g, 0.96 mmol) in dry acetonitrile (5 mL) was cooled to 0–5 °C under nitrogen. Pyridine (0.145 mg, 1.84 mmol) was added slowly over 15 min. After stirring at 20 °C for 15 h the mixture was quenched with water and the aqueous solution extracted with chloroform. The organic layer was separated, dried ($MgSO_4$), and evaporated. Vacuum sublimation of the resulting brown solid (ca. 100 °C, 0.001 mBar Hg) yielded compound **4e** (50 mg, 59%) identical with the sample described above.

Acknowledgment. We thank SERC for funding this work and Professors D. O. Cowan and A. M. Kini for helpful discussions and further details concerning their synthesis of compound **1c**, published in ref 7b. The work in Basel was supported by the Swiss National Science Foundation. The visit by J.H. to Durham was funded by The British Council.

Registry No. **1a**, 1518-16-7; **1b**, 70359-39-6; **1c**, 97218-71-8; **1d**, 138385-47-4; **1e**, 86317-43-3; **2f**, 130891-30-4; **2g**, 130891-33-7; **3a**, 106-51-4; **3b**, 84-65-1; **3c**, 527-17-3; **3d**, 935-92-2; **3e**, 527-61-7; **3f**, 105855-49-0; **3g**, 10251-80-6; **4a**, 83928-83-0; **4b**, 10395-02-5; **4c**, 123849-29-6; **4d**, 123849-28-5; **4e**, 95276-20-3; **4f**, 138385-48-5; **4g**, 130891-41-7; **5a**, 72971-39-2; **5b**, 138385-49-6; **5c**, 97218-72-9; **5d**, 138385-50-9; **5e**, 25751-81-9; **5f**, 138385-51-0; **5g**, 138385-52-1; **6a**, 116267-99-3; **6a** anion, 138385-53-2; **6b**, 116387-65-6; **6c**, 123849-27-4; **6c** anion, 138385-54-3; **6d**, 123849-26-3; **6d** anion, 138385-55-4; **6e**, 123849-25-2; **6e** anion, 138385-56-5; **6f**, 138385-57-6; **6g**, 138385-58-7; **8**, 130891-39-3; **9**, 138385-59-8; **10**, 4102-48-1; **11**, 138385-60-1; **12**, 138385-61-2; **13**, 14384-30-6; **14**, 138385-62-3; malononitrile, 109-77-3; *N,N'*-bis(trimethylsilyl)carbodiimide, 1000-70-0; potassium, 7440-09-7.

Supplementary Material Available: Mass and IR spectroscopic data for compounds **1c**, **4a–4g**, **10**, **11**, **12**, and **14**; mass IR and UV/vis spectroscopic data for compounds **2f**, **2g**, and **6a–6g**; variable-temperature NMR spectra of compound **6e**; complete listings of bond lengths, bond angles, and anisotropic temperature factors for compounds **6c** and **6d** (23 pages). Ordering information is given on any current masthead page.

New Vinylogous Tetrathiafulvalene π-Electron Donors with Peripheral Alkylseleno Substitution

Martin R. Bryce* and Malcolm A. Coffin

Department of Chemistry, University of Durham, Durham, DH1 3LE, U.K.

William Clegg

Department of Chemistry, University of Newcastle, Newcastle upon Tyne, NE1 7RU, U.K.

Received September 26, 1991

Efficient syntheses are described for five new vinylogous π-electron donors, viz. **5**, **6**, and **8–10**, which are related to bis(ethylenediseleno)tetrathiafulvalene (**3**): symmetrical and unsymmetrical systems, containing mixed alkylseleno and alkylthio groups, have been obtained. The solution electrochemical redox properties, studied by cyclic voltammetry, establish that these molecules undergo two, single-electron, oxidations at low potentials. The single-crystal X-ray structure of 4,5-bis(methylseleno)-4′,5′-bis(methylthio)-2,2′-ethanediylidene(1,3-dithiole) (**6**) is reported. Semiconducting complexes of the new donors with tetracyano-*p*-quinodimethane have been obtained.

Quasi-one-dimensional organic metals have been intensively studied since the discovery of high electrical conductivity in the charge-transfer complex of tetrathiafulvalene (TTF) (1) (Chart I) and tetracyano-*p*-quinodimethane (TCNQ).[1] The synthesis of new multichalcogen π-electron donors has remained at the forefront of research,[2] with a few systems, notably, bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF) (2),[3] providing radical cation salts which are superconductors,[4] with T_c values as high as 11.6 K.[5]

The incorporation of conjugated spacers between the 1,3-dithiole ring of TTF has been a prominent theme in the design of new donors. For example, the parent TTF vinylogue **4** has been studied by Yoshida et al.,[6] and recently the BEDT-TTF vinylogue **7** has been synthesised independently by three groups.[7-9] Molecules **4** and **7** were reported to undergo multistage redox reactions with relatively low oxidation potentials; extending the conjugation in this manner stabilized the dication state, relative to TTF (**1**) and BEDT-TTF (**2**), by reducing the intramolecular Coulomb repulsion energy. Salts of extended donors may, therefore, show electronic and magnetic properties that are quite different from salts of donors **1** or **2**. We now describe the synthesis and solution redox behavior of new vinylogues **5**, **6**, and **8–10**, which are the first derivatives of system **4** that have selenium atoms attached to the

---

(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.

(2) (a) Proceedings of the International Conference on Science and Technology of Synthetic Metals, Santa Fe 1988, (ICSM 88), published in *Synth. Metals* **1988**, 27–29; Proceedings of ICSM 90, Tübingen, published in *Synth. Metals* **1991**, 41–43.

(3) (a) Mizuno, M.; Garito, A. F.; Cava, M. P. *J. Chem. Soc., Chem. Commun.* **1978**, 18. (b) Varma, K. S.; Bury, A.; Harris, N. J.; Underhill, A. E. *Synthesis* **1987**, 837.

(4) (a) Murata, K.; Tokumoto, M.; Anzai, H.; Bando, H.; Kajimura, K.; Ishiguro, T.; Saito, G. *Synth. Metals* **1986**, *13*, 3. (b) Williams, J.; Emge, T. J.; Wang, H. H.; Beno, M. A.; Copps, P. T.; Hall, L. N.; Carlson, K. D.; Crabtree, G. W. *Inorg. Chem.* **1984**, *23*, 2558. (c) Williams, J. M.; Beno, M. A.; Wang, H. H.; Leung, P. C. W.; Emge, T. J.; Geiser, U.; Carlson, K. D. *Acc. Chem. Res.* **1985**, *18*, 261. (d) Urayama, H.; Yamochi, H.; Saito, G.; Nozawa, K.; Sugano, T.; Kinoshita, M.; Sato, S.; Oshima, K.; Kawamoto, A.; Tanaka, J. *Chem. Lett.* **1988**, 55. (e) *The Physics and Chemistry of Organic Superconductors*; Saito, G., Kagoshima, S., Eds.; Springer-Verlag: Berlin, 1990.

(5) Kini, A. M.; Geiser, U.; Wang, H. H.; Carlson, K. D.; Williams, J. M.; Kwok, W. K.; Vandervoot, K. G.; Thompson, J. E.; Stupka, D. L.; Jung, D.; Whangbo, M.-H. *Inorg. Chem.* **1990**, *29*, 2555.

(6) (a) Yoshida, Z.; Kawase, T.; Awaji, H.; Sugimoto, I.; Sugimoto, T.; Yoneda, S. *Tetrahedron Lett.* **1983**, *24*, 3469. (b) Sugimoto, T.; Awaji, H.; Sugimoto, I.; Misaki, Y.; Kawase, T.; Yoneda, S.; Yoshida, Z. *Chem. Mater.* **1989**, *1*, 535.

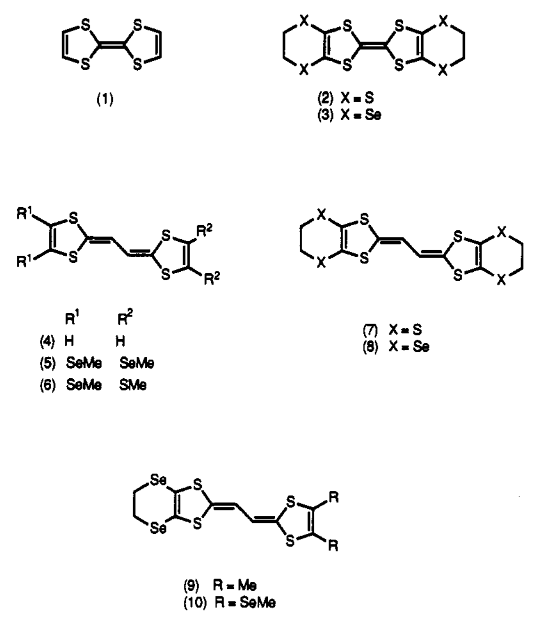
(7) Khodorkovskii, V. Yu.; Veselova, L. N.; Neiland, O. Ya. *Khim. Geterotsikl. Soedin.* **1990**, 130; *Chem. Abstr.* **1990**, *113*, 22868.

(8) (a) Moore, A. J.; Bryce, M. R.; Ando, D. J.; Hursthouse, M. B. *J. Chem. Soc., Chem. Commun.* **1991**, 320. (b) For closely related chemistry, see: Moore, A. J.; Bryce, M. R. *Synthesis* **1991**, 27.

(9) Hansen, T. K.; Lakshmikantham, M. V.; Cava, M. P.; Metzger, R. M.; Becher, J. *J. Org. Chem.* **1991**, *56*, 2720.

0022-3263/92/1957-1696$03.00/0 © 1992 American Chemical Society

Chart I



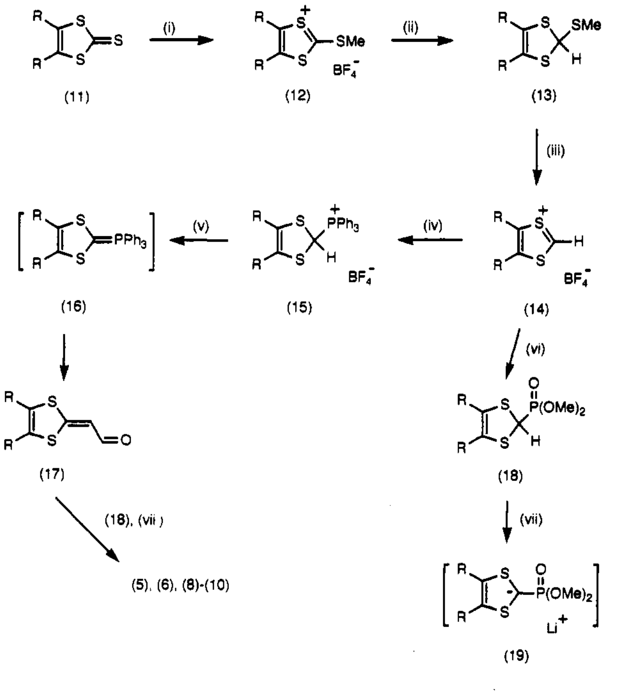
(1)

(2) X = S
(3) X = Se

(7) X = S
(8) X = Se

(9) R = Me
(10) R = SeMe

Scheme I^a



For formulae (11) - (19):
(a) R = SeMe
(b) R— R = -Se-$(CH_2)_2$-Se-

Additionally for formulae (18) and (19):
(c) R = Me
(d) R = SMe

^{a}Reagents and conditions: (i) dimethyl sulfate, 70 °C, then HBF_4, 20 °C; (ii) sodium borohydride, acetonitrile, 20 °C; (iii) acetic anhydride, HBF_4, ether, 0 °C; (iv) triphenylphosphine, acetonitrile, 20 °C; (v) glyoxal, triethylamine, acetonitrile, 20 °C; (vi) trimethylphosphite, sodium iodide, acetonitrile, 20 °C; (vii) *n*-butyllithium, compound 17, THF, -78 °C → 20 °C.

framework. The formation of semiconducting TCNQ complexes of these donors is also reported.

The syntheses are presented in Scheme I. The key step in assembling the vinylogous TTF skeleton is Wittig-Horner reaction of a vinylogous aldehyde (17) with a phosphonate anion (18), as described previously for other vinylogues.[6a,7-9] Starting materials were thiones 11. *S*-Methylation of 11, using neat dimethyl sulfate, yielded the dithiolium cation which was isolated as the crystalline tetrafluoroborate salt 12 in high yield. [An analytically pure sample of thione 11 was essential for clean conversion into salt 12.] Cation salt 12 was reduced by sodium borohydride to yield thioether 13 as a red oil which could be purified by column chromatography. Conversion of compound 13 into dithiolium cation 14 was achieved by treatment with acetic anhydride followed by addition of tetrafluoroboric acid. The overall yield for the three-step sequence 11 → 14 is typically >65%. Salts **14a** and **14b** are both white solids which are notably more air- and moisture-sensitive than the analogous bis(methylthio)[10] and ethylenedithio analogues.[8b]

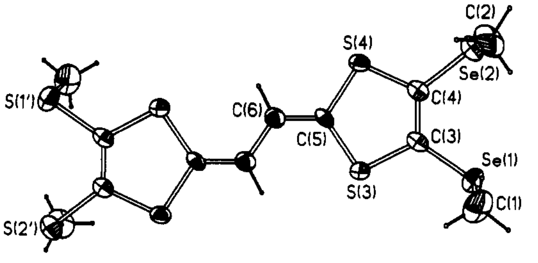


Figure 1. Molecular structure of compound 6 showing the atomic labeling including the S/Se disorder. Thermal motion is depicted as 50% probability ellipsoids except for H atoms.

Cation salt 14, on reaction with triphenylphosphine, yielded phosphonium salt 15, which was not isolated; deprotonation with triethylamine in situ gave the transient ylide 16, which was intercepted with glyoxal to afford the desired vinylogous aldehyde 17 (59–80% yield). Alternatively, cation salt 14 reacted with trimethyl phosphite to yield phosphonate ester 18 in high yield. Compound 18 could be stored for several weeks under vacuum at 20 °C, but rapidly decomposed on exposure to air.

The generation of carbanion 19 from ester 18 was achieved by treatment of the latter compound with *n*-butyllithium at -78 °C; subsequent addition of the appropriate aldehyde 17 gave new vinylogous TTF derivatives 5, 6, and 8–10 in 60–80% yields. Compound 8 has very low solubility in common organic solvents, although solutions can be obtained in carbon disulfide and boiling 1,1,2-trichloroethane. Vinylogues 5, 6, 9, and 10 are soluble in many organic solvents, e.g., dichloromethane.

The molecular structure of compound 6, determined by single-crystal X-ray analysis, is shown in Figure 1. The molecule is disordered over a center of symmetry, so that the terminal methylseleno and methylthio groups are indistinguishable; these heteroatoms were refined as 50% S and 50% Se. The 2,2′-ethanediylidenebis(1,3-dithiole) framework in compound 6 is planar. This is in marked contrast to the nonplanar tetrathiafulvalene framework of analogous tetrakis(alkylchalcogeno)TTF systems,[11] where planarity of the C_6S_8 core is achieved only by attachment of long chains[11] or medium sized rings[12] at the periphery of the molecule. The molecules of compound 6 stack uniformly with several intermolecular S- - -S(Se) contacts close to the sum of the van der Waals radii (Figure 2).

The solution redox properties of donors 5, 6, and 8–10 have been studied by cyclic voltammetry in dichloromethane solutions and the results are collected in Table I. All the compounds undergo two, separate, one-electron oxidations (i.e., sequential formation of the radical cation and the dictation species). The redox waves are reversible for all the compounds except donor 8, for which the reductive scan shows a single two-electron reduction (dica-

---

(10) Moore, A. J.; Bryce, M. R. *Tetrahedron Lett.* In press.

(11) Saito, G. *Pure Appl. Chem.* **1987**, *59*, 999.

(12) Kumar, S. K.; Singh, H. B.; Das, K.; Sinha, U. C.; Mishnev, A. *J. Chem. Soc., Chem. Commun.* **1991**, 952.

Table I. Cyclic Voltammetric Data[a] for Donors 1, 2, and 5–10 and Conductivity Data for TCNQ Complexes

donor	$E_1^{1/2}$, V	$E_2^{1/2}$, V	ΔE	TCNQ complex stoichiometry (donor:TCNQ)[b]	conductivity[c], σ_{rt} S cm^{-1}
TTF (1)	0.340	0.780	0.440		
BEDT-TTF (2)	0.585	0.992	0.407		
5	0.392	0.593	0.201	1:1	10^{-2}
6	0.394	0.571	0.177	1:1	10^{-5}
7	0.480	0.710	0.230		
8	0.407[d]	0.631[d]	0.224[d]	1:1	10^{-2}
9	0.286	0.544	0.258	1:1	10^{-5}
10	0.346	0.562	0.216	1:2	10^{-6}

[a] Experimental conditions: donor (ca. 1 × 10^{-5} mol dm^{-3}), electrolyte $Et_4N^+PF_6^-$ (ca. 1 × 10^{-1} mol dm^{-3}) in dry dichloromethane under nitrogen, 20 °C, vs Ag/AgCl, Pt electrode, scan rate 100 mV s^{-1} using a BAS Electrochemical Analyser. [b] C,H,N analyses were all within acceptable limits. [c] Two-probe compressed pellet measurement. [d] Data for oxidative scan, see text for discussion.

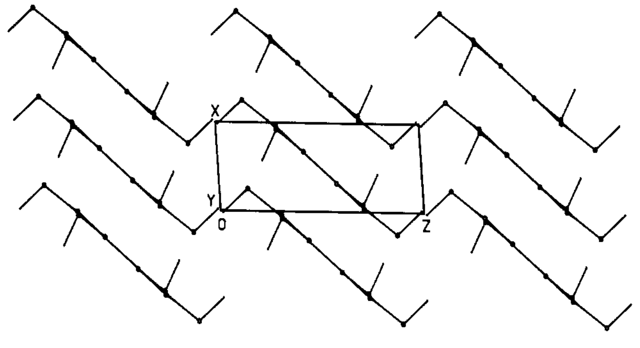


Figure 2. Parallel projection along the *b* axis showing the packing of the molecules of **6**. Intermolecular S---S contacts ≤4.0 Å are S(1)---S(3) 3.963; S(1)---S(4) 3.688; S(2)---S(4) 3.805; S(3)---S(3) 3.918; S(3)---S(4) 3.812. The accepted literature value for S---S van der Waals distance is 3.7 Å (Emsley, J. *The Elements*; Clarendon Press: Oxford, 1989; p 180).

tion → neutral species) at 0.340 V. This behavior for donor **8** is reproducible on repeated recycling of the solution between 0.0 and 1.0 V. Previous work has established that "stretching" the TTF or BEDT-TTF systems by insertion of a vinyl group [viz. molecules **4**[6] and **7**[8,9]] lowers the potential of both the first and second redox waves, $E_1^{1/2}$ and $E_2^{1/2}$, respectively, as well as significantly reducing the difference between them, ΔE. Similar behavior is observed for the new systems described herein. Compound **9** is the best donor in the series (lowest value of $E_1^{1/2}$): this is because two methyl substituents are in place of the alkylthio or alkylseleno groups of the other donors **5–8** and **10**.

Donors **5**, **6**, and **8–10** all form charge-transfer complexes with TCNQ with stoichiometries (donor:acceptor) of 1:1 [for donors **5**, **6**, **8**, and **9**] or 1:2 [for donor **10**]. The highest room temperature conductivity values (two probe, compressed pellet data) are $\sigma_{rt} = 10^{-2}$ S cm^{-1} for the 1:1 complexes of the symmetrical donors **5** and **8** (Table I), which clearly implies that there is segregated stacking and partial charge-transfer from donor to acceptor in these complexes. The infrared stretching frequency of the nitrile group of TCNQ is often used to estimate the degree of charge carried by the acceptor molecule in a complex;[13] however, this method is not reliable for the complexes in Table I. For example, for complex **9**:TCNQ, ν_{max} is 2150 cm^{-1}, which is well outside the usual range of anionic TCNQ.

Experimental Section

General details are the same as those reported recently.[14] Selenium-containing mass peaks are reported for the ^{80}Se isotope. Compound **11b** was prepared by the literature method.[15] Compound **11a** has been mentioned previously but neither synthetic details nor characterisation data were given.[16] Details for **11a** are, therefore, presented here.

4,5-Bis(methylseleno)-1,3-dithiole-2-thione (11a). 1,3-Dithiole-2-thione (2.0 g, 15 mmol) was lithiated and reacted with elemental selenium in THF as described previously.[15] To the resulting diselenate at 0 °C was added methyl iodide (6.0 g, 45 mmol), and the solution was allowed to warm to 20 °C with stirring, which was maintained for 12 h. The mixture was diluted with water and extracted into dichloromethane. The organic layer was separated, dried ($MgSO_4$), and evaporated to yield a red oil. Purification on a silica column (eluent hexane/dichloromethane (3:1 v/v) yielded compound **11a**, which after recrystallization from dichloromethane/hexane was obtained as orange needles (1.44 g, 30%), mp 100–101 °C. NMR: δ_H ($CDCl_3$) 2.41 (s). MS: *m/e* (EI) 322; (CI) 323 (M^+). Anal. Calcd for $C_5H_6S_3Se_2$: C, 18.75; H, 1.89; S, 30.04. Found: C, 18.61; H, 1.80; S, 30.13.

2-(Methylthio)-4,5-bis(methylseleno)-1,3-dithiole (13a). A suspension of compound **11a** (1.0 g; 3.1 mmol) in dimethyl sulfate (5 mL) was heated at 70 °C under nitrogen until dissolution was complete (ca. 1 h). The mixture was cooled to 20 °C and tetrafluoroboric acid (0.6 mL, 3.3 mmol) was added dropwise, followed by dry ether (100 mL). The resulting yellow precipitate was collected, washed with ether, and dried. Salt **12a** (1.21 g, 96%) thus obtained was identified by NMR spectroscopy [δ_H ($CDCl_3$) 3.24 (3 H, s), 2.68 (6 H, s)] and then used directly in the next step. To a solution of salt **12a** (1.21 g, 2.9 mmol) in a mixture of acetonitrile (30 mL) and ethanol (30 mL) was added sodium borohydride (0.15 g, 3.9 mmol), turning the solution from yellow to colorless. After stirring for 1 h at 20 °C, the solvent was evaporated and the residue extracted into dichloromethane, which was washed with water and dried ($MgSO_4$). Evaporation of the organic phase yielded an oil, which was purified by chromatography on a silica column (eluent hexane/dichloromethane, 2:1 v/v) to yield thioether **13a** as a red oil (0.75 g, 78%). NMR: δ_H ($CDCl_3$) 5.90 (1 H, s), 2.29 (6 H, s), and 2.21 (3 H, s). MS: *m/e* (EI) 338; (CI) 339 (M^+).

2-(Methylthio)-5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]diselenin (13b) was similarly prepared from compound **11b** (1.0 g, 3.1 mmol) and isolated by silica column chromatography (eluent hexane/dichloromethane, 1:1 v/v) as a red oil (0.80 g, 83%). NMR: δ_H ($CDCl_3$) 5.86 (1 H, s), 3.30 (4 H, m), and 2.22 (3 H, s). MS: *m/e* (EI) 336; (CI) 337 (M^+).

2-(Formylmethylene)-4,5-bis(methylseleno)-1,3-dithiole (17a). Diethyl ether–tetrafluoroboric acid (0.4 mL, 2.78 mmol) was added dropwise over 15 min to a stirred solution of compound **13a** (0.75 g, 2.23 mmol) in a mixture of acetic anhydride (5 mL) and ether (20 mL) at 0 °C under nitrogen. After stirring for a further 15 min, ether (100 mL) was added and the white solid which had precipitated was removed by filtration, washed with ether, and dried. The air- and moisture-sensitive salt **14a** (0.75 g, 89%) thus obtained was used directly in the next step.

Dithiolium salt **14a** (0.75 g, 2.00 mmol) was dissolved in dry acetonitrile (50 mL) under nitrogen, to which was added tri-

---

(13) Chappell, J. S.; Bloch, A. N.; Bryden, W. A.; Maxfield, M.; Poehler, T. O.; Cowan, D. O. *J. Am. Chem. Soc.* **1981**, *103*, 2442.

(14) Moore, A. J.; Bryce, M. R. *J. Chem. Soc., Perkin Trans. I* **1991**, 157.

(15) Nigrey, P. J.; Morosin, B.; Duesler, E. *Synth. Metals* **1988**, *27*, B481.

(16) Papavassiliou, G. *Pure Appl. Chem.* **1990**, *62*, 483.

phenylphosphine (0.53 g, 2.02 mmol). After 0.5 h at 20 °C, excess glyoxal (10 mL, 40% solution in water) was added, followed by excess triethylamine (ca. 5 mL) and stirring was then continued at 20 °C for 3 h. The solvent was then removed in vacuo and the residue extracted into dichloromethane, which was then washed with water. The organic layer was dried ($MgSO_4$) and evaporated to yield a viscous oil which was purified by chromatography on a silica column (eluent initially hexane/dichloromethane, 1:1 v/v, followed by neat dichloromethane) to afford compound **17a** as a viscous yellow oil [0.47 g, 71%]. NMR: δ_H ($CDCl_3$) 9.27 (1 H, d, J = 1.8 Hz), 6.59 (1 H, d, J = 1.8 Hz), 2.44 (3 H, s), 2.38 (3 H, s). MS: *m/e* (EI) 332; (CI) 333 (M^+).

2-(Formylmethylene)-5,6-dihydro-1,3-dithiolo[4,5-*b*]-[1,4]diselenin (17b) was similarly prepared from compound **13b** (0.80 g) and isolated as a yellow solid (0.55 g, 78%), mp 102–104 °C. NMR: δ_H ($CDCl_3$) 9.36 (1 H, d, J = 1.5 Hz), 6.68 (1 H, d, J = 1.5 Hz), 3.40 (4 H, s). MS: *m/e* (EI) 330; (CI) 331 (M^+). Anal. Calcd for $C_7H_6OS_2Se_2$: C, 25.62, H, 1.84. Found: C, 25.47; H, 1.90.

2-(Dimethoxyphosphoryl)-4,5-bis(methylseleno)-1,3-dithiole (18a). A mixture of dithiolium salt **14a** (0.45 g, 1.20 mmol), trimethyl phosphite (0.15 g, 1.21 mmol), and sodium iodide (0.18 g, 1.2 mmol) in dry acetonitrile (50 mL) was stirred at 20 °C overnight under dry nitrogen. The solvent was evaporated and the residue extracted into dichloromethane, which was washed with water, the organic layer was then dried ($MgSO_4$), and the solvent was removed. The resulting oil was passed down a neutral alumina column, eluting with hexane/dichloromethane (1:1 v/v) to yield compound **18a** as a red oil (0.38 g, 80%). NMR δ_H ($CDCl_3$) 4.81 (1 H, d, J = 4.4 Hz), 3.88 (6 H, d, J = 11.0 Hz), 2.34 (6 H, s).

2-(Dimethoxyphosphoryl)-5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]diselenin (18b) was similarly prepared from salt **14b** (0.50 g) and isolated as a white solid, which rapidly turned black on exposure to air. Recrystallization from dichloromethane/hexane gave 0.31 g, 59%, mp 100–102 °C. NMR: δ_H ($CDCl_3$) 4.83 (1 H, d, J = 6.2 Hz), 3.86 (6 H, d, J = 10.6 Hz), 3.30 (4 H, m). MS: *m/e* (EI) 398; (CI) 399 (M^+). Anal. Calcd for $C_7H_{11}O_3PS_2Se_2$: C, 21.22; H, 2.80. Found: C, 21.79; H, 2.83.

Vinylogous TTF Derivatives 5, 6, and 8–10. General Procedure. A solution of phosphonate ester 18 (1.0 mmol) in dry tetrahydrofuran (THF) (30 mL) was cooled to −78 °C under nitrogen and treated with *n*-butyllithium (1.6 M, 1.1 mmol), causing an immediate color change from red to yellow. After 0.5 h, a solution of aldehyde 16 (0.9 mmol) in THF (10 mL) was added by syringe into the reaction mixture, which was allowed to warm to 20 °C over 16 h. The solvent was then evaporated, and the residue was dissolved in dichloromethane (50 mL), which was washed with water, dried ($MgSO_4$), and evaporated to yield the crude product, which was purified by elution through an alumina column (eluent hexane/dichloromethane ca. 2:1 v/v). The product was recrystallized from hexane/dichloromethane.

4,4′,5,5′-Tetrakis(methylseleno)-2,2′-ethanediylidenebis(1,3-dithiole) (5) was obtained from ester **18a** and aldehyde **17a** and isolated as a orange solid in 58% yield, mp 132–134 °C. NMR: δ_H ($CDCl_3$) 5.78 (2 H, s), 2.32 (12 H, m). MS: *m/e* 605 (M^+). Anal. Calcd for $C_{12}H_{14}S_4Se_4$: C, 23.93; H, 2.34. Found: C, 23.82; H, 2.40.

4,5-Bis(methylseleno)-4′,5′-bis(methylthio)-2,2′-ethanediylidenebis(1,3-dithiole) (6) was obtained from ester **18d**[10] and aldehyde **17a** and isolated as large orange plates in 76% yield, mp 120–122 °C. NMR: δ_H ($CDCl_3$) 5.76 (2 H, s), 2.40 (3 H, s), 2.39 (3 H, s), 2.31 (3 H, s), 2.30 (3 H, s). MS: *m/e* 510 (M^+). Anal. Calcd for $C_{12}H_{14}S_6Se_2$: C, 28.34; H, 2.77. Found: C, 28.37; H, 2.78.

4,5:4′,5′-Bis(ethylenediseleno)-2,2′-ethanediylidenebis-(1,3-dithiole) (8) was obtained from ester **18b** and aldehyde **17b** and isolated as a yellow solid in 55% yield, mp > 340 °C after recrystallization from carbon disulfide/methanol. NMR: δ_H (CS_2) 5.71 (2 H, s) and 3.31 (8 H, s). Anal. Calcd for $C_{12}H_{10}S_4Se_4$: C, 24.09; H, 1.68; S, 21.43. Found: C, 23.85; H, 1.65; S, 21.34. The compound was too involatile to give a mass spectrum (EI, CI, or DCI modes).

4,5-(Ethylenediseleno)-4′,5′-dimethyl-2,2′-ethanediylidenebis(1,3-dithiole) (9) was obtained from ester **18c**[12] and aldehyde **17b** and isolated as a yellow solid in 62% yield, mp 198–200 °C. NMR: δ_H ($CDCl_3$) 5.80 (2 H, dd), 3.33 (4 H, s), 1.90 (3 H, s), 1.89 (3 H, s). MS: *m/e* (EI) 444; (CI) 445 (M^+). Anal. Calcd for $C_{12}H_{12}S_4Se_2$: C, 32.58; H, 2.73. Found: C, 32.78; H, 2.75.

4,5-(Ethylenediseleno)-4′,5′-bis(methylseleno)-2,2′-ethanediylidenebis(1,3-dithiole) (10) was obtained from ester **18a** and aldehyde **17b** and isolated as an orange solid in 65% yield, mp 123–125 °C. NMR: δ_H ($CDCl_3$) 5.81 (2 H, s), 3.33 (4 H, s), 2.31 (3 H, s), 2.30 (3 H, s). MS: *m/e* 604 (M^+). Anal. Calcd for $C_{12}H_{12}S_4Se_4$: C, 24.01; H, 2.01. Found: C, 23.81; H, 1.94.

Complexation of Donors with TCNQ. Equimolar amounts of donor **5**, **6**, and **8–10** and TCNQ were dissolved in boiling dichloromethane [for donors **5**, **6**, **9**, and **10**] or 1,1,2-trichloroethane [for donor **8**] and the dark solution stored at 20 °C for 24 h. The precipitated complex (30–50% yield) was removed by filtration. Data for the complexes are collated in Table I.

Acknowledgment. We thank S.E.R.C. for funding this work.

Registry No. **1**, 31366-25-3; **2**, 66946-48-3; **5**, 138518-80-6; **5**·TCNQ, 138518-81-7; **6**, 138518-82-8; **6**·TCNQ, 138518-83-9; **7**, 127661-08-9; **8**, 138518-84-0; **8**·TCNQ, 138518-85-1; **9**, 138518-86-2; **9**·TCNQ, 138518-87-3; **10**, 138518-88-4; **10**·2TCNQ, 138518-89-5; **11a**, 128346-96-3; **11b**, 118355-60-5; **12a**, 138518-91-9; **13a**, 138518-92-0; **13b**, 138518-93-1; **14a**, 138518-95-3; **14b**, 138518-97-5; **17a**, 138518-98-6; **17b**, 138518-99-7; **18a**, 138519-00-3; **18b**, 138519-01-4; **18c**, 69212-98-2; **18d**, 138519-02-5; 1,3-dithiole-2-thione, 930-35-8; glyoxal, 107-22-2.

Supplementary Material Available: Crystal structure determination (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Piperidinium Tetrathiotungstate as Sulfur Transfer Reagent: Synthesis of Cyclic Disulfides

Preeti Dhar, Nallaperumal Chidambaram, and Srinivasan Chandrasekaran*

Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012, India

Received June 11, 1991

Piperidinium tetrathiotungstate has been found to react with a number of 1,*n*-dihalo compounds to afford the corresponding cyclic disulfides in good yields, under mild reaction conditions. This new methodology has been used as a key step in the synthesis of (±)-lipoic acid (**35**) and asparagusic acid (**37**).

There are a number of methods available in the literature for preparing cyclic disulfides. The preferred method varies with ring size. The common procedures involve either conversion of a dihalide or a ditosylate to a disulfide by displacement with disulfide anion (prepared in situ from sodium sulfide and sulfur)[1] or the oxidation of a

0022-3263/92/1957-1699$03.00/0 © 1992 American Chemical Society