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# Synthesis and Properties of New Bridged Tetrathiafulvalenes

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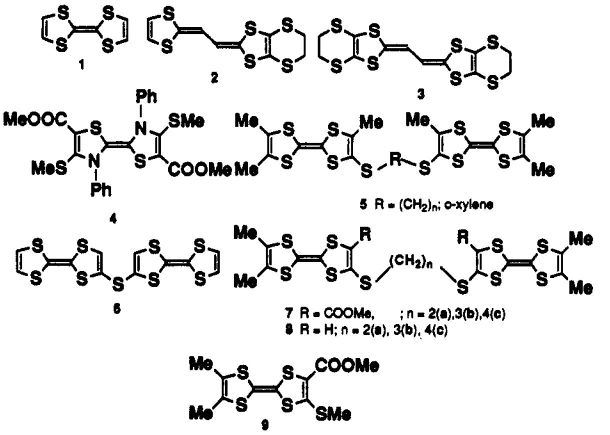
The condensation reaction of dithiole phosphonium perchlorates **17** and **18a–c** with 2-ethylselenodithiolium tetrafluoroborate **16** in the presence of triethylamine was employed for the high-yield synthesis of four new donors **7a–c**, **9** of the tetrathiafulvalene series. The carbomethoxy groups of **7a–c** were removed by basic hydrolysis followed by decarboxylation to give **8a–c**. Electrochemical studies for seven new TTFs were carried out. An unusual effect resulting in an decrease of the first oxidation potential was observed for **7b**. Some properties of the starting 4-mercapto-5-carbomethoxy-1,3-dithiole-2-thione (**10**) are reported.

The high electrical conductivity reported for the tetrathiafulvalene **1** (TTF) complex with tetracyanoquinodimethane (TCNQ) in 1973[1] initiated a tremendous effort aimed at discovering a variety of electron $\pi$-donors of the TTF series.[2] Recent examples include the new TTF vinylogs **2** and **3** and the thiazole analog **4**, which have been synthesized in our laboratories.[3–6] Also, some interesting bridged TTF's (**5** and **6**) have been reported within the past year with the objective of obtaining internal mono- and polycation salts.[7–9]

The idea that systems containing two or more linked donor units might give highly conducting charge-transfer (CT) complexes of higher than one-dimensionality was suggested by Wudl.[10] This concept has led to the preparation of condensed multi-TTF systems,[11] cage-like TTF's,[12] and TTF's linked by heteroatoms,[8,13,14] single bonds, or tertiary carbons.[15] However, very few examples have been described where the effect of the extended $\pi$-electron system can be detected electrochemically.[7,8,11,13,15]

In this paper, we report a high-yield synthesis and some properties of a number of new bridged TTF's (**7a–c** and **8a–c**) and the nonbridged unsymmetrical analog **9**.



4-Mercapto-5-carbomethoxy-1,3-dithiole-2-thione (**10**) was the key intermediate for the series of TTF's **7a–c**. It was synthesized by a modification of the procedure of Augustin and co-workers,[16] who prepared and alkylated the anion of **10**, but did not isolate thiol **10** itself (Scheme I).

Thiol **10** proved to be a surprisingly strong acid, which had a p$K_a$ of 3.6 in aqueous solution. Its UV spectrum was strongly solvent dependent. In chloroform solution, two maxima at 272 and 378 nm were observed, attributable to the unionized thiol **10**. In contrast, three maxima were seen in ethanol at 321, 360, and 418 nm, which we attribute to the anion **10b**. In accord with this interpretation, the crystalline tetrabutylammonium salt **11** of thiol **10** showed the same three anion maxima. Also, addition of hydrochloric acid to an ethanol solution of **10** changed the spectrum to that of the unionized **10**, due to a common ion effect.

The infrared spectrum of **10** in $CS_2$ solution shows two absorption bands at 1077 (strong) and 1095 (weak) cm$^{-1}$, corresponding to $\nu_{C=S}$, two strong bands at 1693 and 1715 cm$^{-1}$ ($\nu_{C=O}$), and a broad band in the region 2420–2460 cm$^{-1}$ ($\nu_{SH}$), testifying to the existence of both forms **10a** and **10**. The 1693 peak disappears in the corresponding

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(1) (a) Ferraris, J. P.; Cowan, D. O.; Walatka, V.; Perlstein, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 948. (b) Coleman, L. B.; Cohen, M. J.; Sandman, D. J.; Yamagishi, F. G.; Garito, A. F.; Heeger, A. J. *Solid State Commun.* **1973**, *12*, 1125.

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(14) Fourmigue, M.; Batail, P. *J. Chem. Soc., Chem. Commun.* **1991**, 1370.

(15) Tatemitsu, H.; Nishikawa, E.; Sakata, Y.; Misumi, S. *Synth. Metals* **1987**, *19*, 565.

(16) Augustin, M.; Dölling, W.; Vogt, A. *Z. Chem.* **1983**, *23*, 333.

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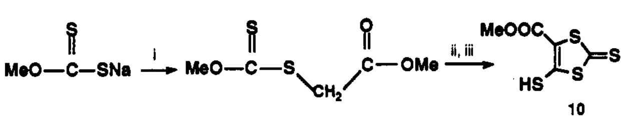
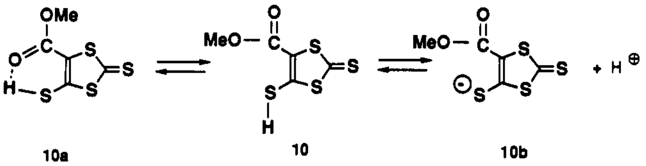
Scheme I$^a$



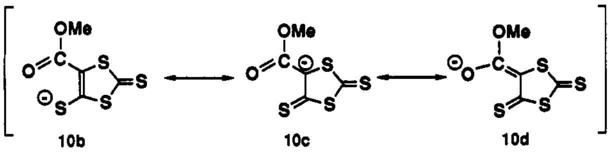
$^a$ (i) ClCH$_2$COOMe, MeOH; (ii) CS$_2$, t-BuONa, DMF; (iii) HCl, 62%.



spectrum of **12a**, which also shows peaks at: 1075 (strong), 1093 (weak) ($\nu_{C=S}$), and 1713 cm$^{-1}$ ($\nu_{C=O}$).

The $^1$H NMR of **10** in CDCl$_3$ solution shows two singlets at $\delta$ 3.89 (3 H, OMe) and 6.18 (1 H, SH). The last signal disappears in acetone-$d_6$ solution, in which dissociation takes place.

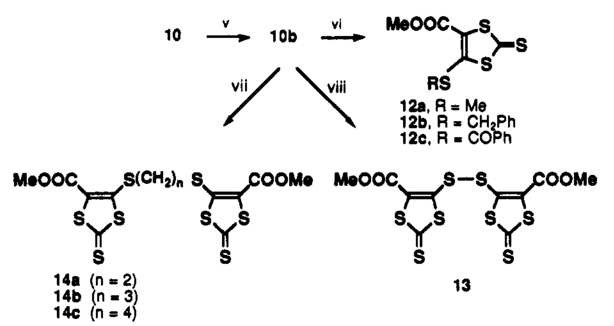
Since resonance form **10c** and **10d** should contribute to the anion of **10** as well as **10b**, the alkylation of the anion with methyl iodide was examined under a variety of conditions in a search for a C- or O-alkylation product. However, only the *S*-methyl derivative **12a** was formed in solvents of different polarity (methanol, benzene, DMF) and using different bases (sodium alkoxides, morpholine, triethylamine).



Several other reactions of the anion of **10** were examined, in all of which the thiolate sulfur participated. Thus, alkylation with benzyl chloride gave **12b** while acylation with benzoyl chloride gave **12c**. Iodine oxidation afforded the disulfide **13**. Dialkylation products **14a–c** were also obtained readily from the appropriate aliphatic dibromides.

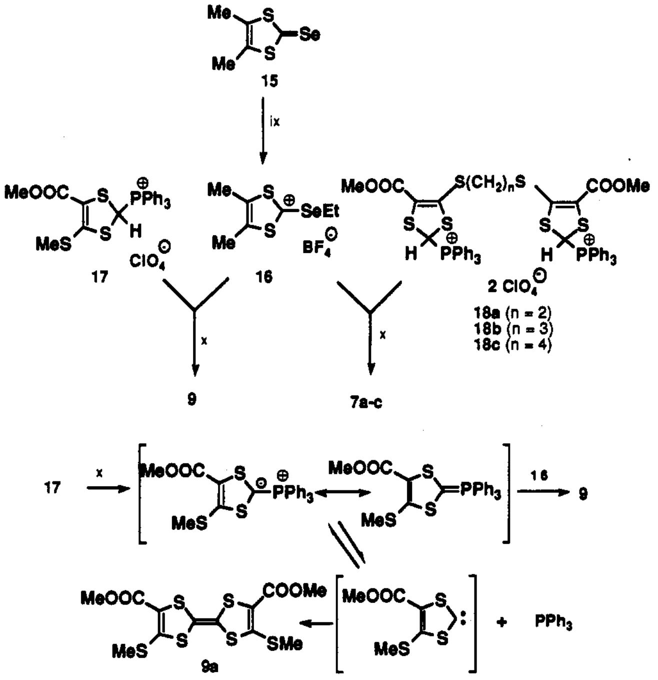
**Tetrathiafulvalenes.** In most cases, unsymmetrical TTFs have been obtained by the cross-coupling of two different 1,3-dithiole fragments;[2] other methods generally do not give yields exceeding 50%.[7,17]

Scheme II$^a$



$^a$ (v) MeONa, MeOH/dioxane; (vi) MeI, 87% (**12a**); PhCH$_2$Cl, 89% (**12b**); PhCOCl, 87% (**12c**); (vii) Br(CH$_2$)$_2$Br, 59% (**14a**); Br(CH$_2$)$_3$Br, 72% (**14b**); Br(CH$_2$)$_4$Br, 75% (**14c**); (viii) I$_2$, Et$_2$O, 67%.

Scheme III$^a$



$^a$ (ix) HC(OEt)$_3$, Et$_2$O·BF$_3$, CHCl$_3$, 100%; (x) NEt$_3$, CH$_3$CN.

We now describe the synthesis of a series of three bridged TTF dimers (**7a–c**) and the related unsymmetrical TTF **9**. The key reaction employed was the recently discovered high-yield condensation of a dithiole phosphonium ylide with an alkylselenodithiolium salt.[18] We consider it to involve a Wittig-like condensation in which a phosphonium ylide generated in situ from the corresponding triphenylphosphonium salt (**17** or **18a–c**) and triethylamine reacts with 2-(ethylseleno)-1,3-dithiolium tetrafluoroborate (**16**), prepared by alkylation of 3,4-dimethyl-1,3-dithiole-2-selone[19] (**15**). The TTF derivatives **9** and **7a–c** were obtained in 61–75% yields (Scheme III), the symmetrical byproduct **9a** being formed in only trace amounts (less than 1%).

Phosphonium salts **17** and **18a–c** were prepared starting from the appropriate 1,3-dithiole-2-thiones **12a** and **14a–c** in 69–78% yields (Scheme IV).

The ester groups of **7a–c** were removed by basic hydrolysis, followed by decarboxylation of the resulting carboxylic acids (Scheme V).

**Cyclic Voltammetry.** Cyclic voltammagrams of **9**, **7a–c**, and **8a–c** were measured at room temperature in acetonitrile solutions with tetrabutylammonium hexaflurophosphate as the supporting electrolyte. The results are presented in Table I. All waves are reversible. The ester groups of **7a–c** raise the first and second oxidation potentials relative to **8a–c**. An interesting effect was found for **7b**. Although for compounds **7a,c** and **8a–c** we observed two reversible waves, as is usual for the most compounds of the TTF family, two additional waves appear for **7b** at 0.40, 0.48, and 0.56 V. These waves probably correspond to the mono- and dication radicals $\mathbf{7b}^{\bullet+}$ (0.40 V, 0.48 V) and $\mathbf{7b}^{(\bullet+)}{}_2$ (0.56 V), respectively. Further two-electron oxidation was observed as a single reversible wave

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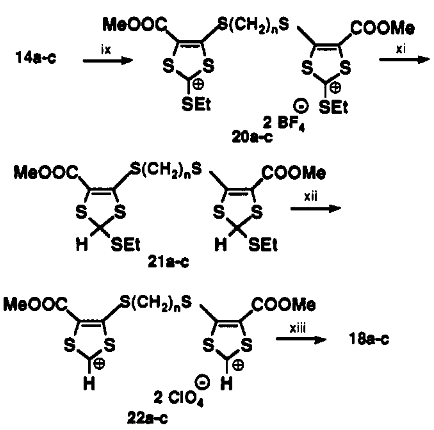
[17] Gonella, N.; Cava, M. P. *J. Org. Chem.* **1978**, *43*, 369.

[18] For another example of the use of this method, see: (a) Khodorkovsky, V. Yu.; Tormos, G. V.; Neilands, O. J.; Kolotilo, N. V.; Il'chenko, A. Ya. *Tetrahedron Lett.* **1992**, *33*, 973. (b) Experimental details for a series of additional unsymmetrical TTF's will be published separately.

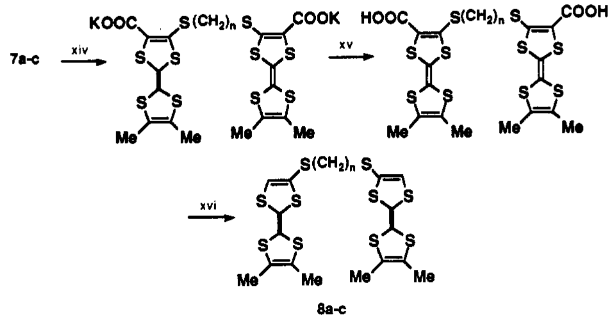
[19] 4,5-Dimethyl-1,3-dithiole-2-thione was obtained as reported: Ferraris, J. P.; Doehler, T. O.; Bloch, A. N.; Cowan, D. O. *Tetrahedron Lett.* **1973**, 2553. The corresponding selone was prepared as described earlier: Khodorkovsky, V. Yu.; Kreicberga, J. N.; Balodis, K. A.; Neilands, O. J. *Izv. AN Latv. SSR, Ser. Khim.* **1988**, *1*, 120 (in Russian).

Scheme IV[a]



[a] (ix) $HC(OEt)_3$, $Et_2O{\cdot}BF_3$, $CHCl_3$; (xi) $NaBH_4$, $CH_3CN$; (xii) 55% aqueous $HClO_4$, $Ac_2O$, $Et_2O$; (xiii) $PPh_3$, $CH_3CN$.

Scheme V[a]



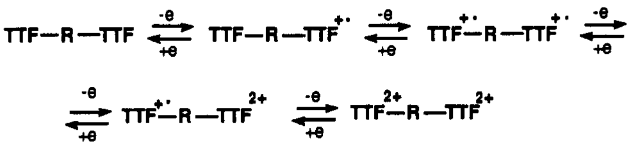
[a] (xiv) KOH, dioxane/$H_2O$; (xv) HCl(aq); (xvi) diglyme, reflux.

**Table I. Cyclic Voltammetry of TTF's 9, 7a–c, 8a–c vs Ag/AgCl, Glassy Carbon Electrode (Scan Speed 100 mV/s)**

| compd | $E_{1/2}^1$ | $E_{1/2}^2$ |
|---|---|---|
| **9** | 0.50 | 0.86 |
| **7a** | 0.60 | 0.94 |
| **7b** | 0.40, 0.48, 0.56 | 0.94 |
| **7c** | 0.56 | 0.91 |
| **8a** | 0.53 | 0.87 |
| **8b** | 0.46 | 0.78 |
| **8c** | 0.44 | 0.78 |

(0.94 V). These results are similar to the situation described for the TTF dimers,[7] in which a decrease of the first oxidation potential leading to $\mathrm{TTF{-}R{-}TTR}^{\bullet+}$ was explained by the possible sharing of the $\pi$-electrons in a sandwich structure resulting in the stabilization of the monocation radical. Removal of the second electron from the positively charged sandwich is more difficult because of Coulombic repulsion between the resulting charged TTF moieties.

To explain our results we assume that **7b** may exist in solution in both the sandwich and the twisted forms. In the first case, the first oxidation potential (0.40 V, $\mathbf{7b}^{\bullet+}$-sandwich) is lower relative to **9**, while the second potential (0.56 V, $\mathbf{7b}^{(\bullet+)}{}_2$) is higher due to Coulombic repulsion. For the twisted or extended form of **7b** we expect the values for both $\mathbf{7b}^{\bullet+}$ and $\mathbf{7b}^{(\bullet+)}{}_2$ to be virtually identical (0.48 V) and comparable to the corresponding potential for **9** (0.50 V). In the cases of **7a,c** the molecules cannot form close sandwiches. However, we still observe a slight increase of the first potential, obviously due to an intramolecular Coulombic effect of the hindered forms. Further two-electron oxidation in all cases was observed as single reversible waves.



In the case of **8a–c**, both TTF moieties in one molecule act independently. X-ray structures, as well as the possibility of producing new conducting charge-transfer salts in this series, are under study in our laboratories.

## Experimental Section

**4-Mercapto-5-carbomethoxy-1,3-dithiole-2-thione (10).** Carbon disulfide (0.34 mL, 5.55 mmol) was added to a solution of carbomethoxymethylxanthogenic acid methyl ester[20] (1 g, 5.55 mmol) in dry DMF (10 mL). The solution was cooled down to 0–5 °C (ice bath) and sodium *tert*-butylate (1.53 g, 11.10 mmol) was added portionwise. After the mixture was stirred for 2 h at room temperature, hydrochloric acid (5%, 100 mL) was added. The precipitate was filtered off, washed with water (4 × 15 mL), dried, and recrystallized from benzene/hexane (1:1) to give 0.77 g (62%) of yellow crystals: mp 134 °C; UV $\lambda_{max}$ ($\log_{10}\epsilon$) EtOH 321 (4.06), 360 (3.96), 4.18 (3.75), $CHCl_3$ 272 (4.00), 378 (4.25) nm; $^1H$ NMR ($CDCl_3$) $\delta$ 3.89 (s, 3 H, OMe), 6.18 (s, 1 H, SH). Anal. Calcd for $C_5H_4O_2S_4$: S, 57.17. Found: S, 57.46.

**Tetrabutylammonium 5-Carbomethoxy-2-thioxo-1,3-dithiole-4-thiolate (11).** A solution of tetrabutylammonium hydroxide (containing 1 mmol of $Bu_4NOH$) in water (3 mL) was added to a hot solution of **10** (0.2 g, 0.89 mmol) in 5 mL of water. The precipitate was filtered off, washed with water (3 × 2 mL), and dried to give 0.28 g (68%) of yellow hydroscopic crystalline material: IR ($CH_3CN$) 1713 (C=O), 1075 (C=S) cm$^{-1}$; UV $\lambda_{max}$ ($\log_{10}\epsilon$) EtOH 322 (4.24), 360 (4.05), 420 (3.90), $CHCl_3$ 322 (3.62) nm; $^1H$ NMR ($CDCl_3$) $\delta$ 0.85–1.10 (m, 12 H, Me), 1.33–1.75 (m, 16 H, $CH_2$), 2.80–3.30 (m, 8 H, $CH_2$), 3.66 (s, 3 H, OMe). Anal. Calcd for $C_{21}H_{39}NO_2S_4$: N, 3.10; S, 27.53. Found: N, 3.10; S, 27.78.

**4-(Benzylthio)-5-carbomethoxy-1,3-dithiole-2-thione (12b).** A solution of sodium methylate (6.24 mmol) in methanol (75 mL) was added under stirring to a suspension of **10** (1.4 g, 6.24 mmol) in methanol (10 mL). The reaction mixture was heated to boiling to form a red solution of sodium thiolate and cooled down to room temperature. Benzyl chloride (0.86 mL, 7.49 mmol) was added. After the mixture was stirred for 8 h, water (200 mL) was added. The precipitate was filtered off, washed with water (4 × 10 mL), and recrystallized from acetic acid to give 1.75 g (89%) of yellow crystals: mp 124 °C; IR (KBr) 1708, 1496, 1268, 1188, 1094, 1068, 1060 cm$^{-1}$; UV $\lambda_{max}$ ($\log_{10}\epsilon$) EtOH 284 (4.04), 381 (4.22), $CHCl_3$ 285 (3.99), 384 (4.19) nm; $^1H$ NMR ($CDCl_3$) $\delta$ 3.75 (s, 3 H, OMe), 4.13 (s, 2 H, $CH_2$), 7.26 (s, 5 H, Ph). Anal. Calcd for $C_{12}H_{10}O_2S_4$: C, 45.83; H, 3.21; S, 40.78. Found: C, 45.92; H, 3.21; S, 40.95.

**4-(Benzoylthio)-5-carbomethoxy-1,3-dithiole-2-thione (12c).** Benzoyl chloride (0.57 mL, 4.91 mmol) was added to the solution of sodium thiolate prepared as described for **12b** from **10** (1 g, 4.46 mmol), MeONa (4.46 mmol), and methanol (26 mL). After the mixture was stirred for 10 min, water (100 mL) was added. The precipitate was filtered off, washed with water (3 × 4 mL), and recrystallized from methanol to yield 1.27 g (87%) of colorless needles: mp 130 °C. Anal. Calcd for $C_{12}H_8O_3S_4$: C, 43.88; H, 2.46; S, 39.05. Found: C, 44.05; H, 2.49; S, 38.93.

**4,4′-Dithiobis(5-carbomethoxy-1,3-dithiole-2-thione) (13).** A solution of iodine (0.3 g, 1.17 mmol) in $Et_2O$ (5 mL) was added to the solution of sodium thiolate prepared as described for **12b** from **10** (0.53 g, 2.34 mmol), MeONa (2.34 mmol), and methanol (30 mL). Water (100 mL) was added, and the precipitate was filtered off, washed with water (3 × 5 mL), dried, and recrystallized from dioxane to give 0.35 g (67%) of orange crystals: mp 215 °C; UV $\lambda_{max}$ ($\log_{10}\epsilon$) $CHCl_3$ 268 (4.10), 373 (4.39) nm; $^1H$ NMR ($CDCl_3$) $\delta$ 3.81 (s, 6 H, OMe). Anal. Calcd for $C_{10}H_6O_4S_8$: S, 57.42. Found: S, 57.70.

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(20) Tröger, J.; Volkmer, F. J. *Prakt. Chem.* **1904**, *70*, 442.

**4,4'-(Alkylenedithio)bis(5-carbomethoxy-1,3-dithiole-2-thiones) (14a–c): General Procedure.** To a solution of sodium thiolate in methanol (20 mL) and dioxane (10 mL), obtained from **10** (8.92 mmol) and MeONa (8.92 mmol), was added dibromoalkane (6.24 mmol). After refluxing for 4 h, the reaction mixture was cooled to room temperature and water (40 mL) was added. The precipitate was filtered off, washed with water (3 × 5 mL), and recrystallized from acetic acid to give the following.

**14a**: 59%; yellow crystals; mp 189–190 °C; UV $\lambda_{max}$ ($\log_{10} \epsilon$) $CHCl_3$ 280 (3.21), 378 (3.44) nm; $^1H$ NMR ($CDCl_3$) $\delta$ 3.25 (s, 4 H, $CH_2$), 3.79 (s, 6 H, OMe). Anal. Calcd for $C_{12}H_{10}O_4S_8$: C, 30.36; H, 2.12; S, 54.04. Found: C, 30.48; H, 2.13; S, 53.85.

**14b**: 72%; yellow crystals; mp 145–6 °C; UV $\lambda_{max}$ ($\log_{10} \epsilon$) $CHCl_3$ 284 (3.23), 385 (3.45) nm; $^1H$ NMR ($CDCl_3$) $\delta$ 2.18 (q, 2 H, $CH_2$), 3.13 (t, 4 H, $SCH_2$), 3.83 (s, 6 H, OMe). Anal. Calcd for $C_{13}H_{12}O_4S_8$: C, 31.95; H, 2.48; S, 52.48. Found: C, 32.06; H, 2.30; S, 52.29.

**14c**: 75%; yellow crystals; mp 181–2 °C; UV $\lambda_{max}$ ($\log_{10} \epsilon$) $CHCl_3$ 284 (4.28), 358 (4.35) (sh), 3.85 (4.50) nm; $^1H$ NMR ($CDCl_3$) $\delta$ 1.51 (s, 4 H, $CH_2$), 3.02 (t, 4 H, $SCH_2$), 3.82 (s, 6 H, OMe). Anal. Calcd for $C_{14}H_{14}O_4S_8$: C, 33.44; H, 2.81; S, 51.02. Found: C, 33.38; H, 2.81; S, 50.89.

**4,4'-(Alkylenedithio)bis[triphenyl(5-carbomethoxy-1,3-dithiol-2-yl)phosphonium perchlorates] (18a–c) and Triphenyl[4-(methylthio)-5-carbomethoxy-1,3-dithiol-2-yl]phosphonium Perchlorate (17).** To a hot solution of 1,3-dithiole-2-thione **12a**[16] or **14a–c** (1.47 mmol) in chloroform (15 mL) were added $HC(OEt)_3$ (3 mL) and $Et_2O{\cdot}BF_3$ (3 mL). The reaction mixture was refluxed for 3 h and cooled down to room temperature. Ether (100 mL) was added. The precipitated oil was separated, washed with ether (3 × 15 ml), and dissolved in acetonitrile (25 mL). Sodium borohydride (2.94 mmol) was added portionwise with stirring to the resulting solution. After the mixture was stirred for 2 h, water (100 mL) was added, and product was extracted with ether (3 × 50 mL). The organic layer was washed with water (3 × 20 mL), dried over $CaCl_2$, and filtered through a short column of silica gel. A mixture of perchloric acid (2 mL) and acetic anhydride (12 mL) was added to the ether solution. The precipitated oil was separated, washed with ether (3 × 20 mL), and dissolved in acetonitrile (25 mL). Triphenylphosphine (2.2 mmol) was added, and the reaction mixture was stirred for 2 h. The product was precipitated by ether (100 mL), dissolved in methanol, and reprecipitated by ether to give the following.

**18a**: 71%. Anal. Calcd for $C_{48}H_{42}Cl_2O_{12}P_2S_6$: C, 50.76; H, 3.70; S, 16.94; Cl, 6.24. Found: C, 51.04; H, 3.58; S, 16.21; Cl, 5.96.

**18b**: 76%. Anal. Calcd for $C_{49}H_{44}Cl_2O_{12}P_2S_6$: C, 51.18; H, 3.83; S, 16.73; Cl, 6.17. Found: C, 51.70; H, 3.62; S, 16.54; Cl, 5.92.

**18c**: 78%. Anal. Calcd for $C_{50}H_{46}Cl_2O_{12}P_2S_6$: C, 51.60; H, 3.95; S, 16.53; Cl, 6.09. Found: C, 52.12; H, 3.80; S, 16.04; Cl, 5.95.

**17**. The procedure requires twice less the amounts of reagents relative to the starting thione **12a**: yield 69%. Anal. Calcd for $C_{24}H_{22}ClO_6PS_3$: C, 50.66; H, 3.90; S, 16.90. Found: C, 50.63; H, 4.25; S, 17.26.

**Synthesis of Tetrathiofulvalenes 9 and 7a–c: General Procedure.** 4,5-Dimethyl-2-(ethylseleno)-1,3-dithiolium tetrafluoroborate (**16**) was prepared from 4,5-dimethyl-1,3-dithiole-2-selone[19] (**15**) (1.76 mmol), $HC(OEt)_3$ (1.5 mL), and $Et_2O{\cdot}BF_3$ (1.5 mL) in $CHCl_3$ (15 mL) as described above for 1,3-dithiole-2-thiones **12a** and **14a–c** (preparation of **17** and **18a–c**). The resulting salt **16** was dissolved in acetonitrile (5 mL) and added to a solution of phosphonium salt **17** or **18a–c**. Triethylamine (1 mL) was added. After 1 h the precipitated crystals were filtered off, washed with methanol (4 × 5 mL), and recrystallized from pyridine/hexane to give the following.

**7a**: 61%; red crystals; mp 183 °C; IR (KBr) 1698, 1540, 1507, 1278, 1090 cm$^{-1}$; UV $\lambda_{max}$ ($\log_{10} \epsilon$) benzene 286 (sh) (4.40), 312 (4.46), 333 (sh) (4.34), 434 (3.60) nm; $^1H$ NMR ($CDCl_3$) $\delta$ 1.94 (s, 12 H, Me), 3.27 (s, 4 H, $CH_2$), 3.77 (s, 6 H, OMe). Anal. Calcd for $C_{22}H_{22}O_4S_{10}$: C, 39.38; H, 3.31; S, 47.78. Found: C, 39.33; H, 3.29; S, 47.79.

**7b**: 68%; red crystals; mp 180–1 °C; IR (KBr) 1684, 1493, 1270, 1085 cm$^{-1}$: UV $\lambda_{max}$ ($\log_{10} \epsilon$) benzene 280 (sh) (4.40), 309 (4.46), 333 (sh) (4.35), 434 (3.60) nm; $^1H$ NMR ($CDCl_3$) $\delta$ 1.93 (s, 12 H, Me), 2.14 (q, 2 H, $CH_2$), 3.12 (t, 4 H, $SCH_2$), 3.77 (s, 6 H, OMe). Anal. Calcd for $C_{23}H_{24}O_4S_{10}$: C, 40.33; H, 3.50; S, 46.82. Found: C, 40.35; H, 3.53; S, 46.68.

**7c**: 75%; red crystals; mp 183–4 °C; IR (KBr) 1695, 1540, 1490, 1255, 1090 cm$^{-1}$; UV $\lambda_{max}$ ($\log_{10} \epsilon$) benzene 280 (sh) (4.46), 309 (4.55), 333 (sh) (4.41), 431 (3.67) nm; $^1H$ NMR ($CDCl_3$) $\delta$ 1.51 (s, 4 H, $CH_2$), 1.93 (s, 12 H, Me), 3.03 (t, 4 H, $SCH_2$), 3.77 (s, 6 H, OMe). Anal. Calcd for $C_{24}H_{26}O_4S_{10}$: C, 41.23; H, 3.74; S, 45.86. Found: C, 41.15; H, 3.75; S, 45.62.

**9**: half the amounts of reagents were used relative to **15**; yield 70%; red crystals; mp 145 °C (from methanol). Anal. Calcd for $C_{11}H_{12}O_2S_5$: S, 47.63. Found: S, 47.81.

**Hydrolysis and Decarboxylation of 7a–c: General Procedure.** To a solution of **7a–c** (0.73 mmol) in dioxane (10 mL) were added potassium hydroxide (2.92 mmol) and water (5 mL). After being refluxed for 3 h with stirring, the reaction mixture was cooled to room temperature, concd hydrochloric acid (10 mL) was added, and the reaction mixture was stirred for 1 h. Water (20 mL) was added, the precipitate was filtered off, washed with water (4 × 10 mL) and acetonitrile (3 × 5 mL), and dried. The intermediate acid was refluxed in diglyme (10 mL) for 20 min and cooled to room temperature, and water (15 mL) was added. The precipitate was filtered off, washed with water (3 × 10 mL), and recrystallized from benzene/hexane to give the following.

**8a**: 78%; orange crystals; mp 116 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 1.93 (s, 12 H, Me), 2.82 (s, 4 H, $SCH_2$), 6.32 (s, 2 H, =CH). Anal. Calcd for $C_{18}H_{18}S_{10}$: C, 38.96; H, 3.24; S, 57.79. Found: C, 39.05; H, 3.45; S, 57.04.

**8b**: 81%; yellow crystals; mp 112–3 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 1.93 (s, 12 H, Me), 2.12 (m, 2 H, $CH_2$), 2.80 (t, 4 H, $SCH_2$), 6.33 (s, 2 H, =CH). Anal. Calcd for $C_{19}H_{20}S_{10}$: C, 40.12; H, 3.52; S, 56.37. Found: C, 40.34; H, 3.45; S, 56.12.

**8c**: 81%; yellow crystals; mp 115–6 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 1.51 (s, 4 H, $CH_2$), 1.93 (s, 12 H, Me), 2.84 (t, 4 H, $SCH_2$), 6.32 (s, 2 H, =CH). Anal. Calcd for $C_{20}H_{22}S_{10}$: C, 41.21; H, 3.77; S, 55.01. Found: C, 41.35; H, 3.82; S, 54.88.

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