An Electron Spin Resonance Study of Radical Intermediates from 1,6,6aλ^4-Triheterapentalenes

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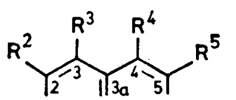
Adduct radicals can be observed by e.s.r. spectroscopy on reaction of some reactive, transient radicals with 1,6,6aλ^4-triheterapentalenes provided the atom at position 1 (and/or 6) is sulphur or selenium. The adduct radicals formed with tri-n-butylstannyl and trithiapentalenes have been studied in most detail. Trithiapentalene itself yields two adduct radicals and 2-t-butyltrithiapentalene yields three adduct radicals. It is concluded that all the adduct radicals are of the pentadienyl type, the $Bu^n{}_3Sn\cdot$ radical adding to S-1 (or S-6) and cleaving the S-1–S-6a (or S-6–S-6a) bond. The observation of more than one adduct radical from a single, symmetric, trithiapentalene is attributed to the fact that the adduct radical can exist in more than one conformation. Structures are tentatively assigned to most of the observed radicals.

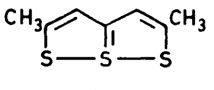
THE reactions of 1,6,6aλ^4-triheterapentalenes (1) with electrophiles and nucleophiles have been examined in some detail[1-12] but their reactions with free radicals have received almost no attention. Radical participation has been suggested in the reaction of arenediazonium fluoroborates with trithiapentalenes (1 ; X = Y = Z = S)[13,14] and radical anions of trithiapentalenes have been generated electrochemically.[15] However, no radical anions were observed on electrolytic reduction of 1,6-dioxa-6aλ^4-thiapentalenes (1 ; X = Y = O, Z = S).[15] In a preliminary communication we reported that photochemically generated trialkylsilyl and trialkylstannyl radicals add to trithiapentalenes to yield a new class of radicals which could be detected by e.s.r. spectroscopy.[16] The spectra indicated that addition occurred exclusively at S-1, there being no sign of addition at the other potential sites, *viz.*, C-2, C-3, C-3a, and S-6a. In this paper we present a full report on our e.s.r. studies of these and related radicals.



(1)

RESULTS

Radical Addition to 2,5-*Dimethyl*-1,6,6aλ^4-*trithiapentalene* (2).—A general survey was carried out of adduct formation by (2) with various types of free radical. The radicals chosen were generated by photolysis directly in the cavity of an e.s.r. spectrometer using benzene, or occasionally toluene, as the solvent. Most spectra were recorded at ambient temperatures since the signal intensities generally decreased with a decrease in temperature, possibly because of the limited solubility of most trithiapentalenes.



(2)

Trimethylsilyl radicals (from trimethylsilane and di-t-butyl peroxide) gave rise to a well resolved spectrum showing hyperfine splittings (h.f.s.s) from two non-equivalent hydrogens and two non-equivalent methyl groups. No e.s.r. signal was obtained in the absence of trimethylsilane and peroxide, nor in the absence of peroxide. Tri-n-butylstannyl (from hexa-n-butylditin with or without added di-t-butyl peroxide) gave a radical with a similar spectrum but with slightly different *g* factor and h.f.s.s. t-Butoxyl radicals (from di-t-butyl peroxide), phenyl radicals (from triphenylarsine and di-t-butyl peroxide), and ethyl radicals (from triethylborane and di-t-butyl peroxide) gave rise to less intense spectra of the same general appearance. The e.s.r. parameters for these radicals are given in Table 1, except for the ethyl adduct for which the spectrum was too weak to analyse completely. Diethoxyphosphoryl radicals $(EtO)_2\dot{P}{=}O$ (from tetraethyl pyrophosphite and di-t-butyl peroxide) and trifluoromethylthiyl radicals (from bis-trifluoromethyl disulphide) did not appear to form adducts with (2).

TABLE 1

E.s.r. parameters for the adduct radicals produced by reaction of various free radicals, R·, with 2,5-dimethyl-1,6,6aλ^4-trithiapentalene (2) at ambient temperatures in benzene

R·	*g*	a^H (1 H)[a]	a^H (1 H)[a]	a^H (3 H)[a]	a^H (3 H)[a]
$Me_3Si\cdot$	2.006 09	0.17	0.24	0.68	0.80
$Bu^n{}_3Sn\cdot$	2.006 10	0.18	0.23	0.67	0.75
$Me_3CO\cdot$	2.005 88	0.16	0.22	0.66	0.78
$C_6H_5\cdot$	2.004 88	0.18	0.21	0.74	1.13
Et·	2.005 60	*b*	*b*	*b*	*b*

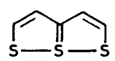
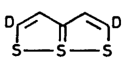
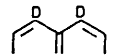
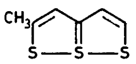
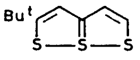
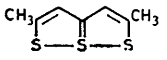
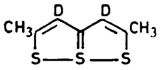
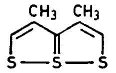
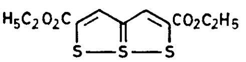
[a] H.f.s.s in mT. [b] Not measurable, see text.

Tri-n-butylstannyl Radical Addition to Trithiapentalenes.—After completion of the above survey, the tri-n-butylstannyl radical was chosen for addition to a variety of other trithiapentalenes. This choice was made because its adduct with (2) exhibited a ' clean ' and relatively intense e.s.r. spectrum. The e.s.r. parameters for this series of adduct radicals are collected in Table 2.

All the trithiapentalenes examined obviously give rather similar adducts with the $Bu^n{}_3Sn\cdot$ radical. However, the parent 1,6,6aλ^4-trithiapentalene (3) and its 2,5-dideuterio-derivative (4) each gave two adduct radicals which have rather similar e.s.r. parameters. These pairs of radicals were not present in equal concentration. The radical with the higher *g* factor gave a spectrum which was *ca.* 2.5 times

TABLE 2

E.s.r. parameters for the adduct radicals produced by reaction of tri-n-butylstannyl radicals with various trithiapentalenes at ambient temperatures in benzene

	Pentalene	g	a^{H} [a]	a^{H} [a]	a^{H} [a]	a^{H} [a]
(3)		2.006 80 2.006 60	0.177 0.169	0.225 0.215	0.698 0.690	0.728 0.720
(4)		2.006 91 2.006 54	0.22 0.225	0.22 0.225	0.12 (D) 0.12 (D)	0.12 (D) 0.12 (D)
(5)		2.006 77	~0.03 (D)	~0.03 (D)	0.725	0.725
(6)		2.006 54	0.19	0 24	0 66 (3 H)	0.73
(7)		2.006 59 P [b] 2.006 40 P [b] 2.004 40 [c] P [b]	0.16 0.15 0.28 [c]	0.23 0.23 0.52 [c]	0.76 0.75 0.81 [c]	
(2)		2.006 10	0.18	0.23	0.67 (3 H)	0.75 (3 H)
(8)		2.006 20	~0.03 (D)	~0.03 (D)	0.75 (3 H)	0.75 (3 H)
(9)		2.004 57	0.18 (3 H)	0.18 (3 H)	0.75	0 75
(10)		2.008 39 P [b]	0.17	0.17	~0.03 (≥4 H) [d]	

[a] H.f.s.s in mT. The value given is for 1 H unless otherwise specified. [b] P = persistent radical. [c] At 170 K. [d] Poorly resolved multiplet.

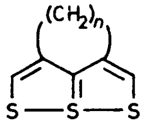
as intense as that of the low g factor radical at ambient temperatures and about twice as intense at 220 K. Two similar radicals were also observed with 2-t-butyl-1,6,6aλ^4-trithiapentalene (7). Again the radical with the higher g factor was present in the higher concentration, by a factor of *ca.* 3.2 at ambient temperatures and *ca.* 4 at 170 K. The spectra of several other $Bu^n_3Sn\cdot$–trithiapentalene adducts listed in Table 2 showed indications of a second radical but definite identification was precluded by extensive overlap with the main spectrum or by the weakness of the signal.

The two adduct radicals formed from (7) at room temperature had relatively intense e.s.r. signals which remained detectable for 2—3 min after the u.v. illumination was cut off. This behaviour contrasts with that of the majority of the adduct radicals observed in this work, which decayed immediately, *i.e.* within the time constant of the spectrometer, on cutting off the light. The decay probably occurs by bimolecular self-reactions and the persistence of the two $Bu^n_3Sn\cdot$–(7) adduct radicals can undoubtedly be attributed to steric factors.[17]

Compound (7) is more soluble than the other trithiapentalenes and this enabled adduct formation to be studied at low temperatures in cyclopropane–benzene as solvent. At 170—200 K a third radical having relatively broad lines (ΔH_{pp} *ca.* 0.12 mT) dominated the e.s.r. spectrum. The two higher temperature adduct radicals, which have quite sharp lines (ΔH_{pp} *ca.* 0.04 mT) like most of the other adduct radicals, were present at low temperatures but were much less persistent than the third radical. A good spectrum of the third radical was obtained by cutting off the light and waiting a few minutes before starting the scan. This low-temperature radical showed h.f.s.s by three non-equivalent hydrogens, just like the two room-temperature radicals. However, it had a lower g factor and one of the h.f.s.s due, presumably, to 2-H or 3-H was significantly larger (0.52 mT) than the values normally found for these hydrogens (*viz.* 0.15—0.24 mT).

The 2,5-bisethoxycarbonyltrithiapentalene (10) adduct with $Bu^n_3Sn\cdot$ is very persistent and has a considerably higher g factor than the adduct radicals formed from any other trithiapentalene.

Tri-n-butylstannyl Radical Addition to Polymethylene-bridged Trithiapentalenes.—The $Bu^n_3Sn\cdot$ adduct with 3,4-dimethyl-1,6,6aλ^4-trithiapentalene (9) and the low-temperature radical from (7) have significantly lower g factors than the adducts formed by trithiapentalene and by the other alkylated trithiapentalenes (see Table 2). In an attempt to throw further light on the structures of the different types of adduct radical the tri-n-butylstannyl radical was generated in the presence of the polymethylene-3,4-bridged trithiapentalenes (11)—(14).

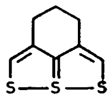
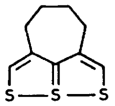
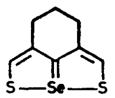


(11) $n = 2$ (12) $n = 3$
(13) $n = 4$ (14) $n = 5$

Compounds (11) and (14) gave weak, poor quality e.s.r. spectra that could not be unequivocally analysed. However, (12) and (13) gave good spectra, the g factors for their Bu$^{n}_{3}$Sn· adducts being similar to those of the Bu$^{n}_{3}$Sn·–(9) adduct. A radical having e.s.r. parameters very similar to that of the radical formed from (12) was obtained with the 6aλ^4-selena analogue of (12), *i.e.* (15). This selenium-containing radical was persistent whereas the Bu$^{n}_{3}$Sn·–(12) adduct was not. The e.s.r. parameters for the adducts derived from (12), (13), and (15) are summarized in Table 3.

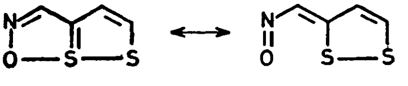
TABLE 3

E.s.r. parameters for the adduct radicals produced by reactions of tri-n-butylstannyl radicals with polymethylene-3,4-bridged trithiapentalenes and a dithiaselenapentalene at ambient temperatures in benzene

	Pentalene	g	a^{H} (2 H) ^{a,b}	a^{H} (4 H) ^{a}	a^{H} ^{a}
(12)		2.004 46	0.78	0.26	~0.04 (2 H)
(13)		2.004 53	0.74	0.19	
(15)		2.004 72 P ^{c}	0.81	0.27	

^{a} H.f.s.s in mT. ^{b} 2- and 5-H. ^{c} P = persistent radical.

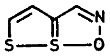
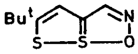
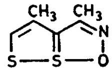
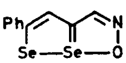
Tri-n-butylstannyl Radical Addition to Some Other Triheterapentalenes.—Well resolved e.s.r. spectra were obtained by reaction of Bu$^{n}_{3}$Sn· radicals with the 1-oxa-6,6aλ^4-dithia-2-azapentalenes (16)—(18). In compounds of this class the S-6a–O bond is long and the nitroso-form (19) is considered to make a significant contribution to the ground state.[18] Our initial hope that the Bu$^{n}_{3}$Sn· radicals would add at the O or N is not supported by the e.s.r. parameters listed in Table 4. These suggest that the adduct radicals formed from (16)—(18) have structures similar to those of radicals derived from trithiapentalenes, *i.e.* radicals formed following the addition of Bu$^{n}_{3}$Sn· to S-1 or -6 (see Discussion section). Furthermore, attack on oxygen is improbable since adduct radicals were not observed with either 1,6-dioxa-6aλ^4-thiapentalene (20) or 3,4-dimethyl-1,6-dioxa-6aλ^4-selena-2,5-diazapentalene (21). In addition, attack at nitrogen, which would yield a nitroxide, is unlikely because the nitrogen h.f.s.s found for Bu$^{n}_{3}$SnN(Ȯ)R radicals are expected to be considerably larger than the values found for the Bu$^{n}_{3}$Sn· adducts with (16)—(18).[19]



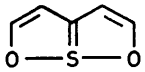
(16) (19)

TABLE 4

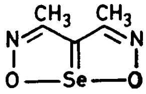
E.s.r. parameters for the adduct radicals produced by reaction of tri-n-butylstannyl radicals with some triheterapentalenes at ambient temperatures in benzene

	Pentalene	g	a^{H} ^{a}	a^{H} ^{a}	a^{H} ^{a}	a^{N}
(16)		2.006 49	0.186	0.186	0.759	0.497
(17)		2.006 35	0.170	0.195		0.536
(18)		2.007 61	0.16 (3 H)	0.16 (3 H)	0.64	0.42
(22)		2.016 9	~0.2	~0.2		~0.6

^{a} H.f.s.s in mT. The value given is for 1 H unless otherwise specified.

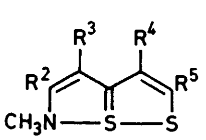


(20)

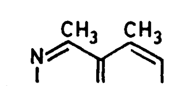


(21)

A radical related to those just described was obtained with 5-phenyl-1-oxa-6,6aλ^4-diselena-2-azapentalene (22) (see Table 4). The g factor of this adduct radical is exceptionally large and the e.s.r. lines are very broad (ΔH_{pp} *ca.* 0.2 mT). Both these phenomena imply that this adduct radical has an appreciable spin on selenium,[20–24] the spin–orbit coupling constant for which is 1 688 cm^{-1} *versus* 382 cm^{-1} for sulphur. It is clear that the substitution of S-1 by selenium has a much greater influence on the g factor of the adduct radical than does a similar substitution at S-6a [*cf.* the Bu$^{n}_{3}$Sn· adducts with (12) and (15) in Table 3].



(23) R^2 = R^5 = CH$_3$, R^3 = R^4 = H
(24) R^2 = R^5 = H, R^3 = R^4 = CH$_3$
(25) R^2 = R^3 = R^4 = H, R^5 = Bu^t

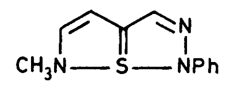


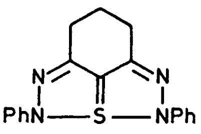
(26)

Reaction of Bu$^{n}_{3}$Sn· radicals with the 6,6aλ^4-dithia-1-azapentalenes (23) and (24) gave e.s.r. spectra which were too weak to analyse. However, (25) gave a strong spectrum showing only *two* non-equivalent hydrogen atoms: g

2.0045, a^{H}(1 H) 2.35 mT, a^{H}(1 H) 0.24 mT. The identity of this radical will not be speculated upon.

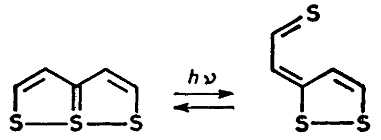
Finally, reaction of $\text{Bu}^{n}{}_{3}\text{Sn}\cdot$ with (26) gave a strong e.s.r. spectrum which was, unfortunately, too complex to analyse. No spectra were obtained with the 1,6-diaza-compounds (27) and (28).


(27)


(28)

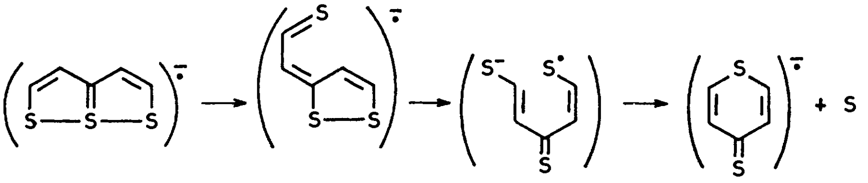
DISCUSSION

The lowest unoccupied molecular orbital (LUMO) of trithiapentalenes is strongly antibonding between the sulphur atoms.[15,25] Fission of the S-1–S-6a bond is therefore a facile process. For example, upon photolysis trithiapentalenes are transformed into the isomeric *trans*-1,2-dithia-3-ylidene-thiones [*e.g.* (29)]. These compounds rapidly decay back to their parent trithiapentalenes at ambient temperatures.[26,27]



(3) (29)

Similarly, at 213 K the radical anions of simple trithiapentalenes [*e.g.* $(2^{\cdot-})$ and $(3^{\cdot-})$] convert, probably *via* the radical anions of the corresponding 1,2-dithia-1-ylidene-thiones [*e.g.* $(29^{\cdot-})$], into the radical anions of 4-thiapyran-4-thiones [*e.g.* $(30^{\cdot-})$] with a loss of sulphur.[15]


$(3^{\cdot-})$ $(29^{\cdot-})$ $(30^{\cdot-})$

g 2·0080

a^{H}(2H) 0·173 mT

a^{H}(2H) 0·672 mT

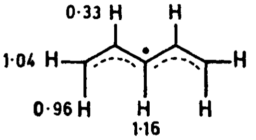
g 2·0068

a^{H}(2H) 0·207 mT

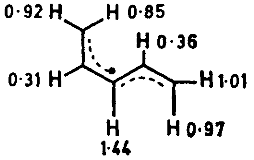
a^{H}(2H) 0·635 mT

This process did not occur (for obvious reasons) with the radical anions of 3,4-trimethylene-bridged trithiapentalenes.[15]

The e.s.r. parameters for all the radicals listed in Tables 1—4 are consistent with their being heteroatom-substituted pentadienyl radicals with appreciable delocalization of unpaired spin onto at least some of the heteroatoms. The parent radical, pentadienyl, exists in two planar conformations,[28-30] a lower energy (more stabilized) *W* structure (31) and a higher energy *Z* form (32). Both conformers have the same *g* factor (2.002 64)[28,30] but they have slightly different h.f.s.s (given in mT on the structures).[30] It should be added that the conformers of substituted pentadienyl radicals do not necessarily have equal *g* factors, *e.g.*[30] for the 3-trimethylsiloxy-substituted radicals, *g* is 2.002 76 for the *W* conformer and 2.002 79 for the *Z* conformer.

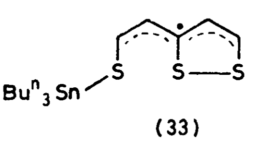


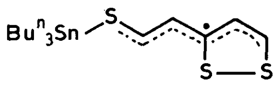
(31)

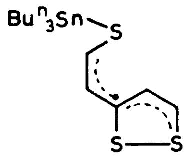


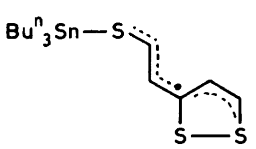
(32)

On the basis of the above information four planar structures (33)—(36) can be suggested for the adduct radicals formed by reaction of $\text{Bu}^{n}{}_{3}\text{Sn}\cdot$ (and other radicals) with the trithiapentalenes (2)—(10). Only the first two of these structures, (33) and (34), could apply to the adduct radicals derived from the polymethylene-3,4-bridged trithiapentalenes (12) and (13).


(33)

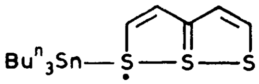

(34)


(35)


(36)

The pentadienyl radical which is first formed must have conformation (33). It will be formed *via* a bimolecular homolytic substitution ($S_{H}2$) reaction[31] of tri-n-butylstannyl radicals at S-1. The cleavage of the S–S bonds of dialkyl and diphenyl disulphides by $\text{Bu}^{n}{}_{3}\text{Sn}\cdot$ radicals is known to be a relatively fast reaction.[31,32] Though many types of sulphuranyl radical have been identified by e.s.r. spectroscopy[33-39] we were unsuccessful in all our attempts to observe such species, *e.g.* (37), in these reactions.

Bond rotation in pentadienyl and some substituted pentadienyls occurs rapidly on the e.s.r. time scale at ambient temperatures.[30] We therefore propose that the adduct radicals derived from the polymethylene-3,4-bridged trithiapentalenes (12) and (13) adopt conformations of type (34) since these will be sterically less congested than conformations of type (33). On the basis of the similarity in *g* factors we further propose that the adduct radical from 3,4-dimethyltrithiapentalene adopts conformations of type (34). In fact, molecular models suggest that (34) will be slightly less hindered than (35) or (36) for this adduct radical. Of course, in this case as in others, strain induced by the substituents may be relieved by a small distortion of the adduct radical from a strictly planar geometry.



(37)

For the adduct radicals obtained from all the other trithiapentalenes at room temperature we suggest that the two conformers (35) and (36) are in equilibrium (on the e.s.r. time scale) though only one conformer may be present in detectable concentrations. Conformer (36) is probably the more stable conformer for the adduct radicals derived from trithiapentalene (3) and the deuterium-substituted trithiapentalenes (4) and (5). We therefore assign conformation (36) to the radicals in each pair with the higher *g* factor and conformation (35) to the radicals with the lower *g* factor. For the adducts from the 2,5-dimethyltrithiapentalenes (2) and (8) conformer (35) should be the less crowded. It is noteworthy that the *g* factors for the only radicals observed with these compounds are relatively low.

There are eight possible structures for the adduct radicals formed from 2-methyl- (6) and 2-t-butyl-trithiapentalene (7) at room temperature. The fact that (7) gives two adduct radicals [presumably (35) and (36)] does suggest that the t-butyl group is on the unopened ring. This is consistent with the expected preference for attack at S-6 because it will be less hindered than S-1. For the adduct radical formed from $\mathrm{Bu^n_3Sn\cdot}$ and (7) at low temperatures we would suggest that bond rotation is ' frozen ' on the e.s.r. time scale (*cf.* pentadienyl) [28-30] and that the observed radical has the ' initial ' structure (33), again with the t-butyl group on the unopened ring. Some distortion from planarity may be the cause of the relatively large 3- or 4-H h.f.s. of 0.52 mT referred to earlier. The most probable conformations of most of the remaining adduct radicals can be deduced by following the same general rules adumbrated above.

Finally, we note that since $\mathrm{Bu^n_3Sn\cdot}$ and the other radicals which were used to form the trithiapentalene adducts were generated photochemically there could be some formation of (35) and (36) by direct addition to the thione sulphur of the photoisomerized *trans*-1,2-dithia-3-ylidene-thione (29). We believe that this is a relatively unimportant process for two reasons. First, the ready formation of adduct radicals from the polymethylene-3,4-bridged trithiapentalenes (12) and (13) indicates the $\mathrm{Bu^n_3Sn\cdot}$ radicals can add to trithiapentalenes with cleavage of the S-1–S-6a bond. Secondly, the thermal generation of triethylsilyl radicals (from triethylsilane and di-t-butyl hyponitrite without a solvent at 324 K) in the presence of (7) was found to yield radicals virtually indistinguishable from those produced using photolytically generated tri-n-butylstannyl radicals.

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