Organosilyl and Organogermyl Nitroxides. A New Radical Rearrangement[1,2]

Robert West* and Philip Boudjouk

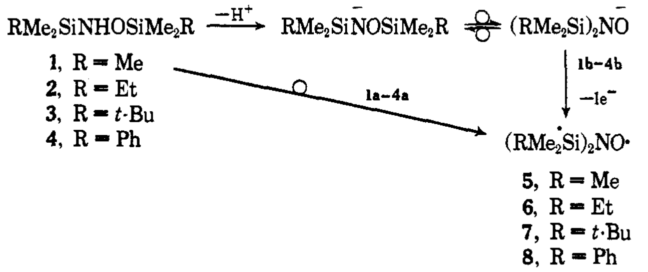
Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received December 20, 1971*

Abstract: Bis(organosilyl) nitroxide radicals $(RMe_2Si)_2NO\cdot$, where R = Me, Et, Ph, *t*-Bu, have been obtained by (1) electrolytic or (2) oxygen oxidation of bis(organosilyl)hydroxylamine anions and by (3) hydrogen abstraction and radical rearrangement of the *N,O*-bis(organosilyl)hydroxylamines (the first example of an O → N radical rearrangement). Esr spectra of bis(organosilyl) nitroxides show very low A_N values of ~6.5 G, consistent with strong dative bonding from nitrogen to silicon and consequent unpaired electron localization on oxygen. $Me_3Ge(t\text{-}BuMe_2Si)\dot{N}O$, $(Me_3Ge)_2\dot{N}O$, and $(t\text{-}BuMe_2Ge)_2\dot{N}O$, also prepared from the corresponding hydroxylamines, showed A_N values of 7.6, 8.8, and 8.8 G, respectively.

Earlier we reported our preliminary results[3] on a new class of nitroxide radicals, bis(organosilyl) nitroxides. In this paper we present details of further investigations of organosilyl nitroxides and the first report of an O → N radical rearrangement.[4-6] Evidence is also presented for the detection of a silyl–germyl nitroxide and two digermyl nitroxides.

Results

Experiments in our laboratories have shown that *N,O*-bis(organosilyl)hydroxylamines, **1**–**4**, when treated with 1 equiv of alkyllithium, form an equilibrium between unrearranged and rearranged anions, **1a**–**4a** and **1b**–**4b**, respectively.[7] Nitroxide radicals **5**–**8** have been generated by (1) electrolytic or (2) oxygen oxidation of the mixture of anions **1a**–**4b**, and by (3) spontaneous rearrangement of radicals resulting from hydrogen abstraction of the parent hydroxylamines **1**–**4**.

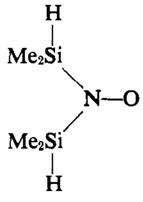


1, R = Me
2, R = Et
3, R = *t*-Bu
4, R = Ph

5, R = Me
6, R = Et
7, R = *t*-Bu
8, R = Ph

These methods produced radicals with nitrogen hyperfine splitting constants (A_N) of approximately 6.5 G. The esr spectrum of **5**, shown in Figure 1, is representative of the spectra obtained from **5** to **8**. For each compound, three lines of equal intensity arising from coupling of the unpaired electron with the ^{14}N nucleus ($I = 1$) are observed. Each of the principal lines is accompanied by a pair of satellites with hyperfine splitting of 5.9 G. The intensities of the satellite lines relative to the ^{14}N absorptions were 4.6%. This value is in good agreement with the calculated intensity (4.7%) for two silicon atoms bonded to nitrogen, and so provides strong evidence that the observed spectra are due to disilyl nitroxide radicals.[8]

N,O-Bis(dimethylsilyl)hydroxylamine (**9**) and *N,O*-bis(*tert*-butylmethylsilyl)hydroxylamine (**10**), prepared by Wannagat's method,[9] were used to make bis(dimethylsilyl) nitroxide (**11**) and bis(*tert*-butylmethylsilyl) nitroxide (**12**), respectively. In isostructural dialkyl nitroxides, for instance, diisopropyl nitroxide, hyperfine splitting by hydrogen attached to the α-carbon atom is observed, but the Si–H coupling constants were too small to be resolved. The esr spectra of **11** and **12** consisted of three broad lines at −70°. Both spectra improved in resolution when the temperature was increased but the radicals proved to be unstable. The half-life of **11** was about 15 min at −30°, while **12** had a half-life of about 20 min at 0°.



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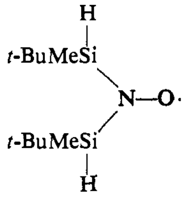

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The radicals **5**–**8** were stable in dilute solution in the absence of air for several days but decomposed upon exposure to the atmosphere. When dry oxygen was bubbled into a solution of **5** in tetrahydrofuran (THF), the 6.5-G signal disappeared and was replaced by a complicated spectrum arising from several radicals. The most stable one of these ($t_{1/2} \approx$ 1 hr at 30°) gave

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[1] It has been suggested that the term "nitroxyls" be used for these radicals rather than the more widely accepted "nitroxides" because the former is more consistent with IUPAC nomenclature and accurately reflects their radical nature: E. G. Rozantsev and V. D. Scholle, *Synthesis*, 4, 190 (1971).

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

[3] (a) R. West and P. Boudjouk, *J. Amer. Chem. Soc.*, **93**, 5901 (1971). (b) For reviews of nitroxides, see A. R. Forrester, J. M. Hay, and R. H. Thomson, "Stable Organic Free Radicals," Academic Press, New York, N. Y., 1968, Chapter 5; E. G. Janzen, *Accounts Chem. Res.*, **2**, 279 (1969); E. G. Rozantsev, "Free Nitroxyl Radicals," Plenum Publishing Co., New York, N. Y., 1970.

[4] The 1,2 N → O rearrangement in tertiary amine oxides (Meisenheimer rearrangement) has recently been observed to follow a radical mechanism: A. R. Lepley, P. M. Cooke, and G. F. Willard, *J. Amer. Chem. Soc.*, **92**, 1101 (1970).

[5] *N,O*-Dialkylhydroxylamines do not undergo radical rearrangement following hydrogen abstraction: W. C. Danen and C. T. West, *ibid.*, **93**, 5582 (1971).

[6] Radical rearrangements involving organosilicon groups have been reviewed: R. A. Jackson, *Advan. Free-Radical Chem.*, **3**, 278 (1969).

[7] R. West, P. Boudjouk, and T. A. Matuszko, *J. Amer. Chem. Soc.*, **91**, 5184 (1969); R. West and P. Boudjouk, **95**, 3987 (1973).

[8] Lines due to coupling of the unpaired electron with silicon-methyl or silicon-phenyl protons were not observed.

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

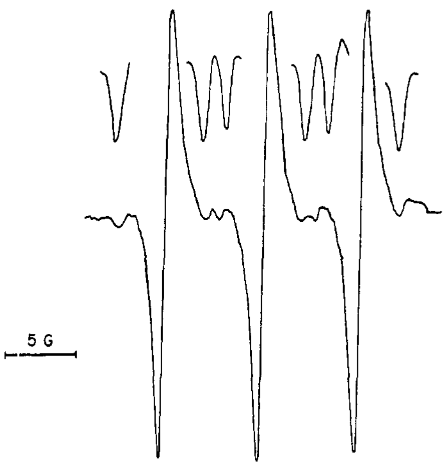


Figure 1. Esr spectrum of **5** at low gain. The ^{29}Si satellites are shown above at high gain and expanded sweep width.

an esr signal of three broad lines of roughly equal intensity with an A_N of approximately 15 G. This is probably the radical observed by Chapelet-Letourneux, Lemaire, and Rassat[10] from the reaction of *p*-nitroperbenzoic acid with hexamethyldisilazane, and reported as the disilyl nitroxide **5**. When **7** was similarly treated with oxygen, the 6.5-G splitting also disappeared, but in this case only one radical was observed ($A_N \approx 15$ G). (The steric hindrance of the *tert*-butyldimethylsilyl groups probably minimizes side reactions.) The spectra obtained for these radicals were poorly resolved (probably because of dissolved oxygen) and no ^{29}Si satellites could be observed. Similar short-lived radicals giving three-line spectra with A_N approximately 15 G were also obtained when hexamethyldisilazane, $(Me_3Si)_2NH$ (**13**), or di-*tert*-butyltetramethyldisilazane, $(t\text{-}BuMe_2Si)_2NH$ (**14**), was treated with *m*-chloroperbenzoic acid in carbon tetrachloride.[11]

Radical Rearrangement of *N*,*O*-Bis(organosilyl)hydroxylamines. When solutions of **1–4** and di-*tert*-butyl peroxide (DTBP) were photolyzed in the esr cavity the radicals **5–8** were observed. These provide the first examples of an O → N radical rearrangement.[4–6] The N–H hydrogen is abstracted by the *tert*-butoxy radical formed when DTBP is exposed to uv light. The hydroxylamine radical formed then rearranges to the bis(organosilyl) nitroxide. The unrearranged radical was not detected even at −80°.

$$t\text{-BuOO-}t\text{-Bu} \xrightarrow{\text{uv}} 2t\text{-BuO}\cdot$$

$$t\text{-BuO}\cdot + R_3SiNHOSiR_3 \longrightarrow R_3Si\dot{N}OSiR_3 + t\text{-BuOH}$$

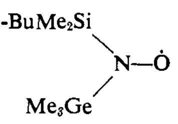
$$R_3Si\dot{N}OSiR_3 \xrightarrow{\frown} (R_3Si)_2NO\cdot$$

Germyl Nitroxides. To obtain A_N values for nitroxides containing organogermanium groups, we synthesized **20**, **23**, and **24**. *O-tert*-Butyldimethylsilylhydroxylamine (**19**), when treated with 1 equiv of *n*-butyllithium and derivatized with trimethylchlorogermane, gave two products, **20** and **21**. Although nmr indicates

$$\underset{\textbf{19}}{H_2NOSiMe_2\text{-}t\text{-Bu}} \xrightarrow[\text{2. Me}_3\text{GeCl}]{\text{1. }n\text{-BuLi}}$$

$$\underset{\textbf{20}}{Me_3GeNHOSiMe_2\text{-}t\text{-Bu or } t\text{-BuMe}_2SiNHOGeMe_3} + \underset{\textbf{21}}{t\text{-BuMe}_2SiOGeMe_3}$$

that **20** is isomerically pure, we cannot decide between the two structures shown (see Experimental Section). When **20** was treated with 1 equiv of alkyllithium and oxidized electrolytically, a radical was observed in the esr that had an A_N of 7.6 G and ^{29}Si satellites 5.9 G apart. The same radical was obtained when a solution of **20** and DTBP was photolyzed in the esr cavity. The *g* value was 2.0087. The relative intensity of the satellites to the main peaks was 2.1 %, which is in good agreement with the calculated value (2.35 %) for a radical with one silicon bonded to nitrogen, consistent with our proposed structure.



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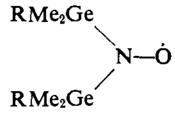
N,*O*-Bis(trimethylgermyl)hydroxylamine (**23**) and *N*,*O*-bis(*tert*-butyldimethylgermyl)hydroxylamine (**24**) were prepared in low yield by Wannagat's method.[9] When solutions of these compounds in THF were treated with an alkyllithium and oxidized, radicals with A_N values of 8.8 G ($g = 2.0075$) were observed. In both cases the spectra consisted of three asymmetric lines of equal intensity. Satellite peaks from the ^{73}Ge nucleus could not be resolved.[13] We believe these radicals have the structures



25, R = Me
26, R = *t*-Bu

Radicals **25** and **26** were also produced by radical rearrangement of the parent hydroxylamines **23** and **24**, respectively.

Discussion

In all of the nitroxides which we have investigated with organosilicon or organogermanium groups bound

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[10] G. Chapelet-Letourneaux, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. Fr.*, 3283 (1965).

[11] (a) On the basis of present evidence we can only speculate on the structures of the 15-G radicals. However, it is reasonable to assume that the reactive Si–N bond might break under oxidizing conditions and form Si–O bonds which are much stronger.[11b] The observation of other radicals in the esr after **5** was exposed to oxygen suggests that cleavage does occur in **7**. The 15-G radicals perhaps result from insertion of oxygen into one or both Si–N bonds of **5** and **7** to form radicals **15–18**. Oxidation of the disilazanes **13** and **14** by *m*-chloroperbenzoic acid could also lead to **15–18** if the nitroxides **5** and **7** were

$$\underset{\textbf{15, 16}}{RMe_2Si\overset{\overset{\displaystyle O\cdot}{|}}{N}OSiMe_2R} \qquad \underset{\textbf{17, 18}}{RMe_2SiO\overset{\overset{\displaystyle O\cdot}{|}}{N}OSiMe_2R}$$

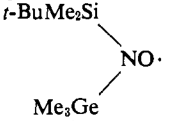
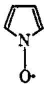
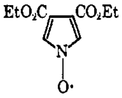
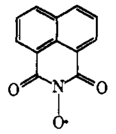
15 R = Me **17**
16 R = *t*-Bu **18**

formed first and then further oxidized. The carbon analogs to **15** and **16** are known[12] and are characterized by high values for A_N of 25–30 G; the presence of a silicon group on nitrogen might reduce the A_N to 15 G. There are no analogs to **17** and **18** and it is difficult to predict the magnitude of the A_N. (b) E. A. V. Ebsworth in "Organometallic Compounds of the Group IV Elements," Vol. 1, A. G. MacDiarmid, Ed., Marcel Dekker, New York, N. Y., 1968, Chapter 1.

[12] A. Mackor, Th. A. J. W. Wajer, Th. J. deBoer, and J. D. W. vanVoorst, *Tetrahedron Lett.*, 385 (1967).

[13] Germanium has only one isotope with spin, ^{73}Ge ($I = {}^9/_2$), and its natural abundance is 7.76 %. Any lines resulting from interaction of the unpaired electron with ^{73}Ge would be very low in intensity and broadened by overlap.

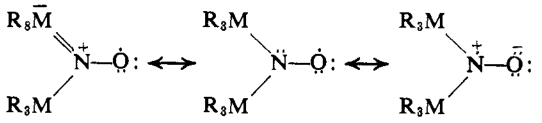
Table I. Electron Spin Resonance Data for Selected Nitroxides

Radical	A_N	g	Solvent	Ref
$Me_2NO\cdot$	17.1	2.0055	Water	*a*
$t\text{-}Bu_2NO\cdot$	15.2	2.0065	Benzene	*b*
$(p\text{-}MeO\text{–}Ph)_2NO\cdot$	10.07	2.0056	Xylene	*c*
$Ph_2NO\cdot$	9.66	2.0056	Xylene	*c*
$(F_3C)_2NO\cdot$	9.3	2.0075	Carbon tetrachloride	*d*
$(RMe_2Ge)_2NO\cdot$ R = Me, *t*-Bu	8.8	2.0075	THF–hexane, DTBP	This work
$(p\text{-}O_2N\text{–}Ph)_2NO\cdot$	8.38	2.0062	Xylene	*c*
 $t\text{-}BuMe_2Si(Me_3Ge)NO\cdot$	7.6	2.0086	THF–hexane, DTBP	This work
$(RMeSiH)_2NO\cdot$ R = Me, *t*-Bu	6.5		THF–hexane	This work
$(RMe_2Si)_2NO\cdot$ R = Me, Et, *t*-Bu, Ph	6.5	2.0093	THF–hexane, DTBP	This work
	4.75	2.0061	Benzene	*e*
	4.58		Benzene	*e*
	4.2		Methylene chloride	10

[a] R. E. Florin, *J. Chem. Phys.*, **47**, 345L (1967); the A_N of $Me_2NO\cdot$ in CCl_4 is 15.2 G. The coupling constant for a hydrogen atom attached to an atom bound to nitrogen in a nitroxide is also affected by the conformation of the entire group bonded to the nitrogen. Thus, $A_{\beta\text{-}H}$ = 10.3 G for $(CH_3CH_2)_2NO\cdot$ and for $[(CH_3)_2CH]_2NO\cdot$, $A_{\beta\text{-}H}$ = 4.5 G; see J. Q. Adams, S. N. Nicksic, and J. R. Thomas, *J. Chem. Phys.*, **45**, 654 (1966).] The A_N's of nitroxides are higher and the *g* values lower in protonic solvents because hydrogen bonding involves the lone pair of electrons on oxygen. This increases the unpaired electron density on nitrogen and lowers the *g* value. The interaction between nitroxides and complexing agents has been the subject of several recent studies: B. M. Hoffman and T. B. Eames, *J. Amer. Chem. Soc.*, **93**, 3141 (1971); Y. Y. Lim and R. S. Drago, *ibid.*, **93**, 891 (1971). [b] A. K. Hoffman and A. T. Henderson, *ibid.*, **83**, 4671 (1961). [c] P. H. H. Fischer and F. A. Z. Neugebauer, *Z. Naturforsch. A*, **19**, 1514 (1966); P. H. H. Fischer and F. A. Z. Neugebauer, *Z. Naturforsch. B*, **21**, 1036 (1966). [d] W. D. Blackley and R. R. Reinhard, *J. Amer. Chem. Soc.*, **87**, 802 (1965). The *g* value was estimated from Figure 8 in T. J. Schaafsma and D. Kivelson, *J. Chem. Phys.*, **49**, 5235 (1968). Apparently there is a typographical error in the original report (Blackley and Reinhard's) which gives a *g* value of 2.0046. [e] R. Rammaseul and A. Rassat, *Bull. Soc. Chim. Fr.*, 4330 (1970).

to nitrogen, the A_N's are reduced significantly from that for typical organic nitroxides. For comparison, several nitroxides, including the new ones described in this paper, are listed in Table I in order of decreasing A_N. Inspection of the table shows that A_N is inversely proportional to the electron-withdrawing power of the groups attached to nitrogen and, of all the known nitroxides, only naphthalenediacyl nitroxide and pyrrole nitroxides have lower A_N's than the bis(organosilyl) nitroxides.[14] We feel that the best explanation for these results is that the lone pair of electrons on nitrogen is withdrawn into the vacant d orbitals on silicon and that the unpaired electron is shifted toward the oxygen. The replacement of an organosilicon by organogermanium groups raises the A_N value to 7.6 G in **22** and to 8.8 G in the bis(organogermyl) nitroxides **25** and **26**. This increase in A_N probably reflects weaker $d_\pi\text{–}p_\pi$ bonding to germanium than to silicon. It is interesting to note, however, that in nitroxides the electron-withdrawing power of organogermyl groups, while apparently less than organosilyl groups, seems to be greater than trifluoromethyl.

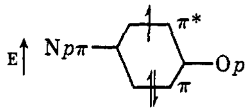
Our results can be interpreted using valence bond theory in which three resonance structures can be considered



I II III

Hyperfine splitting from nitrogen results from contribution of canonical structure III, in which the unpaired electron is localized on the nitrogen atom. In dialkyl nitroxides only canonical structures II and III contribute to the resonance hybrid, and form III is believed to be the more important. The low A_N value for organosilyl nitroxides suggests that III contributes much less to the resonance hybrid for these compounds. In the silyl nitroxides dative bonding from N to Si can take place, represented by a contribution from structure I. The surprisingly low A_N can therefore be explained as due to the dative N → Si bond, shifting the unpaired electron density to oxygen. The contribution of form I appears to be greater for M = Si than for M = Ge, consistent with greater dative π-bonding to silicon than to germanium.

The effect of silicon and germanium on the nitroxide bond can also be described in terms of simple MO theory. The three electrons of the nitroxide bond reside in π and π* orbitals derived from linear combinations of the nitrogen and oxygen pπ orbitals. Two of the electrons occupy the bonding π orbital and the unpaired electron is in the antibonding π* orbital. The effective electronegativity of nitrogen is enhanced when electron-withdrawing groups are attached to it thereby increasing the nitrogen character of the π orbital. Consequently, the oxygen character of the π* orbital holding the unpaired electron is increased.



The small coupling constants for silyl hydrogens in **11** and **12** are consistent with low unpaired electron density on the nitrogen, although other factors[15] may also be responsible for reducing $A_{Si\text{-}H}$.

The *g* values for most organic nitroxides are in the range 2.0060 ± 0.0005, but in bis(organosilyl) nitroxides

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(14) The lower A_N's of aryl and acyl nitroxides are primarily the result of the delocalization of the unpaired electron into the phenyl and carbonyl π systems, respectively. However, the effect of electron-withdrawing and electron-donating substituents in these radicals on the A_N is through the lone pair of electrons on nitrogen.[3b] The mechanism which lowers the A_N for pyrrole nitroxides is not known.

(15) The coupling constant for a hydrogen atom attached to an atom bound to nitrogen in a nitroxide is also affected by the conformation of the entire group bonded to the nitrogen. Thus, $A_{\beta\text{-}H}$ = 10.3 G for $(CH_3CH_2)_2NO\cdot$ and for $[(CH_3)_2CH]_2NO\cdot$, $A_{\beta\text{-}H}$ = 4.5 G; see J. Q. Adams, S. N. Nicksic and J. R. Thomas, *J. Chem. Phys.*, **45**, 654 (1966).

g values are 2.0092 ± 0.0001. The spin–orbit coupling constant for oxygen (151 cm^{-1}) is greater than that for nitrogen (70 cm^{-1}),[16] so the increased *g* values for the disilyl nitroxides are consistent with the much increased unpaired electron density on oxygen in these compounds compared with dialkyl nitroxides.

The stability of the nitroxide three-electron bond apparently provides sufficient driving force to allow migration of organosilyl and organogermyl groups from oxygen to nitrogen following hydrogen abstraction from the parent hydroxylamine. The energy gained from the formation of the nitroxide function must outweigh the differences in Si–O (106 kcal) and Si–N (76 kcal) and Ge–O (~85 kcal) and Ge–N (61 kcal).[11b]

Experimental Section

Analytical and preparative gas chromatography was carried out using a Varian Aerograph Model 90-P chromatograph. Proton nmr were determined with a Varian A-60-A spectrometer, and chemical shifts were obtained by internal referencing with benzene in 15–20% v/v solutions. Ir spectra were obtained as neat liquid films on NaCl plates on a Perkin-Elmer 457 grating spectrophotometer. Esr spectra were recorded on Varian V-4502-13 or E-3 spectrophotometers equipped with variable-temperature attachments. Electrolytic oxidation was carried out in cells of 4-mm Pyrex tubing with platinum wire electrodes.[17] Photolytic reactions were carried out in quartz or Pyrex tubes using an Oriel Model No. C-60-80 mercury lamp focused on the sample tube in the esr cavity. The *g* values for **5–8**, **22**, **25**, and **26** were measured at room temperature using a capillary tube of Fremy's solution as a standard (2.0057 ± 0.0001). The A_N's were measured using Fremy's salt as a standard (A_N = 13.00 ± 0.07) and did not show marked solvent or temperature dependence. The average line widths for **5–8**, **22**, and **25** were 1.6, 1.8, and 2.4 G, respectively.

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. Di-*tert*-butyl peroxide was obtained from Matheson Coleman and Bell and used without further purification. Hexamethyldisilazane was obtained from Dow Chemical Co. and used without further purification.

Hydroxylamine was prepared by the method of Hurd.[18] *tert*-Butyldimethylchlorosilane was obtained from the reaction of 1 equiv of *tert*-butyllithium with dimethyldichlorosilane.[19] Trimethylchlorogermane was obtained from Alfa as a yellow liquid (purity by vpc ~80%) and used without further purification. The preparations of compounds **1–4** and **19** are described elsewhere.[7]

Sample Preparation. All of the nitroxides described in this paper were generated by three different methods with the exception of **11** and **12** which were produced only by the electrolytic oxidation of a solution of the lithium salt of the parent hydroxylamines.

a. Electrolytic Oxidation of the Lithium Salts of Substituted Hydroxylamines. The parent hydroxylamine (1 or 2 g) was treated with 1 equiv of *n*-butyllithium in THF-pentane solution at −78°. A small aliquot (2 or 3 μl) was then removed by syringe and injected into an electrolytic cell containing a degassed THF solution of tetra-*n*-butylammonium perchlorate. The contents of the cell were then degassed by the freeze–thaw technique before electrolysis in the esr cavity. Intense signals were obtained after only a few seconds of electrolysis.

b. Chemical Oxidation by Oxygen. Samples were prepared as above and then treated with oxygen by injecting about 0.1 ml of dry air into the solution. This was sufficient to give an intense signal.

c. Radical Rearrangement. Equal volumes of DTBP and the substituted hydroxylamine were mixed in a dry N_2 filled tube and photolyzed for only a few seconds to generate enough radicals to give an intense signal.

Preparation of *tert*-Butylmethylchlorosilane. To a solution of 57.5 g (0.5 mol) of methyldichlorosilane in 300 ml of ether was added 405 ml (0.5 mol) of 1.24 *M* *tert*-butyllithium at 0°. Salt precipitated immediately. After the solution was stirred overnight at room temperature, lithium chloride was removed by filtration under nitrogen and the pale yellow filtrate was distilled to give 124 g (90%) of *tert*-butylmethylchlorosilane: bp 102–105°; ir (neat) 2980, 2185 (Si–H), 1470, 1260, 900, 840 cm^{-1}; nmr τ 9.83 (d, SiMe, 3), 9.13 (s, Si-*t*-Bu, 9), 5.37 (q, Si–H, 1).

Anal. Calcd for $C_5H_{13}Si_{28}Cl$: C, 43.93; H, 9.59. Found: C, 44.10; H, 9.72.

Preparation of *tert*-Butyldimethylchlorogermane. Dimethyldichlorogermane and *tert*-butyllithium were reacted as described above to give a 60% yield of *tert*-butyldimethylchlorogermane, a waxy solid: mp 93–94°; bp 147–154°; ir (Nujol) 2950, 1250, 1010, 840, 800 cm^{-1}; nmr τ 9.58 (s, $GeMe_2$, 6), 8.99 (s, Ge-*t*-Bu, 9).

Anal. Calcd for $C_6H_{15}GeCl$: C, 36.91; H, 7.74. Found: C, 37.10; H, 7.59.

***N*,*O*-Bis(dimethylsilyl)hydroxylamine (9) and *N*,*O*-Bis(*tert*-butylmethylsilyl)hydroxylamine (10).** Hydroxylamine and triethylamine were reacted with dimethylchlorosilane and *tert*-butylmethylchlorosilane according to Wannagat's procedure[9] giving **9**, bp 40–47° (100 Torr), and **10**, bp 62–65° (2 Torr), in 60 and 75% yields, respectively. Analytical samples were obtained by preparative gas chromatography: ir (**9** neat) 3300 (N–H), 2850, 2110 (Si–H), 1250, 900, 860 cm^{-1}; nmr τ 9.84 (d, $SiMe_2$, 6), 9.74 (d, $SiMe_2$, 6), 5.06 (m, N–H, O–Si–H, N–Si–H, 3); ir (**10**, neat) 3300 (N–H), 2950, 2120 (Si–H), 1250, 840 cm^{-1}; nmr τ 9.86 (d, $SiMe_2$, 3), 9.76 (d, $SiMe_2$, 3), 9.01 (s, Si-*t*-Bu, 9), 8.96 (s, Si-*t*-Bu, 9), 5.66 (q, Si–H, 1), 5.42 (q, Si–H, 1), 5.03 (s, N–H, 1).

Anal. Calcd for $C_4H_{15}NSi_2O$ (**9**): C, 32.17; H, 10.12; N, 9.37; Si, 37.61. Found: C, 32.05; H, 10.10; N, 9.39; Si, 37.85. Calcd for $C_{10}H_{27}NSi_2O$ (**10**): C, 51.43; H, 11.66; N, 6.00; Si, 24.06. Found: C, 51.51; H, 11.47; N, 6.06; Si, 24.31.

Preparation of *tert*-Butyldimethylsilylamine. A solution of 4.5 g (0.03 mol) of *tert*-butyldimethylchlorosilane in 20 ml of pentane at −78° was treated with excess ammonia by bubbling the gaseous ammonia through the reaction mixture for 20–30 min. White precipitate formed immediately. After the ammonia flow was stopped, the reaction mixture was allowed to warm to room temperature and then refluxed for a few hours to remove the unused ammonia. Ammonium chloride was removed by filtration under nitrogen and the solvents were removed by distillation. The product (3 g, 77%), *tert*-butyldimethylsilylamine, was isolated by preparative gas chromatography: ir (neat) 3490, 3450 (NH_2), 2950, 1250, 860, 830 cm^{-1}; nmr τ 9.94 (s, $SiMe_2$, 6), 9.82 (s, NH_2, 1), 9.04 (s, Si-*t*-Bu, 9).

Anal. Calcd for $C_6H_{17}NSi$: C, 54.89; H, 13.05; N, 10.67; Si, 21.39. Found: C, 54.78; H, 12.87; N, 10.41; Si, 21.73.

Preparation of Di-*tert*-butyltetramethyldisilazane (14). A solution of 2.0 g (0.015 mol) of *tert*-butyldimethylsilylamine in 20 ml of ether was treated with 1 equiv of *tert*-butyllithium at −78° followed by derivatization with excess *tert*-butyldimethylchlorosilane. The next day lithium chloride was removed by filtration and the solvents were removed by distillation. The residue was analyzed by glpc and showed one product. **14** (3 g, 81%) was collected by preparative gas chromatography: ir (neat) 3450 (N–H), 2900, 1250, 1175, 930, 830, 790 cm^{-1}; nmr τ 9.82 (s, $SiMe_3$, 12), 8.99 (s, Si-*t*-Bu, 18), 4.4 (s, N–H, 1).

Anal. Calcd for $C_{12}H_{31}NSi_2$: C, 58.70; H, 12.73; N, 5.80; Si, 22.98. Found: C, 58.90; H, 12.85; N, 5.76; Si, 23.01.

Reaction of *O*-*tert*-Butyldimethylsilylhydroxylamine (19) with *n*-Butyllithium and Trimethylchlorogermane. To a solution of 2.0 g (13.6 mmol) of **19** in THF-pentane was added 1 equiv of *n*-butyllithium at −78°. The resulting salt solution was then treated with 2.1 g (13.6 mmol) of trimethylchlorogermane. The next day lithium chloride was removed by filtration under nitrogen through a glass frit and the filtrate distilled. After removal of solvent, 2 ml of a clear pink solution was collected, bp 55–80° (15 Torr). Analysis by glpc showed two major products in a 3:2 ratio which were isolated by preparative gas chromatography. The minor product was identified as *tert*-butyldimethylsilyltrimethylgermyl oxide (**19**): ir (neat) 2950, 1260, 1010, 850 cm^{-1}; nmr τ 9.85 (s, $SiMe_2$, 2), 9.67 (s, $GeMe_3$, 3), 8.93 (s, Si-*t*-Bu, 3). The major product was an isomer of *tert*-butyldimethylsilyltrimethylgermylhydroxylamine (**20**): ir (neat) 3240 (N–H), 2950, 1250, 950, 840, 785 cm^{-1}; nmr τ 9.74 (s, $SiMe_2$, 6), 9.72 (s, $GeMe_3$, 9), 8.91 (s, Si-*t*-Bu, 9), 5.4 (s, N–H, 1). A structural assignment for **20** was not possible because the different electronegativities of germanium and silicon do not allow the use of relative chemical shifts as a method for assigning peaks to protons in groups bound to nitrogen and oxygen as was done for bis(organosilyl)hydroxylamines.[7]

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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]

Robert West* and Philip Boudjouk

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706.

Received December 20, 1971

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]

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

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).