

In summary, the transition metal catalyzed rearrangement of a phenyl-substituted bicyclo[1.1.0]butane leads to an azulene in a process which has potential synthetic utility. The initial formation of a dihydroazulene from a phenyl-substituted bicyclo[1.1.0]butane tends to add support to the proposed intermediacy of a metal-complexed carbene-metal-bonded carbonium ion hybrid in the transition metal promoted rearrangement of bicyclo[1.1.0]butanes. We are continuing to explore the scope and mechanistic detail of this new route to azulenes.

Acknowledgment. We are indebted to the National Science Foundation for partial support of this work.

(12) An alternate path to 3 and 4, which cannot be ruled out on the basis of presently available data, would involve Friedel-Crafts type alkylation of one of the phenyl groups by the initially generated intermediate.

(13) The Ohio State University Postdoctoral Fellow, 1970-1971.

Paul G. Gassman,* Takeshi Nakai¹³

Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Received August 4, 1971

The Formation of Nitrenium Ion Intermediates in the Nitrous Acid Deamination of Dialkylhydrazines¹

Sir:

The recent survey of the chemistry of nitrenium ions has amply illustrated the diversity of applications which these divalent positively charged species have in organic synthesis.² As part of our interest in exploring reactions which involve the generation of nitrenium ion intermediates, we have reinvestigated the nitrous acid deamination of 1,1-disubstituted hydrazines.³ We now wish to report that the reaction of 1,1-disubstituted hydrazines with nitrous acid produced an intermediate which appears to decompose by two alternate routes. One of these reaction paths involves the formation of nitrenium ion intermediates.

In order to establish whether nitrenium ions could be generated *via* the diazotization of hydrazines, in a process analogous to the generation of carbonium ions by the diazotization of aliphatic primary amines,⁴ we chose to investigate a system in which the behavior of the nitrenium ion had been well established.⁵ Both **1**⁵ and **2**⁵ were readily converted into the corresponding *N*-nitroso derivatives, **3** and **4**, respectively, on treatment with nitrosyl chloride.⁷ Reduction of these

(1) Paper XVII in the series "The Chemistry of Nitrenium Ions." For the previous paper in this series see P. G. Gassman and G. A. Campbell, *J. Amer. Chem. Soc.*, **93**, 2567 (1971).

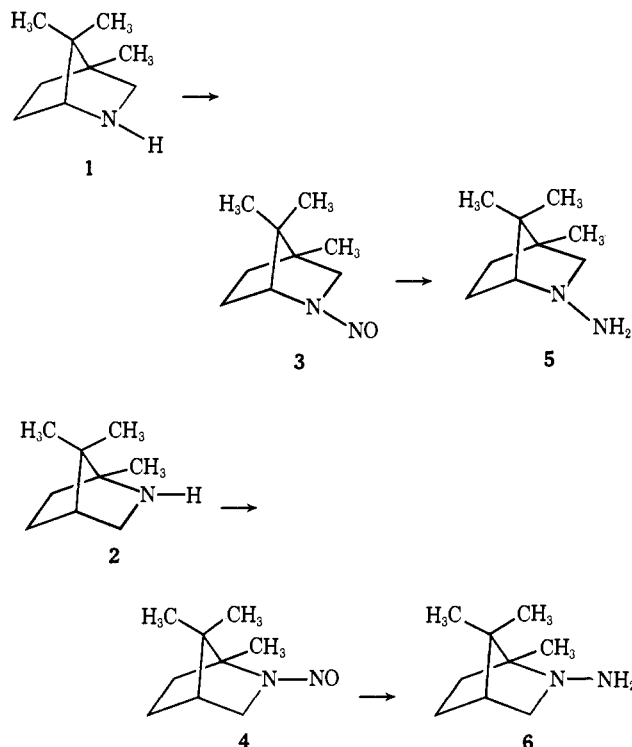
(2) P. G. Gassman, *Accounts Chem. Res.*, **3**, 26 (1970).

(3) The deamination of dialkyl- and diarylhydrazines has been investigated by a variety of workers over the last half-century. [For examples, see J. Thiele, *Justus Liebigs Ann. Chem.*, **376**, 264 (1910); J. Thiele, *Ber.*, **41**, 2806 (1908), and references contained therein]. However, we have found no previous work in the literature which would provide convincing evidence for the intermediacy of nitrenium ions.

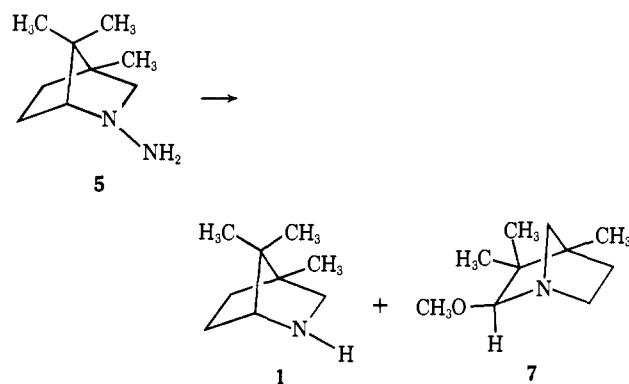
(4) For recent reviews, see E. H. White and D. J. Woodcock in "The Chemistry of the Amino Group," S. Patai, Ed., Wiley, New York, N. Y., 1968, pp 440-483; P. A. S. Smith, "The Chemistry of Open-Chain Organic Nitrogen Compounds," Vol. 1, W. A. Benjamin, New York, N. Y., 1965, pp 33-46; H. Zollinger, "Azo and Diazo Chemistry," Interscience, New York, N. Y., 1961; J. H. Ridd, *Quart. Rev.*, *Chem. Soc.*, **15**, 418 (1961).

(5) P. G. Gassman and R. L. Cryberg, *J. Amer. Chem. Soc.*, **91**, 2047, 1576 (1969).

(6) P. G. Gassman and R. L. Cryberg, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 14-18, 1969, Abstracts, ORGN-14.



N-nitroso compounds with lithium aluminum hydride gave **5** and **6**, respectively, which were isolated as their hydrochlorides.⁸ When the hydrochloride of **5** was treated with 1.1 equiv of isoamyl nitrite at 50° in

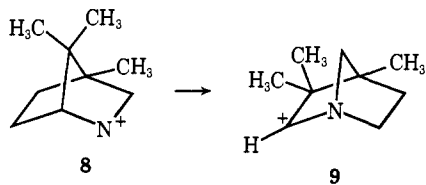


methanol, we obtained 67% of **1** and 21% of **7** for an overall yield of 88%. Both of these products are known to arise from the nitrenium ion, **8**. The formation of the protonated form of **1** is thought to occur *via* the nitrenium ion triplet, while the singlet form of **8** has been shown to rearrange to the carbonium ion **9**.⁵ Attack of the nucleophilic solvent, methanol, on **9** has been shown to yield **7**.^{5,9} The formation of **7** in the deamination of **5** provides convincing evidence for the presence of **9** and hence the initial formation of the nitrenium ion **8**.

(7) Satisfactory elemental analyses were obtained on all new compounds or on derivatives thereof.

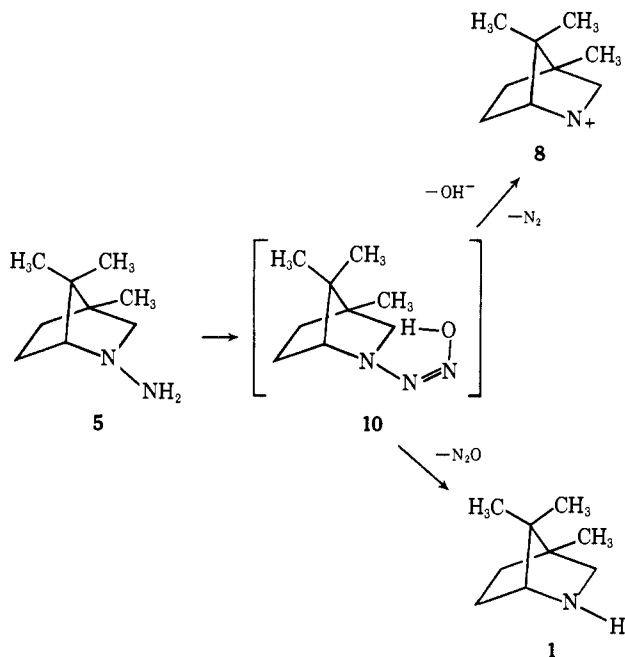
(8) The free hydrazines were readily oxidized in air to the corresponding tetrazines. For an example of the lithium aluminum hydride reduction of *N*-nitroso derivatives to unsymmetrical hydrazines see C. G. Overberger, J. G. Lombardino, and R. G. Hiskey, *J. Amer. Chem. Soc.*, **79**, 6430 (1957).

(9) P. G. Gassman, K. Shudo, and R. L. Cryberg, unpublished results. A detailed account of the nature of **9** will be provided in a forthcoming publication.



The large amount of "reductive" deamination observed in this reaction was cause for concern. The solvolysis of 2-chloro-4,7,7-trimethyl-2-azabicyclo[2.2.1]heptane in methanol produced only 7% of **1**, while yielding 20% of **7** and 59% of 2-chloro-3,3,4-trimethyl-1-azabicyclo[2.2.1]heptane.⁵ Superficially, it might appear that nitrenium ions generated in the deamination of hydrazines were more prone to singlet \rightarrow triplet interconversion than those generated solvolytically. However, closer scrutiny of the reaction indicated that an alternate route to **1**, which did not involve a nitrenium ion intermediate, was involved.

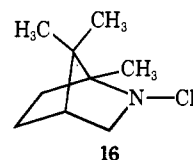
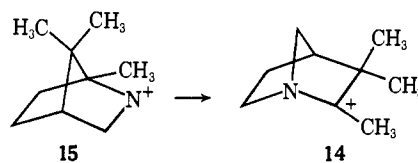
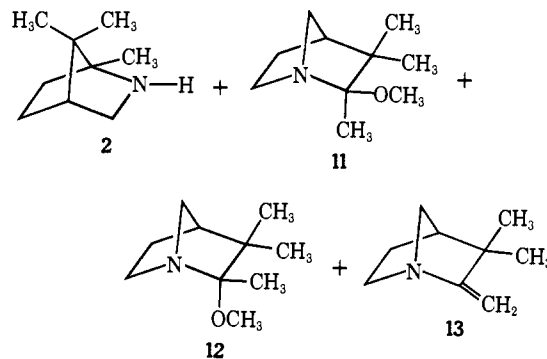
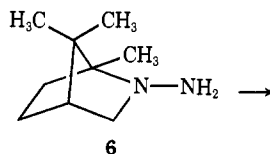
By analogy with the deamination of primary amines,⁴ it is thought that **1** should react with nitrous acid to form the diazotic acid^{3,10} derivative **10**. Loss of hydroxide and nitrogen from **10** would produce the nitrenium ion **8**. An alternate mode of decomposition for **10** would involve hydrogen transfer to the ring nitrogen and loss of nitrous oxide.^{3,10} Evidence for the importance of this latter path in the formation of **1**



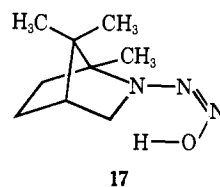
was provided by the isolation and identification of nitrous oxide as a major gaseous product.

Similar results were obtained when the hydrochloride of **6** was treated with 1.1 equiv of isoamyl nitrite in methanol at 50°. This deamination gave 54% of **2**, 16% of **11**, 9% of **12**, and 2% of **13**. The latter three products, which all possess rearranged skeletons, are typical products expected from the carbonium ion **14**. The ion **14** would be derived from the nitrenium ion **15**. The contention that **11**, **12**, and **13** were nitrenium ion products was supported by a detailed study of the silver

(10) For a discussion of this point see N. V. Sidgwick, "The Organic Chemistry of Nitrogen," 3rd ed, Oxford University Press, Oxford, 1966, p 506; P. A. S. Smith, "Open-Chain Nitrogen Compounds," Vol. 2, W. A. Benjamin, New York, N. Y., 1966, p 129.



ion catalyzed solvolysis of **16** which gave 5% of **2**, 64% of **11**, 12% of **12**, and 13% of **13**.¹¹ Again, the large proportion of **2** formed in the "reductive" deamination of **6** was accompanied by the formation of nitrous oxide indicating that two distinct paths were involved in the decomposition of the diazotic acid derivative **17**.



In addition to establishing that nitrenium ions can be generated *via* the deamination of hydrazines, the data discussed above provide an interesting insight into the chemistry of diazotic acid derivatives. The facile loss of nitrous oxide from **10** and **17** has little analogy in the nitrous acid deamination of primary amines. In those special cases where "reductive" deamination of primary amines has been observed, a radical intermediate has been proposed.¹² The steps leading to such radical intermediates are quite different from those which result in "reductive" deamination in the case of **5** and **6**. The exact mechanistic path by which **10** and **17** lose nitrous oxide has not been established and is currently under investigation.

(11) Detailed chemical and spectroscopic evidence for the structural assignments of **11**, **12**, and **13** will be provided in a full paper on this subject.

(12) For a leading reference see K. V. Scherer, Jr., and R. S. Lunt, III, *J. Amer. Chem. Soc.*, **88**, 2860 (1966).

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

Bis(organosilyl) Nitroxides¹

Sir:

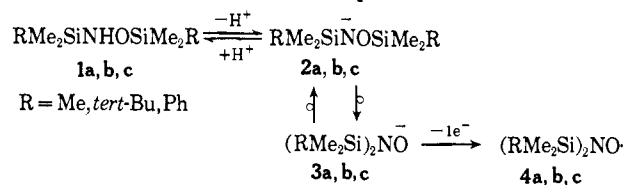
Our investigations of the 1,2 O → N anionic rearrangement of *N,O*-bis(organosilyl)hydroxylamines² have enabled us to synthesize several bis(organosilyl) nitroxide radicals under very mild conditions. When examined by esr spectroscopy, these radicals show a surprisingly low A_N value near 6.5 G, consistent 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 ₃ C) ₂ NO·	15.2	Benzene	<i>a</i>	(F ₃ C) ₂ NO·	9.3	Carbon tetrachloride	<i>c</i>
(MeO-C ₆ H ₄) ₂ NO·	10.07	Xylene	<i>b</i>	(O ₂ N-C ₆ H ₄) ₂ NO·	8.38	Xylene	<i>b</i>
(C ₆ H ₅) ₂ NO·	9.66	Xylene	<i>b</i>	(RMe ₂ Si) ₂ NO·	6.5	THF or 4:1 pentane-THF	This work
				R = Me, <i>tert</i> -Bu, Ph			

^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 laboratories⁴ 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-



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 ¹⁴N ($I = 1$). 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.

(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.

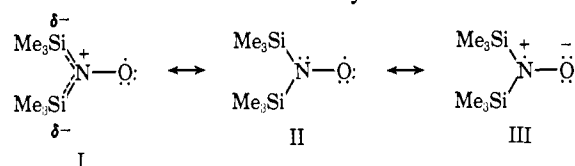
(3) E. G. Janzen, *Accounts Chem. Res.*, **2**, 279 (1969).

(4) R. West and P. Boudjouk, unpublished results.

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

(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

A Novel Thermal Rearrangement of Tris(organosilyl)hydroxylamines¹

Sir:

We recently reported the 1,2 anionic rearrangement of organosilylhydroxylamines² in which migration of

(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).