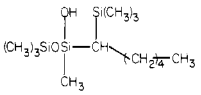


Finally, phenyllithium undergoes substitution at the silyl center in preference to addition to the carbon–carbon double bond of vinylsilanes. Thus I reacts with phenyllithium at 35 °C to yield phenyltrimethylsilane and phenylvinyldimethylsilane as well as siloxane products (eq 12).



(16) G. A. Gornowicz and R. West, *J. Am. Chem. Soc.*, **90**, 4478 (1968).
(17) L. W. Breed, *Inorg. Chem.*, **9**, 1940 (1968).
(18) R. P. Bush, N. C. Lloyd, and C. A. Pearce, *J. Chem. Soc., Chem. Commun.*, 1191 (1968).

Table II. Reaction of Alkyllithium Reagents with Vinyl Siloxanes at Room Temperature. Synthesis of α-Silyl Silanols

siloxane	alkyl-lithium	products	yield, %
 I	*s*-BuLi	 V	100
I	*i*-PrLi	 VII	95
I	*n*-BuLi	 X	86
 II	*s*-BuLi	 XII	95
II	*i*-PrLi	 XIV	100
II	*n*-BuLi	 XVII	52
		 XVIII	40

The extension of this study to polymeric vinyl methyl siloxanes is under active investigation. Clearly, a major problem to be overcome is the solubility of such polymers at the low temperatures required to prevent rearrangement and thus scission of the siloxane polymer backbone.

Experimental Section

All reactions were carried out under an atmosphere of prepurified nitrogen. ^{1}H NMR spectra were obtained on a Varian XL-100 spectrometer operating in the FT mode using 5% solutions in deuteriochloroform. Chloroform was used as an internal standard. The integration of the NMR spectra sometimes gave too small intensities for the Si–CH_3 signals because of saturation problems. However, in all cases the integration was within 10% of the calculated value.[19] IR spectra were obtained on a Perkin-Elmer 281. IR bands were calibrated against known bands of a polystyrene film. The silanols and siloxanes show considerable differences in their IR spectra. The silanols show sharp absorptions at about 3760 cm^{-1} and hydrogen-bonded OH vibrations around 3540 cm^{-1} and no Si–O–Si absorptions between 1100 and 1000 cm^{-1}. Siloxane products, on the other hand, show no absorptions over 3000 cm^{-1} and have very strong Si–O–Si absorptions at 1050 cm^{-1}.[20] Mass spectra were obtained on a Hewlett-Packard 5985 GC/MS. A 6 ft × $^1/_4$ in. 5% OV-101 column was used in the gas chromatograph. GLPC analysis was performed on a

(19) D. E. Leyden and R. H. Cox, "Analytical Applications of NMR", Wiley, New York, 1977, pp 17–18, 260–265.
(20) D. R. Anderson, "Infrared, Raman and Ultraviolet Spectroscopy in Analysis of Silicones", A. L. Smith, Ed.% Wiley, New York, 1979, pp 254, 275.

Hewlett-Packard F&M 700 using a 28 ft × $^1/_4$ in. 20% SE-30 on 60/80 mesh Chromosorb W column. Yields were calculated by using *n*-decane or *n*-hexadecane as internal standards. Elemental analysis were obtained from Galbraith Laboratories, Knoxville, TN. Starting materials are known compounds and had spectra in complete agreement with literature values.

Vinylpentamethyldisiloxane (I) was prepared by the method of Seyferth.[21]

3-Vinylheptamethyltrisiloxane (II) was prepared by cohydrolysis of excess trimethlchlorosilane and methylvinyldichlorosilane.[22]

Vinylheptamethylcyclotetrasiloxane (III) was prepared by cohydrolysis of dimethyldichlorosilane and methylvinyldichlorosilane.[23]

Isopropyllithium[24] was prepared by reaction of isopropyl chloride[25] and lithium shot in olefin-free petroleum ether.

Methyllithium, *n*-butyllithium and *sec*-butyllithium were obtained from Aldrich.

Phenyllithium and *tert*-butyllithium were purchased from Alfa.

Reaction of I with *sec*-Butyllithium. The two general procedures (a) at low temperature and (b) at 0 °C or room temperature described below were used for all of the reactions.

(a) In a 50-mL 2-necked flask equipped with a reflux condenser and a rubber septum were placed 25 mL of ether, I (1.23 g, 7.1 mmol), and a Teflon covered magnetic stirring bar. The solution was cooled to −198 °C. *sec*-Butyllithium (1.4 M in hexane) (5.6 mL, 7.8 mmol) was added slowly by syringe through the rubber septum. After waiting till the *sec*-butyllithium solution was frozen, we put the flask into a dry ice/acetone cooling bath, which caused the mixture to melt. This procedure of initially cooling all reagents to −198 °C prevents premature reaction when *sec*-butyllithium solution (temperature ~20 °C) is added. It was then stirred at −78 °C for 1 h and hydrolyzed by slow addition of a solution of 5 mL of THF and 100 μL of H_2O at −78 °C. The mixture was kept at −78 °C for another 30 min and then allowed to warm to room temperature. More water was added; the organic layer was separated, washed till neutral, and dried over Na_2SO_4. The ether was removed by distillation. GLPC analysis of the residue indicated the formation of 1-(3-methylpentyl)-1,1,3,3,3-pentamethyldisiloxane (IV) in 90% yield. It had the following spectral properties: NMR δ 1.55–1.16 (br m, 5 H), 0.98–0.77 (m, 6 H), 0.65–0.41 (m, 2 H), 0.13 (s, 9 H), 0.09 (s, 6 H); IR $\bar{\nu}$ 1055 cm^{-1} (SiOSi); mass spectrum, *m/e* (relative intensity) 217 (11.6% M^+ − 15), 147 (100.0%), 133 (46.3%), 73 (22.1%). Anal. Calcd for $C_{11}H_{28}O_1Si_2$: C, 56.82; H, 12.14. Found: C, 56.62; H, 12.07.

(b) A mixture of I (1.9 g, 11 mmol), *sec*-butyllithium (8.5 mL, 12 mmol), and 25 mL of ether was prepared as above. The reaction mixture was allowed to come to room temperature and stirred for 12 h. After the reaction mixture was poured into water/ice, the organic layer was separated. It was washed till neutral and dried over Na_2SO_4. The ether was removed by distillation. GLPC analysis of the residue indicated the formation of dimethyl(1-(trimethylsilyl)-3-methylpentyl)silanol (V) in 100% yield. It had the following spectral properties: NMR δ 1.58–1.12 (br m, 6 H), 1.43 (s, 1 H, overlapping the δ 1.58–1.12 (m)), 1.04–0.75 (m, 6 H), 0.20 (s, 6 H), 0.10 (s, 9 H) [the Si–CH–Si signal is obscured by the CH_3Si signals[26]]; mass spectrum, *m/e* (relative intensity) 217 (67.7%, M^+ − 15), 175 (16.8%), 159 (8.3%), 147 (100.0%); IR $\bar{\nu}$ 3760 cm^{-1} (O–H). Anal. Calcd for $C_{11}H_{28}O_1Si_2$: C, 56.82; H, 12.14. Found: C, 56.95; H, 12.34.

Reaction of I with Isopropyllithium. (a) Isopropyllithium (0.65 M in petroleum ether) (14.6 mL, 9.5 mmol) and I (1.5 g, 8.6 mmol) in 25 mL of ether were reacted at −78 °C for 2 h. 1-(3-methylbutyl)-1,1,3,3,3-pentamethyldisiloxane (VI) was formed in 91% yield. It had the following spectral properties: NMR δ 1.65–1.05 (m, 3 H), 0.93 (d, 6 H, J = 7 Hz), 0.53 (m, 2 H, $(J_{AX} + J_{AX'})/2$ = 8 Hz), 0.12 (s, 9 H), 0.09 (s, 6 H); IR $\bar{\nu}$ 1060 cm^{-1} (Si–O–Si); mass spectrum, *m/e* (relative intensity) 218 (3.7%, $M^{+\cdot}$), 203 (7.4%, M^+ − 15), 147 (100.0%), 133 (53.7%), 73 (24.1%). Anal. Calcd for $C_{10}H_{26}O_1Si_2$: C, 54.97; H, 11.99. Found: C, 55.01; H, 11.82.

(b) Isopropyllithium (0.61 M in petroleum ether) (19.7 mL, 12 mmol) and I (1.9 g, 11 mmol) in 25 mL of ether was warmed to room temperature and stirred for 6 h. Dimethyl(1-(trimethylsilyl)-3-(methylbutyl))silanol (VII) was formed in 95% yield. It had the following spectral properties: NMR δ 1.72 (s, 1 H), 1.66–1.22 (m, 3 H), 0.91 (d, 6 H, J = 6 Hz), 0.20 (s, 6 H), 0.11 (s, 9 H) [the Si–CH–Si signal is obscured by the $SiCH_3$ signals[26]]; mass spectrum, *m/e* (relative intensity) 203 (100.0%, M^+ − 15), 175 (21.7%), 147 (87.8%), 133 (61.1%). Anal. Calcd for $C_{10}H_{26}O_1Si_2$: C, 54.97; H, 11.99. Found: C, 54.78; H, 12.06.

Reaction of I with *tert*-Butyllithium. (a) *tert*-Butyllithium (2 M in pentane) (4.1 mL, 8.2 mmol) and I (1.3 g, 7.5 mmol) in 25 mL of ether were reacted at −95 °C (acetone/liquid nitrogen slurry) for 40 min. The clear yellow solution was hydrolyzed very carefully to make sure the reaction temperature did not rise. GLPC analysis indicated the formation of 1-(3,3-dimethylbutyl)-1,1,3,3,3-pentamethyldisiloxane (VIII) and dimethyl(1-(trimethylsilyl)-3,3-(dimethylbutyl))silanol (IX) in 77% and 23% yields, respectively. VIII had the following spectral properties: NMR δ 1.17 (m, 2 H, $(J_{AX} + J_{AX'})/2$ = 8.5 Hz), 0.86 (s, 9 H), 0.43 (m, 2 H, $(J_{AX} + J_{AX'})/2$ = 8.5 Hz), 0.07 (s, 9 H), 0.03 (s, 6 H); mass spectrum, *m/e* (relative intensity) 232 (0.2%, $M^{+\cdot}$), 217 (6.7%, M^+ − 15), 175 (1.6%), 147 (100.0%), 133 (28.5%); IR $\bar{\nu}$ 1060 cm^{-1} (Si–O–Si). Anal. Calcd for $C_{11}H_{28}O_1Si_2$: C, 56.82; H, 12.14. Found: C, 56.89; H, 12.29. IX had the following spectral properties: NMR δ 1.52–1.37 (m, 2 H), 1.48 (s, 1 H, overlapping the δ 1.52–1.37 (m)), 0.87 (s, 9 H), 0.15 (s, 6 H), 0.05 (s, 9 H), −0.09 (t, 1 H, J = 4 Hz); mass spectrum, *m/e* (relative intensity) 217 (47.8%, M^+ − 15), 175 (32.8%), 159 (10.8%), 147 (100.0%), 133 (36.9%); IR $\bar{\nu}$ 3750 cm^{-1} (O–H). Anal. Calcd for $C_{11}H_{28}O_1Si_2$: C, 56.82; H, 12.14. Found: C, 56.67; H, 12.11.

(b) Similar reactions carried out at higher temperatures caused precipitation of a white solid. The formation of a number of products was indicated by GLPC. These have not been identified.

Reaction of I with *n*-Butyllithium. (a) At −78 °C no reaction occurred between I and *n*-butyllithium within 3 h as determined by GLPC analysis. (b) *n*-Butyllithium (1.59 M in hexane) (4.8 mL, 7.6 mmol) and I (1.3 g, 7.5 mmol) in 25 mL of ether were reacted at 0 °C for 2.5 h. Dimethyl(1-(trimethylsilyl)hexyl)silanol (X) was formed in 86% yield. It had the following spectral properties: NMR δ 1.67–1.11 (br m), 1.43 (s, overlapping the δ 1.67–1.11 (m), together 9 H), 1.00–0.72 (m, 3 H), 0.15 (s, 6 H), 0.05 (s, 9 H), −0.4 (t, 1 H, J= 5 Hz); mass spectrum, *m/e* (relative intensity) 217 (100.0%, M^+ − 15), 175 (4.1%), 159 (6.2%), 147 (82.9%), 133 (92.3%); IR $\bar{\nu}$ 3755 cm^{-1} (O–H). Anal. Calcd for $C_{11}H_{28}O_1Si_2$: C, 56.82; H, 12.14. Found: C, 56.95; H, 12.34.

Attempted Reaction of I with Methyllithium. Under reaction conditions either a or b no reaction occurs between I and methyllithium. When THF was used as the solvent, no reaction took place at room temperature. After the reaction mixture was refluxed for 24 h in THF, only unreacted I, vinyltrimethylsilane, and hexamethyldisiloxane could be observed by GC/MS analysis.

Attempted Reaction of I and Phenyllithium. Under reaction conditions either a or b no reaction occurs. When the reaction mixture is refluxed for 4 h, I, phenyltrimethylsilane, 1,3-divinyl-1,1,3,3-tetramethyldisiloxane, vinylphenyldimethylsilane, and hexamethyldisiloxane were observed by GC/MS.

Reaction of II and *sec*-Butyllithium. (a) *sec*-Butyllithium (1.4 M in hexane) (5 mL, 7.0 mmol) and II (1.45 g, 5.9 mmol) in 25 mL of ether were reacted at −78 °C for 1.5 h. 3-(3-Methylpentyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (XI) was produced in 95% yield. It had the following spectral properties: NMR δ 1.52–1.10 (br m, 5 H), 1.04–0.67 (m, 6 H), 0.60–0.32 (m, 2 H), 0.14 (s, 18 H), 0.05 (s, 3 H); mass spectrum, *m/e* (relative intensity) 291 (6%, M^+ − 15), 221 (44.0%), 207 (20.0%), 73 (100.0%); IR $\bar{\nu}$ 1060 cm^{-1} (Si–O–Si). Anal. Calcd for $C_{13}H_{34}O_2Si_3$: C, 50.92; H, 11.18. Found: C, 50.96; H, 11.15.

(b) *sec*-Butyllithium (1.4 M in hexane) (6 mL, 8.4 mmol) and II (1.9 g, 7.7 mmol) in 25 mL of ether were reacted at room

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temperature for 2.5 h. 1-Hydroxy-1-(1-(trimethylsilyl)-3-methylpentyl)-1,3,3,3-tetramethyldisiloxane (XII) was formed in 95% yield. It had the following spectral properties: NMR δ 1.91 (s, 1 H), 1.59–1.15 (br m, 5 H), 1.00–0.73 (m, 6 H), 0.15 (s, 12 H), 0.07 ((s, 9 H) [the Si–Ch–Si signal is obscured by the Si–CH_3 signals[26]]; mass spectrum, m/e (relative intensity) 291 (39%, M − 15), 233 (21.3%), 221 (30.3%), 207 (16.8%), 133 (100.0%); IR $\bar{\nu}$ 3760 (O–H), 1050 cm^{-1} (Si–O–Si). Anal. Calcd for $C_{13}H_{34}O_2Si_3$: C, 50.915; H, 11.175. Found: C, 50.90; H, 11.30.

Reaction of II and Isopropyllithium. (a) Isopropyllithium (0.65 M in petroleum ether) (10.9 mL, 7.1 mmol) and II (1.6 g, 6.5 mmol) in 25 mL of ether were reacted at −78 °C for 2 h. 3-(3-Methylbutyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (XIII) was formed in 91% yield. It had the following spectral properties: NMR δ 1.61–1.09 (m, 3 H), 0.91 (d, 6 H, J = 7 Hz), 0.47 (m, 2 H, $(J_{AX} + J_{AX'})/2$ = 8.5 Hz), 0.15 (s, 18 H), 0.05 (s, 3 H); mass spectrum, m/e (relative intensity) 277 (4.1%), 221 (30.6%), 207 (19.4%), 133 (39.8%), 73 (100.0%); IR $\bar{\nu}$ 1065 cm^{-1} (Si–O–Si). Anal. Calcd for $C_{12}H_{32}O_2Si_3$: C, 49.25; H, 11.02. Found: C, 49.36; H, 11.19.

(b) Isopropyllithium (0.23 M in petroleum ether) (22 mL, 4.9 mmol) and II (1.1 g, 4.4 mmol) in 30 mL of ether were reacted at 0 °C for 3 h. 1-Hydroxy-1-(1-(trimethylsilyl)-3-methylbutyl)-1,3,3,3-tetramethyldisiloxane (XIV) was formed in 100% yield. It had the following spectral properties: NMR δ 1.91 (s, 1 H), 1.75–1.05 (m, 3 H), 0.87 (d of d, 6 H, J = 6 and 2.5 Hz), 0.13 (s, 12 H), 0.06 (s, 9 H), −0.05 (t, 1 H, J = 4 Hz); mass spectrum, m/e (relative intensity) 277 (77.9%, M^+ − 15), 261 (12.3%), 233 (40.2%), 221 (54.6%), 207 (41.6%), 205 (95.8%), 133 (100.0%); IR $\bar{\nu}$ 3760 (O–H), 1050 cm^{-1} (Si–O–Si). Anal. Calcd for $C_{12}H_{32}O_2Si_3$: C, 49.25; H, 11.02. Found: C, 49.25; H, 11.20.

Reaction of II and *tert*-Butyllithium. (a) *tert*-Butyllithium (2 M in pentane) (2.9 mL, 5.8 mmol) and II (1.3 g, 5.2 mmol) in 25 mL of ether were reacted at −95 °C for 5 h. The mixture was hydrolyzed very carefully at this temperature. 3-(3,3-Dimetylbutyl)-1,1,1,3,5,5,5-heptamethyltrisiloxane (XV) and 1-hydroxy-1-(1-(trimethylsilyl)-3,3-dimethylbutyl)-1,3,3,3-tetramethyldisiloxane (XVI) were formed in 75% and 25% yields, respectively. XV had the following spectral properties: NMR δ 1.17 (m, 2 H, $(J_{AX} + J_{AX'})/2$ = 8.5 Hz), 0.84 (s, 9 H), 0.37 (m, 2 H, $(J_{AX} + J_{AX'})/2$ = 9 Hz), 0.10 (s, 18 H), 0.01 (s, 3 H); mass spectrum, m/e (relative intensity) 291 (9.6%, M^+ − 15), 221 (100.0%), 207 (22.4%), 205 (5.7%). IR $\bar{\nu}$ = 1060 cm^{-1} (Si–O–Si). Anal. Calcd for $C_{13}H_{34}O_2Si_3$: C, 50.92; H, 11.18. Found: C, 50.78; H, 11.33. XVI had the following properties: NMR δ 1.58 (s, 1 H), 1.53–1.35 (m, 2 H), 0.87 (s, 9 H), 0.17 (s, 3 H), 0.15 (s, 9 H), 0.09 (s, 9 H), −0.04 to −0.23 (m, 1 H); mass spectrum, m/e (relative intensity) 291 (58.7%, M^+ − 15), 249 (11.9%), 233 (95.8%), 221 (70.9%), 207 (72.1%), 205 (47.7%), 133 (100.0%); IR $\bar{\nu}$ 3755 (O–H), 1050 cm^{-1} (Si–O–Si). Anal. Calcd for $C_{13}H_{34}O_2Si_3$: C, 50.92; H, 11.18. Found: C, 51.02; H, 11.10.

(b) Similar reactions carried out at temperatures higher than −95 °C caused precipitation of a white solid and the formation of a large number of unidentified products.

Reaction of II and *n*-Butyllithium. (a) A mixture of II and *n*-butyllithium in ether was reacted for 7 h at −78 °C. This resulted in negligible reaction.

(b) *n*-Butyllithium (1.59 M in hexane) (4.5 mL, 7.1 mmol) and II (1.6 g, 6.5 mmol) in 25 mL of ether were reacted at 0 °C for 2 h. 1-Butyl-1,3,3,3-tetramethyl-1-vinyldisiloxane (XVII) (52% yield) and 1-hydroxy-1-(1-(trimethylsilyl)hexyl)-1,3,3,3-tetramethyldisiloxane (XVIII) (40% yield) were formed as the main products. XVII had the following properties: NMR δ 6.32–5.44 (m, 3 H), 1.50–1.12 (m, 4 H), 1.06–0.76 (m, 3 H), 0.70–0.39 (m, 2 H, $(J_{AX} + J_{AX'})/2$ = 7 Hz), 0.11 (s, 3 H), 0.09 (s, 9 H); mass spectrum, m/e, (relative intensity) 201 (4.7%, M^+ − 15), 159 (100%, M^+ − 57); IR $\bar{\nu}$ 3098 cm^{-1} (HC═C), 1615 cm^{-1} (C═C), 1065 cm^{-1}Si–O–Si). Anal. Calcd for $C_{10}H_{24}O_1Si_2$: C, 55.49; H, 11.18. Found: C, 55.70; H, 11.10. XVIII had the following properties: NMR δ 1.84 (s, 1 H), 1.61–1.11 (m, 8 H), 1.02–0.76 (m, 3 H), 0.14 (s, 12 H), 0.07 (s, 9 H), 0.00 to −0.23 (m, 1 H); mass spectrum, m/e (relative intensity) 291 (31.5% M^+ − 15), 221 (28.6%), 207 (22.2%), 205 (38.1%), 75 (100.0%); IR $\bar{\nu}$ 3760 cm^{-1} (O–H), 1060 cm^{-1} (Si–O–Si). Anal. Calcd for $C_{13}H_{34}O_2Si_3$: C, 50.92; H, 11.18. Found: C, 51.03; H, 11.10.

Reaction of III and *sec*-Butyllithium. (a) *sec*-Butyllithium (1.4 M in hexane) (3.3 mL, 4.6 mmol) and III (1.3 g, 4.2 mmol) in 25 mL of ether were reacted at −78 °C for 2 h. 1-(3-Methylpentyl)-1,3,3,5,5,7,7-heptamethylcyclotetrasiloxane (XIX) was formed in 90% yield. It had the following spectral properties: NMR δ 1.51–1.07 (m, 5 H), 1.02–0.74 (m, 6 H), 0.64–0.39 (m, 2 H), 0.14 (s, 18 H) , 0.11 (s, 3 H); mass spectrum, m/e (relative intensity) 351 (13.0% M^+ − 15), 276 (100.0%); IR $\bar{\nu}$ 1082 cm^{-1} (Si–O–Si). Anal. Calcd for $C_{13}H_{34}O_4Si_4$: C, 42.57; H, 9.34. Found: C, 42.69; H, 9.10.

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