Rearrangement of Organosilyl Groups between Oxygen and Nitrogen in Tris(organosilyl)hydroxylamines: A Possible Dyotropic Rearrangement[1]

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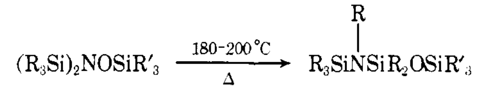
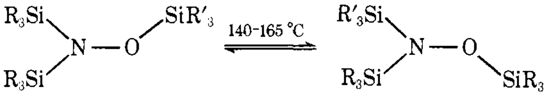
Abstract: Tris(organosilyl)hydroxylamines when heated undergo a reversible 1,2 rearrangement of organosilicon groups between oxygen and nitrogen. The rearrangement was studied by NMR at temperatures ranging from 139 to 162 °C. Kinetic data and activation parameters obtained indicate that the rearrangement is probably occurring by a type 1 dyotropic process, involving a four-centered transition state. Preparation and characterization of several new tris(organosilyl)hydroxylamines are described.

Several years ago, we reported that tris(organosilyl)hydroxylamines were irreversibly thermally isomerized at 180-200 °C to the corresponding silylaminosiloxanes[2] (eq 1).



$$(R_3Si)_2NOSiR'_3 \xrightarrow[\Delta]{180\text{-}200\,^\circ C} R_3Si\overset{\overset{R}{|}}{N}SiR_2OSiR'_3 \qquad (1)$$

It became evident (when R ≠ R′) that the irreversible thermal rearrangement was accompanied in many cases by a reversible rearrangement involving positional exchange between the organosilicon groups on oxygen and nitrogen[3] (eq 2).



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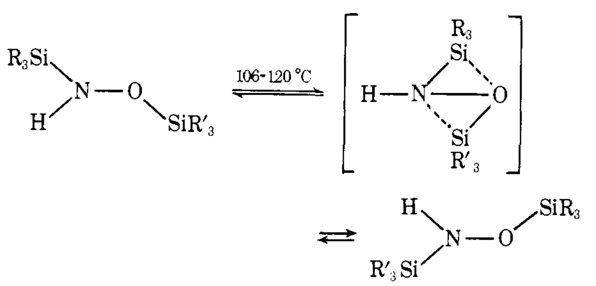
1 **2**

A few other examples of exchange of organosilyl moieties leading to positional isomers are now known. Frainnet and co-workers have described an exchange in bis(organosilyl)-hydroxylamines[4] (eq 3), which they suggest proceeds via a four-center intermediate in which there is (p-d) π interaction of silicon with lone pairs on oxygen and nitrogen.



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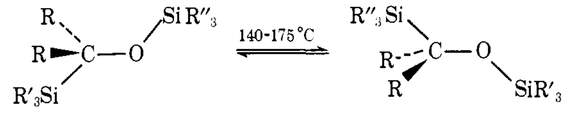
Recently Reetz and co-workers have reported a similar rearrangement in (silyl)methyl silyl ethers (eq 4), which they believe proceeds by a type I dyotropic mechanism.[5,6] A type I dyotropic process involves two migrating groups (e.g., SiR_3, SiR'_3) and two stationary atoms (e.g., C-O or N-O) which may be connected directly or through a conjugated π system. The type I rearrangement is a pericyclic, thermally forbidden, photochemically allowed $[\sigma_{2s} + \sigma_{2s}]$ process involving a concerted shift through a four-membered transition state. The reaction can be changed from a forbidden to an allowed process by utilization of d orbitals on silicon (or any atom with low-lying unfilled d orbitals), which are able to stabilize the four-centered bridged intermediates through interaction with the highest occupied molecular orbital (HOMO) of the X-Y system (eq 5).



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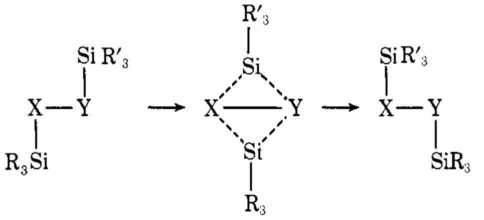

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In this work, we have studied a series of tris(organosilyl)-hydroxylamines in order to determine the generality of the reaction and investigate the effect of change of substituents on silicon upon the course of the rearrangement. In the compounds studied, we have varied the substituents on only one of the organosilyl groups in order to clearly see substituent effects and to minimize gross differences in conformation about the nitrogen-oxygen bond.

Syntheses

Tris(organosilyl)hydroxylamines, mostly new compounds, were synthesized from a bis(organosilyl)hydroxylamine, a chlorosilane, and n-butyllithium (eq 6).[7,8] Synthesis of the unsymmetrical hydroxylamine isomers (**2**) required preparation of the bis(organosilyl)hydroxylamine with two different organosilyl groups, followed by anionic rearrangement and chlorosilane derivatization (eq 7).

$$R_3SiNHOSiR_3 + n\text{-BuLi} \xrightarrow[\substack{\text{hexane-THF}\\ -78^\circ}]{} (R_3Si)_2NO^-Li^+ \xrightarrow{R'_3SiCl} (R_3Si)_2NOSiR'_3 \qquad (6)$$

1a, $R_3 = Me_3$; $R'_3 = Me_2H$
b, $R_3 = Me_3$; $R'_3 = Me_2Ph$
c, $R_3 = Me_3$; $R'_3 = Et_3$
d, $R_3 = Me_3$; $R'_3 = Me_2\text{-}t\text{-}Bu$
e, $R_3 = R'_3 = Me_3$

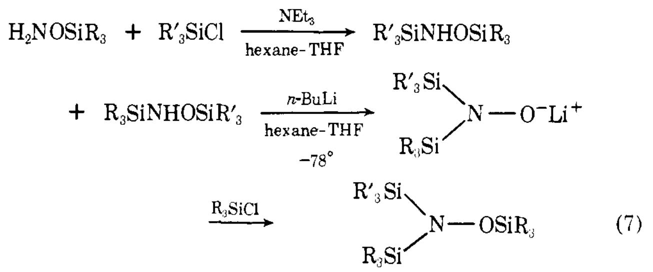
All compounds gave ir and NMR spectra consistent with the proposed structures (see Experimental Section for values).

Table I. Kinetic Data and Activation Parameters for Reversible Rearrangements of Tris(organosilyl)hydroxylamines

	T, °C	$k_1 \times 10^4$, s^{-1}	K_{eq}, [1]/[2]	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta G^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$, (cal deg^{-1} mol^{-1})	E_a, (kcal/mol)
1a → **2a**[a]	139	2.44					
	150	6.78	0.24	29.8 ± 0.2	31.2 ± 0.4	−3.3 ± 0.8	30.6 ± 0.2
	162	17.5					
1b → **2b**[b]	142	0.431					
	148	0.820	0.49	33.0 ± 0.2	37.8 ± 0.2	−11.2 ± 0.8	38.6 ± 0.2
	160	2.98					

[a] Data taken neat, in benzonitrile and in decalin solution. [b] Data taken in benzonitrile only.

Elemental analyses were performed on all new and some previously prepared compounds.


$H_2NOSiR_3 + R'_3SiCl \xrightarrow[\text{hexane-THF}]{NEt_3} R'_3SiNHOSiR_3$

(7)

2a, $R_3 = Me_5$; $R'_3 = Me_2H$

b, $R_3 = Me_3$; $R'_3 = Me_2Ph$

c, $R_3 = Me_3$; $R'_3 = Et_3$

d, $R_3 = Me_3$; $R'_3 = Me_2$-t-Bu

Results and Discussion

Our study showed that the reversible rearrangement (eq 2) apparently is a general reaction for tris(organosilyl)hydroxylamines, but that it is subject to severe hindrance by increasing steric bulk on silicon. Compounds **1d** and **2d** give different products upon thermolysis, so it is obvious that they do not interconvert.[9] Compounds **1c** and **2c** exhibit detectable reversible rearrangement at 170 °C, but also undergo rearrangement to silylaminosiloxane products (eq 1) at comparable rates at this temperature.[9] Product interference does not allow a quantitative measure of the rate of reversible rearrangement in this case. The bis(trimethylsilyl)dimethylsilylhydroxylamines, **1a** and **2a**, and the bis(trimethylsilyl)phenyldimethylsilylhydroxylamines, **1b** and **2b**, were selected for detailed study because in these compounds the reversible rearrangement occurred at low enough temperatures ($T < 165$ °C) to exclude any interference from irreversible rearrangement products. Both reactions were first order in reactant (see Figure 1 for **1a** ⇌ **2a**) and, as in the cases studied by Frainnet[4] and Reetz,[6] completely intramolecular. No crossover products were detectable by NMR or GC analyses in either case. The kinetic rate data and activation parameters are shown in Table I.

The rearrangements were followed by NMR (see Figure 2 for **1a** ⇌ **2a**). The rates were not noticeably affected by change in solvent polarity or concentration. The rate of **1a** ⇌ **2a** was identical when studied neat and in both decalin and benzonitrile at 20% concentration.[10] This insensitivity to solvent polarity indicates that there is little additional solvation of the transition state and little or no charge separation occurs upon going from reactant to transition state.

The transformation **1a** ⇌ **2a** has a slightly lower value of $\Delta H^{\ddagger}$ (~3 kcal/mol) than **1b** ⇌ **2b**. This may be attributed to the increased steric requirement of the phenyldimethylsilyl group. This interpretation is supported by the fact that higher temperatures are required to observe reversible rearrangement in the bis(trimethylsilyl)triethylsilylhydroxylamine system, **1c** ⇌ **2c** (see Figure 3), and the apparent inability of the *tert*-butyldimethylsilyl compounds **1d** and **2d** to undergo interconversion.

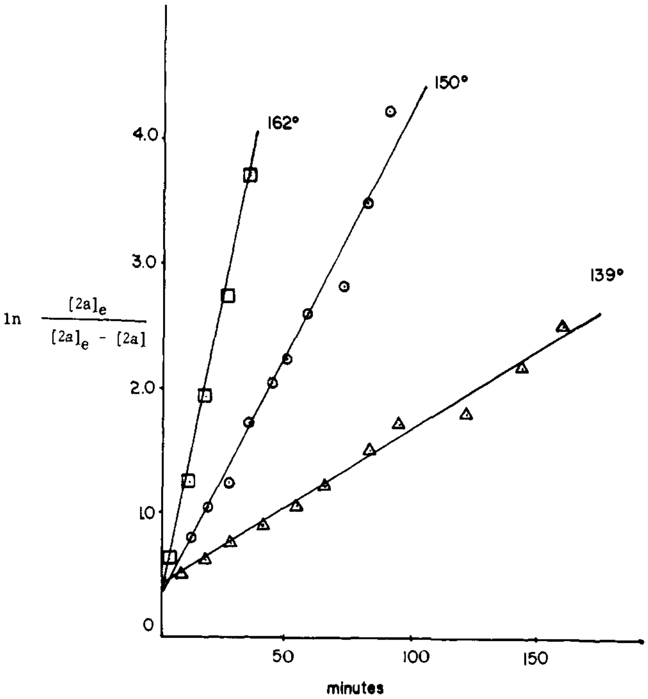


Figure 1. A plot of the logarithm of the concentration of **2a** vs. time at constant temperature is linear for all temperatures employed, indicating that the rearrangement is first order in reactant.

Tris(trimethylsilyl)hydroxylamine, **1e**, was studied by NMR at temperatures up to 200 °C in both benzonitrile and naphthalene solvents in an effort to determine the coalescence temperature for the two trimethylsilyl resonances. Only a moderate peak broadening occurred from 180 to 200 °C (the upper limit of the high temperature probe). Reasoning from the behavior of **1a** ⇌ **2a**, **1b** ⇌ **2b**, and **1c** ⇌ **2c** at lower temperatures, reversible rearrangement of **1e** undoubtedly occurs, but at 200 °C the rate is still slow on the NMR time scale ($k < 2.5 \times 10^{-2}$ s^{-1})[11] so that coalescence is not observed.

The experimental data establish the following order for ease of reversible rearrangement, with Me_3Si most probably falling between HMe_2Si and $PhMe_2Si$:

$$HMe_2Si > PhMe_2Si > Et_3Si > t\text{-}BuMe_2Si$$

The rate of reversible rearrangement appears to depend mainly on the steric requirements of the organosilicon groups. Increased steric bulk apparently decreases the ability to reach the correct geometry to undergo migration.

The experimental values of $\Delta S^{\ddagger}$ obtained are negative and of a magnitude (−10 cal deg^{-1} mol^{-1} or less) consistent with a four-centered asymmetric transition state[5,12,13] (eq 6). The greater negative value of $\Delta S^{\ddagger}$ for the phenyldimethylsilyl compounds is also consistent with the steric arguments con-

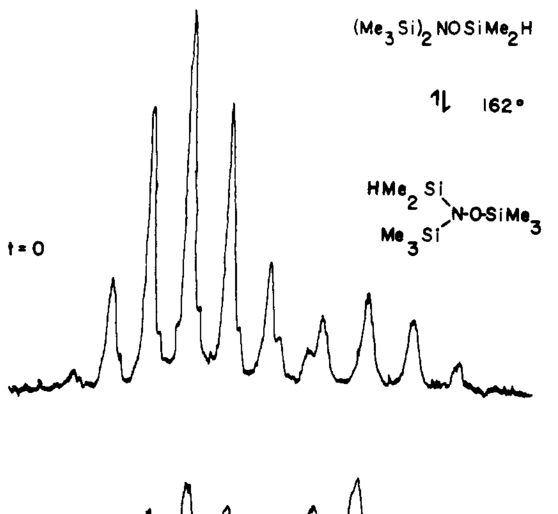


Figure 2. A 60-MHz NMR spectrum (100-Hz sweep width) of **1a** ⇌ **2a** in benzonitrile at 162 °C. At *t* = 0, the ratio of **1a** to **2a** by integration is 2.65:1 (some **2a** was present in the initial sample and could not be separated). At 9 min, the ratio is 1.65:1; at 24 min, 0.33:1; and at 54 min, 0.24:1 (the equilibrium ratio).

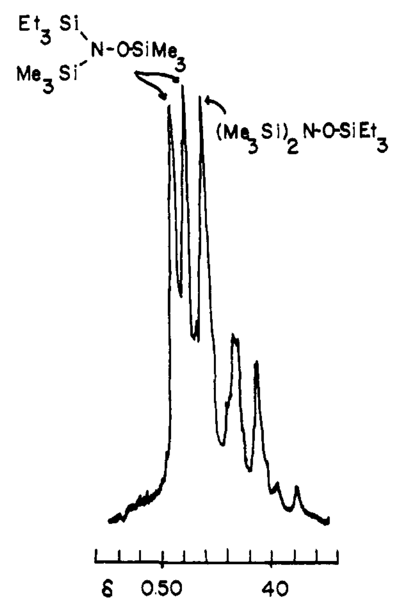
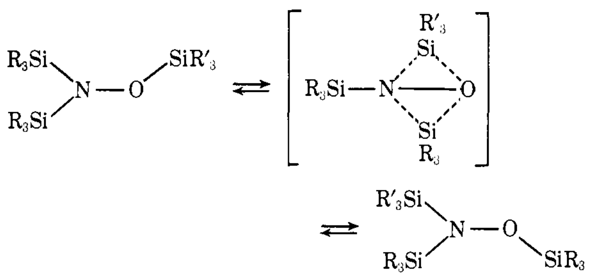


Figure 3. A 100-MHz NMR spectrum (108-Hz sweep width) of **2c** in benzene after 90 min at 196 °C. The peak for $SiMe_3$ protons of **1c** can be clearly seen at δ 0.46, indicating that the reversible rearrangement has occurred. Smaller peaks at δ 0.44 and 0.42 are from irreversible rearrangement products (eq 1) of **1c** and **2c**.

cerning $\Delta H^{\ddagger}$. The similarity of the results obtained for tris(organosilyl)hydroxylamines and those obtained by Reetz for (silyl)methyl silyl ethers ($\Delta H^{\ddagger} = 30.3 \pm 0.6$ kcal/mol, $\Delta S^{\ddagger} = -8.6 \pm 0.3$ cal deg^{-1} mol^{-1}) suggest that our rearrangement is probably also occurring via a type I dyotropic process (eq 8).



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As in the C-O rearrangement, the migrating silicon atoms have unoccupied d orbitals of correct symmetry to remove the orbital symmetry requirements,[14] lowering the energy of the transition state in eq 8. For the C-O rearrangement, Reetz predicts a nonsymmetrical transition state in which the bond to one of the migrating groups has stretched more than the bond to the other, the difference depending upon vibrational coupling between energy levels in the thermally activated molecule.[6] In the N-O rearrangement the transition state may be similarly unsymmetrical.

Experimental Section

All analytical and preparative gas chromatography was done using a Varian Aerograph Model 90-P chromatograph. The analytical columns used were a 15 ft × ¼ in. 20% SE-30 on 60/80 mesh Chromosorb W and a 15 ft × ¼ in. 20% QF-1 on 60/80 mesh Chromosorb W. The preparative column was a 15 ft × ⅜ in. 20% SE-30 on 45/60 Chromosorb W. All columns used were aluminum and were treated with hexamethyldisilazane before each use. The analytical work was done using a helium flow of 100 ml/min, preparative work employed 200 ml/min. Both analytical and preparative separations were done isothermally. Proton NMR spectra were determined on a Varian A60A spectrometer equipped with a variable temperature probe, a Varian T-60 spectrometer, or a JEOL MH-100 spectrometer. Chemical shifts were obtained by internal referencing with benzene in 10% v/v solutions except where noted otherwise. Ir spectra were obtained as neat liquid films on KBr plates on a Perkin-Elmer 457 grating spectrophotometer. All boiling points are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Labs or Galbraith Laboratories, Inc. Analyses are reported for all new compounds and for a few which have been prepared previously.

Materials. All chemicals used were reagent grade materials. Solvents, such as THF, ether, hexane, benzene, decalin, or benzonitrile were refluxed over lithium aluminum hydride or sodium and distilled before use.

Trimethylchlorosilane was obtained from Dow Corning Corporation and was distilled before use. Triethylchlorosilane, phenyldimethylchlorosilane, and dimethylchlorosilane were obtained from PCR, Inc. and were used without further purification. *tert*-Butyldimethylchlorosilane was prepared by treating dimethyldichlorosilane with 1 equiv of *tert*-butyllithium.[15] Hydroxylamine hydrochloride (Mallinckrodt) was placed over Drierite in an evacuated dessicator for 24 h before use. Hydroxylamine was prepared by the method of Hurd.[16] Triethylamine was distilled from barium oxide before use. *O*-Trimethylsilylhydroxylamine, *N*,*O*-bis(trimethylsilyl)hydroxylamine, and tris(trimethylsilyl)hydroxylamine (**1e**) were prepared by the method of Wannagat.[7] Compounds **1a**–**d** were prepared in a similar manner to **1e**. *n*-Butyllithium was obtained as a 1.6 M solution in hexane from Foote Mineral Co.

All preparations, filtrations, and distillations were carried out in Pyrex glassware dried in a 130 °C oven for at least 3 h and then purged with dry nitrogen before use. A nitrogen atmosphere was maintained in all preparations, filtrations, and distillations.

All NMR studies were done in sealed Pyrex NMR tubes (o.d. 5 mm). The tubes were dried for at least 3 h in a 130 °C oven and purged with dry nitrogen before use. Pure samples or 20% v/v solutions of compounds in high boiling solvents were sealed in the tubes with a gas-oxygen torch. The tubes were heated in the variable temperature probe of the Varian A-60A NMR, and at least four integrations of the monitor resonances (Si-H for **1a** $\rightleftharpoons$ **2a**, -SiMe$_3$ for **1b** $\rightleftharpoons$ **2b**) at each measurement interval were taken to obtain an average value of peak area. The measurement intervals at high temperatures (160 °C or above) were initially 5 min, and as the reaction progressed towards equilibrium, 10 min. At lower temperatures they varied from 10 to 30 min. Temperature calibration was done using a separate tube containing ethylene glycol.

Tris(trimethylsilyl)hydroxylamine (1e). General Procedure for Syntheses of all Tris(organosilyl)hydroxylamines. Reaction was done in a jacketed 250-ml three-neck round-bottom flask with an exit stopcock in the bottom. To a solution of 17.7 g (100 mmol) of *N,O*-bis(trimethylsilyl)hydroxylamine in 100 ml of a 4:1 mixture of hexane and THF at −78 °C was added, via syringe, 62.5 ml (100 mmol) of a 1.6 M solution of *n*-butyllithium in hexane. The reaction was allowed to stir and warm to room temperature until a clear solution formed. It was added using the exit stopcock to a solution of 10.9 g (100 mmol) of trimethylchlorosilane in 10 ml of hexane in a 250-ml three-necked round-bottom flask fitted with a reflux condenser, heating mantle, and stirring bar. After a few minutes the reaction mixture became turbid and salt (LiCl) precipitated rapidly. The solution was cooled and filtered under nitrogen and the filtrate distilled to give 22.4 g (90%) of a clear colorless liquid, bp 128 °C (97 Torr); ir (neat) 2950, 2900, 1410, 1250, 970, 850, 760, 690 cm^{-1}; NMR (benzene) δ 0.25 (s, SiMe$_3$, 18 H), 0.30 (s, SiMe$_3$, 9 H).

Anal. Calcd for $C_9H_{27}NSi_3O$: C, 43.31; H, 10.90; N, 5.61; Si, 33.76. Found: C, 43.47; H, 10.81; N, 5.59; Si, 33.81.

***N,N*-Bis(trimethylsilyl)-*O*-dimethylsilylhydroxylamine (1a); *N,N*-Bis(trimethylsilyl)-*O*-phenyldimethylsilylhydroxylamine (1b); *N,N*-Bis(trimethylsilyl)-*O*-triethylsilylhydroxylamine (1c); and *N,N*-Bis(trimethylsilyl)-*O*-*tert*-butyldimethylsilylhydroxylamine (1d).** The procedure described for **1e** was used in all of the above preparations, employing a different chlorosilane to react with the lithium salt of the bis(trimethylsilyl)hydroxylamine in each case. **1a** was obtained in 41% yield, **1b** in 69% yield, **1c** in 65% yield, and **1d** in 31% yield.

1a, isolated by preparative gas chromatography on column C (135 °C, retention time 17 min); ir (neat) 2950, 2900, 2120, 1410, 1250, 960, 910, 840, 760, 680 cm^{-1}; NMR (benzene) δ 0.40 (s, SiMe$_3$, 18 H), 0.54 (d, J = 3.0 Hz, SiMe$_2$, 6 H), 5.03 (septet, J = 3 Hz, Si-H, 1 H).

Anal. Calcd for $C_8H_{25}NSi_3O$: C, 40.29; H, 10.70; N, 5.95; Si, 35.77. Found: C, 40.95; H, 10.74; N, 5.72; Si, 35.51.

1b, bp 82–83 °C (0.1 Torr): ir (neat) 3060, 3040, 2950, 2900, 1550, 1430, 1250, 1120, 970, 850, 710 cm^{-1}; NMR (cyclohexane) δ 0.09 (s, SiMe$_3$, 18 H), 0.44 (s, SiMe$_2$, 6 H), 7.35 (multiplet, Si-Ph, 5 H).

Anal. Calcd for $C_{14}H_{29}NSi_3O$: C, 53.95; H, 9.40; N, 4.49; Si, 27.03. Found: C, 54.43, H, 9.26; N, 4.57; Si, 26.75.

1c, bp 63 °C (15 Torr); ir (neat) 2950, 2900, 2880, 1460, 1410, 1250, 970, 860, 830, 780, 690 cm^{-1}; NMR (benzene) δ 0.46 (s, SiMe$_3$, 18 H), 0.98 (multiplet, SiEt$_3$, 15 H).

Anal. Calcd for $C_{12}H_{33}NSi_3O$: C, 49.42; H, 11.41; N, 4.90; Si, 28.89. Found: C, 49.32; H, 11.41; N, 4.86; Si, 28.67.

1d, bp 80–85 °C (1.5 Torr): ir (neat) 2950, 2920, 2890, 2850, 1460, 1250, 960, 930, 850, 830, 810, 780, 690, 670 cm^{-1}; NMR (benzene) δ 0.42 (s, SiMe$_2$, 6 H), 0.44 (s, SiMe$_3$, 18 H), 1.22 (s, Si-*t*-Bu, 9 H).

Anal. Calcd for $C_{12}H_{33}NSi_3O$: C, 49.41; H, 11.43; N, 4.80; Si, 28.88. Found: C, 49.47; H, 11.24; N, 4.71; Si, 28.51.

***N,O*-Bis(trimethylsilyl)-*N*-dimethylsilylhydroxylamine (2a).** *O*-Trimethylsilylhydroxylamine (10.5 g, 100 mmol) was reacted with 9.4 g (100 mmol) of dimethylchlorosilane and 10.2 g (100 mmol) of triethylamine as in the synthesis of **2c** to give 3.5 g (21%) of a mixture of *O*-trimethylsilyl-*N*-dimethylsilyl- and *O*-dimethylsilyl-*N*-trimethylsilylhydroxylamine; bp 64–68 °C (14 Torr): ir (neat) 3300, 2960, 2900, 2130, 1420, 1340, 1250, 980, 910, 850, 750 cm^{-1}; NMR (benzene) was subject to many overlapping peaks, SiMe$_3$ with SiMe$_2$ and Si-H with N-H, and was not found useful.

Anal. Calcd for $C_5H_{17}NSi_2O$: C, 36.75; H, 10.49; N, 8.58; Si, 34.39. Found: C, 36.71; H, 10.77; N, 8.35; Si, 34.25.

A solution of the lithium salt of the bis(organosilyl)hydroxylamine was prepared by reacting 2.2 g (14 mmol) of the mixture with 8.8 ml (14 mmol) of a 1.6 M solution of *n*-butyllithium in hexane. This was then reacted, as in **2c**, with 1.52 g (14 mmol) of trimethylchlorosilane. The product was purified by preparative gas chromatography using column C (135 °C, 17 min). Isolated yield was 1.51 g of **2** (46%): ir (neat) 2950, 2900, 2130, 1410, 1250, 970, 890, 840, 760, 680, 620 cm^{-1}; NMR (benzene): δ 0.35 (s, SiMe$_3$, 9 H), 0.44 (s, SiMe$_3$, 9 H), 0.46 (d, J = 3.6 Hz, 6 H), 4.82 (septet, J = 3.6 Hz, Si-H, 1 H).

Anal. Calcd for $C_8H_{25}NSi_3O$: C, 40.79; H, 10.70; N, 5.95; Si, 35.77. Found: C, 40.77; H, 10.90; N, 5.93; Si, 36.00.

***N,O*-Bis(trimethylsilyl)-*N*-triethylsilylhydroxylamine (2c).** *O*-Triethylsilylhydroxylamine was prepared in 50% yield by the reaction of triethylchlorosilane, hydroxylamine hydrochloride, and ammonia in ether. It was distilled [bp 47 °C (0.5 Torr)] and used without further purification. It was reacted with equivalent amounts of triethylamine and trimethylchlorosilane as in Wannagat's procedure for the bis(trimethylsilyl) compound[7] to give a 65% yield of a mixture of *O*-triethylsilyl-*N*-trimethylsilyl- and *O*-trimethylsilyl-*N*-triethylsilylhydroxylamine, bp 38 °C (0.15 Torr): ir 3280, 2940, 2900, 2880, 1460, 1410, 1340, 1250, 1020, 970, 870, 850, 800, 750, 690 cm^{-1}; NMR (benzene) δ 0.28, 0.39 (s, SiMe$_3$, integrate together for 9 H), 1.08 (multiplet, SiEt$_3$, 15 H), 4.66, 4.92 (N-H, integrate together for 1 H). A solution of the lithium salt of the bis(organosilyl)hydroxylamine was prepared by reacting 25.8 g (120 mmol) of the mixture with 75 ml (120 mmol) of a 1.6 M solution of *n*-butyllithium in hexane. This was reacted with 13 g (120 mmol) of trimethylchlorosilane. Distillation of the filtrate gave 23 g of **2c** (66%), bp 63–65 °C (15 Torr); ir (neat) 2950, 2900, 2860, 1450, 1410, 1250, 970, 840, 760, 730, 690 cm^{-1}; NMR (benzene) δ 0.43 (s, SiMe$_3$, 9 H), 0.44 (s, SiMe$_3$, 9 H), 1.10 (multiplet, SiEt$_3$, 15 H).

Anal. Calcd for $C_{12}H_{33}N_1Si_3O$: C, 49.42; H, 11.41; N, 4.80; Si, 28.89. Found: C, 49.34, H, 11.28, N, 4.65; Si, 29.05.

***N,O*-Bis(trimethylsilyl)-*N*-phenyldimethylsilylhydroxylamine (2b).** *O*-Phenyldimethylsilylhydroxylamine was prepared in 69% yield by the reaction of 34.1 g (200 mmol) of phenyldimethylchlorosilane, 20.2 g (200 mmol) of triethylamine, and 6.6 g of hydroxylamine. Distillation, bp 151–155 °C (1.25 Torr), yielded 23.7 g of clear colorless liquid: ir (neat) 3350, 3060, 3040, 2950, 2900, 1580, 1420, 1250, 1180, 1110, 940, 840, 800, 740, 710, 650 cm^{-1}; NMR (CCl$_4$) δ 0.40 (s, SiMe$_2$, 6 H), 7.30 (multiplet, Si-Ph, 5 H), NH$_2$ protons not seen. Product was used without further purification.

O-Phenyldimethylsilylhydroxylamine (16.7 g, 100 mmol), 10.1 g (100 mmol) of triethylamine, and 10.9 g (100 mmol) of trimethylchlorosilane were reacted to give 15.0 g (60%) of a mixture of *O*-phenyldimethylsilyl-*N*-trimethylsilyl- and *O*-trimethylsilyl-*N*-phenyldimethylsilylhydroxylamine, bp 102–104 °C (1.25 Torr): ir (neat) 3300, 3060, 3040, 2960, 2900, 1580, 1440, 1250, 1130, 980, 860, 800, 750, 710 cm^{-1}; NMR (CCl$_4$) δ 0.22 (s, SiMe$_2$), 0.33 (s, SiMe$_3$), 0.55 (s, SiMe$_3$), 0.63 (s, SiMe$_2$), 4.68 (s, N-H), 4.87 (s, N-H), 7.30 (multiplet, Si-Ph). The mixture was used without further purification.

A solution of the lithium salt of the bis(organosilyl)hydroxylamine was prepared by reacting 6.0 g (25 mmol) of the mixture with 15.5 ml (25 mmol) of 1.6 M *n*-butyllithium in hexane. This was reacted with 2.7 g (25 mmol) of trimethylchlorosilane to yield 3.68 g of **2b** (47% yield), bp 95–98 °C (2.5 Torr): ir (neat) 3070, 3040, 2950, 2900, 1590, 1420, 1250, 1110, 960, 840, 800, 690 cm^{-1}; NMR (CCl$_4$, cyclohexane standard) δ −0.01 (s, SiMe$_3$, 9 H), 0.05 (s, SiMe$_3$, 9 H), 0.35 (s, SiMe$_2$, 6 H), 7.36 (multiplet, Si-Ph, 5 H).

Anal. Calcd for $C_{14}H_{29}NSi_3O$: C, 53.95; H, 9.40; N, 4.49; Si, 27.03. Found: C, 54.02; H, 9.61; N, 4.62; Si, 26.35 (low).

***N,O*-Bis(trimethylsilyl)-*N*-*tert*-butyldimethylsilylhydroxylamine (2d).** A mixture of *N*-*tert*-butyldimethylsilyl-*O*-trimethylsilyl- and *N*-trimethylsilyl-*O*-*tert*-butyldimethylsilylhydroxylamine was prepared by the procedure of Boudjouk and West.[8] A solution of the lithium salt of the mixture of hydroxylamines was prepared by reacting 1.4 g (6 mmol) of the mixture with 4.1 ml (6 mmol) of a 1.6 M solution of *n*-butyllithium in hexane. This was then reacted with 0.7 g (6 mmol) of trimethylchlorosilane to give **2d**. Compound **2d** was isolated by preparative gas chromatography on column C (165 °C, 9 min) and

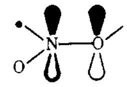
0.55 g was obtained (29% yield): ir (neat) 2950, 2920, 2900, 2850, 1460, 1250, 980, 850, 800, 780, 760, 680 cm^{-1}; NMR (benzene) δ 0.34 (s, SiMe$_2$, 6 H), 0.44 (s, SiMe$_3$, 18 H), 1.27 (s, Si-*t*-**Bu**, 9 H).

Anal. Calcd for $C_{12}H_{33}NSi_3O$: C, 49.41; H, 11.43; N, 4.80; Si, 28.88. Found: C, 49.34; H, 11.43; N, 4.55; Si, 28.40.

References and Notes

(1) Research sponsored by U.S. Air Force Office of Scientific Research (NC)-AFSC, Grant Nos. AF-AFOSR 70-1904 and 74-2644.

(2) P. Boudjouk and R. West, *J. Am. Chem. Soc.*, **93**, 5901 (1971).
(3) R. West, P. Nowakowski, and P. Boudjouk, 3rd International Symposium of Organosilicon Chemistry, Madison, Wisconsin, Aug 1972.
(4) E. Frainnet, F. Duboudin, F. Dabescat, and G. Vincon, *C. R. Acad. Sci., Ser. C*, **276**, 1469 (1973).
(5) M. T. Reetz, *Tetrahedron*, **29**, 2189 (1973).
(6) M. T. Reetz, M. Kliment, and M. Plachkey, *Angew. Chem., Int. Ed. Engl.*, **13**, 813 (1974).
(7) U. Wannagat and O. Smrekar, *Monatsh. Chem.*, **100**, 750 (1969).
(8) R. West and P. Boudjouk, *J. Am. Chem. Soc.*, **95**, 3987 (1973).
(9) **1d** and **2d** undergo reaction according to eq 1 without any evidence of reversible rearrangement, **1d** yielding Me$_3$SiN(Me)SiMe$_2$OSiMe$_2$*t*-Bu and **2d** giving a mixture of Me$_3$SiN(Me)Si(Me)*t*-BuOSiMe$_3$ and *t*-BuMe$_2$SiN(Me)-SiMe$_2$OSiMe$_3$. These reactions and the irreversible rearrangement of all of the above tris(organosilyl)hydroxylamines are discussed in detail in R. West, P. Nowakowski, and P. Boudjouk, *J. Am. Chem. Soc.*, following paper in this issue.
(10) The interconversion of **1b** $\rightleftharpoons$ **2b** was studied neat and in 20% concentration in benzonitrile only.
(11) H. Kessler, *Angew. Chem., Int. Ed. Engl.*, **9**, 219 (1970).
(12) A. G. Brook, D. M. MacRae, and A. R. Bassindale, *J. Organomet. Chem.*, **86**, 185 (1975).
(13) G. L. Larson and Y. V. Fernandez, *J. Organomet. Chem.*, **86**, 193 (1975).
(14) The HOMO in tris(organosilyl)hydroxylamines has been calculated through ab initio Gaussian lobe SCF computations to be i, which has the proper symmetry for the dyotropic process with organosilyl groups to occur: C. Trindle and D. D. Shillady, *J. Am. Chem. Soc.*, **95**, 703 (1973).
(15) R. West, M. Ishikawa, and R. Bailey, *J. Am. Chem. Soc.*, **88**, 4648 (1966).
(16) C. Hurd, *Inorg. Synth.*, **1**, 87 (1939).



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Irreversible Thermal Rearrangement of Tris(organosilyl)hydroxylamines[1]

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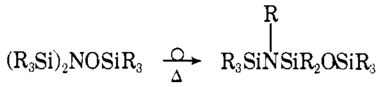
Abstract: Tris(organosilyl)hydroxylamines undergo a general, intramolecular rearrangement at temperatures of 180 °C and above to give silylaminosiloxanes with high product selectivity. An organosilyl group bound to nitrogen appears to insert into the N–O bond (see eq 1 in text). The reactions follow first-order kinetics over at least 4 half-lives with $t_{1/2}$ at 205 °C as follows: (Me$_3$Si)$_2$NOSiMe$_3$ (**1**), 5800; (Me$_3$Si)$_2$NOSiMe$_2$-*t*-**Bu** (**11**), 3600; (Me$_3$Si)$_2$NOSiMe$_2$H (**5**), 2200; and Me$_3$Si(PhMe$_2$Si) NOSiMe$_3$ (**9**), 1800 s. Kinetic evidence and the high product selectivity rule out a simple one- or two-step mechanism. A three-step mechanism which is consistent with kinetic and product data is suggested, involving the formation of a tight radical pair followed by formation of a dipolar intermediate leading to product.

Introduction

In 1971, Boudjouk and West reported preliminary results on the thermal rearrangement of tris(organosilyl)hydroxylamines into isomeric silylaminosiloxane[2,3] (eq 1). This type



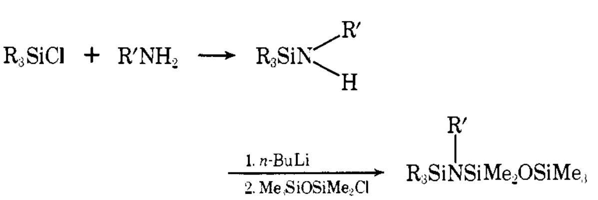
$$(R_3Si)_2NOSiR_3 \xrightarrow[\Delta]{\bigcirc} R_3Si\overset{\overset{\displaystyle R}{|}}{N}SiR_2OSiR_3 \qquad (1)$$

of hydroxylamine rearrangement is unique in both silicon and carbon chemistry.[4,5] It provides the first example of the insertion of an organosilicon moiety into the nitrogen–oxygen bond[6] and is the first clear case in which a substituent is transferred from silicon to nitrogen.[7] The present study was undertaken to study effects of change of organosilyl substituents on the reaction and to try to determine the mechanism of rearrangement.

It was found during this study that tris(organosilyl)hydroxylamines, when heated, undergo a reversible intramolecular 1,2 exchange of organosilyl groups between oxygen and nitrogen. The kinetics and mechanism of this reversible rearrangement are discussed in a companion paper.[8]

Synthesis

The preparations of the tris(organosilyl)hydroxylamines are reported in the accompanying paper.[8] *N*- and *O*-methylbis(trimethylsilyl)hydroxylamines, **25** and **26**, were prepared by the method of Wannagat and Smrekar.[9] Three of the thermolysis products, compounds **10, 13,** and **22,** were synthesized by an alternate route for structure verification. This involved synthesis of an organosilyl-substituted alkyl or aryl amine,[10] which was deprotonated with *n*-butyllithium and treated with pentamethylchlorodisiloxane to give a silylaminosiloxane of



$$R_3SiCl + R'NH_2 \longrightarrow R_3SiN\begin{matrix} R' \\ H \end{matrix} \xrightarrow[2.\ Me_3SiOSiMe_2Cl]{1.\ n\text{-BuLi}} R_3Si\overset{\overset{\displaystyle R'}{|}}{N}SiMe_2OSiMe_3 \qquad (2)$$

10, R_3 = Me$_3$; R′ = Ph
13, R_3 = *t*-BuMe$_2$; R′ = Me
22 R_3 = Et$_3$; R′ = Me

known structure (eq 2). All compounds gave ir and ^{1}H NMR spectra consistent with proposed structures.

Results

The simplest compounds investigated are **1** and **3,** in which only one type of organosilyl group is present in the molecule. Both compounds react cleanly and quantitatively to give the