We are continuing to investigate the synthetic utility of this new method of generating nitrenium ions.

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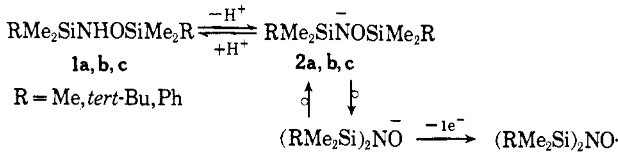
Bis(organosilyl) Nitroxides[1]

Sir:

Our investigations of the 1,2 O → N anionic rearrangement of *N*,*O*-bis(organosilyl)hydroxylamines[2] have enabled us to synthesize several bis(organosilyl) nitroxide radicals under very mild conditions. When examined by esr spectroscopy, these radicals show a surprisingly low A_N value near 6.5 G, consistent with extensive delocalization of the nitrogen lone pair of electrons into the d orbitals on silicon and localization of the unpaired electron largely on the oxygen atom.[3]

Studies in our laboratories[4] have shown that *N*,*O*-bis(organosilyl)hydroxylamines (**1a–c**) form, on the treatment with base, an equilibrium between **2a–c** and **3a–c**. Mild oxidation of the equilibrium mixture electrolytically or with dry oxygen leads to the bis(organosilyl) nitroxide radicals, **4a–c**.



$$\begin{tikzcd} \mathrm{RMe_2SiNHOSiMe_2R} \arrow[r, shift left, "-\mathrm{H}^+"] & \mathrm{RMe_2Si\bar{N}OSiMe_2R} \arrow[l, shift left, "+\mathrm{H}^+"] \arrow[d, shift left] \\ & (\mathrm{RMe_2Si})_2\mathrm{N\bar{O}} \arrow[u, shift left] \arrow[r, "-1e^-"] & (\mathrm{RMe_2Si})_2\mathrm{NO\cdot} \end{tikzcd}$$

1a, b, c **2a, b, c** **3a, b, c** **4a, b, c**

R = Me, *tert*-Bu, Ph

The esr spectrum of **4a** shows three lines of equal intensity arising from ^{14}N ($I = 1$). These are each flanked by a pair of satellite lines, 5.9 G apart with intensity 4.6% of the main line. This agrees well with the theoretical value of 4.7% for two chemically equivalent silicon atoms. Coupling of the unpaired electron with protons of the methyl groups on silicon was not observed indicating that electron pair delocalization and not spin delocalization is responsible for the low A_N. The radicals **4a–4c** all have g values of 2.0092 ± 0.001, and line widths of 1.6 G.

When oxygen is bubbled through a solution of **4a** a yellow color is slowly formed and several new radicals are seen in the esr spectrum. The most stable one ($t_{1/2} \sim 1$ hr) gives an esr signal of three broad lines of roughly equal intensity with an A_N of 15 G. This is probably the radical reported by Chapelet-Letourneaux, *et al.*[5] The presence of other radicals indicates that the 15-G radical might result from cleavage of bonds in **4a**.

Nitroxide radicals with different substituents on the nitrogen and their respective A_N's are listed in Table I. The steady decrease in the A_N as the groups on nitrogen become more electronegative arises from withdrawal of the lone pair of electrons on nitrogen by the substituent,[6] accompanied by the localization of the unpaired electron on the oxygen. Organosilicon groups, by comparison, exhibit a very strong electron-withdrawing influence on nitrogen, apparently even stronger than trifluoromethyl groups. Such extensive delocalization of the nitrogen lone pair could be effected through the use of the vacant 3d orbitals on silicon. In terms of valence bond formulations, I makes a large contribution to the resonance hybrid and III has much less importance than it does for the carbon analog, di-*tert*-butyl nitroxide.[7]

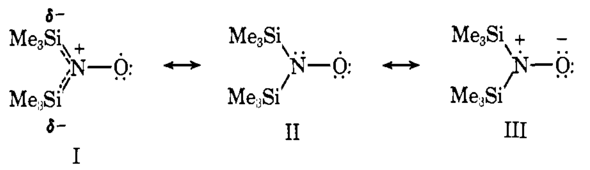
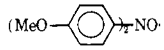
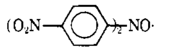
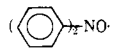


Table I. Electron Spin Resonance Data for Selected Nitroxides

Radical	A_N, G	Solvent	Ref	Radical	A_N	Solvent	Ref
$(Me_3C)_2NO\cdot$	15.2	Benzene	*a*	$(F_3C)_2NO\cdot$	9.3	Carbon tetrachloride	*c*
	10.07	Xylene	*b*		8.38	Xylene	*b*
	9.66	Xylene	*b*	$(RMe_2Si)_2NO\cdot$ R = Me, *tert*-Bu, Ph	6.5	THF or 4:1 pentane–THF	This work

[a] A. K. Hoffman, W. G. Hodgson, D. L. Maricle, and W. H. Jura, *J. Amer. Chem. Soc.*, **86**, 631 (1964). [b] P. H. H. Fischer and F. A. Z. Neugebauer, *Z. Naturforsch. A*, **19**, 1514 (1964); P. H. H. Fischer and F. A. Z. Neugebauer, *ibid.*, *B*, **21**, 1036 (1966). [c] W. D. Blackley and R. R. Reinhard, *J. Amer. Chem. Soc.*, **87**, 802 (1965).

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[1] This research was sponsored by Air Force Office of Scientific Research (SRC)–O.A.R., USAF, Grant No. AF-AFOSR 70-1904.

[2] For a preliminary account of the 1,2 O → N anionic rearrangement of organosilylhydroxylamines, see R. West, P. R. Boudjouk, and T. A. Matuszko, *J. Amer. Chem. Soc.*, **91**, 5184 (1969). A full paper on this rearrangement is in preparation.

[3] E. G. Janzen, *Accounts Chem. Res.*, **2**, 279 (1969).

[4] R. West and P. Boudjouk, unpublished results.

(5) G. Chapelet-Letourneaux, H. Lamaire, and A. Rassat, *Bull. Soc. Chim. Fr.*, 3283 (1965). The authors had assigned the A_N of 15 G to **4a**.

(6) The lower A_N's for aryl compared to dialkyl nitroxides are primarily the result of delocalization of the unpaired electron into the aromatic π systems.

(7) We have assumed that the nitroxides 4a–c have a planar configuration like di-*tert*-butyl nitroxide.

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A Novel Thermal Rearrangement of Tris(organosilyl)hydroxylamines[1]

Sir:

We recently reported the 1,2 anionic rearrangement of organosilylhydroxylamines[2] in which migration of

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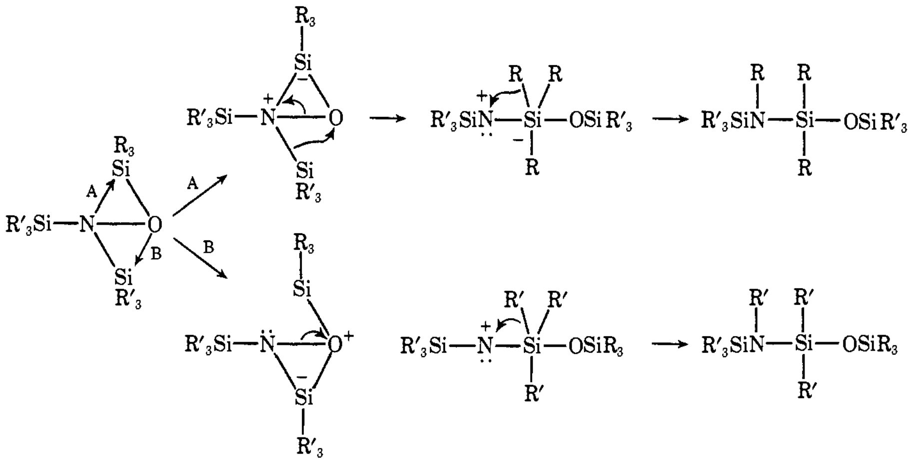
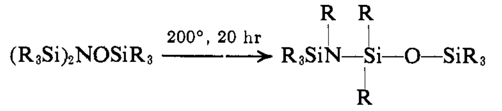
(1) This work was supported by the Air Force Office of Scientific Research (SRC)–O.A.R., Grant No. AF-AFOSR 70-1904.

(2) R. West, P. R. Boudjouk, and T. A. Matuszko, *J. Amer. Chem. Soc.*, **91**, 5184 (1969).

Scheme I



the trimethylsilyl group in the anion of *N*,*O*-bis(trimethylsilyl)hydroxylamine (**1**) provided the first example of a 1,2 O → N anionic rearrangement. In the course of follow-up studies of this rearrangement we have synthesized several tris(organosilyl)hydroxylamines[3,4] by treating deprotonated **1** with various triorganochlorosilanes. To our surprise, we find that tris(organosilyl)hydroxylamines, when heated to 200°, undergo an intramolecular rearrangement involving (1) the insertion of a silicon moiety into the bond between nitrogen and oxygen, and (2) the transfer of an alkyl group from silicon to nitrogen, to form silylaminosiloxanes.



$$(R_3Si)_2NOSiR_3 \xrightarrow{200°,\ 20\ hr} R_3Si\overset{R}{N}-\overset{R}{\underset{R}{Si}}-O-SiR_3$$

2, R = Me　　**4**, R = Me
3, R = Et　　**5**, R = Et

Tris(trimethylsilyl)hydroxylamine (**2**) and tris(triethylsilyl)hydroxylamine (**3**) were prepared by the method of Wannagat and Smrekar.[4] When placed in a sealed tube under nitrogen and heated for 20 hr, **2** is converted almost quantitatively to trimethylsilylaminopentamethylsiloxane (**4**). The structure is proposed on the basis of nmr and ir spectral data and elemental analyses. The nmr of **4** in benzene shows a single resonance with relative intensity 1.0 at τ 7.52, the usual region for *N*-methyl protons, and three absorptions in the Si–C–H region at τ 9.75, 9.76, and 9.77 with relative intensities 3.0:2.0:3.0, consistent with the proposed structure. The infrared spectrum of **4** shows a strong band at 1060 cm^{-1}, diagnostic for siloxanes (ν_{as} Si–O–Si), giving strong support to our structure rather than the isomers, Me$_3$SiSi(Me)$_2$N(Me)OSiMe$_3$ and Me$_3$SiN(Me)OSi(Me)$_2$SiMe$_3$.[5] When treated in a similar manner, **3** converts to **5**, also in nearly quantitative yield.[6]

The high yields and lack of condensation products suggest an intramolecular mechanism for the thermolyses of **2** and **3**. When a mixture of the two is heated to 200° for 20 hr only **4** and **5** are isolated and no crossover products could be observed when the product mixture was analyzed by vpc.

A rearrangement of this kind is unique in both silicon and carbon chemistry. It provides the first example of the insertion of a silicon moiety into a bond between nitrogen and oxygen and is also the first case in which an alkyl group is transferred from silicon to nitrogen.[7] The ease with which the tris(organosilyl)hydroxylamines convert to silylaminosiloxanes leads us to believe that the reaction takes place through a formation of pentacoordinate silicon atoms. Two possible pathways are shown in Scheme I.

The thermolysis products of selected tris(organosilyl)hydroxylamines possessing silicon moieties with different alkyl groups will be investigated in an effort to clarify the mechanism. Thermolyses of alkyl-substituted organosilylhydroxylamines are also under investigation.[9]

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[3] All compounds reported gave satisfactory analyses for C, H, N, and Si.

[4] U. Wannagat and O. Smrekar, *Monatsh. Chem.*, **100**, 750, 760 (1969).

[5] We have prepared several *N*,*O*-bis(organosilyl)-*N*-methylhydroxylamines and their infrared spectra do not show strong absorptions in the 1040–1070-cm^{-1} region.

[6] The thermolyses of **3** and **4** can be carried out within 15 min by passing them through a 15 ft × $^3/_8$ in. column of 20% SE-30 on Chromosorb W at 260°. Samples of **5** and **6** collected in this manner need no further purification.

[7] No analogous rearrangements are known to occur in carbon compounds, although the thermal rearrangements of some oxaziridines[8] have similar features such as cleavage of the bond between nitrogen and oxygen and an alkyl group transfer (from carbon to nitrogen).

[8] For a review of the thermal rearrangements of oxaziridines see M. Lamchen in "Mechanisms of Molecular Migrations," Vol. 1, B. S. Thyagarajan, Ed., Wiley-Interscience, New York, N. Y., 1968, Chapter 1.

[9] *N*,*O*-Bis(trimethylsilyl)-*N*-methylhydroxylamine forms hexamethyldisiloxane and polymer when heated to 200° for 20 hr. This suggests that alkyl-substituted organosilylhydroxylamines may decompose by a different mechanism.

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Epimeric 3-Vinyl-4-piperidineacetic Acids, Synthetic Precursors of Cinchona and Indole Alkaloids

Sir:

The *cis*-3-vinyl-4-piperidineacetic acid, known as meroquinine,[1] was recently described as a synthetic precursor of the quinuclidine ring of quinine and quinidine.[2] Further investigations in our laboratories have revealed that this compound and its trans epimer can also be used as practical synthetic substitutes for bio-

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[1] W. Koenigs, *Chem. Ber.*, **27**, 900, 1501 (1894); W. E. Doering and J. D. Chanley, *J. Amer. Chem. Soc.*, **68**, 586 (1946).

[2] M. Uskoković, J. Gutzwiller, and T. Henderson, *ibid.*, **92**, 203 (1970); J. Gutzwiller and M. Uskoković, *ibid.*, **92**, 204 (1970); M. Gates, B. Sugavanam, and W. L. Schreiber, *ibid.*, **92**, 205 (1970).