Irreversible Rearrangement of Silyl Groups between Oxygen and Nitrogen in Tris(silyl)hydroxylamines

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Diorganofluorosilylation of 1,2-bis(trimethylsilyl)hydroxylamines at low temperatures gives exclusively O-(diorganofluorosilyl)-*N,N*-bis(trimethylsilyl)hydroxylamines **1a,b**. The thermal rearrangement of **1a,b** to the isomeric *N*-(diorganofluorosilyl)-*N,O*-bis(trimethylsilyl)-hydroxylamines **2a,b** is found to be irreversible, and the experimental data suggest an intramolecular course of the isomerization. *Ab initio* and density functional calculations for model compounds demonstrate the dyotropic course of the rearrangement. Anomeric stabilization of **2a,b** by more favorable negative F–Si–N and O–Si–C hyperconjugation is important for the irreversibility of the reaction.
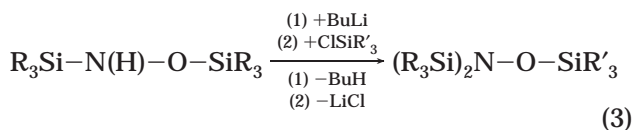
Introduction

The first (organosilyl)hydroxylamines were prepared in 1963 by Wannagat and Pump.[1] It was found that substitution by the first silyl group occurs at oxygen whereas the opposite is true for organyl halides.

$$2H_2NOH + R_3SiCl \rightarrow H_2N-O-SiR_3 + H_2N-OH\cdot HCl \quad (1)$$
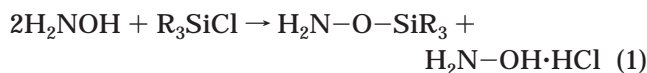
Silicon is normally much more reactive toward the hard Lewis base oxygen than toward the softer Lewis base nitrogen.[2] *N,O*-Bis(organosilyl)hydroxylamines can be prepared from hydroxylamine, triethylamine and a chlorosilane.[2,3]

$$2R_3SiCl + 2Et_3N + H_2N-OH \xrightarrow[-2Et_3N\cdot HCl]{} R_3Si(H)N-OSiR_3 \quad (2)$$
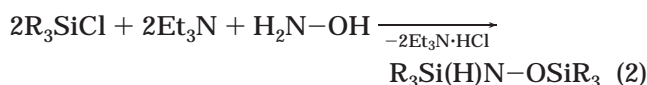
N,N,O-Tris(organosilyl)hydroxylamines can be obtained from the *N,O*-bis(organosilyl)hydroxylamines, butyllithium, and organohalosilanes.[2]

$$R_3Si-N(H)-O-SiR_3 \xrightarrow[\substack{(1)\ -BuH \\ (2)\ -LiCl}]{\substack{(1)\ +BuLi \\ (2)\ +ClSiR'_3}} (R_3Si)_2N-O-SiR'_3 \quad (3)$$

Derivatization with triorganohalosilanes gives, in every case, only the rearranged isomer, in which the new organosilyl group is attached to the oxygen.[2] This result implies an 1,2-anionic silyl group migration from oxygen to nitrogen. The first example of a 1,2-anionic rearrangement in the case of (organosilyl)hydroxylamines

was observed by West, Boudjouk, and Matuszko.[4]

$$R_3Si-N^--O-SiR_3 \xrightarrow{o} (R_3Si)_2N-O^- \quad (4)$$
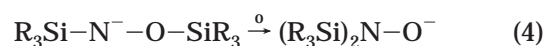
1,2-Silyl shifts in neutral (organosilyl)hydroxylamines have been known since 1973, when Frainnet and Nowakowski described an exchange of trialkylsilyl groups in bis(organosilyl)hydroxylamines.[5] Later West and co-workers found a *reversible* rearrangement involving positional exchange between the organosilicon groups on oxygen and nitrogen in tris(silyl)hydroxylamines,[6] which they suggest proceeds via a dyotropic transition state.[2,7]
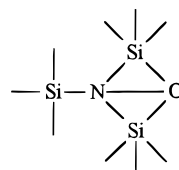
In 1979 we isolated *N*-(arylfluorosilyl)-*N,O*-bis(trimethylsilyl)hydroxylamines[8] in the reactions of arylfluorosilanes and the lithium derivative of *N,O*-bis(trimethylsilyl)hydroxylamine and interpreted this result as an equilibrium of the isomeric bis(trimethylsilyl)hydroxylamide anions[2] (eq 4).

At this time we did not account for the possibility of a consecutive thermal rearrangement. To understand the N-substitution, we carried out the same reactions at low temperatures, e.g. −50 °C, and found that the substitution of the attacking fluorosilyl group occures

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(1) Wannagat, T.; Pump, U. *Monatsh. Chem.* **1963**, *94*, 141.
(2) Boudjouk, P.; West, R. *Intra-Sci. Chem Rep.* **1973**, *7*, 65.
(3) Wannagat, U.; Smrekar, O. *Monatsh. Chem.* **1969**, *100*, 750.

(4) West, R.; Boudjouk, P.; Matuszko, T. A. *J. Am. Chem. Soc.* **1969**, *91*, 5184.
(5) Frainnet, E.; Duboudin, F.; Dabescat, F.; Vincon, G. *C. R. Acad. Sci., Ser. C* **1973**, *276*, 1469.
(6) Nowakowski, P.; West, R. *J. Am. Chem. Soc.* **1976**, *98*, 5616.
(7) Reetz, M. T. *Adv. Organomet. Chem.* **1977**, *16*, 33.
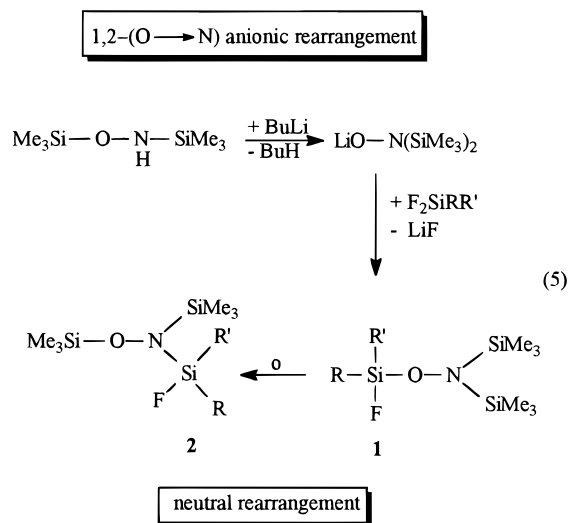(8) Klingebiel, U.; Northe, M. *J. Organomet. Chem.* **1979,** *179*, 391.

exclusively at oxygen. The NMR spectra confirmed a quantitative reaction.[9] Depending on the substituents

$$1,2\text{–}(O \longrightarrow N) \text{ anionic rearrangement}$$

$$\text{Me}_3\text{Si}-\text{O}-\underset{H}{\text{N}}-\text{SiMe}_3 \xrightarrow[-\text{ BuH}]{+\text{ BuLi}} \text{LiO}-\text{N(SiMe}_3)_2$$

$$\downarrow \begin{array}{c} +\text{ F}_2\text{SiRR'} \\ -\text{ LiF} \end{array}$$

(5)

neutral rearrangement

2　　　**1**

at the fluorosilyl group, an exchange of one organosilyl group and the fluorosilyl group occurs at higher temperatures (0−100 °C), leading to the positional isomers **2**. The rearrangement is quantitative and intramolecular, since in crossover experiments no scrambled products are detected.[9] In the tris(organosilyl)hydroxylamine system Nowakowski and West[2,6] observed that the rearrangement is reversible, first order, and completely intramolecular. The rate of reversible rearrangements depends mainly on the steric requirements of the organosilicon groups. Increased steric bulk decreases the ability to reach the correct geometry to undergo migration.[6] Our study showed an irreversible dyotropic rearrangement of fluoro-functional tris(silyl)-hydroxylamines.[9]

For completeness and a better understanding of our results we report here *ab initio* and density functional calculations for model compounds and the neutral rearrangement of the *O*-(diorganofluorosilyl)-*N,N*-bis-(trimethylsilyl)hydroxylamines **1a,b** to the isomeric *N*-(diorganofluorosilyl)-*N,O*-bis(trimethylsilyl)hydroxy-lamines **2a,b** (eq 6).

(6)

1　　　　　**2**
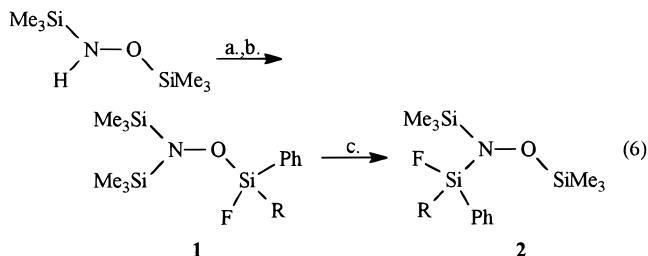
(a) BuLi, rt, hexane. (b) RPhSiF$_2$, hexane. (c) THF, reflux. R = ^{i}C$_3$H$_7$ (**1a,2a**); R = Ph (**1b,2b**).

Compounds **1a** and **1b** were synthesized by reactions of lithiated *N,O*-bis(trimethylsilyl)hydroxylamine with fluorosilanes at low temperatures, e.g. −50 °C to +20 °C. After a solution of **1a** or **1b** was heated in THF— the rearrangement can be monitored by ^{19}F NMR

(9) Wolfgramm, R.; Klingebiel, U. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1031.

**Table 1. $\delta(^{29}\text{Si})$ Chemical Shifts of Tris(silyl)hydroxylamines (in ppm)**

	SiFPhR	SiMe$_3$
1a	−14.00	10.17
1b	−26.83	11.68
2a	−10.06	30.75, 8.27
2b	−21.33	30.68, 9.51

spectroscopy—only the positional isomer **2a** or **2b** could be isolated.

Interestingly, ^{29}Si NMR measurements allow a qualitative prediction of the isomerization. The silyl group, normally the fluorosilyl group, with the highest ^{29}Si NMR upfield chemical shift in **1a** and **1b** will migrate to the nitrogen, suggesting that electronic effects of the migrating group(s) determine the course of the reaction. Table 1 compares the ^{29}Si chemical shifts of **1a** and **1b** with those of **2a** and **2b**.

Ab initio calculations[10] predict that the thermal scrambling of silyl groups in tris(silyl)hydroxylamine **3** proceeds in one step via **TS1**, which is 27.5 kcal mol^{-1} higher in energy than **3** (at MP4(SDTQ)/6-31G*//B3LYP/ 6-31G* + ΔZPVE, see Table 2). This value is in good agreement with ΔH‡ = 29.8 ± 0.2 kcal mol^{-1} for the reversible rearrangement (Me$_3$Si)$_2$NOSiMe$_2$H → (Me$_3$-Si)Me$_2$HSiNOSiMe$_3$ reported by West et al.[6] **TS1** is rather unsymmetrical since the new Si−N bond is nearly formed (r(SiN) = 1.829 Å) while the Si−O distances are still *ca.* 0.45 Å longer than regular Si−O bonds (e.g. 1.634 Å for H$_3$SiOSiH$_3$)[11] (see Figure 1).

Fluorine substitution at one silyl group has only a small influence on the relative stability of both possible regioisomers. The *O*-(trifluorosilyl)-*N,N*-bis(silyl)hy-droxylamine species **4** and *N*-(trifluorosilyl)-*O,N*-bis-(silyl)hydroxylamine species **5** are practically isoenergetic (ΔE = 0.9 kcal mol^{-1}, **5** being the more stable isomer). **4** is separated from **5** by a barrier of 24.8 kcal

(7)

4　　　　　**5**
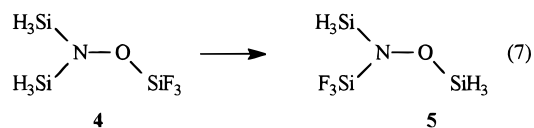
mol^{-1} (at MP4(SDTQ)/6-31G*//B3LYP/6-31G* + ΔZPVE). The activation barrier is 2.7 kcal mol^{-1} smaller than for the degenerate rearrangement of **3**, indicating that fluoro substitution at a migrating silyl group facilitates the rearrangement.

In **TS2,** the transition state for the simultaneous migration of a SiH$_3$ group and the SiF$_3$ group, both migrating groups are in nearly symmetrically bridging positions above the N−O bond with an interplanar angle of 122.1°, characteristic for the transition state of a dyotropic rearrangement (see Figure 1). Alkyl substitution has a small but decisive effect on the relative energies of the isomeric silylhydroxylamines. The *N,O*-

(10) All calculations were performed with Gaussian 94, Revision B1-E1: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Otiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Repogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian 94, Revisions B.1−E1; Gaussian, Inc., Pittsburgh, PA, 1995.
(11) Alemenningen, A.; Bastiansen, O.; Ewing, V.; Hedberg, K.; Traetteberg, M.; *Acta Chem. Scand.* **1963**, *17*, 2455.
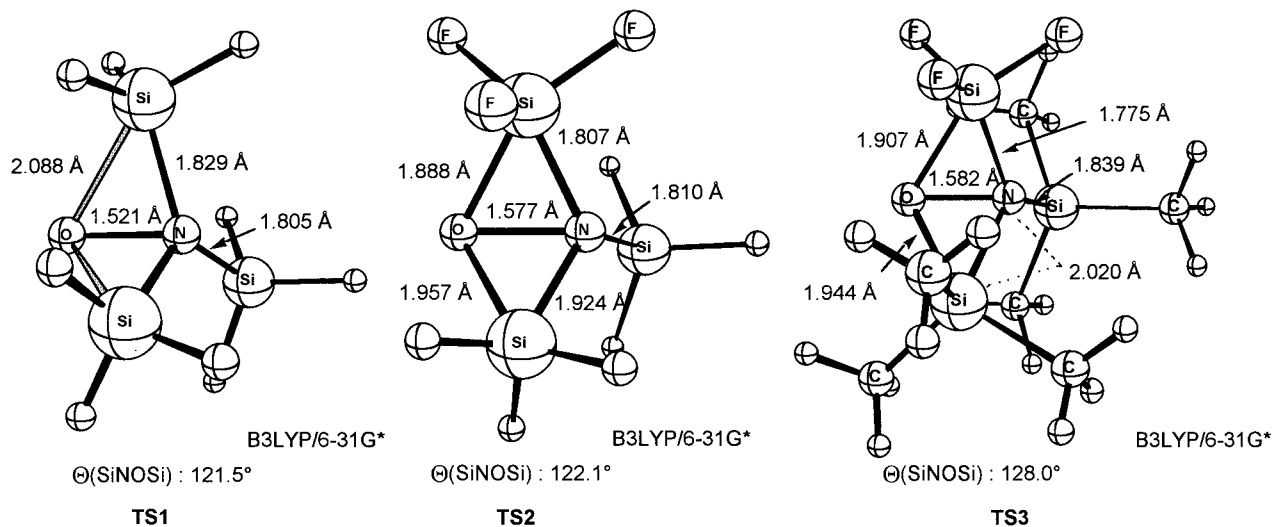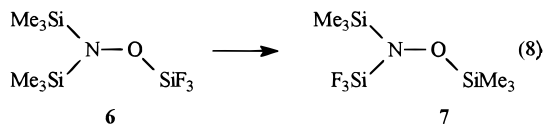
Figure 1. Calculated geometries of the transition states **TS1**-**TS3** (at B3LYP/6-31G*).

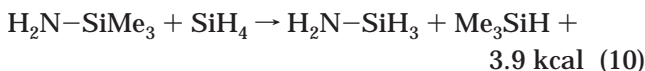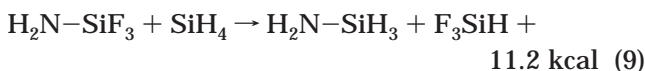**Table 2. Relative Energies (kcal mol^{-1}) of Tris-(silyl)Hydroxylamines and Related Compounds**

compd	HF/ 6-31G*[a]	B3LYP/ 6-31G*[b]	B3LYP/ 6-31G*[b] + ΔZPVE[c]	MP3/ 6-31G*[b] + ΔZPVE[c]	MP4(SDTQ)/ 6-31G*[b] + ΔZPVE[c]
3	0.0	0.0	0.0	0.0	0.0
TS1	37.1	31.7	31.2	31.0	27.5
4	0.0	0.0	0.0	0.0	0.0
5	0.5	0.4	0.5	0.8	−0.9
TS2	40.0	30.0	29.4	30.0	24.8
6	0	0.0	0.0[d]	0.0[d]	
7	−3.2	−3.7	−3.9[d]	−2.5[d]	
TS3	38.9	28.0	27.6[d]	27.6[d]	

[a] A HF/6-31G* optimized geometry was used. [b] A B3LYP/6-31G* optimized geometry was used. [c] At B3LYP/6-31G* unscaled. [d] HF/6-31G* unscaled.

bis(trimethylsilyl)-*N*-(trifluorosilyl)-substituted compound **7** is more stable than the isomeric *N,N*-bis-(trimethylsilyl)-*O*-(trifluorosilyl)-substituted compound **6** by 2.5 kcal mol^{-1} (at MP3/6-31G*//B3LYP/6-31G* + ΔZPVE). Our experience with the isomerization **4 → 5**

$$\underset{\textbf{6}}{\underset{Me_3Si}{\overset{Me_3Si}{\diagdown}}N\!-\!O\underset{SiF_3}{\diagup}} \longrightarrow \underset{\textbf{7}}{\underset{F_3Si}{\overset{Me_3Si}{\diagdown}}N\!-\!O\underset{SiMe_3}{\diagup}} \quad (8)$$

(see Table 2) suggests that more elaborate calculations at the MP4(SDTQ) level would further increase the energy difference between **6** and **7** by ca. 2 kcal mol^{-1}. What is the reason for this small but important stabilization of **7** compared to **6**? Comparison of the isodesmic reactions 9 and 11 suggests that negative F$_3$Si−
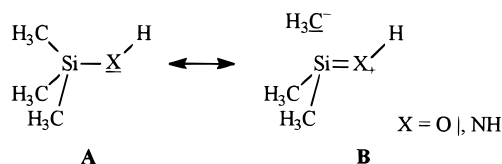
$$H_2N\!-\!SiF_3 + SiH_4 \rightarrow H_2N\!-\!SiH_3 + F_3SiH + \\ 11.2 \text{ kcal} \quad (9)$$

$$H_2N\!-\!SiMe_3 + SiH_4 \rightarrow H_2N\!-\!SiH_3 + Me_3SiH + \\ 3.9 \text{ kcal} \quad (10)$$

$$HO\!-\!SiF_3 + SiH_4 \rightarrow HO\!-\!SiH_3 + F_3SiH + 8.9 \text{ kcal} \quad (11)$$

$$HO\!-\!SiMe_3 + SiH_4 \rightarrow HO\!-\!SiH_3 + Me_3SiH + \\ 6.7 \text{ kcal} \quad (12)$$

$NH_2 \leftrightarrow F|^-F_2Si\!=\!N^+H_2$ hyperconjugation[12,13] is more advantageous than the geminal F$_3$Si−OH $\leftrightarrow$ F|$^-$F$_2$Si$=$O$^+$H interaction by 2.3 kcal mol^{-1}. More

Table 3. Orbital Occupancies (e) and Second-Order Pertubation Energies, ΔE_{ij} (kcal·mol^{-1}), Derived from NBO Analysis of Me$_3$SiOH and Me$_3$SiNH$_2$ (MP2/6-31G*)

	Me$_3$SiXH$_n$	
	XH$_n$ = NH$_2$	XH$_n$ = OH
occupancy of lpX	1.941	1.952; 1.976
occupancy of σ^*_{SiMe}	0.044; 0.044; 0.031	0.054; 0.031; 0.030
ΔE_{ij}(lpX → σ^*_{SiMe})	13.71, 2.85; 2.50	8.58; 8.58; 3.71; 1.78, 1.79

important, inspection of eqs 10 and 12 reveal that geminal alkyl and hydroxy substitution stabilizes a silane by 2.8 kcal mol^{-1} compared to geminal alkyl and amino substitution (at MP4(SDTQ)/6-31G*//B3LYP/6-31G* + ΔZPVE).

The superiority of the geminal methyl/hydroxy interaction at silicon over geminal methyl/amino delocalizations is supported by an NBO analysis[14] of the MP2/6-31G* wave functions of Me$_3$SiOH and Me$_3$SiNH$_2$. The occupancies of the nitrogen or oxygen lone pairs in both compounds are significantly depleted in respect to the ideal value of 2e, and the occupancies of the σ^*_{SiMe} orbitals are significantly larger (see Table 3) than in the reference compound Me$_3$SiH (0.022e). This indicates the occurrence of noteworthy negative hyperconjugation, which is described in valence bond terms by the canonicals **A** and **B**.

$$\underset{\textbf{A}}{\underset{H_3C}{\overset{H_3C}{\diagup}}\underset{H_3C}{\diagdown}\!Si\!-\!\underline{X}\!-\!H} \quad\longleftrightarrow\quad \underset{\textbf{B}}{\underset{H_3C}{\overset{H_3\underline{C}^-}{\diagup}}\underset{H_3C}{\diagdown}\!Si\!=\!X^+\!-\!H} \quad X = O\,|, NH$$

The lp(X) → σ^*_{SiMe} interactions described by the structure **B** are significant in both Me$_3$SiNH$_2$ and Me$_3$-

(12) Müller, T.; Apeloig, Y.; Hemme, I.; Klingebiel, U.; Noltemeyer, M. *J. Organomet. Chem.* **1995**, *494*, 133.
(13) (a) Reed, A. E.; Schleyer, P. v. R. *Inorg. Chem.* **1988**, *27*, 3969. (b) Schleyer, P. v. R.; Jemmins, E. D.; Spitznagel, G. W. *J. Am. Chem. Soc.* **1985**, *107*, 6393. (c) Schleyer, P. v. R.; Reed, A. E. *J. Am. Chem. Soc.* **1987**, *109*, 7362. (d) Schleyer, P. v. R.; Kos, A. *Tetrahedron* **1983**, *39*, 1141. (e) Apeloig, Y.; Stanger, A. *J. Organomet. Chem.* **1988**, *346*, 305. (f) Reed, A. E.; Schade, C.; Schleyer, P. v. R.; Kamath, P. V.; Chandrasekhar, J. *J. Chem. Soc., Chem. Commun.* **1988**, 67.
(14) (a) Glendening, E. D.;. Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. NBO 4.0; Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 1996. (b) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

SiOH. Although the second-order perturbative term ΔE_{ij}[15] for the interaction between the lp(N) and the anti-oriented σ^*_{SiMe} orbital in Me₃SiNH₂ is the largest term of all geminal interactions in Me₃SiOH and Me₃SiNH₂, the sum of ΔE_{ij} values describing all possible lp(X) → σ^*_{SiMe} interactions is 5.4 kcal mol⁻¹ larger for Me₃SiOH than for Me₃SiNH₂ (see Table 3). Thus, according to the NBO analysis the more pronounced lp(O) → σ^*_{SiMe} delocalizations in Me₃SiOH contributes to its higher thermodynamic stabilization compared to Me₃SiNH₂.

Both geminal interactions, the more efficient F₃Si−NH₂ ↔ F⁻F₂Si=N⁺H₂ and the more advantageous lp(O) → σ^*_{SiMe} delocalizations, favor **7** relative to **6**, resulting in a higher thermodynamic stability of **7**.

Methyl substitution at the silyl groups influences also the calculated barrier for the dyotropic isomerization reaction. The activation energy for the transformation **6** → **7** is slightly lower than predicted for **4** → **5** (by 2.4 kcal mol⁻¹ at MP3/6-31G*//B3LYP/6-31G* + ΔZPVE). Our MP4 results for the isomerizations of **3** and **4** (see Table 2) suggest that also the barrier for the rearrangement **6** → **7** is actually 3−5 kcal mol⁻¹ smaller than anticipated from the MP3 calculations. Thus, our calculations for the isomeric hydroxylamines **6** and **7** suggest that the N-fluorosilyl isomer **7** dominates in the equilibrium **6** → **7** and might be even the only observable species. This is in agreement with our experimental finding that **1a,b** cleanly rearranges thermally to **2a,b**. Anomeric stabilization by more favorable negative F−Si−N and O−Si−C hyperconjugation is important in the irreversibility of the reaction. Furthermore, the calculations demonstrate the dyotropic course of the isomerization.

Theoretical Methods

Structures **3**−**7** and **TS1**−**TS3** were initially fully optimized at the SCF/6-31G* level of theory and refined employing Becke's three-parameter hybrid method using the LYP correlational functional (B3LYP) and the 6-31G* basis set. Frequency calculations at this level were used to characterize stationary points. Transition structures were located using the ts routine of Gaussian 94 and the intrinsic reaction coordinate (IRC) method. The energies of the calculated structures were evaluated at the MP4(SDTQ)/6-31G* level and further refined by adding unscaled zero-point energy differences (ΔZPVE). For **6**, **7**, and **TS3** frequency calculations were performed at the SCF/6-31G* level and the energies were evaluated at the MP3/6-31G*//B3LYP/6-31G* level.[16] NBO analyses of the MP2/6-31G* wave functions were performed with the NBO 4.0 program.[14a]

Experimental Section

All experiments were performed in oven-dried glassware under purified nitrogen or argon using standard inert-atmosphere and vacuum-line techniques. All NMR spectra were obtained on either a Bruker AM-250 or MSL-400

(15) The second-order perturbative energy ΔE_{ij}, the stabilization energy associated with the interaction between orbital i and orbital j, is given by the following equation: $\Delta E_{ij} = -2F_{ij}2/\Delta e_{ij}$, where $\Delta e_{ij} = e_j - e_j$. The Fock matrix element F_{ij} is roughly proportional to the corresponding overlap matrix element, S_{ij}, of the interacting orbitals, and e_i and e_j are the energies of the corresponding orbitals.

(16) For an introduction to the applied methods and basis sets, see: (a) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986. (b) Foresman, J. B.; Frisch, Æ. *Exploring Chemistry with Electronic Structure Methods*, 2nd ed.; Gaussian Inc., Pittsburgh, PA, 1996.

spectrometer with SiMe₄ as internal reference or C₆F₆ as external reference. The data are reported in mass to charge units (*m/z*) with their relative intensities in parentheses. The NMR spectra confirmed the purity of **1** and **2**.

O-**(Fluoroisopropylphenylsilyl)-*N,N*-bis(trimethylsilyl)-hydroxylamine (1a).** To a solution of 10.0 g (0.056 mol) of *N,O*-bis(trimethylsilyl)hydroxylamine in hexane was added dropwise 23.8 mL of a solution of *n*-butyllithium in hexane (23%). The mixture was heated to reflux for 3 h. The white suspension was added dropwise to 10.5 g (0.056 mol) of *i*PrPhSiF₂ in hexane at 0 °C. The mixture was warmed to ambient temperature and refluxed for 20 min. After this mixture was cooled to room temperature, the product was condensed *in vacuo* into a trap cooled with liquid nitrogen. The clear liquid obtained was fractionally distilled under reduced pressure to yield 10.9 g (56%), bp 71 °C/0.01 mbar. ¹H NMR (C₆D₆): δ 7.73−7.63 (m, 2 H, phenyl H), 7.18−7.13 (m, 3 H, phenyl H), 1.44−1.30 (m, 1H, CH), 1.22−1.14 (m, 6 H, C(CH₃)₂), 0.13 (d, ⁶J_{HF} = 0.7 Hz, 9 H, Si(CH₃)₃). ¹³C NMR (C₆D₆): δ 135.27 (d, ³J_{CF} = 2.5 Hz, phenyl C2/C6), 131.47 (d, ²J_{CF} = 21.5 Hz, phenyl C1), 130.96 (d, ⁵J_{CF} = 0.5 Hz, phenyl C4), 128.01 (d, ⁴J_{CF} = 0.7 Hz, phenyl C3/C5), 17.75 (d, ³J_{CF} = 1.4 Hz, C*C*H₃), 17.40 (s, C*C*H₃), 12.57 (d, ²J_{CF} = 16.4 Hz, *C*H-(CH₃)₂), 0.77 (d, ⁵J_{CF} = 1.6 Hz, Si(CH₃)₃). ¹⁹F NMR (C₆D₆): δ 16.79 (s, SiF). ²⁹Si NMR (C₆D₆): δ 10.17 (s, Si(CH₃)₃), −14.00 (d, ¹J_{SiF} = 304.5 Hz, SiF). MS (FI): *m/z* 343 (100) [M]⁺. Anal. Calcd for C₁₅H₃₀FNOSi₃ (343.16): C, 52.50; H, 8.81. Found: C, 52.28; H, 8.59.

N-**(Fluoroisopropylphenylsilyl)-*N,O*-bis(trimethylsilyl)-hydroxylamine (2a).** A solution of 10 g (0.03 mol) of **1a** in THF was heated to reflux for 4 days. The reaction can be monitored by ¹⁹F NMR spectroscopy. The solvent was removed by distillation. **2a** was purified by distillation under reduced pressure to yield 8.5 g (84%), bp 71 °C/0.01 mbar. ¹H NMR (CDCl₃): δ 7.73−7.71 (m, 2 H, phenyl H), 7.46−7.43 (m, 3 H, phenyl H), 1.54−1.49 (m, 1 H, CH), 1.24 (s, 3H, C*C*H₃), 1.13 (s, 3H, C*C*H₃), 0.31 (d, ⁵J_{HF} = 1.1 Hz, 9 H, NSi(CH₃)₃), 0.08 (s, 9 H, OSi(CH₃)₃). ¹³C NMR (CDCl₃): δ 134.82 (d, ³J_{CF} = 2.1 Hz, phenyl C2/C6), 132.68 (d, ²J_{CF} = 19.5 Hz, phenyl C1), 130.54 (d, ⁵J_{CF} = 0.5 Hz, phenyl C4), 127.82 (d, ⁴J_{CF} = 0.7 Hz, phenyl C3/C5), 17.51 (d, ³J_{CF} = 1.4 Hz, C(*C*H₃)), 17.16 (s, C(*C*H₃)), 12.15 (d, ²J_{CF} = 18.2 Hz, *C*H(CH₃)₂), 0.60 (d, ⁴J_{CF} = 2.4 Hz, NSi(CH₃)₃), 0.36 (d, ⁵J_{CF} = 0.6 Hz, OSi(CH₃)₃). ¹⁹F NMR (CDCl₃): δ 14.02 (s, SiF). ²⁹Si NMR (CDCl₃): δ 30.75 (s, OSi(CH₃)₃), 8.27 (d, ³J_{SiF} = 1.2 Hz, NSi(CH₃)₃), −10.06 (d, ¹J_{SiF} = 287.9 Hz, SiF). MS (EI): *m/z* 343 (8) [M]⁺, 251 (14) [M − CH₃]⁺. Anal. Calcd for C₁₅H₃₀FNOSi₃ (343.16): C, 52.50; H, 8.81. Found: C, 52.59; H, 8.95.

O-**(Fluorodiphenylsilyl)-*N,N*-bis(trimethylsilyl)hydroxylamine (1b).** To a solution of 10.0 g (0.056 mol) of *N,O*-bis(trimethylsilyl)hydroxylamine in hexane was added dropwise 23.8 mL of a solution of *n*-butyllithium (23%) in hexane. The mixture was refluxed for 3 h. When the lithiation was complete, the white suspension was added dropwise to 14.4 g (0.056 mol) of Ph₂SiF₂ in hexane at 0 °C. The mixture was warmed slowly to ambient temperature and stirred for 1 h. The product was separated from LiF by centrifuging. The product can only be characterized in solution. ¹H NMR (CDCl₃/hexane): δ 7.90−7.75 (m, 4 H, phenyl H), 7.60−7.40 (m, 6 H, phenyl H), 0.28 (d, ⁵J_{HF} = 0.6 Hz, 18 H, Si(CH₃)₃). ¹³C NMR (CDCl₃/hexane): δ 135.85 (d, ³J_{CF} = 1.6 Hz, phenyl C2/C6), 131.22 (d, ²J_{CF} = 22.7 Hz, phenyl C1), 131.10 (d, ⁴J_{CF} = 0.5 Hz, phenyl C3/C5), 127.95 (s, phenyl C4), 0.64 (d, ⁵J_{CF} = 1.6 Hz, Si(CH₃)₃). ¹⁹F NMR (CDCl₃/hexane): δ 24.25 (s, SiF). ²⁹Si NMR (CDCl₃/hexane) δ 11.68 (s, Si(CH₃)₃), −26.83 (d, ¹J_{SiF} = 293.4 Hz, SiF).

N-**(Fluorodiphenylsilyl)-*N,O*-bis(trimethylsilyl)hydroxylamine (2b). Method 1.** To a solution of 10.0 g (0.056 mol) of *N,O*-bis(trimethylsilyl)hydroxylamine in hexane was added dropwise 23.8 mL of a solution of *n*-butyllithium in hexane (23%). The mixture was refluxed for 3 h. The suspension was

added dropwise to 14.4 g (0.056 mol) of Ph_2SiF_2 in THF and heated to reflux for 1 h. For separation the product was condensed *in vacuo* into a trap cooled with liquid nitrogen and purified by distillation at 123 °C/0.01 mbar to yield 10.2 g (48%).

Method 2. By heating or trying to distill compound **1b**, only the isomer **2b** can be isolated. ^{1}H NMR (C_6D_6): δ 7.76−7.74 (m, 4 H, phenyl H), 7.13−7.11 (m, 6 H, phenyl H), 0.15 (s, 9 H, NSi$(CH_3)_3$), 0.02 (s, 9 H, OSi$(CH_3)_3$). ^{13}C NMR (C_6D_6): δ 135.71 (d, $^3J_{CF}$ = 1.5 Hz, phenyl C6/C2), 132.62 (d, $^2J_{CF}$ = 21.8 Hz, phenyl C1), 131.02 (d, $^4J_{CF}$ = 0.5 Hz, phenyl C3/C5), 128.16 (s, phenyl C4), 0.63 (d, $^4J_{CF}$ = 2.1 Hz, NSi$(CH_3)_3$), 0.56 (d, $^5J_{CF}$ = 0.6 Hz, OSi$(CH_3)_3$). ^{19}F NMR (C_6D_6) δ 8.08 (s, SiF). ^{29}Si NMR (C_6D_6): δ 30.68 (s, OSi$(CH_3)_3$), 9.51 (d, $^3J_{SiF}$ = 0.9 Hz, NSi$(CH_3)_3$), −21.33 (d, $^1J_{SiF}$ = 280.3 Hz, SiF). MS (FI) m/z 377 (100) [M]$^+$. Anal. Calcd for $C_{18}H_{28}FNOSi_3$ (377.15): C, 57.32; H, 7.48. Found: C, 57.56; H, 7.65.

Supporting Information Available: Tables giving absolute energies (*H*) of trisilylhydroxylamines and related compounds and *XYZ* coordinates of the B3LYP/6-31G* optimized geometries of compounds **3**−**7** (9 pages). Ordering information is given on any current masthead page.

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