# Electrochemical Reduction of Diaryl Trithiocarbonates and Related Compounds

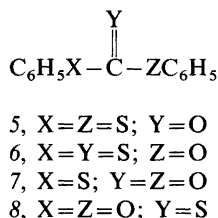M. FALSIG,[a] H. LUND,[a] L. NADJO[b] and J. M. SAVÉANT[b]

[a] Department of Organic Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark and [b] Laboratoire d'Electrochimie, Université de Paris 7, 2 Place Jussieu, F-75221 Paris, Cedex 05, France

Electrochemical reduction of diaryl trithiocarbonates (1) in aprotic medium followed by alkylation gives a mixture of Z- and E-tetrathioethylenes (2) and thioanisoles (3) in which the Z:E ratio is approximately 1:10. The influence of different parameters on the yield of 2 and 3 has been investigated, and these results together with those from a kinetic investigation published elsewhere have been used in a discussion of the reaction mechanism.
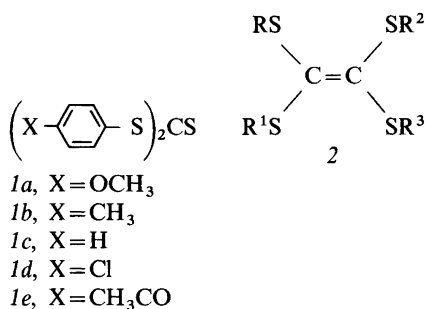
Tetrathioethylenes have lately attracted much attention, mainly in connection with the electrical properties of certain derivates.[2–5] A number of methods have been used for the preparation of tetrathioethylenes.[6–15] Thus, pyrolysis of orthothiooxalates,[6–10] synthesized either by reductive electrochemical dimerization of trithiocarbenium ions[6,8] or by chemical methods,[9,10] metalation of orthothioformate by means of either amide ions in liquid ammonia[11,12] or organolithium compounds[13,14] and cleavage of 1,3,4,6-tetrathiapentalene-2,5-dione by strong bases, followed by alkylation[15] seem to be the methods with the broadest scope.

In this series electrochemical reactions leading to tetrathioethylenes have been investigated with the aim of elucidating both their preparative value and their mechanism. In the report below the emphasis is laid on the preparative results of the electrolysis of some diaryl trithiocarbonates (1) and related compounds (5 – 8); a kinetic analysis of the reduction of these compounds has been published elsewhere.[1]

$$\left(X-\!\!\!\left\langle\bigcirc\right\rangle\!\!\!-S\right)_2 CS$$

1a, X = OCH_3
1b, X = CH_3
1c, X = H
1d, X = Cl
1e, X = CH_3CO

$$C_6H_5X-\overset{\overset{Y}{\|}}{C}-ZC_6H_5$$

5, X = Z = S; Y = O
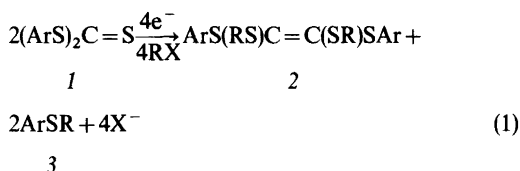6, X = Y = S; Z = O
7, X = S; Y = Z = O
8, X = Z = O; Y = S

RESULTS AND DISCUSSION

Electrolysis of diaryl trithiocarbonates (1) followed by alkylation by an alkyl halide gives a mixture of Z- and E-tetrathioethylenes (E:Z ~ 10:1) and thioanisoles (3) in an overall 2-electron reduction. The yield of 3 is generally > 50 %, whereas that of 2 mostly is < 50 % (Table 1). For some of the substrates a one-carbon segment is thus not accounted for in eqn. 1 which just shows the compounds isolated; stoichiometrically it could be carbon sulfide, CS, (4) but this has not been detected. The diaryltetrathioethylene dianion formed during the reduction is rather unstable; the reduction is therefore performed in the presence of an alkylating agent.

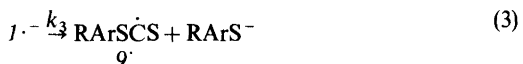*Table 1.* Yields (%) from the electrochemical reductions, followed by alkylation, of diaryl trithiocarbonates $(RC_6H_4S)_2CS$ (*1*).

R =	OCH_3	CH_3	H	Cl	CH_3CO
2	7 – 12	15 – 26	23 – 41	40 – 62	6 – 8
3	85 – 90	70 – 80	55 – 72	34 – 35	57 – 90

$$2(ArS)_2C = S \xrightarrow[4RX]{4e^-} ArS(RS)C = C(SR)SAr +$$

$$\underset{1}{} \qquad \underset{2}{}$$

$$2ArSR + 4X^- \qquad (1)$$
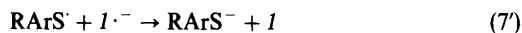
$$\underset{3}{}$$

The product distribution between *2* and *3* suggests a competition between a cleavage and a coupling reaction. This competition should be influenced by variations of operational parameters such as initial concentration and stirring rate. It was, indeed, observed that increasing the concentration of *1* fivefold raised the yield of *2* by 10 – 20 %; increasing the stirring rate with a factor 5, corresponding to the decrease of the diffusion layer thickness by a factor of about 2, raised the yield of *2* by 6 – 13 %.

The yield of *3* is higher than that of *2;* one possibility could be that the dianion of *2* was decomposed before the alkylation but two facts do not agree with that assumption. Firstly, the nature of the alkylating agent did not significantly influence the yield of *2*; the yield of *2* would be expected to be higher the more reactive the alkylating agent was. Secondly, no two-carbon segments, oxalic or glyoxalic acid derivatives, were isolated.

The peak potential (E_p) of *1* in cyclic voltammetry (CV) is independent of the concentration[1] so the further reaction of *1*$^{\cdot-}$ in CV is not a dimerization, but rather a cleavage. This is also in agreement with the observation that the shift of E_p is -30 mV per decade at low v, *i.e.*, under conditions where the initial electron transfer step is not rate controlling.[1]
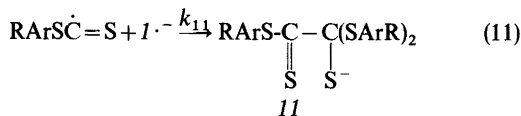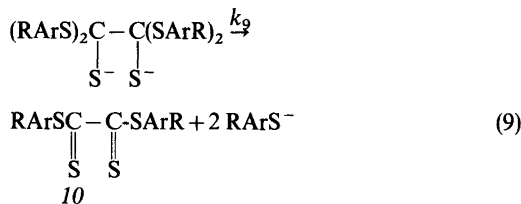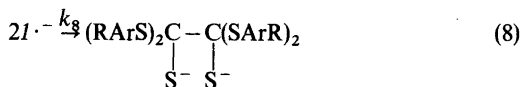
$$RArSCSSArR + e^- \rightleftharpoons (RArSCSSArR)^{\cdot-} \qquad (2)$$

$$\underset{1}{} \qquad\qquad \underset{1^{\cdot-}}{}$$

$$1^{\cdot-} \xrightarrow{k_3} RArS\dot{C}S + RArS^- \qquad (3)$$

$$\underset{9^{\cdot}}{}$$

Further cleavage occurs conceivably along the reaction sequences (4) – (7').

$$9^{\cdot} \xrightarrow{k_4} RArS^{\cdot} + CS \qquad (4)$$

$$9^{\cdot} + e^- \rightarrow RArS\bar{C} = S \qquad (5)$$

$$\underset{9^-}{}$$

$$9^{\cdot} + 1^{\cdot-} \xrightarrow{k_D} 9^- + 1 \qquad (5')$$

$$9^- \xrightarrow{k_6} RArS^- + CS \qquad (6)$$

$$RArS^{\cdot} + e^- \rightarrow RArS^- \qquad (7)$$

$$RArS^{\cdot} + 1^{\cdot-} \rightarrow RArS^- + 1 \qquad (7')$$

i.e. a cleavage (eqn. 4) followed by electron transfer at the electrode (eqn. 7) or in the solution (eqn. 7') in the first case or an electron transfer step occurring at the electrode (eqn. 5) or in the solution (eqn. 5') followed by a cleavage reaction (eqn. 6). Species, such as 9$^{\cdot}$ and RArS$^{\cdot}$, are likely to be reduced much more easily than *1*. The rate of the solution electron transfer reactions is thus likely to be close to the diffusion limit. Whether the solution electron transfer route predominates over the heterogenous electron transfer or not is primarily related to the rate of the initial cleavage reaction (eqn. 3). If this is slow, 9$^{\cdot}$ is formed far from the electrode surface and the further reactions including the electron transfers will occur before the reaction species can diffuse back to the electrode and be reduced there. Conversely, if reaction 3 were fast, the electrode reaction would predominate. *1a*$^{\cdot-}$ – *1e*$^{\cdot-}$ have cleavage rates[1] in the interval $1 - 100 \text{ s}^{-1}$ so the solution electron transfer is the most likely route for the further reduction of 9$^{\cdot}$ or RArS$^{\cdot}$. More precisely, the reaction path (eqns. 3, 5 and 5') is a typical case of an "ece-disp" competition, the kinetics of which has been amply discussed in the context of kinetic techniques such as CV and potential step chronopotentiometry[16-18] and of preparative scale electrolysis (PSE).[19] In PSE the competition parameter between the homogeneous and heterogenous electron transfers is $(k_D/k_3^{3/2})$ $(C^{\circ}D^{1/2}/\delta)$ where C° is the initial concentration of the substrate, D the average value of the diffusion coefficients, and δ the thickness of the diffusion layer. Using plausible values for the parameters ($C^{\circ} = 10^{-2}$ M, $D = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $\delta = 10^{-2}$ cm, $k_D = 10^{10}$ M^{-1} s^{-1}) the competition parameters are between 3×10^7 and 3×10^4 for *1a* – *1e*, *i.e.* much larger than 1. It can thus be concluded that solution electron transfer will be the only mode of reduction of 9$^{\cdot}$ and that reaction

5 can be neglected in the following. An identical conclusion is valid for eqns. 7 and 7' if the plausible assumption is made that reaction 4 is faster than reaction 3.

The coupling reactions 8, 10, 11, and 12 will be considered.

$$2 1 \cdot^{-} \xrightarrow{k_8} (RArS)_2 C - C(SArR)_2 \quad (8)$$
$$\begin{array}{cc} | & | \\ S^- & S^- \end{array}$$

$$(RArS)_2 C - C(SArR)_2 \xrightarrow{k_9}$$
$$\begin{array}{cc} | & | \\ S^- & S^- \end{array}$$

$$RArSC - C - SArR + 2 RArS^- \quad (9)$$
$$\begin{array}{cc} \| & \| \\ S & S \\ \mathbf{10} \end{array}$$

$$2RAr\dot{S}C = S \xrightarrow{k_{10}} \mathbf{10} \quad (10)$$

$$RAr\dot{S}C = S + 1 \cdot^{-} \xrightarrow{k_{11}} RArS - C - C(SArR)_2 \quad (11)$$
$$\begin{array}{cc} \| & | \\ S & S^- \\ & \mathbf{11} \end{array}$$

$$RArS\bar{C} = S + \mathbf{1} \xrightarrow{k_{12}} \mathbf{11} \quad (12)$$

The coupling reactions are followed by a cleavage (13) of $\mathbf{11}$ to $\mathbf{10}$ plus benzenethiolate and a two-electron reduction (eqn. 14) of $\mathbf{10}$ by $\mathbf{1}^{\cdot-}$ to the dianion of diaryltetrathioethylene rather than an electrode reduction for the same reasons as discussed above.

As regards the competition between the two modes of cleavage, eqns. 4 and 7' $vs.$ 5' and 6, a minimal value of k_4 can be estimated for the first path to predominate over the second one. The parameter for the second path over the first one is $(k_D/k_3^{1/2}k_4)(C^\circ D^{1/2}/\delta)$ in the context of PSE.[20] For average electrolysis conditions, taking $k_D = 10 \text{ M}^{-1}$

s^{-1}, it is found that k_4 should be larger than 3×10^8 s^{-1} for $\mathbf{1a}$ and $3 \times 10^7 \text{ s}^{-1}$ for $\mathbf{1e}$ in order that the cleavage-reduction route (eqns. 4 and 7') competes efficiently with the reduction-cleavage path (eqns. 5' and 6).

The parameters for the competition[21] between a given mode of dimerization and each of the two modes of cleavage are given in Table 2. Although it is not possible from the data to establish the reaction route, a number of the possibilities can be shown to be less likely.

It was mentioned above that reaction 8 was not important in CV, but the conditions are somewhat different at PSE. The competition parameters for CV and PSE are $(k_8/k_3^{3/2})[C^\circ(vF/RT)^{1/2}]$ and $(k_8/k_3^{3/2})(C^\circ D^{1/2}/\delta)$, respectively. If these are compared using reasonable estimates of the paramters $(C = 10^{-3}$ M for CV and 10^{-2} in PSE, $v = 1$ V s^{-1} $(vF/RT = 40)$, $D = 6 \times 10^{-6}$ cm^2 s^{-1}, $\delta = 10^{-2}$ cm$)$, then the following values are obtained, $C^\circ(vF/RT)^{1/2} = 6 \times 10^{-3}$ and $C^\circ D^{1/2}/\delta = 2.4 \times 10^{-3}$ showing that the dimerization would interfere as much in CV as in PSE, essentially because the effect of the change in concentration is compensated by the change in diffusion rate. The observation of $dE_p(d \log C)^{-1} = 0$ and $dE_p(d \log v) = -30$ mV in CV is thus meaningful also with regard to PSE.

The reaction schemes (reactions 5', 6 competing with 10, 14 and 5', 6 competing with 11, 13, 14) can be ruled out since they would lead to a variation of the product distribution with concentration and stirring rate different from the observed one.

The interference of reactions 10 and 14 in competition with the other mode of cleavage (eqns. 4 and 7') can also be disregarded for the following reasons. It has been mentioned above that k_4 should be at least 3×10^8 s^{-1} for $\mathbf{1a}$ and 3×10^7 s^{-1} for $\mathbf{1e}$ in order that the route (eqns. 4 and 7') could interfere efficiently. If we consider the most favourable case for the interference of reaction 10 (largest k_3 and smallest k_4 which is the case of $\mathbf{1e}$), the competition parameter is seen to have a maximal value of 3.5×10^{-7} if we

Table 2. Parameters for the competition between a given mode of coupling and each of the two possible modes of cleavage.

Coupling	Cleavage (5')+(6)	Cleavage (4)+(7)
(8)+(9)+(14)	$(k_8/k_3^{3/2})(C^\circ D^{1/2}/\delta)$	$(k_8/k_3^{3/2})(C^\circ D^{1/2}/\delta)$
(10+(14)	$(k_3^{3/4}k_{10}^{1/2}/k_D)/(C^\circ D^{1/2}/\delta)$	$(k_3^{1/2}k_{10}/k_4^2)(C^\circ D^{1/2}/\delta)$
(11)+(13)+(14)	k_{11}/k_D	$(k_{11}/k_3^{1/2}k_4)(C^\circ D^{1/2}/\delta)$
(12)+(13)+(14)	$(k_{12}/k_3^{1/2}k_6)(C^\circ D^{1/2}/\delta)$	$(k_D/k_3^{1/2}k_4)(C^\circ D^{1/2}/\delta)$

$$\text{RArS}-\overset{\cdot}{\text{C}}=\text{S} \overset{4}{\rightarrow} \text{RArS}^{\cdot} + \text{CS} \underset{7'}{\overset{I^{\cdot-}}{\rightleftharpoons}} \text{RArS}^{-} + 1$$

9·

$$[\text{RArS}-\overset{-}{\text{C}}=\text{S}+1] \overset{6}{\rightarrow}$$
$$\text{RArS}^{-}+\text{CS}$$

I·⁻ | 11

1·⁻ | 5′

| 1

| 12

$$\underset{S\ \ S^{-}}{\text{RArSC}-\text{C(SArR)}_2} \overset{-\text{RArS}^{-}}{\underset{13}{\longrightarrow}} \underset{S\ \ S}{\text{RArSC}-\text{CSArR}}$$

11

14 | 2 *1*·⁻

$$\underset{S^{-}\ \ S^{-}}{\text{RArS}-\text{C}=\text{C}-\text{SArR}}$$

Scheme 1.

take for k_{10} a maximal value of 10^{10} M^{-1} s^{-1} corresponding to diffusion control; this reaction path is thus clearly unlikely.

Thus, there remain three mechanistic possibilities, either reactions 5′ and 6 in competition with reaction 12 or reactions 4 and 7′ in competition with reactions 11 or 12. Scheme 1 can thus be proposed for the reactions after reactions 2 and 3.

The yield of 2 is low for *1a* and *1e* but higher for *1b* − *1d*: a plot of the yield *vs.* Hammett σ-values gives a non-linear curve. The rate of reaction 4 would be expected to show a non-monotonous variation with the Hammett substituent constant σ, due to a mutual conjugation in the transition state between the substituent R and the reaction centre; a similar non-linear Hammett plot is found, *e.g.*, when the rate of the reaction of methyl methacrylate radicals with substituted styrenes[22] is plotted *vs.* Hammett's σ-values. The transition state of this radical addition is analogous to that of the radical cleavage, eqn. 4. Reaction 6 would probably give a linear Hammett plot as the leaving group ability of RArS⁻ would be linearly dependent on the σ-value of R. Similarly, reaction 11 would be expected to lead to a linear Hammett correlation as the substituents at the two coupling species are the same and no mutual conjugation thus is found. The nucleophilicity of RArSC̄=S and the electrophilicity of *1* would be

expected to vary linearly with σ, so eqn. 12 would also be expected to exhibit a linear Hammett correlation.

Since k_3 has been shown[1] to be linearly correlated with the Hammett σ-values and taking into account the rate dependence of the competition parameters in Table 2, it can be concluded that the most likely mode of cleavage would be reaction 4.

In the scheme two coupling routes are depicted, eqn. 11 and eqns. 5′, 12, but the question is how much are they different? This is related to the distance at which an electron can be transferred from *1*·⁻ to *9*·, and the distance at which bond formation starts in the nucleophilic addition of *9*⁻ to *1*. On approaching *9*·, *1*·⁻ would be able to transfer an electron to *9*· at a diffusion controlled rate; a nucleophilic attack of *9*⁻ on *1*, if occurring, would involve a carbon−carbon bond formation, where *9*⁻ delivered both electrons. Such a donation and back-donation of electrons as distinct events seems questionable which could suggest that only one transition state existed.

The fate of the central carbon atom *1* is uncertain; in the scheme it has been accounted for as carbon sulfide (4). *4* is formed during the electrolysis of carbon disulfide[23] and was trapped as a rhodium complex. *4* might be of interest in synthetic organic chemistry so several reagents, including electrophiles, nucleophiles, dienes, and dienophiles, were used in attempts to trap *4*, but without any success.

S,S-Diphenyl dithiocarbonate (*5*) gives on reduction followed by methylation a nearly quantitative yield of *3*, whereas *O,S*-diphenyl thiocarbonate (*7*) under similar contions gives *3* and anisole, but neither *5* nor *7* give any substituted ethylenes.

O,S-Diphenyl dithiocarbonate (*6*) and *O,O*-diphenyl thiocarbonate (*8*) give a low yield of 1,2-bis(methylthio)-1,2-bisphenoxyethylene. None of the compounds *5* to *8* are thus useful for the preparation of substituted ethylenes.

In conclusion, substituted diphenyl trithiocarbonates are useful for the preparation of substituted *E*-1,2-bis(alkylthio)-1,2-bis(arylthio)ethylene, but the yield depends on the substituents. Strongly electron-attracting or electron-donating substituents lower the yield. The most likelt mechanism for the reaction involves the expulsion of a benzenethiolate moiety from the initially formed anion radical (eqn. 3). The resulting neutral radical (*9*·) would then undergo two competitive reactions: cleavage with loss of CS (eqn. 4) and coupling with the initially formed anion radical *1*·⁻.

EXPERIMENTAL

Apparatus. An H-type 3-electrode cell[24] of conventional design was used in combination with a JUUL Electronic 300V/1A potentiostat. Temperature control of the cell was performed by means of a HETOFRIG CD 122 cryostat. ^{1}H NMR spectra were recorded on a Varian A 60 NMR spectrometer and mass spectra on a Micromass 70 −70F or a CEC 21−104 mass spectrometer. Melting and boiling points are uncorrected. GLC analyses were performed on a Hewlett-Packard 5711 A gas chromatograph with a Hewlett-Packard 3370 B integrator, using a 2 m SS-column, containing 15 % SE 30 on Chromosorb WAW (80−100 mesh). HPLC analysis was performed on a system consisting of a Rheodyne 6-way valve injectionport, an ALTEX 110 A pump and a CECIL UV detector, CE 212 (200−450 nm) or a JOPLING R.I. detector. 30 cm 6 mm columns were packed using a slurry technique with Lichrosorb. R. P. 18.5 μm (Merck) as packing material, the pressure provided by a Magnus Scientific pump at 3.5×10^7 N m^{-2}. The system was connected to a Hewlett-Packard 3380S integrator. X-Ray analysis was performed by means of a diffractometer of the Arndt and Philips type (1961).[25]

Materials. The trithiocarbonates *1a−1e* were synthesized according to published methods,[26−29] with the slight modification that acetonitrile deaerated by nitrogen was used as solvent. This generally increases the yield considerably. O,O-Diphenyl thiocarbonate *8*,[30] S,S-diphenyl dithiocarbonate *5*,[31] O,S-diphenyl thiocarbonate *7*,[31] and O,S-diphenyl dithiocarbonate *6*,[32] were prepared according to the references given. Spectroscopic data for all the synthesized compounds were in agreement with those given in the literature.[26−32] N,N-Dimethylformamide (DMF) and tetrabutylammonium iodide (TBAI) were used as received. The DMF was stored over 4 Å molecular sieves. All other compounds were commercially available and recrystallized or redistilled before use, if purity tests by GLC or HPLC showed it necessary.

General procedure for electrolysis. All the electrolyses were performed in DMF/0.1 M TBAI at 10 °C under nitrogen. The working electrode was a mercury pool or a platinum net and as reference electrode an Ag/AgI electrode was used in the same solvent/electrolyte system.

Procedure A. The reductions were performed in the presence of a suitable alkylating agent. After completion of the electrolysis, the catholyte was diluted with water and extracted three times with diethyl ether. The combined organic phases were dried over MgSO$_4$, and after evaporation of the solvent the crude product was separated by column chromatography, GLC and/or HPLC.

Procedure B. The reductions were performed

without any alkylating agent present. After completion of the electrolysis excess of an alkylating agent was added and, after 2 h of stirring, the products were extracted and worked up in a manner similar to that of method A.

Reduction of diphenyl trithiocarbonate (1c) in the presence of methyl iodide. One g of *1c* was reduced at −0.9 V in the presence of 2 ml of methyl iodide (*10*), $n=2.05$ F mol^{-1}. After the extraction the crude product was separated on silica, gradually changing the eluent from light petroleum (b.p. <50 °C) to diethyl ether. Isolated were thioanisole (0.71 g, 75 %) and Z- and E-1,2-bis(methylthio)-1,2-bis(phenylthio)ethylene (0.261 g, 41 %). Recrystallization of the $Z−E$ mixture from 5 % diethyl ether/95 % light petroleum gave exclusively one of the isomers. The mother liquor was separated by preparative HPLC, using methanol/water/11/2 as eluent. The isomer distribution was 1:9. X-Ray analysis[25] of the major isomer characterized it as the E isomer. E-1,2-Bis(methylthio)-1,2-bis(phenylthio)ethylene (0.224 g, 35 %). Anal. C$_{16}$H$_{16}$S$_4$: C, H, S; m.p. 116 °C. ^{1}H NMR spectrum (CCl$_4$): δ 2.23 (3 H, s), 7.24 (5 H, m). Mass spectrum (*m/e*): 336, 289, 227, and 109. Z-1,2-Bis(methylthio)-1,2-bis(phenylthio)ethylene (0.027 g, 4 %), m.p. 48−50 °C. ^{1}H NMR (CCl$_4$): δ 2.31 (3 H, s), 7.26 (5 H, m). Mass spectrum (*m/e*): 336, 289, 227, and 109.

Reduction of diphenyl trithiocarbonate (1c) in the presence of ethyl iodide. One g of *1c* was reduced at −0.9 V in the presence of 5 ml of ethyl iodide at 10 °C; $n=2.05$ F mol^{-1}. After a work up procedure, similar to that described above, were isolated: Ethyl phenyl sulfide (0.76 g, 72 %) and E-1,2-bis(ethylthio)-1,2-bis(phenylthio)ethylene (0.264 g, 38 %), m.p. 103 °C. ^{1}H NMR spectrum (CCl$_4$): δ 1.28 (3 H, t, J 6 Hz), 2.88 (2 H, q, J 6 Hz), 7.0−7.8 (5 H, m). MS (*m/e*): 364, 335, 302, 255, 109, 77. Z-1,2-Bis(ethylthio)-1,2-bis(phenylthio)ethylene was not isolated. The $Z:E$ ratio was estimated from the ^{1}H NMR spectrum; $Z:E=1:10$. Separation of the Z isomer from the E isomer by HPLC was unsuccessful. ^{1}H NMR spectrum (CCl$_4$): δ 1.31 (3 H, t, J 6 Hz), 2.9 (2 H, q, J 6 Hz), 7.0−7.8 (5 H, m).

Reduction of diphenyl trithiocarbonate (1c) in the presence of isopropyl iodide. One g of *1c* was reduced at −0.9 V in the presence of 4 ml of isopropyl iodide at 10 °C; $n=2.06$ F mol^{-1}. Work up as above. Isolated were: Isopropyl phenyl sulfide (0.824 g, 71 %) and E-1,2-bis(isopropylthio)-1,2-(phenylthio)ethylene (0.285 g, 38 %), m.p. 121 °C. ^{1}H NMR spectrum (CDCl$_3$): δ 1.17 (6 H, d, J 8 Hz), 3.42 (1 H, sept., J 8 Hz), 7.1−7.3 (5 H, m). Mass spectrum (*m/e*): 392, 349, 317, 283, 107, 77. Z-1,2-Bis(isopropylthio)-1,2-bis(phenylthio)ethylene was not isolated. However, from HPLC using a 30 cm 6 mm column containing 5 μm R. P. 18 packings, eluent CH$_3$CN:water (10:3), the $Z:E$ ratio was measured to

be 1:11, assuming that both isomers had the same refractive index.

Reduction of di(4-methoxyphenyl) trithiocarbonate (1a) in the presence of 10. Two g of *1a* were reduced at −1.25 V in the presence of 5 ml of *10; n* = 1.97 F mol⁻¹. Work up procedure as for *1c*. Isolated were 4-methoxyphenyl methyl sulfide (1.91 g, 91 %) and *E*-1,2-bis(methylthio)-1,2-bis(4-methoxyphenylthio) ethylene (0.135 g, 11 %), m.p. 129 °C. ^{1}H NMR (CDCl₃) δ 2.23 (3 H, s), 3.7 (3 H, s), 7.36 (4 H, m). Mass spectrum (*m/e*): 396, 349, 257, 139, 107. The *Z:E* ratio was measured to be 1:11 by HPLC as described above.

Reduction of di-4-tolyl trithiocarbonate (1b) in the presence of 10. One g of *1b* was reduced at −1.1 V in the presence of 2 ml of *10; n* = 2.01 F mol⁻¹. Work up as described above. Isolated were methyl 4-tolyl sulfide (0.801 g, 84 %) and *E*-1,2-bis(methylthio)-1,2-bis(4-tolylthio)ethylene (0.144 g, 23 %), m.p. 118 °C. ^{1}H NMR spectrum (CDCl₃) δ 2.23 (3 H, s), 2.33 (3 H, s), 7.18 (4 H, m). Mass spectrum (*m/e*): 364, 349, 317, 241, 123, 91. *Z*-1,2-Bis(methylthio)-1,2-bis(*p*-tolylthio)ethylene was not isolated pure, but identified from the ^{1}H NMR spectrum (CCl₄): δ 2.29 (3 H, s), 2.31 (3 H, s), 7.15 (4 H, m). The *Z:E* ratio was measured by HPLC to be 1:9, assuming that both isomers had the same refractive index.

Reduction of di-(4-chlorophenyl) trithiocarbonate (1d) in the presence of 10. One g of *1d* was reduced at −0.75 V in the presence of 2 ml of *10; n* = 2.06 F mol⁻¹. Work up as for *1a*. Isolated were 4-chlorophenyl methyl sulfide (0.61 g, 63 %) and *E*-1,2-bis(methylthio)-1,2-bis(4-chlorophenylthio)ethylene (0.36 g, 60 %), m.p. 127 °C. ^{1}H NMR spectrum (CDCl₃): δ 2.29 (3 H, s), 7.16 (4 H, m). Mass spectrum (*m/e*): 404, 357, 261, 143, 121. The *Z:E* ratio was measured to be 1:10 by HPLC as described above. *Z*-1,2-Bis(methylthio)-1,2-bis(4-chlorophenylthio)-ethylene was not isolated pure, but identified from the ^{1}H NMR spectrum (CDCl₃): δ 2.36 (3 H, s), 7.17 (4 H, m).

Reduction of di-(4-acetylphenyl) trithiocarbonate (1e) in the presence of 10. 1.5 g of *1e* was reduced at −0.8 V in the presence of 3.5 ml of *10* at 10 °C; *n* = 2.01 F mol⁻¹. Work up procedure as for *1a*. Isolated were 4-acetylphenyl methyl sulfide (1.34 g, 93 %) and *E*-1,2-bis(methylthio)-1,2-bis(4-acetyl-phenylthio)ethylene (0.064 g, 7 %), m.p. 137 °C. ^{1}H NMR spectrum (CDCl₃): δ 2.31 (3 H, s), 7.39 (4 H, m). Mass spectrum (*m/e*): 420, 373, 269, 151. The *Z* isomer was not isolated. The *Z:E* ratio was measured to be 2:21 using HPLC as described above.

Reduction of *1a* − *1e* according to *method B* decreased the yields of the dimers significantly; *n* ~ 2 F mol⁻¹; only traces of dimeric species were found.

Reduction of S,S-diphenyl dithiocarbonate (5) in the presence of dimethyl sulfate (11). One g of *5* was reduced at −1.5 V in the presence of 3 ml of dimethyl sulfate, *11; n* = 2.0 F mol⁻¹. Work up procedure as described above. Isolated was thioanisole (0.97 g, 96 %). No traces of other compounds were detected.

Reduction of O,S-diphenyl dithiocarbonate (6) in the presence of 11. Two g of *6* were reduced at −1.1 V in the presence of 3 ml of *11; n* = 2.05 F mol⁻¹. Work up procedure as described above. Isolated were anisole (0.880 g, 93 %) and thioanisole (1.01 g, 94 %). 1,2-Bis(methylthio)-1,2-bis(phenoxy)ethylene was not isolated pure, probably due to its instability towards oxygen,[33] but identified from spectroscopic data: ^{1}H NMR spectrum (CDCl₃): δ 2.31 (3 H, s), 7.2 (5 H, m). Mass spectrum (*m/e*): 304, 257, 211, 93. The yield was less than 5 %.

Reduction of O,S-diphenyl thiocarbonate (7) in the presence of 11. Two g of *7* were reduced at −1.7 V in the presence of 4 ml of *11; n* = 1.97 F mol⁻¹. Work up procedure as described above. Isolated were anisole (0.86 g, 94 %) and thioanisole (0.97 g, 94 %).

Reduction of O,O-diphenyl thiocarbonate (8) in the presence of 11. Two g of *8* were reduced at −1.0 V in the presence of 4 ml of *11; n* = 1.94 F mol⁻¹. Isolated was anisole (1.64 g, 91 %). 1,2-Bis(methylthio)-1,2-bis(phenoxy)ethylene was identified from spectroscopic data as above. The yield was less than 5 %.

Trapping experiments of carbon monosulfide. During electrolysis of *1c* the nitrogen, which had passed through the catholyte, was bubbled through a suitable solution (DMF or THF) or a trapping agent (typical 0.1 M solution) at −10 °C. As trapping agents were used: Cyanide, thiocyanide, sodium diethylmalonate, butyllithium, methylmagnesium bromide, maleic anhydride, tetracyanoethylene, furan, phenyl azide, ethyl cinnamate and diphenyl disulfide. CS or derivatives of CS were not trapped in any of the cases.

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