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THE ELECTROCHEMISTRY OF ORGANIC SULFUR COMPOUNDS. PART III. ANODIC OXIDATION OF 1,2-DITHIOL-3-THIONES TO DISULFIDE LINKED BIS(DITHIOLYLIUM) DICATIONS.

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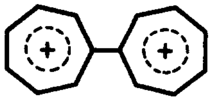
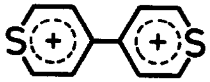
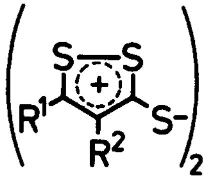
The observation of ditropylium dication (I) by Vol'pin et al. (2) has inspired investigations to find other similar systems in which positive charges in two adjoining rings are found in the same molecule. For example, the dithiopyrylium dication (II) has recently been synthesized (3). We now report several examples of dications in which the dithiolylium ions, isoelectronic with tropylium ion, are linked together through a disulfide linkage to give the dimer (III). In the previous communication we demonstrated that bis(dithiolylium) dications are not formed from anodic oxidation of the corresponding bis(1,2-dithiole-3-yl) but instead cleavage of the bond connecting the two rings occurs to regenerate the dithiolylium ions (4).



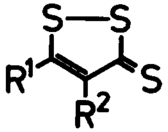
I



II



III



IV

Preparative oxidation of IVb in MeCN resulted in the precipitation of essentially pure dimeric perchlorate. The ^{1}H nmr spectrum in DMSO-d_6 exhibited a dithiole proton at δ 8.40 which is indicative of a dithiolylium structure as III. In 5-anisyl-3-methylthio-1.2-dithiolylium methosulphate the dithiole proton is found at δ 8.68 in DMSO-d_6, whereas in neutral 1.2-dithiole derivatives the dithiole proton occurs ca. 1 ppm at higher field. Oxidation of IVa gave rise to a MeCN soluble perchlorate, the structure of which is unambiguous since a C-C dimer is impossible.

The voltammetric curves were very similar to Figure b of the previous paper (4). The voltammetric and coulometric behaviour of a series of compounds are summarized in the Table.

TABLE

Voltammetry and Coulometry of Aryl Substituted 1,2-Dithiol-3-thiones in MeCN

		Peak Potential (vs. SCE)		Coulometric n	
	Substrate	Oxidation	Reduction	Oxidation	Reduction
a.	4-An; 5-An	+ 1.23	- 0.05	1.0	1.0
b.	4-H ; 5-An	+ 0.76	+ 0.32	1.0	1.0
c.	4-Ph; 5-Ph	+ 1.32	- 0.06	1.0	0.7
d.	4-Ph; 5-H	+ 0.92	+ 0.25	1.0	0.7
e.	4-H ; 5-Ph	+ 0.80	+ 0.24	1.0	0.6

A striking feature of the data in the Table is that both the oxidation and reduction potentials are markedly influenced by the substitution on the ring. The mono substituted compounds are oxidized more easily to compounds more easily reduced than the corresponding disubstituted compounds. On the other hand, the nature of the aryl group does not influence the voltammetry, p-anisyl groups behave almost identical to phenyl groups. The origin of this effect is most likely steric in nature, and in support of this is the fact that the corresponding dimethyl compound, in which much less interaction would be expected between the two substituents, behaves almost identical to the mono aryl substituted compounds. The anisyl groups are apparently more effective than phenyl in stabilizing the oxidation products as evidenced by the fact that almost identical oxidation and reduction coulometric n values were observed while the corresponding phenyl compounds gave reduction n values which are about 70% the oxidation values.

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