

Reaction of Free Radicals with 1,6,6a λ^4 -Trithiapentalenes

By KEITH U. INGOLD,† DAVID H. REID, and JOHN C. WALTON*

(*Department of Chemistry, The University, St. Andrews, Fife KY16 9ST, and*

†N.R.C. Canada, Division of Chemistry, Ottawa, Canada K1A 0R6)

Summary Free radicals centred on tin and silicon react with 1,6,6a λ^4 -trithiapentalenes (**1**) at the 1(6)-position to give substituted pentadienyl radicals (**3**) which have been studied by e.s.r. spectroscopy.

STUDIES of the reactivity of 1,6,6a λ^4 -trithiapentalenes (**1**) have mainly been confined to reactions with electrophiles.¹ The essential step in this process is addition of the electrophile at position 3 or 4 of the substrate with accompanying

breaking of the S-1-S-6a or S-6-S-6a bond and formation of a stable 6 π -electron monocyclic cation.² Recent work³ suggests that these reactions may be accompanied by, or preceded by, electrophilic attack at a heteroatom (S-1 or S-6).

Apart from an e.s.r. study of electrochemically generated radical anions of 1,6,6a λ^4 -trithiapentalenes (**1**)⁴ no attention has been given to homolytic reactions of triheterapentalenes. We have generated trimethylsilyl and tri-n-butyltin radicals

in the presence of (1) and studied the resulting intermediates by means of e.s.r. spectroscopy. Photolysis of a mixture of 2,5-dimethyl-1,6,6a λ^4 -trithiapentalene (1, R¹ = R² = Me), di-*t*-butyl peroxide, and trimethylsilane in a benzene solution gave rise to a radical whose spectrum is shown in the Figure. No e.s.r. signal was obtained in the

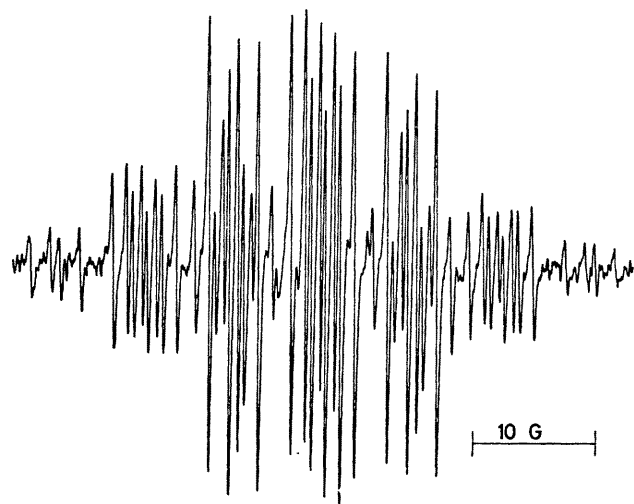
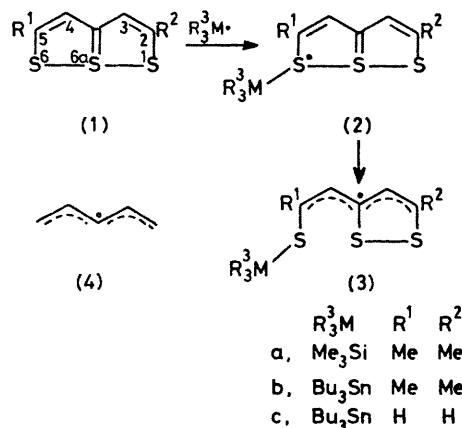


FIGURE. E.s.r. spectrum of the radical (3a) in benzene solution at 9.14 GHz.

absence of Bu^tOObu^t and Me₃SiH or in the absence of Bu^tOObu^t, indicating that the radical is not a product of the direct photolysis of (1, R¹ = R² = Me) but arises from attack of trimethylsilyl radicals on the substrate.

None of these radicals showed any persistence on cutting off the u.v. irradiation, and the e.s.r. signal intensities decreased appreciably during the time of irradiation (*ca.* 30 min). We attribute the e.s.r. spectra to trithiapentadienyl radicals (3) which are formed either directly by concerted attack at S-1(6) and breaking of the S-1-S-6a bond, or *via* sulphuranyl radicals (2) as intermediates.



The overall process can be classified as a homolytic substitution reaction, S_H2, at sulphur. Attempts to detect the sulphuranyl radical (2) at lower temperatures were unsuccessful. The h.f.s. of the trithiapentadienyl radicals (3) are significantly lower than those of the pentadienyl radical (4) itself, and the *g*-factor is considerably higher,⁵ indicating significant delocalization of unpaired spin onto sulphur (see Table). The h.f.s. from the radical anion of (1; R¹ = R² = H)⁴ are slightly smaller in magnitude than those of the neutral radicals reported here and, of course,

TABLE. E.s.r. parameters of trithiapentadienyl radicals.

Radical	Temp./K	<i>g</i> -Factor	h.f.s./G		
(3a)	293	2.00609	1.69 (1H),	2.40 (1H),	6.75 (3H), 8.00 (3H)
(3b)	290	2.00610	1.75 (1H),	2.33 (1H),	6.74 (3H), 7.50 (3H)
(3c)	294	2.00680	1.77 (1H),	2.25 (1H),	6.98 (1H), 7.28 (1H)
(4) ^a	233	2.00264	3.22 (2H),	9.62 (2H),	10.40 (2H), 11.58 (1H)

^a See ref. 5.

The spectrum can be analysed in terms of two non-equivalent methyl groups and two non-equivalent hydrogen atoms; the e.s.r. parameters are given in the Table. Tri-*n*-butyltin radicals, generated by photolysis of hexa-*n*-butylditin, also reacted with (1, R¹ = R² = Me) to give a radical whose e.s.r. spectrum was very similar in appearance, but with slightly different *g*-factor and hyperfine splittings (h.f.s.). 1,6,6a λ^4 -Trithiapentalene (1, R¹ = R² = H) itself reacted with tri-*n*-butyltin radicals to give a radical showing h.f.s. by four non-equivalent hydrogens.

correspond to two equivalent pairs of hydrogen atoms. There appears to be slightly more spin density on sulphur in the radical anions. Radical attack on triheterapentalenes appears to be analogous to the recently discovered electrophilic attack at the heteroatom.³

Preliminary investigations indicate that other types of 1,6,6a λ^4 -triheterapentalenes also form radicals in analogous reaction systems.

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