Synthesis of Sulfur-Rich 1,2- and 1,3-Dithiolo Disulfides and Thiodesaurines from Diisopropyl Sulfide

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The reaction of diisopropyl sulfide and S_2Cl_2 in chlorobenzene, in the presence of DABCO, gives 4-isopropylthio-5-isopropyldithio-1,2-dithiole-3-thione (**1**) and the dimeric 5,5′-dithiobis(4-isopropylthio-1,2-dithiol-3-thione) (**2**). If the reaction is performed in the presence of diisopropyl disulfide at the last stage of the reaction, disulfide **1** is selectively obtained. Some interconversions between **1** and **2** under UV irradiation are described, and a coherent set of reaction pathways for the formation of **1** and **2** are proposed. Treatment of **1** with DMAD in benzene gives the 1:1 adduct **9** in high yield; analogously the bisdithiolo disulfide **2** gives the 1:2 adduct **10**, a very sulfur-rich molecule. Treatment of **1** with 1.27 equiv of triphenylphosphine in dichloromethane gives 4,5-di-(isopropylthio)-1,2-dithiole-3-thione (**11**), but the treatment of **1** with 2 equiv of Ph_3P affords thiodesaurine **12** ($Z + E$ isomers), which was converted into desaurines **14** and **15** by treatment with nitrile oxide **16**.

Introduction

The chemistry of sulfur-containing heterocycles has blossomed since the discovery of tetrathiafulvalene superconductive charge-transfer salts[1] and polythiophene electronic and optical molecular switches.[2] Related research areas are also intensely studied, especially those dealing with the natural and synthetic 1,2-dithiolethiones with antioxidant, chemotherapeutic, radioprotective, and cancer chemoprotective properties.[3] One substituted dithiolethione, Oltipraz [5-(2-pyrazinyl)-4-methyl-1,2-dithiole-3-thione], originally an antischistosomal agent,[4] has been shown to protect against chemically induced carcinogenesis[5] and was effective at inhibiting human immunodeficiency virus type-1 (HIV-1) replication.[6] Therefore, the search for new structures with potentially attractive characteristics yet to be exploited needs effective syntheses to polysulfur heterocycles. We have previously described transformations of cyclic oximes with disulfur dichloride, S_2Cl_2, into fully unsaturated heteroaromatic systems[7] and pseudoazulene discotic liquid crystals.[8,9] In connection with this work we found that *N*-alkyldiisopropylamines reacted with S_2Cl_2 to give bis-[1,2]dithiolo[1,4]thiazines,[10] bis[1,2]dithiolopyrroles,[11] and a [1,2]dithiolo[1,4]thiazine.[12] In all these cases, the first

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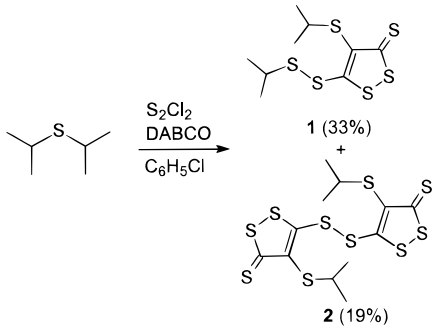
Scheme 1



step is oxidation of an *N*-isopropyl group by S_2Cl_2 to give a stable isopropyl iminium ion that is further sulfurated.[13] Seeking other isopropyl groups that could give useful intermediates in synthesis of heterocycles, we saw that ethers are easily cleaved by electrophiles[10,13,14] but dialkyl sulfides give stable dialkylthiosulfonium salts.[15] We now describe the unprecedented reaction of diisopropyl sulfide and S_2Cl_2 which affords, in one pot, new 1,2-dithiole-3-thiono-5-disulfides that are easily converted into other polysulfur heterocyclic systems.

Results and Discussion

Diisopropyl sulfide was treated with an excess of S_2Cl_2 in chlorobenzene in the presence of 1,4-diazabicyclo-[2.2.2]octane, DABCO, for 3 days at room temperature followed by refluxing for 3 h. In these conditions, compounds **1**, dark red oil (33%), and **2**, mp 162−163 °C (19%), were obtained by repeated column chromatography (Scheme 1). ^{1}H NMR of **1** showed two different isopropyl groups, confirmed by ^{13}C NMR, that showed, in addition, three sp^2-tertiary carbon atoms. One of them, at δ 212, was assigned to a C═S group, confirmed by a strong IR absorption at 1239 cm^{-1}. Mass spectrometry of **1** showed a very weak molecular peak of 314 amu corresponding to $C_9H_{14}S_6$, confirmed by HRMS and microanalysis, but the main peak was 239 amu, $C_6H_7S_5^+$, confirmed by HRMS, in which a fragment of 75 amu (Pr^{i}S) was lost. We concluded that all the C−H bonds of only one isopropyl group of diisopropyl sulfide had been cleaved and that the group had been fully sulfurated. The fact that two isopropyl groups were still present in **1** and one of them was easily removed (in the formation of **2**) was intriguing, suggesting that an addition of an isopropylthio group had occurred during the formation of **1**, affording a labile disulfide bond. If the carbon connectivity of the starting isopropyl sulfide is retained, there are few reasonable structures possible for the product, and the spectroscopic data all pointed to what we considered to be the most stable possibility, 4-isopropylthio-5-isopropyldithio-1,2-dithiole-3-thione **1**. On the other hand, the ^{1}H NMR of **2** showed one isopropyl group, confirmed by ^{13}C NMR, which showed also three sp^2-tertiary carbon atoms. One of them, at δ 212, was assigned to a C═S group, confirmed by a strong IR absorption at 1240 cm^{-1}. The extremely simple IR spectrum suggested a symmetric structure. EI mass spectrometry of **2** showed the main peak at 239 amu, $C_6H_7S_5^+$, confirmed by HRMS, but an FAB spectrum showed, in addition to the peak at 239 amu, a peak at 479 amu, assigned to the $[M + 1]^+$ peak, suggesting for **2** the dimeric structure 5,5′-dithiobis(4-isopropylthio-1,2-dithiol-3-thione).

Irradiation of a solution of **2** and an excess of diisopropyl *di*sulfide in cyclohexane, with a low-pressure mercury UV lamp (250 W), in the presence of 9-fluorenone for 30−45 min, gave a mixture of **1** and **2**. Mixtures of **1** and **2**, increasingly enriched in **2**, were also obtained by sunlight irradiation of solutions of **1** in cyclohexane for 2−12 h or UV irradiation (250 W) in the presence of 9-fluorenone for 30 min. These experiments support the existence of an S−S bond in the structures of **1** and **2**. They also suggested that compound **2** could have originated from **1** and its formation might be suppressed in the presence of excess diisopropyl *di*sulfide. Thus, diisopropyl sulfide (1 equiv) was treated with S_2Cl_2 (10 equiv) in chlorobenzene in the presence of DABCO (10 equiv) for 3 days at room temperature followed by addition of diisopropyl *di*sulfide (5.5 equiv) and the mixture refluxed for 1.5 h. In these conditions, compound **1** was obtained in better yield (48%) after repeated chromatography, as the only recognizable product. Treatment of diisopropyl *di*sulfide with an excess of S_2Cl_2 and DABCO in chlorobenzene for 3 days at room temperature followed by refluxing for 3 h afforded only baseline material on TLC (petroleum ether−CH_2Cl_2 1:1 as eluent). The absence of compound **1** indicated that it was formed from diisopropyl sulfide but not from diisopropyl *di*sulfide; the action of diisopropyl disulfide at a late stage of the reaction was attributed to inhibition of the equilibrium formation of **2**. Treatment of **1** (1 equiv) with S_2Cl_2 (10 equiv) for 3 days at room temperature and then refluxing the mixture for 1.5 h afforded unchanged **1** (60%) and minor unstable products that did not include **2**.

In this one-pot conversion of diisopropyl sulfide into **1** and **2** the 7 C−H bonds of one isopropyl group have been replaced by 5 C−S bonds and one carbon−carbon double bond, while the other isopropyl group has been untouched. This provides a striking example of activation of only one isopropyl group by the initial sulfide atom; this activation is suppressed when the isopropyl sulfide is bonded to a dithiolethione group. This is in strong contrast with the results obtained with tertiary diisopropylamines, in which nitrogen activates both isopropyl groups to reaction with S_2Cl_2.[10−13]

We propose that the first step in these reactions is oxidation of an isopropyl group in diisopropyl sulfide by S_2Cl_2 (or its more reactive complex with DABCO) to give the sulfonium ion **3** (Scheme 2). Deprotonation of sulfonium ion **3** gives the isopropenyl sulfide **4**, which reacts with S_2Cl_2 (or its DABCO complex) to give the 1,2-dithiole **5** which would be expected to react further with S_2Cl_2 to give the dithiolium salt **6**. Apparently the dithiolium ring in this compound is sufficiently electron withdrawing to prevent oxidation of the other isopropyl group. This key intermediate reacts with sulfur nucleophiles to give the thione group, and further reaction with S_2Cl_2 could give the sulfenyl chloride **7** that may then react with a second molecule of diisopropyl sulfide, affording the thiosulfonium cation **8** and hence **1**. Disulfides are unstable in

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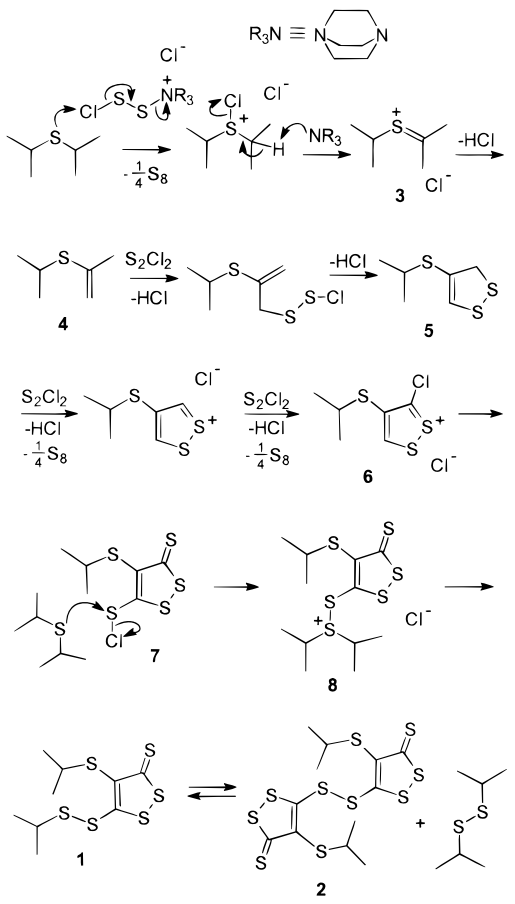
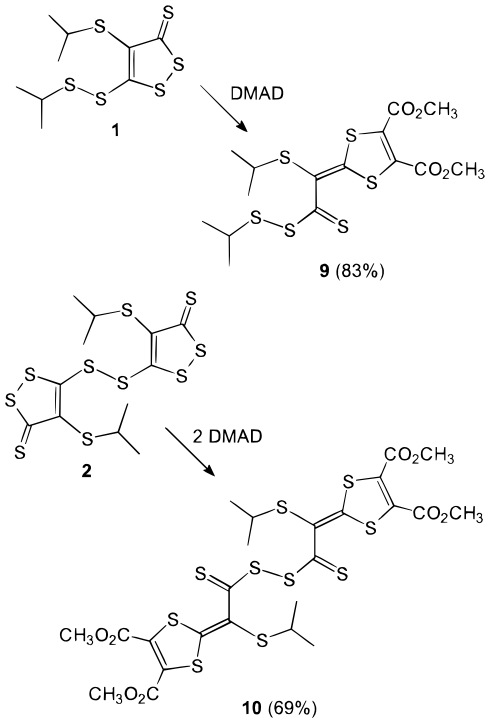
Scheme 2



Scheme 3



the presence of other electrophiles, and unsymmetrical disulfides are readily transformed into a mixture including the two symmetrical disulfides.[16] Whatever the precise mechanism, the transformation of diisopropyl sulfide into **2** via **1** requires four molecules of starting sulfide, so from a mechanistic point of view the yield for **2** is 19%.

1,2-Dithiole-3-thiones can act as 1,3-dipoles.[17] Treatment of compound **1** with dimethyl acetylenedicarboxylate, DMAD (2.5 equiv), in refluxing benzene for 10 min gave the 1:1[18] adduct **9** as an orange solid, mp 91−93 °C (83%), as the only product (Scheme 3). ^{1}H NMR spectroscopy showed the presence of two different isopropyl groups in addition to two ester methyl groups. ^{13}C NMR showed, in addition to the isopropyl groups, two methoxycarbonyl groups, a thiono group at δ 211 (confirmed by IR), and four other distinct sp^2-tertiary carbon atoms. Mass spectrometry showed a very weak molecular peak at 456 amu, confirmed by FAB, which corresponded to $C_{15}H_{20}O_4S_6$, confirmed by HRMS and microanalysis. The main peak found in all MS experiments was 349 amu that corresponded to the loss of an isopropyldithio fragment from **9**.

In an analogous reaction, bisdithiolo disulfide **2** gave the 1:2 adduct **10** as a dark red solid, mp 208−210 °C (69%). Both ^{1}H and ^{13}C NMR spectroscopy showed the presence of one isopropyl and two different methoxycarbonyl groups, and the ^{13}C NMR spectrum also showed the presence of the thiono group at δ 205 (confirmed by IR) and four other distinct sp^2-tertiary carbon atoms, closely equivalent to the corresponding signals for **9**. The FAB spectrum of **10** gave the molecular peak, 762 amu ($C_{24}H_{26}O_8S_{10}$), but the main peak was 349 amu, exactly the same as found for **9**, indicating a dimeric structure for **10**. Compound **10**, a very sulfur-rich molecule, was obtained from commercial diisopropyl sulfide in two steps in 14% unoptimized overall yield.

Disulfides are converted into sulfides by P^{III} reagents.[19] Treatment of compound **1** with 1.27 equiv of triphenylphosphine in dichloromethane gave compound **11**, red solid, mp 51−53 °C (57%) (Scheme 4). ^{1}H and ^{13}C NMR spectra of **11** were similar to those corresponding to **1**, but mass spectrometry of **11** showed a molecular ion for one sulfur less than **1**, and this was confirmed by HRMS and microanalysis. The main peak in the MS spectrum of **11**, 239 amu ($C_6H_7S_5$, confirmed by HRMS), corresponded to the loss of isopropyl from the molecular ion, indicating that the disulfide bond was not present and supporting the 4,5-di(isopropylthio)-1,2-dithiole-3-thione structure **11**. Surprisingly, compound **1** was regenerated from **11** in low yield (26%), by treatment of **11** with S_2Cl_2 in the same conditions initially used for converting diisopropyl sulfide into **1** and **2**. In this case, chlorination of the thiono group in **11** could give the intermediate **7** (with loss of propene). The reaction of **7** with a second molecule of **11**, acting as source of isopropylthio group, would give **1** by the same mechanism as that proposed above.

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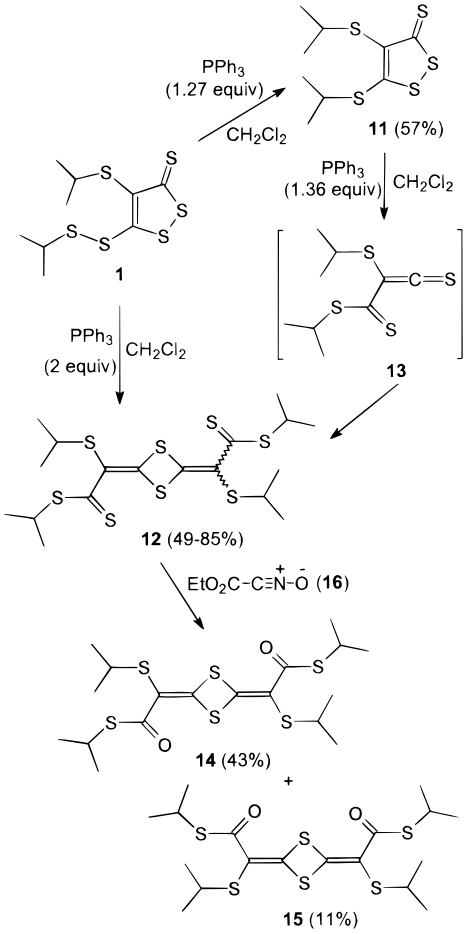
Scheme 4



On the other hand, treatment of compound **1** with 2 equiv of triphenylphosphine under similar conditions afforded **12**, red solid, mp 161−163 °C (49%). The same compound **12** (85%) was obtained by reaction of **11** and 1.36 equiv of triphenylphosphine under the same conditions. Mass spectrometry of **12** showed a molecular peak of 500 amu ($C_{18}H_{28}S_8$, confirmed by HRMS and microanalysis), corresponding to a dimer of (**11** − S). The ^{1}H NMR spectrum of **12** showed the presence of two isopropyl groups, and the ^{13}C NMR spectrum showed also a thiono group at δ 209, confirmed by IR, and two other sp^2-tertiary carbon atoms. Although the compound was homogeneous on TLC, three signals in the ^{13}C NMR spectrum, corresponding to C═S, C═C, and one tertiary hydrogen, appeared doubled with lower signals, indicating that **12** consisted of an inseparable mixture of isomers. The only structure that appears consistent with the spectral data and exists in two geometric isomers is the thiodesaurine[20] structure **12**, obtained by dimerization of intermediate thioketene **13**, formed by sulfur abstraction from the dithiole ring.[20b] Application of the nitrile oxide method for converting thiocarbonyl into carbonyl groups[10−11,13] readily gave the corresponding desaurines **14**, yellow solid, mp 144−146 °C (43%), and **15**, yellow solid, mp 114−116 °C (11%), by treatment of thiodesaurine **12** in THF at 0 °C for 15 min with an excess of the nitrile oxide **16** generated from ethyl chlorooximidoacetate and triethylamine. Desaurines **14** and **15** could be separated by preparative TLC; they had very similar spectral properties, as expected. Mass spectrometry of both **14** and **15** showed the molecular peak 468 amu ($C_{18}H_{28}S_6O_2$, confirmed by HRMS and microanalysis), in which two sulfur atoms were replaced by two oxygen atoms. The appearance of a signal at δ 192 for **14** and δ 191 for **15** in their ^{13}C NMR spectra indicated the newly formed carbonyl groups, confirmed by IR. We assigned to the less polar and more abundant isomer the *E*-geometry **14** and to the less abundant isomer the *Z*-geometry **15**, in accordance with the calculated dipole moments for **14** and **15**.[20b,21]

Conclusions. In summary, we have shown that diisopropyl sulfide is readily transformed in a one-pot process to give the hitherto unknown[22] disulfides bearing one or two 1,2-dithiole-3-thione rings. Heterocyclic disulfides are of interest in pharmacology as analogues of the cytotoxic agent polycarpine.[23] The present reaction provides a new route to 1,2-dithiolo-3-thiones, normally prepared by heating organic substrates with sulfur,[17,24] and the products obtained are readily transformed into sulfur-rich 1,3-dithiole and 1,3-dithietane derivatives.

Experimental Section

Disulfur dichloride, diisopropyl sulfide, DABCO, and DMAD were purchased from Aldrich and used without further purification. Chlorobenzene was distilled from phosphorus pentoxide. Melting points were determined using a Kofler hot-stage apparatus. Column chromatography was carried out on a medium-pressure Gilson liquid chromatography apparatus, with silica gel C60 (Merck). Light petroleum refers to the fraction bp 40−60 °C.

General Procedure for 1 and 2. Disulfur dichloride (S_2Cl_2, 16.8 mL, 210 mmol) was added dropwise to a cooled solution (−40 °C) of diisopropyl sulfide (3 mL, 20.7 mmol) and 1,4-diazabicyclo[2.2.2]octane (DABCO, 23.4 g, 209 mmol) in chlorobenzene (300 mL). The mixture was stirred under nitrogen at room temperature for 72 h and then refluxed for 3 h. The crude mixture was filtered through Celite and the solvent removed in the rotary evaporator. After repeated medium-pressure liquid chromatography (MPLC) (silica gel Merck 60, petroleum ether to dichloromethane−petroleum ether, 6:4), two main products were separated and characterized.

4-Isopropylthio-5-isopropyldithio-1,2-dithiole-3-thione (1): dark red oil (1.068 g, 33%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (hept, J = 6.7 Hz, 1H, SC*H*(CH$_3$)$_2$), 3.32 (hept, J = 6.7 Hz, 1H, SSC*H*(CH$_3$)$_2$), 1.42 (d, J = 6.7 Hz, 6H, SCH(C*H*$_3$)$_2$), 1.27 (d, J = 6.7 Hz, 6H, SSCH(C*H*$_3$)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.4 (*C*═S), 185.0 (SS*C*SS), 133.4 (S*C*C═S), 43.4 (S*C*H(CH$_3$)$_2$), 37.9 (SS*C*H(CH$_3$)$_2$), 23.1 (SCH(*C*H$_3$)$_2$), 22.5 (SSCH(*C*H$_3$)$_2$); IR (neat, cm^{-1}) ν 1412, 1239 (C═S), 1153; MS (EI, 70 eV) *m*/*z* 314 (M$^+$, 2), 282 (M − 32, 2), 239 (M − 78, 100); HRMS, M$^+$ = 313.9435 $C_9H_{14}S_6$ requires 313.9420; HRMS, M$^+$ = 238.9158 $C_6H_7S_5$ requires 238.9151. Anal. Calcd for $C_9H_{14}S_6$: C, 34.36; H, 4.49. Found: C, 34.45; H, 4.19.

5,5′-Dithiobis(4-isopropylthio-1,2-dithiol-3-thione) (2): light brown solid (petroleum ether/(CH_2Cl_2) (466 mg, 10%); mp 162−163 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (hept, J = 6.7 Hz, 1H, SC*H*(CH$_3$)$_2$), 1.32 (d, J = 6.7 Hz, 6H, SCH(C*H*$_3$)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.5 (C═S), 176.3 (SS*C*SS), 135.6 (S*C*C═S), 38.3 (S*C*H(CH$_3$)$_2$), 23.3 (SCH(*C*H$_3$)$_2$); IR (CCl_4,

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(21) Dipolar moments for **14** and **15** were calculated with HyperChem 5.0 on PM3 optimized geometries.

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(24) Aimar, M. L.; Rossi, R. H. *Tetrahedron Lett.* **1996**, *37*, 2137.

cm^{-1}) ν 1423, 1240 (C═S), 1062; MS (EI, 70 eV) *m/z* 239 ($^1/_2M^+$, 40), 207 ($^1/_2M - 32$, 20), 198 (40), 133 (70); MS (FAB+) *m/z* 479 ($M^+ + 1$, 15), 239 ($^1/_2M^+$, 19); HRMS, $M^+ = 238.9154$ $C_6H_7S_5$ requires 238.9151. Anal. Calcd for $C_{12}H_{14}S_{10}$: C, 30.10; H, 2.95. Found: C, 30.38; H, 2.80.

Alternative Procedure for 1. Disulfur dichloride (S_2Cl_2, 11.2 mL, 140 mmol) was added dropwise to a cooled solution (−40 °C) of diisopropyl sulfide (2 mL, 13.8 mmol) and DABCO (15.62 g, 139 mmol) in chlorobenzene (180 mL). The mixture was stirred under nitrogen at room temperature for 72 h, and then disopropyl disulfide (12 mL, 75 mmol) was added and the mixture refluxed for 1.5 h. Similar workup of the reaction residue afforded **1** (1.050 g, 48%).

Dimethyl 6-Isopropylthio-6-[(isopropyldithio)thiocarbonyl]-1,4-dithiafulvene-2,3-dicarboxylate (9). Dimethyl acetylenedicarboxylate (0.060 mL, 0.49 mmol) was added to a solution of **1** (60 mg, 0.19 mmol) in benzene (15 mL). The resulting solution was refluxed for 10 min. The solvent was removed in the rotatory evaporator, and the resulting solid was purified by MPLC (silica gel Merck 60, petroleum ether to petroleum ether/CH_2Cl_2, 1:1) to give **9** as a dark orange solid (petroleum ether/CH_2Cl_2) (72 mg, 83%): mp 91−93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.93 (s, 6H, 2xCO_2CH_3), 3.58 (hept, J = 6.7 Hz, 1H, SC*H*$(CH_3)_2$), 3.12 (hept, J = 6.7 Hz, 1H, SSC*H*$(CH_3)_2$), 1.38 (d, J = 6.7, 6H, SCH(C*H*$_3)_2$), 1.31 (d, J = 6.7, 6H, SSCH(C*H*$_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.7 (*C*═S), 170.2 (C═*C*S_2), 160.2 (*C*═O), 159.9 (*C*═O), 133.4 (*C*CO_2-CH_3), 132.1 (*C*CO_2CH_3), 118.4 (*C*═CS_2), 53.7 (CO_2CH_3), 53.6 (CO_2CH_3), 41.2 (S*C*H$(CH_3)_2$), 40.8 (SS*C*H$(CH_3)_2$), 23.0 (SCH-(*C*H$_3)_2$), 22.7 (SSCH(*C*H$_3)_2$); IR (KBr, cm^{-1}) ν 1751 (C═O), 1721 (C═O), 1392, 1229 (C═S), 1093; MS (EI, 70 eV) *m/z* 456 (M^+, 1.3), 382 (M − 74, 3), 349 (M − 107, 100); MS (FAB+) *m/z* 457 ($M^+ + 1$, 14), 413 (M − 43, 3), 381 (M − 75, 11), 349 (M − 107, 100); HRMS, $M^+ = 455.9691$ $C_{15}H_{20}O_4S_6$ required 455.9686. Anal. Calcd for $C_{15}H_{20}O_4S_6$: C, 39.45; H, 4.41. Found: C, 39.59; H, 4.47.

Tetramethyl α,α′-Dithiobis(6-isopropylthio-6-thiocarbonyl-1,4-dithiafulvene-2,3-dicarboxylate) (10). Dimethyl acetylenedicarboxylate (0.053 mL, 0.43 mmol) was added to a solution of **2** (40 mg, 0.08 mmol) in benzene (15 mL). The resulting solution was refluxed for 10 min. The solvent was removed in the rotary evaporator, and the resulting solid was purified by MPLC (silica gel Merck 60, petroleum ether to dichloromethane) to give **10** as a dark red solid (CH_2Cl_2) (42 mg, 69%): mp 208−210 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.93 (s, 6H, 2 × CO_2CH_3), 3.90 (s, 6H, 2 × CO_2CH_3), 3.87 (hept, J = 6.7 Hz, 2H, 2 × SC*H*$(CH_3)_2$), 1.47 (d, J = 6.7 Hz, 12 H, 2 × SCH(C*H*$_3)_2$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 205.1 (*C*═S), 170.0 (C═*C*S_2), 160.0 (C═O), 159.8 (C═O), 133.5 (*C*CO_2CH_3), 132.2 (*C*CO_2CH_3), 118.5 (*C*═CS_2), 53.7 (CO_2CH_3), 53.6 (CO_2CH_3), 41.6 (S*C*H$(CH_3)_2$), 23.2 (SCH(*C*H$_3)_2$); IR (KBr, cm^{-1}) ν 1752 (C═O), 1726 (C═O), 1383, 1256 (C═S), 1226 (C═S), 1095; MS (FAB+) *m/z* 762 (M^+, 2), 698 (M − 64, 2), 382 ($^1/_2M + 1$, 7), 349 ($^1/_2M$ − S, 100). Anal. Calcd for $C_{24}H_{26}O_8S_{10}$: C, 37.78; H, 3.43. Found: C, 37.96; H, 3.54.

4,5-Diisopropylthio-1,2-dithiole-3-thione (11). Triphenylphosphine (212 mg, 0.81 mmol) was added to a solution of **1** (200 mg, 0.64 mmol) in dichloromethane (14 mL), under nitrogen. After 5 min, the reaction was monitored by TLC, showing that all of **1** and most of the triphenylphosphine had disappeared and a more polar fluorescent yellow spot (probably corresponding to a phosphorus intermediate) appeared. The mixture was then refluxed under nitrogen for 5 h, until TLC showed the complete transformation of the fluorescent yellow spot into a new yellow product. The solvent was removed in the rotary evaporator, and the resulting solid was purified by MPLC (silica gel Merck 60, petroleum ether to petroleum ether/CH_2Cl_2 7:3) to give **11** as a red solid (CH_2Cl_2) (102 mg, 57%): mp 51−53 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (hept, J = 6.8 Hz, 1H, C*H*$(CH_3)_2$), 3.72 (hept, J = 6.7 Hz, 1H, C*H*$(CH_3)_2$), 1.48 (d, J = 6.7 Hz, 6H, CH(C*H*$_3)_2$), 1.19 (d, J = 6.8 Hz, 6H, CH(C*H*$_3)_2$);^{13}C NMR (100 MHz, $CDCl_3$) δ 210.0 (*C*═S), 179.4 (C═*C*S_2), 134.8 (*C*═CS_2), 38.1 (S*C*H$(CH_3)_2$), 37.6 (S*C*H$(CH_3)_2$), 23.7 (SCH(*C*H$_3)_2$), 23.1 (SCH(*C*H$_3)_2$); IR (KBr, cm^{-1}) ν 1382, 1246, and 1230 (C═S), 1058; MS (EI) *m/z* 282 (M^+, 28), 239 (M − 43, 100), 207 (M − 75, 33); HRMS, $M^+ = 281.9711$ $C_9H_{14}S_5$ requires 281.9699. Anal. Calcd for $C_9H_{14}S_5$: C, 38.26; H, 4.99. Found: C, 38.39; H, 5.06. Some **12** (6 mg, 4%) and recovered **1** (20 mg, 10%) were also obtained.

Diisopropyl (*Z*+*E*)-2,2′-(1,3-Dithietane-2,4-diylidene)-bis[2-(isopropylthio)dithioacetate] (12). A solution of **1** (83 mg, 0.26 mmol) and triphenylphosphine (143 mg, 0.55 mmol) in dichloromethane (6 mL) was refluxed under nitrogen for 5 h. The solvent was removed in the rotary evaporator, and the resulting solid was purified by MPLC (silica gel Merck 60, petroleum ether to petroleum ether/CH_2Cl_2 8:2) to give **12** as a red solid (petroleum ether/CH_2Cl_2) (32 mg, 49%): mp 161−163 °C. By a similar procedure, a solution of **11** (102 mg, 0.36 mmol) and triphenylphosphine (129 mg, 0.49 mmol) in dichloromethane (6 mL), refluxed under nitrogen for 8 h, gave **12** (75 mg, 83%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.70 (hept, J = 6.9 Hz, 2H, 2 × C*H*$(CH_3)_2$), 3.37 (hept, J = 6.6 Hz, 2H, 2 × C*H*$(CH_3)_2$), 1.35 (d, J = 6.9 Hz, 12H, 2 × CH(C*H*$_3)_2$), 1.27 (d, J = 6.6 Hz, 12H, 2 × CH(C*H*$_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) *E*-**12**, δ 209.0 (*C*═S), 162.8 (C═*C*S_2), 124.9 (*C*═CS_2), 41.6 (S*C*H-$(CH_3)_2$), 40.9 (S*C*H$(CH_3)_2$), 23.1 (SCH(*C*H$_3)_2$), 21.6 (SCH(*C*H$_3)_2$); *Z*-**12**, δ 208.6 (C═S), 161.1 (C═*C*S_2), 127.0 (*C*═CS_2), 41.8 (S*C*H-$(CH_3)_2$); IR (KBr, cm^{-1}) ν 1475, 1178 (C═S), 1011; MS (EI) *m/z* 500 (M^+, 20), 457 (M − 43, 45), 175 ($^1/_2M$ − 75, 100); HRMS, $M^+ = 499.9891$ $C_{18}H_{28}S_8$ requires 499.9957. Anal. Calcd for $C_{18}H_{28}S_8$: C, 43.16; H, 5.63. Found: C, 42.95; H, 5.52.

General Procedure for 14 and 15. Triethylamine (140 μL, 1.00 mmol) was added dropwise to a solution of **12** (100 mg, 0.20 mmol) and ethyl chlorooximidoacetate (130 mg, 0.86 mmol) in dry THF (4 mL), at 0 °C. The mixture was stirred for 15 min at 0 °C and a further 15 min at room temperature. The reaction mixture was filtered through Celite, and the solvent was removed in the rotary evaporator. The residue was purified twice by preparative TLC (silica gel Merck 60 F_{254}, petroleum ether/CH_2Cl_2 8:2). Two separated pale yellow bands were collected, the less polar **14** and the more polar **15**.

(*S*,*S*)-Diisopropyl (*E*)-2,2′-(1,3-dithietane-2,4-diylidene)-bis[2-(isopropylthio)thioacetate] (14): yellow solid (petroleum ether/CH_2Cl_2) (40 mg, 43%); mp 144−146 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.58 (hept, J = 6.9 Hz, 2H, 2 × C*H*$(CH_3)_2$), 3.32 (hept, J = 6.9 Hz, 2H, 2 × C*H*$(CH_3)_2$), 1.35 (d, J = 6.9 Hz, 12H, 2 × CH(C*H*$_3)_2$), 1.30 (d, J = 6.9 Hz, 12H, 2 × CH-(C*H*$_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6 (*C*═O), 155.0 (C═*C*S_2), 118.4 (*C*═CS_2), 41.1 (S*C*H$(CH_3)_2$, DEPT), 35.9 (S*C*H-$(CH_3)_2$, DEPT), 23.3 (SCH(*C*H$_3)_2$, DEPT), 22.9 (SCH(*C*H$_3)_2$, DEPT); IR (KBr, cm^{-1}) ν 1612 (C═O), 1500, 1384, 1135; MS (EI) *m/z* 468 (M^+, 71), 425 (M − 43, 4), 393 (M − 75, 78), 323 (M − 145, 100); HRMS, $M^+ = 468.0412$ $C_{18}H_{28}S_6O_2$ requires 468.0414. Anal. Calcd for $C_{18}H_{28}S_6O_2$: C, 46.12; H, 6.02. Found: C, 46.32; H, 6.17.

(*S*,*S*)-Diisopropyl (*Z*)-2,2′-(1,3-dithietane-2,4-diylidene)-bis[2-(isopropylthio)thioacetate] (15): yellow solid (petroleum ether/CH_2Cl_2) (10 mg, 11%); mp 91−93 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.60 (hept, J = 6.8 Hz, 2H, 2 × C*H*$(CH_3)_2$), 3.33 (hept, J = 6.8 Hz, 2H, 2 × C*H*$(CH_3)_2$), 1.34 (d, J = 6.8 Hz, 12H, 2 × CH(C*H*$_3)_2$), 1.29 (d, J = 6.8 Hz, 12H, 2 × CH-(C*H*$_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.7 (*C*═O), 154.3 (C═*C*S_2), 119.3 (*C*═CS_2), 41.1 (S*C*H$(CH_3)_2$, DEPT), 35.9 (S*C*H-$(CH_3)_2$, DEPT), 23.16 (SCH(*C*H$_3)_2$, DEPT), 22.9 (SCH(*C*H$_3)_2$, DEPT); IR (KBr, cm^{-1}) ν 1610 (C═O), 1559, 1501, 1132; MS (EI) *m/z* 468 (M^+, 90), 425 (M − 43, 5), 393 (M − 75, 95), 323 (M − 145, 100); HRMS, $M^+ = 468.0388$ $C_{18}H_{28}S_6O_2$ requires 468.0414. Anal. Calcd for $C_{18}H_{28}S_6O_2$: C, 46.12; H, 6.02. Found: C, 46.32; H, 5.93.

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