Table II. Bond Distances and Angles and Their Estimated Standard Errors

Atoms	Distance, Å	Angle	Degrees
N-1-C-2	1.487 (3)	C-2-N-1-C-5	116.2 (2)
N-1-C-5	1.479 (4)	C-2-N-1-O-6	120.8 (2)
N-1-O-6	1.272 (3)	C-5-N-1-O-6	122.8 (2)
C-2-C-3	1.554 (4)	N-1-C-2-C-3	99.3 (2)
C-2-C-7	1.531 (4)	N-1-C-2-C-7	108.1 (2)
C-2-C-8	1.512 (4)	N-1-C-2-C-8	109.8 (2)
C-3-C-4	1.520 (5)	C-3-C-2-C-7	114.5 (3)
C-3-C-9	1.515 (4)	C-3-C-2-C-8	113.4 (3)
C-4-C-5	1.533 (4)	C-7-C-2-C(8)	111.0 (3)
C-5-C-12	1.504 (5)	C-2-C-3-C-4	104.2 (2)
C-5-C-13	1.527 (5)	C-2-C-3-C-9	113.0 (3)
C-9-O-10	1.187 (4)	C-4-C-3-C-9	112.7 (3)
C-9-O-11	1.305 (4)	C-3-C-4-C-5	105.8 (2)
		N-1-C-5-C-4	100.4 (2)
		N-1-C-5-C-12	110.5 (3)
		N-1-C-5-C-13	108.4 (3)
		C-4-C-5-C-12	112.9 (3)
		C-4-C-5-C-13	113.2 (3)
		C-3-C-9-O-10	124.7 (3)
		C-3-C-9-O-11	113.6 (3)
		O-10-C-9-O-11	121.6 (3)

O-6 distance of 1.27 Å lies between that expected for a single bond (1.44 Å) and a double bond (1.20 Å).[10] Similar N–O distances have been observed in other *N*-oxides[11] and are indicative of a semipolar N→O bond. The conformation of the ring may be described by considering that O-6, C-3, and C-9 are displaced 0.21, −0.57, and −0.20 Å, respectively, from the least-squares plane defined by N-1, C-2, C-4, and C-5. Atoms C-2, C-5, N-1, and O-6 are nearly planar with N-1 displaced 0.03 Å from the plane of C-2, C-5, and O-6. Planarity of the C(NO)C group has also been observed in X-ray crystallographic determinations of the structures of the potassium salt and amide of a pyrrolinyl nitroxide,[12,13] but in three piperidinyl nitroxides, the N–O bonds have been found to make angles of 16, 30.5, and 18.2°, respectively, with the C–N–C planes.[11,14-16]

Several optically active derivatives of (+)-I have been synthesized using reactions expected to proceed with retention of configuration at C-3. The *m*- and *p*-nitrophenyl esters of (+)-I prepared by coupling the acid with the corresponding nitrophenols have been employed in the investigation of enantiomeric specificity in ester hydrolysis catalyzed by α-chymotrypsin and cyclohexaamylose.[2,17] We are now using the (+)-amide, mp 198–198.5°, $[\alpha]^{25}\mathrm{D}$ +116° (*c* 0.15, EtOH), formed by the reaction of liquid ammonia with the *p*-nitrophenyl ester of (+)-I as a precursor for the establishment of the absolute configuration of the enantiomers of 3-amino-2,2,5,5-tetramethyl-1-pyrrolidinyloxy and related derivatives, racemic forms of which have been employed in spin-label studies of many biological systems.[18]

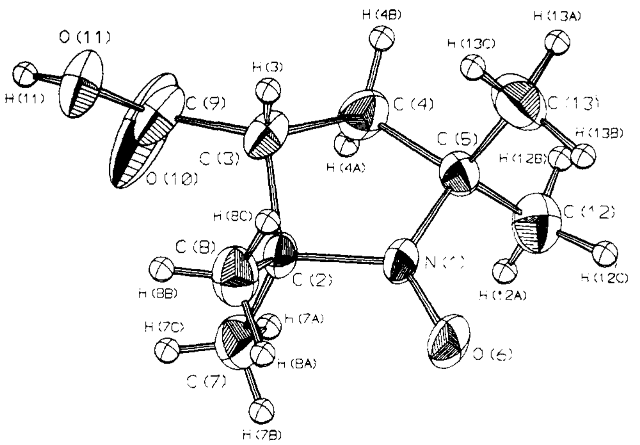

Figure 1. ORTEP II drawing of the *R* configuration of (+)-I with thermal ellipsoids representing 50% probability. Hydrogen atoms are drawn with an arbitrary radius of 0.10 Å.

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Organosilylhydrazyl Radicals and a Possible Triazyl Radical[1]

Sir:

Although certain triarylhydrazyls are very stable,[2] alkylhydrazyl radicals are extremely reactive, having been observed only as products of X-irradiation of the parent hydrazines in adamantane matrix.[3] We find that tris(organosilyl)hydrazyls, although less stable than triarylhydrazyls such as diphenylpicrylhydrazyl (DPPH), can be prepared and studied by electron spin resonance spectroscopy in solution at room temperature. These are apparently the first examples of organometal-substituted hydrazyls.

Tris(trimethylsilyl)hydrazyl (**1**) and tris(*tert*-butyldi-

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(1) This work was supported by the U. S. Air Force Office of Scientific Research (NC)-OAR, USAF Grant No. AF-AFOSR-70-1904.

(2) A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals," Academic Press, New York, N. Y., 1968, Chapter 4.

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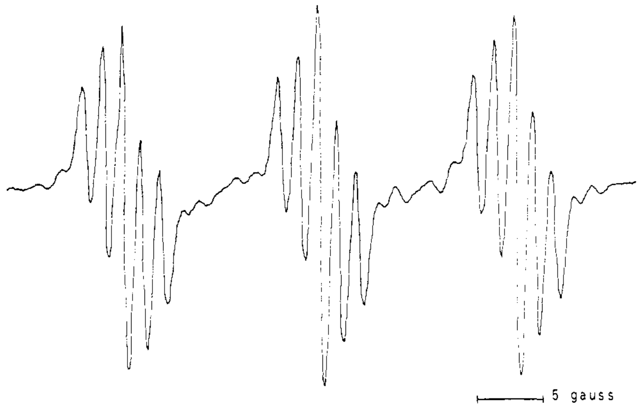
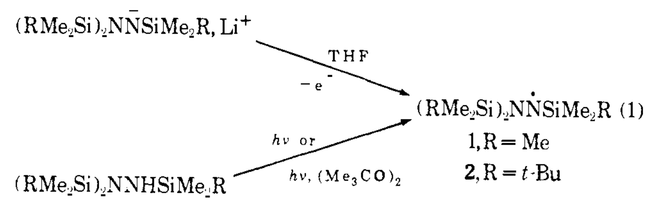


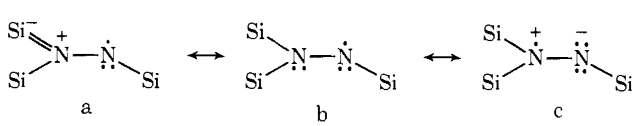
Figure 1. Esr spectrum of new radical from photolysis of tris(trimethylsilyl)hydrazine, believed to be tetrakis(trimethylsilyl)triazyl, $(Me_3Si)_2N\dot{N}N(SiMe_3)_2$.

methylsilyl)hydrazyl (2) were obtained[4] by two general methods: (1) electrolytic oxidation of a dilute solution of the lithium salt of the parent hydrazine in THF, and (2) ultraviolet photolysis of the parent hydrazine,[5] with or without the assistance of di-*tert*-butyl peroxide[6] (eq 1). Hydrazyls **1** and **2** are far more stable than the



alkylhydrazyls. Apparent half-times for decomposition, which is approximately first order for several lifetimes, are 25 min for **1** and 30 hr for **2**, at 30°.

The esr spectrum of **1** consists of nine lines attributed to interaction of the unpaired electron with two nonequivalent nitrogens, with a_N values of 11.1 and 4.2 G. The spectrum of **2** is almost identical with a_N values of 11.2 and 4.3 G. The large difference between the a_N values is unprecedented (compare DPPH, a_N = 9.65 and 8.03 G,[7] and other data in ref 2) and suggests marked restriction of the spin density to one nitrogen (we believe to the monosubstituted nitrogen). Such localization of spin could result from lone-pair delocalization from the disubstituted nitrogen onto silicon through dative bonding, as proposed earlier to explain the unusual esr spectra of organometal-substituted nitroxides.[8] In valence bond notation, this would be represented by a significant contribution of canonical forms like a to the resonance hybrid.



Photolysis of tris(trimethylsilyl)hydrazine (**3**) for an extended period in the presence of di-*tert*-butyl peroxide led also to the formation of secondary radical products. When **3** was photolyzed for 1 hr and then allowed to stand in the dark for 10 hr to permit decay of **1**, the esr spectrum shown in Figure 1 was obtained. The spectrum shows coupling of the unpaired electron with two equivalent and one unique nitrogen atoms (a_N = 14.6 and 1.48 G). Side bands attributable to hyperfine interaction with ^{29}Si are also observed; these have the proper intensity for coupling with *four* equivalent silicon atoms. The new spectrum is tentatively assigned to the tetrakis(trimethylsilyl)triazyl radical, $(Me_3Si)_2N\dot{N}N(SiMe_3)_2$; if this assignment is correct this is the first triazyl radical to be observed.[9] Our continuing research will examine the reasons for the relative stability of these radical systems and explore for other new organometallic hydrazyls.[10]

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(4) All experiments were carried out after extensive degassing of the sample by the freeze-thaw method utilizing a high vacuum system.

(5) (a) U. Wannagat and H. Niederprüm, *Z. Anorg. Allg. Chem.*, **310**, 32 (1961). (b) Satisfactory elemental analyses and nmr, ir, and mass spectra were obtained for the new compound tris(*tert*-butyldimethylsilyl)hydrazine.

(6) The hydrazines were photolyzed with a General Electric 100-W mercury spot lamp focused on a Suprasil quartz tube esr cell. Radical **1** was generated from a neat or di-*tert*-butyl peroxide (DTBP) solution of the parent hydrazine; radical **2** was generated either from hydrocarbon solution with or without the aid of DTBP or from DTBP solution.

(7) Yu. M. Ryzhmanov, Yu. V. Yablokov, B. M. Kozyrev, R. O. Matevosyan, and L. I. Stashkov, *Dokl. Akad. Nauk SSSR*, **156**, 106 (1964).

(8) R. West and P. Boudjouk, *J. Amer. Chem. Soc.*, **93**, 5901 (1971).

(9) Triazyl radicals have, however, been proposed as reaction intermediates. See L. Holleck and G. Kazemifrad, *Monatsh. Chem.*, **103**, 1427 (1972); J. Hollaender, W. P. Neumann, and G. Alester, *Chem. Ber.*, **105**, 1540 (1972).

(10) NOTE ADDED IN PROOF. Very recently bicyclic hydrazyls have been reported (S. F. Nelson and R. T. R. T. Landis, II, *J. Amer. Chem. Soc.*, **95**, 6454 (1973)), and 1,1-dialkylhydrazyls have been detected in solution by esr (V. Malatesta and K. U. Ingold, *ibid.*, **95**, 6110 (1973)).

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Viscosity Dependence of the Nitropentaamminecobalt(III) Photochemistry. Evidence for Radical Cage Recombination

Sir:

The photochemistry of Co(III) complexes is characterized by the extensive occurrence of redox decomposition reactions.[1–3] It is now generally agreed that the redox decomposition arises from a homolytic metal–ligand bond fission occurring in excited states of ligand-to-metal charge transfer (LMCT) character. However, since the earlier investigations in this field, there has been some dispute on the mechanism of the redox decomposition process.[3–10] Although the terms of the dispute have often been ambiguously stated,[11] it

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(1) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, New York, N. Y, 1970.

(2) V. Balzani, L. Moggi, F. Scandola, and V. Carassiti, *Inorg. Chim. Acta Rev.*, **1**, 7 (1967).

(3) A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, *Chem. Rev.*, **68**, 541 (1968).

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(8) A. Vogler and A. W. Adamson, *J. Phys. Chem.*, **74**, 67 (1970).

(9) V. Balzani, R. Ballardini, N. Sabbatini, and L. Moggi, *Inorg. Chem.*, **7**, 1398 (1968).

(10) D. Valentine, *Advan. Photochem.*, **6**, 186 (1968).

(11) Most of the ambiguity stems from the fact the term "radical pair mechanism" has assumed a dual meaning, *i.e.*, that (i) all LMCT states of Co(III) complexes quantitatively dissociate to give a radical pair (in other words, a LMCT state is just equivalent to a radical pair) and (ii) the radical pair formed from bond homolysis of a LMCT state can undergo radical cage recombination and/or back electron transfer. Actually, the two points are quite independent from one another, and separate criticisms are needed in any discussion of this mechanism.