The Radical-anion of Thioxanthen *SS*-Dioxide and its 9-Substituted Derivatives

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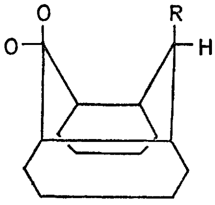
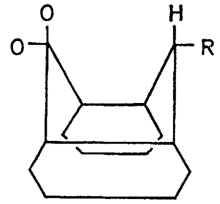
The radical-anion of thioxanthen *SS*-dioxide is non-planar. The spectra of the 9-methyl and 9-phenyl derivatives show that in these radical-anions the substituent, contrary to the situation in the neutral parent, is in the boat-equatorial position. These radicals are unstable and the solutions, at low temperature in contact with potassium give fluorene or biphenyl radical-anions or their derivatives.

9-SUBSTITUTED derivatives of thioxanthen *SS*-dioxide can in principal exist either with the substituent in the boat-axial or boat-equatorial configurations (I) or (II). N.m.r. studies have indicated[1] that (I) is the usually adopted form and this structure has been confirmed for the 9-isobutyl derivative by *X*-ray crystallography.[2]



(I)



(II)

Aromatic sulphones have been shown to form radical-anions in which the spin density is largely concentrated on the *ortho-* and *para*-positions of the benzene ring.[3] This fact together with the well known angular dependence of the coupling constant of methyl protons adjacent to a π-type radical[4] indicates that whereas a radical-anion in form (I) would exhibit only a small coupling constant from the remaining proton in the 9-position, in form (II) an appreciable coupling constant of the order of 1.0 mT should be apparent thus making straightforward the differentiation between the two forms. We report here the e.s.r. spectra of a number of such radical-anions together with those of various decomposition products.

EXPERIMENTAL

All sulphones were prepared by the usual oxidation of the corresponding thioxanthens by 30% hydrogen peroxide in acetic acid.[5] Thioxanthen was a commercial product. 9-Methyl-,[6] 9-phenyl-,[6] 9,9-dimethyl-,[1] 9-methyl-9-phenyl-,[7] and 2,7-dimethyl-9-phenyl-thioxanthen[8] were prepared by published methods. 9-Perdeuteriomethyl and 9-perdeuteriophenyl derivatives were prepared using trideuteriomethyl iodide and pentadeuteriobromobenzene respectively as the source of the appropriate Grignard reagent.

Dimethoxyethane was dried over and distilled from lithium aluminium hydride and the radicals were prepared by reaction at $-80°$ with a bright mirror of potassium under nitrogen in a sealed tube. E.s.r. spectra were measured on a JEOL ME/X1 spectrometer using 100 KHz field modulation. The final analysis of spectra was based on simulation using the Q.C.P.E. program 160.

The identity of all compounds was checked by the measurement of their ^{1}H n.m.r. spectra on Perkin-Elmer R12 (60 MHz) and Varian XL100 (100 MHz) spectrometers.

RESULTS AND DISCUSSION

(A) *Radical-anions of Sulphones*.—The e.s.r. spectrum of the radical-anion of thioxanthen *SS*-dioxide is shown in the Figure and the e.s.r. parameters of this and of its related radical-anions are shown in the Table. The assignments to the ring protons are made on the basis of the results for diphenyl sulphone[3] where the spin density in the *para-* is about twice that in the *ortho*-position while that of the *meta*-position is very small. Hence the assignment of the small coupling to either the 1,8- or 3,6-positions is completely uncertain.

The spectrum of the thioxanthen *SS*-dioxide radical-anion itself shows that, on the e.s.r. time-scale, the molecule is not inverting rapidly between the two possible conformers since the two methylene protons are not equivalent. The n.m.r. spectrum however, measured in solution in CD_2Cl_2, shows equivalent methylene protons (δ 4.24) down to $-80°$ while the e.s.r. spectrum shows inequivalent methylene protons up to $-30°$, at which temperature decomposition takes place. Of course the time-scales of the n.m.r. and e.s.r. experiments are different so these differences may not reflect any very great difference in the barriers to inversion in the neutral molecule and radical-anion respectively.

The relative values of the two methylene coupling constants show that the one with the low coupling of 0.057 mT must lie approximately in the intersection of the planes of the benzene rings and hence that the dihedral angle between the other C–C–H fragment and the corresponding benzene ring is *ca.* 60°. For the neutral molecule a recent *X*-ray structure determination[9] showed that one CH bond has a dihedral angle of 76° while the other lies 15° from the molecular plane. With these angles the coupling constants of the two methylene protons would be approximately in the ratio $\cos^2 14°/\cos^2 75° = 14$ compared with the

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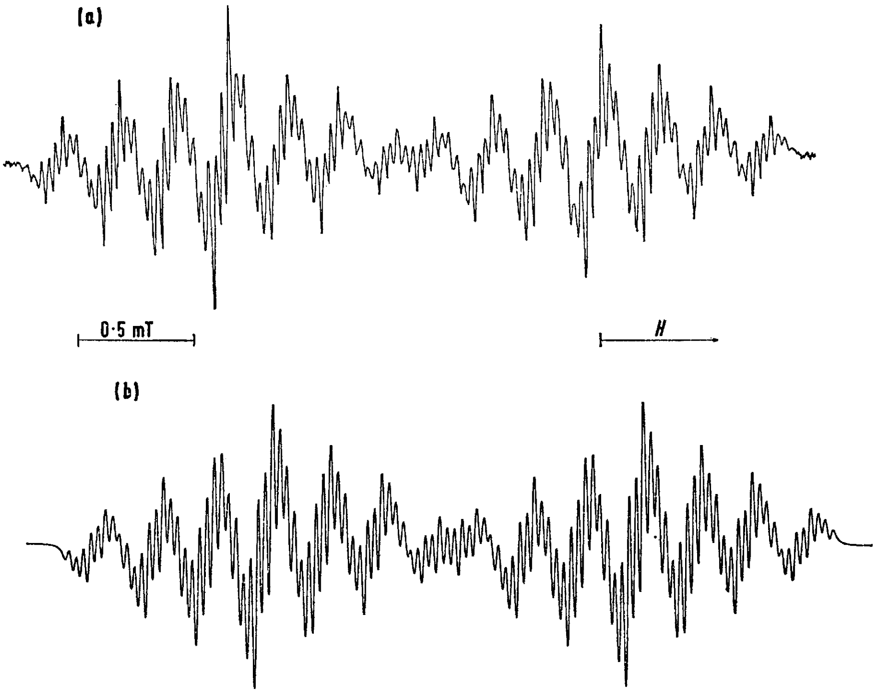
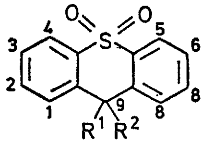
experimental ratio of 28. The dihedral angles 60° and 0° together with Whiffen's modification[10] of the McConnell equation for bridging methylene groups[4] indicate that this coupling constant corresponds to a spin density at the neighbouring carbon atom of *ca.* 0.1, in excellent agreement with the *ortho*-ring-proton coupling (0.241 mT) in diphenyl sulphone[3] and with the coupling of 0.250 mT assigned to the 4,5-protons in the present molecule.



(a) E.s.r. spectrum of the thioxanthen *SS*-dioxide radical-anion; (b) computer simulation based on the coupling constants given in the Table

Coupling constants (mT) of thioxanthen *SS*-dioxide and several of its derivatives



Radical-anion	R^1	R^2	$a_{1,8}$	$a_{2,7}$	$a_{3,6}$	$a_{4,5}$	a_{R1}	a_{R2}
Thioxanthen *SS*-dioxide	H	H	0.033	0.476	0.065	0.253	1.621	0.057
9-Methylthioxanthen *SS*-dioxide	H	CH_3	0.022	0.460	0.062	0.225	1.270	0.022
9-Perdeuteriomethylthioxanthen *SS*-dioxide	H	CD_3	0.022	0.460	0.062	0.225	1.270	0.000
9,9-Dimethylthioxanthen *SS*-dioxide	CH_3	CH_3	0.030	0.454	0.064	0.236	0.030	<0.010
*9,9-Dideuteriomethylthioxanthen *SS*-dioxide	CD_3	CD_3	0.030	0.454	0.064	0.236	<0.005	<0.005
9-Phenylthioxanthen *SS*-dioxide	H	C_6H_5	<0.020	0.470	0.079	0.238	1.564	<0.020
9-Methyl-9-phenylthioxanthen *SS*-dioxide	CH_3	C_6H_5	<0.020	0.445	0.077	0.208	<0.013	<0.020

* $g = 2.0028 \pm 0.0001$.

The most important conclusion from the high methylene coupling constant is however that the sulphone group conjugates *via* an orbital which is symmetric with respect to reflection in the SO_2 plane, for otherwise the coefficients of the 11- and 12-carbon atoms in the molecular orbital containing the unpaired electron would be of opposite sign and hence[10] would give rise to a very small value of the coupling constant of the methylene protons. This result is in agreement with the previous hypothesis of Gerdil and Lucken.[3]

The persistence of a large coupling constant in the 9-monosubstituted derivatives shows unambiguously that the substituent is in the boat-equatorial position (II). Thus the radical-anions and neutral molecules have different conformations.

Both 9-methyl- and 9,9-dimethyl-thioxanthen *SS*-dioxide radical-anions show small couplings from the three protons of *one* methyl group. Thus a methyl group in the boat-axial position gives a coupling constant <0.01 mT. Unlike the radical-anions of 9-phenylxanthene no coupling is present from the phenyl group of 9-phenylthioxanthen *SS*-dioxide radical-anion.

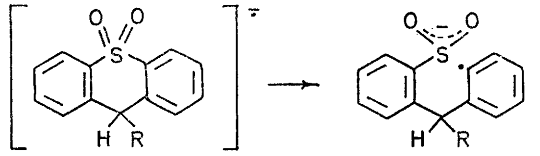
(B) *Decomposition Products*.—Unless great care is taken to exclude all traces of oxygen from the system, including oxygen in the form of slight oxidation of the potassium mirror, attempts to observe the radical-anion of thioxanthen *SS*-dioxide yield the radical-anion of thioxanthone *SS*-dioxide.[11] This spectrum shows, as is usual for ketones, a temperature-dependent splitting from ^{39}K varying from 0.009 at −70 to 0.048 mT at 0°.

If contact with the potassium mirror is maintained at −40°, some 40° higher than that appropriate for the formation of the radical-anion of thioxanthen *SS*-dioxide, then the radical-anion of fluorene [12] is observed. Similarly the dioxides of 9-methyl- and 9,9-dimethylthioxanthen give 9-methylfluorene [13] and 9,9-dimethylfluorene radical-anions respectively. This last radical, which was identified by comparison with the radical-anion obtained directly from 9,9-dimethylfluorene, displays as expected coupling constants arising from four pairs of equivalent protons with the values 0.522, 0.402, 0.091, and 0.091 mT which, by analogy with the assignments for the fluorene radical-anion,[12] are assigned to the 2,7-, 4,5-, 1,8-, and 3,6-protons respectively. Under higher gain satellites presumably arising from ^{13}C may be observed, which, on the basis of their relative intensities are assigned to two equivalent ^{13}C atoms with a coupling constant 0.566 mT and one ^{13}C atom with a coupling of 0.500 mT. We may unambiguously assign this latter value to the carbon atom in position 9 while the former coupling is most likely to arise from the carbon atom in position 2. 9-Methyl-9-phenylthioxanthen *SS*-dioxide gives a spectrum which is almost identical with this, coupling constants 0.535, 0.400, 0.090, and 0.090 mT, which presumably arises from the 9-methyl-9-phenylfluorene radical-anion. This radical was also observed as a product of the reaction between 9-methyl-9-phenylxanthen and potassium.[14]

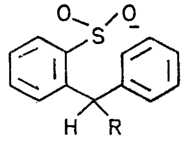
9-Phenylthioxanthen *SS*-dioxide radical-anion under the above conditions shows a spectrum which clearly arises from two separate species. If the temperature is allowed to rise to 10°, in contact with metallic potassium, a spectrum identified as that of the 9-phenylfluorenyl radical-dianion is obtained.[13]

If the initial decomposition of 9-phenylthioxanthen *SS*-dioxide is allowed to take place at −20° the spectrum of the biphenyl radical-anion is observed.[15] If 9-perdeuteriophenylthioxanthen *SS*-dioxide is employed then a spectrum corresponding to the radical-anion of a 2 : 1 mixture of biphenyl and 2,3,4,5,6-pentadeuteriobiphenyl is observed. This behaviour should be contrasted with that we have observed with 9-pentadeuteriophenylxanthen where only the radical-anion of the pentadeuteriated species was observed.[14]

The lines of the spectrum of the decomposition product of 2,7-dimethyl-9-phenylthioxanthen *SS*-dioxide are large but the spectrum is apparently identical with the radical-anion of either 3-methyl- or 3,3′-dimethyl-biphenyl.[16] (The uncertainty arises from the fact that the coupling from the methyl group in the 3-position is less than the line-width.) No biphenyl-type decomposition products were observed with any of the other thioxanthen *SS*-dioxides studied here. In the absence of further and more detailed studies no definite interpretation of the above results can be given. However one possible explanation is that scission of the carbon–sulphur bond takes place in two stages with the initial formation of the anion (III). At low temperatures the adjacent ' phenyl ' radical attacks the sulphur-bearing carbon atom and eliminates SO_2 to form a fluorene but at higher temperatures it picks up a hydrogen atom from the solvent to yield the neutral species (IV).



(III)



(IV)

It may then be supposed that the biphenyl radical-anion is a product of the action of potassium on what amounts to triphenylmethane although the observation of the formation of undeuteriated biphenyl from the decomposition of 9-pentadeuteriophenylxanthen *SS*-dioxide indicates that removal of the SO_2 group occurs before the carbon–carbon bond is attached. Furthermore the absence of a 4-methylbiphenyl radical-anion, easily recognisable in view of the high spin density in the 4-position, from 2,7-dimethyl-9-phenylxanthen *SS*-dioxide shows that the removal of the SO_2 group probably takes place independently of the formation of biphenyl. Cleavage of the carbon–carbon bond of triphenylmethane by potassium in ether solvents has previously been reported [17,18] although biphenyl was not reported as a product. However in an e.s.r. study such as this it is always possible that the radical detected be only a

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by-product while the main reaction yields products, for example benzene, which do not readily form radical-anions.

Conclusions.—Like the parent molecule the radical-anion of thioxanthen *SS*-dioxide is non-planar and inversion of this radical is slow on the e.s.r. time-scale. Unlike the parent molecules however the substituent in the 9-position adopts the boat-equatorial conformation.

We thank the Swiss National Research Fund for their support of this work.

[5/1138 *Received*, 10*th June*, 1975]