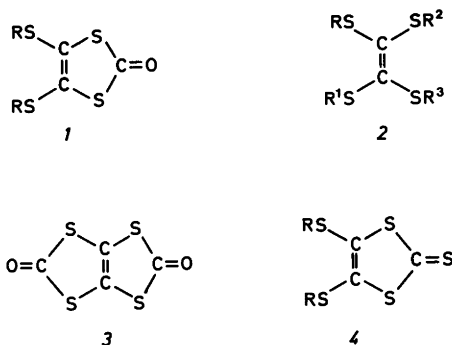


## Electrochemical Synthesis of Tetrathioethylenes

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Electrochemical reduction of 4,5-bis(alkylthio)-1,3-dithiol-2-ones (*1a–d*) in aprotic medium, followed by alkylation, gives tetrathioethylenes (*2*) in nearly quantitative yield. A similar reduction and alkylation of 1,3,4,6-tetrathiopentalene-2,5-dione (*3*) leads to *1* in almost quantitative yield. 4,5-Bis(alkylthio)-1,3-dithiole-2-thiones (*4*) gives tetrathioethylenes under similar conditions although in lower yields than *1*. The mechanism of the reactions is discussed on the basis of the preparative and cyclic voltammetric results.



Electrochemical reduction of carbon disulfide in aprotic media, followed by alkylation, gives 4,5-bis(alkylthio)-1,3-dithiole-2-thiones (*4*),<sup>1–6</sup> which may be converted to 4,5-bis(alkylthio)-1,3-dithiol-2-ones (*1*) on treatment with mercuric acetate.<sup>5</sup> *4* and *1*, as well as trithiocarbonates<sup>7</sup> may be used for the preparation of tetrathioethylenes (*2*).

Below are reported the results of a cyclic voltammetric and preparative investigation of *1* and *4* and related compounds (*3*).

*1a*, R = CH<sub>3</sub>; *1c*, R = (CH<sub>3</sub>)<sub>2</sub>CH; *2a*, R,R<sup>1</sup>,R<sup>2</sup>,R<sup>3</sup> = CH<sub>3</sub>; *2b*, R,R<sup>1</sup>,R<sup>2</sup>,R<sup>3</sup> = C<sub>2</sub>H<sub>5</sub>; *2c*, R,R<sup>1</sup>,R<sup>2</sup>,R<sup>3</sup> = (CH<sub>3</sub>)<sub>2</sub>CH; *2d*, R,R<sup>1</sup>,R<sup>2</sup>,R<sup>3</sup> = C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>; *2e*, R<sup>1</sup>,R<sup>2</sup> = C<sub>2</sub>H<sub>5</sub>, R,R<sup>3</sup> = C<sub>2</sub>H<sub>5</sub>; *4a*, R = CH<sub>3</sub>; *4b*, R = C<sub>2</sub>H<sub>5</sub>; *4c*, R = (CH<sub>3</sub>)<sub>2</sub>CH; *4d*, R = C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>.

(*i<sub>p</sub>v<sup>-3</sup>*) varies less than 10% on changing *v* from 0.04 V s<sup>-1</sup> to 1000 V s<sup>-1</sup>. At *v* = 0.4 V s<sup>-1</sup> *E<sub>p</sub>* (*1a*) = -2.12 V vs. SCE.

The heterogeneous charge transfer is thus rather slow and the rate of the follow-up chemical reactions is relatively fast (>10<sup>4</sup> s<sup>-1</sup>); this is generally found when the follow-up reaction is a cleavage of a -C(=O)-S bond. The CV-curves are neither purely diffusion nor kinetically controlled, but both factors are involved. This is similar to the behaviour of related compounds.<sup>7,8</sup>

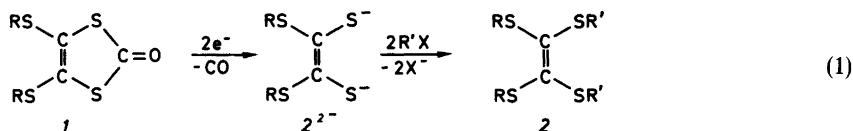
Constant potential electrolysis of *1* yields the dianion of *2*, which may be alkylated; *n* is close to 2 F mol<sup>-1</sup> and the yield is almost quantitative.

If R' of the alkylating agent is different from the alkyl R in *1* the *Z* isomer is obtained; in the reduction of diaryl trithiocarbonates<sup>7</sup> the predominant isomer is the *E* form.

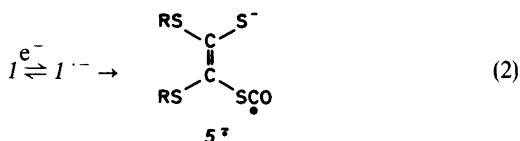
The results from CV indicate a fast chemical reaction after the charge transfer, which most likely

### RESULTS AND DISCUSSION

4,5-Bis(alkylthio)-1,3-dithiol-2-ones, *1*. Cyclic voltammetry (CV) of *1a* and *1c* in *N,N*-dimethylformamide (DMF) containing 0.1 M tetrabutylammonium iodide (TBAI) at a hanging mercury electrode (HMD) shows an irreversible peak, which does not become reversible within the available range of scan rates (*v*) (0.04 V s<sup>-1</sup> < *v* < 1000 V s<sup>-1</sup>). At constant sweep rate the peak potential is independent of the concentration of *1* (1 to 10 mM). For *1a* the peak potential shifts 58 mV to more negative values for a tenfold increase in the scan rate (*v*). The relative current function



is an opening of the ring of  $1^{2-}$  to  $5^{2-}$ .  $5^{2-}$  reacts then further either by loss of carbon monoxide, followed by an uptake of an electron either from  $1^{2-}$  or the electrode, or by an electron uptake followed by a loss of CO.



Products formed by the dimerization of the sulfur analogue of  $5^{2-}$  are obtained from the reduction of  $4$  (*vide infra*); such compounds have not been detected during the reduction of  $1$ .

[1,3]Dithiolo[4,5-d]-1,3-dithiole-2,5-dione,  $\mathbf{3}$ . Cyclic voltammetry of  $\mathbf{3}$  in DMF/0.1 M TBAI at the HMD shows one peak which is irreversible at all  $v$  used (0.04–1000 V s<sup>-1</sup>). The relative current function varies less than 10% on changing  $v$ . These results indicate that a fast chemical reaction follows after the heterogeneous charge transfer. At  $v=0.4$  V s<sup>-1</sup>  $E_p(\mathbf{3})=1.60$  V vs. SCE.

Constant potential electrolysis of  $\mathbf{3}$  produced  $1^{2-}$  in a two-electron reduction;  $1^{2-}$  may be alkylated to  $\mathbf{1}$ ; the yield of  $\mathbf{1}$  from  $\mathbf{3}$  is almost quantitative.  $1^{2-}$  is not further reducible in the accessible potential region.

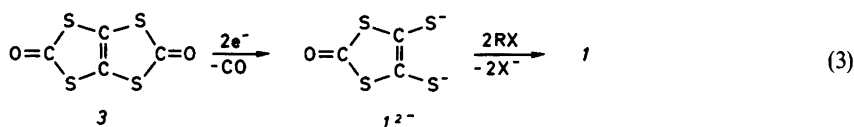


Table 1. Electrochemical data from a cyclic voltammetric analysis of a series of 4,5-bis(alkylthio)-1,3-dithiole-2-thiones.  $C$  = concentration,  $v$  = sweep rate.

	R	C/mM	$E^\circ$ /V vs. Ag/AgI	$k^{\text{cleavage } a}/$ s <sup>-1</sup>	$dE_p \text{ d log } v^{-1}/$ mV	$dE_p \text{ d log } C^{-1}$
4a	CH <sub>3</sub> CH <sub>2</sub>	1.14	-1.205	40	30	0
4b	CH <sub>3</sub>	1.57	-1.225	53	29	0
4c	(CH <sub>3</sub> ) <sub>2</sub> CH	1.63	-1.135	<2.5	30	0
4d	PhCH <sub>2</sub>	1.29	—	>10 <sup>4</sup>	30	0

<sup>a</sup> Determined by the intersection method.<sup>9</sup>

4,5-Bis(alkylthio)-1,3-dithiole-2-thione,  $\mathbf{4}$ . The cyclic voltammetric data of  $\mathbf{4a}$  to  $\mathbf{d}$  are given in Table 1. The behaviour of  $\mathbf{4a}$ ,  $\mathbf{4b}$  and  $\mathbf{4c}$  is similar although there is some difference in the rate of cleavage,  $\mathbf{4a}$  having the highest and  $\mathbf{4c}$  the lowest rate. On CV are seen two peaks in DMF/0.1 M TBAI at an HMD, the first peak being partly reversible at low sweep rates; it gradually becomes reversible with increasing  $v$  whereas the most negative peak is irreversible at all sweep rates. The peak to peak separation is close to 60 mV at  $v < 500$  V s<sup>-1</sup>, at higher  $v$  it tends to increase, which indicates that the heterogeneous charge transfer is gradually becoming the rate determining step (Fig. 1).

The peak potentials are independent of the concentration of  $\mathbf{4}$ ; the current function, relative to that of a one-electron reaction, decreases from 1.4 to 1.0 with increasing  $v$ . At low  $v$  the peak potential shifts about 30 mV to more negative values for a tenfold increase of  $v$ , whereas  $E_p$  becomes independent of  $v$  at higher scan rates. The slope,  $dE_p \text{ (d log } v)^{-1} = -30$  mV, is consistent<sup>9</sup> with a rapid chemical reaction following the charge transfer step; the rate of the cleavage reaction can be determined from the value of  $v$  at the intersection between the two lines,  $dE_p \text{ (d log } v)^{-1} = -30$  mV and  $dE_p \text{ (d log } v)^{-1} = 0$ .<sup>9</sup>

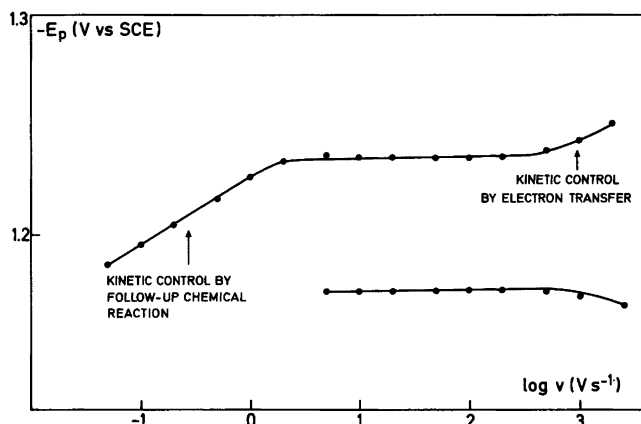
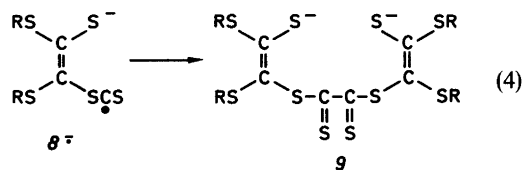


Fig. 1. Variation of the peak potential with scan rate for 1.14 mM 4,5-bis(ethylthio)-1,3-dithiole-2-thione in DMF/0.1 M TBAI at an HMD.

CV of *4d* is slightly different from *4a–4c*; both peaks are irreversible at all sweep rates employed. The shift of  $E_p$  with  $v$  is about 30 mV for a tenfold increase of  $v$  for  $v < 1 \text{ V s}^{-1}$  and increases gradually to about 60 mV at very high sweep rates.

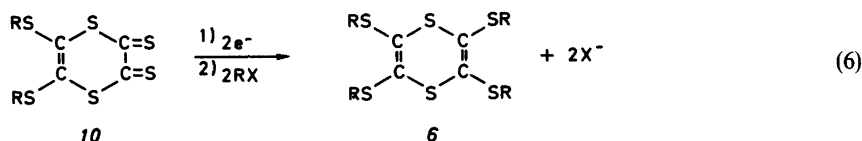
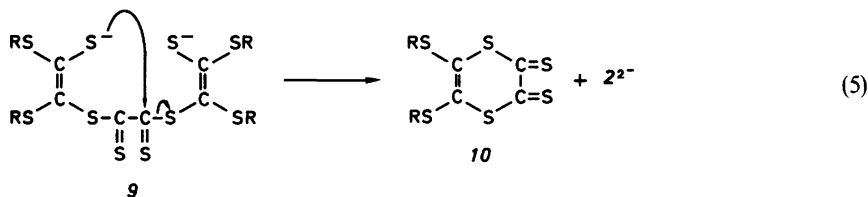
Controlled potential electrolysis of *4* gives the dianion of dialkyltetrathioethylene (*2*) in moderate yields (<45%), polymeric material, and minor amounts of other compounds. Thus, from the reduction of *4a* is isolated some tetrakis(methylthio)-1,4-dithiin (*6*)<sup>1</sup> and from *4d* some 4-benzylthio-1,3-dithiole-2-thione (*7*).

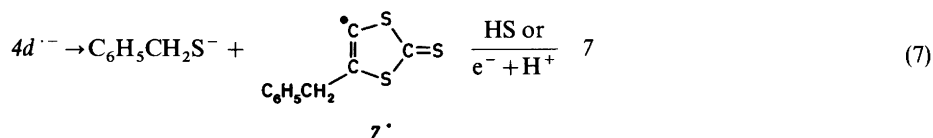
The reaction leading to *2* is analogous to the reduction of *1* to *2*; *6* is probably formed through a dimerization to (*9*) of the sulfur analogue of  $5^{\cdot-}$  ( $8^{\cdot-}$ ), followed by a ring closure with elimination of  $2^{2-}$ . A faster cleavage of  $5^{\cdot-}$  compared to that of  $8^{\cdot-}$  might explain the lack of dimeric products from the reduction of *1*.



The yield of *6* (22%) indicates that a considerable part of *2* (38%) is formed through this pathway, the other route being one analogous to that of *1*.

When  $\text{RS}^-$  is a sufficiently good leaving group, the anion radical of *4* may react by loss of  $\text{RS}^-$  rather than by ring opening. *4d*, where  $\text{RS}^-$  is phenylmethanethiolate, reacts partly in this way, and the resulting radical forms *7* on hydrogen atom abstraction or by electron transfer and protonation; the yield of *7* is low (6%).





*1,3-Benzodithiole-2-thione* (11). The CV of 11 is similar to that of 4; two peaks are observed. The first one, corresponding to the formation of the anion radical, is partly reversible at low  $v$  and becomes reversible at  $v > 1 \text{ V s}^{-1}$ ; the second peak is irreversible at all  $v$ .

The peak to peak separation of the first wave is 60 mV even at high sweep rates indicating a relatively fast heterogeneous charge transfer reaction. The relative current function is constant for  $1 \text{ V s}^{-1} < v < 1000 \text{ V s}^{-1}$ , but at lower  $v$  it increases and is 1.33 at  $v = 0.04 \text{ V s}^{-1}$ . At  $v = 0.4 \text{ V s}^{-1}$   $E_p(11) = -1.64 \text{ V vs. SCE}$ .

*Tetrakis(alkylthio)ethylene, 2*. The polarographic half-wave potential of tetrakis(methylthio)ethylene, 2a, has been reported;<sup>1</sup> here is briefly described the CV of *E*-1,2-bis(ethylthio)-1,2-bis(phenylthio)ethylene (2e,  $\text{R,R}^3 = \text{C}_2\text{H}_5$ ;  $\text{R}^1, \text{R}^2 = \text{C}_6\text{H}_5$ ) which has  $E_p = -2.08 \text{ V vs. SCE}$  at  $v = 0.4 \text{ V s}^{-1}$ .

The relative current function changes from 2 to 1 on increasing the scan rate from 0.04 to  $1000 \text{ V s}^{-1}$ . The variation of  $E_p$  with  $v$  shows a behaviour similar to that of 1. Besides the reduction peak, 2e gives on CV an anodic peak which coincides with that of benzenethiolate.

In conclusion, the best route for the preparation of 2 from carbon disulfide seems to be an electrochemical reduction of carbon disulfide to 4, conversion of 4 to 1, followed by an electrochemical reduction of 1 to 2. The loss of material in the conversion of 4 to 1 is more than compensated by the almost quantitative yield in the reduction of 1 to 2.

## EXPERIMENTAL

*Materials.* The 4,5-bis(alkylthio)-1,3-dithiole-2-thiones (4),<sup>1-6</sup> 4,5-bis(alkylthio)-1,3-dithiol-2-ones (1),<sup>5</sup> 1,3,4,6-tetrathiapentalene-2,5-dione (3),<sup>10</sup> and 1,3-benzodithiole-2-thione (11)<sup>11</sup> were prepared according to the given references. For preparative purpose *N,N*-dimethylformamide (DMF) was used as received, after storage over 4A molecular sieves, whereas freshly distilled DMF was used for cyclic

voltammetry. Tetrabutylammonium iodide (TBAI) was used as received.

*Apparatus.* The electroanalytical equipment<sup>12-13</sup> and the set-up for preparative electrolysis<sup>14</sup> have been described elsewhere. Potentials are measured against the saturated calomel electrode (SCE).

*Reduction of carbon disulfide.* Carbon disulfide (5–10 ml) was dissolved in dry DMF (190 ml) containing TBAI (20 g) and reduced at  $0^\circ \text{C}$  under nitrogen at a mercury pool (area  $32 \text{ cm}^2$ ) at  $-1.4 \text{ V vs. SCE}$ .  $n = 1.7 \text{ F mol}^{-1}$ . After completion of the electrolysis excess of an alkylating agent was added to the catholyte and after stirring for 0.5 h the catholyte was diluted with water. The products were extracted with diethyl ether, from which DMF and basic impurities were removed by washing with dilute acid and water. The organic phase was dried over  $\text{MgSO}_4$ , and after evaporation of the solvent the crude product was separated by means of column chromatography on alumina, gradually changing the eluent from light petroleum (b.p.  $< 50^\circ \text{C}$ ) to diethyl ether. As alkylating agents were used: Methyl iodide, ethyl iodide, isopropyl iodide and benzyl chloride. The yield of 4 was 60–66%. 19–23% of the corresponding dialkyl trithiocarbonates was found besides 4. No 4-alkylthio-1,3-dithiole-2-thione was isolated.

The use of potassium in DMF/0.2 M TBAI as reducing agent gives 50–53% of 4 and 14–17% of the corresponding trithiocarbonate.

Attempts to synthesize 4,5-bis(arylthio)-1,3-dithiole-2-thiones by arylation of 4,5-dimercapto-1,3-dithiole-2-thione with benzenediazonium chloride, diphenyliodonium chloride, 1,3-dinitro-4,6-dichlorobenzene or 1,3-dinitro-4-chlorobenzene analogously to the procedure for the aliphatic ones were unsuccessful.

*General procedure for reduction of 1, 2 and 3.* The substrate (1 g) was dissolved in dry DMF (150 ml) containing TBAI (7.5 g) and reduced under nitrogen at a mercury pool ( $25 \text{ cm}^3$ ) on the plateau of the first wave. After completion of the electrolysis, excess of an alkylating agent was added to the catholyte and after stirring for 0.5 h, the catholyte was diluted with water and the products extracted with toluene–diethyl ether (1:1) from which DMF and basic impurities were removed by washing with dilute acid and water.

The organic phase was dried over  $\text{MgSO}_4$  and after evaporation of the solvent the crude product was, if necessary, separated by means of column chromatography on silica, gradually changing the eluent from tetrachloromethane to diethyl ether.

**Reduction of 1a.** Potential:  $-2.25\text{ V}$ ,  $n=1.98\text{ F mol}^{-1}$ . Methyl iodide (2 ml) was used as alkylating agent. Isolated was tetrakis(methylthio)ethylene (0.93 g, 93%), m.p. =  $60^\circ\text{C}$ .<sup>15,16</sup> MS (*m/e*): 212, 164, and 118.

**Reduction of 1c.** Potential:  $-2.3\text{ V}$ , Isopropyl iodide (2 ml) was used as alkylating agent. Isolated was tetrakis(isopropylthio)ethylene (1.14 g, 99%), m.p. =  $83^\circ\text{C}$ .<sup>15,17</sup>

**Reduction of 3.** Potential:  $-1.7\text{ V}$ ;  $n=2.02\text{ F mol}^{-1}$ . (a): Methyl iodide or (b): Isopropyl iodide was used as alkylating agents. Isolated was (a): 4,5-Bis(methylthio)-1,3-dithiol-2-one (0.97 g, 96%), m.p. =  $63.5^\circ\text{C}$ .<sup>5</sup>  $^1\text{H NMR}$  ( $\text{CCl}_4$ ):  $\delta=2.5$  (s). MS (*m/e*): 210, 195, 182, and 163. (b): 4,4-Bis(isopropylthio)-1,3-dithiol-2-one (1.21 g, 94%), m.p. =  $53^\circ\text{C}$ .  $^1\text{H NMR}$  ( $\text{CCl}_4$ ):  $\delta$  1.37 (6 H, d;  $J=8\text{ Hz}$ ) and 3.40 (1 H, sept,  $J=8\text{ Hz}$ ). MS (*m/e*): 268, 240, 225, and 191. If the excess of methyl iodide in (a) is removed by passing nitrogen through the catholyte for an appropriate time and the electrolysis is resumed at  $-2.25\text{ V vs. SCE}$ .  $n=3.91\text{ F mol}^{-1}$ . If the product then is methylated with methyl iodide after the electrolysis, 91% of tetrakis(methylthio)ethylene is isolated.

**Reduction of 4a.** Potential:  $-1.5\text{ V}$ ;  $n=1.7\text{ F mol}^{-1}$ . Methyl iodide (2 ml) was used as alkylating agent. Isolated was tetrakis(methylthio)ethylene (0.36 g, 38%) and tetrakis(methylthio)-1,4-dithiin (a dark red oil) (0.15 g, 22%).

**Reduction of 4b.** Potential:  $-1.5\text{ V}$ ;  $n=1.8\text{ F mol}^{-1}$ . Ethyl iodide was used as alkylating agent. Isolated was tetrakis(ethylthio)ethylene (0.43 g, 41%), m.p. =  $52^\circ\text{C}$ .<sup>17,18</sup>

**Reduction of 4c.** Potential:  $-1.5\text{ V}$ ;  $n=1.85\text{ F mol}^{-1}$ . Isopropyl iodide (2 ml) was used as alkylating agent. Isolated was tetrakis(isopropylthio)ethylene (0.495 g, 43%).

**Reduction of 4d.** Potential:  $-1.6\text{ V}$ ;  $n=1.9\text{ F mol}^{-1}$ . Benzyl chloride was used as alkylating agent. Isolated was dibenzyl sulfide (0.068 g, 12%), m.p. =  $49^\circ\text{C}$ .<sup>18</sup> 4-Benzylthio-1,3-dithiole-2-thione (0.04 g, 6%), m.p. =  $48^\circ\text{C}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  = 3.88 (2 H, s), 6.91 (1 H, s), 7.15–7.83 (5 H, m). MS (*m/e*): 256 and 180. Tetrakis(benzylthio)ethylene (0.37 g, 28%), m.p. =  $113^\circ\text{C}$ .<sup>19</sup>

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