Homolytic Ring-opening of Thietans by Oxygen-centred Radicals: S_H2 Attack at Sulphur

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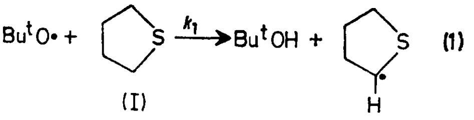
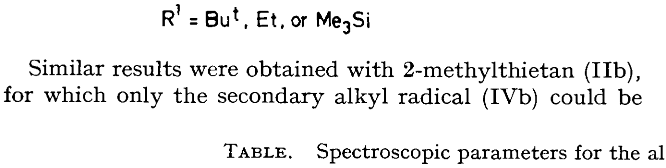
Summary t-Butoxyl, ethoxyl, or trimethylsiloxyl radicals attack at sulphur in thietan or 2-methylthietan to bring about rapid homolytic ring-opening.

The reactions of t-butoxyl radicals with acyclic dialkyl sulphides, thiolan (I) [reaction (1)], or thian (thiacyclohexane) in non-aqueous solvents have been shown by e.s.r. spectroscopy to involve abstraction of hydrogen from a C–H bond adjacent to sulphur.[1] Norman and his co-workers[2] have examined the reactions of hydroxyl radicals with a variety of sulphur-containing compounds, including (I),[2b] in aqueous solution and have found contrasting results. Under these conditions (I) gives rise to the e.s.r. spectra of the cation radical $(\overline{CH_2[CH_2]_3S}\text{-}\overline{S[CH_2]_3CH_2})^{+\cdot}$ and of the radical $\cdot\overline{CH[CH_2]_2SCH_2}$.[2b]



(I)

Using e.s.r. spectroscopy we have examined the interaction of thietans with photochemically-generated oxygen-centred radicals in cyclopropane solvent and have found that in this case attack occurs at sulphur to bring about ring-opening. Irradiation of di-t-butyl, diethyl, or bis(trimethylsilyl) peroxides in the presence of thietan (IIa), whilst the sample was in the spectrometer cavity, gave rise to strong spectra assigned to the alkyl radicals (IVa; $R^1 = Bu^t$, Et, or Me_3Si).



(IIa); $R^2 = H$ (III) (IVa); $R^2 = H$

(IIb); $R^2 = Me$ (IVb); $R^2 = Me$

$R^1 = Bu^t$, Et, or Me_3Si

Similar results were obtained with 2-methylthietan (IIb), for which only the secondary alkyl radical (IVb) could be detected. The spectroscopic parameters for (IV; $R^1 = Bu^t$) are given in the Table, and the spectrum of (IVa; $R^1 = Bu^t$) is shown in the Figure.

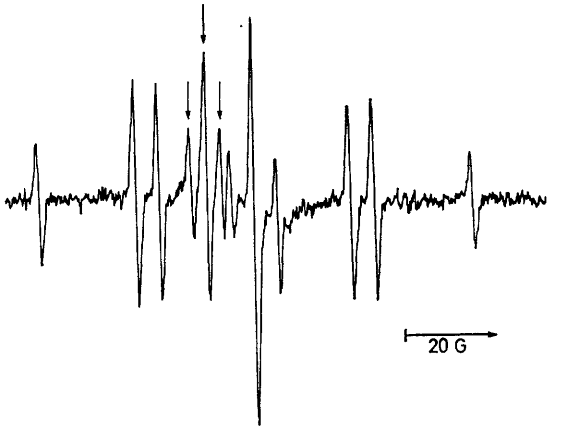


Figure. E.s.r. spectrum of the radical $Bu^tOSCH_2CH_2\dot{C}H_2$, generated by photolysis of a mixture containing di-t-butyl peroxide, thietan, and cyclopropane (3 : 1 : 1 by volume) at 230 K. The arrows mark the positions of the triplet, assigned to a sulphinyl radical, which is very intense at lower temperatures.

The 4-membered ring in thietan is appreciably strained (strain energy[3] 82·4 kJ mol^{-1}), and comparison of the reactivity of (IIa) with that of (I) (strain energy[2] 8·4 kJ mol^{-1}) is particularly relevant. The rate constants for the reactions (1) and (2; $R^1 = Bu^t$, $R^2 = H$) were determined by causing (I) or (IIa) to compete with tri-isobutylborane[4] for t-butoxyl radicals, whence $k_1 = 2 \times 10^6$ l mol^{-1} s^{-1} and k_2 ($R^1 = Bu^t$, $R^2 = H$) $= 6 \times 10^6$ l mol^{-1} s^{-1} at 243 K were determined.

In contrast, both thietan and thiolan react with pentafluorophenyl radicals (generated by photolysis of C_6F_5I in the presence of $Me_3SnSnMe_3$) to undergo exclusively ring-opening, as judged by e.s.r. spectroscopy. Thus if ring-opening of (I) were to compete with reaction (1) to any appreciable extent it should have been detectable by e.s.r. spectroscopy. It follows that the sulphur centre in thietan is very much more reactive than that in thiolan towards attack by t-butoxyl radicals, and this difference may be attributed to the relief of ring strain on passing from (II) to the transient intermediate sulphuranyl radical (III).†

Table. Spectroscopic parameters for the alkyl radicals (IV; $R^1 = Bu^t$) in cyclopropane.

Radical	Temp./K	*g*-Factor	Hyperfine splittings/G $a(H_\alpha)$	 $a(H_\beta)$	 $a(H_\gamma)$
$Bu^tOS[CH_2]_2\dot{C}H_2$	208	2·0029	21·9 (2H)	27·5 (2H)	0·6 (2H)
$Bu^tOS[CH_2]_2\dot{C}HMe$	228	2·0028	21·4 (1H)	24·5 (5H)	0·7 (2H)

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† The adduct (III) may be a transition state, although analogies with phosphoranyl radical chemistry (R. W. Dennis and B. P. Roberts, *J.C.S. Perkin II*, 1975, 140) suggest that the sulphuranyl radical will represent a potential energy minimum [in (III), when $R^2 = Me$, the methyl group may alternatively be attached to the apical carbon atom].

At low temperatures (<230 K) an intense e.s.r. signal, ascribed to a sulphur-centred radical (g = 2·0098) showing a 1:2:1 triplet splitting [a(H) = 3·5 G at 208 K], was detected alongside that of (IVa) during the photolysis of di-t-butyl peroxide in the presence of thietan (see Figure). A similar species was detected using bis(trimethylsilyl) peroxide, but not with diethyl peroxide. We attribute this signal to a sulphinyl-type radical ($\mathrm{RCH_2\dot{S}{=}O}$) rather than to the sulphuranyl radical (III), for the following reasons. At 166 K, when the photolysis was interrupted, the radical (IVa; $\mathrm{R^1 = Bu^t}$) decayed to 5% of its original concentration within 15 ms, during which time the sulphur-centred radical had decayed by only 9%: thus the latter radical cannot be the precursor of (IVa). The g-factor of the sulphur-centred radical is close to that obtained previously for species thought to be sulphinyl radicals (2·00965 for $\mathrm{Me\dot{S}O}$,[5a] 2·0106 for $\mathrm{Bu^t\dot{S}O}$[5b]) and somewhat higher than values obtained for sulphuranyl radicals[6] (2·005—2·009).

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