the data, it is important to generate a trace such that each x value is associated with just one y value. In order to do this, we have preferred to generate our own software, rather than use the one available from the manufacturer. For every x value, the y values are averaged if more than one is available or interpolated if that x channel contains no y information associated with it. In processing the data in this manner, one must use very strict criteria in evaluating the quality of a given trace, since it would be very easy to generate excellent looking traces from very little information, by simply playing a game of interpolations and extrapolations. By properly tuning the instrument, we found that it was easy to work under conditions where over 99% of the data was contained in the original trace recorded (i.e., less than 1% interpolation), and values as high as 99.7% were not unusual. Traces where 3% or more of the y values were generated by software were regarded as unacceptable. The video display unit was quite valuable in optimizing the experimental conditions.

A programmable photomultiplier power supply has been recently incorporated to the system and was used for the last group of experiments. The unit has been built around a Model LR-2N, Venus PMT power supply (Subtech Ltd.). The computer has been programmed to set the high voltage so that a suitable current will be drawn from the photomultiplier, based on wavelength, signal during previous shots, etc. The computer commands are fed into the power supply via one channel (″170442) from a DEC-AAV11-A 12-bit D/A converter. This unit was extremely useful for the automatic recording of transient spectra.

In general, the time resolution (in terms of interval between points) that can be achieved with the R7912 digitizer amply exceeds that necessary for nanosecond experiments; we have generally preferred to handle 100 points, rather than 512. To do this, the 400 points in the center of the trace were "nested" in groups of four, leading to the 100 points generally displayed in our traces (see Figures 1, 3, and 5); elimination of the edges of the trace makes the tuning of the instrument simpler. As a rule, we have averaged between 5 and 30 traces to carry out the kinetic measurements and 3–8 traces at each wavelength for the spectra, even if in many cases a single shot could have sufficed.

After the data had been processed, all graphic outputs were displayed in a Tektronix 4010-1 terminal, and a 4631 Tektronix unit provided hardcopy facilities. The results were also stored in double-density flexible disks.

The risetime of the system was ca. 1 ns, but the actual 'window' in which measurements could be carried out was 10 ns to 500 μs. The rate at which data could be gathered was ca. 1 trace every 3 s, though it should be noted that this rate is at present controlled by the rate at which the capacitors used for the lamp pulser are recharged.

Acknowledgment. I am grateful to Dr. D. F. Williams for his help in setting up the laser system and for valuable discussions, to S. E. Sugamori for his technical assistance, and to G. Charette for designing and building the computer interfaces.

An Electrically Neutral σ-Sulfuranyl Radical from the Homolysis of a Perester with Neighboring Sulfenyl Sulfur: 9-S-3 Species[1]

C. W. Perkins,[†] **J. C. Martin,***[†] **A. J. Arduengo,***[†] **W. Lau,**[‡] **A. Alegria,**[‡] **and J. K. Kochi***[‡]

Contribution from the Departments of Chemistry, University of Illinois, Urbana, Illinois 61801, and Indiana University, Bloomington, Indiana 47401. *Received June 9, 1979*

Abstract: The cyclic sulfuranyl radical **2** is generated by the low-temperature photolysis of *tert*-butylperoxy 2-(methylsulfenyl)benzoate (**1**) in methylene chloride solutions. The ESR spectrum of **2**, centered at $\langle g \rangle = 2.008_0$, shows proton hyperfine splittings by a methyl group ($a_{3H} = 9.0$ G) and H_6 ($a_H = 1.5$ G) but no resolved coupling (<0.1 G) to other protons. The pattern of coupling was unambiguously established through studies of four different regiospecifically deuterated samples of **1**. The ESR results are best interpreted in terms of a bridged radical, a 9-S-3 (nine-electron, three-coordinate sulfur) system with an S–O bond, in which the odd electron is in a σ-type orbital with large spin density on sulfur, and a σ-sulfuranyl radical. We discuss the implications of this finding in terms of earlier observations of anchimeric acceleration of thermal bond homolysis in **1** and its analogues.

Radical-forming thermolyses of *tert*-butylperoxy benzoates which have sulfenyl sulfur substituents ortho to the carboxy function (either phenylsulfenyl or, as in the case of **1**, methylsulfenyl) have been shown[2] to proceed with anchimeric acceleration factors of as much as 10^6. Substituent effects on rate showed the decomposition of the phenylsulfenyl-substituted perbenzoate to occur via a very polar transition state with the development of positive charge on the sulfur atom.[2c,d] It has been suggested[2] that the acceleration results from S–O bonding in a transition state leading to bridged sulfuranyl radicals such as **2**. An unstable intermediate sulfurane, which would result from recombination of the *tert*-butoxy radical (formed by O–O bond homolysis) with the simultaneously formed sulfuranyl radical, has been directly observed[2d] in the thermolysis of a close analogue of **1** (eq 1).

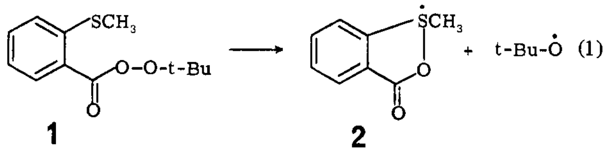
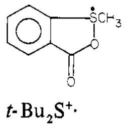


Table I. ESR Parameters of Some Oxysulfuranyl Radicals

structure	⟨g⟩	proton hyperfine splittings, G: CH_3S	proton hyperfine splittings, G: others	ref
$(CH_3)_2\dot{S}OSi(CH_3)_3$	2.0076	7.7	0.2[a]	*e*
$CH_3\dot{S}(O\text{-}t\text{-}Bu)_2$	2.0096	6.5		*f*
$\dot{S}(OCH_3)_3$	2.0067		1.7[b]	*g*
	2.008_0	9.0	1.5[c]	This work
$t\text{-}Bu_2S^{+\cdot}$	2.0130		*d*	*e*

[a] From $(CH_3)_3Si$. [b] From CH_3O. [c] From H_6. [d] *t*-Bu not resolved, $a_S = 32.5$ G. [e] W. B. Gara, J. R. M. Giles, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1444 (1979). [f] W. B. Gara, B. P. Roberts, B. C. Gilbert, C. M. Kirk, and R. O. C. Norman, *J. Chem. Res., Miniprint*, 1748 (1977). [g] J. S. Chapman, J. W. Cooper, and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, 835 (1976).

Sulfuranyl radicals (e.g., **2**) are tricoordinate species in which the valence shell of sulfur has been, at least formally, expanded

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[†] University of Illinois.
[‡] Indiana University.

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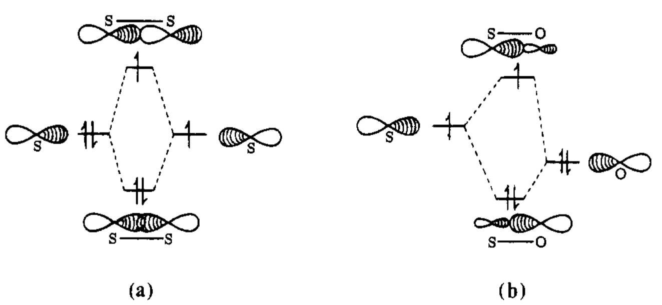


Figure 1. Schematic MO representation of a two-center, three-electron (2c,3e) bond joining (a) S to S and (b) S to O.

to nine. Using a classification scheme which we propose herewith,[1] we may call this a 9-S-3 species. Several lines of evidence indicate the existence of such species. (a) Studies of radical selectivities in chlorinations led Russell[3] to suggest in 1958 that species which can be formulated as sulfuranyl radicals are formed by the reaction of chlorine atoms with diphenyl sulfide. (b) Analogous reactions of electronegative alkoxy radicals with compounds containing sulfenyl sulfur to give sulfuranyl radicals such as **3** have been confirmed by ESR.[4,5] (c) The γ irradiation of SF_6 gives the trifluorosulfuranyl radical which is observable by ESR.[6] (d) One-electron oxidations[7] of sulfides with suitably situated nucleophilic neighboring groups lead to sulfuranyl radicals such as **4**. (e) One-electron reduction[8] of the corresponding disulfide gives the anionic sulfuranyl radical **5**.

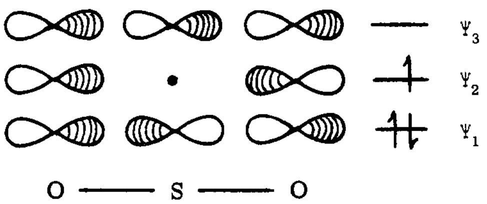


Figure 2. The approximate hypervalent[12] bonding scheme for a σ-sulfuranyl radical.

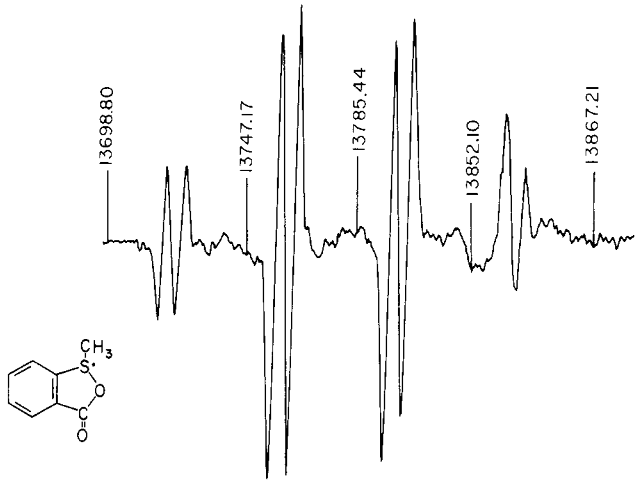
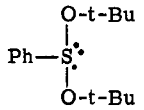
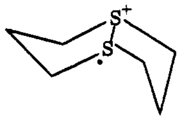


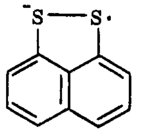
Figure 3. ESR spectrum obtained for the photolysis of *tert*-butylperoxy 2-(methylsulfenyl)benzoate in methylene chloride solution at −85 °C. Proton NMR field markers are in kHz.



3 (9-S-3)



4 (9-S-3 and 8-S-3)



5 (9-S-2 and 10-S-2)

$(CH_3)_3SiO\dot{\underset{..}{S}}(CH_3)_2$

6 (9-S-3)

We may illustrate three approximate bonding models[9a,b] for

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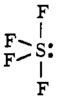
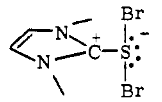
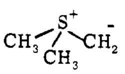
[1] The increasing interest in molecules with electron-rich multicenter (hypervalent) bonding such as that postulated here for **2** has prompted us to devise a systematic classification scheme which includes a concise description of such bonding. We here propose a generally useful system to designate the bonding about any atom (X) in a resonance structure in terms of the number of valence shell electrons (*N*) formally associated directly with that atom and the number of ligands (*L*) directly bonded to it. Such a bonding system is described as an *N*-X-*L* system. A sulfuranyl radical such as **2** thus contains the 9-S-3 system. Nine electrons are formally associated with sulfur to which three ligands are bound. The usual structure drawn for a sulfurane such as SF_4 (below) contains a 10-S-4 system, as well as four 8-F-1 systems. The following examples serve to illustrate the application of this system of classification for several types of compounds or transition states, some having hypervalent bonds and others having only normal bonds or electron-deficient bonds.



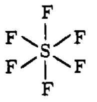
10-S-4



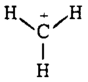
10-S-3



8-S-3



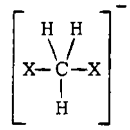
12-S-6



6-C-3

CH_5^+

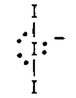
8-C-5



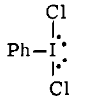
10-C-5

$:CH_2$

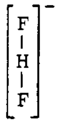
6-C-2



10-I-2



10-I-3



4-H-2

$[H_3C\cdots\dot{H}\cdots Cl]$

3-H-2

(2) (a) J. C. Martin and W. G. Bentrude, *Chem. Ind.* (*London*), 192 (1959); (b) W. G. Bentrude and J. C. Martin, *J. Am. Chem. Soc.*, **84**, 1561 (1962); (c) J. C. Martin, D. L. Tuleen, and W. G. Bentrude, *Tetrahedron Lett.*, 229 (1962); (d) D. L. Tuleen, W. G. Bentrude, and J. C. Martin, *J. Am. Chem.*, **85**, 1938 (1963); (e) T. H. Fisher and J. C. Martin, *ibid.*, **88**, 3382 (1966); (f) P. Livant and J. C. Martin, *ibid.*, **98**, 7851 (1976).

(3) G. A. Russell, *J. Am. Chem. Soc.*, **80**, 4987 (1958).

(4) B. C. Gilbert, C. M. Kirk, R. O. C. Norman, and H. A. Laue *J. Chem. Soc., Perkins Trans 2*, 497 (1977) have reinterpreted the spectra ascribed by T. Kawamura, P. J. Krusic, and J. K. Kochi, *Tetrahedron Lett.*, 4075 (1972), to methanesulfinyl radical resulting from the irradiation of *tert*-butyl methanesulfenate and have concluded that the spectra are in fact attributable to the methylbis(*tert*-butoxysulfuranyl) radical.

(5) (a) B. C. Gilbert, D. K. C. Hodgeman, and R. O. C. Norman, *J. Chem. Soc., Perkins Trans. 2*, 1748 (1973); (b) W. B. Gara, B. P. Roberts, B. C. Gilbert, C. M. Kirk, and R. O. C. Norman, *J. Chem. Res. Miniprint*, 1748 (1977); (c) J. S. Chapman, J. W. Cooper, and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, 835 (1976); (d) W. B.Gara and B. P. Roberts, *J. Organomet. Chem.*, **135** (1977), C20–C22.

(6) J. R. Morton and K. F. Preston, *J. Phys. Chem.*, **77**, 2645 (1973); A. J. Colussi, J. R. Morton, K. F. Preston, and R. W. Fessenden, *J. Chem. Phys.*, **61**, 1247 (1974).

(7) W. K. Musker and T. L. Wolford, *J. Am. Chem. Soc.*, **98**, 3055 (1976); R. S. Glass, J. R. Duchek, J. T. Klug, and G. S. Wilson, *ibid.*, **99**, 7349 (1977); G. S. Wilson, D. D. Swanson, J. T. Klug, R. S. Glass, M. D. Ryan, and W. K. Musker, *ibid.*, **101**, 1040 (1979); W. K. Musker, T. L. Wolford, and P. B. Roush, *ibid.*, **100**, 6416 (1978); W. K. Musker, A. S. Hirschon, and J. T. Doi, *ibid.*, **100**, 7754 (1978); K.-D. Asmus, H. A. Gillis, and G. G. Teather, *J. Phys. Chem.*, **82**, 2677 (1978). For a recent review see K.-D. Asmus, *Acc. Chem. Res.*, **12**, 436 (1979).

(8) A. Zweig and A. K. Hoffman, *J. Org. Chem.*, **30**, 3997 (1965).

(9) (a) J. C. Martin, *ACS Symp. Ser.*, No. **69**, 71 (1978). (b) A fourth bonding scheme may be considered for radicals having a phenyl ring adjacent to sulfur. This model has a "tetrahedral" structure about sulfur and unpaired electron density located primarily in the lowest π^* orbital of the phenyl ring with the sulfur lying in the nodal plane. Since there is a lack of appreciable unshared electron density on the sulfur atom, a molecule described by this bonding scheme is, by definition, not a sulfuranyl radical. This structure may be more appropriately considered a sulfonium species with a phenyl radical anion ligand. Analogous phosphonium species have been postulated.[14c,d]

such species. (a) The odd electron in **3** has been postulated,[5b] from ESR evidence, to be in a π-orbital delocalized over the phenyl ring. In such a structure the two alkoxy ligands are joined to sulfur with a three-center, four-electron (3c,4e) bond of the type postulated[10] for many isolable sulfuranes.[11] Results of a CIDNP study[12] of the thermolysis of **1** have been interpreted in terms of such a π-radical description for **2**.

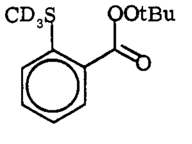
(b) Radicals **4**[7] and **5**[8] are thought to be σ radicals which can be described approximately[9a] in terms of a structure with the odd electron in an orbital which is essentially an antibonding combination of sulfur 3p atomic orbitals, as in Figure 1a. Radical **6**, an even closer analogue of **2**, has been described[5d] as a σ radical with the odd electron in an antibonding σ combination of sulfur and oxygen orbital, as in Figure 1b.

Since the bonding MO is doubly occupied while the antibonding MO is only singly occupied, one may see an overall bonding interaction between a sulfur cation radical and any neighboring nucleophile such as the carboxylate oxygen in **2** (Figure 1b).

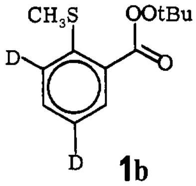
(c) A third possible bonding scheme of **2** requires the methyl carbon to be roughly collinear with the S–O bond, with the singly occupied MO being made up primarily of the σ bonds in what has been approximately described[9] as a three-center, three-electron (3c,3e) bond.

The ESR spectrum of the trifluorosulfuranyl radical has been interpreted[6] in terms of a T-shaped structure entirely analogous to this model for **2**. The odd electron is in an orbital ($^2A_1$) which is essentially the central nonbonding hypervalent MO in the simplified description of Musher.[13] An antibonding interaction of Ψ_2 (Figure 2) with the sulfur 3s orbital gives a better approximation to the $^2A_1$ orbital which accommodates the odd electron.[14] Radical **6**, which shows equal hyperfine coupling to the six *S*-methyl protons, could also be described by this bonding scheme with an O–S–C three-center bond if the methyl ligands exchange rapidly enough to average the hfsc in the ESR.[5d]

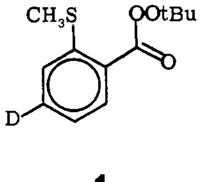
We here report the result of an ESR study of **2**, together with studies of radicals from regiospecifically deuterated derivatives of **1** (**1a–d**), which establishes it to be a σ-type radical, best approximately described by bonding model c.



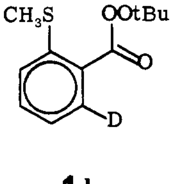
1a



1b



1c



1d

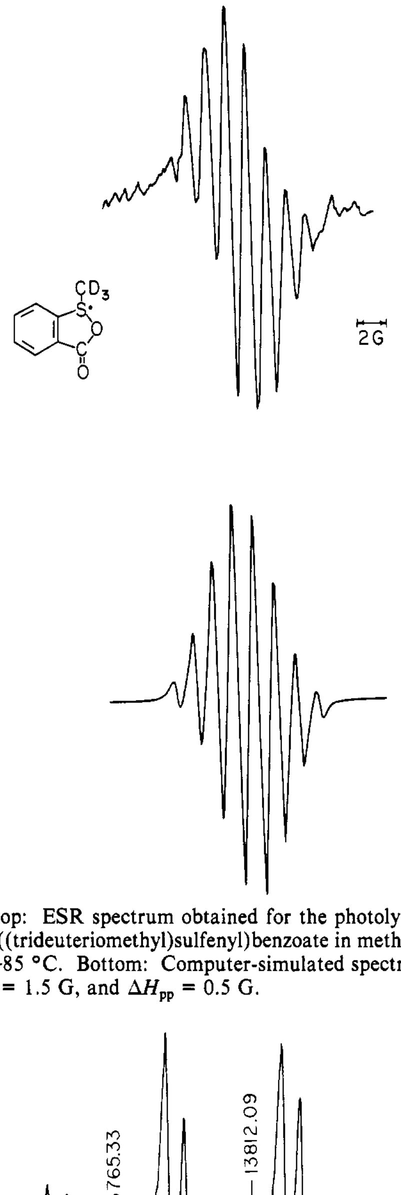


Figure 4. Top: ESR spectrum obtained for the photolysis of *tert*-butylperoxy 2-((trideuteriomethyl)sulfenyl)benzoate in methylene chloride solution at −85 °C. Bottom: Computer-simulated spectrum using a_{3H} = 1.4 g, a_H = 1.5 G, and ΔH_{pp} = 0.5 G.

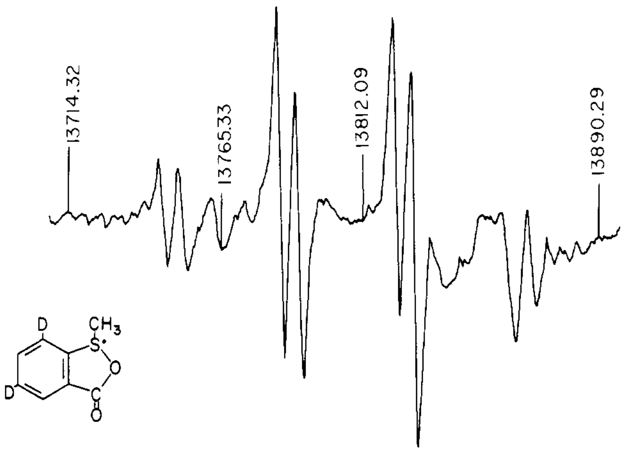


Figure 5. ESR spectrum obtained from the photolysis of 3,5-dideuterio analogue **1b** at −85 °C in methylene chloride solution.

Results

The well-resolved, but somewhat broadened ($\Delta H_{pp} \approx 0.5$ G), ESR spectrum shown in Figure 3 was obtained from the photolysis of a solution of *tert*-butylperoxy 2-(methylsulfenyl)benzoate **1** in methylene chloride at −85 °C. The same spectrum was obtained in the completely deuterated solvent CD_2Cl_2. A variety of other solvents were also examined but afforded spectra with reduced amplitudes owing largely to limited solubility of the perester. The ESR spectrum was unchanged between −40 and −100 °C, the freezing point of the solvent. The hyperfine splitting pattern in Figure 3 clearly consists of a doublet of 1:3:3:1 quartets with $g = 2.008_0$. The binomial intensity ratios are correct for a splitting from a set of three equivalent protons and a unique proton. (Note

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(10) J. C. Martin and E. F. Perozzi, *Science (Washington, D. C.)*, **191**, 154 (1976).

(11) Direct observations of anionic tricoordinate sulfur analogues of **3**, sulfuranide anions, have recently been reported by P. H. W. Lau and J. C. Martin, *J. Am. Chem. Soc.*, **100**, 7077 (1978), and neutral zwitterionic analogues by A. J. Arduengo and E. M. Burgess, *ibid.*, **99**, 2376 (1977).

(12) W. Nakanishi, S. Koike, M. Inoue, Y. Ikeda, H. Iwamura, Y. Imahashi, K. Kihara, and M. Iwai, *Tetrahedron Lett.*, 81 (1977).

(13) J. I. Musher, *Agnew. Chem., Int. Ed. Engl.*, **8**, 54 (1969).

(14) Related 3c,3e bond types have been deduced for 9-P-4 phosphoranyl radicals. (a) T. Gillbro and F. Williams, *J. Am. Chem. Soc.*, **96**, 5032 (1974); (b) A. Hasegawa, K. Ohnishi, K. Sogabe, and M. Miura, *Mol. Phys.*, **30**, 1367 (1975); (c) J. A. Baban and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, 537 (1979). Even more closely related are the anion radicals of tricoordinate phosphorus (9-P-3): (d) G. Boekestein, E. H. J. M. Jansen, and H. M. Buck, *ibid.*, 118 (1974) and references cited therein. For a review of phosphoryl radical chemistry see W. G. Bentrude in "Free Radicals", Vol. II, J. K. Kochi, Ed., Wiley, New York, 1973, Chapter 22.

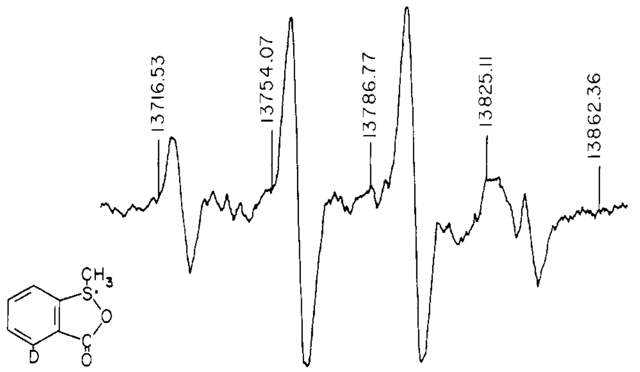


Figure 6. ESR spectrum obtained from the photolysis of the 6-deuterio analogue **1d** in methylene chloride solution at −85 °C.

the high field doublet is partially obscured by an overlapping line from a solvent-derived radical.)

The quartet splitting of 9.0 G is unambiguously assigned to the protons on the methylsulfenyl substituent, since the photolysis of the trideuterio analogue **1a** afforded the spectrum in Figure 4 (top), in which the quartet splitting has been reduced by a factor of 6.5 ($\gamma_H/\gamma_D = 6.514$) to 1.4 G as shown by a comparison with the computer-simulated spectrum in Figure 4 (bottom).

The remaining doublet splitting of 1.5 G cannot be due to the ring protons at either 3- or 5-position, since the ESR spectrum in Figure 5, obtained for the photolysis of **1b**, is essentially identical with that shown in Figure 3 (i.e., $a_{3H} = 9.0$ G, $a_H = 1.5$ G, $g = 2.008_0$). Similarly, photolysis of the 4-deuterio analogue **1c** afforded the same ESR spectrum with a_{3H} and $a_H = 9.0$ and 1.5 G, respectively, and $g = 2.008_2$. However, the doublet splitting is absent from the ESR spectrum in Figure 6, obtained from the 6-deuterio analogue **1d**. The quartet splitting of 9.0 G with $g = 2.008_0$ is the same as that in Figure 3. An expected deuterium splitting of 1.5/6.5 or 0.2 G is unresolved but readily accommodated within in the envelope of the increased linewidths ($\Delta H_{pp} \approx 1.6$ G) in Figure 6.

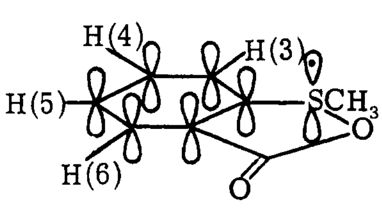
Discussion

The sulfuranyl radical **2** obtained from the homolytic cleavage to *tert*-butylperoxy 2-(methylsulfenyl)benzoate derives part of its stability from its cyclic nature. This is concluded because attempts to generate similar structures by an intermolecular process involving the addition of oxyl radicals to phenyl methyl sulfide, i.e., eq 2, when X = *t*-Bu and COPh, have been unsuccessful. The sulfuranyl radical **2** is formally a member of a class of three-coordinate sulfur-centered radicals (9-S-3 systems[1]) containing an alkoxy ligand. As such, the ESR parameters of **2** are compared in Table I with those presented in the extant literature for similar paramagnetic species. Indeed the proton splitting of 9.0 G by the methylsulfenyl group in **2** is close to that reported for the closest acyclic analogue, the monooxysulfuranyl radical $(CH_3)_2\dot{S}OSi(CH_3)_3$, in Table I. It is noteworthy that the isotropic g values of the two species are also comparable. We believe that the observation of the relatively large doublet splitting by the aromatic proton at position 6 provides an unusual insight into the structure of **2**. Let us consider some structural possibilities.

(2)

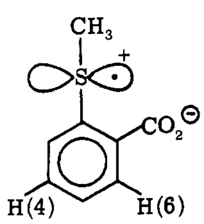
The relatively large quartet splitting is qualitatively in accord with the conclusion, previously drawn from the results of a CIDNP study,[12] that the radical has the π-type structure illustrated in **7**. In that study, a nuclear spin polarization was seen for the methyl protons in stable products from the homolysis of **1**. The results of CNDO/2 calculations of **7**, carried out without optimization of geometry, were also cited in support of this structural hypothesis.

Structure **7** however, appears inconsistent with the smaller doublet structure which we have shown to result from hyperfine coupling to H(6). A π-delocalized structure, **7**, might be expected to have comparably large spin density at H(3) and H(5). Such an expectation was a part of the argument presented[5b] in support of the conclusion that **3** is a π-sulfuranyl radical. The fact that coupling to these protons is negligible, compared to that to H(6), suggested the inadequacy of π-delocalized structure **7** as a model. Another structural hypothesis is required which is consistent both with the ESR and CIDNP results. Proton spin polarization was observed in protons absorbing in the aromatic region of the product NMR in the CIDNP experiment, but no assignments were made.



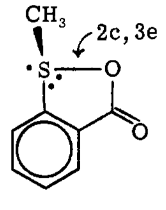
7

A 7-S-2 structure such as **8**, which resembles a sulfur cation radical without an S–O bond, with the odd electron in an orbital in the plane of the aromatic ring, also seems unlikely. Such a structure might be expected to show comparable hyperfine interactions with H(6) and H(4). Coupling to H(4) is not observable. Furthermore the g value for such a sulfonium structure is expected to be larger than 2.008 (compare $t\text{-}Bu_2S^{+}\cdot$ in Table I).

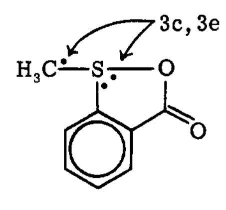


8

All observations are in qualitative accord with structural hypotheses represented by **9** or **10**, σ-sulfuranyl radicals with bonding models b or c discussed above. In such structures the S–O bond renders H(4) and H(6) nonequivalent with respect to hyperfine interactions.

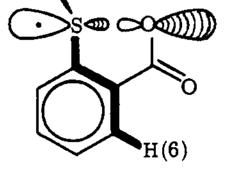


9

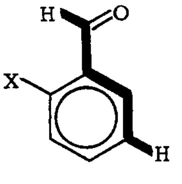


10

The odd electron in **9** is part of a 2c,3e bond in an orbital approximately described as the antibonding combination of S and O atomic orbitals, as in **9a**. By analogy to the long-range nuclear spin–spin coupling observed[15] for benzaldehydes by way of the



9a



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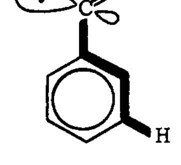

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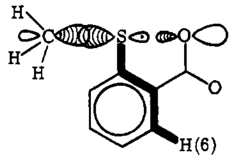
[15] G. J. Karabatsos and F. M. Vane, *J. Am. Chem. Soc.*, **85**, 3886 (1963).

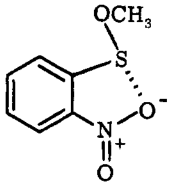
extended zigzag chain of bonds illustrated in **11**, one might expect the hyperfine coupling to H(6), through a similar chain of bonds, to be appreciable. Such a coupling to the meta protons is also seen in benzoyl radicals[16] (although the rapid rotation about the C-phenyl bond renders both meta protons equivalent).

The alternative formulation for a σ-sulfuranyl radical, **10**, bonding model (c), has the odd electron in an orbital which is approximately described, as in **10a**, as part of a 3c,3e bond. It is constituted in such a way as to facilitate σ delocalization to H(6). While we may therefore state with some confidence that **2** is a σ radical, a choice between bonding models **9a** and **10a** requires more detailed analysis of the system.

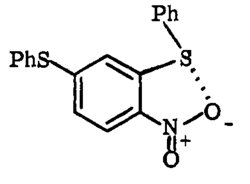


10a

We have examined sulfuranyl radical **2**, the corresponding sulfonium cation **12**, and sulfuranide anion **13**, as well as the *o*-nitrosulfenic ester **14** by using the energy geometry optimized SCF-MINDO/3 procedure and for the open-shell molecules MINDO with unrestricted Hartree-Fock, MINDO-UHF.[17] Sulfuranyl radical **2** was also examined by an INDO procedure employing the parameterization of Gordon et al.[18a] and that of Santry and Segal.[18b]



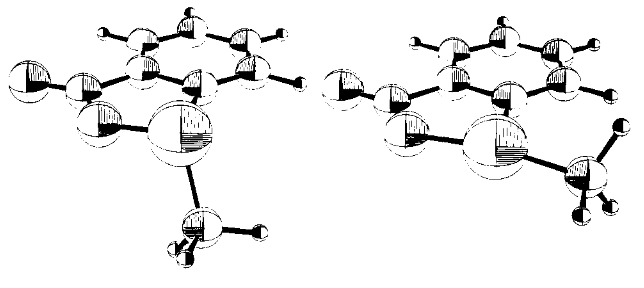
14



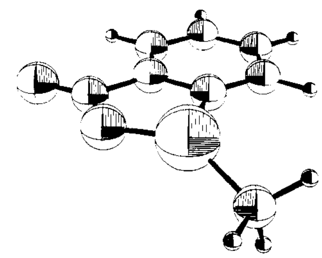
15

The minimum energy geometry for **2** (Figure 7) places the odd electron in a SOMO (Figure 8) which is not π-like but rather a σ system of largely methyl, sulfur, and oxygen contributions. This SOMO which is qualitatively similar in MINDO/3, MINDO-UHF, and INDO structures is characterized by an electron distribution which appears to be in essence an antibonding combination of the sulfur s orbital lone pair and the symmetric nonbonding highest occupied level from the three-center hypervalent bonding system of the sulfurane. It should be noted that the deviation of the methyl group from the molecular plane at 23° has allowed a slight contribution of the p-type sulfur lone pair to the SOMO system.

The calculated geometry for **2** is intermediate between the geometries calculated by MINDO/3 for sulfuranide anion, **13**, and sulfonium cation, **12** (Figure 7). It is useful to view the structure of radical **2** as lying along a smooth surface which upon successive electron removal converts the ψ-TBP geometry of the anion **13** to the ψ-tetrahedral geometry of the cation **12**. The MINDO-UHF structure for **2** shows a C(methyl)-S-O angle of 140.7° while the C-S-O angle in **13** is 163.8° and the C-S-O angle in **12** is 110.3°. The methyl carbon is in the plane of the molecule for anion **13**. In radical **2** the methyl is bent out of the plane by 23° and in cation **12** by 65°. The structure for radical **2** more closely resembles planar anion **13** than pyramidal cation **12**. The structure of cation **12** is unexceptional and in line with what would be expected for a sulfonium ion.



12, Sulfonium cation **13**, Sulfuranide anion



2, Sulfuranyl radical

Figure 7. Energy-minimized geometries from MINDO-UHF calculations for radical **2** and its cationic (**12**) and anionic (**13**) analogues.

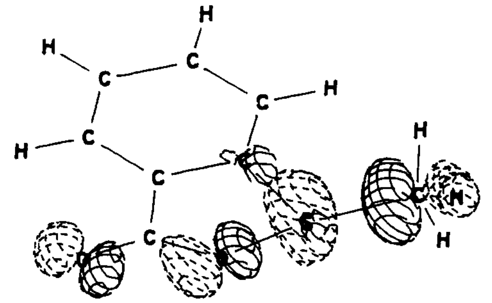


Figure 8. The SOMO of **2** calculated by MINDO-UHF.

A striking feature of the structures for radical **2** and anion **13** is the rather short S-O interatomic distance: r_{S-O} in **2** is 1.63 Å and r_{S-O} in **13** is 1.74. Sulfenate ester **14** is sufficiently similar to anion **13** in electronic structure to make it a useful model. The structure calculated for **14** is very similar to the observed[19a] geometry except for the shortness of the S-O bond (1.68 Å) compared with the observed bond distance of 2.44 Å. The more closely analogous **15** has an even longer S-O bond distance, 2.64 Å. (Both S-O distances are less than the sum of the van der Waals radii, 3.25 Å.) Attempts to reparameterize the hypervalent S-O bond in MINDO to give a longer S-O bond, more in accord with that expected from a consideration of these model compounds, met with no success. The problem of choosing bicentric parameters for the MINDO procedure when structures like **2** and **13** are calculated is difficult since it can be seen that there are also two types of S-C bonds, normal and hypervalent, which may need different parameter sets. The more extensive data base used to obtain the S-C parameters may, however, make the choice of "special" parameters less important for sulfur-carbon bonds.

The energy minimum for the final calculated structure in **2** is shallow. The energy required to move the methyl group into the

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(16) P. J. Krusic and T. A. Rettig, *J. Am. Chem. Soc.*, **92**, 722 (1970).

(17) (a) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285 (1975). (b) MINDO-UHF is a version of the MINDO procedure developed by M. J. S. Dewar which allows INDO calculations on open-shell molecules by using the unrestricted Hartree-Fock technique. We are thankful to Dr. D. A. Pensak for kindly providing a copy of the MINDO-UHF program. (c) See P. Bischof, *J. Am. Chem. Soc.*, **98**, 6844 (1976). The bicentric parameters, β_{so} and α_{so}, required to modify the core repulsion and resonance integrals were initially taken from the work of A. J. Arduengo and E. M. Burgess, *J. Am. Chem. Soc.*, **98**, 5021 (1976).

(18) (a) M. S. Gordon, M. D. Bjorke, F. J. Marsh, and M. S. Korth, *J. Am. Chem. Soc.*, **100**, 2670 (1978); (b) D. P. Santry and G. A. Segal, *J. Chem. Phys.*, **47**, 158 (1967).

(19) (a) W. C. Hamilton and S. J. LaPlaca, *J. Am. Chem. Soc.*, **86**, 2289 (1964); (b) J. D. Korp, I. Bernal, R. F. Miller, J. C. Turley, L. Williams, and G. E. Martin, *J. Cryst. Mol. Struct.*, **8**, 127 (1978).

plane of the molecule, setting the C–S–C angle equal to that calculated for the anion, was small enough (ca. 2.1 kcal/mol) to make it impossible to make a definite statement as to the magnitude of the deviation from planarity, if indeed there is one. Positioning the methyl to produce the more pyramidal geometry of the cation is more costly in energy (ca. 8.6 kcal/mol). Since we expect the S–O bond distance to be greater than that predicted by the MINDO–UHF calculations, it is not likely that the calculation understates the barrier for bending deformations of the O–S–C(methyl) angle.

The pictured (Figure 7) structure for **2** is, however, a reasonable approximation except that the S–O bond is perhaps too short, and the molecule is easily deformed to move the methyl group into the plane.

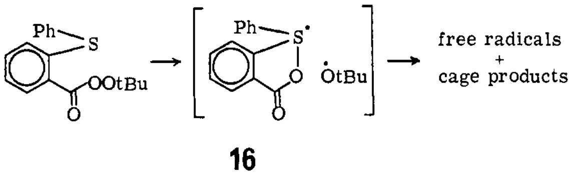
The spin densities calculated for **2** by MINDO–UHF are listed in Table II. The magnitudes calculated for the various protons in the molecule are in the same order as the magnitudes of the observed hyperfine coupling constants. These results are difficult to interpret, however, since the magnitudes of the calculated spin densities are small in magnitude and markedly dependent on relatively small changes in the geometry of **2**. Bischof[17b] has reported spin densities calculated by MINDO–UHF for various radicals involving first-row elements. The agreement with experiment is not close.

The factor relating MINDO–UHF spin densities to hyperfine coupling constants is not expected to be the same as the factor used with other INDO calculations. A statistical fit of a large set of experimentally determined hyperfine coupling constants would be required to obtain an optimum conversion factor.

The calculation of properties of compounds of second-row elements using the INDO procedure has often required the generation of new sets of parameters. We used two of these sets of parameters[18a,b] in attempts to fit our data. Neither gave spin densities for the ring protons of **2** with magnitudes in the proper order. The MINDO–UHF spin densities, while not giving a satisfactory quantitative fit to experiment, are qualitatively in accord with our observations.

Both MINDO and INDO give a SOMO which is qualitatively a σ radical, as pictured in Figure 8, with a rather large energy separation between the sigma SOMO and the π-type orbital next higher in energy.

A fact[20] which must be accommodated by any adequate structural hypothesis for **2** is that the sulfuranyl radical of radical pair, **16**, a close analogue to **2**, gives products different from those derived from ion pair **17**. The perester decompositions lead predominantly to products which may be expected from radical intermediates (eq 3).[2b] Products from the ion pair reaction, in contrast, do not include those characteristic of the free radicals of this system.[20]



(3)

16

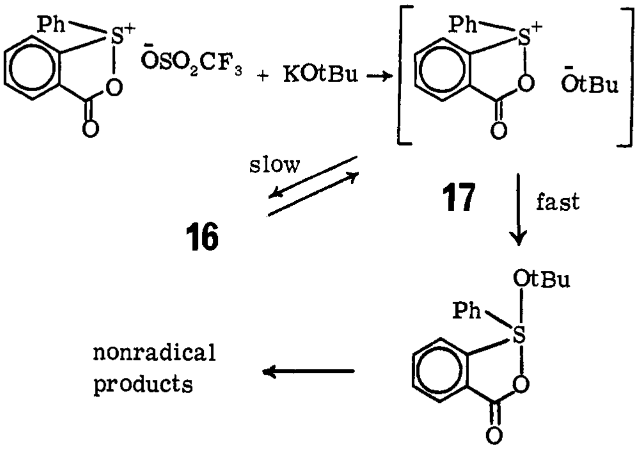
The apparent unimportance of the one-electron transfer that would interconvert the ion pair and the radical pair is documented and discussed elsewhere.[20] The factor that is probably responsible for the lack of crossover between the radical pair and the ion pair is the difference in geometry about the sulfur in the sulfuranyl radical and the sulfonium ion. If failure to see crossover is to be explained by invoking the Frank–Condon principle, there must be a substantial difference in the geometry of the sulfonium ion and the sulfuranyl radical, as is in fact seen in our calculated geometries. Given that this is the case it is possible that one might observe a substantial energy barrier for the equilibrium of **16** and **17** and observe products from each with minimal crossover (Scheme I).

Table II. Calculated Spin Densities (MINDO-UHF) and Observed Hyperfine Coupling Constants for Radical 2

protons	s-orbital spin densities	obsd hyperfine coupling constants
CH_3[b]	−0.00495	8.966
H(3)	−0.00028	*a*
H(4)	0.00060	*a*
H(5)	−0.00048	*a*
H(6)	−0.00097	1.456

[a] Not resolved in spectra. [b] Positional average.

Scheme I



Thermal homolyses of closely related analogues of **1** such as **16** are shown by substituent effects to develop positive charge on sulfur.[2d] The calculated electronic structure for the product radical from **1** is seen to have positive charge at S (charge +0.316). The 3c,3e bond is polarized, as expected on the basis of the known great polarizability of 3c,4e bonds in sulfuranes,[21] toward the more electronegative oxygen (charge −0.494), although the methyl carbon at the other apical position is also negatively charged (−0.029). The large polar solvent effects on rate and kinetic salt effects observed[2c,d] for thermal bond homolyses of these same compounds reflect a large charge separation in the transition state of these reactions. Our calculations on the bridged sulfuranyl radical product show a dipole moment of 5.95 D for this species. The observations[2c,d] related to the polar character of the transition states in these radical-forming reactions may therefore be largely explicable on the basis of the resemblance of the transition state to the product radicals.

Summary

We conclude that radical **2** is best described as a slightly distorted 9-S-3 ψ-TBP species with a 3c,3e bond, i.e., a σ-sulfuranyl radical in which the apical positions are very unsymmetrically substituted, with a carboxy oxygen and a methyl group. When taken with the earlier conclusion[6] that the symmetrically substituted trifluorosulfuranyl radical ($F_3S\cdot$) has the same type of structure, this suggests that 9-S-3 sulfuranyl radicals might quite generally have such structures. Indeed our calculated results, which suggest that **2** is a sigma radical, bring into question the electronic structure of **3**, which was postulated[5h] to be a π-sulfuranyl radical.

Evidence for related σ-phosphoranyl radicals has been presented (e.g., ref 14a), as has evidence[14d] for 9-P-3 anion radicals which might be expected to be isoelectronic with the neutral 9-S-3 radicals. Observations of ESR spectra of hexacoordinate silicon anion radicals (11-Si-6 species) have been reported[22] which are

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(20) P. Livant and J. C. Martin, *J. Am. Chem. Soc.*, submitted for publication.

(21) P. Livant and J. C. Martin, *J. Am. Chem. Soc.*, **99**, 5761 (1977).

also consistent with this general picture, although other explanations were provided for the observations.

It is clear that 3c,3e bonds may play an important role in free-radical chemistry, both in the set of observable species discussed here and, as has long been recognized, in the transition states for radical abstraction reactions of many types. It is helpful to view such species as hypervalent analogues of the closed-shell species such as sulfuranes and phosphoranes, which are directly observable and for which, therefore, structure-reactivity relationships are more fully understood.

Experimental Section

***tert*-Butylperoxy 2-(Methylthio)benzoate (1).** In an adaptation of the method of Lorand and Bartlett[23] **1** was prepared by boiling a mixture of 1 g (6 mmol) of unlabeled acid, 10 mL (140 mmol) of $SOCl_2$, and 10 mL of CCl_4 for 10 min. The CCl_4 and $SOCl_2$ were removed in vacuo. The crude product was dissolved in ether and decolorized with charcoal. Evaporation of the ether left white crystalline acid chloride. A suspension of 0.80 g (7 mmol) of potassium *tert*-butyl hydroperoxide[24] in 15 mL of ether was added in one portion to a solution of this white crystalline solid in 15 mL of ether at −20 °C. The mixture was stirred for 16 h and then filtered into a flask precooled to −30 °C. Ether was removed at −30 °C and (0.1 torr) until a white precipitate began to appear. The solution was left overnight at −78 °C. White crystals were obtained upon filtration. Pentane was added to the filtrate until a precipitate appeared. A second crop obtained after addition of pentane gave additional **1**, a total of 0.89 g. Recrystallization from ether–pentane gave 0.80 g (51%), mp 56–56.5 °C (lit. 55.2–55.7 °C).[2b]

The appropriate acid precursors to **1c,d** were prepared by thiomethylating lithium derivatives of phenyloxazoline in which a specific position had been deuterated.[25] For the 4-deuterio-, 6-deuterio-, and 3,5-dideuterio-2-(methylthio)benzoic acids the predicted positions of deuteration were verified by NMR. The percent deuteration for the 4-deuterio and 6-deuterio compounds was determined by both NMR and mass spectrometry while the percent deuteration of the 3,5-dideuterio was verified by mass spectrometry only. The 3,5-dideuterio compound showed the expected area reduction of the two upfield aromatic peaks [δ 7.2 (H(3)), δ 7.3 (H(5))] accompanied by the expected simplification of the two downfield peaks [H(4) and H(6)]. The NMR of the 6-deuterio acid showed the expected reduction of the most downfield peak (δ 8.13, H ortho to the CO_2H). The 4-deuterio analogue showed a reduction of the peak area at δ 7.55 and broadening in the other aromatic peaks.

3,5-Dideuterio-2-(methylthio)benzoic acid was prepared by the reaction of 1.9 g (11 mmol) of unlabeled acid and 35 g of an 80% w/w mixture of triflic acid-*d* and D_2O. After 56 h at ambient temperatures, the mixture was poured into ice and extracted with ether. Ether was removed in vacuo. White crystals of **1b** obtained upon recrystallization from ethanol–water weighed 1.7 g (0.10 mmol): mp 169.5–170.0 °C;[26] ^1H NMR ($CDCl_2$) δ 8.12 (s, 100), 7.55 (s, 96), 2.47 (s, 500); mass spectrum (70 eV), *m/e* (relative intensity) 170 (100 $M^{+\cdot}$, d_2), 155 (38.06, $M^{+\cdot} - CH_3$), 124 (35.65, $M^{+\cdot} - H_2O$, CO), 123 (42.74, $M^{+\cdot} - SCH_3$), 169 (22.66 $M^{+\cdot}$, d_1), 168 (2.01, $M^{+\cdot}$, d_0). Percent deuteration by mass spectrometry: d_2, 78%; d_1, 20%; d_0 2%.

(Trifluoromethane)sulfonic acid-*d* was prepared by combining 2.90 g (10 mmol) of triflic anhydride with 234 mg of D_2O (11.7 mmol) and heating to 70 °C for 1 h.

2-(Methylthio)benzoic acid-*O*-*d* was prepared from 1.68 g (10 mmol) of the unlabeled acid and 1.8 g (100 mmol) of D_2O in tetrahydrofuran under N_2. The mixture was heated to dissolve the material, and hexane was added. Upon cooling of the mixture, white crystals were obtained (1.5 g, 0.9 mmol): mp 170–175 °C; mass spectrum (70 eV), *m/e* (relative intensity) 169 (100.00 $M^{+\cdot}$, d_1), 168 (21.92, $M^{+\cdot}$, d_0), 151 (17.07, $M^{+\cdot} - OD$), 150 (13.51, $M^{+\cdot} - HOD$), 153 (27.31, $M^{+\cdot} - COD$). The percent deuteration estimated by mass spectrometry was 82%.

2-(4-Deuterio-2-(methylthio)phenyl)-4,4-dimethyl-Δ^2-oxazoline was prepared by adding 70 mL (105 mmol) of 1.5 M *n*-BuLi in hexane dropwise to a solution of 17.5 g (100 mmol) of 2-(4-deuteriophenyl)-4,4-dimethyl-Δ^2-oxazoline[25] in 300 mL of tetrahydrofuran. After 1.5 h at −40 °C (chlorobenzene–liquid nitrogen slush) 28.3 g (300 mmol) of dimethyl disulfide was added. The reaction mixture was poured into water, extracted with ether, and dried, and solvent was removed in vacuo. The crude product was recrystallized once from hexane and once from $MeOH/H_2O$ to give **1c**: 15 g (68 mmol); mp 100–101 °C; ^1H NMR ($CDCl_3$) δ 1.41 (s, 6), 2.39 (s, 3), 7.09 (s, 1), 7.18 (s, 1), 7.39 (m, 0.2), 7.25 (d, 1).

2-(6-Deuterio-2-(methylthio)phenyl)-4,4-dimethyl-Δ^2-oxazoline was prepared in the same manner as described in the preceding paragraph from the 6-deuteriooxazoline except that in this case the carbanion was allowed to stir for 6 h at −45 °C. ^1H NMR ($CDCl_3$): δ 1.41 (s, 6), 2.39 (s, 3), 7.09 (s, 1), 7.18 (d, 1), 7.39 (t, 1), 7.75 (d, 0.3).

4-Deuterio-2-(methylthio)- and 6-deuterio-2-(methylthio)benzoic acids were prepared by hydrolyzing the oxazoline precursors in a large excess of 4.5 N HCl for 5 h. The melting point values for the 4-deuterio and the 6-deuterio species were 169–170 °C (lit. mp 170–171 °C).[26]

4-Deuterio-2-(methylthio)benzoic acid gave the following spectroscopic data: mass spectrum (70 eV), *m/e* (relative intensity) 172 (0.84), 171 (6.9), 170 (19.4, $M^{+\cdot}$, + 1, d_1), 169 (100, $M^{+\cdot}$, d_1), 168 (20.1, $M^{+\cdot}$, d_0); ^1H NMR (CD_2Cl_2) δ 2.5 (s, 3), 7.2 (d, 1), 7.3 (s, 1), 7.55 (s, 0.25), 8.1 (d, 1). Percent deuteration by mass spectrometry: d_1, 82%; d_0, 18%.

6-Deuterio-2-(methylthio)benzoic acid gave the following spectroscopic data: mass spectrum (70 eV), *m/e* (relative intensity) 170 (11.0, $M^{+\cdot}$ + 1, d_1), 169 (100, $M^{+\cdot}$, d_1), 168 (46.8, $M^{+\cdot}$, d_0); ^1H NMR (CD_2Cl_2) δ 2.5 (s, 3), 7.20 (br, 1), 7.32 (d, 1), 7.54 (t, 1), 8.13 (d, 0.3). Percent deuteration by mass spectrometry: d_1 65%; d_0 35%.

Deuterated peresters, 1a–d, were prepared by the procedure described above for **1**.

ESR Measurements. All experiments were performed on a Varian E112 spectrometer equipped with a Hewlett-Packard 5248L electronic counter and a 5255A frequency converter together with a Harvey Wells G502 gaussmeter. The photolyses of the perester solutions were carried out at variable temperature by direct irradiation of the sample tube, which was contained in a quartz Dewar within the cavity, with a Hanovia (Model 977B) 1-kW mercury–xenon lamp. All *g* values are corrected relative to the perylene cation radical ($g = 2.002\,569 \pm 0.000\,006$) used as a standard.

Reagent grade methylene chloride was dried over calcium hydride and degassed by three successive freeze–pump–thaw cycles. Solutions were made up by vacuum transfer of the solvent (~0.4 mL) into a 2-mm i.d. suprasil quartz tube containing approximately 30 mg of the appropriate perester. The tubes were sealed in vacuo and kept frozen until used.

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Supplementary Material Available: Complete results for the MINDO–UHF calculation for **2** and the MINDO/3 calculations for **12** and **13** (30 pages). Ordering information is given on any current masthead page.

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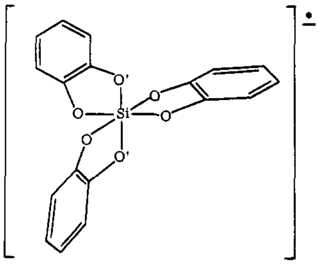
(22) For a review see N. N. Bubnov, S. P. Solodovnikov, A. I. Prokof'ev and M. I. Kabachnik, *Russ. Chem. Rev.* (*Engl. Transl.*), **47**, 579 (1978). The low-temperature ESR spectrum for anion radical **18** shows a triplet which was ascribed to hyperfine coupling to two protons in a single catechol ligand. An alternative formulation for this 11-Si-6 species would invoke equal hyperfine coupling to the two pictured protons in a structure in which one of the three O–Si–O hypervalent bonds (the one involving O′ atoms) is a 3c,3e bond and the other two O–Si–O bonds are 3c,4e bonds. Observable coupling only to the pictured ring protons meta to the hypervalent bond would be analogous to our observations for **2**.



18

(23) J. P. Lorand and P. D. Bartlett, *J. Am. Chem. Soc.*, **88**, 3294 (1966).

(24) Caution should be exercized when this reagent is used. Use of a plastic spoon and Teflon bottles is standard precaution. P. D. Bartlett and H. Minato, *J. Am. Chem. Soc.*, **85**, 1858 (1963).

(25) The deuterated oxazolines were prepared by the method of A. I. Meyers and E. D. Mihelich, *J. Org. Chem.*, **40**, 3158 (1975).

(26) A. Kucsman and T. Kremmer, *Acta Chim. Acad. Sci. Hung.*, **34** (1), 75 (1962).