Tetrahedron Letters,Vol.24,No.22,pp 2299-2302,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain

ESR IDENTIFICATION AND CONFORMATION OF A PERSISTENT FREE RADICAL IN THE (4+2)-CYCLOADDITION REACTION OF XANTHENETHIONE WITH PHENYLALLENE

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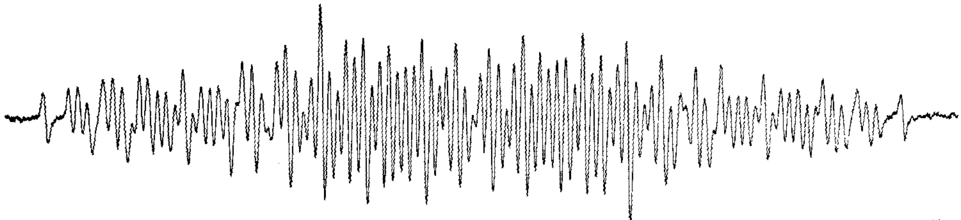
Abstract: In the (4+2)-cycloaddition reaction of xanthenethione 1 with phenylallene 2 to give amongst other, thiopyran derivative 6 and thiopyran 7 as the isolable product, a ketyl radical has been found and identified by ESR spectroscopy. Its conformation and role in the formation of compound 6 are discussed.

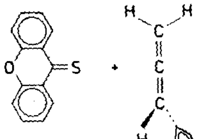
In our recent paper [1] on the thermal reaction of xanthenethione 1 to substituted allenes, e.g. phenylallene 2, we reported the observation of a strong ESR signal. This 1,4-biradical intermediated $[_{\pi}2_{s}+_{\pi}2_{s}+_{\pi}2_{s}]$ cycloaddition reaction gives rise to (2+2)-cycladducts 3 and 4 and (4+2)-cycloadducts 5 and 6 [1,10] (see Schemes I and II).

Computer processing[2] of the observed ESR-spectrum has shown that the hyperfine structure arises from interaction of the unpaired spin with nine different protons which have the following splitting constants a_2 = 0.734 G, a_3 = 3.414 G, a_4 = 0.580 G, a_5 = 0.630 G, a_6 = 3.616 G, a_7 = 0.784 G, a_8 = 3.146 G, a_A = 1.654 G and 0.440 G (± 0.004 G) (anticipating the numbering as been taken from Scheme I 6 *rad*). The simulated spectrum based on these splitting constants matches the experimental spectrum in all details (Fig. I).

Fig. I

Experimental spectrum





1 2

Simulated spectrum

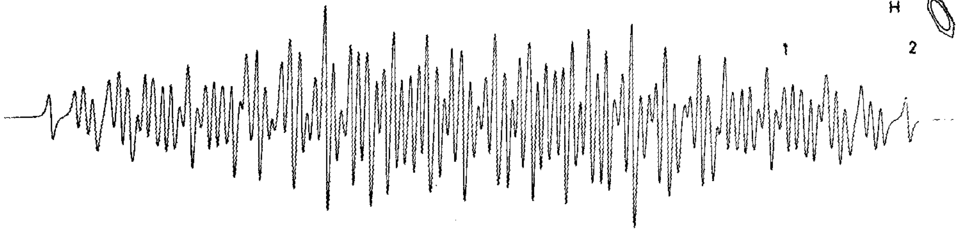
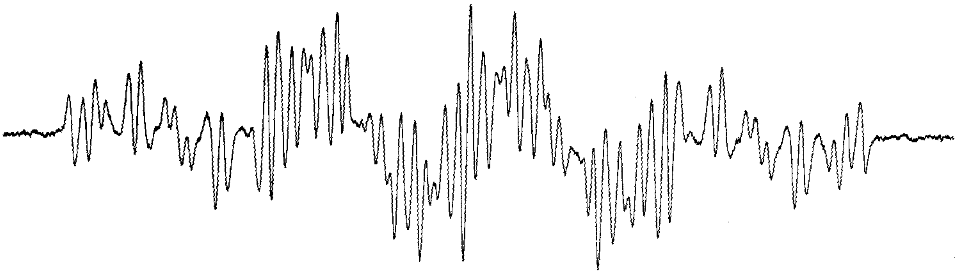
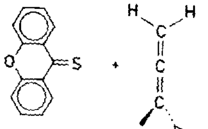


Fig. II

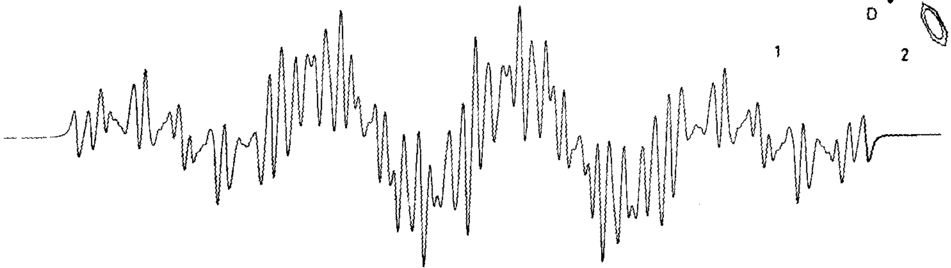
Experimental spectrum





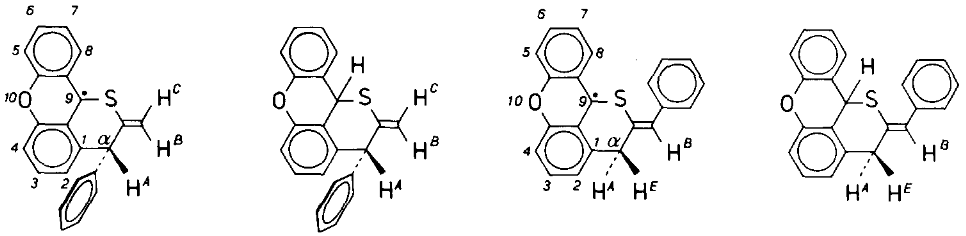
1 2

Simulated spectrum



Comparison of the g-value (2.0033) and the splitting constants with those of other xanthenyl radicals [3,4,5] shows that we can assign seven splitting constants to a xanthenyl radical that is substituted at the 9- and 1-position. The a_A = 1.654 G splitting constant could be assigned to the α-hydrogen of the phenylallene moiety. When we used deuterated phenylallene ($PhCD=C=CH_2$) in the reaction with xanthenethione, this splitting constant disappeared and a triplet splitting constant (1:1:1) a = 0.246 G appeared (a_D/a_H = 0.15). Again the simulated spectrum reproduces the experimental spectrum excellently (Fig. II). We therefore conclude that the phenylallene moiety is involved in the free radical that produces the ESR signal. When we used some *ortho*-, *meta*-, or *para*-substituted phenylallenes the signal did not change, thus the aromatic protons of the phenylallene moiety do not interact with the free electron system. The remaining splitting constant must be assigned to one of the methylene protons. We conclude that 5 *rad* or 6 *rad* are the most probable structures.

Scheme I



6 *rad* 6 5 *rad* 5

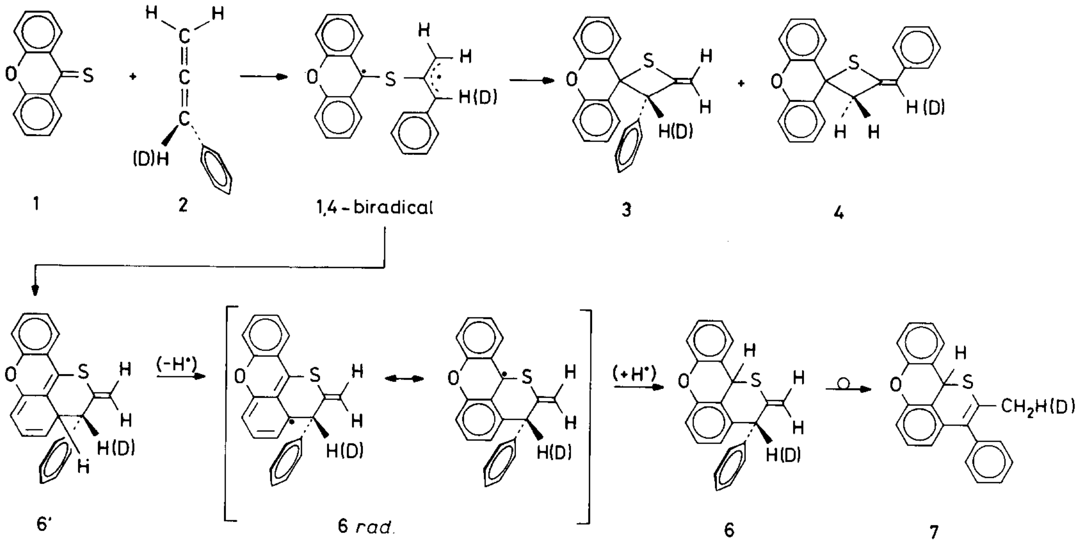
The splitting constant for a proton at the C(α)-position is given by a $a_0 \cos^2\Theta$, where Θ is the torsion angle between the 2 p_z orbital at C(1) and the C(1)-C(α)-H plane and a_0 for a benzylic proton can be estimated to be 6 to 7 Gauss [6,7]. It is clear that for structure 5 *rad* there is no conformation for the two α-protons (H^A, H^E) that will give splitting constants of 0.440 G and 0.0 Gauss.

We conclude therefore that we are dealing with 6 *rad*. The splitting constant of 1.654 G for the C(α)-proton shows that Θ is approximately 60°, which means that the phenylgroup is in the position of minimal steric hindrance with the xanthene moiety. (Dreiding and SASM-models). The magnetic non-equivalence of the two olefinic protons is in agreement with the splitting constants found for the but-3-en-1-yl radical $H_2C=CH-CH_2-\dot{C}H_2$ [8,9].

Structure 6 *rad* plays a role in the formation of the (4+2)-cycloadduct 6 (see Scheme II). The formation of 6 *rad* from 6 can be excluded, because at the commencement of the reaction, measurement of the ESR signal gave maximum intensity. When phenylallene is in excess over xanthenethione, the concentration of the radical fits a second order kinetic equation, which is in agreement with our proposed mechanism. The radical 6 *rad* will be formed from the (4+2)-cycloadduct 6' in a hydrogen abstraction reaction. The nature of this hydrogen abstraction reaction is not understood and will be of interest for further investigations. The (back)donation of hydrogen to 6 *rad* will lead to 6.

The rearrangement of 6 into the thiopyran 7 is probably acid catalyzed. This type of prototropy has been effectuated at low temperature under the influence of para toluenesulfonic acid [10].

Scheme II



Acknowledgement: This investigation was supported by the Netherlands Foundation of Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Researhc (ZWO). We thank Mr. A.V.E. George for his assistence, and Dr. R.J.M. Nolte for the fruitful discussions on this subject. Also, we would like to thank Messrs. P.D.J. Grootenhuis, A.P. Ruijter and G. Hofstra for their enthusiastic cooperation.

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(Received in UK 24 March 1983)