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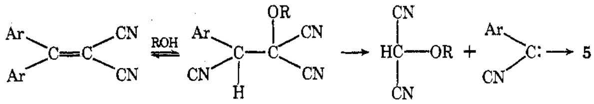

If one assumes that solvolysis of the carbene by ethanol is not a rapid reaction, this suggestion certainly appears feasible. Information to be presented in a future publication, however, will show that the formation of **5** is inhibited when a base is present in the reaction mixture.
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Electrochemical Reduction of Ethylene Trithiocarbonate. Reactions of Trithiocarbonyl Radical Anions

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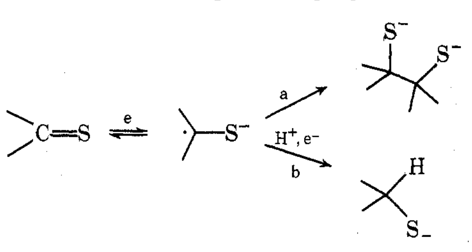
The electrochemical reduction of ethylene trithiocarbonate (1) has been studied in *N,N*-dimethylformamide–tetra-*n*-butylammonium bromide solutions at a platinum electrode. Reduction proceeds through the radical anion of 1 which reacts via anionic elimination of a molecule of ethylene. At potentials on the foot of the voltammetric wave the major electrolysis product is a bis(trithiocarbonate) dianion which was isolated as the methyl or ethyl ester after aklylation with the alkyl iodide. Alkylation with either 1,2-dibromoethane or 1,2-diiodoethane produced 1,4,6,9-tetrathiospiro[4.4]nonane as the major product. Reduction with sodium metal gives larger amounts of products derived from trithiocarbonate dianions. A mechanism is proposed for the reduction which accounts for the observed potential dependence of the electrolysis products.

Previous work in this laboratory has shown that several cyclic trithiocarbonates are electrochemically reduced under voltammetric conditions via an ECE pathway.[1] For ethylene trithiocarbonate cyclic voltammograms at fast sweep rates (ca. 75 V sec^{-1}) demonstrated the presence of a reversible one-electron couple in acetonitrile solutions at −1.76 V vs. a saturated calomel electrode (SCE). As the rate of the potential scan was decreased, the one-electron wave was transformed into an irreversible two-electron wave with a peak width of ca. 50 mV. This type of behavior has become familiar in recent years and is characteristic of an electrode process for which Nernstian electron transfer reactions are maintained and the irreversibility is caused by a chemical step involving the radical anion intermediate (an ECE pathway).[2]

By analogy to the well-studied electroreduction of carbonyl compounds, two possible pathways are suggested for the radical anion of thiocarbonyl groups: thiopinacol and mercaptan formation. In aqueous 2-propanol buffers two-electron reductions of the thiocarbonyl group have been observed for a variety of thiones.[3] In nonaqueous solvents, however, the low proton availability would favor pathway a in eq 1 over b. In fact addition of proton donors such as phenol or water to DMF solutions did not appreciably decrease the lifetime of the radical anion in the voltammetric experiments,[1] a result which suggests pathway a. Further support for this pathway comes from work of Astruc et al.,[4] in which a dimeric product was obtained from the electroreduction of a 1,2-dithiole-3-thione.



(1)

The dimercaptide dianion which would result from the 2,2′ coupling of two ethylene trithiocarbonate radical anions represents a potentially useful synthetic intermediate as a ligand or a nucleophile for the preparation of new transition metal complexes or multisulfur heterocycles. Electrogenerated mecaptides have been used successfully for the preparation of compounds in the tetrathiofulvalene series[5] and it was our hope to carry out similar reactions using ethylene trithiocarbonate (1) instead of carbon disulfide. However, the radical anion of 1 was found to react by an unexpected pathway which is described below.

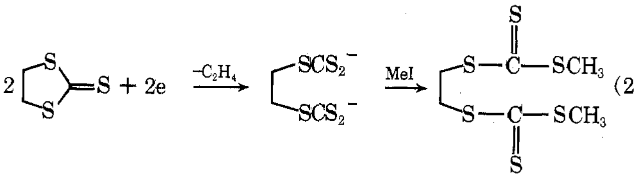
Results

Alkylation with Alkyl Iodides. Electrolyses in DMF–TBABr solutions of ca. 1-g quantities of 1 at potentials between −1.4 and −1.6 V vs. SCE consumed an average of 0.98 F/mol of electricity. Usually the electrolysis was complete within 1 hr, at which point the solution had acquired a light brown color. Addition of an excess of alkylating agent, e.g., CH_3I, caused the color to change from brown to yellow. Product isolation gave yellow needles, mp 59.0–59.8°, in greater than 50% current yield (based on 1 F/mol) after two recrystallizations from acetonitrile. No attempt was made to maximize the yield of the major product. In addition a yellow oil was isolated as a minor product after column chromatography on silica gel of the residue left after recrystallization.

The oil was shown to be dimethyl trithiocarbonate (2) by comparison of its ir and NMR spectra to that of an authentic sample and published spectra.[6,7] NMR spectra of the crude reaction product indicated that 2 was present at a concentration up to 40% of the major product in some electrolyses.

The analytical data on the solid product gave $C_6H_{10}S_6$ as the empirical formula, which implies the loss of an ethylene molecule for every two molecules of 1 in the reduction process. The loss of ethylene was verified by passing the effluent gas stream from a closed electrolysis cell through a solution of bromine in CH_2Cl_2. A substantial quantity of 1,2-dibromoethane was subsequently isolated from the CH_2Cl_2 solution and identified by its ir and NMR spectra.

The major product of the electrolysis was determined to be 1,2-ethanebis(methyl trithiocarbonate) (3), based on the following spectral evidence. The NMR spectrum of 3 in deuteriochloroform contained two singlets at 3.67 and 2.78 ppm from Me_4Si with relative areas of 2.0–3.0. For comparison, the NMR spectrum of 2 exhibits a singlet at 2.73 ppm in CCl_4[6] and the value of 3.67 ppm for the methylene protons is consistent with NMR spectra of a variety of multisulfur heterocycles which contain $-SCH_2CH_2S-$ linkages.[8,9] Addition of a shift reagent, tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate)europium(III), failed to resolve the singlets in deuteriobenzene. A ^{13}C NMR spectrum contained signals which could be assigned to the methyl and methylene carbon atoms in approximately a 1:1 ratio at 34.84 and 20.29 ppm from Me_4Si.



(2)

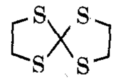
3

The presence of a trithiocarbonate group was clearly indicated by the strong absorption at 1050 cm^{-1} in the ir spectrum.[10] This functionality is also indicated by the uv spectrum of 3, which exhibits bands at 309 and 431 nm with molar absorptivities of 30 000 and 85 M^{-1} cm^{-1}, respectively. Furthermore, in accord with the bifunctionality of 3, these absorptivities are close to twice the values reported by Muller and Krebs for simple trithiocarbonates.[11] Cyclic voltammograms of 3 contained two irreversible reduction waves at −1.58 and −1.76 V vs. SCE (peak potentials). These waves had current functions and peak widths characteristic of successive reduction of the two trithiocarbonate groups in 3.

The mass spectrum of the electrolysis product showed the parent peak at *m/e* 274 and a fragmentation pattern consistent with the assigned structure (see Experimental Section).

Alkylation with ethyl iodide gave the 1,2-ethanebis(ethyl trithiocarbonate) as yellow, crystalline flakes, mp 34.5–35.5°. Details are given in the Experimental Section.

Alkylation with 1,2-Dibromo- or 1,2-Diiodoethane. The exhaustive reduction of ethylene trithiocarbonate followed by alkylation with either 1,2-dibromoethane or 1,2-diiodoethane produced three isolated compounds: a yellow, insoluble material (0.16 g per 0.75 g of 1 reduced), 1,4,6,9-tetrathiaspiro[4.4]nonane (4), and starting material. A yield of 4 based on isolated product was not determined, but NMR spectra showed that 4 was present in twice the concentration of 1 in the crude product.



4

The yellow material precipitated from solution soon after the addition of the alkylating agent. It was found to be slightly soluble in hot DMF, but otherwise insoluble in 14 solvents that encompassed a wide range of polarity. Upon heating, the color gradually turned brown beginning at 90° and at 140° the material was tarlike.

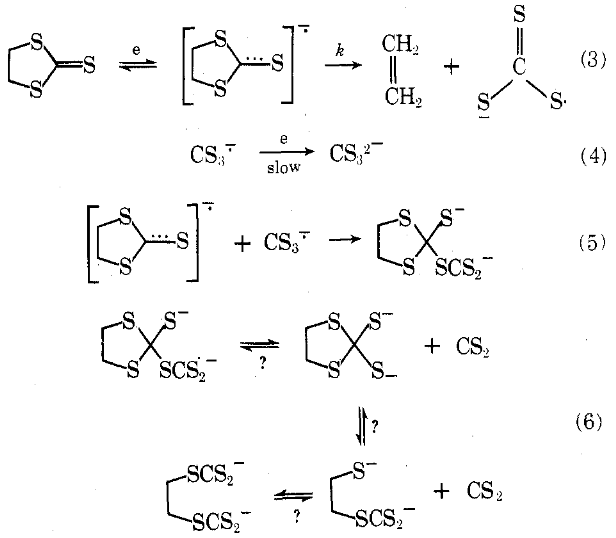
The ir spectrum, the uv spectrum, and cyclic voltammograms of the yellow material indicated the presence of trithiocarbonate groups. The indicators of this functionality were the strong ir band at 1055 cm^{-1}, the absorption bands at 312 and 430 nm in the electronic spectrum, and the peak voltammogram at −1.71 V vs. SCE.

The material may be a polymer with an ethylene trithiocarbonate repeating unit: $-CH_2CH_2SCS_2-_n$. The color, decomposition point, and ir spectrum are similar to those of pentamethylene and hexamethylene polytrithiocarbonates reported by Braun and Kiessel.[12]

The spiro compound, 4, was recrystallized from acetonitrile as a white, fluffy powder, mp 139–140°. The compound was identified by comparison of the mass, ir, and NMR spectra with the data reported by D'Amico and Campbell.[13]

Discussion

The above results can be accommodated by a relatively simple mechanism which is consistent with the voltammetric behavior of 1, eq 3–6. The key step in this mechanism is the anionic elimination of ethylene from the radical anion of 1, eq 3. This reaction, which is suggested to be the chemical step which produces the ECE voltammetric behavior, has precedent in analogous oxygen compounds.[14] At potentials on the rising portion of the voltammetric wave, where the electrolyses were carried out, addition of an electron to $CS_3\cdot^-$ is slow and this species is viewed to couple with the radical anion of 1, eq 5. The mechanism is completed by a sequence of equilibria (eq 6) involving CS_2 additions which lead to the resonance stabilized bis(trithiocarbonate) dianion. The question marks under the equilibrium signs in eq 6 are meant to indicate that the reversibility of these steps has not been directly established in this study.



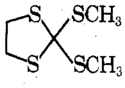
Reaction of the trithiocarbonate radical anion, $CS_3\cdot^-$, with 1 followed by an electron transfer is a possible alternative to the reaction in eq 5. Experimental evidence for or against the radical coupling reaction is lacking, since this step follows the irreversible fragmentation in the proposed mechanism. We favor the radical coupling reaction owing to the known propensity of electrogenerated radical anions to couple in DMF solutions.[15,16]

The effect of potential on the reduction process is readily rationalized by this scheme. Under voltammetric conditions the addition of a second electron to $CS_3\cdot^-$ is rapid in the region of the peak potential and a two-electron wave results. Sodium metal reduction of 1 in DMF followed by addition of CH_3I gave twice as much **2** as **3** based on NMR analysis of the crude mixture. Thus sodium, which is a powerful enough reducing agent to carry out eq 4, favors the voltammetric pathway to a greater extent than electrolysis on the foot of the wave.

In several control experiments potassium or sodium trithiocarbonate solutions in DMF were treated with excess **1** and allowed to stand overnight. Only methyl trithiocarbonate was recovered from the mixtures after addition of CH_3I. Thus reaction of 1 with CS_3^{2-} under electrolysis conditions is unlikely.

Several experiments were also carried out in which CS_2 was added to the solution after completion of the electrolysis and before addition of CH_3I. If CS_2 is involved in the equilibria of eq 6, then an increased yield of **3** could result by this procedure. Upon addition of CS_2 a transient red color developed in solution and an oxidation wave in the region of 0.0 V vs. SCE became less prominent in cyclic voltammograms of the solution, but no increase in yield of **3** appeared to result. It is likely that the equilibria in eq 6 lie in favor of the bis(trithiocarbonate) dianion and that the yield of **3** is determined by losses during the work-up.

Finally, it should be mentioned that, although the scheme rationalizes the presence of all the alkylated products, it also suggests the presence of several which were not found. In particular, compound **5** would be expected since



5

the dianion precursor was trapped by addition of the dihalogenoethane. Apparently this compound is either thermally unstable or, more likely, was lost in the work-up in the presence of excess **2** and **3**.

Experimental Section

Chemicals. *N,N*-Dimethylformamide was purified by the procedure of Faulkner and Bard.[17] Tetra-*n*-butylammonium bromide (TBABr) was obtained from Eastman Kodak Co. and used as received. It was the electrolyte for all electrolyses of **1**. Practical grade ethylene trithiocarbonate (Aldrich Chemical Co.) was recrystallized twice from acetonitrile. Methyl and ethyl iodide (Eastman), 1,2-dibromoethane (Fisher), and 1,2-diiodoethane (Aldrich) were used without further purification. Potassium trithiocarbonate (Alpha Inorganics) was also used as received. Sodium trithiocarbonate was synthesized by dissolving 0.23 g of reagent grade anhydrous sodium sulfide in 10 ml of DMF and adding 0.25 g of carbon disulfide. This solution was then used in subsequent experiments.

Procedures. Bulk electrolyses were performed in a three-compartment cell which was cooled with tap water. The cell was filled with 1 *M* TBABr in DMF and the platinum working electrode compartment (ca. 40 ml) was stirred with nitrogen gas throughout the experiment. After ca. 10 min of deaeration, between 0.5 and 1.5 g of **1** was added to the working electrode compartment. The working electrode potential was maintained between −1.4 and −1.6 V and the current averaged ca. 175 mA throughout most of the electrolyses. Usually electrolyses were terminated when the current dropped to less than 5 mA.

Product isolation was as follows. An excess of alkylating agent was added directly to the working electrode compartment. The solution was collected and poured into 500 ml of water and then extracted with ether which then was dried with anhydrous magnesium sulfate and evaporated on a rotoevaporator. Recrystallization of the resulting oil from acetonitrile gave the main product and the residue was separated by column chromatography on silica gel using hexane–methylene chloride mixtures as the eluent.

Voltammetric parameters of the isolated alkylated products were obtained in acetonitrile, 0.1 *M* tetraethylammonium perchlorate solutions using procedures given elsewhere.[1]

Physical Characteristics of Isolated Compounds. 1,2-Ethanebis(methyl trithiocarbonate). Most of the spectral parameters for **3** are given above. The ir spectrum (KBr) showed bands at the following frequencies: 820, 860, 960, 1050, 1135, 1205, 1385, 1410 cm^{-1}. The electron-impact mass spectrum at 20 eV gave the following major *m/e* peaks and assigned fragments: 274 (parent mass), 183 ($CH_3SCS_2CH_2CH_2S^+$), 138 ($CH_3SCS_2CH_3^+$), 136 ($CH_3SCS_2CH^+$), 91 ($SCSCH_3^+$), 76 (SCS^+, base peak), 60 ($SCH_2CH_2^+$), 59 ($SCHCH_2^+$), 47 (SCH_3^+), and 45 (SCH^+). All of these fragments are readily derived from the structure of **3** except for the peak at *m/e* 138, which may result from an impurity of **2** in the sample.

Anal. Calcd for $C_6H_{10}S_6$: C, 26.25; H, 3.67; S, 70.07. Found: C, 26.30; H, 3.66; S. 69.99.

1,2-Ethanebis(ethyl trithiocarbonate). The NMR spectrum of this compound in deuteriochloroform contains a singlet at 3.75 ppm, a quartet centered at 3.38 ppm, and a triplet centered at 1.38 ppm. Integration of the peak areas yielded a ratio of 2:2:3, respectively. The ir spectrum gave absorption bands at the following frequencies: 815, 1025, 1065, 1135, 1205, 1260, 1390, 1405, 1450 cm^{-1}. The uv spectrum in chloroform yielded wavelength maxima at 310 and 434 nm with corresponding molar absorptivities of 40 000 and 105 M^{-1} cm^{-1}. The mass spectrum at 10 eV gave the following major *m/e* peaks and assigned fragments: 302 (parent), 197 ($C_2H_5SCS_2CH_2CH_2S^+$, base peak), 168 ($SCS_2CH_2CH_2S^+$), 136 ($SCS_2CH_2CH_2^+$), 105 ($SCSCH_2CH_3^+$), 76 (SCS), and 61 ($SCH_2CH_3^+$). Cyclic voltammograms of the ethyl derivative showed two irreversible waves at −1.58 and −1.73 V vs. SCE.

1,4,6,9-Tetrathiaspiro[4.4]nonane:[13] NMR ($CDCl_3$) 3.40 ppm, singlet; ir (KBr) 1410, 1270, 965, 945, 845, 795, 755 cm^{-1}. The mass spectrum gave the parent mass at *m/e* 196. Cyclic voltammograms yielded two irreversible oxidation waves at 0.99 and 1.53 V vs. SCE.

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Registry No.—1, 822-38-8; 3, 57443-63-7; 4, 13145-46-5; DMF, 68-12-2; TBABr, 1643-19-2; methyl iodide, 74-88-4; ethyl iodide, 75-03-6; 1,2-dibromoethane, 106-93-4; 1,2-diiodoethane, 624-73-7; 1,2-ethanebis(ethyl trithiocarbonate), 57443-64-8.

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