duced in the rest of the series, or other effects such as a different mode of cleavage for **1d**.[7] Indeed, considering these possible differences, it is remarkable that the other seven compounds gave as good a correlation as they did.

Experimental Section

All ^{13}C nmr spectra were recorded with a Varian Associates XL-100-15 nmr spectrometer utilizing complete ^{1}H decoupling at 100 MHz with simultaneous ^{13}C observation at 25.2 MHz. Mass spectra were recorded on a CEC 21-104 analytical mass spectrometer.

Each imide, **1a-h**, was prepared by adding the appropriate aniline derivative slowly (at ~25°) to an excess of the dichloromaleic anhydride in glacial acetic acid. After several hours of stirring at 25°, each system was refluxed for 1 hr and cooled. The products crystallized from the solution on cooling and were readily isolated and purified. Each gave the expected ^{1}H and ^{13}C nmr spectra and mass spectra and showed strong C=O absorption in the ir at ~1725 cm^{-1}. Other analytical data are given in Table I.

Registry No.—**1a**, 34379-53-8; **1b**, 34281-45-3; **1c**, 29244-55-1; **1d**, 34281-46-4; **1e**, 3876-05-9; **1f**, 29236-09-7; **1g**, 34281-49-7; **1h**, 34281-50-0.

Acknowledgments.—The authors are indebted to Dr. G. C. Levy and J. D. Cargioli for their assistance in interpreting the ^{13}C nmr spectra.

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(7) Analogous behavior of the *p*-phenyl substituent has been noted before in another kind of correlation: M. M. Bursey and F. W. McLafferty, *J. Amer. Chem. Soc.*, **88**, 529 (1966).

Deuterium and Sulfur-34 Isotope Effects in the Thermal Decomposition of Some Cyclic Sulfones

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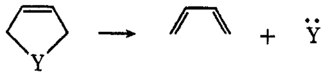
The k_H/k_D ratios in the decomposition of 2,5-dihydrothiophene-*2,2,5,5*-d_4 1,1-dioxide (II) at 120° and 2,4-dimethyl-2,5-dihydrothiophene-*5,5*-d_2 1,1-dioxide (IV) at 105° have been determined in the melt to be 1.094 ± 0.014 and 1.054 ± 0.019, respectively. The sulfur-34 isotope effect in the decomposition of the undeuterated analog of II has also been measured in the melt and in the diethylene glycol diethyl ether solution and $^{32}k/^{34}k$ ratio found to be 1.009 at 99.5°. Both deuterium and sulfur-34 isotope effects can well be accommodated by a concerted mechanism. The deuterium isotope effects are unusually small (about 3.3% per atom D extrapolated to room temperature). Possible explanations of this observation are mentioned.

The mechanism of addition of sulfur dioxide to conjugated acyclic dienes and the retro reaction, the thermal decomposition of cyclic sulfones, has been extensively studied. The two-step mechanism involving dipolar or diradical intermediates has been suggested mainly in earlier work,[1-5] though a concerted mechanism taking place in disrotatory manner has been also proposed.[6]

Woodward and Hoffman[7] predicted on the basis of orbital symmetry arguments that the concerted five-membered ring thermal fragmentation of the type

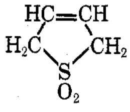


(Y can be SO$_2$, CO, NH, $\overset{+}{N}=\overset{-}{N}$, N–N=O) should be a disrotatory process. Experimental support for this prediction has been presented.[8,9] On the other hand, the photochemical SO$_2$ extrusion from sulfones occurs by concerted fragmentation[10] in a conrotatory manner, as also predicted by Woodward–Hoffman rules.[7]

We studied the effect of deuteration on the rate of thermal decomposition of sulfolene I (II) and its 2,4-dimethyl analog III (IV). The kinetic sulfur-34 isotope effect in the reaction of I has also been measured. The intent of this work was to gain additional information about the mechanism of these reactions with respect to the timing of the bond-breaking processes and the structure of the transition state.

Results

The kinetics of the thermal decomposition of I were previously studied.[2] We determined energy of activation, frequency factor, and entropy of activation as 33.2 kcal mol^{-1}, 7.1 × 10^{14} sec^{-1}, and 7.0 eu, which is in good agreement with published data (33.6 kcal mol^{-1}, 7.0 × 10^{14} sec^{-1}, and 8.9 eu).[2a,b] Using the sealed tube technique for the kinetic measurements, the rates of decomposition of I, of its tetradeuterated analog II, of 2,4-dimethyl-2,5-dihydrothiophene 1,1-dioxide (III) and of its deuterated analog IV, were determined.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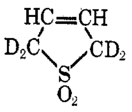
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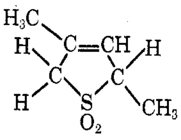
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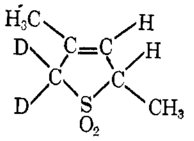
IV

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(1) L. R. Drake, S. C. Stowe, and A. M. Partansky, *J. Amer. Chem. Soc.*, **68**, 2521 (1946).

(2) (a) O. Grummitt, A. E. Ardis, and J. Fick, *ibid.*, **72**, 5167 (1950); (b) O. Grummitt and H. Leaver, *ibid.*, **74**, 1595 (1952); (c) O. Grummitt and J. Splitter, *ibid.*, **74**, 3924 (1952); (d) O. Grummitt and A. L. Endrey, *ibid.*, **82**, 3614 (1960).

(3) R. C. Krug and J. A. Rignay, *J. Org. Chem.*, **27**, 1305 (1962).

(4) (a) L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Amer. Chem. Soc.*, **86**, 622 (1964); (b) P. D. Bartlett, G. E. H. Wallbillick, and L. K. Montgomery, *J. Org. Chem.*, **32**, 290 (1967).

(5) T. J. Wallace, J. E. Hofmann, and A. Schriesheim, *J. Amer. Chem. Soc.*, **85**, 2739 (1963).

(6) W. L. Bailey and E. W. Cummins, *ibid.*, **76**, 1936, 1940 (1954).

(7) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965); R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965).

(8) (a) W. L. Mock, *ibid.*, **88**, 2857 (1966); (b) W. L. Mock, *ibid.*, **92**, 7610 (1970).

(9) D. McGregor and D. M. Lemal, *ibid.*, **88**, 2858 (1966).

(10) J. Saltiel and L. Metts, *ibid.*, **89**, 2232 (1967).

TABLE I

A TYPICAL KINETIC RUN. RATE OF DECOMPOSITION OF 2,5-DIHYDROTHIOPHENE 1,1-DIOXIDE AT 120 ± 0.15° [a]

Time, sec	HCl, ml	% Completion	$k \times 10^4$, sec^{-1}
0	27.62	0	
600	25.22	12.4	2.21
900	24.20	17.7	2.16
1200	22.98	24.0	2.30
1500	22.28	27.7	2.17
1800	21.38	32.4	2.18
2100	20.45	37.2	2.22
2400	19.62	41.5	2.24
3000	18.28	48.5	2.21
3600	17.32	53.3	2.13
4800	15.20	64.6	2.16
7200	12.64	77.8	2.10
24 hr	8.37	99.0	

$k_{av} = 2.19 \pm 0.05$[b]

[a] The sealed tubes containing 0.0004 mol of the sulfone were broken and 15 ml of 0.0756 *M* NaOH was added. The excess of the base was titrated with 0.00411 *M* HCl. [b] Standard deviation of the mean.

Table I shows the results of a typical kinetic run (see Experimental Section).

Table II summarizes the results.

The rates of decomposition of compounds I and II were also measured in 1-butanol. At 116° k_H for I was found to be $(1.34 \pm 0.02) \times 10^{-4}$, and k_D for II $(1.18 \pm 0.04) \times 10^{-4}$ sec^{-1} (uncertainties are standard deviation of the mean of seven kinetic measurements). The rate in 1-butanol is only slightly lower (for about 10%) than the rate in the melt, suggesting that the mechanism is unchanged. The deuterium isotope effect was found to be 13.6 ± 4.7%, which is not significantly different from the value obtained in the melt (9.4 ± 1.4%).

The sulfur-34 isotope effect in the decomposition of I was also determined. The reaction was carried out either in the melt or in diethylene glycol diethyl ether solution at 95.5°. One of the authors found that the isotope effect in the melt was 0.74 ± 0.19% (corrected for ^{18}O, 0.81%) and in diethylene glycol diethyl ether 0.81 ± 0.23% (corrected 0.89%). Another author, using a different mass spectrometer, determined the isotope effect in the melt as 0.90 ± 0.19% (corrected 0.97%). It can be concluded that the ^{34}S isotope effect is about 0.9%.

The maximum isotope effect for breaking a C–S bond can be calculated from Bigeleisen theory.[11] Assuming a C–S stretching frequency[12] of 700 cm^{-1}, the maximum isotope effect for decomposition of the hypothetical C–S molecule was calculated to be 1.28% at 99.5°.

Discussion

Experimental evidence[8,9] indicates that the thermally induced extrusion of sulfur dioxide from sulfolene is a concerted, disrotatory process. The orbital symmetry consideration[7] predicts that this concerted process is disrotatory. Our results can also be best accommodated by this reaction mechanism. Thus, the magnitude of rate deceleration brought about by two deuteriums in IV (5.4 ± 1.9%) is just about half of that for four deuteriums as measured with II (9.4 ± 1.4%). These results indicate that both carbons bound to sulfur in compounds I–IV are probably involved in the reaction transition state in a similar manner, which is in accord with a concerted mechanism. It should be pointed out that essentially the same experimental method has been used by Seltzer[13] in the study of the retrograde Diels–Alder reaction. Although the possibility of a two-step mechanism cannot be excluded on grounds of our results alone, the interpretation of the observed isotope effects in these terms is difficult.

Thus, if such a mechanism were operative, the attachment of a methyl group to one of the carbons bound to sulfur, as in III and IV, would be expected to result in the preferential prior cleavage of that C–S bond which gives rise to a secondary allyl radical. If this first step is rate determining, then the isotope effect observed with IV could be explained in terms of hyperconjugative electron release from the CD bonding orbitals to the neighboring allyl radical. Indeed, small secondary β-deuterium isotope effects have been observed in free radical reactions.[14] However, there is no evidence in the literature that such effects are transmitted through double bonds. Moreover, such β effects are significantly smaller than the corresponding α effects and could be expected to be further reduced if transmitted from a vinylogous position. Therefore it is difficult, if not impossible, to explain in terms of this mechanism the fact that the isotope effect observed with IV is just about one-half of that observed with II. Alternatively, a two-step mechanism with the second step rate determining can be considered. In this case the observed rate constant would be the product of the first step equilibrium constant times the second step rate constant. Ignoring the mentioned vinylogous β-deuterium effect, the observed isotope effect with IV is then due only to the kinetic α effect on the second step, while with II it is due to the product of α isotope effects on the first step equilibrium constant times that on the second step rate constant. If such were the case, the isotope effect with II could be expected to be larger than twice that measured with IV. Hyperconjugative electron release from CD bonds, if operative, would influence the reaction of II and IV in a similar manner and would therefore not change the above expectation.

The secondary deuterium isotope effect found in this work, which in case of a concerted mechanism can be considered as analogous to α effects in solvolyses reactions,[15] is surprisingly small (2.4% per deuterium atom at 120°). Using the equation $\ln (k_H/k_D)_{T_1} = T_2/T_1 \ln (k_H/k_D)_{T_2}$, the isotope effect per deuterium atom at 20° was calculated to be 3.3%, which is much less than usually observed.[16] There is ample evidence in the

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[11] J. Bigeleisen and M. G. Mayer, *J. Chem. Phys.*, **15**, 261 (1947); J. Bigeleisen, *ibid.*, **17**, 675 (1949).

[12] W. O. George, R. C. W. Goodman, and J. H. S. Green, *Spectrochim. Acta*, **22**, 1749 (1966).

[13] (a) S. Seltzer, *J. Amer. Chem. Soc.*, **83**, 1861 (1961); (b) *Tetrahedron Lett.*, 457 (1962); (c) *J. Amer. Chem. Soc.*, **85**, 1360 (1963); (d) *ibid.*, **87**, 1534 (1965); (e) *ibid.*, **85**, 14 (1963).

[14] S. Seltzer and E. J. Hamilton, Jr., *J. Amer. Chem. Soc.*, **88**, 3775 (1966); T. Koenig and R. Wolf, *ibid.*, **89**, 2948 (1967); **91**, 2574 (1969).

[15] W. H. Saunders, Jr., S. Ašperger, and D. H. Edison, *ibid.*, **80**, 2421 (1958); K. Mislow, S. Borčić, and V. Prelog, *Helv. Chim. Acta*, **40**, 2477 (1957); A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Amer. Chem. Soc.*, **80**, 2326 (1958).

[16] A. Streitwieser, Jr., "Solvolytic Displacement Reaction," McGraw-Hill, New York, N. Y., 1962, p 173.

TABLE II

RATES OF THERMAL DECOMPOSITION OF COMPOUNDS I–IV

Compd	Atoms of D per molecule	Temp, °C	$k_H \times 10^4$, sec^{-1}	$k_D \times 10^4$, sec^{-1}	k_H/k_D
I	None	120 ± 0.15	2.21 ± 0.02[a]		
II	3.88	120 ± 0.15		2.02 ± 0.01[a]	1.094 ± 0.014
III	None	105 ± 0.10	3.34 ± 0.04[a]		
IV	1.95	105 ± 0.10		3.17 ± 0.02[a]	1.054 ± 0.019

[a] Standard deviation of the mean of five kinetic measurements.

literature[13e,17] that the magnitude of the α effect is correlated to the amount of bond breaking between the deuterated reaction center and the "leaving group" in the reaction transition state. Consequently, an obvious explanation of the observed reduced α effects would be that the reaction transition state is reactant-(sulfolene) like, with little C–S bond stretching. In this respect the measured primary sulfur-34 isotope effect is of interest. Unfortunately, the observed effect of 0.9% can give us only limited information on the extent of C–S bonds weakening in the transition state, since the maximum isotope effect for simultaneous breaking of both C–S bonds is not known.

The experimental value can only be compared with the maximum effect (1.3%) calculated for complete bond cleavage in a hypothetical C–S molecule, which is not a good model for the reaction studied.

It should be noticed that the sulfur-34 isotope effect in the elimination reaction of 2-phenylethyldimethylsulfonium ion with lyate ion[18] and the nitrogen-15 isotope effect in the elimination from the corresponding ammonium ion[19] are roughly $^1/_3$ of the maximum isotope effect for breaking a hypothetical C–S and C–N molecule, respectively. The corresponding α-deuterium isotope effect in ammonium salt is less than 2% per deuterium atom both in aqueous and ethanolic solutions.[20,21]

There are several other factors which, acting singly or in concert, could be responsible for the low α effects observed. Thus, the neighboring SO_2 dipole could influence the C–H (D) vibrational frequencies in sulfolenes, an inductive effect which would be operative in the ground state and largely lost in the transition state.[22] Another possible explanation seems to be in terms of steric hindrance of the C–H (D) bending frequencies.[24] Further, from the proposed geometry of the transition state[8,9] it appears that the reaction coordinate is not associated with a particular vibrational mode but with a combination thereof, which makes the evaluation of expected isotope effects difficult.

At present, it is not possible to make a clear-cut decision about the relative contribution of all these factors to the composite isotope effect observed.

Experimental Section

Materials.—**2,5-Dihydrothiophene 1,1-dioxide** (I) (Fluka) was purified by several recrystallizations from ethanol–ether solution, mp 63–64°.

2,5-Dihydrothiophene-*2,2,5,5-d*$_4$ 1,1-dioxide (II) was prepared according to the literature.[25] Nmr analysis showed 3.88 deuterium atoms per molecule.

2,4-Dimethyl-2,5-dihydrothiophene 1,1-Dioxide (III).—4-Methyl-1,3-pentadiene was first prepared following the published procedure.[26] The cyclization with SO_2 was carried out according to the literature[27] and 2,5-dihydrothiophene-2,2-dimethyl 1,1-dioxide should have been obtained. Nmr analysis showed that III was obtained in accordance with recent observation.[4b]

Anal. Calcd for $C_6H_{10}SO_2$: C, 49.29; H, 6.89; S, 21.93. Found: C, 49.49; H, 7.00; S, 22.16.

2,4-Dimethyl-2,5-dihydrothiophene-*5,5-d*$_2$ 1,1-dioxide (IV) was prepared by deuteration of the corresponding sulfone according to Cope's procedure.[25]

Kinetics.—The reactions in sealed tubes were carried out with about 0.0004 mol of the sulfone thermostated at 105 ± 0.10° or 120 ± 0.15° (or better) using an electronically controlled oil thermostat. At definite intervals the sealed tubes were cooled with liquid air and broken in excess of aqueous sodium hydroxide. Oxidation with 1% H_2O_2 converted sulfite to sulfate,[28] and the excess of base was titrated with hydrochloric acid.

When the reaction was carried out in the melt, the thermostated reaction vessel was evacuated to a pressure of 0.5 mm, and about 0.003 mol of the sulfone was introduced into the vessel. The vessel was closed and the change in pressure was measured on a mercury manometer.

Kinetic measurements in 1-butanol were carried out with specially dried solvent.[29] Sulfur dioxide was expelled from the reaction solution by a stream of highly pure nitrogen (carefully freed from carbon dioxide). SO_2 was absorbed in aqueous sodium hydroxide of pH 10. At that pH the absorption of SO_2 was complete and the interference of CO_2 from the atmosphere was negligible. The pH was kept constant with a 4 *N* NaOH solution using a pH-Stat.

The first-order rate constants were calculated with a computer using a least squares program.

Mass Spectrometry.—A Nier-type single collector mass spectrometer, produced at the Institute "Jožef Stefan," Ljubljana, Yugoslavia, and a single collector CSF M 500 (French) mass spectrometer were used. SO_2 was expelled from the reaction vessel by a stream of nitrogen, and butadiene was removed with P_2O_5. The low-temperature distillation using liquid air and Dry Ice removed traces of butadiene and carbon dioxide. Samples of SO_2 gas from the reaction carried out to about 2% completion

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[17] V. J. Shiner, Jr., M. W. Rapp, and H. R. Pinnick, Jr., *J. Amer. Chem. Soc.*, **92**, 232 (1970); K. Humski, R. Malojčić, S. Borčić, and D. E. Sunko, *ibid.*, **92**, 6534 (1970); H. G. Bull, K. Koehler, T. C. Pletcher, J. J. Ortiz, and E. H. Cordes, *ibid.*, **93**, 3002 (1971).

[18] W. H. Saunders, Jr., A. F. Cockerill, S. Ašperger, L. Klasinc, and D. Stefanović, *ibid.*, **84**, 848 (1966).

[19] A. N. Bourns and P. J. Smith, *Proc. Chem. Soc.*, 366 (1964).

[20] S. Ašperger, L. Klasinc, and D. Pavlović, *Croat. Chem. Acta*, **36**, 159 (1964).

[21] The α-deuterium effect in sulfonium salt cannot be determined with certainty because of fast α-deuterium exchange: S. Ašperger, N. Ilakovac, and D. Pavlović, *J. Amer. Chem. Soc.*, **83**, 5032 (1961); *Croat. Chem. Acta*, **34**, 7 (1962).

[22] A complete vibrational analysis is available for the dimethyl sulfone molecule.[23] Indeed, in this compound the C–H bending modes occur at lower frequencies than in methyl groups of hydrocarbons, which could cause a lowering of the α-deuterium effect.

[23] W. R. Feairheller, Jr., and J. E. Katon, *Spectrochim. Acta*, **20**, 1099 (1964).

[24] There is evidence of strong steric interactions between substituents at C_2 and C_5 in the transition state. Thus *cis*-2,5-dimethylsulfolene decomposes at a temperature 50[8] to 90°[9] lower than the trans isomer. Such an interaction in sulfolenes I–IV would tend to *increase* the force constants for a bending vibration of the affected C–H (D) bonds. α effects are due to a *decrease* in this particular C–H (D) frequency which becomes an out-of-plane vibration in the sp^2-hybridized product.

[25] A. C. Cope, G. A. Berchthold, and D. L. Ross, *J. Amer. Chem. Soc.*, **83**, 3860 (1961).

[26] G. B. Backmann and Ch. J. Goebel, *ibid.*, **64**, 787 (1942).

[27] G. B. Backmann and R. E. Hatton, *ibid.*, **66**, 1513 (1944).

[28] E. Taylor and H. F. Johnstone, *Ind. Eng. Chem., Anal. Ed.*, **1**, 197 (1929).

[29] A. Vogel, "Practical Organic Chemistry," Longmans, London, 1959, p 168.

and to complete decomposition of the cyclic sulfone, respectively, were collected in a liquid air trap and purified on a vacuum line, and the $^{32}S/^{34}S$ mass ratios were determined as previously described.[30]

Nmr spectra were recorded on a Varian A-60A instrument.

Registry No.—I, 77-79-2; II, 20966-34-1; III, 10033-92-8; IV, 34206-55-8; deuterium, 7440-51-9; sulfur-34 isotope, 13965-97-4.

Acknowledgment.—The authors thank Professor Maurice Kreevoy and Professor Elliot N. Marvell for most helpful discussions. Thanks are due to Dr. J. Popović for help in measuring mass spectra.

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[30] W. H. Saunders, Jr., and S. Ašperger, *J. Amer. Chem. Soc.*, **79**, 1612 (1957).

α-Phenylnitroxide Radicals from α-Phenylnitrones[1]

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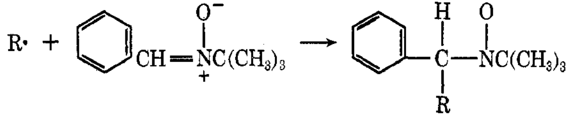
Irradiation of α-phenyl-*N*-*tert*-butylnitrone in benzene in the presence of some organometallic reagents traps short-lived radicals. The nitroxide radical formed is dependent on the amount of oxygen in solution. The inherent quality of α,*N*-diphenylnitrone to lose oxygen on irradiation allows only one of the above type nitroxide radicals. Nitroxide radicals are also formed when the phenylnitrones are irradiated in benzene containing alcohols. This reaction apparently does not proceed *via* the usual trapping mode. The reactions and structures of the nitroxides are discussed.

In a recent study we reported that α-phenylnitrones[2] on irradiation with ultraviolet light gave rise to *N*-benzoylnitroxide radicals.[3] The spin trapping characteristic of α-phenyl-*N*-*tert*-butylnitrone (PBN) has been dealt with in a number of papers.[4] In the spin trapping technique, a reactive free radical adds to PBN to produce a stabler nitroxide radical. The hyperfine splitting constants (hfsc's), from esr measurements, of the α-hydrogen and nitrogen atoms show slight variations with different trapped radicals, R·. This paper describes additional radicals arising from nitrones that we have detected under various conditions.



Results

Nitroxide Radicals from α-Phenyl-*N*-*tert*-butylnitrone.—When we irradiated, with ultraviolet light, benzene solutions of PBN to which organolead and -mercury compounds had been added, the esr signal obtained depended on the degree of deoxygenation of the solution. Incompletely deaerated solutions of PBN in benzene containing dimethylmercury, diethylmercury, triethyllead acetate, tetra-*n*-butyllead, or diphenylmercury yielded radicals whose hfsc's differed from those reported by Janzen and Blackburn,[5,6] but still showed the typical splitting pattern, a triplet of doublets, arising from a sharing of the odd electron between the nitrogen and α-hydrogen atoms. When fresh solutions were completely deaerated and then irradiated, the splitting constants agreed with the values reported. The splitting constants are listed in Table I. In the deoxygenated solutions, the radical which attached to the nitrone system was either a methyl, ethyl, *n*-butyl, or phenyl radical, depending on the radical source.[5,6] The hydrogen and nitrogen coupling constants which arose from incompletely deoxygenated solutions showed very little variation in value, which may indicate that a similar type of reactive species added to the nitrone function. We also observed that, when the totally deoxygenated solutions were irradiated briefly, for about 15 sec, the radicals detected were the ones with smaller hfsc's, shown in Table I. These signals were stable if the solutions were kept in the dark. On further irradiation, about 1–3 min, the nitroxide radicals with larger splitting constants were found. In partially deoxygenated solutions, the nitroxide with larger splitting constants was never observed, even after extended irradiation. Figure 1 shows the changes in the esr spectra during progressive stages of irradiation of a deoxygenated benzene solution of PBN containing diethylmercury. Figure 1b shows the esr signal as a mixture

TABLE I

HYPERFINE SPLITTING CONSTANTS OF NITROXIDES FROM α-PHENYL-*N*-*tert*-BUTYLNITRONE[a]

Radical source	$A^{N\,b}$	$A_\alpha{}^{H\,b}$	$A^{N\,c}$	$A_\alpha{}^{H\,c}$	$A^{N\,d}$	$A_\alpha{}^{H}$
$(CH_3)_2Hg$	13.74	1.99	14.79	3.73	14.82	3.60
$(CH_3CH_2)_2Hg$	13.80	1.97	14.68	3.25	14.62	3.33
$(CH_3CH_2)_3PbOAc$	13.75	1.95	14.54	3.30	14.50	3.35
n-Bu_4Pb	13.65	1.97	14.64	3.21	14.62	3.27
$(C_6H_5)_2Hg$	13.65	1.97	14.47	2.18	14.42	2.21
$(C_6H_5)_3CN{=}NC_6H_5$[e]			14.48	2.17[e]	14.43	2.18

[a] In benzene at room temperature. The splittings are in gauss. [b] Photolysis of incompletely deoxygenated solutions of PBN and radical source. [c] Photolysis of totally dexoygenated solutions of PBN and radical source. [d] Values from Janzen and Blackburn adjusted upwards by 4.4%.[6] [e] By thermal decomposition.

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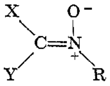
[1] Presented in part at the 9th National Meeting of the Society for Applied Spectroscopy, New Orleans, La., Oct 1970.

[2] In this paper the carbon substituents X and Y are prefixed by α, and the substituent on the nitrogen (R) is prefixed by N.



$XYC{=}\overset{+}{N}(O^-)R$

Hyperfine splitting constants from esr measurements referring to the hydrogen on the carbon atom are designated as $A_\alpha{}^H$.

[3] A. L. Bluhm and J. Weinstein, *J. Amer. Chem. Soc.*, **92**, 1444 (1970).

[4] See E. G. Jantzen, *Accounts Chem. Res.*, **4**, 31 (1971), for a review of spin trapping including the nitrones and references thereto.

[5] E. G. Janzen and B. J. Blackburn, *J. Amer. Chem. Soc.*, **90**, 5909 (1968).

[6] E. G. Janzen and B. J. Blackburn, *ibid.*, **91**, 4481 (1969).