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Electrochemical Reduction of Carbon Disulfide in Dimethylformamide

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The electrolytic reduction of carbon disulfide in dimethylformamide followed by alkylation with methyl iodide gave 4,5-bis(methylthio)-1,3-dithiole-2-thione. This compound was identical with the product formed by the sodium amalgam reduction of carbon disulfide and erroneously reported as dimethyl tetrathiooxalate. The lower melting product in the latter work was found to be 4-methylthio-1,3-dithiole-2-thione. The structure proof for both compounds was based on spectral and polarographic data and chemical reaction with morpholine. 4,5-Bis(methylthio)-1,3-dithiole-2-thione was converted by alkaline hydrolysis and by electrolytic reduction followed by alkylation with methyl iodide into tetrakis(methylthio)ethylene.

The recent report[2] of the preparation of dialkyl oxalates and dialkyl carbonates by the electrochemical reduction of carbon dioxide in dimethylformamide followed by treatment with alkyl halides suggested the present study of the electrochemical reduction of carbon disulfide as a method for preparing dimethyl tetrathiooxalate. The results obtained were different from those expected and will be presented here.

Carbon disulfide gave two one-electron polarographic waves at −0.99 (Hg pool) (I_d = 2.34) and −2.21 V (Hg pool) (I_d = 2.04) in dimethylformamide containing 0.2 *M* tetrabutylammonium bromide. Electrolysis was carried out using a saturated calomel electrode as a reference electrode at a controlled potential of −1.40 and of −1.80 V, and at an uncontrolled potential, followed by alkylation with methyl iodide, and gave 4,5-bis(methylthio)-1,3-dithiole-2-thione (1) as the major product in yields varying from 12.5 to 41.5%.

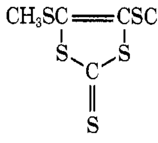
Evidence for structure 1 was the spectral and polarographic data and its chemical reactions. The melting point of 101° was in agreement with that of the products obtained by the sodium amalgam reduction of carbon disulfide followed by alkylation with methyl chloride and formulated as dimethyl tetrathiooxalate. This reduction

Table I
Polarographic Reduction of 1, 2, and Related Compounds in Dimethylformamide Containing 0.2 *M* Tetrabutylammonium Bromide

Compd	Concn, mmol/l.	$E_{1/2}$ (Hg pool)	$I_d{}^a$
1	3.20	−0.94	1.80
		−1.81	2.18
		−2.20	1.22
2	0.89	−0.94	2.20
		−1.86	1.31
		−2.16	1.18
$(CH_3S)_2C{=}S$	3.26	−1.00	4.50
$(CH_3S)_2C{=}C(SCH_3)_2$	0.80	−1.62	1.75

[a] $I_d = i_d/Cm^{2/3}t^{1/6}$.

also yields a compound melting at 71° which was considered to be an isomer of dimethyl tetrathiooxalate.[3] Repetition of this work showed that the 101° melting compound was identical with that isolated from the electrochemical reduction. The 71° melting compound, upon the basis of its spectral and polarographic data and reaction with morpholine, was 4-methylthio-1,3-dithiole-2-thione (2).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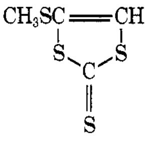
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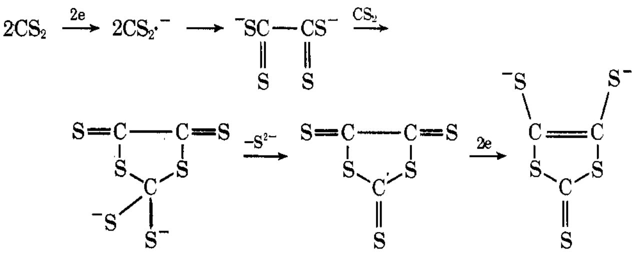
Compound 1 showed a carbon–sulfur double bond at 9.41 μ in the ir spectrum, a singlet (δ 2.48) in the nmr, and a molecular ion at *m/e* 226 and (M − CS_2 at *m/e* 150 in the mass spectrum. The 71° melting compound (2) gave a similar absorption (9.45 μ) in the infrared, two singlets in the nmr at δ 2.50 (3 H) and 6.93 (1 H), and a molecular ion at *m/e* 180 and M − CS_2 at *m/e* 104 in the mass spectrum. Strong Raman absorptions at 6.70 (2) and 6.80 μ (1) were obtained for the carbon–carbon double bond. The ultraviolet spectra of 1 [216 nm (ε 8000), 379 (6000)] and 2 [228 nm (ε 4300), 369 (5650)] compared favorably with that reported for 4,5-dimethyl-1,3-dithiole-2-thione [233 nm (ε 8900), 372 (15000)].[4]

The polarographic behavior of 1 and 2 in dimethylformamide was compared with that of dimethyl trithiocarbonate and is shown in Table I.

The similarity of the half-wave potentials for 1, 2, and dimethyl trithiocarbonate suggests that reduction of the carbon–sulfur double bond is involved. Based on differences in diffusion coefficients, it is assumed that the reduction involved two electrons. The second wave for 1 and 2 is probably associated with the reduction to the carbon-carbon double bond. Such a supposition is based on the report that tetrakis(alkylthio)ethylenes are unreactive toward electrophilic reagents. The alkylthio group is therefore electron withdrawing and the carbon–carbon double bond is "electron poor."[5]

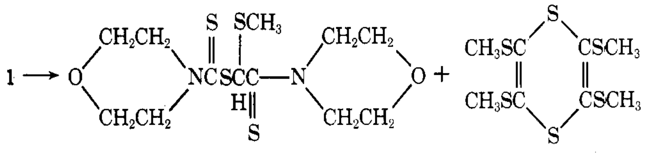
The half-wave potentials of −1.81 and −1.86 V for 1 and 2 are more negative than that [−1.62 V (Hg pool)] for tetrakis(methylthio)ethylene and may be caused by the fact that the resulting product from the reduction step of 1 and 2 is negatively charged.

The formation of 1 in the electrolysis probably occurs by an ECCE mechanism. The formation of an anion radical from carbon disulfide would be followed by dimerization to the tetrathiooxalate ion. This species would add to carbon disulfide and form 1,3-dithiole-2,4,5-trithione, which is reduced electrochemically to the species that is converted by alkylation to 1.



Chemical reactions were carried out mainly with 1 because of its availability. Treatment of 1 with tetrabutylammonium hydroxide in dimethylformamide under nitrogen followed by alkylation with methyl iodide gave a mixture of 12 products from which tetrakis(methylthio)ethylene was isolated in a 4% yield. The same product was isolated in a better yield from the controlled-potential electrolysis at −1.40 V (sce) of 1 followed by alkylation with methyl iodide. A by-product in this reaction was dimethyl trithiocarbonate.

The reaction of 4,5-bis(methylthio)-1,3-dithiole-2-thione (1) with morpholine gave a complex mixture of products.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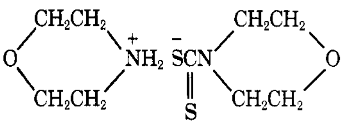
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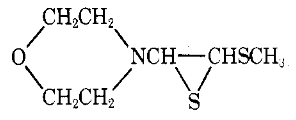
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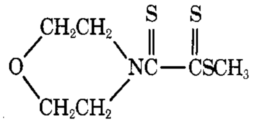
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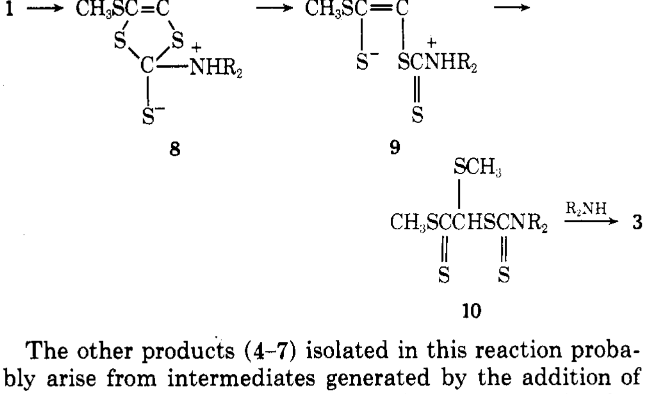
α-Methylthio-α-*N*-morpholinodithiocarboxythioacetomorpholide (3), which was isolated in the largest amount, was characterized by its nmr and mass spectra and elemental analysis. This compound (3) would be formed by a nucleophilic attack of the carbon–sulfur double bond by morpholine(R_2NH) with subsequent ring opening to 9 which would tautomerize to 10. Reaction of 10 with morpholine would form 3.


8 9 10

The other products (4–7) isolated in this reaction probably arise from intermediates generated by the addition of morpholine to the carbon–carbon double bond. This behavior would parallel in certain respects that observed with tetrakis(trifluoromethyl)ethylene and diethylamine.[6]

Morpholinum *N*-morpholinodithiocarboxylate (5) was identified by comparison with an authentic sample.[7]

Table II
Effect of Solvents on the Nmr Spectrum of 4

Solvent	Chemical shift, δ			
CCl_4	2.35	2.39	2.47	2.52
C_6D_6	2.15	2.22	2.25	
$CDCl_3$	2.41	2.43	2.57	2.59
	2.39[a]	2.41[a]	2.51[a]	2.55[a]
CD_3COCD_3	2.39	2.40		2.60

[a] At 120°.

Structure assignments for **4**, **6**, and **7** were made on the basis of mass and nmr spectra and elemental analysis.

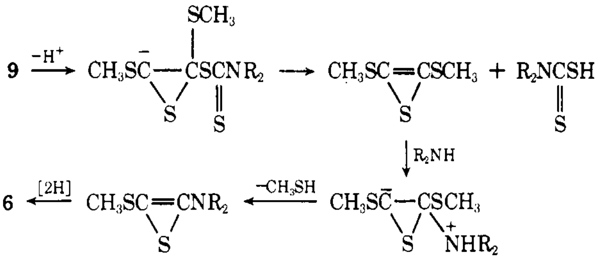
Tetrakis(methylthio)-*p*-dithiin (**4**) showed a molecular ion M^+ at *m/e* 300. The next major peak at $M^+ - 32$, which can be accounted for by the loss of sulfur and formation of the related thiophene, may be either a fragmentation peak or may result from the thermal decomposition of **4**. A similar thermal decomposition to sulfur and 2,5-thiophene has been observed with 2,5-diphenyl-*p*-dithiin.[8]

The nmr spectrum was solvent dependent and is shown in Table II.

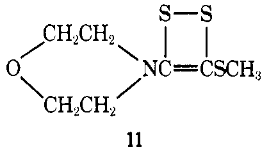
The observation of four different singlets can be explained by restricted rotation of the methylthio groups; differences in chemical shifts would be caused by the differences in proximity of the methyl groups to the ring sulfurs. This interaction through space would be expected to be solvent dependent. The boat form of the dithiin ring is apparently difficult to invert since no coalescence of the singlets occurred in deuteriochloroform at 120°.

Further evidence for the proposed structure of **4** was the uv spectrum. Compound **4** showed peaks at 264 nm (ε 6100); *p*-dithiin gave a peak at 262 nm (ε 5400).[9]

Compound **6** gave a molecular ion in the mass spectrum at *m/e* 191 with a major fragment at *m/e* 86 (morpholine). The nmr spectrum showed a multiplet at δ 4.17–4.43 that integrated for two protons in addition to a singlet at δ 2.30 for the thiomethyl group and a multiplet at δ 3.60–3.90 for the morpholine methylene groups. The multiplet at δ 4.17–4.43 would point to the presence of cis–trans hydrogens on the thiirane ring. This compound **6** could result from **9** by the following steps.



Structure **7** is based on the mass spectrum, which showed a molecular ion at *m/e* 221 and a M − 47 peak due to the loss of a thiomethyl group. The nmr spectrum showed two different thiomethyl groups at δ 2.47 and 2.70 and can be explained by the existence of an equilibrium between the dithione structure **7** and the dithiete form **11** in a ratio of 1:1.1. A similar equilibrium has recently been observed for a dithiobenzil.[10]



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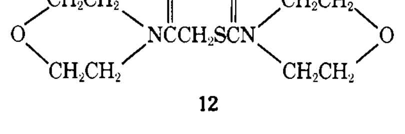

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4-Methylthio-1,3-dithiole-2-thione (**2**) was converted by morpholine into α-*N*-morpholinodithiocarboxythioacetomorpholide (**12**), **5**, and **6**. The morpholide **12** is formed by the addition of morpholine to the carbon–sulfur double bond in a similar fashion to that given for the formation of **3** from **1**. The formation of **5** and **6** would probably parallel that postulated for the formation of these compounds from **1**.

The reactions of **1** with methyl iodide and mercuric chloride did not form complexes; only decomposition of was observed. No Diels–Alder reaction occurred between **1** and either 1,3-cyclohexadiene or 1,4-diphenylisobenzofuran. The reaction with tri-*n*-hexyl phosphite at 150° did not produce bis(methylthio)acetylene. This type of reaction has been used successfully to produce *trans*-cyclooctene from *trans*-1,2-cyclooctene trithiocarbonate.[11]

Experimental Section[12]

Polarography. Polarographic measurements were made using a Sargent Model XXI recording polarograph. The capillary constant was 1.71 mg ⅔ $sec^{-1/2}$ at a mercury reservoir height of 70 cm.

Electrolytic Reduction of Carbon Disulfide. A. The electrolysis was carried out in a double H cell. One arm of this cell was separated from the cathode compartment with a medium-porosity glass frit and contained a platinum cylinder anode. The cathode compartment contained the mercury cathode (19.6 cm^2), a stirrer, and a nitrogen inlet tube and was connected to a saturated calomel electrode by a 70% dimethylformamide–agar bridge.

A solution of carbon disulfide (3.8 g, 0.05 mol) in dimethylformamide (100 ml) containing 0.5 *M* tetrabutylammonium bromide was electrolyzed at −1.40 V (sce) using a PAR Model 173 automatic potentiostat. The initial current was 44 mA. Electrolysis caused the solution to turn deep red and was terminated after 11 hr, when the frit between the anode and cathode compartment became clogged with a black solid. Approximately 1500 C of electricity was employed. The mercury was separated from the red solution, and methyl iodide (4.4 g, 0.04 mol) was added. After this addition, which was accompanied by a mild exothermic reaction, the red solution was stirred at room temperature for 2 hr and poured into water (500 ml). Extraction with hexane (200 ml) followed by drying ($MgSO_4$) and concentration to about half the volume gave yellow needles of **1** (0.47 g). Recrystallization from hexane gave a sample of **1** melting at 100–101°; ir (KBr) 6.80 (C=C), 9.41 μ (C=S); Raman ($CHCl_3$) 6.80 (C=C), 9.40 μ (C=S); nmr ($CDCl_3$) δ 2.48 (s, SCH_3); uv (cyclohexane) λ_{max} 379 nm (ε 6000), 295 (2600), 266 (4300), 230 (s, 4750), 216 (s, 8000); mass spectrum *m/e* (rel intensity) 226 (100), 150 (50, M − CS_2).

Anal. Calcd for $C_5H_6S_5$: C, 26.52; H, 2.61. Found: C, 26.62; H, 2.92.

B. Electrolysis, using a potential of −1.65 V (sce), of carbon disulfide (3.8 g) gave an initial current of 0.11 A, and was terminated after 5 hr because of a clogged frit. Approximately 1800 C of electricity was used. Treatment of the solution with methyl iodide (14.2 g, 0.1 mol) for 3 hr was followed by the addition of water (500 ml) and extraction with two 600-ml portions of hexane. Concentration of the hexane gave yellow needles of **1** (1.56 g), which after recrystallization from hexane melted at 100–101.5°. The hexane filtrate gave upon removal of the solvent a yellow oil (1.04 g). Analysis by gas chromatography (column, 10 ft × 0.25 in.; 15% SE-30 on 100–120 mesh Chromosorb P at 150°, injection port 220°, detector 265°) showed the presence of four compounds with retention times of 3.3, 5.0, 5.6, and 20.4 min. The component with a retention time of 20.4 min made up approximately 10% of the mixture and was identified as dimethyl trithiocarbonate by comparison with an authentic sample.

C. Reduction of carbon disulfide (22.8 g, 0.3 mol) in dimethylformamide (300 ml) containing 0.5 *M* tetrabutylammonium bromide was carried out in a 600-ml Berzelius breaker at a mercury cathode (44.2 cm^2). The anode compartment was a porcelain cup (6 in. high × 2 in. diameter) and was fitted with a platinum foil cylindrical anode (1 in. high × 1 in. diameter). Stirring was carried out magnetically. A potential of 14 V gave a current of 0.4–0.5 A. Higher currents than these caused heating. The electrolysis was allowed to proceed for 5 hr, and, after removal of the mercury, methyl iodide (42.6 g, 0.3 mol) was added and the solution was stirred for 12 hr. The work-up in the usual manner gave **1** in yields of 3.2–4 g, mp 100–101°.

Reduction of Carbon Disulfide with 0.8% Sodium Amalgam. Repetition of the directions in the literature[3] and substituting methyl iodide for the methyl chloride gave 1.33 g of **1**, which after successive recrystallization from hexane and from ethanol using decolorizing carbon melted at 100–101°. A mixture melting point with a sample from the electrolysis melted at the same point. The filtrate, upon removal of the solvent, gave a dark red oil (19.54 g) which by tlc analysis on silica using benzene showed the presence of at least six components. Chromatography on silica gel (500 g) using petroleum ether (bp 60–68°), benzene, and ethyl acetate as eluting solvents gave two major fractions. Petroleum ether eluted a clear yellow oil (4.18 g) which by gas chromatography consisted of approximately 40% of dimethyl trithiocarbonate. Benzene eluted a reddish-orange oil (4.50 g) which solidified on standing. Recrystallization successively from hexane, methanol, ethyl acetate, and 50:50 methanol–chloroform gave yellow crystals of **2** melting at 72–73°: ir (KBr) 9.45 μ (C=S); Raman ($CHCl_3$) 6.70 (C=C), 9.34 μ (C=S); nmr ($CDCl_3$) δ 2.50 (s, 3 H, SCH_3), 6.93 (s, 1 H, =CH); uv (cyclohexane) λ_{max} 369 nm (ϵ 5650), 260 (2500), 228 (4300); mass spectrum *m/e* (rel intensity) 180 (100), 104 (50, M − CS_2).

Anal. Calcd for $C_4H_4S_4$: C, 26.64; H, 2.23; S, 71.13. Found: C, 26.43; H, 2.18; S, 71.22.

Tetrakis(methylthio)ethylene. A. A solution of 4,5-bis(methylthio)-1,3-dithiole-2-thione (**1**, 5.18 g) in dimethylformamide (100 ml) was deoxygenated with nitrogen and treated with a solution of 1.08 *N* tetrabutylammonium hydroxide in methanol (84 ml) at 55° for 22 hr. Tlc analysis on silica using benzene as a solvent indicated the absence of **1**. The solution was cooled and after treatment with methyl iodide (5.7 ml) was allowed to stand at room temperature for 9 hr. The resulting solution was added to water (500 ml) and extracted with two 600-ml portions of petroleum ether. Removal of the solvent gave a dark red oil (2.82 g) which by tlc analysis on silica using benzene and carbon tetrachloride as solvents consisted of 12 compounds. Chromatography on silica gel preparative layer plates using benzene and carbon tetrachloride as solvents gave a yellow oil which slowly solidified on standing. The yellow solid melted at 56.5–59° and on sublimation gave white crystals of tetrakis(methylthio)ethylene melting at 60–61° (lit.[13] mp 60–61°). The ir and nmr spectra were identical with Sadtler (nmr No. 8515, ir No. 37240); mass spectrum *m/e* 212.

B. A solution of **1** (2.84 g) in dimethylformamide (100 ml) containing 0.5 *M* tetrabutylammonium bromide was reduced electrochemically at −1.40 V constant potential (sce) using the double H cell described earlier and a nitrogen atmosphere. The initial current was 80 mA and the electrolysis was terminated after 6 hr, during which time approximately 1800 C was used. Removal of the mercury was followed by the addition of methyl iodide (1 ml) to the solution. The resulting solution was stirred for 18 hr at room temperature, poured into water, and extracted with hexane. Removal of the hexane gave a red oil (1.80 g) which by tlc analysis on silica using benzene and carbon tetrachloride as solvents showed ten components. A portion of the oil (1.16 g) was chromatographed on four silica gel preparative layer plates using benzene and carbon tetrachloride as eluents. The two main fractions obtained were a yellow oil (0.35 g) and a red oil (0.72 g). Analysis of the yellow oil by gas chromatography indicated that it was dimethyl trithiocarbonate. The red oil, upon vacuum distillation, gave a solid which sublimed into the distilling head. Recrystallization from petroleum ether gave white needles of tetrakis(methylthio)ethylene melting at 60–61°.

Reaction of 4,5-Bis(methylthio)-1,3-dithiole-2-thione with Morpholine. A solution of **1** (9.77 g) and morpholine (9.40 g) in benzene (500 ml) was refluxed for 11 hr. During this period methyl mercaptan was evolved and a white solid (6.00 g) was formed. The white solid was identified as morpholinium *N*-morpholinodithiocarboxylate (**5**) by comparison with an authentic sample.[6] Removal of the benzene gave a brown oil (13.20 g) which by tlc analysis on silica using chloroform as a solvent contained at least five components. Chromatography on silica preparative layer plates using benzene or carbon tetrachloride as developing solvents gave the following compounds in the order of their initial elution with chloroform. Components present in amounts smaller than 5% of the crude mixture were not investigated.

A. Starting material **1** (1.32 g) was obtained.

B. Tetrakis(methylthio)-*p*-dithiin (**4**) was a reddish-brown oil: yield 1.45 g; ir (neat) 3.42, 7.07, 7.40, 7.68, 7.99, 9.40, 10.32, 10.50, 11.32, 12.95 μ; nmr, see Table II; mass spectrum molecular ion *m/e* 300; uv (cyclohexane) λ_{max} 314 nm (ϵ 5300), 264 (6100), 224 (8700).

Anal. Calcd for $C_8H_{12}S_6$: C, 31.96; H, 4.03; S, 64.01. Found: C, 32.22; H, 3.97; S, 63.82.

C. Methyl dithiooxalmorpholide [3-methylthio-4-(*N*-morpholino)dithiete] (**7, 11**) was a reddish-brown oil (1.03 g): ir (neat) 3.51, 6.95, 7.40, 7.71, 8.15, 8.82, 9.00, 9.70, 10.15, 10.46, 11.02, 11.70, 12.40, 13.05 μ; nmr ($CDCl_3$) δ 2.47, 2.70 (two singlets in ratio of 1.1:1, 3 H, SCH_3), 3.50–3.90 [m, 4 H, $O(CH_2)_2$], 4.00–4.40 [m, 4 H, $N(CH_2)_2$]; mass spectrum *m/e* 221.

Anal. Calcd for $C_{17}H_{11}NOS_3$: C, 37.97; H, 5.01; N, 6.33. Found: C, 37.83; H, 5.22; N, 6.55.

D. ***cis*- and *trans*-(2-Methylthio-3-(*N*-morpholino)thiirane (6)** was a solid which melted at 78.5–80.5° after recrystallization from hexane: yield 3.24 g; ir (KBr) 3.37, 3.38, 3.41, 6.12, 6.69, 6.83, 6.94, 7.63, 7.79, 7.96, 8.66, 9.01, 9.06, 9.41, 9.69, 10.20, 10.75, 10.98, 11.77, 12.18, 14.50, 16.00, 16.50, 18.18 μ; nmr ($CDCl_3$) δ 2.30 (s, 3 H, SCH_3), 3.60–3.90 [m, 8 H, $O(CH_2CH_2)_2N$], 4.17–4.43 (m, 2 H, CHCH); mass spectrum *m/e* 191.

Anal. Calcd for $C_7H_{13}NOS_2$: C, 43.94; H, 6.85; N, 7.32. Found: C, 43.87; H, 6.85; N, 7.24.

E. α′-Methylthio-α-*N*-morpholinodithiocarboxythioacetomorpholide (**3**) was a colorless, viscous oil: yield 3.30 g; ir (neat) 3.45, 6.02, 6.95, 8.00 (broad), 8.34, 9104, 9.41, 9.80, 10.08, 10.30, 11.20, 11.53, 11.74, 12.18, 12.24, 12.86, 14.80 μ (broad); nmr ($CDCl_3$) δ 2.30 (s, 3 H, SCH_3), 3.60–3.95 [m, 8 H, $(O(CH_2)_2)_2$], 3.95–4.50 [m, 8 H, $(N(CH_2)_2)_2$], 6.88 (s, 1 H, CH); mass spectrum major fragments *m/e* 191 and 76.

Anal. Calcd for $C_{12}H_{20}N_2O_2S_4$: C, 40.88; H, 5.72; N, 7.95. Found: C, 41.14; H, 5.79; N, 7.63.

Reaction of 4-Methylthio-1,3-dithiole-2-thione (2) with Morpholine. A solution of **2** (0.73 g) and morpholine (1.75 g) in benzene (50 ml) was refluxed for 3 hr. Methyl mercaptan was liberated and a white solid was found during this period. The white solid (0.15 g) was identified as **5**. Removal of the benzene from the filtrate gave a brown semisolid (1.22 g) which upon the basis of the tlc analysis on silica using chloroform consisted of two major compounds. Preparative layer chromatography on silica of a 0.45-g sample gave α-*N*-morpholinodithiocarboxythioacetomorpholide (**12**, 0.33 g) and **6** (0.11 g). The first compound melted at 130.5–132° after recrystallization from a mixture of methylene chloride–ethanol: ir (KBr) 3.36, 3.38, 3.39, 3.42, 6.14, 6.80, 7.02, 7.21, 7.35, 7.66, 7.84, 7.86, 7.92, 8.13, 9.01, 9.42, 9.76, 10.05, 10.75, 11.05, 11.17, 11.62, 12.20, 16.00, 16.52, 18.62, 24.10, 25.00 μ; nmr ($CDCl_3$) δ 3.60–3.90 [m, 8 H, $(O(CH_2)_2)_2$], 4.00–4.40 [m, 8 H, $(NCH_2)_2)_2$], 4.78 (s, 2 H, CH_2); mass spectrum *m/e* 306.

Anal. Calcd for $C_{11}H_{18}N_2O_2S_3$: C, 43.11; H, 5.92; N, 9.14. Found: C, 43.03; H, 6.06; N, 8.85.

Registry No. 1, 49638-64-4; **2,** 49687-08-3; **3,** 49638-65-5; **4,** 49638-66-6; *cis*-**6,** 49638-67-7; *trans*-**6,** 49687-09-4; **7,** 49687-10-7; **11,** 49638-68-8; **12,** 49638-69-9; carbon disulfide, 75-15-0; dimethylformamide, 68-12-2.

References and Notes

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