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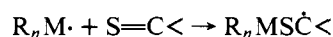
Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. 25. Radicals Formed by Spin Trapping with Di-*tert*-butyl Thioketone¹

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Abstract: A variety of transient $R_nM\cdot$ radicals ($M = C, Si, Sn,$ and P , but not O) have been trapped with di-*tert*-butyl thioketone and the persistent adduct radicals, $R_nMSC(CMe_3)_2$ (**1**), have been examined by EPR spectroscopy. From a comparison of the hyperfine splittings by M in **1** and in $R_nMCH_2C(CMe_3)_2$ and analogous radicals, and from a consideration of the g values for **1** (2.0024–2.0033), it is concluded that the R_nM group eclipses the C_α $2p_z$ orbital. Competitive experiments involving the reaction of *tert*-butyl with thione or oxygen at $-80^\circ C$ and the reaction of methyl with thione or Me_3CNO at $-40^\circ C$ indicate that alkyl addition to the thione has a rate constant of ca. $10^6 M^{-1} s^{-1}$ at these temperatures. The $CH_3SC(CMe_3)_2$ radical exists in equilibrium with a dimer at temperatures in the range -70 to $-110^\circ C$: $\Delta H = 9.6 \pm 1.5$ kcal/mol; $\Delta S = 32 \pm 3$ gibbs/mol. Above $-50^\circ C$ the $CH_3SC(CMe_3)_2$ radical decays with the first-order kinetics. It is concluded that $CH_3SC(CMe_3)_2$ and $SiH_3SC(CMe_3)_2$ decay by an intramolecular transfer of H from M to C_α . The $CF_3SC(CMe_3)_2$ radical is extremely persistent. The $(n-Bu)_3SnSC(CMe_3)_2$ radical decays with second-order kinetics. Arrhenius parameters for some of the decay reactions are reported.

The carbon-sulfur double bond in thioketones is known to be a fairly good trap for carbon-centered³⁻⁷ and sulfur-centered⁶ free radicals.



This reaction appears to be important during the photolysis of thioketones in solutions containing good hydrogen donors, R_nMH .^{5,6} The EPR spectra of a few R_nMSCAr_2 radicals obtained by the addition of carbon-centered radicals to thiobenzophenones have been reported.^{5,6} Similar radicals have been produced by the reaction of simple alkyl Grignards (e.g., $MeMgBr$) with thiobenzophenone,⁸ thiopivalophenone,^{9a} 22,5,5-tetramethylcyclopentanethione,^{9b} and thiofenchone.^{9b} However, no detailed EPR spectroscopic study of carbon-centered or heteroatom-centered radical additions to dialkyl thioketones has yet been undertaken. For this reason, we have examined the reactions of a variety of transient radicals with di-*tert*-butyl thioketone. The adduct radicals produced, $R_nMSC(CMe_3)_2$ (**1**), were generally quite persistent and gave excellent EPR spectra as we would expect from our earlier work on spin trapping with 1,1-di-*tert*-butylethylene¹⁰⁻¹² and di-*tert*-butylketimine.¹³ We conclude from the EPR parameters of a variety of the adduct radicals that the R_nM group is in the eclipsed position with respect to the C_α $2p_z$ orbital. We have also measured the rate of trapping of transient carbon-centered radicals by this thione using competitive techniques and have studied the kinetics of decay of several **1**. A few experiments were also carried out with thiobenzophenone and adamantaneethione.

Experimental Section

Di-*tert*-butyl thioketone was prepared from di-*tert*-butylketimine by reaction first with methyllithium and then with carbon disulfide according to the method of Barton et al.¹⁴ It was purified by vacuum distillation and was stored under argon at $-20^\circ C$. Fortunately, the extinction coefficients of this thione (viz., λ_{max} 531 nm, ϵ 6.45 $cm^{-1} M^{-1}$; no other maxima until $\lambda < 275$ nm; at 313 nm, ϵ 13.46) are low enough to allow the transient $R_nM\cdot$ radicals to be generated photochemically in its presence. The radicals were generated directly in the cavity of a Varian E-4 EPR spectrometer by previously described procedures.¹¹⁻¹³

Thiobenzophenone¹⁵ was prepared by reaction of benzophenone with gaseous H_2S and HCl . Adamantaneethione was prepared by the method of Greidanus¹⁶ from adamantaneone and P_2S_5 .

Results and Discussion

1. EPR Spectra. The EPR spectral parameters for the di-*tert*-butyl thioketone spin adducts are listed in Table I. Most of these radicals were quite persistent (see below) and their spectra were therefore sufficiently intense (see e.g., Figures 1, 2, 3, and 4) to observe splitting by magnetic nuclei in low natural abundance, e.g., ^{13}C , ^{29}Si , ^{119}Sn , ^{117}Sn , and even ^{33}S .

For any particular R_nM group, the hyperfine splittings by H_γ , $^{13}C_\alpha$, $^{13}C_\gamma$, and particularly M (see Table II) in the $R_nMSC(CMe_3)_2$ radicals are very similar to the splittings found for the additions of the same $R_nM\cdot$ to di-*tert*-butylethylene,¹² i.e., **2**, and to di-*tert*-butylvinylidenetetramethylcyclopropane,¹⁷ i.e., **3**. Since all **2** and **3** have the R_nM group in the eclipsed position with respect to the C_α $2p_z$ orbital we conclude that all **1** adopt the same eclipsed conformation.

Table I. EPR Parameters for $R_n\text{MSC}(\text{CMe}_3)_2$ Radicals (Hyperfine Splittings are Given in Gauss)^a

$R_n\text{M}$	g	$a^{13\text{C}_\alpha}$	$a^{33\text{S}_\beta}$	$a^{13\text{C}_\gamma}$	a^{M_γ}	a^{H_δ}	a^{R_δ}
H_3C	2.0027	45.3	8.2 ^b	9.6	23.5	0.51	<i>c, d</i>
$(\text{CH}_3)_3\text{C}$	2.0026	44.3	<i>c</i>	9.3	20.1	0.57 ^e	0.19 ^f
F_3C	2.0024	43.9	<i>c</i>	9.4	38.6	0.52	3.9
H_3Si	2.0029	50.0	<i>c</i>	<i>c</i>	33.0	0.34 ^g	<i>c</i>
$(\text{CH}_3)_3\text{Si}$	2.0033	49.7	<i>c</i>	9.2	23.5	0.36 ^h	0.12 ^f
$(n\text{-Bu})_3\text{Si}$	2.0033	47.6	<i>c</i>	9.4	<i>c</i>	0.48	<i>c</i>
$(\text{CH}_3)_3\text{Sn}$	2.0028	47.2	10.4	8.9	243.3 ^{i-k} 254.5 ^{j-l}	0.49 ^m	0.16 ^f
$(n\text{-Bu})_3\text{Sn}$	2.0028	48.7	<i>c</i>	8.8	197.4 ^{i-k} 209.9 ^{j-l}	<i>c</i>	<i>c</i>
$(\text{EtO})_2\text{P}=\text{O}^n$	2.0026	<i>c</i>	<i>c</i>	9.5	101.0 ^j	0.45	<i>c</i>

^a Hfsc's are essentially independent of temperature unless otherwise noted. Spectra were recorded at temperatures of -20 to 25 °C, except for the H_3Si adduct which was recorded at -50 °C. Positions are designated as in the following example: $\text{R}_\delta\text{M}_\gamma\text{S}_\beta\text{C}_\alpha[\text{C}_\beta(\text{C}_\gamma\text{H}_\delta)]$. ^b ± 0.4 G. The ^{33}S $m = \pm 3/2$ lines overlap with the $\text{M} (= ^{13}\text{C})$ lines. The ^{33}S hfsc was determined from the relative intensities of the hyperfine splitting pattern in this region of the spectrum. ^c Not resolved. ^d Probably ≤ 0.05 G. The spectra for the CH_3 and CD_3 adducts were identical except for the line widths which were 0.15 and 0.11 G, respectively, at -17 °C. This result implies that the large splittings (1.0 to 1.22 G) reported for the CH_3 protons in the methyl adducts and CH_2 protons in the ethyl adducts to thiopivalophenone, 2,2,5,5-tetramethylcyclopentanethione, and thiofenchone (ref 9b) are in error. ^e At all temperatures the line spacing is ca. 0.19 and we presume a^{H_δ} has about three times this value. At 20 °C the hfs pattern of lines forms a single smooth envelope, but at -60 °C the lines break into groups of four with a spacing between groups of ca. 0.85 G. This is probably due to hindered rotation about the $\text{S}-\text{CMe}_3$ bond. ^f Due to the protons in R. ^g Observed hfsc's for H_3Si and D_3Si adducts. ^h By comparison of the $(\text{CH}_3)_3\text{Si}$ and $(\text{CD}_3)_3\text{Si}$ adducts. ⁱ 117 Sn. ^j Corrected using the Breit-Rabi equation. ^k Measured at -30 °C. This hfsc has a temperature coefficient of ca. $+58$ mG/°C over a temperature range from -60 to 25 °C. ^l 119 Sn. ^m The line spacing is 0.162 and we presume a^{H_δ} has about three times this value (see Figure 3). ⁿ Under continuous irradiation at 25 °C there is a second ^{31}P containing radical ($a^{\text{P}} = 113$ G) present in about 6% of the concentration of the main adduct. This radical is absent at low temperatures (≤ 0 °C) where the main adduct is persistent and so is observed without continuous photolysis.

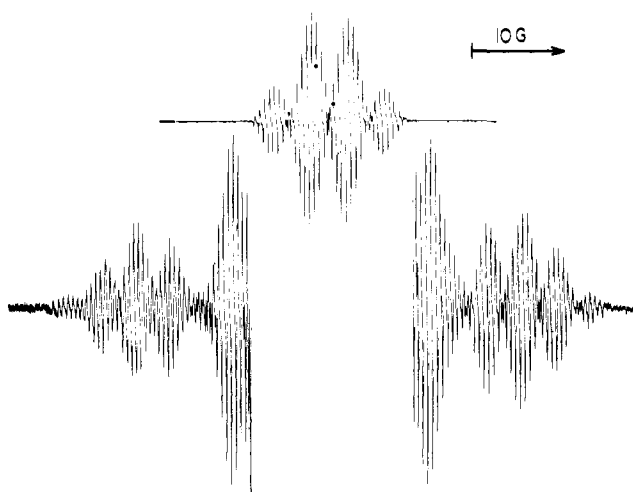


Figure 1. EPR spectrum of $\text{F}_3\text{CSC}(\text{CMe}_3)_2$ recorded at -10 °C with a modulation amplitude of 0.12 G and with the light shut off after a brief irradiation of CF_3I , $(n\text{-Bu})_3\text{SnSn}(n\text{-Bu})_3$, and $(\text{Me}_3\text{C})_2\text{C}=\text{S}$ in cyclopentane. The side lines are due to ^{13}C in natural abundance. They were recorded at 125 times the gain used for the central lines.

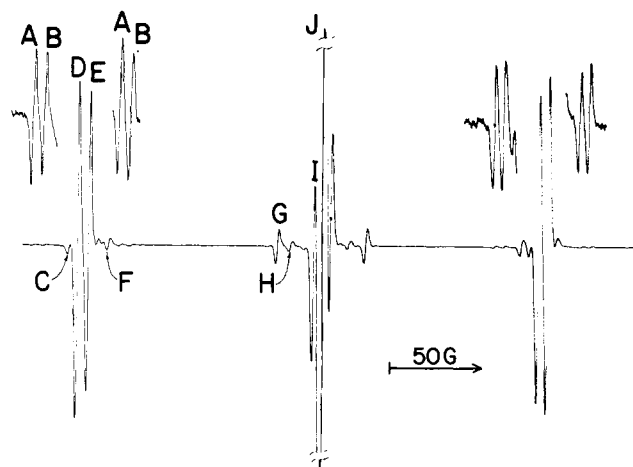
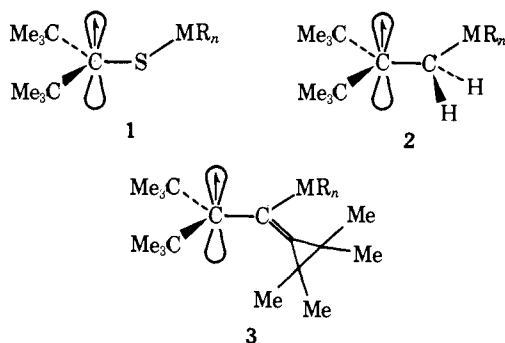


Figure 2. EPR spectrum of $\text{Me}_3\text{SnSC}(\text{CMe}_3)_2$ recorded at -30 °C with a modulation amplitude of 1.25 and with the light shut off after a brief irradiation of $\text{Me}_3\text{SnSnMe}_3$ and $(\text{Me}_3\text{C})_2\text{C}=\text{S}$ in cyclopentane. A and B are the $^{13}\text{C}_\alpha$ side lines of the ^{119}Sn (D) and ^{117}Sn (E) satellites, respectively. They were recorded at 75 times the gain used for the other lines. C is the $^{13}\text{C}_\gamma$ side line of the ^{119}Sn (D) satellite. D is the ^{119}Sn and E is the ^{117}Sn satellite of the central line (J). F is due to an impurity. G is the $^{13}\text{C}_\alpha$ satellite of J. The $^{13}\text{C}_\gamma$ side lines of G are also visible. H is the ^{33}S satellite and I is the $^{13}\text{C}_\gamma$ satellite of the central line J.



The a^{M} values in **3** are always $67 \pm 5\%$ of the a^{M} values in **2**.¹⁷ This has been attributed¹⁷ to the greater $\text{C}_\alpha\text{-M}$ distance and the greater $\text{C}_\alpha\text{-C}_\beta\text{-M}$ angle in **3**. Except for $\text{M} = \text{Si}$, the

a^{M} values in **1** are more comparable to those found in **2** than in **3** (see Table II). We presume that the potential reduction in a^{M} consequent upon the larger size of sulfur compared with carbon is largely off-set by smaller C_αSM angles¹⁸ in **1** than the $\text{C}_\alpha\text{-C}_\beta\text{-M}$ angles in **2**.

The majority of alkylthiylalkyl radicals previously reported have g values in the range 2.0044–2.0049.^{19–23} The g values for the $R_n\text{MSC}(\text{CMe}_3)_2$ radicals are much lower, most being of similar magnitude to the g factors of alkyl radicals having only carbon or hydrogen in the β position (viz.,¹⁹ 2.0025–2.0027). These low g values provide additional evidence that $R_n\text{MSC}(\text{CMe}_3)_2$ radicals adopt conformation **1**. Thus, unhindered alkylthiylalkyl radicals adopt a conformation, **4**, in

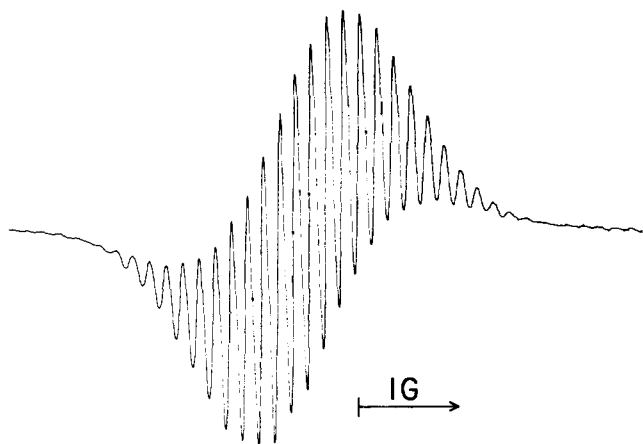


Figure 3. The central line (J) of $(\text{CH}_3)_3\text{SnSC}(\text{CMe}_3)_2$ recorded at -30°C with a modulation amplitude of 0.02 G.

Table II. Hyperfine Splittings by M in **1**, **2**, and **3**

R_nM	a^M, G		
	1	2 ^a	3 ^b
H_3C	23.5	(22.0) ^c	(18) ^d
F_3C	38.6	30.1	
Me_3Si	23.5	35.0	23.9
$(\text{EtO})_2\text{P}=\text{O}$	101.0	109.4	75.9

^a Reference 12. ^b Reference 17. ^c Twice the γ -carbon coupling in $(\text{Me}_3\text{C})_3\text{C}\cdot$. ^d 1,1-Di-*tert*-butyl-2-methylallyl (H. Regenstein and A. Berndt, *Angew. Chem., Int. Ed. Engl.*, **13**, 145 (1974)).

which the S-MR_n bond is in the C_α 2p_z nodal plane because the unpaired electron is delocalized onto the sulfur, i.e., $\text{>C}\cdot\text{-}\ddot{\text{S}}\leftrightarrow\text{>C}^-\text{-}\ddot{\text{S}}^+$.²⁴ With increasing steric hindrance the R_nM group is increasingly forced out of the nodal plane. Gilbert, Larkin, and Norman²² have shown that this produces a decrease in the *g* factor. Thus, for the series H₂CSR, H(Me)CSR, and Me₂CSR, with R = CH₂CH₂OH, the *g* values are 2.0048, 2.0044, and 2.0037, respectively.²² These workers point out that as the coplanar conformation, **4**, becomes disfavored there is less effective conjugation between C_α and S which causes a reduction in the spin density at sulfur and "in turn, the spin-withdrawing parameter for the sulfur substituent would fall, the *g*-factor would be reduced (tending ultimately to the value for a hydrocarbon-like radical). . . ." It would seem that R_nMSC(CMe₃)₂ radicals have reached the limit prophesied by Gilbert et al. and that the R_nM group is indeed perpendicular to the nodal plane.²⁵

The R_nMSC(CMe₃)₂ radicals probably have a negative spin density at the sulfur since, in conformation **1**, spin can reach this atom more easily by spin polarization than by conjugative electron delocalization. The reverse situation obtains in alkylthiylalkyl radicals that adopt conformation **4** and so such radicals will have ³³S_β hfsc's more positive than ca. -8 G. We are not aware of any previous measurements of ³³S_β hfsc's in monoalkylthiylalkyl radicals,²⁹ but note that (c-C₆H₁₁S)₃C and (Me₃CS)₂C $\dot{\text{M}}$ have ³³S hfsc's of 3.8 G³⁰ and <5.0 G,³¹ respectively.

Since the S-M bond in **1** will be longer than the C_β-M bond in **2**, the R_nM group should be less rigidly held in the former class of radicals. This relative freedom of motion of R_nM in **1** serves to explain certain differences in the epr spectra of the two types of radical. For example, addition of C₆F₅· to the ethylene gives a radical with a large ¹⁹F hfsc (17.6 G) due to a single ortho fluorine.^{12,32} The C₆F₅ ring must therefore be

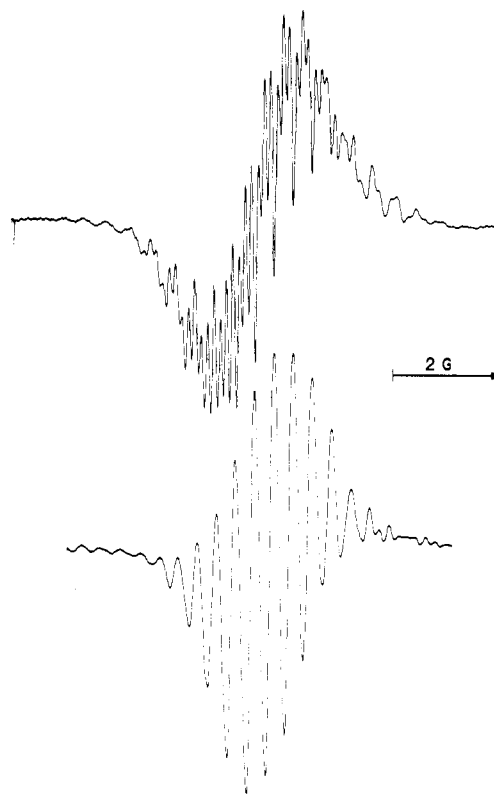
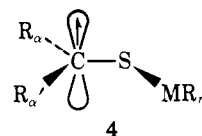


Figure 4. Top spectrum: Central line of $(\text{CH}_3)_3\text{SiSC}(\text{CMe}_3)_2$ recorded at -40°C with a modulation amplitude of 0.05 G. Bottom spectrum: Same with $(\text{CD}_3)_3\text{SiSC}(\text{CMe}_3)_2$.

held with one edge pointing toward the α carbon. Addition of C₆F₅· to the thione gave a complex multiplet (overall width ca. 8 G, *g* = 2.0032) with overlapping lines from a second radical which prevented its unequivocal identification. However, there was certainly no large coupling by a single fluorine.

As a second example, the majority of a^M values in **1** and **2** are essentially temperature independent. However, ¹¹⁷Sn and ¹¹⁹Sn hfsc's in **1** increase with increasing temperature (footnote *j*, Table I). If increasing the temperature produced a significant increase in the amplitude of rocking of the R₃Sn groups about the C_α-S bond the Sn hfsc's would decrease. (In conformation **4** the Sn hfsc would be very small.) We are therefore forced to



conclude that with R₃SnSC(CMe₃)₂ radicals raising the temperature promotes bending about the C_α-S-Sn angle to a greater extent than it promotes rocking about the C_α-S bond. That is, increased bending will bring the C_α and Sn closer together, and so it will increase the Sn hfsc. For other M (all of which are much smaller atoms than tin) the effect of temperature on the amplitudes of the bending and rocking motions would appear to cancel out one another in so far as a^M values are concerned. In this connection, it is worth noting that a high sensitivity of the Sn hfsc to the C_α-S-Sn angle is implied by their magnitudes for the Me₃Sn adduct (e.g., ¹¹⁷Sn = 243.3 G) and for the (*n*-Bu)₃Sn adduct (¹¹⁷Sn = 197.4 G). The latter adduct, having the more bulky R_nM group, is expected to have the larger C_α-S-Sn angle and hence the lower Sn hfsc.

A few other points relating to spin trapping with di-*tert*-butyl thioketone are worth noting. In an attempt to add CF₃S radicals, by photolyzing CF₃SSCF₃, we obtained a spectrum identical with that for CF₃ radical addition (from CF₃I and

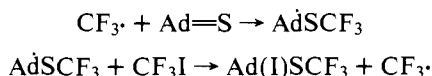
$\text{Me}_3\text{SnSnMe}_3$). Clearly, photolysis of this disulfide must give some C-S cleavage in addition to the usual S-S cleavage.³³ Since there is independent evidence^{6,34} that alkylthiyl radicals can add to thiones, we conclude that the addition of CF_3S is either much slower than the addition of CF_3 and/or that the CF_3S adduct is much less persistent than the CF_3 adduct.

We were not successful in adding $\text{Me}_3\text{CO}\cdot$ or $\text{CF}_3\text{O}\cdot$ radicals to di-*tert*-butyl thioketone. This spin trap therefore exhibits the unique ability to trap carbon-centered but not oxygen-centered radicals.

Although $\text{Cl}_3\text{C}\cdot$ did appear to add to the thioketone the spectrum obtained was too weak and complex for unequivocal identification. The $\text{Cl}_3\text{Si}\cdot$ radical did not add to the thioke-

tone. An attempt to generate **1** with $\text{R}_n\text{M} = \text{Et}_2\text{B}$ by a homolytic substitution at boron by thione in its triplet state was also unsuccessful.³⁵ Irradiation of the long wavelength band of the thione in the presence of Et_3B gave a weak EPR spectrum (multiplet, $a \sim 0.51$ G) in which no coupling by boron-11 could be identified.

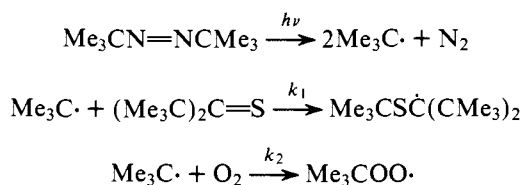
A few experiments with thiobenzophenone and adamantanethione showed that although these compounds could act as spin traps the EPR spectra of the adducts were never as intense nor as informative as those obtained with di-*tert*-butyl thioketone. For example, $\text{Ph}_2\text{C}=\text{S}$ appeared to trap $(n\text{-Bu})_3\text{Si}\cdot$ radicals but only coupling to the ring protons could be observed ($a^{\text{ortho}} = 2.86$, $a^{\text{meta}} = 1.26$, $a^{\text{para}} = 3.15$ G at 60 °C in *n*-pentane). One problem with this thione is its strong absorption of light at the wavelengths used to generate $\text{R}_n\text{M}\cdot$ radicals. Although this is not a problem with adamantanethione, there were other difficulties. For example, the addition of $\text{CF}_3\cdot$, generated from the iodide, gave a very complex spectrum and the thione was very rapidly consumed, presumably via the chain sequence:



Even with $(\text{EtO})_2\text{P}(\text{=O})\text{SAd}$ the only coupling that could be identified was that due to the phosphorus, $a^{\text{P}} = 60$ G at -50 °C.

2. Rates of Spin Trapping. Competitive methods were used to estimate the rates of spin trapping of two carbon-centered radicals by di-*tert*-butyl thioketone.

(a) Competition with Oxygen. Irradiation in the EPR spectrometer of an air saturated, isooctane solution of $(\text{Me}_3\text{C})_2\text{C}=\text{S}$ and $\text{Me}_3\text{CN}=\text{NCMe}_3$ at -80 °C gave detectable concentrations of both the $\text{Me}_3\text{CSC}(\text{CMe}_3)_2$ radical and the $\text{Me}_3\text{COO}\cdot$ radical.

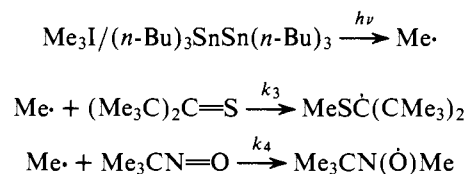


The $\text{Me}_3\text{CSC}(\text{CMe}_3)_2$ radical is persistent under these conditions³⁶ and so builds-up as the photolysis is continued. The $\text{Me}_3\text{COO}\cdot$ radical is transient and rapidly reaches a steady concentration. The desired rate constant, k_1 , can be obtained from the concentrations of the two radicals at a given time, t , after the initiation of photolysis, provided allowance is made for the $\text{Me}_3\text{COO}\cdot$ radicals that have decayed in this period. That is,

$$k_1 = \frac{k_2[\text{Me}_3\text{CSC}(\text{CMe}_3)_2]_t[\text{O}_2]}{\left(-\frac{\partial[\text{Me}_3\text{COO}\cdot]}{\partial t}\right)_t[(\text{Me}_3\text{C})_2\text{C}=\text{S}]}$$

where $(-\partial[\text{Me}_3\text{COO}\cdot]/\partial t)$ is the rate of decay of the *tert*-butylperoxy radicals which was determined by chopping the light using the usual^{1,11,17} kinetic EPR technique. The half-life for the peroxy radicals was ca. 0.25 s at $(\text{Me}_3\text{C})_2\text{C}=\text{S}$ concentrations of ca. 0.08 M. Taking $[\text{O}_2]^{-80^\circ\text{C}} = 4.8 \times 10^{-3}$ M³⁷ and assuming that $k_2^{-80^\circ\text{C}} = 10^9 \text{ M}^{-1} \text{ s}^{-1}$ gave $k_1^{-80^\circ\text{C}} = (1.3 \pm 0.6) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ (from three independent series of measurements at thione concentrations in the range 0.05 to 0.11 M).

(b) Competition with 2-Methyl-2-nitrosopropane. Photolysis of cyclopentane solutions of $(\text{Me}_3\text{C})_2\text{C}=\text{S}$, Me_3CNO , CH_3I , and $(n\text{-Bu})_3\text{SnSn}(n\text{-Bu})_3$ gave $\text{MeSC}(\text{CMe}_3)_2$ and $\text{Me}_3\text{CN}(\dot{\text{O}})\text{Me}$.



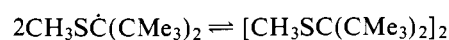
At -40 °C the nitroxide is persistent and the $\text{MeSC}(\text{CMe}_3)_2$ decays rather slowly. The spectrum was overmodulated and the high field line (due only to $\text{Me}_3\text{CN}(\dot{\text{O}})\text{Me}$) and center line (due to both radicals) were recorded immediately before and immediately after a series of 0.2-s flashes of light. Comparison of the rates at which these two lines grew gave $k_3^{-40^\circ\text{C}}/k_4^{-40^\circ\text{C}} \sim 7.5$. Taking $k_4^{-40^\circ\text{C}} \geq 1.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ³⁸ gives $k_3^{-40^\circ\text{C}} \geq 1.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$.

Although both measurements of the rate constants for spin trapping by the thione are very imprecise, they do indicate that this reaction is extremely fast. In fact, the rate constant for trapping unhindered and nonresonance stabilized carbon-centered radicals at ambient temperatures can hardly be less than $10^7 \text{ M}^{-1} \text{ s}^{-1}$. These high rates probably reflect, among other factors, the rather small contribution toward the C-S bond strength in thiones made by the π bond (ca. 40-55 kcal/mol⁴¹ compared with 70-80 kcal/mol for ketones⁴⁵).

3. Decay Kinetics for $\text{R}_n\text{MSC}(\text{CMe}_3)_2$ Radicals. Rates of decay of **1** were easy to measure since the EPR signals are strong and the radicals are all fairly persistent. However, for some **1** the interpretation of the decay rates was not straightforward since decay occurred with noninteger kinetic orders. For example, the order in **1** concentration was ca. 1.2-1.3 for $\text{R}_n\text{M} = (\text{EtO})_2\text{P}=\text{O}$ (from $\text{Me}_3\text{CO}\cdot + (\text{EtO})_2\text{POP}(\text{OEt})_2$) and for $\text{R}_n\text{M} = \text{Me}_3\text{Sn}$ (from $\text{Me}_3\text{SnSnMe}_3$). With $\text{R}_n\text{M} = \text{Me}_3\text{Si}$ (from $\text{Me}_3\text{CO}\cdot + \text{Me}_3\text{SiH}$) the rate of decay depended somewhat on the concentration of the reagents, possibly indicating a radical chain reaction. A chain reaction is also certainly involved for $\text{R}_n\text{M} = (n\text{-Bu})_3\text{Sn}$ when this radical was generated from $(n\text{-Bu})_3\text{SnH}$ since the reagents were very quickly consumed.

Fortunately, for some **1** it was possible to find experimental conditions (e.g., a range of temperatures) where decay occurred with "clean" first- or second-order kinetics when the light was cut-off. The results of these experiments are summarized in Table III. This table lists the kinetic order, half-lives ($\tau_{1/2}$) at 25 °C for those radicals that decay with first-order kinetics, and the Arrhenius parameters for decay.

At temperatures in the range -110 to -70 °C the initial decay of $\text{CH}_3\text{SC}(\text{CMe}_3)_2$ radicals occurred with second-order kinetics, but the radical concentration did not decrease to zero. Instead it reached an equilibrium value which could be increased or decreased reversibly by raising and lowering the temperature. The radical must therefore be in equilibrium with a diamagnetic dimer.⁴⁶



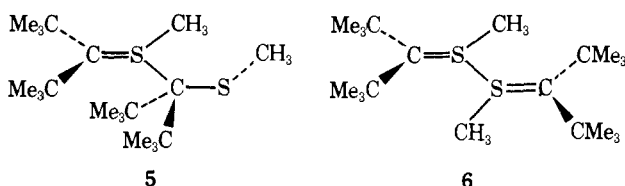
At concentrations of [radical] + 2[dimer] of ca. 10^{-6} M the

Table III. Kinetic Orders and Arrhenius Parameters for the Decay of $R_nM\dot{S}C(CMe_3)_2$ Radicals

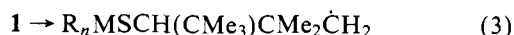
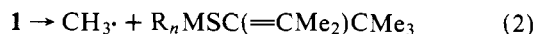
R_nM	Decay kinetics ^a (temp range, °C)	$\tau_{1/2}^{25^\circ C}$, s	Log A^b	E , kcal/mol	Dimer ^c
H_3C^d	1 (-55 to 30)	1	7 ± 2	10 ± 3	Yes
$(CH_3)_3C^e$	1 (-15 to 150)	0.8	9.6 ± 0.8	13.4 ± 1.0	No
F_3C^f	1 (-100 to 20)	$\gg 10^4$	Persistent		No
H_3Si	1 (-85 to -25)	0.017	8.7 ± 0.6	9.7 ± 0.7	No
$(n-Bu)_3Sn$	2 (-35 to 35)		11.1 ± 0.9	9.2 ± 1.2	Yes

^a 1 = first-order decay of the radical over the indicated temperature range; 2 = second-order decay. ^b A in units of s^{-1} for first-order decays and $M^{-1} s^{-1}$ for second-order decays. ^c See text. ^d Decay rates refer to $CH_3\cdot$ generated from $Me_3COOCMe_3 + (CH_3)_3B$. When the $CH_3\cdot$ were generated from $CH_3I + (n-Bu)_3SnSn(n-Bu)_3$ the $CH_3\dot{S}C(CMe_3)_2$ radicals decayed about ten times more slowly, perhaps because of a chain reaction. Because of this problem the kinetics for the decay of the $CD_3\cdot$ adduct (from CD_3I and ditin) were not studied. ^e Azoisobutane and di-*tert*-butyl ketone as $(CH_3)_3C\cdot$ sources gave data in excellent agreement at temperatures $> -20^\circ C$. At lower temperatures the azo compound gives anomalous results because of the slow thermal decomposition of photochemically generated *cis*-azoisobutane (cf. T. Mill and R. S. Stringham, *Tetrahedron Lett.* 1853 (1969)). ^f From CF_3I and $(n-Bu)_3SnSn(n-Bu)_3$. The radicals are not produced thermally in this system.

change in the equilibrium concentration of radicals with temperature could be correlated by the van't Hoff relation, $K = e^{\Delta S/R} e^{-\Delta H/RT}$, with $\Delta S = 32 \pm 3$ gibbs/mol and $\Delta H = 9.6 \pm 1.5$ kcal/mol. The change in entropy is of the magnitude expected for a simple dimerization.^{46,47} Since 1,1-di-*tert*-butylalkyl radicals appear never to dimerize^{11,13,17,48} it seems very improbable that the $CH_3\dot{S}C(CMe_3)_2$ dimer could be head-to-head coupled. We therefore propose that it has either a head-to-tail structure, **5**, or, perhaps, a tail-to-tail structure, **6**.



At temperatures above ca. $-50^\circ C$ under our normal experimental conditions the concentration of dimer would be negligible. At these higher temperatures the $CH_3\dot{S}C(CMe_3)_2$ radical decays with "clean" first-order kinetics. However, for some undiscovered reason the rates of decay were less reproducible than the rates for the other **1**. For this radical, as for the other **1**'s listed in Table III that decay with first-order kinetics, the decay reaction might, in principle, involve loss of $R_nM\cdot$, loss of $CH_3\cdot$, or an intramolecular atom transfer, i.e.,



The A factors for decay (Table III) seem unduly low for either of the β -scission reactions,⁴⁷ i.e., 1 or 2. However, they are not inconsistent with an intramolecular atom transfer since this would involve a highly strained four-membered cyclic transition state for reaction 3 and for reaction 4 except in the case of $R_nM = (CH_3)_3C$. I decay occurred by reaction 3 all **1** might be expected to decompose at similar rates. Since this is manifestly not the case (Table III) and since radical lifetimes increase along the series $R_nM = H_3Si, H_3C, F_3C$, it seemed likely that reaction 4 must be the "normal" decay process when R is an atom. The $R_{n-1}MSCR(CMe_3)_2$ radical formed in reaction 4 would decay rapidly by reaction with a second radical since it is not sterically hindered.

Product studies, which could in principle distinguish between reactions 1-4, were not attempted. This was because we have never succeeded (despite many attempts) in identifying the decay products of persistent radicals when the latter have been

generated by the addition of a transient radical to an unsaturated molecule. However, we did examine the decay of $H_3Si\dot{S}C(CMe_3)_2$ and $D_3Si\dot{S}C(CMe_3)_2$ after their generation under identical conditions from thione, di-*tert*-butyl peroxide, and SiH_4 or SiD_4 . Decay curves were obtained without changing spectrometer or temperature-controller settings between measurements on the normal and deuterated radical. The ratio of the rate constants for decay of the H_3Si and D_3Si adducts, k_H/k_D , were 1.6 at $-20^\circ C$ and 2.3 at $-45^\circ C$, both with error limits of $\pm 10\%$. These kinetic isotope effects, while not large, clearly point to a primary isotope effect in the decay process. We believe they fully confirm that decay can occur by reaction 4 and imply that reaction 4 may be important for other R_nM groups.

We conclude by noting that **1** having $R_nM = (CH_3)_3C, F_3C,$ and H_3Si gave no indication that a dimer was formed at low temperatures. However, the occurrence of second-order decay kinetics for $R_nM = (n-Bu)_3Sn$ suggests that a dimer may be the initial product of this reaction.

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- orbit coupling constant for sulfur compared with oxygen.
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- (25) It is possible that the low g values of $R_nMSC(Me_3)_2$ radicals are also, in part, a consequence of nonplanar geometry at the α carbon since it is known that the g factors of $(RO)_{3-n}CH_n$ ²⁶ and of $F_{3-n}CH_n$ ²⁷ decrease with increased bending at C_α . However, the $a^{13C\alpha}$ values for $R_nMSC(Me_3)_2$ radicals are of comparable magnitude to those of $R_nMCH_2C(Me_3)_2$ radicals¹² and most of the latter are believed to be planar¹² or close to it.²⁸ Moreover, a β sulfur is less effective than a β oxygen at inducing deformation at the α carbon.²²
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Photoelectron Spectra of Sterically Congested Alkenes and Dienes

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Abstract: The He I photoelectron spectra of tetraisopropylethylene and several other tetrasubstituted ethylenes (including adamantylideneadamantane) have been recorded. Although NMR spectra of tetraisopropylethylene have indicated strong steric interactions between the alkyl groups, analysis of the vibrational structure in the photoelectron spectra of these compounds affords no evidence for unusual distortions of the double bonds arising from steric congestion. The values of ionization potentials, Franck-Condon band profiles, and Raman spectra of these compounds reinforce this conclusion. In contrast, the photoelectron spectra of three dehydro derivatives of tetraisopropylethylene do provide clear evidence of sterically induced skewing about the single bond joining the formally conjugated double bonds. The dihedral angles in the diene systems of 3,4-diisopropyl-2,5-dimethyl-2,4-hexadiene and 1,2-diisopropylidene-3,3,4,4-tetramethylcyclobutane have been estimated to be 83 – 97° and about 40° , respectively, from the PES data.

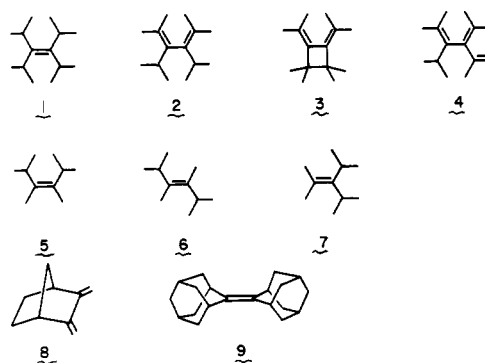
Introduction

Sterically crowded alkenes have attracted considerable interest because of the possibility that strong nonbonded interactions among bulky substituent groups may produce structural distortions about the double bond.² Sterically crowded dienes are of interest for similar reasons, and for the additional reason that atropisomerism may occur if severe nonbonded interactions prevent facile enantiomerization processes involving torsion about the central single bond.³

Continuing an investigation of the properties of sterically congested alkenes,⁴ the present study examines the He I photoelectron spectra of tetraisopropylethylene (**1**), three of its dehydro analogues (**2**, **3**, **4**), two related congested alkenes (**5** and **6**), and adamantylideneadamantane (**9**).

Results and Discussion

The significant steric interactions in **1** are evident from its NMR spectra: both ¹H and ¹³C NMR spectra exhibit two



isopropyl methyl resonances and two isopropyl methine resonances, consistent with its expected conformation (Figure 1); from a line broadening analysis, the activation barrier to interconversion of the nonequivalent pairs of isopropyl groups at $24^\circ C$ has been calculated to be $\Delta G^\ddagger = 17$ kcal/mol.^{4b,5}