Radicals Derived from 1,2-Dithiolylium Ions, a New Class of Stable Organic Free Radicals

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Summary Cathodic reduction of 3,5-diaryl-1,2-dithiolylium ions produces the corresponding stable neutral free radical which is in equilibrium with its dimer at lower temperature.

We report a new class of stable organic free radicals formed by cathodic reduction of the corresponding 1,2-dithiolylium salts. The radicals are stable at room temperature in carefully purified acetonitrile in the absence of oxygen, and exist in equilibrium with the dimers at lower temperature. With the exception of the trithienylmethyl radical, this is, to our knowledge, the only report of stable free radicals in sulphur containing heterocyclic rings.[1a] In fact, although radical ions are common very few sulphur containing stable free radicals are known.[1b]

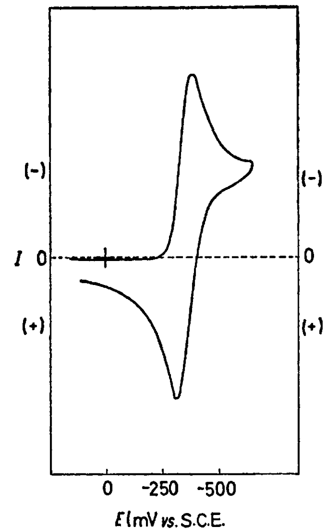
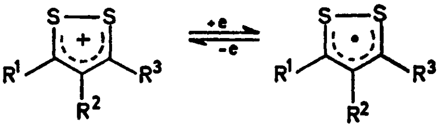


Figure 1. *Cyclic voltammogram for the reduction of* 3,5-*diphenyl*-1,2-*dithiolylium ion in acetonitrile containing sodium perchlorate* (0·1 M). *Substrate concentration* = 1·0 mM, *voltage sweep rate* = 150 mV s^{-1}.

The cyclic voltammogram of 3,5-diphenyl-1,2-dithiolylium ion (Ia)[1c] in acetonitrile is shown in Figure 1. A reduction peak is observed at −380 mV and on the anodic scan the corresponding peak for oxidation of (IIa; $R^1 = R^3 = Ph$, $R^2 = H$) appears at −320 mV.† Exhaustive coulometric reduction[1d] was accompanied by the consumption of precisely 1·0 F mol^{-1} and the quantitative formation of (IIa) as shown by cyclic voltammetry.



(I) (II)

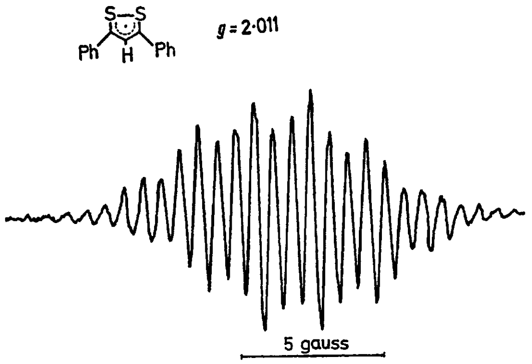


Figure 2. *E.s.r. spectrum of* (IIa) *in acetonitrile.*

The e.s.r. spectrum of (IIa) (Figure 2) in acetonitrile consisted of *ca.* 26 resolved lines when measured at 8°. The intensity of the spectrum was found to be markedly dependent on the temperature, becoming vanishingly weak at −35°. On warming, the signal reappeared showing the same temperature dependence as was observed during cooling

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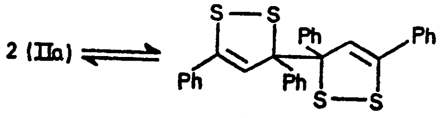
† All voltages refer to oxidation or reduction at a platinum electrode *versus* the aqueous saturated calomel electrode.

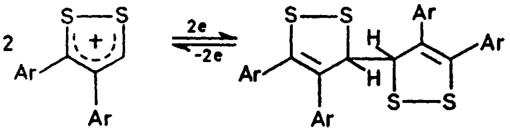
indicating the existence of an equilibrium with a non-radical species, most probably the dimer (III).

The stability of radicals of structure (II) appears to be a general phenomenon when both R^1 and R^3 are aryl groups.‡



(III)

We have examined the reduction of 5-*p*-anisyl-3-phenyl-, 3,5-di-*p*-anisyl-, and 5-*p*-dimethylaminophenyl-3-phenyl-1,2-dithiolylium ions and in all cases observed the formation of stable free radicals comparable to (IIa). We have previously shown that 3,4-diaryl-1,2-dithiolylium ions (IV) are reduced to dimers (V) which on oxidation quantitatively regenerate the substrates,[3] in complete analogy to the iso-electronic tropylium–bitropenyl system.[4] Thus, it appears that the steric interaction of groups situated on the carbon atoms where the two rings join is an important factor in determining whether the radical or the dimer of type (III) or (V) is the favoured species. When these groups are aryl there is considerable steric interaction and the room temperature equilibrium favours the radical while there is no tendency for (V) to dissociate. Preliminary studies on compounds where R^1 is aryl and R^3 is methyl as well as those in which both R^1 and R^3 are methyl show that methyl does not inhibit reductive dimerization, no radicals being detected by cyclic voltammetry and reduction of these compounds parallels that of (IV). Further work is in progress to see if more bulky alkyl groups incorporated as R^1 and R^3 will enhance radical stability and thus provide information of the relative importance of steric and electronic factors in the stabilization of (II).



(IV) (V)

The stability of 1,2-dithiolylium ions (I) is generally attributed to aromaticity, being isoelectronic with tropylium ion.[5] Sulphur in a conjugated system can usually be considered as equivalent to an ethylene linkage and thus (II) can be considered to be isoelectronic with a substituted tropenyl radical, none of which have been reported as stable entities. Thus, it appears that there may be an inconsistency in the isoelectronic analogy since there seems to be inherent stability in the structure (II) as dimerization by opening of the normally weak S–S bond is a feasible but unobserved reaction pathway.

(*Received*, 21*st February* 1972; *Com.* 281.)

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‡ While this manuscript was in preparation a theoretical paper[2] appeared which predicted the stability of structures such as (II).

[1] (a) A. Mangini, C. F. Pedulli, and M. Tiecco, *Tetrahedron Letters*, 1968, 4941; (b) A. R. Forrester, J. M. Hay, and R. H. Thomson, 'Organic Chemistry of Stable Free Radicals', Academic Press, New York, 1968, pp. 352—355; (c) For the preparation of 3,5-di-substituted-1,2-dithiolylium salts see: H. Hartman, K. Fabian, B. Bartho, and J. Faust, *J. prakt. Chem.*, 1970, **312**, 1197; (d) The constant current coulometric method has previously been described, V. D. Parker, *Acta Chem. Scand.*, 1970, **24**, 2768.

[2] R. Zahradnik, P. Čársky, S. Hunig, G. Kiesslich, and D. Scheutzow, *Internat. J. Sulfur Chem. C*, 1971, 109.

[3] C. Th. Pedersen and V. D. Parker, *Tetrahedron Letters*, 1972, 767.

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[5] E. Klingsberg, *J. Amer. Chem. Soc.*, 1961, **83**, 2934; G. Bergson, *Arkiv. Kemi*, 1962, **19**, 181; R. Zahradnik and C. Párkányi, *Coll. Czech. Chem. Comm.*, 1965, **30**, 3016.