

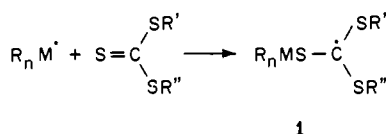
An Electron Paramagnetic Resonance Study of Free-Radical Additions to Trithiocarbonates and of the Formation and Destruction of Tetrathiafulvalene by Free-Radical Processes¹

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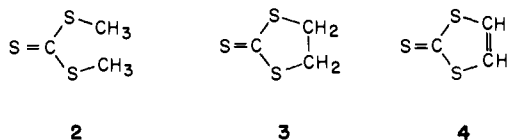
Abstract: Tris(organothiyl)methyl radicals, $R_nMS\dot{C}(SR')_2$, have been generated by the addition of a variety of transient $R_nM\cdot$ radicals to the thione sulfur of three trithiocarbonates (dimethyl trithiocarbonate (2), 1,3-dithiolane-2-thione (3), and 1,3-dithiole-2-thione (4)) and their EPR parameters have been measured. All adducts to 3 and 4 adopt a conformation in which the R_nM group and the semioccupied orbital at C_{α} are eclipsed, but the adducts to 2 adopt noneclipsed conformations. This behavior is attributed to differences in the extent of conjugative electron delocalization to the p-type lone pair of the sulfur which bears the R_nM group. Tetrathiafulvalene (6) is formed by reaction of $R_3Sn\cdot$ radicals with 4 (cf. ref 17). Its yield passes through a maximum because the $R_3Sn\cdot$ can attack 6 at sulfur via an S_H2 process. This produces acetylene and persistent 1-thiaallyl radicals, $R_3SnS\dot{C}(S)C(SCH)_2$, which exist in equilibrium with their diamagnetic dimers at ambient temperatures.

There have been comparatively few studies of the chemistry, conformation, and EPR spectroscopy of tris(organothiyl)methyl radicals.³ Those radicals whose EPR spectra have been recorded have been generated either by the thermolysis of hexakis(organothiyl)ethanes and tetrakis(organothiyl)methanes⁴⁻⁹ or by hydrogen atom abstraction from tris(organothiyl)methanes.¹⁰ Our recent studies on radical additions to carbon-sulfur double bonds¹¹⁻¹³ have shown that this functional group is frequently a surprisingly effective spin trap.¹⁴ This fact suggested to us that the addition of transient radicals, $R_nM\cdot$, to trithiocarbonates might provide a simple and more versatile alternative route to tris(organothiyl)methyl radicals, 1. Uneyama et al.'s⁴ product study of the phenyl



radical-diphenyl trithiocarbonate reaction also suggested that this would prove a viable route to the desired radicals.

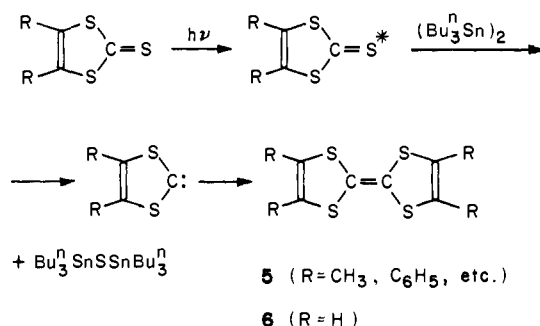
In this paper we report an EPR spectroscopic study of the adduct radicals, 1, produced by the addition of a variety of $R_nM\cdot$ to one acyclic and two cyclic trithiocarbonates, namely, dimethyl trithiocarbonate (2), 1,3-dithiolane-2-thione (3), and 1,3-dithiole-2-thione (4). The last two compounds were ex-



pected to show some differences because 4 is a planar molecule having a completely delocalized n, π electron system,¹⁵ whereas 3 has a puckered ring¹⁶ and is not stabilized by delocalization of the n and π electrons.^{15b}

We were also prompted to study the reaction of free radicals with compound 4 by a recent communication¹⁷ which reports the synthesis of tetrasubstituted tetrathiafulvalenes,¹⁸ 5, by the photolysis of disubstituted 1,3-dithiole-2-thiones in the presence of hexabutylditin. It was suggested¹⁷ that the photoexcited thione reacted with the ditin to produce a carbene which then dimerized to 5, viz.,

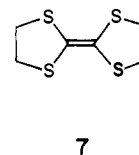
A radical process involving initial homolysis of the Sn-Sn bond was considered unlikely because 5 were not produced by heating the two reagents in the presence of azobisisobutyro-



nitrile (AIBN), radicals from which were expected to cleave the ditin.¹⁷ However, carbene dimerizations are generally disfavored because of the high reactivity of such species.^{19,20} Furthermore, UV photolysis of hexaalkylditins is known to produce trialkyltin radicals, albeit with a low quantum efficiency,²¹ and the radicals so produced form adducts with various spin traps.^{11,12,22} It was therefore thought warranted to investigate the role, if any, played by trialkyltin radicals in the formation of the parent tetrathiafulvalene 6 from 4 and hexa-*n*-butylditin and this, in turn, led to a study of the reactions of trialkyltin and other radicals with 6.

Experimental Section

Materials. Dimethyl trithiocarbonate (2) was prepared by the general method of Runge et al.²³ mobile yellow liquid; ¹H NMR in CDCl₃ δ 2.72 ppm. 1,3-Dithiolane-2-thione (3) was prepared by the same procedure²³ and was recrystallized from toluene/pentane at -78 °C; yellow crystals; mp 36-37 °C (lit.²⁴ 36 °C); ¹H NMR in CDCl₃ δ 3.88 ppm. 1,3-Dithiole-2-thione (4) was prepared by Chen's method;²⁵ yellow crystals; mp 48.5-50 °C (lit.²⁵ 49-50 °C); ¹H NMR in CDCl₃ δ 6.99 ppm. Bis(trimethyltin) sulfide, Me₃SnSSnMe₃, was prepared by the procedure of Harada;²⁶ colorless liquid; ¹H NMR in CCl₄ δ 0.39 ppm (lit.²⁷ δ 0.39 ppm) and in C₆D₆ δ 0.31 ppm. 2-(1,3-Dithiolan-2-ylidene)-1,3-dithiolane (7) was prepared from 2,2'-



bi-1,3-dithiolane²⁸ by the method of Coffen and Garrett²⁹ and was purified by preparative VPC to give a light yellow solid, mp 195-198 °C (lit.²⁹ 200-202 °C), ¹H NMR in C₆D₆ δ 2.66 ppm. Tetrathiafulvalene (6) was obtained in 99% purity from Aldrich and was used

without further purification, ^1H NMR in CDCl_3 δ 6.22 ppm.

Radical Generation. The following transient $\text{R}_n\text{M}\cdot$ radicals were generated photochemically, as previously described,³⁰ directly in the cavity of a Varian E-4 EPR spectrometer: $\text{Me}_3\text{Sn}\cdot$, $n\text{-Bu}_3\text{Sn}\cdot$, $\text{Me}_3\text{Si}\cdot$, $\text{Me}_3\text{C}\cdot$, $\text{CH}_3\cdot$, $\text{CF}_3\cdot$, $\text{C}_6\text{H}_5\cdot$, $\text{Me}_3\text{CO}\cdot$, $\text{C}_6\text{H}_5(\text{CH}_3)_2\text{CO}\cdot$, $\text{CF}_3\text{S}\cdot$, $\text{Me}_3\text{CS}\cdot$, $n\text{-BuS}\cdot$, and $(\text{EtO})_2\text{P}(\text{O})\cdot$. Each of these radicals was generated in the presence of the three trithiocarbonates using toluene as the solvent. The trialkyltin, alkoxy, and alkylthiyl radicals were generated from their dimers, and *tert*-butyl was generated from azoisobutane. Trimethylsilyl was produced by the $\text{Me}_3\text{CO}\cdot + \text{Me}_3\text{SiH}$ reaction. Methyl and trifluoromethyl were generated by photolysis of their iodides and a hexaalkylditin. Although a direct reaction between methyl iodide and **4** is known to occur in nitromethane,²⁴ no reaction could be detected by NMR in C_6D_6 after 15 h at room temperature and recovered **4** was shown to be pure. Similarly, there was no reaction in C_6D_6 between CF_3I and **4**.

The phenyl radical had to be generated by reaction of $\text{Me}_3\text{CO}\cdot$ with $(\text{C}_6\text{H}_5)_3\text{As}$ because the $\text{R}_3\text{Sn}\cdot + \text{C}_6\text{H}_5\text{I}$ system gave only $\text{R}_3\text{Sn}\cdot$ adducts while $(\text{C}_6\text{H}_5)_2\text{Hg}$ did not give any adducts. The diethylphosphonyl adducts could only be detected when $(\text{EtO})_2\text{P}(\text{O})\cdot$ was produced by reaction of $\text{Me}_3\text{CO}\cdot$ with $(\text{EtO})_2\text{POP}(\text{OEt})_2$. They were not observed in the $\text{Me}_3\text{CO}\cdot + (\text{EtO})_2\text{POH}$ system.³¹

Several of the above-mentioned $\text{R}_n\text{M}\cdot$ radicals were also generated in the presence of tetrathiafulvalene, using toluene as solvent.

Formation of Tetrathiafulvalene from Hexaalkylditin and **4. The Photochemical Reaction.** Hexamethylditin (0.32 mmol) and **4** (0.14 mmol) were dissolved in C_6D_6 (0.30 cm^3), degassed, sealed under vacuum in a silica tube, and irradiated with light of wavelength 300 nm in a Rayonet photochemical reactor at room temperature. The progress of the reaction was monitored by NMR spectroscopy. After 174 h of irradiation the reaction ceased and $\geq 96\%$ of **4** had been consumed. The final yield of tetrathiafulvalene (**6**) was 28% (0.02 mmol), but some of this compound was itself consumed toward the end of the reaction (see below). The maximum yield of **6** was ca. 33%. This low yield is, at least in part, a consequence of side reactions. The NMR spectra suggest that ca. 20% of **4** is converted to a product which would appear to be an unsymmetrically substituted cis olefin (two doublets, $J = 8$ Hz, at δ 5.98 and 6.64 ppm). The NMR spectra also indicated that $\text{Me}_3\text{SnSSnMe}_3$ was a major product, as would be expected.¹⁷ However, very little acetylene or compound **8** (see below) were formed.

A rather similar experiment with hexa-*n*-butylditin (0.46 mmol) and **4** (0.23 mmol) in C_6D_6 gave, upon completion of the reaction (174 h), a 78% consumption of **4** and a final yield of **6** of 17%. The maximum yield of **6** was ca. 25%. Some cis olefin also appeared to be formed.

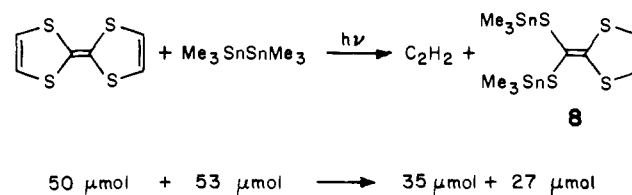
The Thermal Reaction. The cleavage of Sn-Sn bonds by an $\text{S}_\text{H}2$ reaction involving attack of the stabilized³² $(\text{CH}_3)_2\dot{\text{C}}\text{CN}$ radical (from AIBN) on hexa-*n*-butylditin (as attempted by Ueno et al.¹⁷) is not expected to be a very facile process.³³ However, the $\text{S}_\text{H}2$ reaction between a *tert*-butoxy radical and a ditin is known to be rapid and efficient^{21a,33,34} and so the following experiment was carried out.

Hexamethylditin (0.85 mmol), **4** (0.11 mmol), and di-*tert*-butyl hyponitrite³⁵ (0.37 mmol) were dissolved in C_6D_6 (0.30 cm^3), degassed, sealed under vacuum in a silica tube, and heated to 65 °C³⁶ in the dark. The progress of the reaction was monitored by NMR spectroscopy. After 95 min more than 97% of **4** had been consumed and **6** was produced in a final yield of 31%.³⁷ The maximum yield of **6** was ca. 35%. Under similar conditions but without the ditin some 90% of **4** was destroyed but no **6** was formed. No reaction occurred on heating the ditin and **4** to 65 °C in the absence of the hyponitrite.

Photoreaction of Hexamethylditin with **6.** In the reaction of $\text{R}_3\text{Sn}\cdot$ radicals with **4** the yield of **6** goes through a maximum (see above). This implies that $\text{R}_3\text{Sn}\cdot$ radicals can react with **6**, and this conclusion is supported by our EPR studies (see below). In order to determine the principal position at which **6** is attacked by trialkyltin radicals the following experiment was carried out.

Hexamethylditin (94 μmol) and **6** (75 μmol) were dissolved in C_6D_6 (0.30 cm^3), degassed, sealed under vacuum in a silica tube, and photolyzed at room temperature with the unfiltered light from a 250-W high-pressure mercury lamp. The progress of the reaction was monitored by NMR spectroscopy. The solution gradually darkens and this brought the reaction almost to a halt after 22 h. At this time, 66% of **6** and ca. 56% of the ditin had been consumed and 35 μmol of acetylene (δ 1.38 ppm, confirmed subsequently by VPC) and 8 μmol of

$\text{Me}_3\text{SnSSnMe}_3$ (δ 0.31 ppm) had been produced. (In the absence of the ditin, but under otherwise identical conditions, 20% of **6** was consumed and 8 μmol of acetylene was produced.) There were only two other major new peaks in the NMR spectrum. One of these (which was not formed in the absence of the ditin) was in the vinylic region at δ 5.53 ppm (**6** has δ 5.38 ppm in C_6D_6): yield 27 μmol (assuming two olefinic protons, i.e., one $-\text{CH}=\text{CH}-$ group). The other major new peak occurred in the methyl region at δ 0.41 ppm ($\text{Me}_3\text{SnSSnMe}_3$ has δ 0.25 ppm) and a partially purified sample showed combined ^{117}Sn and ^{119}Sn satellite peaks, $J = 54$ Hz: yield 26 ± 3 μmol (assuming two Me_3Sn groups). It appeared likely that both major new peaks arose from one compound, **8**, and an attempt was therefore made to isolate it starting with ca. 15 times as much material. Unreacted **6** was removed from the products by four recrystallizations from *n*-pentane/dichloromethane and a light brown solid (66 mg) containing 72% **8** and 28% **6** was crystallized from the final liquors. None of the usual separation techniques yielded analytically pure **8** because the product mixture decomposed very readily. However, the 5.53 ppm/0.41 ppm NMR peak ratio remained unchanged throughout the various workups, which confirms that these peaks came from the same compound. A mass spectrum of the mixture showed a parent ion from **6** but not one due to **8**, presumably because the latter compound was thermally unstable at the temperatures required for it to volatilize. The overall reaction can probably be represented as follows.



An attempt to study the thermal reaction between $\text{Me}_3\text{Sn}\cdot$ radicals and **6** was foiled by a direct reaction between **6** and di-*tert*-butyl hyponitrite which occurred at ambient temperatures and yielded a red-brown precipitate. This reaction was not examined further.

Competitive Photoreaction of Hexamethylditin with **6 and **7**.** Having established that the attack of $\text{Me}_3\text{Sn}\cdot$ radicals on **6** yielded acetylene it became of interest to determine whether ethylene would be formed by attack of $\text{Me}_3\text{Sn}\cdot$ on **6**'s tetrahydro derivative, **7**. This latter reaction was found to occur and, as the following experiment demonstrates, it is far more facile than C_2H_2 formation from **6**.

Hexamethylditin (109 μmol), **6** (52 μmol), and **7** (49 μmol) were dissolved in C_6D_6 (0.30 cm^3), degassed, and sealed under vacuum in a silica tube. The solution was photolyzed and monitored by NMR spectroscopy as before. Ethylene (δ 5.16 ppm) was formed preferentially. Only after 91% of the **7** had been consumed was there any significant consumption of **6** and any detectable formation of acetylene and **8**. After 18 h the reaction had almost ceased and all **7** and 45% **6** had been consumed. Overall, 91 μmol of $\text{Me}_3\text{SnSSnMe}_3 + 49$ μmol of **7** + 24 μmol of **6** yielded 24 μmol of $\text{C}_2\text{H}_4 + 11$ μmol of $\text{C}_2\text{H}_2 + 9$ μmol of **8**. Under similar conditions, but in the absence of the ditin, 32% of the **7** was consumed and 9.5 μmol of ethylene was formed, there being no appreciable decomposition of **6**.

Results

The principal EPR parameters of the radical adducts, **1**, formed from the three trithiocarbonates are listed in Table I. Only $(\text{MeS})_3\text{C}\cdot$ has been reported previously.¹⁰ All **1** had rather broad spectral lines ($0.2 \text{ G} \leq \Delta H_{\text{pp}} \leq 1.0 \text{ G}$) and were transient species that decayed with second-order kinetics at rates approaching the diffusion-controlled limit. Alkylthiyl radicals did not form adducts with any of the trithiocarbonates.

The reaction of tri-*n*-butyltin radicals with 1,3-dithiole-2-thione (**4**) gave the expected adduct initially and so, apparently, did trimethyltin radicals (see Table I). However, after irradiation for 1 or 2 min the spectra of the $\text{R}_3\text{SnSC}(\text{SCH})_2$ radicals decreased in intensity and a spectrum due to a persistent radical appeared. This radical was present even after prolonged irradiation. It could also be produced by photolysis of the ditin in the presence of tetrathiafulvalene (**6**) and in this

Table I. EPR Parameters for Radicals, 1, Derived from Trithiocarbonates, 2, 3, and 4^a

R _n M	R _n MS̄C(SCH ₃) ₂			R _n MS̄C(SCH ₂) ₂			R _n MS̄C(SCH) ₂			a ^{other}
	g	a ^H (CH ₃ S) ₂	a ^M	g	a ^H (CH ₂ S) ₂	a ^M	g	a ^H (CHS) ₂	a ^M	
Me ₃ Sn	2.0051	1.25	108 ^b	2.0047	1.21 ^c	176, ^d 184 ^e	2.0050	f	f	f
n-Bu ₃ Sn	2.0052	1.23	91.5 ^b	2.0046	0.95	153, ^d 160 ^e	2.0048	0.8	154, ^d 162 ^e	43.0 ^g
Me ₃ Si	2.0056	1.40	h	2.0053	1.03	h	i			
Me ₃ C	2.0052	1.78 ^j	h	2.0049	1.45 ^k	h	2.0053	0.94 ^{l,m}	h	
H ₃ C	2.0052 ⁿ	1.15 ⁿ	7.10 ^{o,p}	2.0051 ^q	1.70 ^q	17.12 ^{o,q}	2.0054 ^q	0.92 ^{l,q}	17.35 ^{o,q}	0.46 ^{l,r}
F ₃ C	2.0053 ^s	2.20	(3.80) ^{s,t}	2.0052 ^q	1.73 ^q	(4.0) ^{q,t}	2.0056 ^q	1.15 ^q	(4.49) ^{q,t}	
C ₆ H ₅	2.0052 ^u	1.63	h	2.0053	1.44	(0.4) ^{l,v}	i			
Me ₃ CO	2.0051 ^w	1.43 ^w	h	2.0046 ^q	1.98 ^q	h	i			
Ph(Me) ₂ CO	2.0051	1.3	h	2.0046 ^q	2.05 ^q	h	i			
(EtO) ₂ P(O)	2.0053 ^x	1.85	71.2 ^x	2.0052 ^x	1.73	83.2 ^x	2.0052 ^{q,x}	h	80.2 ^{q,x}	h

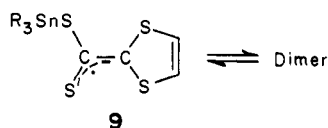
^a Hyperfine splitting constants are given in gauss. Data were obtained at 25 °C in toluene unless otherwise specified. ^b ¹¹⁷Sn and ¹¹⁹Sn not resolved. ^c Additional splitting by Me₃Sn protons at low temperatures, a^H = 0.27 G at -65 °C. ^d ¹¹⁷Sn. ^e ¹¹⁹Sn. ^f Not measurable because of the rapid decrease in signal intensity on continued photolysis. ^g ¹³C_α. ^h Not resolved. ⁱ An adduct does not appear to be formed. ^j Also, a^H(Me₃C) = 0.50 G. ^k Also, a^H(Me₃C) = 0.48 G. ^l Poorly resolved. ^m Also, a^H(Me₃C) = 0.47 G. ⁿ Values reported in ref 10 are g = 2.0057, a^H(CH₃S)₃ = 1.5 G, and a¹³C_α = 54.25 G at 25 and 50 °C. In the present work, decreasing the temperature to -65 °C increased a^H to 1.23 G. ^o Obtained by generating methyl radicals from ¹³CH₃I (90 atom % ¹³C). ^p a¹³C = 6.67 G at -65 °C. ^q At ca. -60 to -70 °C. ^r Additional splitting by CH₃ protons. ^s For comparison,^{9,10} (CF₃S)₃C• has g = 2.0044 and a^F = 2.88 G. ^t a^F (3F). ^u For comparison,⁸ (C₆H₅S)₃C• has g = 2.004 95 and a¹³C_α = 42.2 G. ^v Additional splitting by 3 H. ^w In C₆H₆ at 25 °C. g = 2.0052 and a^H(CH₃S)₂ = 1.40 G. This rules out any possibility that PhCH₂S̄C(SCH₃)₂ was the radical formed in toluene. ^x Corrected by the Breit-Rabi equation.

Table II. EPR Parameters for Some Radicals Generated from Tetrathiafulvalene (6)^a

	Radical	g	a ^H	a ^{other}
9 (R = Me)	Me ₃ SnS̄C(S̄)C̄(SCH) ₂	2.0116	1.00 (2 H)	3.2 (1 Sn), ^{b,c} 10.8 (1 ¹³ C) ^d
9 (R = n-Bu)	n-Bu ₃ SnS̄C(S̄)C̄(SCH) ₂	2.0118	1.02 (2 H)	2.7 (1 Sn), ^b 8.3 (1 ¹³ C)
10	Me ₃ SnS̄C(S̄)C̄(SCH ₂) ₂ ^e	2.014	1.7 (4 H) ^f	
12 ^g	[(CHS) ₂ C=C(SCH) ₂] ⁺	2.0081	1.25 (4 H)	4.06 (4 ¹³ S)

^a Hyperfine splittings are given in gauss. Data were obtained in toluene and at 25 °C unless otherwise specified. ^b ¹¹⁷Sn and ¹¹⁹Sn not resolved. ^c At -70 °C. ^d At 0 °C. ^e Tentative identification only. ^f Some lines masked by **9** (R = Me). ^g In EtOH-toluene (1:5). For comparison: g = 2.0080, a^H = 1.22 G in neat toluene (this work); g = 2.008 38, a^H = 1.26 G in H₂O-CH₃CN at 25 °C or EtOH at -50 °C;³⁹ the structurally related [(MeS)₂C=C(SMe)₂]⁺ enriched in ¹³C at the ethylenic positions has a¹³C (2 C) = 3.72 G at 30 °C.^{43b}

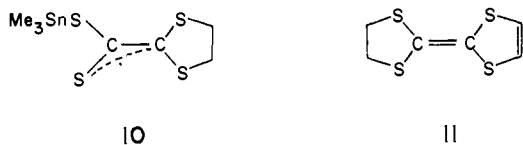
case it was produced immediately after the photolysis was begun. These radicals are assigned structure **9** (see Discussion)



and their EPR parameters are listed in Table II. They exist in equilibrium with a diamagnetic dimer since their concentration can be increased and decreased reversibly by raising and lowering the temperature.

Two other persistent radicals were formed in low concentrations (relative to **9**) by prolonged photolysis of hexamethylditin with either **4** or **6**. The EPR parameters for these radicals (g = 2.0069 and 2.0105, a^H(2H) = 1.1 G for both) did not provide sufficient information for structures to be assigned.

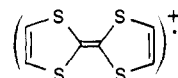
Photolysis of hexamethylditin and **7** in toluene gave a strong EPR signal from the persistent radical **9** (R = Me), which partly masked a weaker signal coming from a less persistent species, **10**. On the basis of its EPR parameters (Table II) we tentatively assign **10** a 1-thiaallyl structure similar to **9**. In this



experiment, the most probable source of radical **9** (R = Me) was 2-(1,3 dithiol-2-ylidene)-1,3-dithiolane (**11**), which is a by-product in the synthesis of **7**. Although **11** was present only

in trace amounts, the EPR spectrum is dominated by **9** because of the greater persistence of the latter radical.

Photolysis of **4** in the presence of either di-*tert*-butyl peroxide or diethyl phosphite alone gave no EPR signals. However, photolysis of a toluene solution containing all three compounds gave the distinctive EPR spectrum of the persistent radical cation of tetrathiafulvalene,^{39,40} **12**, rather than the expected adduct radical.⁴¹ Radical **12** is well known and can be produced



12

from **6** in various ways^{39,40} including, we have found, by photolysis of a toluene solution of **6**, peroxide, and phosphite. However, the spectrum of **12** was much more poorly resolved in this last system than when **4** was used as its precursor unless a *very* dilute solution of **6** was employed and the temperature was lowered. It would appear that when **12** is generated in the presence of any appreciable concentration of **6** there is a rapid electron exchange reaction which causes line broadening and loss of resolution. As a corollary, this implies that the yield of **6** should be small in the peroxide-phosphite-**4** reaction and this was confirmed by our failure to detect **6** by NMR spectroscopy even after prolonged photolysis of these reactants. In this reaction system **12** was moderately persistent (first-order decay with τ_{1/2} = 4 min at -24 °C). The signal intensity due to **12** could be increased and decreased reversibly by raising and lowering the temperature without there being any significant changes in line width. This implies that the radical cation is in thermal equilibrium with its dimer⁴² or its disproportionation products.^{39,40}

Radical **12** was also produced in a thermal reaction between **6** and bis(trifluoromethyl) disulfide in toluene at room temperature. A violet^{39,40} precipitate was formed which, when dissolved in ethanol-toluene (1:5), gave a green solution at 25 °C which showed a well-resolved spectrum of **12**. This was sufficiently intense that lines which we attribute to the two outer sets of satellites arising from the four equivalent ³³S atoms could be observed (Table II).^{43a} Hyperfine splitting by ³³S has not been reported previously for **12** nor for related cation radicals.^{43b} On cooling this solution the color changed from green to violet and the concentration of free **12** decreased.

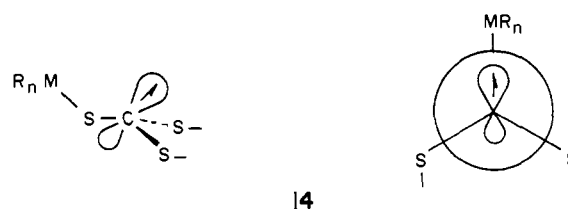
Discussion

Trithiocarbonate Radical Adducts 1. It can be seen from Table I that whereas dimethyl trithiocarbonate (**2**) and 1,3-dithiolane-2-thione (**3**) can trap a wide variety of transient radicals, 1,3-dithiole-2-thione (**4**) is much more discriminating since it does not give adducts with Me₃Si·, C₆H₅·, Me₃CO·, or Ph(Me)₂CO· radicals. None of the trithiocarbonates trap alkylthiyl radicals, though such species are readily trapped by thioketones.^{13,14} It is even more surprising that alkoxy radicals are trapped by **2** and **3** since these radicals are not trapped by di-*tert*-butylthioketone,¹¹ nor by thio esters,¹² nor can the *tert*-butyl radical be trapped by (Me₃C)₂C=S=O.⁴⁴ Of course, alkoxy trapping must be fairly slow or it would not have been possible to detect the adducts of Me₃Si·, C₆H₅·, and (EtO)₂P(O)·, since these radicals were all generated indirectly via *tert*-butoxy.

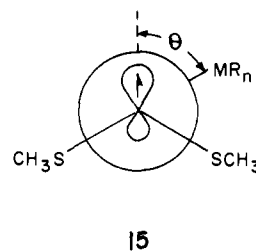
Configuration⁴⁵ of 1. The only ¹³C_α hyperfine splitting that could be measured was that for *n*-Bu₃SnSC(SCH)₂. Its value was 43.0 G, which is comparable to the values reported for some tris(arylthio)methyls, e.g.,⁸ 42.2 G for (C₆H₅S)₃C·, and some tris(alkylthiomethyls), e.g., 41.0 G for (*c*-C₆H₁₁S)₃C·⁸ and 54.25 G for (CH₃S)₃C·.¹⁰ For these acyclic radicals it has been calculated⁸ that the unpaired electron is in an orbital with 8–9% *s* character and that there is an 11–12° deviation from planarity at C_α.

Conformation⁴⁵ of 1. The three trithiocarbonates should all give sufficiently unhindered adducts that their conformations should not be determined (as is so often the case)^{11,30,32,46} entirely by steric factors. In these radicals the dihedral angle, θ , between the R_nM-S bond and the C_α2p_z direction can be roughly estimated from the magnitude of *a*^M. Hyperfine splittings by M in natural abundance could be measured for R_nM = Me₃Sn, *n*-Bu₃Sn, and (EtO)₂P(O), and for R_nM = H₃C using carbon-13 enriched methyl radicals. In order to determine the conformation of any **1** it is necessary to compare its *a*^M value with that found for an analogous radical of known conformation. The safest comparison is with R_nMSC(CMe₃)₂ since these radicals all adopt a conformation, **13**, in which R_nM group is eclipsed by the C_α2p_z orbital (i.e., $\theta = 0$) and *a*^M has its maximum value.¹¹ If any **1** were to adopt a similar eclipsed conformation, **14**, it would be expected to have a somewhat lower *a*^M value than the corresponding **13** for two reasons. In the first place, the spin density at C_α which is available to interact with M will be less in **14** than in **13**. This is because the spin in **1** will be conjugatively delocalized by the two thyl sulfurs of the trithiocarbonate moiety via their p-type lone pairs. Secondly, because **1** are probably⁴⁷ more bent at C_α than **13**, the distance between M and the semioccupied orbital will be greater in **14** than in **13**.

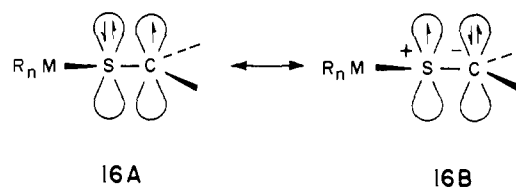
The *a*^M values reported¹¹ for **13** are 243 (¹¹⁷Sn) and 254 (¹¹⁹Sn) G for R_nM = Me₃Sn; 197 and 209 G for *n*-Bu₃Sn; 23.5 G for ¹³CH₃; and 101 G for (EtO)₂³¹P(O). Comparison with the data in Table I shows that the *a*^M values for the R₃Sn, CH₃, and (EtO)₂P(O) adducts to the two cyclic trithiocarbonates, **3** and **4**, are all about 20–25% lower than the *a*^M values for **13**. We conclude, therefore, that all adducts to **3** and **4** adopt an



eclipsed, or nearly eclipsed, conformation, **14**. In contrast, although the (EtO)₂P(O) adduct to the acyclic trithiocarbonate, **2**, may have adopted an eclipsed conformation, there can be no doubt that the R₃Sn and CH₃ adducts to **2** adopt a staggered conformation, **15**, with θ having a not insignificant value.⁴⁸



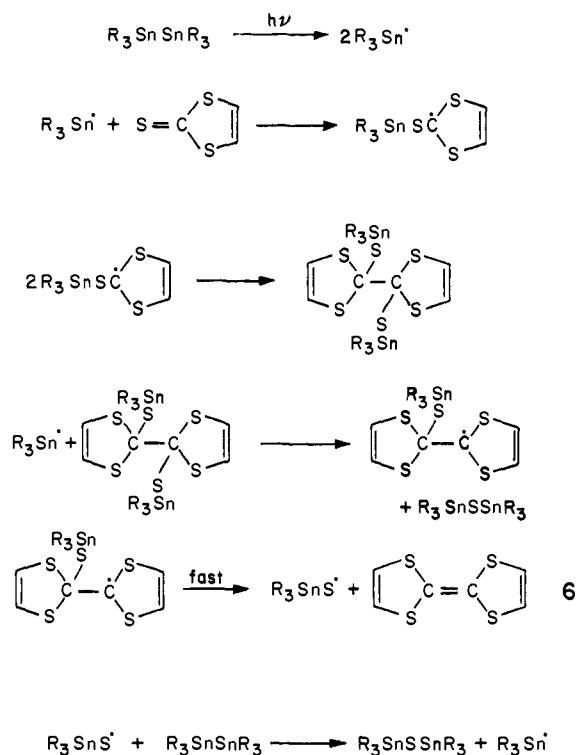
The conformational preferences of the different tris(organothyl)methyl radicals can be rationalized in the following manner. The force which promotes the staggered conformation¹⁵ arises from conjugative delocalization between the unpaired electron and the p-type lone pair on the sulfur of the R_nMS group (**16A** ↔ **16B**) while the forces which favor the



eclipsed conformation, **14**, arise from steric repulsion between R_nM and the α substituents and from hyperconjugation of the unpaired electron into the R_nM-S bond. In the cyclic radicals the two sulfur atoms in the ring have their p-type lone pairs almost⁴⁹ ideally oriented for conjugative delocalization of the unpaired electron and so the spin density available for conjugative delocalization to the R_nMS sulfur is reduced. As a result, steric and/or hyperconjugative forces dominate and cause the cyclic radicals to adopt an eclipsed conformation. However, in the acyclic radicals the three sulfurs are more nearly (or even exactly) equivalent and so conjugative delocalization to the R_nMS sulfur atom becomes more important. The opposing forces then achieve a balance which produces a partially staggered conformation for the acyclic radicals with θ being larger for the more electropositive R_nM (CH₃ and R₃Sn)⁴⁸ because such groups help to stabilize canonical structure **16B** and smaller for the more electronegative groups, (EtO)₂P(O)⁴⁸ and CF₃,⁵⁰ which destabilize this structure.

Tetrathiafulvalene (6). Mechanism of Formation of 6 from 4 and Trialkyltin Radicals. Two lines of evidence indicate that Ueno et al.'s carbene mechanism¹⁷ is not the route by which

Scheme I

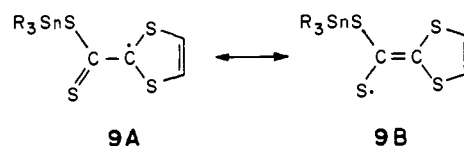


6 was formed during the photolysis of **4** and a hexaalkylditin. Firstly, the $n\text{-Bu}_3\text{SnSC}(\text{SCH})_2$ radical was certainly formed during the photolysis of **4** and hexa- n -butylditin. Secondly, the reaction of **4** with thermally generated $\text{Me}_3\text{Sn}\cdot$ radicals gave **6** in yields comparable to the photoreaction⁵¹ (see Experimental Section). We conclude that the photoreaction yields **6** by a radical mechanism and we presume that photolysis of ditins with disubstituted 1,3-dithiole-2-thiones also yields the tetrasubstituted tetrathiafulvalenes **5** by a radical process. The most probable route for the conversion of **4** to **6** is shown in Scheme I. The initial adducts are presumed to undergo a head-to-head dimerization because this is consistent with the observation that $n\text{-Bu}_3\text{SnSC}(\text{SCH})_2$ (and analogous radicals) decayed with second-order kinetics. The route by which the dimer is then converted to **6** is uncertain, but that indicated would seem quite plausible.

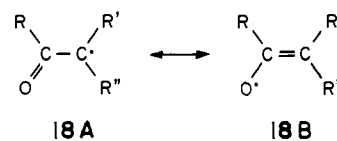
Reaction of $\text{R}_3\text{Sn}\cdot$ with **6.** In both the photo- and the thermal reaction of $\text{R}_3\text{Sn}\cdot$ with **4** the yield of **6** passed through a maximum of ca. 30% and then decreased (see Experimental Section). This implied that **6** was destroyed by $\text{R}_3\text{Sn}\cdot$ radicals and this conclusion was confirmed by product and by EPR studies. The major products identified were acetylene and $(\text{Me}_3\text{SnS})_2\text{C}=\text{C}(\text{SCH})_2$ (**8**). In the EPR study a persistent radical was formed which, for reasons outlined below, we identify as a 1-thiaallyl radical, **9**. Such radicals do not appear to have been observed previously in solution.⁵² The probable mechanism by which **6** is destroyed by $\text{R}_3\text{Sn}\cdot$ radicals is shown in Scheme II. It involves an initial $\text{S}_{\text{H}2}$ reaction in which $\text{R}_3\text{Sn}\cdot$ attacks a thiole sulfur to form acetylene and radical **9**. The olefin, **8**, is presumed to be formed by the coupling of $\text{R}_3\text{Sn}\cdot$ with **9** (which is persistent and so is present in relatively high concentrations). We assume that **8** will eventually be destroyed by further reactions with $\text{R}_3\text{Sn}\cdot$ radicals.

The assignment of the 1-thiaallyl structure to **9** rests on the following observations.

(1) **EPR Parameters (See Table II).** The high g values indicate that the spin density on sulfur is much higher than that in tris(alkylthiyl)methyl radicals. In structure **9**, the unpaired electron can be delocalized onto the thione sulfur, i.e.,



The hyperfine splitting by two equivalent hydrogens and by one tin atom is also consistent with structure **9**. The unique carbon-13 atom which gives rise to the splitting of ca. 10 G must, we presume, be at the 2 position in the 1,3-dithiole ring (i.e., the α position in **9A**). The low magnitude of this splitting suggests that radical **9** can be better represented by canonical structure **9B** than **9A**. That is, **9** should be regarded as partly delocalized thiyl radicals rather than as partly delocalized alkyl radicals. It would appear that **9** are more closely related to arylthiyls (in which there is relatively little delocalization of the unpaired electron from the sulfur into the aromatic ring)⁵³⁻⁵⁶ than to their closest oxygen analogues, the alkanoylalkyls, **18**.⁵⁷⁻⁶¹ In these last-named radicals, a $^{13}\text{C}\alpha$ is ca. 27 G and the contribution of the canonical structure having the unpaired electron on oxygen, **18B**, has been calculated to be only about 15%.⁶⁰ Differences in the electronegativities of oxygen, carbon, and sulfur provide a simple explanation for this difference between **9** and **18** because radical stabilization energies^{32,62} are strongly influenced by the electronegativity of the atom bearing the unpaired electron. The stabilization energies of a series of structurally related oxygen, carbon, and sulfur centered radicals increase in this order.⁶³ For this reason, **18A** is favored over **18B** but **9B** is favored over **9A**. Alterna-



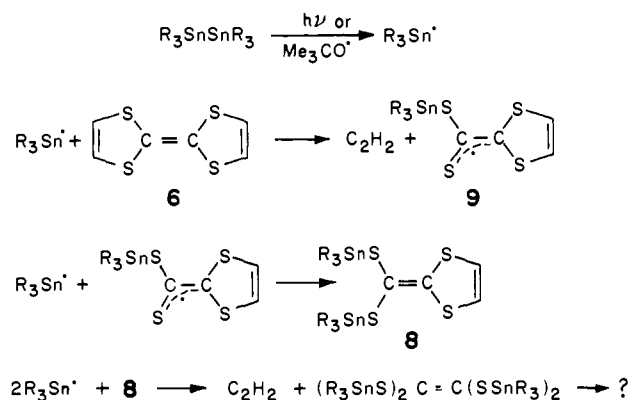
tively,⁶⁴ the differences in structure between **18** and **9** can be rationalized in terms of the greater strength of the $\text{C}=\text{O}$ π bond (~ 90 kcal/mol) compared with the strength of the $\text{C}=\text{S}$ π bond (~ 55 kcal/mol).

(2) **Formation of **9** from **6**.** Radical **9** is immediately produced upon UV irradiation of a toluene solution of **6** and a hexaalkylditin. It is not formed immediately and directly from **4**.

(3) **Production of Acetylene.** A radical having structure **9** must be formed as an intermediate if acetylene⁶⁵ is to be produced by the reaction of **6** with $\text{Me}_3\text{Sn}\cdot$ radicals. (Similarly, radical **10** must be formed if ethylene is to be produced from **7** and $\text{Me}_3\text{Sn}\cdot$ radicals. We are not aware of any other $\text{S}_{\text{H}2}$ reactions which lead to the extrusion of C_2H_2 or C_2H_4 from a ring.)

(4) **Formation of a Dimer.** Although **9** is persistent, it does exist in thermal equilibrium with a diamagnetic dimer at ambient temperatures and below. This is also true of sterically

Scheme II



hindered arylthiyls^{54,55} and, by analogy with these species, we suggest that the dimer of **9** is S-S coupled. It is not obvious why **10** should be less persistent than **9**, though this may come about because the unpaired electron is more strongly delocalized in the latter radical.⁶⁴

To conclude, it should be pointed out that while the maximum yield of **6** was ca. 35% (based on **4**), Ueno et al.'s¹⁷ yields of tetrasubstituted tetrathiafulvalenes, **5**, were in the range 50–77% under comparable conditions. Whether this difference is simply due to steric factors which better protect **5** from wastage via R₃Sn· attack or to some more subtle electronic factor remains to be determined.

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- Suggested by a referee.
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