The ESR Spectra of Some Thienylphenyl- and Trithienylmethyl Radicals

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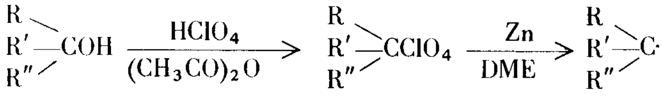
Sir:

Our interest on the homolytic reactivity of heterocyclic compounds containing sulphur (1,2) as well as on the relative perturbation by oxygen and sulphur on π radicals (3,4), induced us to undertake a study of the electron spin resonance spectra of some thiophene analogs of triphenylmethyl radicals. Thus, we have recently reported (5) that the 2-trithienylmethyl (IA) and the 3-trithienylmethyl (IB) radicals can be conveniently generated by heating an oxygen free mixture of the corresponding perchlorates with zinc powder in dimethoxyethane. The ESR spectra of these two radicals are interpreted as the result of the coupling of the unpaired electron with three series of three equivalent protons. The relative hyperfine splitting constants have been assigned to the various hydrogens by means of deuterated derivatives (6).

We have now extended our research to some mixed triarylmethyl radicals (IC-IF) in order to obtain information about the spin density distribution in the different aromatic nuclei; the efficiency of the phenyl, 2-thienyl and 3-thienyl groups, in delocalizing the odd electron, could thus be tested. The triarylmethyl radicals investigated are listed in the following scheme in which the reactions employed for their preparation are also outlined.



$$\begin{matrix}\mathrm{R}\\ \mathrm{R'}-\mathrm{COH}\\ \mathrm{R''}\end{matrix} \xrightarrow[(\mathrm{CH_3CO})_2\mathrm{O}]{\mathrm{HClO_4}} \begin{matrix}\mathrm{R}\\ \mathrm{R'}-\mathrm{CClO_4}\\ \mathrm{R''}\end{matrix} \xrightarrow[\mathrm{DME}]{\mathrm{Zn}} \begin{matrix}\mathrm{R}\\ \mathrm{R'}-\mathrm{C}\cdot\\ \mathrm{R''}\end{matrix}$$

IA : R = R′ = R″ = 2-thienyl
IB : R = R′ = R″ = 3-thienyl
IC : R = R′ = 2-thienyl, R″ = 3-thienyl
ID : R = 2-thienyl, R′ = R″ = 3-thienyl
IE : R = R′ = 3-thienyl, R″ = phenyl
IF : R = 3-thienyl, R′ = R″ = phenyl

Owing to a larger number of non-equivalent protons, the spectra of the radicals IC-IF are more complicated than those of IA and IB. The interpretation of these spectra was therefore accomplished by means of a simulator programme run in a digital computer provided with a plotter.

The hyperfine coupling constants, in the radicals IC, ID and IF, were assigned to the 2-thienyl, 3-thienyl and phenyl on the basis of the number of equivalent hydrogens. As far as the radical IE is concerned the hfs constants were assigned on the analogy of the symmetrical derivatives; the values of those constants in fact are not very different in the two cases.

The values of the hyperfine coupling constants, as well as their assignments to the various aromatic nuclei, are collected in Table 1.

The data reported in the table clearly indicate that the odd electron distribution is remarkably influenced by the nature of the aromatic group linked to the central carbon atom. Moreover, from the experimental hyperfine splitting constants, it is apparent that, while the 3-thienyl group behaves approximately as the phenyl group, the 2-thienyl substituent is much more efficient in delocalization of the odd electron. Such behaviour is consistent with the observed reactivities of the 2- and 3-position and with the relative reactivity of thiophene (1), as well as with the observed reactivity of 2-thienyl, 3-thienyl and phenyl radicals (2).

We are now carrying out a McLachlan-type molecular orbital calculation to correlate the experimental and the calculated spin density distribution in the radicals IA-IF.

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TABLE I

Hyperfine Splitting Constants (Gauss) of the Hydrogens on the 2-Thienyl, 3-Thienyl and Phenyl Groups in the Radicals IA-IF.

Radicals	Aromatic Nucleus								
	2-Thienyl			3-Thienyl			Phenyl		
IA (a)	3.86	2.98	0.77	–	–	–	–	–	–
IB (a)	–	–	–	4.83	1.12	0.62	–	–	–
$Ph_3C\cdot$ (b)	–	–	–	–	–	–	2.81	2.57	1.12
IC	4.73	3.98	0.94	2.31	0.71	0.55	–	–	–
ID	5.32	4.53	1.06	3.51	0.94	0.58	–	–	–
IE	–	–	–	4.54	1.13	0.65	2.58	2.41	1.09
IF	–	–	–	4.80	1.11	0.63	2.70	2.49	1.11

(a) See ref. 5. (b) These values were obtained from the spectrum of the trityl radical generated under the experimental conditions employed for the radicals IA-IF.

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