Hz upfield of Me_4Si. At this point, the 1-bridgehead proton was 334 Hz, the *endo*-3-proton is 320 Hz, the *exo*-3-proton is 610 Hz, the *syn*-7-proton is 472 Hz, and the *anti*-7-proton is 208 Hz upfield of Me_4Si. Integration of the *syn*- and *anti*-7-proton signals relative to the other four protons indicates 99 ± 3% D incorporation and an anti/syn deuterium ratio of 1.33 ± 0.02 (syn or anti is relative to the benzo ring).

Stereochemistry of the Reaction of *exo*-2-Chloronorbornane with LiDBB. To a solution of LiDBB made under conditions A and cooled to −78 °C was added *exo*-2-chloronorbornane (2 × 100 μL) prepared from norbornene and HCl by the method of Schmerling.[52] After 30 s, 1 mL of D_2O was added, and the clear solution was warmed to 0 °C and worked up in the usual manner followed by GC collection from column C at 70 °C. IR analysis at 858 cm^{-1} for the exo and 836 cm^{-1} for the endo isomer as recommended by Nickon and Hammons[53] indicates a 5:1 exo to endo ratio, assuming equal molar extinction coefficients. The analysis is less than fully satisfactory, however, due to severe overlap of absorptions in this region.

In like fashion, reaction of the title chloride (320 mg, 5% excess) with LiDBB solution (from which 2 mL had been removed for other purposes) was followed by quenching within 30 s with excess ethylene dibromide. The solution was warmed to 0 °C and worked up in the usual way. GC analysis showed only one peak in the bromide region. GC collection and NMR analysis of this peak indicates it to be a mixture of 91% *exo*- and 9% *endo*-bromides. The ratio was determined by NMR integrations of the proton α to bromine which for the *exo*-bromide falls at δ 3.9, cleanly separated from the α proton of the *endo*-bromide which falls at δ 4.2.[54]

(52) Schmerling, L. *J. Am. Chem. Soc.* **1946**, *68*, 195.
(53) Nickon, A.; Hammons, J. *J. Am. Chem. Soc.* **1964**, *86*, 3323.

Stereochemistry of the Reaction of 4-Chloro-*tert*-butylcyclohexane with LiDBB. To a THF solution of LiDBB at −78 °C made under conditions B was added ca. 220 mg of the title chloride prepared by the method of Glaze et al.[55] (cis/trans ratio of 4). After 5 min, D_2O (2 mL) was added, followed by the usual workup. The product was separated from the DBB by bulb to bulb distillation with an Aldrich Kugelrohr apparatus at 210 °C for 10 min. GC collection (column C at 120 °C) was followed by ir analysis in the C-D stretching region. The spectrum was calibrated with an indene external standard by using the 2305-, 2173-, and 2050-cm^{-1} bands. The ratio of equatorial to axial deuteration is at least 14:1 on using the frequencies given by Glaze et al. for the axial and equatorial compounds and assuming that the molar extinction coefficients for the two compounds are approximately the same.

Registry No. 1, 61217-61-6; *anti*-**2**-Cl, 6518-27-0; *anti*-**2**-D, 52882-75-4; *syn*-**2**-D, 52882-74-3; *anti*-**3**-Br, 1121-41-1; *syn*-**3**-Br, 1121-40-0; *anti*-**3**-Cl, 18688-21-6; *syn*-**3**-Cl, 18688-22-7; *anti*-**3**-D, 87461-78-7; *syn*-**3**-D, 87461-79-8; *anti*-**9**-Br, 55027-63-9; *syn*-**9**-Br, 13307-66-9; *anti*-**9**-D, 87481-43-4; *syn*-**9**-D, 87481-44-5; *syn*-**10**-Br, 20047-65-8; *anti*-**10**-D, 20664-22-6; *syn*-**10**-D, 37907-29-2; *anti*-**11**-Cl, 10239-89-1; *anti*-**11**-D, 31893-09-1; *syn*-**11**-D, 51348-79-9; *endo*-**12**-Br, 13237-87-1; *exo*-**12**-Br, 2534-77-2; *exo*-**12**-Cl, 765-91-3; *endo*-**12**-D, 22642-75-7; *exo*-**12**-D, 22642-76-8; *cis*-**13**-Cl, 13131-74-3; *trans*-**13**-Cl, 13145-48-7; *cis*-**13**-D, 53042-76-5; *trans*-**13**-D, 17553-36-5; $C_2H_4Br_2$, 106-93-4; BuLi, 109-72-8; 7,7-dibromonorcarane, 2415-79-4; *anti*-7-methylnorcarane, 14135-43-4; *syn*-7-methylnorcarane, 14222-39-0.

(54) Applequist, D. E.; Chmurny, G. N. *J. Am. Chem. Soc.* **1967**, *89*, 875.
(55) Glaze, W. H.; Selman, C. M.; Ball, A. L., Jr.; Bray, L. E. *J. Org. Chem.* **1969**, *34*, 641.

Chemistry en Route to $\Delta^{2,2'}$-Bithieno[3,4-*d*]-1,3-dithiole (DTTTF) and Its Selenium Analogue

Long-Yong Chiang

Corporate Research Laboratory, Exxon Research and Engineering Company, Linden, New Jersey 07036

Paul Shu, Dennis Holt, and Dwaine Cowan*

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

Received March 18, 1983

Thieno[3,4-*d*]-1,3-dithiole-2-thione (**4**) and its selenium analogue (**11**) were prepared by utilizing the insertion reaction of elemental sulfur and selenium into the carbon–lithium bond as a key step. The coupling reaction of selone **6** or carbene **9**, which were efficiently derived from the corresponding thione through a common intermediate, hexafluorophosphate salt **5**, gave DTTTF (**1**). A similar approach to the synthesis of DTTSF (**2**) and its key intermediate selone **13** is also described. The repeated insertion reaction of microcrystalline tellurium with lithiated thiophene followed by the treatment with thiocarbonylbis(imidazole) gave a mixture of tellurium compounds **16** and **17**.

Salts of certain planar π-electron donor and acceptor molecules form crystals consisting of parallel chains of stacked molecular ions. This class of compounds displays a range of electrical conductivity[1,2] from insulators [DBTTF–TCNQ] to anisotropic metals [TTF–TCNQ] and superconductors [$(TMTSF)_2ClO_4$]. Studies of these and related compounds have provided a better understanding of charge and spin density waves, Peierls transitions, Kohn

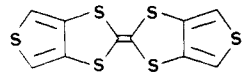
(1) (a) Cowan, D.; Kini, A.; Chiang, L-Y.; Lerstrup, K.; Talham, D.; Poehler, T.; Bloch, A. *Mol. Cryst. Liq. Cryst.* **1982**, *86*, 1741–66. (b) Cowan, D.; Shu, P.; Hu, C.; Krug, W.; Carruthers, T.; Poehler, T.; Bloch, A. "*Chemistry and Physics of One-Dimensional Metals*"; Plenum: New York, 1977; pp 25–46. (c) Bloch, A. N.; Carruthers, T. F.; Poehler, T. O.; Cowan, D. O. *Ibid.* pp 47–85. (d) Jerome, D.; Schulz, H. J. *Adv. Phys.* **1982**, *31*, 299–490.

(2) Jerome, D.; Mazaud, A.; Ribault, M.; Bechgaard, K. *J. Phys. Lett. (Orsay, Fr.)* **1980**, *41*, 95–98. Ribault, M.; Benedek, G.; Jerome, D.; Backgaard, K. *J. Phys. Lett.* **1980**, *41*, 397. Bechgaard, K.; Corneiro, K.; Olsen, M.; Rasmussen, F.; Jacobsen, C. *Phys. Rev. Lett.* **1981**, *46*, 852. Gubser, D. U.; Fuller, W. W.; Poehler, T. O.; Cowan, D. O., Lee, M.; Potember, R. S.; Chiang, L-Y.; Bloch, A. N. *Phys. Rev. B*, **1981**, *24*, 478.

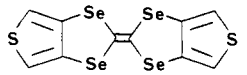
0022-3263/83/1948-4713$01.50/0

anomalies, and Mott–Hubbard insulators and in general how low dimensionality and narrow bands affect the electrical conductivity and magnetic susceptibility of organic radical ion salts. This sensitivity to molecular structure presents an exceptional opportunity to chemically control the electrical properties of these solids.[1]

One important aspect of our continuing study of highly conducting organic materials is an attempt to increase the interchain interactions that could in principle suppress the Peierls transitions.[1a-c,3] The Peierls transition can open a gap in the density of states at the Fermi level and thus convert an organic metal into a small band gap semiconductor. We describe in this paper a new set of compounds, $\Delta^{2,2'}$-bithieno[3,4-*d*]-1,3-dithiole[4] (DTTTF, **1**) and $\Delta^{2,2'}$-bithieno[3,4-*d*]-1,3-diselenole (DTTSF, **2**), which possess



1



2

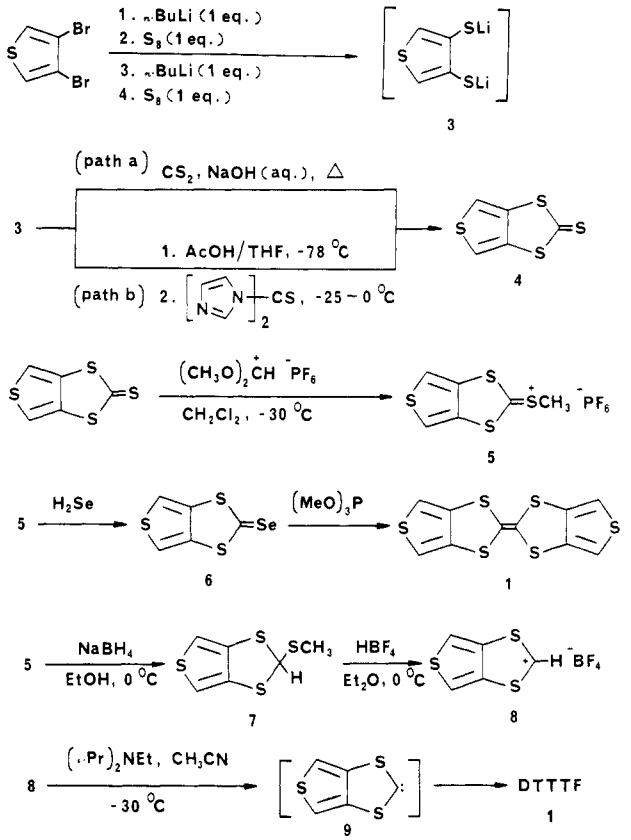
a polarizable heteroatom in the exocyclic rings and consequently could increase interchain interactions in the solid state.

Our approach to the syntheses of compounds **1** and **2** has focused on the efficient generation of key intermediates—thiones **4** and **11**, corresponding selones **6** and **13**, or carbene **9**. DTTTF (**1**) was prepared in higher than 10% overall yield from 3,4-dibromothiophene. However, the coupling reaction of thieno[3,4-*d*]-1,3-diselenole-2-selone (**13**), prepared in 12% yield from 3,4-dibromothiophene, with trialkyl phosphite or triphenylphosphine gave only a low yield of DTTSF (**2**), and this reaction was not reproducible.

Results and Discussion

Our synthesis of DTTTF and attempted synthesis of DTTSF is based on the Gronowitz[5] study of the reaction of sulfur with organolithium compounds derived from thiophene. There are now several other studies that also make use of this reaction. For example, in the syntheses of naphthalene and acenaphthylene dichalcogenides,[6] the insertion reaction of two chalcogen atoms into the carbon–lithium bond of 1,8-dilithionaphthalene and 5,6-dilithioacenaphthylene was found to be a successful synthetic methodology in the construction of an aryl heterocyclic skeleton of organic donors. The method is especially useful in the preparation of certain tellurium analogues of organic donors, such as hexamethylenetetratellurofulvalene[7] and dibenzotetratellurofulvalene.[8] We have utilized this

Scheme I



synthetic strategy to construct DTTTF and DTTSF. Although 3,4-dilithiothiophene could not be generated by treatment of 3,4-dibromothiophene with 2 equiv of an alkyllithium reagent, as in the case of dibromonaphthalene and dibromoacenaphthylene, two consecutive stepwise treatments of 3,4-dibromothiophene with equivalent amounts of alkyllithium reagent and chalcogen metal enabled us to prepare the dilithium salt of 3,4-thiophenedichalcogenides (**3**). In general, *n*-butyllithium is the most efficient reagent for the lithium–bromine exchange reaction. However, the reaction proceeded with a considerable amount of monoalkylated and dialkylated chalcogenides, which were generated from the reaction of lithium chalcogenide and alkyl bromide. Although *tert*-butyllithium may be less efficient in the lithium–bromine exchange reaction, the replacement of *n*-butyllithium by 2 equiv of *tert*-butyllithium gives an easier to purify product mainly due to the consumption of alkyl bromide by the second equivalent of *tert*-butyllithium. As shown in Schemes I, thieno[3,4-*d*]-1,3-dithiole-2-thione (**4**) was prepared by a convenient one-flask reaction in which 3,4-dibromothiophene was twice treated with *n*-butyllithium (1 equiv) or *tert*-butyllithium (2 equiv) followed by elemental sulfur (1 equiv) to produce lithium 3,4-dimercaptothiophene (**3**). Without the isolation of intermediate **3**, the reaction mixture was allowed to react with carbon disulfide in aqueous alkaline solution at refluxing temperature or with an excess of thiocarbonylbis(imidazole) in a dilute solution in THF to afford **4** in 33–39% yield.

The attempted coupling reaction of 1,3-dithiole-2-thione (**4**) with trialkyl phosphite was not successful. This in in contrast to the previous observation that electron-withdrawing substituted 1,3-dithiole-2-thiones may be coupled via desulfurization with trivalent phosphorus compounds

(3) (a) Phillips, T.; Kistenmacher, T. J.; Bloch, A. N.; Cowan, D. O. *J. Chem. Soc., Chem. Commun.* **1976**, 334. (b) Krug, W. P.; Bloch, A. N.; Cowan, D. O. *Ibid.* **1977**, 660. (c) Krug, W. P.; Bloch, A. N.; Poehler, T. O.; Cowan, D. O. *Ann. N. Y. Acad. Sci.* **1978**, *313*, 366–368. Other groups have also been interested in increasing the dimensionality of the organic charge transfer salts; see for example (d) Berg, C.; Bechgaard, K.; Andersen, J. R.; Jacobsen, C. S. *Tetrahedron Lett.* **1976**, 1719–1720. (e) Engler, E. M.; Patel, V. V.; Andersen, J. R.; Schumaker, R. R.; Fukushima, A. A. *J. Am. Chem. Soc.* **1978**, *100*, 3769–3776. (f) Kaplan, M. L., Haddon, R. C. Wudl, F.; Feit, E. D. *J. Org. Chem.* **1978**, *43*, 4642–4646. (g) Mizuno, M.; Garito, A. F.; Cava, M. P. *J. Chem. Soc., Chem. Commun.* **1978**, 18–19.

(4) Shu, P.; Chiang, L.; Emge, T.; Holt, D.; Kistenmacher, T.; Lee, M.; Stokes, J.; Poehler, T.; Bloch, A.; Cowan, D. *J. Chem. Soc., Chem. Commun.* **1981**, 920–21.

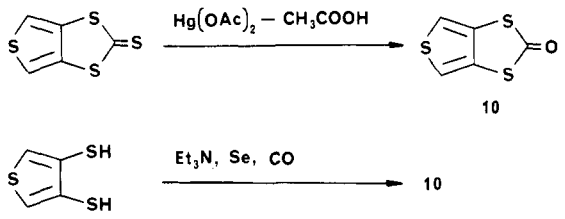
(5) Gronowitz, S.; Moses, P. *Acta Chem. Scand.* **1962**, *16*, 105–110.

(6) Meinwald, J.; Dauplaise, D.; Wudl, F.; Hauser, J. *J. Am. Chem. Soc.* **1977**, *99*, 255–57. Meinwald, J.; Dauplaise, D.; Clardy, J. *J. Am. Chem. Soc.* **1977**, *99*, 7743–44. Chiang, L., Meinwald, J. *Tetrahedron Lett.* **1980**, *21*, 4565–68.

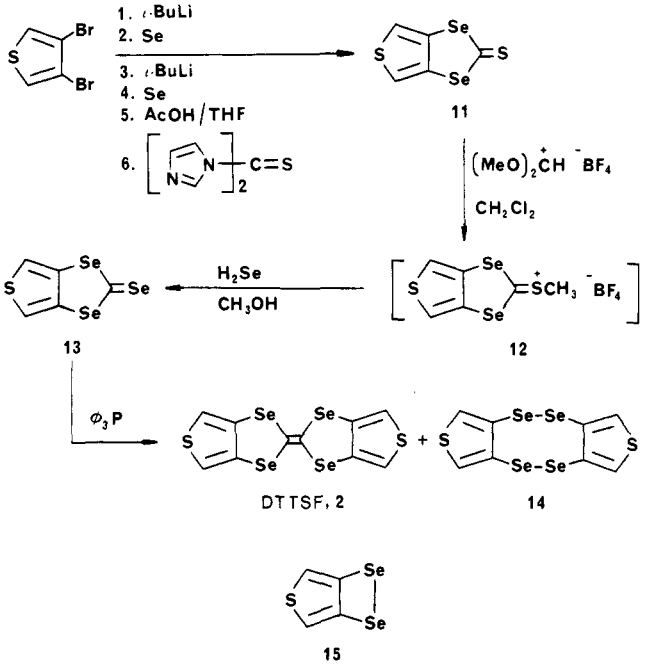
(7) Wudl, F.; Aharon-Shalom, E. *J. Am. Chem. Soc.* **1982**, *104*, 1154–56.

(8) Lerstrup, K.; Talham, D.; Bloch, A.; Poehler, T.; Cowan, D. *J. Chem. Soc., Chem. Commun.* **1982**, 336–7.

Scheme II



Scheme III

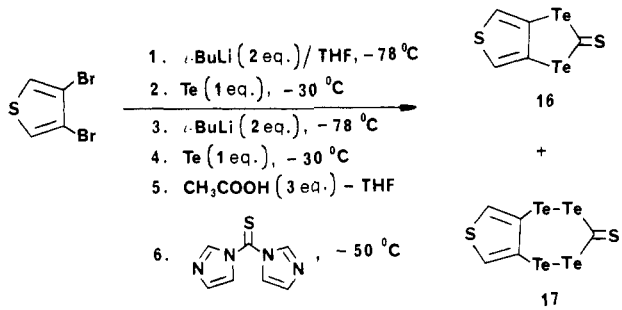


to TTF derivatives. For example, dibenzotetrathiofulvalene (DBTTF)[9a] has been prepared by this route. Therefore, thione **4** was converted to the corresponding selone, **6**, via methylation of the thione with dimethoxycarbenium tetrafluoroborate or hexafluorophosphate followed by treatment of the resulting tetrafluoroborate or hexafluorophosphate salt **5** with hydrogen selenide. Selone **6** was coupled with trimethyl phosphite to give DTTTF (**1**) in 58% yield without any scrambled byproducts.[9b] Also, the preparation of DTTTF was achieved by the coupling reaction of thieno[3,4-d]-1,3-dithiole-2-carbene (**9**), which was produced by the deprotonation of thieno-[3,4-*d*]-1,3-dithiolium cation (**8**) with tertiary amine in the deoxygenated acetonitrile, in 31% yield from **4**.

Thieno[3,4-*d*]-1,3-dithiole-2-one (**10**) was also prepared in order to examine its coupling reaction with trivalent phosphorus. Thus, thione **4** was allowed to react with mercury(II) acetate in a saturated solution of acetic acid to afford the dithiocarbonate **10** in 30% yield as shown in Scheme II. Alternately, dithiocarbonate **10** could be synthesized from the reaction of thiophene-3,4-dithiol with carbonyl selenide (SeCO), formed in situ by reaction of selenium with carbon monoxide in the presence of triethylamine as a catalyst,[10] under pressure, in 48% yield. Unfortunately, the coupling reaction of **10** with triethyl phosphite did not give DTTTF.

The synthetic approach to the preparation of $\Delta^{2,2'}$-bithieno[3,4-*d*]-1,3-diselenole (**2**) is described in Scheme III.

Scheme IV



Two consecutive treatments of 3,4-dibromothiophene with 2 equiv of *tert*-butyllithium and 1 equiv of elemental selenium produced the dilithium salt of thiophene-3,4-diselenol, which was protonated with glacial acetic acid and was reacted with an excess of thiocarbonylbis(imidazole) to obtain thieno[3,4-*d*]-1,3-diselenole-2-thione (**11**) in 30% yield in a one-flask sequence. Methylation of thione **11** with dimethoxycarbenium tetrafluoroborate in methylene chloride gave the tetrafluoroborate salt **12**. After the excess methylation agent was destroyed by methanol, the resulting mixture was treated with hydrogen selenide to give thieno[3,4-*d*]-1,3-diselenol-2-selone (**13**) as red crystals in 39% yield. The coupling reaction of selone **13** was attempted with a variety of trivalent phosphorus reagents, such as trimethyl and triethyl phosphite, triphenylphosphine, and trimorpholinophosphine. The desired donor, DTTSF (**2**), was either not formed or was formed in very low yields. Its presence in some reactions in small amounts could be deduced from the appropriate molecular ion cluster in the mass spectrum of the product. However, we have been unable, to date, to obtain a synthetically useful procedure for the coupling of this selone. The major product was identified as the dimer of 3,4-diselenothiophene (**14**), and no starting material selone **13** could be detected in the product. Apparently, the heterocyclic ring opening of **13** occurred during the reaction. The intermediate **15** could be a precursor in the formation of **14**.

In the case of the analogous reaction with tellurium, it proved necessary to use recently prepared finely divided tellurium[11] and to carry out the reaction at a somewhat elevated temperature (−30 °C). The commercially available tellurium (40–60 mesh, Alfa) exhibited a very low reactivity toward the insertion reaction. Hence, microcrystalline tellurium was prepared either by oxidation of tellurium to tellurium oxide followed by reduction according to the procedure described in the literature[12] or by pretreating the surface of tellurium metal with concentrated sulfuric acid followed by neutralization and then mechanical grinding of the tellurium in a high-speed ball mill. The tellurium insertion reaction was carried out in sequence under the conditions indicated in Scheme IV, and the product was isolated by chromatography (Florisil, R_f = 0.6 with hexane–ether 5:1 (v/v) as eluent) in 14% yield. The mass spectral analysis of the product indicated the presence of a two-component mixture, thieno[3,4-*d*]-1,3-ditellurole-2-thione (**16**) and thieno[3,4-*d*]-1,3-tetratelluro-2-thione (**17**).

We have been able to provide a good synthesis for the new organic *p*-donor, DTTTF, and for several potential intermediates in the synthesis of its selenium analogue,

(9) (a) Hunig, S.; Kliesslich, G.; Quast, H.; Schentzow, D. *Liebigs Ann. Chem.* **1973**, *310*. (b) Engler, E. M.; Patel, V. V.; Schumaker, R. R. *J. Chem. Soc.* **1977**, 835–836.

(10) Kooh, P.; Perrotti, E. *Tetrahedron Lett.* **1974**, 2899–900.

(11) Surface oxidation of metallic grey tellurium, when it is exposed to air for a long period, results in a black powder which is apparently inactive toward the tellurium insertion reaction into the carbon–lithium bond.

(12) Clauder, O. E. *Z. Anal. Chem.* **1932**, *89* 270.

DTTSF. We are continuing work on the synthesis of DTTSF and DTTTeF as well as exploring the solid-state properties of complexes and salts derived from DTTTF.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. The following spectrometers were used: IR, Perkin-Elmer 347; ^{1}H NMR, Varian EM-360L, CFT-20, and Jeol MH-100; and MS, Associated Electronic Industries MS-902 and Finnigan GC/MS 3300 (mass spectroscopy facilities of Cornell University). Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Thieno[3,4-*d*]-1,3-dithiole-2-thione (4). Method A. A solution of 3,4-dibromothiophene[13] (4.36 g, 18 mmol) in anhydrous diethyl ether (30 mL) was stirred and cooled to −78 °C (dry ice and acetone bath) under argon while *n*-butyllithium (11.3 mL, 18 mmol, 1.6 M in hexane) was added via syringe. The solution was stirred for 0.5 h, then sulfur (576 mg, 18 mmol) was added. After being stirred for 1 h, *n*-butyllithium (11.3 mL, 18 mmol) was added via syringe and the reaction mixture was stirred at −78 °C for 30 min. Sulfur (576 mg, 18 mmol) was added and the mixture was stirred for an additional 1 h to give a yellow solution. A few drops of water were then added and the solution was allowed to come to ambient temperature while the ether was removed under vacuum. After removal of the ether, 2 N sodium hydroxide solution (30 mL) and carbon disulfide (12 mL) were added. This mixture was refluxed under argon for 4 h in a heated oil bath (90 °C) and then allowed to stand at room temperature overnight. The excess of carbon disulfide was removed in vacuo. Filtration of the dark reaction mixture gave a yellow solid. Recrystallization of the solid from dichloromethane–hexane (1:5 (v/v)) gave 1.13 g (33% yield) of thieno[3,4-*d*]-1,3-dithiole-2-thione (**4**) as amber needles, mp 142–143 °C (lit.[5] mp 142 °C).

Method B. A solution of 3,4-dibromothiophene (1.2 g, 5 mmol) in THF (40 mL, distilled from sodium benzophenone ketyl) was stirred and cooled to −78 °C (dry ice and acetone bath) under argon while *tert*-butyllithium (4.4 mL, 10 mmol, 2.3 M in pentane) was added via syringe. The solution was stirred for 0.5 h, and sulfur (160 mg, 5 mmol) was added. After being stirred for 1 h, *tert*-butyllithium (4.4 mL, 10 mmol) was added and the reaction mixture was stirred at −78 °C for 0.5 h followed by the addition of sulfur (160 mg, 5 mmol). The resulting mixture was maintained at −78 °C for an additional hour to afford an orange–yellow solution. After quenching with glacial acetic acid (0.7 mL) in THF (5 mL), thiocarbonylbis(imidazole) (890 mg, 5 mmol) in THF (30 ml) was added slowly. The solution was allowed to warm to room temperature in 5 h and stirred at that temperature overnight. The reaction mixture was then partitioned between dilute hydrochloric acid and dichloromethane. The organic phase was separated, washed with water and brine, and dried over $MgSO_4$. Column chromatography (silica gel, EtOAc–hexane 1:10 (v/v)) gave 370 mg (39% yield) of thieno[3,4-*d*]-1,3-dithiole-2-thione (**4**).

Thieno[3,4-*d*]-1,3-dithiol-2-ylidenemethylsulfonium Hexafluorophosphate (5). A solution of thieno[3,4-*d*]-1,3-dithiole-2-thione (**4**) (1 g, 5.25 mmol) in dichloromethane (30 mL) was added to a suspension of dimethoxycarbenium hexafluorophosphate (3 g, 14 mmol) in dichloromethane (20 mL) which had been cooled to −30 °C under argon. The mixture was stirred at −30 °C for half an hour. It was then allowed to warm to room temperature slowly and stirred for an additional half-hour period. Ethyl acetate (300 mL) was added and stirring continued for 20 to 30 min. The precipitation of product was noticeable at this stage. After further crystallization of product by cooling the solution in a freezer, crude product was collected by filtration. Recrystallization from acetonitrile–ether gave 1.5 g (82% yield) of hexafluorophosphate salt (**5**): mp 165 °C dec; IR (KBr) 3120 (w), 1385 (m), 1115 (m), 840 (s), and 560 (m) cm^{-1}; NMR (CD_3CN) δ 3.00 (s, 3), 8.05 (s, 2). Anal. Calcd for $C_6H_5S_4PF_6$: C, 20.57; H, 1.44; S, 36.61. Found: C, 20.65; H, 1.45; S, 37.07.

Thieno[3,4-*d*]-1,3-dithiole-2-selone (6). A solution of hexafluorophosphate salt **5** (700 mg, 2 mmol) in absolute methanol (30 mL) was cooled to −30 °C under argon. An excess of hydrogen selenide was added through argon flow. The mixture was allowed to warm to 0 °C and stirring continued for 4 h. After removal of the excess hydrogen selenide (destroyed in a trap containing a mixture of aqueous potassium hydroxide and hydrogen peroxide), dichloromethane (50 mL) was added and the solution was washed with water and brine, dried ($MgSO_4$), filtered, and concentrated in vacuo. Column chromatography (silica gel, EtOAc–hexane 1:5 (v/v)) and recrystallization from dichloromethane–hexane gave 470 mg (quantitative yield) of thieno-[3,4-*d*]-1,3-dithiole-2-selone (**6**) as purple needles: mp 141–142 °C; IR (KBr) 1386 (m), 947 (w), 880 (vw), 840 (vw), 760 (w), and 595 (w) cm^{-1}; NMR ($CDCl_3$) δ 6.0; MS, *m/e* (relative intensity) 238 (M^+, 35), 158 (23), 126 (25), 69 (100), and 44 (40). Anal. Calcd for $C_5H_2S_3Se$: C, 25.31; H, 0.85; S, 40.55. Found: C, 25.26; H, 0.86; S, 40.34.

2-(Methylthio)thieno[3,4-*d*]-1,3-dithiole (7). Sodium borohydride (500 mg, 13 mmol) was added in several portions under argon into a suspension of thieno[3,4-*d*]-1,3-dithiol-2-ylidenemethylsulfonium hexafluorophosphate (**5**) (980 mg, 2.8 mmol) in absolute ethanol (25 mL) cooled in an ice bath. After half an hour, the reaction mixture was allowed to warm to room temperature and stirring continued until all unreacted sodium borohydride had disappeared. It was then worked up by washing with water and extracting with ether followed by drying over $MgSO_4$ and removal of solvent. A yellowish viscous liquid was obtained and it was chromatographed to give a quantitative yield of 2-(methylthio)thieno[3,4-*d*]-1,3-dithiole (**7**): NMR ($CDCl_3$) δ 2.3 (s, 3), 6.5 (s, 1), 6.9 (s, 2); MS, *m/e* (relative intensity, %) 206 (M^+, 15), 189 (19), 174 (35), 159 (100), 146 (51), and 101 (19).

$\Delta^{2,2'}$-Bithieno[3,4-*d*]-1,3-dithiole (1) from Compound 7. A solution of 2-(methylthio)thieno[3,4-*d*]-1,3-dithiole (**7**) (515 mg, 2.5 mmol) in a mixture of diethyl ether–acetic anhydride (100 mL, 20:1 (v/v)) was cooled to ice bath temperature under argon. To this chilled solution HBF_4–Et_2O (5 mL) was added, which instantly resulted in the formation of a bright yellow precipitate. The product was filtered and transferred into an argon-filled flask to avoid decomposition. After brief dyring under vacuum (10 min), dried and deoxygenated acetonitrile was added while the flask was cooled to −30 °C to obtain a saturated solution of the thiolium salt. Diisopropylethylamine (5 mL) was added immediately, and the mixture was stirred at −30 °C for 0.5 h and then was allowed to warm up to room temperature. Stirring was continued for 1 h. Water was added and the mixture was placed in a refrigerator to promote precipitation. After filtration and recrystallization from 1:5 dichloromethane–hexane (v/v), it afforded 245 mg (31% yield) of $\Delta^{2,2'}$-bithieno[3,4-*d*]-1,3-dithiole (**1**): mp 259–260 °C dec; IR (KBr) 3100 (vw), 1386 (w), 1322 (w), 836 (w), 770 (w), 750 (m), and 707 (w) cm^{-1}; NMR (CS_2) δ 6.9 (s); MS, *m/e* (relative intensity, %) 316 (M^+, 100), 158 (30), and 82 (15). Anal. Calcd for $C_{10}H_4S_6$: C, 37.91; H, 1.27; S, 60.78. Found: C, 37.96; H, 1.29; S, 60.43.

$\Delta^{2,2'}$-Bithieno[3,4-*d*]-1,3-dithiole (1) from Selone 6. A solution of thieno[3,4-*d*]-1,3-dithiole-2-selone (**6**) (476 mg, 2 mmol) and trimethyl phosphite (excess, 2 mL) in toluene (10 mL) was heated at 75 °C under argon for 1 day. The reaction mixture was cooled to −30 °C to complete precipitation. The crude product was filtered and recrystallized from dichloromethane–hexane 1:5 (v/v) to give 183 mg (58% yield) of DTTTF (**1**).

Thieno[3,4-*d*]-1,3-dithiol-2-one (10) from Thiophene-3,4-dithiol. Into a 500-mL stainless steel reaction cylinder was placed thiophene-3,4-dithiol (1 g, 6.7 mmol), selenium powder (30 mg, 0.4 mmol), triethylamine (170 mg, 1.7 mmol), and tetrahydrofuran (10 mL). The cylinder was twice purged with carbon monoxide and pressurized to 100 psi with carbon monoxide. The reaction cylinder was then pressurized an additional 15 psi with oxygen. This mixture was magnetically stirred at room temperature for 24 h. The cylinder was depressurized to atmospheric pressure and the reaction products were washed out of the cylinder with THF. The resulting brown solution was dried over $CaCl_2$ and the solvent removed, leaving a brown crude solid product. Recrystallization from dichloromethane yielded 570 mg (48%) of **10** as a white solid: mp 107–108 °C; IR (KBr) 3100 (m), 1635 (s), 1385 (m), 1315 (m), 975 (m), 880 (m), 860 (m), 850 (m), 825 (m), and 785 (s) cm^{-1}; NMR (C_6D_6) δ 6.29 (s); Anal. Calcd for $C_5H_2S_3O$: C, 34.46; H, 1.16; S, 55.20. Found: C, 34.31; H, 1.15; S, 54.99.

Thieno[3,4-*d*]-1,3-dithiol-2-one (10) from Thione 4. A saturated solution of mercury(II) acetate (1.92 g, 6 mmol) in acetic acid was added to a saturated solution of thieno[3,4-*d*]-1,3-di-

(13) Gronowitz, S.; Moses, P.; Hakansson, R. *Ark. Kemi* **1960**, *16*, 267.

thiole-2-thione (**4**) (300 mg, 1.58 mmol) in dichloromethane. The mixture was stirred at room temperature for 3 h. The resulting mixture was filtered and the filtrate diluted with dichloromethane, washed with water repeatedly, dried ($MgSO_4$), and filtered. The solvent was evaporated to obtain a white solid. Recrystallization of this white residue from the dichloromethane–hexane gave 78 mg (30% yield) of thieno[3,4-*d*]-1,3-dithiol-2-one (**10**).

Thieno[3,4-*d*]-1,3-diselenole-2-thione (11). A solution of 3,4-dibromothiophene (1.45 g, 6 mmol) in THF (50 mL, distilled from sodium benzophenone ketyl) was stirred and cooled to −78 °C (dry ice and acetone bath) under argon while *tert*-butyllithium (5.3 mL, 12 mmol, 2.3 M in pentane) was added via syringe. After the mixture was stirred for 30 min, selenium powder (480 mg, 6 mmol) was added and the solution stirred for 1.5 h until the selenium suspension disappeared. A second portion of *tert*-butyllithium (5.3 mL, 12 mmol) was added via syringe and the reaction mixture was stirred at −78 °C for half an hour followed by the addition of selenium powder (480 mg, 6 mmol). The resulting mixture was maintained at −78 °C for an additional 1.5 h to obtain an orange solution. After the mixture was quenched with glacial acetic acid (1.2 mL) in THF (5 mL), thiocarbonylbis(imidazole) (1.07 g, 6 mmol) in THF (50 mL) was added. The solution was allowed to warm slowly to −25 °C and stirred at −25 °C for 3 h and then at room temperature overnight. The mixture was then partitioned between dilute hydrochloric acid and dichloromethane. The organic phase was separated, washed with water and brine, and dried ($MgSO_4$), and the solvent evaporated. Column chromatography (silica gel, 1:10 EtOAc–hexane v/v)) gave 515 g (30% yield) of thieno[3,4-*d*]-1,3-diselenole-2-thione (**11**) as a yellow solid: mp 123–124 °C; IR (KBr) 1400 (w), 1308 (w), 1035 (s), 1020 (s), 842, 775, 763 cm^{-1}; NMR ($CDCl_3$) δ 7.55 (s); MS, *m/e* (relative intensity) 286 (M^+, 100), 242 (85), 117 (26), and 82 (92). Anal. Calcd for $C_5H_2S_2Se_2$: C, 21.13; H, 0.70; S, 22.54; Se, 55.63. Found: C, 21.32; H, 0.80;, S, 22.31; Se, 55.71.

Thieno[3,4-*d*]-1,3-diselenole-2-selone (13). To a solution of thione **11** (286 mg, 1 mmol) in dichloromethane (10 mL, distilled from CaH_2), maintained at −10 °C under argon, was added dimethoxycarbenium tetrafluoroborate (0.3 mL) via syringe. The mixture was stirred at −10 °C for 30 min and at 10 °C for 1 h. Without the isolation of the tetrafluoroborate salt **12**, absolute methanol (4 mL) was added and the resulting solution was stirred at room temperature for 20 min and then cooled to −30 °C. An excess of hydrogen selenide was added through the argon flow. The solution turned to a white suspension immediately. It was then allowed to warm to room temperature graduately over a 3-h period. The stirring was continued for an additional 6 h to obtain a red solution with the disappearance of white solid. The excess of hydrogen selenide was removed and destroyed in a trap containing a mixture of aqueous potassium hydroxide and hydrogen peroxide. The resulting solution was diluted with dichloromethane, washed with water, and dried over $MgSO_4$. Immediate column chromatography (silica gel, hexane) gave 129 mg (39% yield) of thieno[3,4-*d*]-1,3-diselenole-2-selone (**13**) as red crystals: mp 134 °C; IR (KBr) 1398 (w), 1305 (w), 1028, 890 (s), 864, 840 (s), and 770 (s) cm^{-1}; NMR ($CDCl_3$) δ 7.45 (s); MS, *m/e* (relative intensity) 332 (M^+, 100), 252 (12), 240 (35), 174 (46), 117 (27), and 82 (65). Anal. Calcd for $C_5H_2SSe_3$: C, 18.13; H, 0.60; S, 9.67; Se, 71.60. Found: C, 18.38; H, 0.82; S, 9.82; Se, 71.09.

Coupling Reaction of Thieno[3,4-*d*]-1,3-diselenole-2-selone (13). The various reagents including trimethyl phosphite, triethyl phosphite, triphenylphosphine, and trimorpholinophosphine were used in the coupling reaction of selone **13**. A typical example of the reaction conditions is as follows.

A solution of thieno[3,4-*d*]-1,3-diselenole-2-selone (**13**) (66 mg, 0.2 mmol) and triphenylphosphine (114 mg, 0.44 mmol) in acetonitrile or benzene (1.5 mL) was stirred at room temperature under argon. It gave a yellow solution within 10 min. The stirring was continued for 1 day to give an orange-yellow suspension. The precipitate was filtered and washed with a small amount of acetonitrile to afford a yellowish orange solid (4 mg). Mass spectral analysis of this solid showed a weak relative intensity of *m/e* 504, which was corresponding to the molecular ion cluster $\Delta^{2,2'}$-bithieno[3,4-*d*]-1,3-diselenole (**2**), and a strong relative intensity of a group of peaks centered at *m/e* 480 corresponding to the molecular ion cluster of compound **14**: MS, *m/e* (relative intensity, %) 506 (3), 504 (2), 486 (20), 485 (6), 484 (45), 483 (13), 482 (58), 481 (23), 480 (52), 479 (23), 478 (38), 477 (18), 476 (20), 324 (14), 322 (14), 320 (11), 244 (35), 242 (90), 241 (10), 240 (80), 239 (27), 238 (46), 237 (12), and 236 (17).

Thieno[3,4-*d*]-1,3-ditellurole-2-thione (16). A solution of 3,4-dibromothiophene (725 mg, 3 mmol) in THF (50 mL) was stirred and cooled to −78 °C under argon while *tert*-butyllithium (2.7 mL, 6 mmol, 2.3 M in pentane) was added via syringe. After the mixture was stirred for 30 min, tellurium powder (381 mg, 3 mmol) was added and the solution stirred for 1.5 h at −30 °C until the tellurium suspension disappeared. Another portion of *tert*-butyllithium (2.7 mL, 6 mmol) was added via syringe and the reaction mixture was stirred at −78 °C for half an hour followed by the addition of tellurium powder (381 mg, 3 mmol). The resulting mixture was maintained at −30 °C for an additional 1.5 h. After the mixture was quenched with glacial acetic acid (0.6 mL) in THF (5 mL), thiocarbonylbis(imidazole) (588 mg, 3.3 mmol) in THF (25 mL) was added. The solution was allowed to warm slowly to −25 °C and stirred at −25 °C for 3 h and then at room temperature for overnight. The mixture was then partitioned between dilute hydrochloric acid and dichloromethane. The organic phase was separated, washed with water and brine, and dried ($MgSO_4$), and the solvent evaporated. Immediate chromatography (Florisil, hexane-ether 5:1 (v/v), R_f 0.6) gave 160 mg of reddish brown solids: MS, *m/e* (relative intensity, %) 642 (4), 640 (5), 638 (5), 636 (3), 634 (3), 515 (7), 514 (12), 513 (9), 512 (19), 511 (13), 510 (20), 509 (11), 508 (16), 507 (8), 506 (11), 480 (16), 478 (24), 473 (21), 386 (5), 384 (11), 382 (14), 380 (8), 352 (25), 350 (45), 348 (44), 347 (12), 346 (30), 345 (11), 344 (17), 296 (19), 295 (31), 294 (100), 293 (30), 292 (86), 291 (24), 290 (57), 289 (16), 288 (20), 213 (48), 211 (42), and 209 (27).

Acknowledgment. This work was supported by a grant from the National Science Foundation (DMR-8015318).

Registry No. **1**, 80229-45-4; **2**, 87207-35-0; **4**, 80229-39-6; **5**, 87207-37-2; **6**, 87207-38-3; **7**, 80229-42-1; **8**, 87207-44-1; **10**, 87207-39-4; **11**, 81794-52-7; **13**, 87207-40-7; **16**, 87207-41-8; **17**, 87207-42-9; 3,4-dibromothiophene, 3141-26-2; thiocarbonylbis(imidazole), 6160-65-2; dimethoxycarbenium hexafluorophosphate, 50318-32-6; thiophene-3,4-dithiol, 87207-45-2.