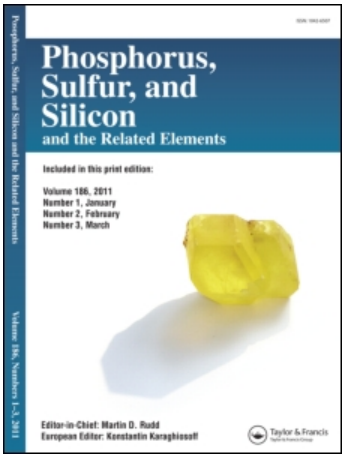

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ELECTROREDUCTION OF ORGANIC COMPOUNDS, 29*

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ELECTROREDUCTION OF ORGANIC COMPOUNDS, 29*

Electroreduction of ω-Haloalkyl Dithiopivalates and O-Methyl Thiopivalate in Methanol and Methan[D]ol

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O-Methyl thiopivalate **3** yields bis(1-methoxy-2,2-dimethylpropyl)disulfane **6** and 3,5-di-*tert*-butyl-1,2,4-trithiolane **8** on electroreduction in methanol. Thiono ester **3** formed by transesterification is also the source of **6** which is found as product on electroreduction of 4-chlorobutyl (**1**) and 5-chloropentyl dithiopivalate **2**.—The deutero derivatives **12** and **13** result from the electroreduction of **3** in methan[D]ol.

Keywords: Electroreduction; O-methyl thiopivalate; disulfide; 1;2;4-trithiolane; deuteration

As described in our previous publication[3] the electroreduction of 4-chlorobutyl dithiopivalate **1** in methanol under galvanostatic conditions yields the disulfide **6** as one of the products. We ascribed the formation of **6** to the intermediate solvolysis of **1** to form **4** and O-methyl thiopivalate **3** which is then electroreduced. In the following we report on further experiments, which we undertook to support our assumption and to get more information on the course of these electrolyses.

Since the disulfide **6** was not detected among the products of electroreduction of 2-chloroethyl or 3-chloropropyl dithiopivalate (**10**)[3] we first studied the higher homologue of **1**, 5-chloropentyl dithiopivalate **2**.—After its electroreduc-

*Part 28: Ref. [1]

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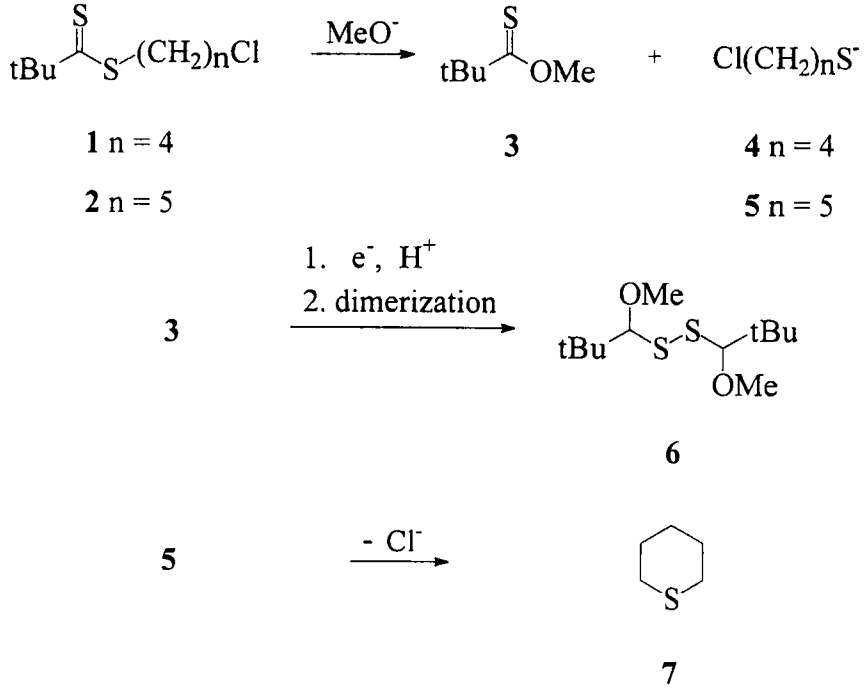
tion in methanol under the same conditions as applied for **1** we obtained tetrahydrothiopyran **7** as the main product (57%)[4]. The disulfide **6** was formed as minor product and **3** (15%) could also be detected in the reaction mixture. Accordingly, transesterification obviously occurs with **2** in the same way as with **1**. 5-Chloropentanethiolate **5** is released together with **3** and cyclizes to form **7**.

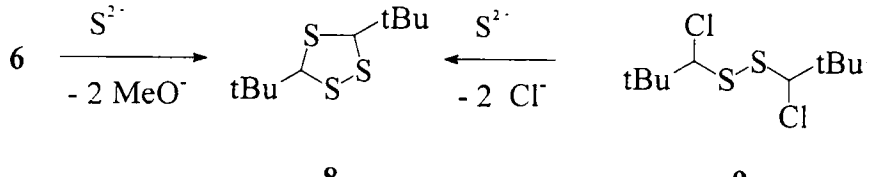
Neither **3** nor **7** are formed *via* reduction. A real reduction product, on the other hand, is 3,5-di-*tert*-butyl-1,2,4-trithiolane **8** which we isolated as a mixture of diastereoisomers (*meso*: *d,l* ≈ 1:1) with 43% yield.[4]

In completion of our previous results[3] we also found a small amount of the trithiolane **8** to be formed if **1** was electroreduced under potentiostatic instead of galvanostatic conditions.

After being successful in preparing the elusive O-methyl thiopivalate **3**, which is very sensitive to oxidation and smokes if exposed to air, in an at least preparatively useful (3 g) though low (9%) yield we have studied its electroreduction. All electrolyses were performed under rigorous exclusion of oxygen. Therefore, strict tightness of the cell and a nitrogen atmosphere were maintained during the electrolysis and the gas phases of the cathodic and the anodic compartments were connected with each other to achieve a balance of pressure.



SCHEME 1



8 **9**

SCHEME 2

Nevertheless the overall yield was low (36%). The 1,2,4-trithiolane **8** was produced as main product (18%) and the expected disulfide **6** (12%) was formed too together with 6% neopentyl dithiopivalate as by-product which is also formed on electroreduction of **1**.[3]

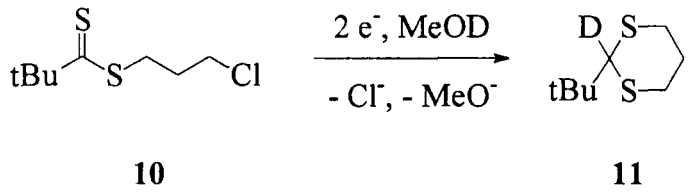
The formation of **6** from **3** does not unequivocally prove **3** to be an intermediate during the electroreduction of **1**. However, it shows a reaction *via* **3** to be possible and probable.

The formation of **8** from **2** or **3** can be explained in the following way. The known conventional preparation of **8** starts from the disulfide **9** which is cyclized by nucleophilic substitution of the chloride with sodium sulfide.[5] One may therefore assume that the disulfide **6** which is present in the reaction mixture undergoes an analogous substitution reaction with sulfide anions formed during the electroreduction of dithioesters[6,7] and with methoxide instead of chloride as leaving group.

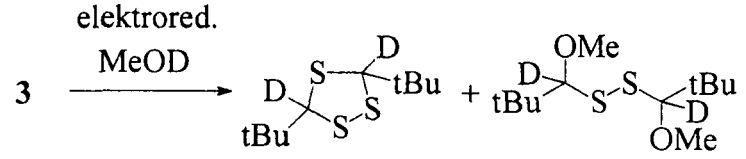
The *EHC*-mechanism which we assume for the formation of **6** is accepted for similar cases[3,8]. It is characterized by the protonation of a radical anion in the second step. In order to answer the question wether the protons needed for this step stem from the solvent or traces of water or originate from a Hofmann-type elimination of the quaternary ammonium salt used as supporting electrolyte and electrogenerated bases, we have performed electrolyses in methan[D]ol. For this purpose purest tetraethylammonium bromide was carefully dried over phosphorus pentoxide. The water content of this salt as well as the deuterated methanol as checked by NMR spectroscopy was less than 1%. All parts of the cell were particularly carefully dried.

As a test, 3-chloropropyl dithiopivalate **10** was studied from which 2-*tert*-butyl-1,3-dithiane is formed in methanol with a good yield.[3] Using deuteromethanol we obtained the deuterated dithiane **11** with a content of less than 1% non-deuterated product according to its NMR and MS analyses.

The thiono ester **3** was also cleanly electroduced in methan[D]ol to form the two characteristic deuterated products **12** and **13**, each as a mixture of diastereoisomers. Again the contents of the corresponding non-deuterated compounds **6** and **8** were below 1%.—One can, therefore, conclude that protonation of the anionic species which are formed as intermediates during the electroreduction of



10 **11**



12 **13**

SCHEME 3

thiono and dithioesters in methanol is exlusively brought about by the alcoholic solvent. Hofmann-type elimination does not play a role as product determining step under the applied conditions of the electrolyses. Likewise, traces of water in the solvent-supporting-electrolyte system can be excluded as the proton source.

EXPERIMENTAL

Boiling points were determined during distillation.—IR: Perkin-Elmer 399 and FTIR 1720.—^{1}H NMR: Bruker AC 250 P and AMX 400 ($CDCl_3$, TMS as internal standard).—^{13}C NMR: Bruker WM 250 P and WM 400 ($CDCl_3$, δ_c = 77.0 as internal standard).—MS: Varian MAT CH7 and VG 250 S (HRMS).—GC-MS-Coupling: HP-GC 5970; fused silica column (50 m); SE 54 as stationary phase; mass selective detector.

O-Methyl 2,2-dimethylpropanethioate (O-methyl thiopivalate) (**3**): 21.0 g (0.25 mol) pivalonitrile and 8.0 g (0.25 mol) methanol were dissolved under N_2 in 80 ml dry diethyl ether. During permanent stirring an excess of gaseous HCl was bubbled through the solution at 0°C. After stirring over night the precipitate of *O-methyl 2,2-dimethylpropanimidoate hydrochloride* was filtered off and dried *i. vac.* The dry crystals were dissolved in dry pyridine under N_2 and H_2S was bubbled through the solution for 8 h. The yellow solution was poured on a mixture of 150 g ice and 200 ml 2n HCl. The yellow oil which separated was extracted with diethyl ether and the extract dried over Na_2SO_4. The solution was concentrated and cautiously distilled *i. vac.* into an ice-cooled flask to yield 3.0

g (9%) **3** as yellow liquid, which decomposes on exposure to air.—B.p. 24–26°C/0.2 Torr.—IR: ν = 2971 cm^{-1}, 1477, 1439, 1211, 1157, 1122 (C=S).—^1H NMR (250 MHz): δ = 1.29 (s, 9H, *t*Bu), 4.07 (s, 3H, OCH_3).—^{13}C NMR: δ = 29.2 [$C(CH_3)_3$], 47.1 [$C(CH_3)_3$], 59.2 (OCH_3), 232.2 (C=S).—MS (70 eV): *m/z* (%) = 102 (7) [M^+—CH_2O], 101 (100) [M^+—CH_3O], 86 (13) [M^+—CH_2S], 85 (14) [M^+—CH_3S], 75 (22) [M^+—C_4H_9], 69 (37) [$C_5H_9^+$], 57 (61) [$C_4H_9^+$].—$C_6H_{12}OS$: calcd. 132.0609, found 132.0613 (MS-CI).

5-Chloropentyl 2,2-dimethylpropanedithioate (5-chloropentyl dithiopivalate) (**2**): 1.85 g (10.0 mmol) 1-bromo-5-chloropentane in 30 ml $CHCl_3$ and 0.50 g (2.7 mmol) benzyltrimethylammonium chloride in 20 ml H_2O were stirred at room temp. with a solution of 2.30 g (12.0 mmol) of sodium dithiopivalate dihydrate[3] in 20 ml H_2O until the aqueous phase was colourless. The organic layer was separated, washed 3x with H_2O, dried over $MgSO_4$ and concentrated *i. vac.* Distillation of the residue yielded 1.44 g (60%) **2** as orange oil.—B.p. 106°C/0.15 Torr.—IR: ν = 2990 cm^{-1}, 2900, 1460, 1105 (C=S), 920.—^1H NMR (400 MHz): δ = 1.45 (s, 9H, tBu), 1.57 (m, 2H, 3′-H), 1.70 (qn, J = 7.5 Hz, 2H, 2′-H), 1.82 (qn, J = 7.1 Hz, 2H, 4′-H), 3.18 (t, J = 7.4 Hz, 2H, SCH_2), 3.56 (t, J = 6 Hz, 2H, $ClCH_2$).—^{13}C NMR (100 MHz): δ = 26.41, 26.43, 32.10 (3 CH_2), 31.67 [$C(CH_3)_3$], 36.31 (CH_2Cl), 44.51 (CH_2S), 52.01 [$C(CH_3)_3$], 248.0 (C=S).—MS (70 eV): *m/z* (%) = 238 (10) [M^+], 149 (4), 134 (36), 101 (29), 92 (9), 85 (8), 78 (6), 69 (17), 67 (15), 59 (9), 57 (100) [$C_4H_9^+$].—$C_{10}H_{19}ClS_2$ (238.9). calc. C 50.29, H 8.02, Cl 14.84, S 26.85; found C 49.58, H 7.93, Cl 15.10, S 26.73.

Electrolyses were performed galvanostatically[3,6] (if not stated otherwise) by means of a Hewlett Packard power supply 6274 B at 1 A (120 Am^{-2}) in a cooled tight cylindrical cell with a concentric arrangement of graphite anode, diaphragm (tube-shaped G3 glass frit) and lead cathode (80 cm^2, see Figure 1). Tetraethylammonium bromide (0.2 M) in 60 ml methanol was used as solvent-supporting-electrolyte. When the electrolysis was finished the catholyte was removed immediately. It was diluted with the fivefold amount of H_2O and extracted first with n-hexane then with diethyl ether. The combined extracts were washed with H_2O, dried over Na_2SO_4 and concentrated *i. vac.* The residue was purified by column chromatography or distillation.—Minor products were detected and identified by GC and, especially, GC-MS-coupling techniques. Product yields in mixtures were determined NMR spectroscopically, i.e. known amounts of 1,2-diphenylethane were added as standard to aliquot parts of the mixture and the composition was calculated from the signal integrals.

Electrolysis of 2.1 g (8.8 mmol) **2** until the consumption of 1.5 F and column chromatography (hexane/ethyl acetate 100:1) yielded:

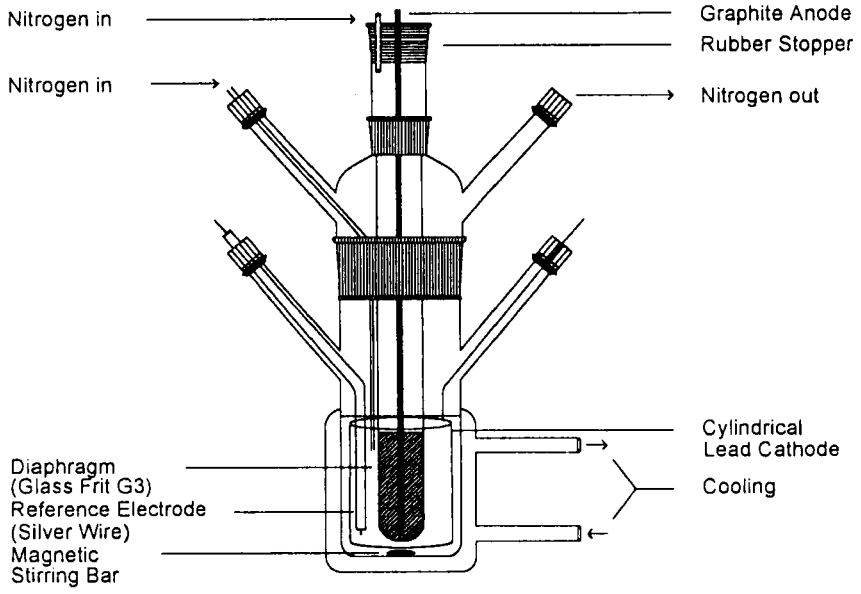


FIGURE 1 Electrolysis Cell

0.50 g (57%) *Tetrahydrothiopyran* **7**, yellowish liquid; IR-, ^{1}H NMR-[(400 MHz): δ = 1.58 (m, 2H, 4-H), 1.81 (m, 4H, 3-H, 5-H), 2.59 (m, 4H, 2-H, 6-H)], and ^{13}C NMR spectra in agreement with an authentic sample.[9]

0.48 g (43%) *3,5-Di-tert-butyl-1,2,4-trithiolane* **8** (1:1-mixture of *cis/trans* isomers), light yellow oil.—IR: ν = 2959 cm^{-1}, 2924, 2851, 1482, 1366, 1170, 907.—^{1}H NMR (400 MHz): δ = 1.15/1.16 (each s, 18H, tBu), 4.69/4.85 (each s, 2H, 3-H, 5-H).—MS (70 eV): *m/z* (%) = 236 (32) [M^+], 179 (40) [M^+—*t*Bu], 109 (38) [M^+—C_5H_{10}], 102 (39) [M^+—*t*BuCHS], 101 (44), 87 (17), 74 (24), 70 (59) [$C_5H_{10}^+$], 69 (100), 57 (58) [$C_4H_9^+$]. The spectra agree with the data from ref..[3]

Bis(1-methoxy-2,2-dimethylpropyl)disulfane **6** (3%) [^{1}H NMR (400 MHz): δ = 1.03/1.04 (each s, 18H, tBu), 3.50/3.52 (each s, 6H, OCH_3), 4.10/4.11 (each s, 2H, CH)] and *O-methyl 2,2-dimethylpropanethioate* **3** (15%) were spectrocopically detected in the product mixture.

Electrolysis of 0.60 g (2.67 mmol) **1** at a constant potential (potentiostat Bank ST 72) of −1.6 V *vs.* sce as described previously[10] gave after the usual work-up (extraction with hexane) 90 mg of an oily crude product, which mainly consisted of **6** and *neopentyl 2,2-dimethylpropanedithioate*[3] but according to its GC-MS and ^{1}H NMR spectrum contained *cis*- and *trans*-**8** (yield: 2.5%).

Electrolysis of 1.20 g (9.1 mmol) **3** until the consumption of 1.2 F and column chromatography (CCl_4/CH_2Cl_2 100:1) yielded:

0.19 g (18%) **8** (mixture of diastereoisomers), identical with **8** obtained from **2** according to its IR-, ^{1}H NMR- and MS.

0.15 g (12%) **6** (mixture of diastereoisomers) light yellow oil, spectra identical with data from ref..[3]

0.11 g (6%) *Neopentyl 2,2-dimethylpropanedithioate*, yellow oil, spectra identical with data from ref..[3]

Electrolysis of 2.20 g (10.4 mmol) **10**[3] in methan[D]ol (Janssen) until the consumption of 2 F and distillation (Kugelrohr, 1 Torr) yielded:

0.45 g (25%) *[2-D]-2-tert-Butyl-1,3-dithiane* **11**, colourless liquid.—IR: ν = 3022 cm^{-1}, 2946, 1450, 1360, 1275, 1256, 895, 773.—^{1}H NMR (250 Mhz): δ = 1.10 (s, 9H, tBu), 1.50–2.33 (m, 2H, CH_2), 2.75–3.00 (m, 4H, SCH_2).—^{13}C NMR (63 MHz): δ = 26.0 (CH_2), 27.8 [$C(CH_3)_3$], 31.2 (SCH_2), 35.9 [$C(CH_3)_3$]. The signal of C-2 (δ = 61.9[2]) is missing. Instead, expectedly, a very weak *C*D triplet is detected at 61.9 ppm.—MS (70 eV): *m/z* (%) = 177 (6) [M^+], 176 (54), 121 (23) [M^+—C_4H_8], 119 (100) [M^+—C_4H_8D], 106 (7), 85 (6), 75 (5).

Electrolysis of 1.30 g (9.8 mmol) **3** in methan[D]ol (Janssen) until the consumption of 2.3 F and column chromatography (petroleum ether 60–70°C/ethyl acetate 30:1) yielded:

0.15 g (12%) *[3,5-D_2]-3,5-Di-tert-butyl-1,2,4-trithiolane* **12**, colourless liquid.—IR: ν = 2952 cm^{-1}, 2920, 1486, 1361, 1178, 900.—^{1}H NMR (250 MHz): δ = 1.18 (s, 18H, tBu). The CH-signals of **8** are missing.—MS (70 eV): *m/z* (%) = 238 (55) [M^+], 181 (11) [M^+—C_4H_9], 110 (49), 104 (21), 103 (91), 102 (23), 101 (26), 88 (24), 74 (37), 71 (62), 70 (100), 59 (59), 57 (92) [$C_4H_9^+$].

0.14 g (10%) *Bis([1-D]-1-methoxy-2,2-dimethylpropyl)disulfane* **13**, colourless oil.—IR: ν = 2958 cm^{-1}, 1450, 1095.—^{1}H NMR (250 MHz): δ = 1.08 (s, 18H, tBu), 3.55, 3.58 (each s, 6H, OCH_3). The CH-signals of **6** are missing.—MS (70 eV): *m/z* (%) = 268 (0.3) [M^+], 166 (5), 104 (12), 103 (8), 102 (6), 70 (82), 69 (25), 59 (15), 57 (100) [$C_4H_9^+$], 56 (26).

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References

[1] S. Anowski and J. Voss, *J. Prakt. Chem.*, **338**, 337–344 (1996).
[2] T. Gade, Ph.D. Thesis, University of Hamburg (1990).

[3] T. Gade, M. Streek and J. Voß, *Chem. Ber.*, **121**, 2245–2249 (1988).
[4] Considering the yields one has to take into account that 1 mole of **5** or **7** *plus* 1 mole of **3** or 0, 5 mole of the disulfide **6** or the trithiolane **8** can be formed from 1 mole of **2**. The total amount of products may, therefore, reach apparant 200%.
[5] S.B. Tjan, J.C. Haakman, C.J. Teunis and H.G. Peer, *Tetrahedron*, **28**, 3489–3500 (1972).
[6] T. Gade, M. Streek and J. Voß, *Chem. Ber.*, **125**, 127–141 (1992).
[7] G. Adiwidjaja, L. Kistenbrügger and J. Voss, *J. Chem. Res. (S)*, **1981**, 88–89 (1981); *J. Chem. Res. (M)*, 1227–1253.
[8] L. Eberson and H. Schäfer, *Fortschr. Chem. Forschg.*, **21**, 1–128, esp. p. 8 (1971).
[9] R.L. Crumbie and D.D. Ridley, *Aust. J. Chem.*, **32**, 2777–2781 (1979).
[10] M. Streek and J. Voß, *Chem. Ber.*, **121**, 2251–2253 (1988).