As anticipated, IIa gives a Cotton effect amplitude opposite to Ia and Ib but similar in sign and magnitude to its carbocyclic analog, phenylalanine. In the case of the acid IIIb, unfavorable ring size requirements will prevent the ligand from acting as a tridentate. Thus, IIIb behaves as a simple amino acid (compare with L-2-aminobutyric acid and L-norvaline complexes in ref 1).

**Acknowledgment.** We wish to thank the U. S. Public Health Service (1 RO1 GM 13,962-01) and the United Health Foundation of Western New York (G-65-UB-4) for partial support of this work.

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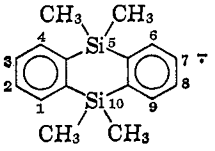
## Line Broadening in Electron Spin Resonance Spectra of 5,10-Dihydrosilanthrene Radical Ion Pairs[1]

*Sir:*

Previous electron spin resonance studies of organosilane anion radicals have provided evidence for spin delocalization into silicon 3d orbitals.[2,3] A radical anion with the unpaired electron entirely delocalized in overlapping silicon d orbitals has been made by alkali metal reduction of dodecamethylcyclohexasilane in ether solvents.[4]

We have made an esr study of the radical anions of certain 5,10-dihydrosilanthrene, dibenzasilole, and silacyclopentadiene derivatives. Spin densities obtained from Hückel–McLachlan MO calculations correlate well with experimentally obtained coupling constants.[5] In this communication we report on the effect of solvent and metal ion on the esr spectrum of 5,5,10,10-tetramethyl-5,10-dihydrosilanthrene radical anion (I).



I

Radical anion I is readily obtained by sodium or potassium reduction in 1,2-dimethoxyethane (DME) at room temperature. The esr spectrum at low resolution consists of five lines due to four equivalent hydrogens, $A_H$ = 2.2 gauss. From MO calculations[5] and by analogy to similar radicals[6] the hyperfine coupling is assigned to hydrogens in the 2, 3, 7, and 8 positions. Under better resolution more lines with 0.18-gauss spacing due to methyl hydrogens are obtained (Figure 1). This radical is probably the free ion since identical spectra are obtained using either sodium or potassium as gegenion. The spectrum does not change at lower temperature (−52°) except that the lines sharpen. In tetrahydrofuran (THF) potassium reduction gives the same spectrum at room temperature, but at lower temperatures (−87°) marked line-width alternation is observed (Figure 1).[7] At −115° broadening has progressed to the point that the observed intensity sequence of the multiplet is approximately 1:0.5:4:0.5:1, as compared to the normal 1:4:6:4:1 expected for four equivalent hydrogens. In diethyl ether (DEE) similar results are obtained within the same temperature range. At lower temperatures the intensity sequence becomes 1:0.1:1.4:0.1:1 at −125° and 1:0:1:0:1 at −141°.

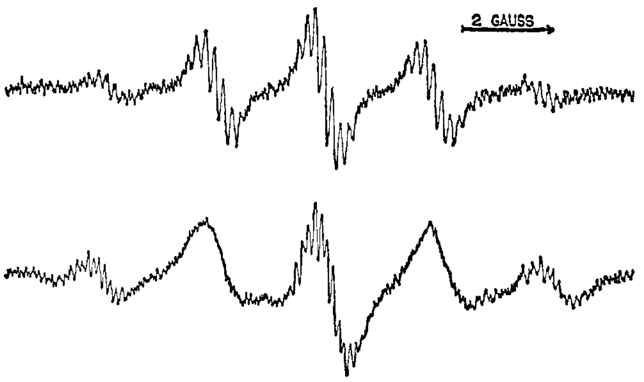
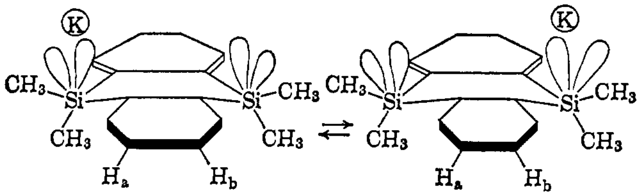


Figure 1. Esr spectrum of tetramethyl-5,10-dihydrosilanthrene radical anion in dimethoxyethane at room temperature (top) and in tetrahydrofuran at −87° (bottom). Gegenion is potassium in both cases.

The line-broadening process observed in THF and DEE (to −115°) comes from rapid interchange of two slightly different coupling constants in the molecule. Since in these solvents ion pairing usually takes place, the line broadening could be caused by rapid interchange of the location of potassium ion in the molecule. A choice location would seem to be a silicon 3d orbital since MO calculations place the largest spin density (and hence charge) on this atom (almost 20% per silicon atom). We suggest that the following equilibrium exists in solutions of I in THF or DEE.[8]



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[1] Organometallic Radicals. I. This work is supported by a grant from Dow Corning Corp. Grateful acknowledgment is hereby made.

[2] M. G. Townsend, *J. Chem. Soc.*, 51 (1962); J. A. Bedford, J. R. Bolton, A. Carrington, and R. H. Prince, *Trans. Faraday Soc.*, **59**, 53 (1963); R. D. Cowell, G. Urry, and S. I. Weissman, *J. Am. Chem. Soc.*, **85**, 822 (1963).

[3] M. D. Curtis and A. L. Allred, *ibid.*, **87**, 2554 (1965).

[4] G. R. Husk and R. West, *ibid.*, **87**, 3993 (1965).

[5] Presented at the Southeastern Regional Meeting of the American Chemical Society, Louisville, Ky., Oct 27–29, 1966, Paper No. 119.

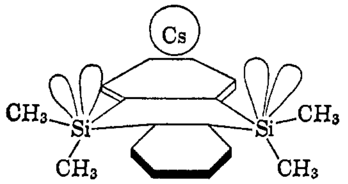
[6] *E.g.*, thianthrene S,S,S′-tetroxide: R. Gerdil and E. A. C. Lucken, *Mol. Phys.*, **9**, 529 (1965); E. T. Kaiser and D. H. Eargle, Jr., *J. Am. Chem. Soc.*, **85**, 1821 (1963).

[7] For a review and discussion of line-width alternation and broadening processes in anion radical ion pairs see M. C. R. Symons, *J. Phys. Chem.*, 71, 172 (1967).

[8] No definitive information regarding the structure of 5,10-disilanthrenes or the radical anions is available at this time. The line width of the methyl proton nmr peak is not temperature dependent at temperatures down to −75° (private communication from Dr. W. H. Atwell). Models show small barriers to bond inversion about the silicon atom but considerable steric interaction between one pair of methyl groups in a nonplanar structure. In the contact radical ion pair a small deviation from planarity would seem to provide better d-orbital bonding facilities for the metal ion than a completely planar structure. Our data for the free radical anion are consistent with either a planar or rapidly inverting structure while for the contact ion pair a structure deviating slightly from planarity is suggested. An analogous sulfur compound, 5,10-thianthrene dioxide, exhibits an inversion rate of greater than 100 sec$^{-1}$: K. F. Purcell and J. R. Berschied, Jr., *J. Am. Chem. Soc.*, **89**, 1579 (1967).

At room temperature the potassium ion jump is rapid enough so that an average coupling constant for $H_a$ and $H_b$ is observed but, as the temperature is lowered, the ion jump becomes slower, $H_a$ and $H_b$ become distinguishably different, and line broadening sets in. At temperatures below −115° (in DEE) further broadening takes place because the pairs of previously equivalent hydrogens now also become slightly different. This could be the result of the potassium ion locating itself nearer one benzene than the other.

Further evidence for this interpretation is found when cesium is used as gegenion. In DME, THF, and DEE a 12-line spectrum is obtained. The splitting pattern is consistent with approximately equal coupling to four equivalent hydrogens and one cesium ion ($I = {}^7/_2$) of 2.17, 2.16, and 2.44 gauss at room temperature and 2.15, 2.55, and 2.44 gauss at −60° for DME, THF, and DEE, respectively. In THF and DEE the 12 lines have approximately the intensities predicted. These results clearly point to a contact ion pair which may in fact have a chelate structure.[9]



It is clear that much can be learned about the structure and bonding in organosilane radical anions from temperature studies of the esr spectra of the ion pairs. To the extent bonding to potassium takes place in the ion pairs silicon can be considered pentacoordinated.[10] Trigonal-bipyramidal structures have been suggested in some cases.[11] However, all our data when taken together are more consistent with the use of unhydridized silicon 3d orbitals for delocalization of spin from neighboring aromatic $\pi$ systems. Further studies of organosilane radical ion pairs are in progress.[12]

**Acknowledgment.** We are grateful to Dr. W. H. Atwell of the Dow Corning Corporation for providing us with the organosilanes used in this study.

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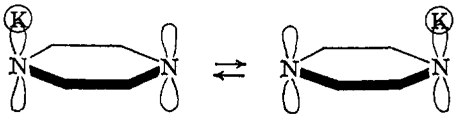
(9) Spectra of sodium and potassium ion pairs of pyrazine radical anion also exhibit line-width alternation at −68° in THF and −58° in DME, respectively. A similar mechanism for line broadening has been suggested (approximately 45% of the spin resides on each nitrogen atom): N. M. Atherton and A. E. Goggins, *Mol. Phys.*, **8**, 99 (1964); J. D. Santos-Veiga and A. F. Neiva-Correia, *ibid.*, **9**, 395 (1965); see also C. A. McDowell and K. F. G. Paulus, *Can. J. Chem.*, **43**, 224 (1965).



(10) C. L. Frye, *J. Am. Chem. Soc.*, **86**, 3170 (1964); C. L. Frye, G. E. Vogel, and J. A. Hall, *ibid.*, **83**, 996 (1961).

(11) J. Y. Corey and R. West, *ibid.*, **85**, 4034 (1963); R. Rudman, S. Novick, and W. C. Hamilton, Abstracts of Papers, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 10–14, 1967, No. R188; see also L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965; L. H. Sommer, G. A. Parker, N. C. Lloyd, C. L. Frye, and K. W. Michael, *J. Am. Chem. Soc.*, **89**, 857 (1967).

(12) Preliminary results have been obtained on the carbon analog of I, 9,9,10,10-tetramethyldihydroanthracene radical anion. However, these spectra are different and not well understood at this time.

(13) NASA Traineeship, 1965–1967.

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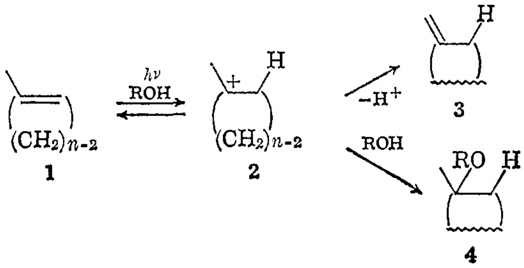
## Photochemistry of Cycloalkenes. II. Cyclopentenes and Norbornenes

*Sir:*

Recent studies have shown that irradiation of alcoholic solutions of 1-alkylcyclohexenes and -heptenes (*cf.* **1**) in the presence of aromatic hydrocarbon photosensitizers such as benzene, toluene, or xylene results in protonation of the double bond followed by three competing processes: (a) formation of the corresponding exocyclic isomer **3**, (b) addition of solvent to afford a tertiary cycloalkyl ether (**4**), and (c) regeneration of the starting olefin **1**.[1,2] As a consequence of this behavior, irradiation in methanol-O-*d* leads to extensive incorporation of deuterium in both the products and the recovered starting olefin.[1] Analogous behavior is exhibited by cyclohexenes and -heptenes bearing no substituents about the double bond, except that in these cases photosensitized cyclodimerization competes with ether formation.[1,3] By contrast, larger ring cycloalkenes and their acyclic analogs, which are well known to undergo facile *cis–trans* photoisomerization,[4] show no evidence of either isomerization or ether formation under these conditions.[1] The difference in behavior of these various systems is almost surely related to the relative ease with which the carbon skeleton can accommodate an orthogonally oriented $\pi,\pi^*$ triplet species and, perhaps, a *trans*-substituted double bond.[1] We wish now to report yet another type of behavior, of a radical rather than ionic nature, displayed under these conditions by norbornenes and cyclopentenes—olefins which are substantially less flexible than those previously found to exhibit ionic behavior.



Irradiation of 1-methylcyclopentene in methanol–xylene affords principally 1-methylcyclopentane (46%), accompanied by a smaller amount of methylenecyclopentane (24%) but no methyl 1-methylcyclopentyl ether,[5] the expected product of ionic addition.[1,2,6] Although some exocyclic isomer is formed in this case, labeling studies have shown that *the isomerization does not involve protonation of the starting olefin:* irradiation of 1-methylcyclopentene in xylene–methanol-O-*d*, under conditions in which 1-methylcyclohexene and its photoproducts incorporated deuterium extensively (33–92%), afforded 1-methylcyclopentane and methylenecyclopentane *without any measurable incorporation of*

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(1) Part I: P. J. Kropp, *J. Am. Chem. Soc.*, **88**, 4091 (1966).

(2) J. A. Marshall and R. D. Carroll, *ibid.*, 88, 4092 (1966).

(3) P. J. Kropp, unpublished observations.

(4) See, for example, the discussion by R. B. Cundall, *Progr. Reaction Kinetics*, **2**, 165 (1964).

(5) Direct comparison was made with an authentic specimen prepared independently by acid-catalyzed addition of methanol.

(6) All products were identified by direct spectral comparison with commercial samples or authentic specimens prepared as previously described in the literature.