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

**Acknowledgment.** We are indebted to the National Cancer Institute of the Public Health Service for support of this investigation.

**Paul G. Gassman,* Koichi Shudo**
*Department of Chemistry, The Ohio State University*
*Columbus, Ohio 43210*
*Received August 9, 1971*

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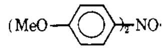
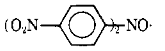
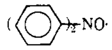
## Bis(organosilyl) Nitroxides[1]

*Sir:*

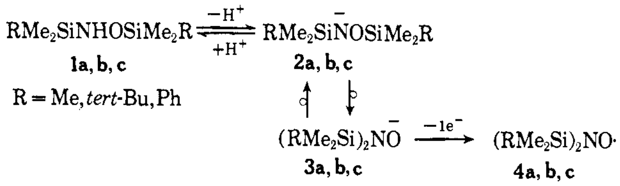
Our investigations of the 1,2 O → N anionic rearrangement of *N*,*O*-bis(organosilyl)hydroxylamines[2] have enabled us to synthesize several bis(organosilyl) nitroxide radicals under very mild conditions. When examined by esr spectroscopy, these radicals show a surprisingly low $A_N$ value near 6.5 G, 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]

**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* | $(RMe_2Si)_2NO\cdot$<br>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).

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 elec-



$$\begin{tikzcd}[column sep=small] RMe_2SiNHOSiMe_2R \arrow[r, shift left, "-H^+"] & RMe_2Si\bar{N}OSiMe_2R \arrow[l, shift left, "+H^+"] \arrow[d, shift left] & \\ & (RMe_2Si)_2N\bar{O} \arrow[u, shift left] \arrow[r, "-1e^-"] & (RMe_2Si)_2NO\cdot \end{tikzcd}$$

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

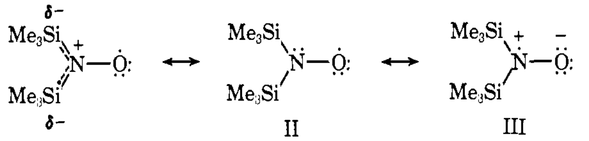
R = Me, *tert*-Bu, Ph

trolytically or with dry oxygen leads to the bis(organosilyl) nitroxide radicals, **4a–c**.

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



I II III

less importance than it does for the carbon analog, di-*tert*-butyl nitroxide.[7]

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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.

**Robert West,* Philip Boudjouk**
*Department of Chemistry, University of Wisconsin*
*Madison, Wisconsin 53706*
*Received July 8, 1971*

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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).