to give a center cut of 1.11 g (49%) of **13a** as a clear, viscous oil (pure by GC analysis): NMR ($CDCl_3$) δ 8.3–8.0 (m, 3), 7.85–7.45 (m, 5), 3.8 (s, 3); IR (film) 1725 cm^{-1}.

Anal. Calcd for $C_{17}H_{11}F_3N_2O_2S$: C, 56.04; H, 3.04. Found: C, 55.94; H, 3.05.

Methyl 2-[5-(4-Chlorophenyl)-1,2,4-thiadiazol-3-yl]benzoate (13b). The above procedure was applied, with 3.5 g of sodium nitrite added during 1 h to 1.95 g of **12b** in 40 mL of 75% sulfuric acid at 70–80 °C. The crude acid (1.93 g, mp 171–174 °C) was converted to 1.80 g of crude ester. Kugelrohr distillation of the ester at 120–140 °C (0.04 mm) gave 1.01 g (50%) of clear viscous oil that crystallized after 1 week: mp 84–85 °C; IR (melt) 1722 cm^{-1}; NMR ($CDCl_3$) δ 8.2–7.4 (m, 8), 3.8 (s, 3).

Anal. Calcd for $C_{16}H_{11}ClN_2O_2S$: C, 58.09; H, 3.35. Found: C, 57.95; H, 3.39.

Registry No. 6a, 76010-55-4; **6b**, 76010-56-5; **6c**, 76010-57-6; **6d**, 76010-58-7; **6e**, 76010-59-8; **6f**, 76010-60-1; **7**, 76010-61-2; **8**, 76010-62-3; **9**, 17174-98-0; **10**, 52059-77-5; **11a**, 76010-63-4; **11b**, 76010-64-5; **12a**, 76010-65-6; **12b**, 76010-66-7; **13a**, 76010-67-8; **13b**, 76010-68-9; phthalonitrile, 91-15-6; 5-phenyl-1,3,4-oxathiazol-2-one, 5852-49-3; methyl *o*-cyanobenzoate, 6587-24-2; 5-(4-chlorophenyl)-1,3,4-oxathiazol-2-one, 17452-79-8; 5-[3-(trifluoromethyl)phenyl]-1,3,4-oxathiazol-2-one, 57459-15-1; (chlorocarbonyl)sulfenyl chloride, 2757-23-5; *m*-(trifluoromethyl)benzonitrile, 368-77-4; 2-(2-oxo-1,3,4-oxathiazol-5-yl)benzonitrile, 52059-77-5; *p*-chlorobenzonitrile, 623-03-0; 2-[5-(4-chlorophenyl)-1,2,4-thiadiazol-3-yl]benzoic acid, 76010-69-0.

Electrochemical Reduction of Carbon Disulfide. Synthesis of Carbon Sulfide Heterocycles[1]

Michael F. Hurley and James Q. Chambers*

Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37916

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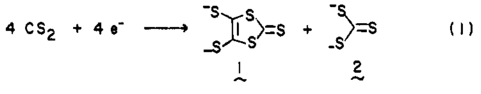
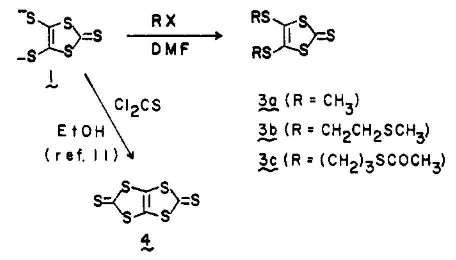
Detailed procedures for the electrochemical reduction of carbon disulfide in *N,N*-dimethylformamide and acetonitrile are given. The synthetic utility of the method is demonstrated by the preparation of several thio-substituted derivatives of tetrathiafulvalene. Cyclic voltammograms of the tetrapotassium salt of the tetrathio anion of tetrathiafulvalene indicate four successive electron-transfer steps and in situ formation of a C_6S_8 species. Oxidation of the CS_2 electrolysis solutions produces a compound which is tentatively identified as [1,3]dithiolo[4,5-*d*]-1,2,3-trithiole-5-thione.

The reduction of carbon disulfide in aprotic media provides synthetic entry into multisulfur species based on the 1,3-dithiole ring structure. Although the sodium amalgam reduction of CS_2 was studied 50 years ago,[2] only recently was the structure of the key product, the 4,5-dimercapto-1,3-dithiole-2-thione dianion (**1**), elucidated by Wawzonek and Heilmann.[3] Under suitable conditions this species can be prepared in close to stoichiometric amounts either by active metal[4] or electrochemical reduction according to eq 1. We and others have exploited this chemistry for the synthesis of multisulfur electron donors in the tetrathioethylene series.[5-14] The yields in the electrochemical reduction of CS_2 can be low, because at intermediate stages of these electrolyses, complex mixtures of anionic multisulfur species are produced which are potential, concentration, and time dependent.[15,16] However, essentially stoichiometric yields of **1** can be obtained by electrochemical reduction of CS_2 in either DMF or CH_3CN. The procedures, which are relatively simple, do not require high-purity solvents or electrolytes and can be performed without sophisticated electrochemical gear. These procedures are reported in this paper along with the synthesis of several new carbon–sulfur compounds.



(1)

Scheme I



Following the chemistry of Engler and Schumaker[17] and Krug et al.,[11] we have used these procedures to prepare the 1,3,5,7-tetrathiapentalene ring system and derivatives of tetrathiotetrathiafulvalene. The cyclic voltammetry of these compounds is also reported in this paper.

Results and Discussion

The electrochemical reduction of CS_2 provides a convenient synthetic entry into the 1,3-dithiole ring system via the dianion **1** as shown in Scheme I. Alkylation yields thiones such as **3a–c**, while treatment of **1** with thio-

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[1] Taken from the Ph.D. Thesis of M.F.H., University of Tennessee, Knoxville, TN, 1980.

[2] Fetkenheuer, B.; Fetkenheuer, H.; Lecus, H. *Chem. Ber.* **1927**, *60*, 2528.

[3] Wawzonek, S.; Heilmann, S. M. *J. Org. Chem.* **1974**, *39*, 511.

[4] Steimecke, G.; Sieler, H. J.; Kirmse, R.; Hoyer, E. *Phosphorus Sulfur* **1979**, *7*, 49.

[5] Moses, P. R.; Chambers, J. Q. *J. Am. Chem. Soc.* **1974**, *96*, 945.

[6] Harnden, R. M.; Moses, P. R.; Chambers, J. Q. *J. Chem. Soc., Chem. Commun.* **1977**, 11.

[7] Moses, P. R.; Harnden, R. M.; Chambers, J. Q. *J. Electroanal. Chem.* **1977**, *84*, 187.

[8] Engler, E. M.; Green, D. C.; Chambers, J. Q. *J. Chem. Soc., Chem. Commun.* **1976**, 148.

[9] Syper, L.; Sucharda-Sobczyk, A. *Bull. Acad. Pol. Sci., Ser. Sci. Chim.* **1975**, *23*, 563.

[10] Mizuno, M.; Cava, M. P.; Garito, A. F. *J. Org. Chem.* **1976**, *41*, 1484.

[11] Krug, W. P.; Bloch, A. N.; Cowan, D. O. *J. Chem. Soc., Chem. Commun.* **1977**, 660.

[12] Bontempelli, G.; Magno, F.; Mazzocchin, G. A.; Seeber, R. *J. Electroanal. Chem.* **1975**, *63*, 231.

[13] Reuter, U.; Gattow, G. *Z. Anorg. Allg. Chem.* **1976**, *421*, 143.

[14] Jeroschewski, P. *Z. Chem.* **1978**, *18*, 27.

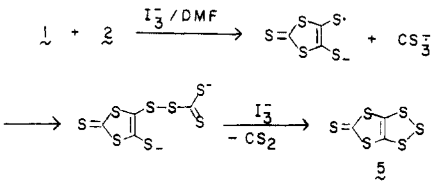
[15] Lodmell, J. C. M.S. Thesis, University of Tennessee, Knoxville, TN, 1980.

[16] Lodmell, J. C.; Hurley, M. F.; Chambers, J. Q., submitted for publication.

[17] Schumaker, R. R.; Engler, E. M. *J. Am. Chem. Soc.* **1977**, *99*, 5521.

0022-3263/81/1946-0775$01.00/0

Scheme II



phosgene in ethanol, following Krug et al.,[11] gives tetrathiapentalene-2,6-dithione 4. In agreement with Steimecke et al.,[4] we find that potassium (best) or sodium metal reduction of CS_2 in DMF produced 1 in excellent yield. The electrochemical procedure circumvents the hazards associated with the use of active metals and is most convenient for small-scale reductions (up to 100 mmol), while the metal reductions can be carried out on a molar scale. The electrochemical procedure does not require high-purity solvents or electrolytes. The electrolyses were carried out in a hood, care was not taken to dry the solvents other than distillation, and the TBAI electrolyte did not have to be recrystallized in order to obtain excellent yields of 1.

Oxidation of the electrolysis solution of 1 and 2 by combination of the working- and counter-electrode compartments, the latter of which contains a I_3^-/I^- mixture after completion of the electrolysis, yields a sparingly soluble yellow solid in almost quantitative yield. Elemental analyses indicated a carbon sulfide with the formula CS_x, $1.75 < x < 2.08$; after recrystallization from carbon disulfide, analysis gave $CS_{1.98}$. Structure 5, obtained by oxidative addition of sulfur to the 4,5-dimercapto-1,3-dithiole-2-thione dianion, is tentatively assigned to this compound. The high yield of 5, as well as the failure of a good dienophile such as benzoquinone to add to any intermediates in this process, suggests the reactions shown in Scheme II to account for the formation of 5.

Assignment of the structure of 5 rests on the elemental analysis, the mass spectra which contained a parent peak at *m/e* 228, and the IR spectrum. The latter exhibited strong bands at 1465 (C=C) and 1070 cm^{-1} (SCS_2); compare 1470 and 1069 cm^{-1} for 3a and 1461 and 1080 cm^{-1} for C_4S_6 (4).[11] While the mass spectrum indicates that some elemental sulfur was present in the samples, no evidence of S_8 was obtained from the attempted voltammetric investigation of 5 in DMF. The latter experiments were thwarted by the low solubility and apparent decomposition of 5 in solution. Under these conditions the reduction waves of sulfur[18] would have been readily detected. Attempts to obtain ^{13}C NMR spectra of saturated carbon disulfide solutions of 5 (ca. 50 mg/10 mL) in the presence or absence of chromium(III) acetoneacetonate also were unsuccessful. Nor were we successful in obtaining crystals suitable for X-ray analysis.

Substituted 1,3-dithiole-2-thiones can be elaborated further by a variety of coupling methods[19] which lead to substituted tetrathiafulvalenes. Since we were not successful in coupling compounds 3b or 3c by the simple procedure of refluxing the thione in the presence of a phosphorous(III) compound [$P(OCH_3)_3$, $P(OCH_2CH_3)_3$, or $P(C_6H_5)_3$], an alternate strategy was adopted. The chemistry of Schumaker and Engler[17] was employed (Scheme III) to produce the highly interesting potassium salt of the tetraanion, $C_6S_8^{4-}$. This salt was readily alkylated in DMF to form the substituted tetrathiafulvalenes 7a–c. These compounds are good electron donors with almost identical voltammetric behavior. The cyclic voltammograms of 7a–c show the two reversible TTF oxidation waves at ca. 0.2 and 0.4 V ($E_{1/2}$ values) vs. a silver reference electrode. Half-wave potentials are given in Table I.

Scheme III

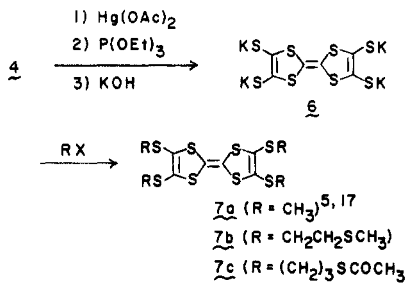


Table I. Voltammetric Parameters of Substituted Tetrathiafulvalenes in Acetonitrile 0.1 M in NEt_4ClO_4

compd	$E_{1/2}{}^1$,[a] V	$E_{1/2}{}^2$,[a] V	CF[b]
7a[c]	0.17	0.41	
7b	0.22	0.47	0.44
7c	0.19	0.42	0.46

[a] $E_{1/2} = (E_p{}^a + E_p{}^c)/2$ vs. Ag|AgNO$_3$ (0.01 M). [b] CF = $i_p/ACv^{1/2}$, amp cm^{-2} M^{-1} $(s/V)^{1/2}$. [c] Reference 5.

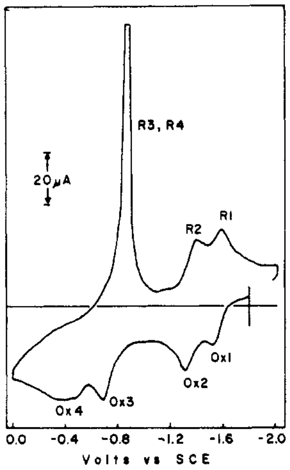


Figure 1. Cyclic voltammogram of 0.4×10^{-3} M 6 with 0.1 M TEAP in DMF: platinum disk electrode; sweep rate 50 mV s^{-1}.

The cyclic voltammetry of 6 (Figure 1) was more interesting. Four oxidation waves (Ox1–Ox4) are evident at rather negative potentials. The open-circuit rest potential of the DMF solution of 6 is ca. −1.6 V which indicates not only that 6 is very easily oxidized but also that the DMF solution of 6 is partially oxidized, presumably by trace amounts of oxygen in the electrochemical cell. This is confirmed by the strong electron spin resonance signal obtained from DMF solutions of 6 at open circuit.

The first two couples in the voltammograms of 6 exhibited almost reversible ($\Delta E_p \simeq 70$ mV) to quasireversible behavior. This indicates a facile electron-transfer equilibrium between the tetraanion, the radical trianion, and the dianion. Half-wave potential data, $(E_p{}^a + E_p{}^c)/2$ vs. SCE, are given in eq 2. When the electrode potential is

$$C_6S_8^{4-} \xrightleftharpoons[-1.56\ V]{-e} C_6S_8^{3-} \xrightleftharpoons[-1.35\ V]{-e} C_6S_8^{2-} \xrightleftharpoons[-0.72\ V]{-e} C_6S_8^{-} \xrightleftharpoons[-0.5\ V]{-e} C_6S_8^{0} \quad (2)$$

scanned past the peak potential of wave Ox4, the platinum working electrode becomes coated with a golden yellow film. In spite of this, coulometric oxidation of 6 at 0.0 V

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(18) Martin, R. P.; Doub, W. H., Jr.; Roberts, J. L., Jr.; Sawyer, D. T. *Inorg. Chem.* **1973**, *12*, 1921.

(19) Narita, M.; Pittman, C. U., Jr. *Synthesis* **1976**, 489.

vs. SCE proceeded smoothly and indicated a total *n* value of 4 electrons/molecule. On reversal of the potential sweep, a large, sharp "stripping wave" (R3, R4) is observed in the region of −0.8 to −0.9 V vs. SCE, presumably due to the reduction of the neutral C_6S_8 film on the electrode surface. If the potential sweep is reversed just positive of Ox3, the Ox3/R3 couple appears to be reversible. Thus, the voltammetry is consistent with four successive electron transfers (eq 2) relating the five species from $C_6S_8^{4-}$ to $C_6S_8^{\circ}$ with the latter being insoluble in DMF. Work is continuing to characterize more completely the golden yellow film presumed to be the neutral species C_6S_8.

The ESR spectra obtained from DMF solutions of 6 were complex. The spectra exhibited an intense narrow line at $g = 2.0153$ and a cluster of four unevenly spaced relatively weak lines around $g = 2.0112$. In situ electrolysis in the spectrometer cavity at potentials between Ox1 and Ox2 increased the height of all these lines. Oxidation at −0.6 V immediately eliminated the lines around $g = 2.0112$ and greatly decreased the intensity of the line at $g = 2.0153$. The significant observation is that the ESR spectra correlate with the voltammetric behavior shown in Figure 1. The main ESR signal is assigned to the $C_6S_8^{3-}$ species or a protonated form of this trianion.

Experimental Section

Chemicals. Acetonitrile and *N,N*-dimethylformamide (DMF) were the principal solvents used for the electrolyses in this work. Spectrograde acetonitrile (Aldrich) was used without further purification. DMF was purified by vacuum distillation (0.1 mmHg, 28 °C) over anhydrous $CuSO_4$ (10 g/750 mL of DMF) after being stirred at room temperature overnight.[20] Ethanol was distilled twice, first from KOH (40 g/2.0 L of drug-grade 100% ethanol) and then over magnesium turnings (30 g).

Tetrabutylammonium iodide (TBAI, Eastman), which was the supporting electrolyte for all bulk electrolyses, was used without further purification. Tetraethylammonium perchlorate (TEAP, Eastman) and tetrabutylammonium perchlorate (TBAP, Eastman) were recrystallized three times from water and dried in vacuo for 2 days prior to use in voltammetric studies.

Certified ACS reagent grade CS_2 (Fisher) was used with no further purification.

Elemental analyses were performed by Galbraith Laboratories.

Instrumentation. Most of the electrolyses were carried out by using a PAR Model 173 potentiostat equipped with a PAR Model 176 current follower and a Koslow Scientific Model 541 coulometer. A Lambda power supply (0–200 V at 1 A) with manual control of the applied voltage was employed for some of the electrolyses.

Electron-spin resonance spectra were obtained by using standard in situ electrolysis techniques with a Varian E-line spectrometer (Model E-109S) equipped with E-101 microwave bridge. Experiments carried out under an inert atmosphere (argon) were performed in a Vacuum Atmospheres Model 43-2 drybox equipped with a Model HE-493 dry train.

Cells and Electrodes. Since the CS_2 reduction products react readily with triiodide formed at the anode, all electrolyses were carried out in three compartment cells in which medium-porosity glass frits (20-mm diameter) separated the compartments. A cell which had two separate 20-mm-diameter arms connecting the counter- and working-electrode compartments smoothly handled currents of 0.2 A which permitted approximately 0.05–0.10 faraday of electricity to be passed over a 8-h period. The bottom of the working-electrode compartment was a medium-porosity frit which allowed for deaeration and stirring of the solution by the purging gas during the electrolyses. The working-electrode compartment generally contained 100–200 mL of 0.4 M TBAI in either acetonitrile or DMF.

A platinum foil working electrode (28 cm²), a saturated calomel reference electrode, and a carbon-rod counter electrode were used. The working electrode for voltammetry was a polished 0.22-cm² platinum disk.

General Electrolysis Procedure. Typically, solutions which were 1–5% (v/v) in CS_2 were electrolyzed at a current of 0.2 A. Higher currents resulted in excessive heating of the frits in the electrolysis cell. The working electrode potential was maintained between −1.8 and −2.1 V vs. SCE and additional amounts of CS_2 were added when the potential became more negative than ca. −2.1 V or when the solution volume in the cell decreased. It should be mentioned that Bontempelli et al.[12] obtained evidence for formation of gaseous carbon monosulfide at potentials more negative than −2.2 V vs. SCE. When DMF was the solvent, the next step was carried out directly in the cell after the electrolysis. For example, to a DMF/CS_2 electrolysis solution through which 0.030 faraday had been passed was added 4.3 g (30 mmol) of methyl iodide (Aldrich). The mixture was stirred with gentle warming for 1 h and then treated with 100 mL each of water and methylene chloride. The organic layer was washed five times with water and dried with $MgSO_4$. Chromatographic separation on an alumina column with benzene as the eluant afforded an oil which crystallized from CH_3CN to give light brown needles of 4,5-bis(methylthio)-1,3-dithiole-2-thione (**3a**)[3,5] in 90% yield based on 7.5 mequiv of 1 being formed in the electrolysis.

For electrolyses in 0.4 M TBAI/CH_3CN, the solution was evaporated to dryness prior to further manipulation. The resulting deep red salt cake, which consists of a mixture of the tetrabutylammonium salt of 1, TBAI, and other electrolysis products, is air sensitive and decomposes upon being allowed to stand after 1–2 days.

When the platinum cathode potential is maintained positive of −1.7 V vs. SCE in 0.4 M TBAI/DMF, an apparently oligomeric form of the CS_2 reduction product is formed. This product was isolated by addition of the contents of the working electrode compartment to 500 mL of a saturated aqueous solution of KI. The resulting solid was washed with 0.5 M aqueous KI solution, until the washings became clear, and then with small amounts of cold water. The resulting brick-red solid was more air stable than the above salt mixture and decomposed only slowly in air. Based on the amount of isolated product, the apparent *n* values for these electrolyses varied between 0.15 and 0.25 faraday/mol of CS_2. Treatment of this material with CH_3I in DMF resulted in the formation of **3a** but in yields of less than 50%.

[1,3]Dithiolo[4,5-*d*]-1,2,3-trithiole-5-thione (5). Carbon disulfide was reduced in 0.4 M TBAI/DMF as described above. After passage of 0.030 faraday, the electrolysis was halted, and the contents of all three compartments were combined. The resulting yellow precipitate was separated by filtration and washed with 50-mL portions each of ethanol, benzene, and ether successively. An amorphous yellow solid which analyzes for CS_x, $1.75 < x < 2.1$, is realized in almost quantitative yield. Crystallization from CS_2 gives an off-yellow solid which decomposes upon being heated at 138–140 °C: IR (KBr) 1725 (w), 1465 (s), 1405 (w), 1383 (w), 1245 (m), 1171 (m), 1110 (m), 1070 (s, br), 929 (m), 890 (s), 802 (w), 743 (m) cm^{-1}; mass spectrum (70 eV), *m/e* (relative intensity, assignment) 44 (6.5, CS^+), 64 (3.9, S_2^+), 76 (100.0, CS_2^+), 78 (7.8, 76 + 2), 160 (4.3, S_5^+), 192 (7.3, S_6^+), 228 (4.7, $C_3S_6^+$). Anal. Calcd for C_3S_6: C, 15.77; S, 84.23. Found: C, 15.81; S, 83.66.

Several attempted reactions of 5 with benzoquinone were unsuccessful. A mixture of 0.1 g of 5 and 0.1 g of benzoquinone was refluxed for 1 h in either ether, ethanol, benzene, or methylene chloride. The yellow solid darkened but did not dissolve, and benzoquinone was recovered from the supernatant liquids in almost quantitative yields. A similar result was obtained when benzoquinone was added to the DMF/CS_2 electrolysis solution prior to combining the contents of the compartments.

4,5-Bis[[2-(methylthio)ethyl]thio]-1,3-dithiole-2-thione (3b). To a DMF solution of 7.5 mmol of the CS_2 reduction product was added 0.50 mL of 2-chloroethyl methyl sulfide (Aldrich). By use of the above procedure for **3a**, the thione was isolated in 70% yield: mp 40–42 °C; IR (KBr) 2900 (w), 1453 (m), 1413 (m), 1253 (w), 1204 (s), 1125 (m), 1060 (vs), 945 (w), 890 (m), 745 (w), 725 (w), 700 (w), 675 (m) cm^{-1}; NMR ($CDCl_3$) δ 2.2 (s, 3 H), 2.4 (m, 4 H). Anal. Calcd for $C_9H_{14}S_7$: C, 31.18; H, 4.07; S, 64.75. Found: C, 30.92; H, 4.12; S, 64.45.

4,5-Bis[[3-(thioacetoxy)-1-propyl]thio]-1,3-dithiole-2-thione (3c). To a DMF solution of 7.5 mmol of the CS_2 reduction product

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(20) Faulkner, L. R.; Bard, A. J. *J. Am. Chem. Soc.* **1968**, *90*, 6284.

was added 0.50 mL of 3-chloropropyl thioacetate. Following the above procedure the thione **3c** was isolated in 70% yield after recrystallization from $CHCl_3$: mp 48–50 °C; IR (KBr) 2910 (w), 1710 (s), 1430 (w), 1388 (m), 1360 (w), 1300 (w), 1250 (w), 1145 (m), 1110 (w), 1060 (s), 1040 (w), 915 (m), 890 (w) cm^{-1}; NMR ($CDCl_3$) δ 2.0 (m, 2 H), 2.1 (s, 3 H), 2.7 (m, 4 H).

1,3,5,7-Tetrathiapentalene-2,6-dithione (4). This compound was prepared following the procedure of Krug et al.[11] The salt cake obtained from the acetonitrile–CS_2 electrolysis solution was dissolved in deaerated ethanol and treated with thiophosgene until the solution was decolorized. An amorphous yellow solid was obtained in quantitative yield based on the stoichiometry of eq 1: mp 208–210 °C dec (compare lit.[17] mp 207–210 °C dec); IR (KBr) 1068 (vs), 959 (m), 900 (w), 776 (m) cm^{-1}; mass spectrum (70 eV), *m/e* (relative intensity, assignment) 44 (20.9, CS^+), 64 (7.5, S_2^+), 76 (100, CS_2^+), 88 (85.1, $C_2S_2^+$), 240 (88.1, $C_4S_6^+$), 242 (20.9, M + 2).

1,3,5,7-Tetrathiapentalene-2,6-dione. This compound was prepared by $Hg(OAc)_2$ hydrolysis of **4** following the procedure of Rae.[21] The yellow solid which was obtained by sublimation (90 °C, 0.05 mmHg) was purified further by recrystallization from acetonitrile. Fine white needles were realized in 22% yield: mp 150 °C; IR (KBr) 1727 (m), 1678 (s), 973 (w), 914 (w) cm^{-1}.

Tetrapotassium 2,2′-Bis(1,3-dithiole 4,5-disulfide) (6). A mixture of 100 mL of ethanol, 10 g of KOH, and 1.0 g of 2,2′-bis(1,3,5,7-tetrathiapentalen-6-one), prepared by coupling 1,3,5,7-tetrathiapentalene-2,6-dione,[17] was stirred 10 h under an inert atmosphere. The resulting pink salt was isolated by filtration and washed with a 10-mL portion of EtOH under an argon atmosphere. The salt which darkens upon drying was realized in 90% yield: mp 120 °C; IR (KBr) 1730 (m), 1610 (s), 1440 (s), 1385 (s), 1305 (s), 1140 (m), 1105 (m), 1050 (w), 990 (s), 870 (m), 750 (w), 740 (w), 680 (m), 650 (m) cm^{-1}.

Exhaustive coulometry was carried out by dissolving 40 mg of this salt in a deaerated solution of 0.1 M TEAP in DMF and oxidizing the mixture at 0.0 V vs. SCE. An *n* value of 4 faradays/mol of **6** was obtained.

2,2′-Bis[4,5-bis[[2-(methylthio)ethyl]thio]-1,3-dithiole] (7b). A mixture of 0.5 g of **6**, 25 mL of DMF, and 7.6 mL of 2-chloroethyl methyl sulfide was stirred for 10 h under argon. A 50-mL portion of water was added slowly with stirring and the mixture extracted with chloroform. After being dried with $MgSO_4$, the brown solution was eluted on neutral alumina with chloroform. The solid was recrystallized from acetonitrile to give golden brown needles in 60% yield: mp 110 °C; IR (KBr) 2960 (w), 2910 (m), 1424 (s), 1320 (w), 1262 (m), 1204 (s), 1126 (w), 1100 (w), 1023 (w), 961 (w), 913 (w), 886 (m), 805 (m), 772 (m), 731 (w), 710 (w), 682 (m) cm^{-1}. Anal. Calcd for $C_{18}H_{28}S_{12}$: C, 34.35; H, 4.49; S, 61.15. Found: C, 34.22; H, 4.64; S, 60.98.

2,2′-Bis[4,5-bis[[3-(thioacetoxy)-1-propyl]thio]-1,3-dithiole] (7c). A mixture of 0.5 g of **6**, 25 mL of DMF, and 3.0 mL of 3-chloropropyl thioacetate was stirred under argon for 10 h. The solution was worked up in the same manner as for **7b** and was eluted on silica gel with a chloroform–ether mixture. The brown solid was realized in 60% yield: mp 95 °C; IR (KBr) 2910 (w), 1710 (s), 1420 (m), 1390 (w), 1300 (w), 1253 (m), 1135 (s), 1107 (s), 948 (m), 874 (w), 766 (w) cm^{-1}. Anal. Calcd for $C_{26}H_{36}O_4S_{12}$: C, 39.16; H, 4.55; S, 48.26. Found: C, 38.97; H, 4.56; S, 48.37.

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Registry No. 3a, 49638-64-4; **3b**, 75949-39-2; **3c**, 75961-52-3; **4**, 64394-46-3; **5**, 75949-40-5; **6**, 75949-41-6; **7b**, 75949-42-7; **7c**, 75949-43-8; CS_2, 74-15-0; methyl iodide, 74-88-4; 2-chloroethyl methyl sulfide, 542-81-4; 3-chloropropyl thioacetate, 13012-54-9; 1,3,5,7-tetrathiapentalene-2,6-dione, 64394-45-2; 2,2′-bis(1,3,5,7-tetrathiapentalen-6-one), 64394-47-4.

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[21] Rae, I. D. *Int. J. Sulfur Chem.* **1973**, *8*, 273.

Synthesis of Indoles from *N*-(Trifluoroacetyl)-2-anilino Acetals[1]

J. Eric Nordlander,* David B. Catalane, Kirtivan D. Kotian, Randall M. Stevens, and Jerome E. Haky

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

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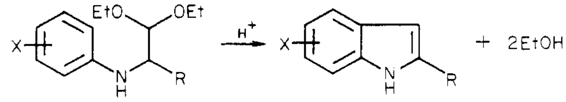
N-(Trifluoroacetyl)indoles (**3**) are produced in high yield from appropriately ring-substituted *N*-(trifluoroacetyl)-2-anilino acetals (**2**) in boiling trifluoroacetic acid containing excess trifluoroacetic anhydride. Mild saponification provides the free indoles nearly quantitatively. The scope of the reaction is discussed. The ring closure follows solvolytic substitution of a trifluoroacetoxy group for one of the ethoxy groups in **2**. The method has been extended to cyclization of *N*-(trifluoroacetyl)-α-anilinoacetone in hot polyphosphoric acid followed by saponification to yield 3-methylindole.

The biochemical importance of many indole derivatives[2] has spurred continual efforts toward new or improved methods for synthesis of the indole nucleus.[2-4] One early concept for indole construction, eq 1, was acid-catalyzed



(1)

cyclization–elimination of 2-anilino acetals,[5] readily

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[1] Presented in part at the 178th National Meeting of the American Chemical Society, Washington, DC, Sept 1979; Abstract ORGN 20.

[2] (a) Neuss, N. In "Chemistry of the Alkaloids"; Pelletier, S. W., Ed.; Van Nostrand-Reinhold: New York, 1970; Chapter 9. (b) Houlihan, W. J., Ed. "Indoles"; Wiley-Interscience: New York, 1972; Parts 1 and 2; *Ibid.*, Part 3, 1979. (c) Stoll, A., Hofmann, A. In "Chemistry of the Alkaloids"; Pelletier, S. W., Ed.; Van Nostrand-Reinhold: New York, 1970, Chapter 10. (d) Taylor, W. I. "Indole Alkaloids", Pergamon: New York, 1966. (e) Manske, R. H. F., Ed. "The Alkaloids"; Academic Press: New York, 1965; Vol. VIII. (f) Bentley, K. W. "The Alkaloids"; Wiley-Interscience: New York, 1957; Part I, Chapters 7 and 8. (g) Bentley, K. W. *Ibid.*; Wiley-Interscience: New York, 1965; Part II, Chapter 6.

[3] (a) Sundberg, R. J. "The Chemistry of Indoles"; Academic Press, New York, 1970; Chapter 3. (b) Brown, R. K. In "Indoles"; Houlihan, W. J., Ed.; Wiley-Interscience: New York, 1972; Part 1, Chapter 2. (c) Kutney, J. P. In "The Total Synthesis of Natural Products"; ApSimon, J., Ed.; Wiley-Interscience: New York, 1977; Vol. 3, pp 274–278.

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