Anal. Calcd for $C_9H_{24}SiGeO$ (**21**): C, 43.42; H, 9.72; Si, 11.28. Found: C, 43.70; H, 10.01; Si, 11.58. Calcd for $C_9H_{25}NSiGeO$ (**20**): C, 40.95; H. 9.55; N, 5.31; Si, 10.64. Found: C. 40.67; H, 9.81; N, 5.10; Si, 10.97.

***N*,*O*-Bis(trimethylgermyl)hydroxylamine** (**23**). Hydroxylamine (2.7 g, 0.082 mol). triethylamine (16.4 g, 0.163 mol), and trimethylchlorogermane (25 g, 0.163 mol) were reacted according to Wannagat's procedure.[9] After removal of the triethylamine hydrochloride by filtration under nitrogen, the solvent was removed by distillation. The residue was then vacuum distilled to give 6.3 g (30% yield) of crude **23** at 70–75° (2 Torr). Analytical samples were obtained by preparative gas chromatography.

Thermal decomposition of this compound occurs at about 140°, necessitating a short, low load column (5 ft × $^3/_8$ in. packed with 5% SE-52 on Chromosorb W): ir (neat) 3300 (N–H, very weak), 3000, 2830, 1410, 1240, 820, 760 cm^{-1}; nmr τ 9.65 (s, $GeMe_3$, 9), 9.62 (s, $GeMe_3$, 9), 4.11 (s, N–H, 0.9).

Anal. Calcd for $C_6H_{19}NGe_2O$: C, 27.05; H, 7.19; N, 5.25; Ge, 54.50. Found: C, 27.08; H, 7.12; N, 5.05; Ge, 54.43.

***N*,*O*-Bis(*tert*-butyldimethylgermyl)hydroxylamine** (**24**). To a slurry of 2.0 g (0.06 mol) of hydroxylamine and 12.2 g (0.12 mol) of triethylamine in 200 ml of ether was added 23.4 g (0.12 mol) of *tert*-butyldimethylchlorogermane dissolved in 60 ml of hexane. Formation of triethylamine hydrochloride occurred immediately. The next day the solid was removed by filtration under nitrogen and the amber-colored filtrate distilled to give *tert*-butyldimethylchlorogermane, bp 83° (100 Torr). When the temperature of the distilling flask exceeded 120°, the color of the residue (~5 ml) darkened and the distillation was stopped. Attempts to analyze the residue by glpc gave broad temperature-dependent peaks. Nmr showed several peaks in the Ge–C–H and Ge–*t*-Bu regions. This residue was used in experiments to generate the digermyl nitroxide, **26**, by the three methods described above.

Acknowledgments. We wish to thank Dr. D. Galen Reese for his assistance in obtaining some of the esr spectra and Miss Kathy Kiehnau for her help in preparing some of the starting materials.

New Anionic Rearrangements. XV.[1] 1,2-Anionic Rearrangement of Organosilylhydroxylamines[2,3]

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Abstract: Mono- and bis(organosilyl)hydroxylamines, when treated with 1 equiv of alkyllithium, undergo 1,2-anionic rearrangement with migration of the organosilicon group from oxygen to nitrogen. The rearrangement of bis(organosilyl)hydroxylamines was studied in detail; ir, nmr, and chemical evidence shows that, upon deprotonation, migration of the organosilyl group occurs intramolecularly to form an equilibrium mixture of unrearranged and rearranged anions and that the rearranged anion is predominant. This is the first example of a 1,2-anionic rearrangement from oxygen to nitrogen.

Organosilicon groups exhibit unprecedented migratory aptitude in anionic rearrangements.[4] The faster rates of rearrangement of organosilicon groups compared to purely organic migrating groups can be explained by the greater ease with which silicon forms a bridged pentacoordinate transition state. We have extended our studies to heteroatomic systems,[5,6] and, in the case of organosilylhydroxylamines, we have observed the first example of a 1,2-anionic rearrangement from oxygen to nitrogen.[7]

$$R_3Si\bar{N}OSiR_3 \xrightarrow{e} (R_3Si)_2NO^-$$

To investigate this rearrangement, we have synthesized several mono- and bis(organosilyl)hydroxylamines and examined their anions chemically and spectroscopically. Bis(organosilyl)hydroxylamines were studied in greater detail because of their better suitability for nmr and ir studies and the greater stability of their anions.

Syntheses. Bis(organosilyl)hydroxylamines were prepared in good yield by Wannagat's[8] procedure from hydroxylamine, triethylamine, and a chlorosilane (eq 1).

$$2RMe_2SiCl + 2Et_3N + H_2NOH \longrightarrow RMe_2SiNHOSiMe_2R + 2Et_3N \cdot HCl \quad (1)$$

1, R = Me
2, R = Et
3, R = Ph
4, R = *t*-Bu

These compounds gave ir and nmr spectra consistent with the proposed structures (see Table I for nmr data). *N*,*O*-Bis(trimethylsilyl)hydroxylamine (**1**) can also be prepared in 70% yield by the reaction of excess hexamethyldisilazane and hydroxylamine hydrochloride in a mixture of tetrahydrofuran (THF) and pentane. The advantage of this route over Wannagat's method[8] is the elimination of the synthesis and isolation of free hydroxylamine. That **1** is the N,O isomer is shown by

$$(Me_3Si)_2NH + NH_2OH \cdot HCl \longrightarrow \mathbf{1} + NH_4Cl$$

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[1] Previous paper in this series: R. West and B. Bichlmeir, *J. Amer. Chem. Soc.*, **94**, 1649 (1972).

[2] For a review of silyl anionic rearrangements, see R. West, *Pure Appl. Chem.*, **19**, 291 (1969).

[3] Research sponsored by Air Force Office of Scientific Research (NC), OAR, USAF Grant No. AF-AFOSR 70-1904.

[4] For a preliminary account of this rearrangement, see R. West, P. Boudjouk, and T. A. Matuszko, *J. Amer. Chem. Soc.*, **91**, 5184 (1969). Bis(organosilyl)hydroxylamines will also undergo radical rearrangement: R. West and P. Boudjouk, *J. Amer. Chem. Soc.*, **95**, 3983 (1973).

[5] Several organosilyl anionic rearrangements involving carbanions have been studied in our laboratories and have been recently reported: 1,2 (O → C) [R. West, R. Lowe, H. F. Stewart, and A. Wright, *ibid.*, **93**, 282 (1971)]; 1,3 (O → C) [R. West and G. A. Gornowicz, *J. Organometal. Chem.*, **28**, 25 (1971)]; 1,2 (S → C) [A. Wright, D. Ling, P. Boudjouk, and R. West, *J. Amer. Chem. Soc.*, **94**, 4784 (1972)].

[6] 1,4 O → N anionic rearrangements of bis(organosilyl)ethanolamines have also been observed.[2] A 1,4 S → N anionic rearrangement has also been observed in ethanethiolamines: R. West and P. Boudjouk, unpublished results.

[7] For reviews of heteroatomic anionic rearrangements involving carbon migrating groups, see A. R. Lepley and A. G. Giumanini in "Mechanisms of Molecular Migrations," Vol. 3, B. S. Thyagarajan, Ed., Interscience, New York, N. Y., 1971, p 297; and U. Schöllkopf, *Angew. Chem., Int. Ed. Engl.*, **9**, 763 (1970).

[8] U. Wannagat and O. Smrekar, *Monatsh. Chem.*, **100**, 750 (1969).

Table I. Proton Nmr Data for Organosilylhydroxylamines[a]

Compd	$(CH_3)_3Si$	$(CH_3)_2Si$	*t*-BuSi	EtSi	PhSi	N–H	$N–CH_3$	$O–CH_3$
1	9.84, 9.75					5.4		
2		9.85, 9.78		9.1		5.4		
3		9.75, 9.71			2.6	5.3		
4		9.83, 9.74	8.96, 8.91			5.2		
5	9.80					5.4		
6		9.79	8.95			5.4		
7	9.77					5.2	7.51	
8	9.85, 9.75						7.12	
9	9.75							6.55
10	9.72			9.02				
11	9.69	9.76	8.89					
12		9.78		9.1				6.55
13		9.78			2.5			6.72
14		9.87, 9.77	8.96, 8.94				7.13	
15		9.78	8.90					6.58
19	9.73	9.84	8.97			5.2		
20	9.84	9.73	8.91			5.2		
21	9.75						7.40	
22	9.86	9.79	8.96				7.14	

[a] All data presented above were measured in benzene except for **3** and **13** which were measured in cyclohexane.

the presence of two equally intense[9] methylsilyl resonances in its nmr spectrum at τ 9.92 and 9.85 and a N–H absorption at τ 5.4. *O*-Trimethylsilylhydroxylamine (**5**) and **1** can be obtained in equal amounts from

$$2(\text{Me}_3\text{Si})_2\text{NH} + 3\text{H}_2\text{NOH}\cdot\text{HCl} + \text{Et}_3\text{N} \longrightarrow \underset{\mathbf{5}}{2\text{H}_2\text{NOSiMe}_3} + \mathbf{1} + 2\text{NH}_4\text{Cl} + \text{Et}_3\text{N}\cdot\text{HCl}$$

the same reagents if triethylamine is used. The derivatives are easily separated by distillation, the mono- and bis(trimethylsilyl) compounds boiling at 98–100° and 137–139°, respectively. *O-tert*-Butyldimethylsilylhydroxylamine (**6**) was isolated in small amounts by preparative gas chromatography as a by-product in the synthesis of **4**. *O*-Trimethylsilyl-*N*-methylhydroxylamine (**7**) was prepared by the reaction of *N*-methylhydroxylamine hydrochloride with triethylamine followed by treatment with excess hexamethyldisilazane.[10]

$$\text{MeNHOH}\cdot\text{HCl} + \text{Et}_3\text{N} \xrightarrow{(\text{Me}_3\text{Si})_2\text{NH}} \underset{\mathbf{7}}{\text{MeNHOSiMe}_3} + \text{Et}_3\text{N}\cdot\text{HCl}$$

When carried out in pentane, this reaction gave only **7**. When THF was used and the reaction mixture was refluxed for 24 hr, the disilylated product, *N*,*O*-bis(trimethylsilyl)-*N*-methylhydroxylamine (**8**), was also formed but in low yield. However, when *O*-methylhydroxylamine hydrochloride was treated with hexamethyldisilazane in refluxing THF only *N*,*N*-bis(trimethylsilyl)-*O*-methylhydroxylamine (**9**) was obtained and in high yield (85%).

Anionic Rearrangements. Bis(organosilyl)hydroxylamines. The bis(organosilyl)hydroxylamines were deprotonated by reaction with 1 equiv of alkyllithium at −78° in THF–pentane forming a clear solution of the lithium salt, which was added to a solution of the derivatizing agent in the same solvents. These reactions are characterized by high yields and an isomeric distribution of products that is independent of the temperature of the reactants and of the order of addition but greatly dependent on the derivatizing agent used (Table II).

Table II. Anionic Rearrangement of Organosilylhydroxylamines

Compd	Derivatizing agent	% rearranged isomer
1, 4, 7	$RR_2'SiCl$[a]	100
5, 6	$RR_2'SiCl$[a]	75
1, 2, 3, 4	H^+	0
1, 2, 3	MeI	100
4	MeI	50
7	MeI	0

[a] R = R′ = Et for **1**; R = R′ = Me for **4** and **6**; R = *t*-Bu, R′ = Me for **7** and **5**.

We believe the results of all of the derivatization experiments are best interpreted in terms of an equilibrium between the isomeric anions **1a**–**4a** and **1b**–**4b**.

$$\text{RMe}_2\text{Si}\overset{\text{Li}^+}{\bar{\text{N}}}\text{OSiMe}_2\text{R} \underset{\circ}{\overset{\circ}{\rightleftharpoons}} (\text{RMe}_2\text{Si})_2\text{N}\bar{\text{O}}\text{Li}^+$$

1a	R = Me	**1b**
2a	R = Et	**2b**
3a	R = Ph	**3b**
4a	R = *t*-Bu	**4b**

Triorganochlorosilanes give, in every case, only the rearranged isomer, in which the new organosilyl group is attached to the oxygen. For example, when *N*,*O*-bis(trimethylsilyl)hydroxylamine (**1**) is treated with alkyllithium and quenched with triethylchlorosilane, only *N*,*N*-bis(trimethylsilyl)-*O*-triethylsilylhydroxylamine (**10**) is isolated and no trace of the *N*,*O* isomer is detected.[11] Similarly, the lithium salt of *N*,*O*-bis(*tert*-

$$\underset{\mathbf{1}}{\text{Me}_3\text{SiNHOSiMe}_3} \xrightarrow[\text{2. Et}_3\text{SiCl}]{\text{1. RLi}} \underset{\mathbf{10}}{(\text{Me}_3\text{Si})_2\text{NOSiEt}_3}$$

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[9] The nmr spectrum of 1 reported by Wannagat and Smrekar[8] showed two unequal methylsilyl resonances. The authors suggested that the larger downfield peak resulted from the presence of some of the rearranged isomer, $(Me_3Si)_2NOH$, whose methylsilyl protons were accidentally degenerate with one of the peaks of 1. Our results indicate that the impurity is the hydrolysis product, hexamethyldisiloxane. We obtain a spectrum resembling that reported by Wannagat and Smrekar[8] if our sample is exposed to air for a few hours. In a separate experiment, it was shown that the addition of hexamethyldisiloxane to 1 increases the area of the downfield peak in the methylsilyl region.

[10] While this work was in progress, compounds 5, 7, 8, and 9 were prepared by a different method: O. Smrekar and U. Wannagat, *Monatsh. Chem.*, 100, 760 (1969).

[11] Recently, tris(organosilyl)hydroxylamines have been found to undergo a novel intramolecular thermal rearrangement to form silylaminosiloxanes: P. Boudjouk and R. West, *J. Amer. Chem. Soc.*, 93, 5901 (1971).

butyldimethylsilyl)hydroxylamine gives only *N*,*N*-bis(*tert*-butyldimethylsilyl)-*O*-trimethylsilylhydroxylamine (**11**) when treated with trimethylchlorosilane. These results can be explained by a preference of the chlorosilanes for reaction with the oxyanions **1b**–**4b**.

Upon protonation of the lithium salts of the bis(organosilyl)hydroxylamines, ($\mathrm{RMe_2SiNHOSiMe_2R}$), with pyrrole, starting material was recovered quantitatively. No evidence for the formation of $\mathrm{(RMe_2Si)_2NOH}$ isomers was observed. Protonation of the lithium salts of these compounds in an nmr tube at −60° produced the two methylsilyl resonances of the starting compound immediately. If an $\mathrm{(RMe_2Si)_2NOH}$ compound was formed, a single peak at a chemical shift different from the anion peak (peak iii, Figure 1) should be observed. This result implies that anions **1a**–**4a** are stronger bases than **1b**–**4b** although protonation of the rearranged anions **1b**–**4b** followed by instantaneous rearrangement to starting material cannot be ruled out. The absence of disproportionation products in this reaction, however, argues against this possibility.

While only the *O*-methyl isomers **9**, **12**, and **13** are

$$\mathrm{RMe_2SiNHOSiMe_2R} \xrightarrow[\text{2. MeI}]{\text{1. RLi}} \mathrm{(RMe_2Si)_2NOMe}$$

$$\begin{array}{ll} \mathbf{1}, \mathrm{R = Me} & \mathbf{9}, \mathrm{R = Me} \\ \mathbf{2}, \mathrm{R = Et} & \mathbf{12}, \mathrm{R = Et} \\ \mathbf{3}, \mathrm{R = Ph} & \mathbf{13}, \mathrm{R = Ph} \end{array}$$

obtained from **1**, **2**, and **3**, respectively, both the *O*-methyl and *N*-methyl derivatives are isolated in nearly equal amounts from **4** with methyl iodide (eq 2). The

$$\underset{\mathbf{4}}{t\text{-}\mathrm{BuMe_2SiNHOSiMe_2}\text{-}t\text{-}\mathrm{Bu}} \xrightarrow[\text{2. MeI}]{\text{1. RLi}}$$

$$\underset{\mathbf{14}}{t\text{-}\mathrm{BuMe_2SiN(Me)OSiMe_2}\text{-}t\text{-}\mathrm{Bu}} + \underset{\mathbf{15}}{(t\text{-}\mathrm{BuMe_2Si)_2NOMe}} \quad (2)$$

isolation of both **14** and **15** from this reaction provides good evidence for an equilibrium between the rearranged and unrearranged anions of **4** (eq 3). The formation of both isomers could be the result of two factors: (1) that the distribution of anions is such that **4a** is present in greater quantity than the anions **1a**–**3a** in their equilibrium mixtures with **1b**–**3b** and that derivatization with methyl iodide more closely reflects the distribution of anions; or (2) that k_1/k_2 is larger for **4a,b** than for the anions **1a,b**–**3a,b**. An increase in k_1/k_2 could result from a greater increase in steric hindrance in **4b** relative to **4a**. Or, the two $t\text{-}\mathrm{BuMe_2Si}$-groups on nitrogen might reduce intra- or intermolecular coordination of the lithium ion with nitrogen in **4b** (see discussion on ir studies below). Localization of the lithium ion on the oxygen might reduce its nucleophilicity sufficiently to inhibit its reaction with methyl iodide.

$$\begin{tikzcd} \underset{\mathbf{4a}}{t\text{-}\mathrm{BuMe_2Si\bar{N}OSiMe_2}\text{-}t\text{-}\mathrm{Bu}} \arrow[r, shift left] \arrow[d, "k_1"] & \underset{\mathbf{4b}}{(t\text{-}\mathrm{BuMe_2Si)_2NO^-}} \arrow[l, shift left] \arrow[d, "k_2"] \\ \mathbf{14} & \mathbf{15} \end{tikzcd} \quad (3)$$

To establish the inter- or intramolecular nature of the rearrangement, a crossover experiment was carried out. A solution of **1** and **2** was reacted with 1 equiv of alkyllithium followed by addition of the salt solution to a THF–pentane solution of $\mathrm{CH_3I}$. Only **9** and *N*,*N*-bis(ethyldimethylsilyl)-*O*-methylhydroxylamine (**12**) were isolated, no crossover products being detected by glpc. This indicates that the rearrangement is intramolecular as are the anionic rearrangements of silylhydrazines,[12] silylethylenediamines,[13] and silyl-*O*-phenylenediamines.[14]

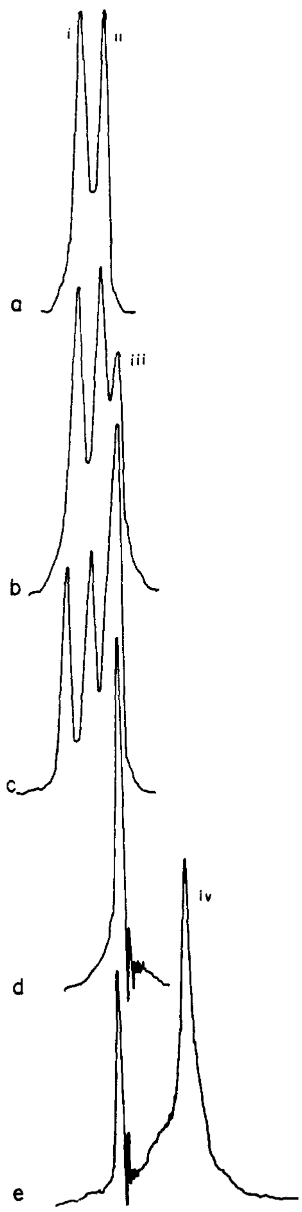

Figure 1. Nmr spectrum of **1** in THF–pentane solution with various amounts of *n*-butyllithium added, showing conversion of **1** to its lithium salt and eventual cleavage to lithium hexamethyldisilazane with excess *n*-BuLi: (a) no *n*-BuLi; (b) 0.25 equiv; (c) 0.50 equiv; (d) 1.00 equiv; (e) 2.00 equiv.

Nmr Studies of Bis(organosilyl)hydroxylamines. The effect of base stoichiometry on the proton nmr of **1** is shown in Figure 1. When **1** was treated with 0.25 equiv of alkyllithium, a third peak (iii) appeared in the methylsilyl region of the nmr with an intensity two-thirds of each of the methylsilyl resonances (i, ii) of **1**. This corresponds to 25% conversion to anionic species. At 0.50 equiv, iii increased to roughly twice the intensity of

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[12] R. West, M. Ishikawa, and R. E. Bailey, *J. Amer. Chem. Soc.*, **89**, 4068 (1967).

[13] R. West, M. Ishikawa, and S. Murai, *ibid.*, **90**, 727 (1968).

[14] H. F. Stewart, D. G. Koepsell, and R. West, *ibid.*, **92**, 846 (1970).

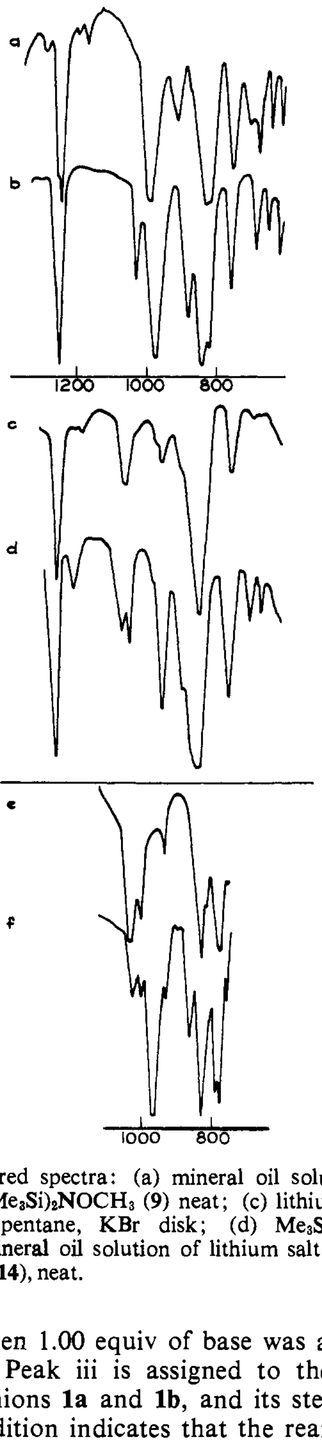


Figure 2. Infrared spectra: (a) mineral oil solution of lithium salt of **1**; (b) (Me$_3$Si)$_2$NOCH$_3$ (**9**) neat; (c) lithium salt of **1** precipitated from pentane, KBr disk; (d) Me$_3$SiN(CH$_3$)OSiMe$_3$ (**8**), neat; (e) mineral oil solution of lithium salt of **4**; (f) (*t*-BuMe$_2$Si)$_2$NOCH$_3$ (**14**), neat.

i and ii. When 1.00 equiv of base was added only iii was visible. Peak iii is assigned to the equilibrium mixture of anions **1a** and **1b**, and its stepwise growth with base addition indicates that the rearrangement is not catalytic as in the case of organosilylhydrazines.[12]

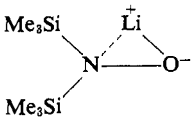
An intramolecular exchange of protons involving **1**, **1a** and/or **1b**, which was slow on the nmr time scale and which would give similar spectra, was ruled out by showing that when **1** was added to a solution of **2a** and **2b** the nmr spectrum of **1** was unchanged. The absence of a peak attributable to the anions of **1** (peak iii, Figure 1) proves that the anions of bis(organosilyl)hydroxylamines are not sufficiently strong bases to deprotonate the parent compounds.

When a solution of **1** in THF–pentane in an nmr tube at -60° was treated with 1.0 equiv of base the two methylsilyl resonances disappeared and were replaced by one peak in less than 45 sec. The same experiment was done with **4** with identical results. These experiments suggest that deprotonation and equilibration of anions are complete within the time of mixing at this temperature.

The nmr spectrum of the solution of the anions **1a,b** was studied at low temperature to see if interconversion of the anions could be observed. However, the single peak (iii) for **1a,b** remained sharp to -80°. The same experiment was then tried with **4** to see if the increased bulk of the organosilicon groups would slow the rate of exchange between **4a** and **4b** or shift the equilibrium constant to allow detection of the individual anions. A single peak was observed over the range 25 to -60° at which temperature the liquid began to glass causing the peak to broaden slightly. These observations can be explained by (1) rapid equilibrium between anions in the temperature range monitored which averages the separate resonances for all three types of protons, or (2) predominance of **1b** and **4b** in the equilibrium mixtures so that only signals from protons in these isomers are observed, or (3) an accidental degeneracy of the chemical shifts of the N-Si-C-H and O-Si-C-H protons in **1a,b** and **4a,b**. The third possibility is very unlikely in view of the different environments of these protons.

Structure of the Anions in Solution. A crude estimate of the equilibrium concentrations of **1a,b** and **4a,b** was obtained from their infrared spectra in solution (Figures 2a and 2e). In both cases, the ir spectra of the salt solutions strongly resemble those of the methyl derivatives of the rearranged anions, **9** and **15**, respectively and suggest that the equilibria may lie far toward **1b** and **4b**.

The Si–N–Si asymmetric stretching absorptions in the salt solutions of both **1** and **4** are at higher frequency than in **9** and **15**. This might be expected because the high electron density on the oxyanion could repel the lone pair of electrons on nitrogen and make them more available to the d orbitals on silicon for back-bonding, thus strengthening Si–N bonds. The ν_{as} Si–N–Si which appears at 970 cm^{-1} for both **9**[15] and **15** is shifted to 990 cm^{-1} for **1b** and to 1035 cm^{-1} in **4b**. The reason for this large difference between **1b** and **4b** is not obvious; if the frequency shift were the result of bond angle changes in the Si–N–Si linkage from steric effects one would expect the ir of **15** to be similarly affected. In **1b**, the lithium ion may be coordinated to some extent by nitrogen either intramolecularly as in I, or intermolecularly, while in **4b** steric hindrance might inhibit this coordination. The lower frequency observed for the Si–N–Si asymmetric stretching frequency in **1b** could then be explained by weak coordination of the lone pair of electrons on nitrogen to lithium making them less available for withdrawal into the d orbitals of silicon than they are in **4b**.



I, **1b**

Structure of the Solid Lithium Salt of *N*,*O*-Bis(trimethylsilyl)hydroxylamine (1). When **1** was treated with 1 equiv of alkyllithium in pentane a white solid precipitated immediately. Addition of this slurry to a

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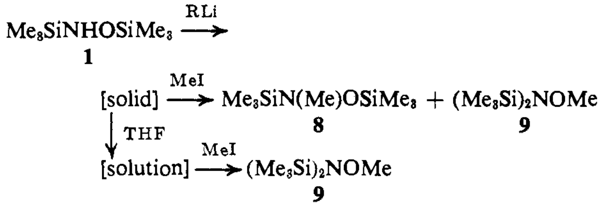
(15) H. Bürger, K. Burczyk, and O. Smrekar, *Monatsh. Chem.*, **100**, 766 (1966).

solution of excess methyl iodide in pentane–THF at −78° produced **8** and **9** in nearly equal amounts. When the slurry was added quickly to a methyl iodide solution at room temperature, **8** and **9** were isolated in a 1 : 19 ratio; slow addition gave only **9**. Solutions of the lithium salt of **1** added to methyl iodide yielded only **9** over a wide range of conditions (eq 4). Investigation of the infrared spectrum of lithium salt of **1** before and after dissolution provides an explanation for these results. In Figure 2c the ir spectrum of the lithium salt of **1** before it has dissolved is shown to be similar to that of **8** (Figure 2d). A solution of this lithium salt in Nujol gives a new spectrum (Figure 2a) characterized by a strong absorption 990 cm^{-1} (ν_{as} Si–N–Si) and resembling the ir spectrum of **9** (Figure 2b). This suggests that the lithium salt precipitates as the unrearranged anion **1a**[16] and rearranges when dissolved. The isolation of **8** from reactions of methyl iodide with slurries of **1a** apparently results from solid **1a** reacting before it has an opportunity to rearrange.



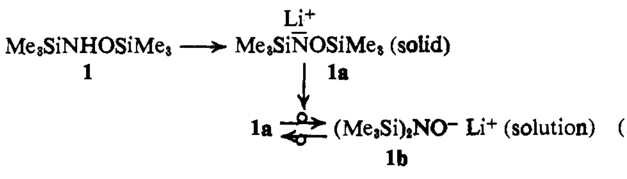
$$\underset{1}{\mathrm{Me_3SiNHOSiMe_3}} \xrightarrow{\mathrm{RLi}}$$

$$[\text{solid}] \xrightarrow{\mathrm{MeI}} \underset{8}{\mathrm{Me_3SiN(Me)OSiMe_3}} + \underset{9}{\mathrm{(Me_3Si)_2NOMe}} \qquad (4)$$

$$\downarrow \mathrm{THF}$$

$$[\text{solution}] \xrightarrow{\mathrm{MeI}} \underset{9}{\mathrm{(Me_3Si)_2NOMe}}$$

Nmr and ir spectra are consistent with the structures proposed for **8** and **9**. Further support was obtained by independent syntheses of **8** and **9** by silylation of *N*-methylhydroxylamine hydrochloride and *O*-methylhydroxylamine hydrochloride, respectively, with hexamethyldisilazane (eq 5).

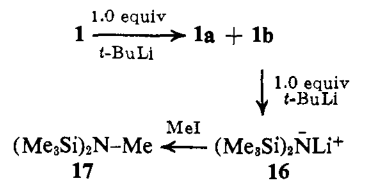


$$\underset{1}{\mathrm{Me_3SiNHOSiMe_3}} \longrightarrow \mathrm{Me_3Si\overset{Li^+}{\bar{N}}OSiMe_3}\ (\text{solid})\ \ \mathbf{1a}$$

$$\downarrow$$

$$\mathbf{1a} \overset{\Delta}{\rightleftharpoons} \underset{\mathbf{1b}}{\mathrm{(Me_3Si)_2NO^-\ Li^+}}\ (\text{solution}) \qquad (5)$$

Cleavage Reactions of 1. When excess alkyllithium was added to **1**, a new peak iv (Figure 1) appeared upfield from iii. Unlike iii, it broadened and separated into two resonances at lower temperatures. This new peak is assigned to the lithium salt of hexamethyldisilazane (**16**). The low temperature nmr spectra we observed are similar to those reported by Kimura and Brown[17] and attributed to monomer–dimer equilibria in **16**. Further support for the assignment of iv to the protons of **16** comes from a preparative scale reaction. Treatment of **1** with 2.0 equiv of *tert*-butyllithium at −78° followed by derivatization with methyl iodide gave a 70% yield of heptamethyldisilazane (**17**) (eq 6).



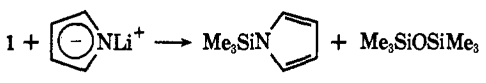
$$1 \xrightarrow[t\text{-BuLi}]{1.0\ \text{equiv}} \mathbf{1a} + \mathbf{1b}$$

$$\downarrow \tfrac{1.0\ \text{equiv}}{t\text{-BuLi}} \qquad (6)$$

$$\underset{17}{\mathrm{(Me_3Si)_2N{-}Me}} \xleftarrow{\mathrm{MeI}} \underset{16}{\mathrm{(Me_3Si)_2\bar{N}Li^+}}$$

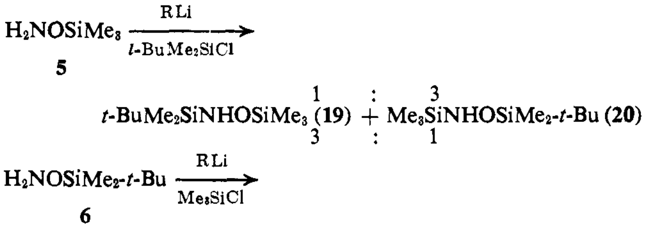
The cleavage of the N–O bond in alkylhydroxylamines by alkyllithiums is a known route to amines[18] but this is the first example of such a cleavage in organosilylhydroxylamines and is potentially valuable as a method of generating unsymmetrical disilazanes.

If **1** is refluxed in solution with the pyrrole anion for 48 hr the latter attacks the Si–N bond and two new products, *N*-trimethylsilylpyrrole (**18**) and hexamethyldisiloxane, are formed at the expense of **1**. The same results can be obtained if equivalent amounts of **1** and pyrrole are refluxed in THF after a catalytic amount of alkyllithium has been added.



18

Mono(organosilyl)hydroxylamines. Anionic rearrangement of mono(organosilyl)hydroxylamines was observed for *O*-trimethylsilylhydroxylamine (**5**), *O-tert*-butyldimethylsilylhydroxyamine (**6**), and *O*-trimethylsilyl-*N*-methylhydroxylamine (**7**). Reaction of the lithium salt of **5** with *tert*-butyldimethylchlorosilane gave **19** and **20** in a 1:3 ratio in 40% yield. If **6** is reacted with *n*-butyllithium and derivatized with trimethylchlorosilane, **19** and **20** are obtained in a 3 : 1 ratio in 60% yield. Thus in each of these reactions about 75% of the rearranged derivative was obtained. This result is probably fortuitous, since the proportion of product isomers need not reflect the equilibrium concentration of anions. Both isomers can also be obtained when a weaker base is used. For example, when **5** is reacted with equivalent amounts of triethylamine and *tert*-butyldimethylchlorosilane, **19** and **20** are obtained in a 3 : 1 ratio. No crossover products are detected, suggesting that anionic rearrangement may be responsible for the presence of both isomers rather than intermolecular exchange. The predominance of the unrearranged isomer (**19**) in this reaction probably reflects the weaker basicity of triethylamine compared to *n*-butyllithium resulting in the formation of fewer anions.

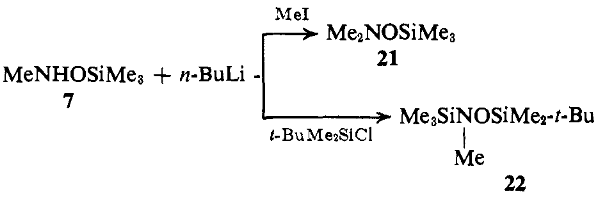


$$\underset{5}{\mathrm{H_2NOSiMe_3}} \xrightarrow[t\text{-}\mathrm{BuMe_2SiCl}]{\mathrm{RLi}}$$

$$\underset{\substack{1\\3}}{} \quad t\text{-}\mathrm{BuMe_2SiNHOSiMe_3}\ (\mathbf{19}) + \mathrm{Me_3SiNHOSiMe_2}\text{-}t\text{-}\mathrm{Bu}\ (\mathbf{20}) \quad \begin{matrix}1 : 3\\ 3 : 1\end{matrix}$$

$$\underset{6}{\mathrm{H_2NOSiMe_2}\text{-}t\text{-}\mathrm{Bu}} \xrightarrow[\mathrm{Me_3SiCl}]{\mathrm{RLi}}$$

When *O*-trimethylsilyl-*N*-methylhydroxylamine (**7**) is treated with alkyllithium in pentane at room temperature a vigorous reaction occurs but no salt precipitates. Derivatization with methyl iodide gives only the unrearranged isomer, *N*,*N*-dimethyl-*O*-trimethylsilylhydroxylamine (**21**). However, if lithiated **7** is treated



$$\underset{7}{\mathrm{MeNHOSiMe_3}} + n\text{-}\mathrm{BuLi} \begin{cases} \xrightarrow{\mathrm{MeI}} \underset{21}{\mathrm{Me_2NOSiMe_3}} \\ \xrightarrow[t\text{-}\mathrm{BuMe_2SiCl}]{} \underset{22}{\mathrm{Me_3Si\underset{Me}{\underset{|}{N}}OSiMe_2}\text{-}t\text{-}\mathrm{Bu}} \end{cases}$$

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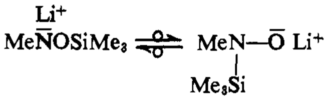
[16] The assignment of the ir spectrum in Figure 2c to **1a** is based not only on its similarity to that of **8** but also on the fact that there is no band in the region 830–1250 cm^{-1} assignable to ν_{as} Si–N–Si. This rules out the possibility that the ir spectrum in Figure 2c is that of an associated form of 16.

[17] B. Y. Kimura and T. L. Brown, *J. Organometal. Chem.*, **26**, 57 (1971).

[18] P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," Vol. 2, W. A. Benjamin, New York, N. Y., 1966, Chapter 1.

with *tert*-butyldimethylchlorosilane, the rearranged isomer (**22**) is obtained. The difference in the isomeric structure of the products reflects the selectivity of the derivatizing agent toward the unrearranged and rearranged anions, which are probably in equilibrium. Apparently, methyl iodide reacts much faster with **7a** than **7b**, whereas *tert*-butyldimethylchlorosilane reacts



$$\overset{Li^+}{\text{MeNOSiMe}_3}\ \underset{\circ}{\overset{\circ}{\rightleftharpoons}}\ \text{MeN(SiMe}_3\text{)}\text{—}\bar{\text{O}}\ \text{Li}^+$$

7a **7b**

preferentially with **7b**. The solubility of the lithium salt in pentane suggests that it may not be monomeric in solution.

Discussion

The course of the rearrangement of organosilylhydroxylamine anions seems to be governed largely by electronic factors. The greater stability of the oxyanion compared to the nitrogen anion apparently outweighs the difference in the Si–O and Si–N bond energies (106 and 76 kcal, respectively). Although the rate of migration from oxygen to nitrogen could not be deter-

$$R_3Si\bar{N}OSiR_3 \underset{\circ}{\overset{\circ}{\rightleftharpoons}} (R_3Si)_2N\bar{O}$$

mined exactly, our nmr studies show that equilibration of hydroxylamine anions occurs in less than 45 sec at −60°, and from ir data we estimate that the equilibrium lies far to the right. This facile migration of organosilicon groups suggests that the transition state is of relatively low energy in which silicon utilizes its vacant d orbitals to form a pentacoordinate bridged structure between oxygen and nitrogen.

Experimental Section

Analytical and preparative gas chromatography was carried out using a Varian Aerograph Model 90-P chromatograph. The analytical columns used were 0.25 in. × 16 ft aluminum columns packed with 20% SE-30, 20% QF-1 or 20% Carbowax 20M liquid substrates on 60–80 mesh Chromosorb W with a helium flow of 60 ml/min. The preparative separations were carried out using a $^3/_8$ in. × 6 ft stainless steel column packed with 20% SE-30 silicone fluid on Prep Grade Chromosorb W and a helium flow of 200 ml/min. Both analytical and preparative separations were done isothermally, usually at temperatures 30–75° below the boiling point of the desired compound. Proton nmr spectra were determined with a Varian A-60A spectrometer equipped with a variable-temperature probe. Chemical shifts were obtained by internal referencing with benzene in 15–20% v/v solutions. Nmr data are summarized in Table I. Ir spectra were obtained as neat liquid films or Nujol mulls on NaCl plates on a Perkin-Elmer 457 grating spectrophotometer and were consistent with the proposed structures in every case. All boiling points and melting points were uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc.

Materials. All chemicals were reagent grade materials. Solvents such as THF, petroleum ether, decalin, benzene, and ether were further purified by refluxing over lithium aluminum hydride or sodium followed by fractional distillation just before use.

Triethylchlorosilane and phenyldimethylchlorosilane were obtained from Pierce Chemical Co. and used without further purification. Hydroxylamine hydrochloride (Mallinckrodt), *O*-methylhydroxylamine hydrochloride, and *N*-methylhydroxylamine hydrochloride (Aldrich) were placed over Drierite in an evacuated desiccator for 24 hr before using. Hydroxylamine was prepared by the method of Hurd.[19] Triethylamine was distilled from barium oxide immediately before use. Ethyldimethylchlorosilane was prepared by the action of ethylmagnesium bromide on dimethyldichlorosilane. *tert*-Butyldimethylchlorosilane was prepared by treating dimethyldichlorosilane with 1 equiv of *tert*-butyllithium.[20] The purity of these chlorosilanes was checked prior to use by analytical gas chromatography and infrared spectroscopy. Methyl iodide and pyrrole were distilled immediately before use.

All reactions were carried out in Pyrex glassware dried in a 160° oven for at least 3 hr and then purged with dry nitrogen before use. A nitrogen atmosphere was used in all preparations. Filtrations were carried out by nitrogen pressure filtration through a glass frit, and the filtrates were collected in dry nitrogen-filled flasks. Distillations were conducted under nitrogen or at reduced pressure.

***N*,*O*-Bis(trimethylsilyl)hydroxylamine (1).** To a well-stirred slurry of 69.5 g (1.0 mol) of hydroxylamine hydrochloride in 300 ml of pentane and 100 ml of THF was added 305 ml (249 g, 1.5 mol) of hexamethyldisilazane. The mixture was refluxed for 20 hr followed by filtration of NH_4Cl and distillation to yield 142 g (80%) of crude **1**. A second filtration was necessary to remove additional precipitated NH_4Cl. Distillation through a spinning band column gave pure **1** (126 g, 71%), bp 137–139°. The proposed structure was consistent with the nmr[9] and ir spectra.

Anal. Calcd for $C_6H_{19}NSi_2O$: C, 40.62; H, 10.80; N, 7.94; Si, 31.66. Found: C, 40.87; H, 10.81; N, 7.69; Si, 31.92.

One-Step Synthesis of 1 and *O*-Trimethylsilylhydroxylamine (5). To a well-stirred slurry of 34.8 g (0.5 mol) of hydroxylamine hydrochloride and 35.1 ml (25.3 g, 0.25 mol) of triethylamine in 200 ml of pentane was added 102 ml (80.5 g, 0.5 mol) of hexamethyldisilazane. This reaction mixture was allowed to stir overnight at room temperature and refluxed for a few hours prior to work-up to ensure completion. Filtration of the salts under nitrogen was followed by distillation on the spinning band column. **5** (33 g), bp 98–100°, and 31 g of **1**, bp 137–139°, were collected for yields of 62 and 70%, respectively.

Anal. Calcd for $C_3H_{11}NSiO$: C, 34.25; H, 10.53; N, 13.31; Si, 26.70. Found: C, 34.41; H, 10.60; N, 13.28; Si, 26.91.

***N*,*O*-Bis(ethyldimethylsilyl)hydroxylamine (2), *N*,*O*-bis(phenyldimethylsilyl)hydroxylamine (3), and *N*,*O*-bis(*tert*-butyldimethylsilyl)hydroxylamine (4)** were prepared in yields of 65–70% by Wannagat's method[8] from hydroxylamine, triethylamine, and a chlorosilane. The boiling points of **2**, **3**, and **4** were 180–182°, 112–115° (0.2 Torr), and 72° (2 Torr), respectively.

Anal. Calcd for $C_8H_{23}NSiO$ (**2**): C, 46.76; H, 11.28; N, 6.81; Si, 27.34. Found: C, 46.70; H, 11.35; N, 6.97; Si, 27.39. Calcd for $C_{16}H_{23}NSi_2O$ (**3**): C, 63.73; H, 7.69; N, 4.65; Si, 18.63. Found: C, 63.88; H, 7.91; N, 4.85; Si, 18.50. Calcd for $C_{12}H_{31}NSi_2O$ (**4**): C, 55.11; H, 11.95; N, 5.36; Si, 21.48. Found: C, 54.91; H, 11.72; N, 5.63; Si, 21.73.

From a lower boiling fraction, 80–100° (60 Torr), obtained in the synthesis of **4**, 2 g of *O*-*tert*-butyldimethylsilylhydroxylamine (**6**), mp 63–64°, was isolated by preparative glpc. A small amount of *tert*-butyldimethylchlorosilane was also recovered.

Anal. Calcd for $C_6H_{17}NSiO$ (**6**): C, 48.93; H, 11.63; N, 9.51; Si, 19.07. Found: C, 49.04; H, 11.64; N, 9.78; Si, 19.34.

***O*-Trimethylsilyl-*N*-methylhydroxylamine (7).** To a well-stirred slurry of 10 g (0.12 mol) of MeNHOH·HCl in 50 ml of pentane was added 16.8 ml (12.1 g, 0.12 mol) of Et_3N at room temperature. Reaction occurred immediately causing the solvent to reflux and the formation of a clumpy white solid. After the mixture was stirred at room temperature for 12 hr, 29.8 ml (19.3 g, 0.12 mol) of hexamethyldisilazane was added *via* syringe through a rubber septum. This reaction mixture was stirred for 24 hr at room temperature and then filtered to remove the solid. The clear amber filtrate was distilled on a spinning band to give 10.5 g (72%) of **7**, bp 95°.

Anal. Calcd for $C_4H_{13}NSiO$: C, 40.29; H, 10.99; N, 11.75; Si, 23.55. Found: C, 40.37; H, 10.79; N, 11.59; Si, 23.80.

***N*,*O*-Bis(trimethylsilyl)-*N*-methylhydroxylamine (8).** The procedure described for the synthesis of **7** was followed except that THF was used as a solvent instead of pentane. Distillation of the filtrate gave 9.0 g of **7** and 4.0 g of **8**, bp 85° (97 Torr).

Anal. Calcd for $C_7H_{21}NSi_2O$: C, 43.91; H, 11.05; N, 7.35; Si, 29.33. Found: C, 43.96; H, 11.01; N, 7.22; Si, 29.21.

***N*,*N*-Bis(trimethylsilyl)-*O*-methylhydroxylamine (9).** To a slurry of 8.35 g (0.10 mol) of *O*-methylhydroxylamine hydrochloride in 35 ml of THF was added 41.5 ml (0.10 mol) of hexamethyldisilazane. The reaction mixture was refluxed for 24 hr, then filtered under nitrogen, and distilled, bp 90° (97 Torr), to give 16.2 g (85%) of **9**.

Anal. Found: C, 43.84; H, 10.91; N, 7.21; Si, 29.41.

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[19] C. D. Hurd, *Inorg. Syn.*, 1, 87 (1939).

[20] R. West, M. Ishikawa, and R. E. Bailey, *J. Amer. Chem. Soc.*, **88**, 4648 (1966).

Anionic Rearrangement Reactions. a. General Procedure. The anionic species of the organosilylhydroxylamine substrates were generated at −78° in a modified reaction vessel consisting of a 100-ml, three-necked, round-bottomed flask fitted with an exit stopcock at the bottom. The reaction vessel was encased in a 1000-ml beaker fitted just above the stopcock. This apparatus allowed temperature control of the solution of anions. Reagents were added by syringe through a rubber serum stopper or *via* a small addition funnel. The reaction mixture was stirred by a motor driven stirrer operated through the center neck. A nitrogen atmosphere was maintained at all times. Solutions of the deprotonated organosilylhydroxylamines were derivatized by adding them to a pentane–THF solution of the trapping agent. The temperature of the derivatizing solution was controlled using suitable baths. Salts resulting from these reactions were removed by nitrogen pressure filtration through a glass frit or by high vacuum distillation of the liquid at the lowest possible temperatures. Reaction products were then isolated by distillation or preparative gas chromatography. For compounds **1**, **2**, **3**, and **4** derivatization with pyrrole gave back starting material quantitatively.

b. Nmr Investigations of the Anions of 1 and 4. Two methods were used to prepare nmr samples. (1) The general procedure outlined in **a** was followed and a small aliquot of the salt solution was removed from the flask by syringe technique and injected into a dry, N_2-filled nmr tube fitted with a rubber septum. (2) An nmr tube, after being dried and purged with nitrogen, was fitted with a serum cap and a needle attached to a nitrogen line. Solvent, substrate, and base were then added to the nmr tube using a syringe. The base was slowly added to the reaction mixture at −78° and was allowed to run down the walls of the tube. The contents of the tube were shaken at intervals during the addition to ensure good mixing.

The effect of base stoichiometry was determined by stepwise addition of alkyllithium (0.25, 0.50, 1.00, and 2.00 equiv) to **1** and following the progress of the reaction by scanning the methylsilyl region of the nmr. Both procedures for preparing samples described above were used to carry out these experiments.

To an nmr tube containing 0.037 g (0.14 mmol) of **2** in a THF–pentane solution was added 0.07 mmol of *n*-butyllithium. To this was added 0.025 g (0.14 mmol) of **1**. Scanning of the methylsilyl region of the nmr showed only two equally intense peaks. The nmr spectrum remained unchanged over a 2-hr period.

To measure the rate of deprotonation and the rate of equilibration of anions a solution of **1** in THF–pentane at −78° was treated with 1.0 equiv of base in an nmr tube. The contents of the tube were mixed by shaking the tube in a Dry Ice–acetone bath. The tube was then quickly wiped dry and inserted into the nmr probe which had been cooled to −60° and the methylsilyl region was scanned at 100 sec sweep time. The time elapsed between the complete addition of base and the scan of the methylsilyl region was about 45 sec.

c. Infrared Spectra of the Lithium Salts of 1 and 4. To a solution of 1.0 g (5.7 mmol) of **1** dissolved in 3 ml of pentane was added 2.8 ml (5.7 mmol) of 1.6 *M* *n*-butyllithium in hexane at −78°. A white solid precipitated immediately. The solid was allowed to settle to the bottom of the flask and most of the liquid was drawn off with a syringe. The remaining solvent was pumped off. A small amount of the dry solid was then mixed with dried, finely ground KBr in a nitrogen-filled glove bag and the mixture molded into a pellet. The infrared spectrum of this salt is shown in Figure 2c and compared with that of **8** (Figure 2d). To obtain the spectrum of the salt in solution (Figure 2a) a small amount of the solid was dissolved in Nujol. The ir spectrum of the solution of the lithium salt of **4** (Figure 2c) was obtained in the same manner and is compared with the spectrum of **15** (Figure 2f). The ir spectra of **8**, **9**, and **15** were taken as neat liquid films on sodium chloride plates.

Reactions of Deprotonated *N*,*O*-Bis(trimethylsilyl)hydroxylamine (1). i. With Methyl Iodide. A salt solution of **1** was prepared as described above and added to a threefold excess of methyl iodide in a pentane–THF solution. The LiI formed was removed by filtration under nitrogen, and the filtrate was distilled to give 4.0 g (91%) of **9**, bp 90° (97 Torr). Nmr supported the proposed structure and further confirmation was obtained by comparing the ir spectrum of **9** with that of a sample prepared from hexamethyldisilazane and *O*-methylhydroxylamine hydrochloride. When **1** was reacted with base in pentane and the salt was allowed to precipitate, reaction with methyl iodide in pentane–THF at −78° gave two products in approximately equal amounts. These were isolated by gas chromatography. One of these was **9**, and nmr spectral data for the other product were consistent with structure **8**. The structure of **8** was further confirmed by comparison of its ir spectrum with that of a sample synthesized from hexamethyldisilazane and *N*-methylhydroxylamine hydrochloride.

ii. With Triethylchlorosilane. A salt solution of **1** prepared as described above was slowly added to a solution of excess triethylchlorosilane in pentane and THF. The next day LiCl was removed by filtration and the clear yellow filtrate was distilled to give 4.6 g (69%) of **10**, bp 63° (15 Torr).

Anal. Calcd for $C_{12}H_{33}NSi_3O$: C, 49.42; H, 11.41; N, 4.80; Si, 28.89. Found: C, 49.32; H, 11.41; N, 4.86; Si, 28.67.

Reaction of Deprotonated *N*,*O*-Bis(phenyldimethylsilyl)hydroxylamine (3) with Methyl Iodide. A salt solution of **3** was prepared as described above and added to a solution of excess methyl iodide in pentane and THF. After filtration of LiI, the liquid was distilled to give 3 g of a clear oily liquid, bp 112–117° (0.4 Torr). Glpc analysis showed two products in a 19:1 ratio. The minor product gave ir and nmr spectra consistent with the siloxane, $(PhMe_2Si)_2O$, and is probably the result of hydrolysis during the work-up. The major product, **13**, was isolated by preparative gas chromatography, yield 85%.

Anal. Calcd for $C_{17}H_{25}NSi_2O$: C, 64.71; H, 7.99; N, 4.44; Si, 17.80. Found: C, 64.62; H, 8.16; N, 4.19; Si, 18.08.

Reactions of Deprotonated *N*,*O*-Bis(*tert*-butyldimethylsilyl)hydroxylamine (4). i. With Methyl Iodide. A salt solution of **4** was prepared as described above and added to excess methyl iodide in pentane and THF. Glpc analysis of the residue obtained after removal of LiI and solvents showed two major products. These were isolated by preparative gas chromatography and gave nmr spectra consistent with the isomers **14** and **15**.

Anal. Calcd for $C_{12}H_{33}NSi_2O$: C, 56.66; H, 12.07; N, 5.08; Si, 20.38. Found (**14**): C, 56.38; H, 12.06; N, 5.27; Si, 20.16. Found (**15**): C, 56.62; H, 12.15; N, 4.95; Si, 20.61.

ii. With Trimethylchlorosilane. A salt solution of **4** prepared as described above was added to a solution of excess trimethylchlorosilane in pentane and THF. After removal of LiCl the clear orange filtrate was distilled giving 4.8 g (88%) of **11**, bp 102° (4 Torr).

Anal. Calcd for $C_{12}H_{39}NSi_3O$: C, 53.98; H, 11.79; N, 4.20; Si, 25.25. Found: C, 54.11; H, 11.65; N, 4.21; Si, 25.51.

The Crossover Experiment. A solution of 2.70 g (13.1 mmol) of **2** and 3.15 g (17.8 mmol) of **1** in 40 ml of a 3:1 hexane–THF mixture was treated with 20 ml (32 mmol) of 1.6 *M* *n*-butyllithium at −78°. After the mixture was stirred for 2 hr, the salt solution was slowly added to a room-temperature solution of 12.8 g (90 mmol) of methyl iodide in a hexane–THF solution. The next day the solid was removed by filtration under nitrogen and solvent was removed by distillation. The residue was analyzed by glpc and showed only two products. Isolation by glpc preparative methods gave **9** and **12**. No crossover products were detected indicating that the rearrangement occurs intramolecularly. Ir and nmr spectra for **12** were consistent with the proposed structure.

Anal. Calcd for $C_9H_{25}NSi_2O$: C, 49.25; H, 11.48; N, 6.38; Si, 25.60. Found: C, 49.09; H, 11.36; N, 6.50; Si, 25.76.

Reaction of *O*-Trimethylsilylhydroxylamine (5) with Triethylamine and *tert*-Butyldimethylchlorosilane. To a solution of 1.05 g (10 mmol) of **5** and 1.8 g (10 mmol) of triethylamine in 20 ml of ether at −78° was added a solution of 1.5 g (10 mmol) of *tert*-butyldimethylchlorosilane in 15 ml of pentane. The reaction mixture was allowed to warm to room temperature and stir overnight. Triethylamine hydrochloride was removed by filtration under nitrogen and the solvent was removed by distillation. Although analysis by glpc showed only one product, two isomers were visible in the nmr, and from measurements of peak height, the ratio of **19** to **20** estimated to be 4:1. The nmr of the mixture showed five resonances at τ 9.84, 9.73, 8.97, 8.91, and 5.2 with relative intensities of 33, 42, 36, 9, and 9, respectively. The relative areas of the Si-*t*-Bu peaks at τ 8.97 and 8.91 give the ratio of the two isomers. The absorption at τ 8.91 is assigned to O–Si-*t*-Bu protons and the resonances at τ 8.97 to the N–Si-*t*-Bu protons. The methylsilyl region is complicated by two cases of accidental degeneracy. The O–Si–C–H protons of **19** and **20** absorb at τ 9.73 while the N–Si–C–H protons resonate at τ 9.84. The relative areas of these peaks agree with the theoretical value for a 4:1 mixture of isomers. The two isomers could not be separated and were analyzed as a mixture.

Anal. Calcd for $C_9H_{25}NSi_2O$: C, 49.25; H, 11.48; N, 6.38; Si, 25.59. Found: C, 49.49; H, 11.31; N, 6.47; Si, 25.36.

Reaction of Deprotonated 5 with *tert*-Butyldimethylchlorosilane. To 1.0 g (10 mmol) of **5** dissolved in a 4:1 pentane–THF mixture at −78° was added 1 equiv of *n*-butyllithium. After 10 min 1.5 g (1.0 mmol) of *tert*-butyldimethylchlorosilane dissolved in 10 ml of pentane was added to the salt solution. After removal of salts and solvent the products were isolated by preparative glpc. **19** and **20** were obtained in a 1:3 ratio, respectively (estimated by nmr). Total yield was about 40%.

Reaction of Deprotonated *O-tert*-Butyldimethylsilylhydroxylamine (6) with Trimethylchlorosilane. To a solution of 0.25 g (1.7 mmol) of **6** dissolved in a 4:1 pentane–THF mixture at −78° was added 1 equiv of *n*-butyllithium. After 10 min 0.2 g (1.8 mmol) of trimethylchlorosilane was added to the solution. The salts and solvent were removed and the products isolated by glpc preparative methods. **19** and **20** were obtained in a 3:1 ratio, respectively (estimated by nmr). Total yield was about 60%.

Cleavage Reactions of 1. Cleavage of the N–O Bond in the Lithium Salt of 1 by *tert*-Butyllithium. To a stirred solution of 10 ml (8.0 g, 45 mmol) of **1** in 35 ml of pentane was added 73 ml (90 mmol) of 1.24 *M tert*-butyllithium over a 30-min period producing a white slurry. After the mixture was stirred at room temperature for 24 hr, the slurry was slowly added to a solution of 15 g (105 mmol) of MeI in 50 ml of pentane at −78°, which dissolved the salt immediately. After the mixture was stirred for 10 min, 10 ml of THF was added causing solid to precipitate. The reaction mixture was warmed slowly to room temperature and stirred overnight. The next day the liquid was removed from the reaction vessel by vacuum distillation and collected in a Dry Ice trap. Glpc analysis of the crude reaction mixture showed one major product. Distillation of the product mixture afforded 6.1 g (77%) of heptamethyldisilazane (**17**).[21] The ir of this compound was superimposable with that of a known sample.

Cleavage of the Si–N Bond in 1 by the Lithium Salt of Pyrrole. A solution of 4.05 g (22.9 mmol) of **1** in THF–pentane was reacted with 1 equiv of *n*-butyllithium at −78°. The salt solution was then treated with 1.5 g (23 mmol) of pyrrole producing an amber colored solution. This reaction mixture was then refluxed for 48 hr. The liquid was removed from the reaction vessel by vacuum distillation and collected in a Dry Ice trap. Glpc analysis of this liquid showed two products. They were isolated by glpc preparative methods. The product with shorter retention time was identified as hexamethyldisiloxane. *N*-Trimethylsilylpyrrole (**18**) was also isolated (1 g, 30%), and its structure was confirmed by comparison of its ir and nmr spectra with that of a sample prepared from the reaction of potassium pyrrole and trimethylchlorosilane.[22] The same products were obtained when equivalent amounts of **1** and pyrrole were refluxed in THF and a catalytic amount of alkyllithium was added.

Anal. Calcd for $C_7H_{13}NSi$: C, 60.37; H, 9.41; N, 10.06; Si, 21.17. Found: C, 60.29; H, 9.45; N, 10.16; Si, 20.34.

Reactions of Deprotonated *O*-Trimethylsilyl-*N*-methylhydroxylamine (7). i. With Methyl Iodide. To a solution of 4.0 g (33 mmol) of **7** dissolved in 20 ml of pentane was added 21 ml (23.6 mmol) of 1.6 *M n*-butyllithium at room temperature. Sufficient heat to reflux pentane was evolved and a clear colorless solution was formed. After the mixture was stirred for 24 hr at room temperature the solution had become slightly cloudy and was added to a pentane–THF solution of excess methyl iodide. Precipitation of a white solid occurred immediately. This reaction mixture was stirred overnight at room temperature. The liquid was removed from the solid by vacuum distillation at 25° and was collected in a Dry Ice trap. The clear colorless solution was distilled at atmospheric pressure and 3.8 g (86%) of **21** was collected at 40–45° (97 Torr). Ir and nmr spectra were consistent with the proposed structure. Analytically pure samples were obtained by preparative gas chromatography.

Anal. Calcd for $C_5H_{15}NSiO$: C, 45.06; H, 11.35; N, 10.51; Si, 21.07. Found: C, 44.94; H, 11.44; N, 10.61; Si, 21.30.

ii. With *tert*-Butyldimethylchlorosilane. To a solution of 1.22 g (10.22 mmol) of **7** in 10 ml of pentane was added 6.5 ml (10.4 mmol) of 1.6 *M n*-butyllithium in pentane–THF. The reaction mixture changed to pale yellow but salt did not precipitate for several hours. Analysis of the reaction mixture by glpc showed one product. The solid was removed by filtration and the product was isolated (1.65 g, 70%) by glpc preparative methods. Ir and nmr spectra were consistent with the proposed structure for **22**.

Anal. Calcd for $C_9H_{25}NSi_2O$: C, 51.44; H, 11.66; N, 6.00; Si, 24.06. Found: C, 51.33; H, 11.71; N, 6.06; Si, 23.87.

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Hydrolysis of Acyl-Activated Thiol Esters. Acid Catalysis and Acid Inhibition[1a]

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Abstract: The hydrolysis of 11 acyl-activated thiol esters RCOSR′ has been studied in the pH range 0–12 at 30°. Strongly acyl-activated thiol esters ($R = CF_3, CCl_3, CF_3CF_2$) show pronounced acid inhibition of the rate of hydrolysis at pH <2. Weakly acyl-activated thiol esters ($R = CH_2Cl, NO_2CH_2$) undergo acid-catalyzed hydrolysis. Thiol esters with electron-withdrawing substituents of intermediate strength ($R = CHF_2, CH_3SCO, CHCl_2$) show either modest acid inhibition or inhibition followed by acid catalysis as acidity increases further. A general mechanism which includes anionic, neutral, and cationic tetrahedral intermediates is proposed to account for the observed pH–rate profiles, with the existence of acid inhibition being directly related to the ratio of the rate constants for breakdown of the neutral intermediate to products and reactants.

In weakly acidic solution, the hydrolysis of thiol esters derived from acetic acid,[2] formic acid,[3] and benzoic[4] acid exhibits acid catalysis. In intriguing contrast, the rate of hydrolysis of thiol esters derived from trifluoroacetic acid is inhibited at acid concentra-

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