Tetrahedron Letters No.47, pp. 4941-4944, 1968. Pergamon Press. Printed in Great Britain.

ESR INVESTIGATION OF THE TRITHIENYLMETHYL RADICALS

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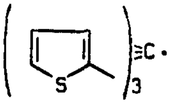
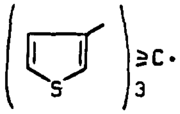
(Received in UK 6 August 1968; accepted for publication 19 August 1968)

The study of the homolytic reactions in the field of the heterocyclic compounds and of spin density distribution in oxygen or bivalent sulphur containing radicals has been the object of our recent researches. Thus our attention has been devoted both to the reactions of thiophene with phenyl and substituted phenyl radicals(1), and to the behaviour of 2- and 3-thienyl radicals(2) as arylating agents, as well as to the study of the relative perturbation by oxygen(3) and sulphur(4) on π-radicals to see whether the sulphur d-orbital partecipation can play a role in conjugation(5).

In connection with these investigations, we wish now to report the preliminary results on the electron spin resonance spectra of the α-trithienylmethyl (α-TTM) (I) and β-trithienylmethyl (β-TTM) (II) radicals.



(I)



(II)

The aim of this work was to find the experimental conditions under which these two radicals could be generated and to study their relative stability. Moreover, the spin density distribution in these radicals should be very sensitive to sulphur d-orbital partecipation in π-bonding and could, therefore, give useful information about this problem.

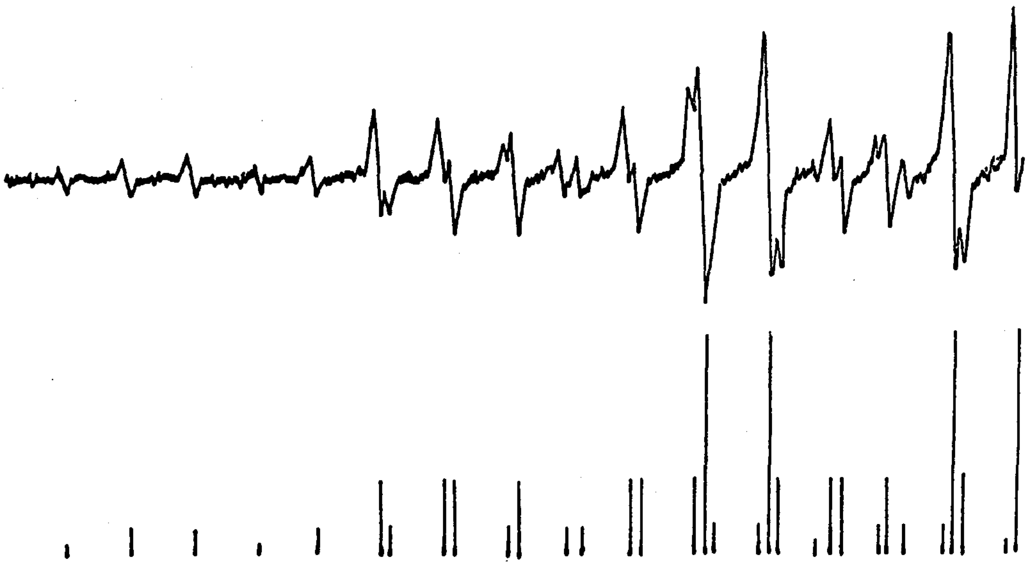
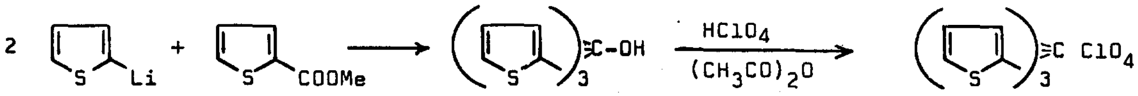


Figure 1: Experimental and reconstructed half spectrum of the α-trithienylmetyl radical (I).

The starting products employed to generate the two radicals were the α- and β-trithienylmethyl perchlorates, the syntheses of which were accomplished according to the scheme here reported for the α-isomer:



By heating a oxygen-free mixture of the perchlorates and zinc powder in dimethoxyethane the two isomeric radicals could be obtained; the experimental spectra of α-TTM (I) and β-TTM (II) are shown in Fig. 1 and Fig. 2 respectively. They are easily interpreted as the result of the coupling of the unpaired electron with three series of three equivalent protons; the spectral reconstructions, reported

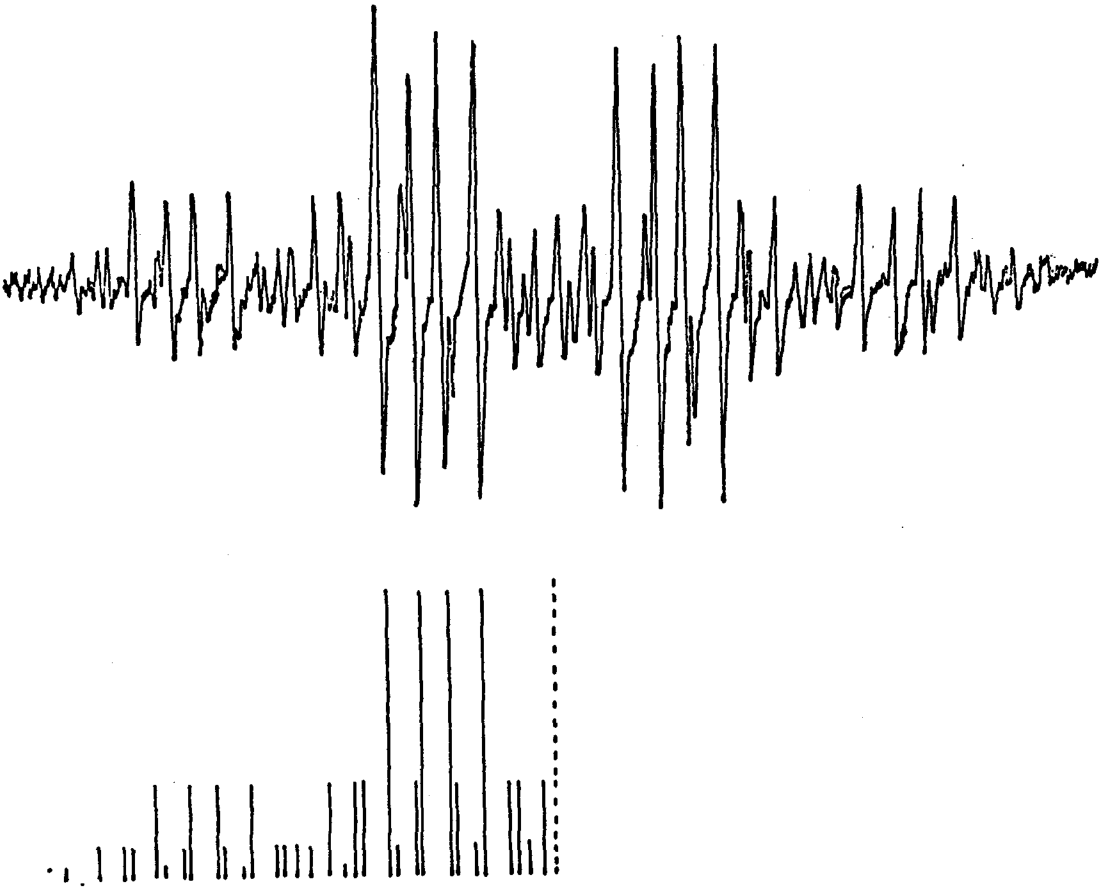


Figure 2: Experimental and reconstructed spectrum of the β-Trithienylmethyl radical (II).

lower in the figures, were based on the hyperfine coupling constants which are listed in table 1.

Table 1

Hyperfine splitting constants in the α-TTM and β-TTM radicals

	a_1	a_2	a_3
α-TTM	3.86	2.98	0.77
β-TTM	4.38	1.12	0.62

Further work is in progress to assign the hfs constants to the various hydrogens by means of deuterated derivatives.

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