Selective Syntheses of Bis[1,2]dithiolo[1,4]thiazines and Bis[1,2]dithiolopyrroles from Hünig's Base

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The reaction of *N*,*N*-diisopropylethylamine (Hünig's base) and disulfur dichloride in 1,2-dichloroethane, in the presence of DABCO, gives 4-ethylbis[1,2]dithiolo[5,4-*b*][4′,5′-*e*][1,4]thiazine-3,5-dithione (**1**), or, by addition of oxygen donors, the 3-oxo-5-thione **2** or 3,5-dione **3** derivatives are selectively obtained. When the first reaction is performed in boiling chlorobenzene, 4-ethylbis-[1,2]dithiolo[4,5-*b*][5′,4′-*d*]pyrrole-3,5-dithione (**4**) is obtained by sulfur extrusion from **1**, and in the presence of oxygen donors, the 3-oxo-5-thione **5** or 3,5-dione **6** derivatives are selectively obtained. Some interconversions of compounds **1**−**6** are described, and a coherent set of reaction pathways for the formation of all six products is proposed. X-ray diffraction shows that the new bis-dithiolothiazine ring system of **1**−**3** is folded out of planarity about the thiazine N−S vector, with the *N*-ethyl group folded back over the thiazine ring in a scorpion-like conformation. The new bis-dithiolopyrrole ring system of **4**−**6** is planar and extensively delocalized.

Introduction

The search for new materials has focused largely on sulfur heterocycles since the discovery of superconducting tetrathiafulvalene charge-transfer complexes[1] and molecular switches,[2] thiazole and thiadiazole liquid crystals[3] and thiophene nonlinear optical materials.[4] Polysulfur−nitrogen heterocycles and sulfur-bearing pseudoazulenes[5] are a good source of new structures with potentially attractive characteristics yet to be exploited, but practical syntheses on a multigram scale are rarely available. We have previously described remarkably extensive transformations of simple saturated oximes with disulfur dichloride, S_2Cl_2, into fully unsaturated and chlorinated heteroaromatic systems,[6] and liquid crystalline pseudoazulene 1,2-dithioles and 1,2-thiazines[7] from new molecular rearrangements. In connection with this work we discovered that *N*,*N*-diisopropylethylamine (Hünig's base), initially added as an inert base, reacted with disulfur dichloride to give the first examples of the bis[1,2]-dithiolo[5,4-*b*][4′,5′-*e*][1,4]thiazine ring system.[8] The potential for sulfur extrusion[9] of these new 1,4-thiazines led us to study their thermal behavior, and we found that they underwent very clean and selective thermal extrusion of one sulfur atom only to give the first examples of bis[1,2]dithiolo[4,5-*b*][5′,4′-*d*]pyrroles.[10] These unusual reactions have now opened a very short pathway for the preparation of new heterocyclic systems from commercial reagents. Their main features are the large number of steps involved in each transformation, and the isolation of different compounds from the same reagents by changing the reaction conditions. We have made a systematic study of these reactions in an attempt to understand how the conditions affect the nature of the final product, and to isolate any intermediates in order to establish a coherent mechanism for the reaction. We now report the precise conditions for the selective syn-

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(5) For a review on pseudoazulenes, see: Timpe, H.-J.; El'tsov, A. V. *Adv. Heterocycl. Chem.* **1983**, *33*, 185.

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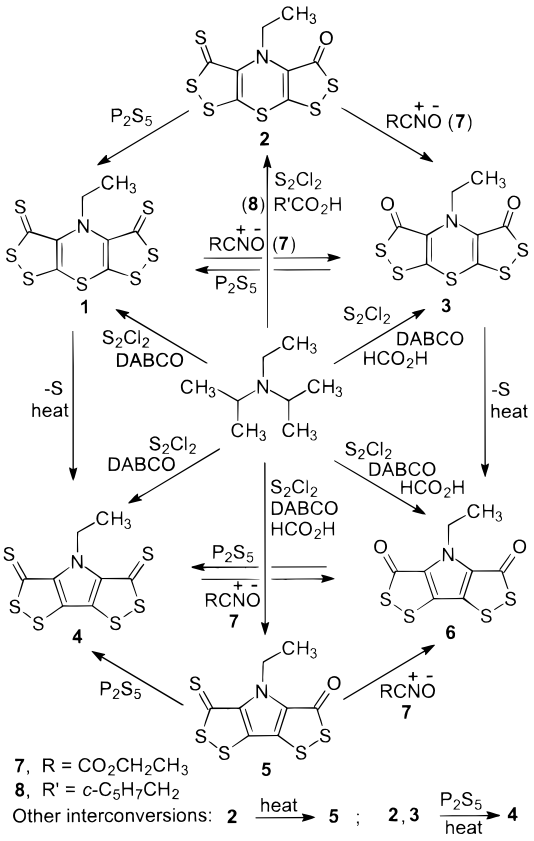
Scheme 1



thesis of each individual compound, mechanistic proposals based on isolated intermediates, and the structures and crystal packing obtained from X-ray diffraction analysis.

Results and Discussion

Hünig's base is a valuable hindered base, very efficient in deprotonation reactions associated with the extensive aromatization and chlorination steps performed by disulfur dichloride on saturated substrates.[6,7] This base did not react when mixed with S_2Cl_2 during several days at temperatures up to 4 °C, thus acting as an inert base, but higher temperatures promoted a slow sulfuration process of the base, affording a variety of heterocyclic compounds in surprisingly good yields. Modification of solvent, refluxing temperature, and time, and addition of a stronger base or an oxygen donor, permitted the selective synthesis of each of the various products. Thus Hünig's base was treated with 10 equiv of S_2Cl_2 in 1,2-dichloroethane in the presence of 10 equiv of 1,4-diazabicyclo[2.2.2]octane (DABCO) for 3 days at room temperature, followed by refluxing for 2 h. In these conditions compound **1**, mp 202−203 °C (40%), was obtained by chromatography as black needles with a metallic luster (Scheme 1). These conditions promoted selectively the full sulfuration of all the C−H bonds of the two isopropyl groups, converting the initial $EtN{\cdot}C_6H_{14}$ into $EtN{\cdot}C_6S_7$, as shown by mass spectrometry, HRMS, and microanalysis of **1**. The presence of the *N*-ethyl group was detected in the ^1H and ^{13}C NMR spectra of **1**, suggesting the structure 4-ethylbis[1,2]dithiolo[5,4-*b*]-[4′,5′-*e*][1,4]thiazine-3,5-dithione (**1**), in which the carbon connectivity is retained, as the most probable, and this was confirmed by X-ray crystallography.[19]

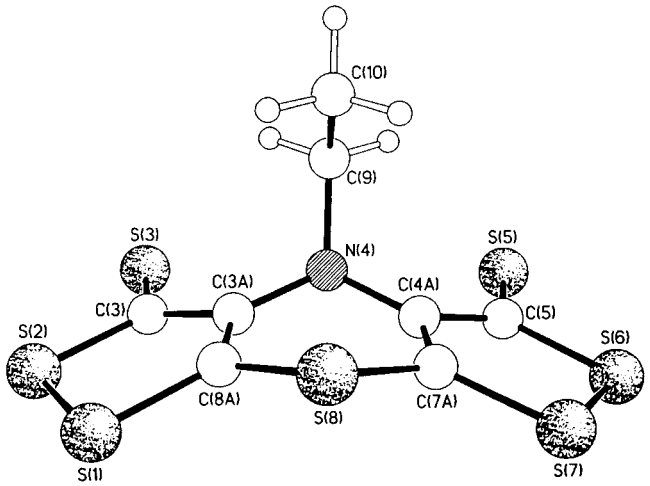


Figure 1. The molecular structure of **1**.

Table 1. Selected Bond Lengths and Derived Parameters for Compounds 1−3, 5, and 6

	1	2	3	5	6
S(1)−S(2)	2.059(1)	2.048(1)	2.053(1)	2.073(1)	2.070(1)
S(1)−C(8A)	1.723(3)	1.727(2)	1.731(2)	–	–
S(1)−C(7B)	–	–	–	1.728(4)	1.735(2)
S(2)−C(3)	1.729(3)	1.790(3)	1.779(2)	1.802(5)	1.801(2)
C(3)−C(3A)	1.436(4)	1.463(3)	1.455(2)	1.456(5)	1.439(3)
C(3A)−N(4)	1.405(3)	1.409(3)	1.402(2)	1.363(5)	1.370(2)
C(3A−C(7B)	–	–	–	1.390(5)	1.392(3)
C(3A)−C(8A)	1.365(4)	1.350(3)	1.351(2)	–	–
N(4)−C(4A)	1.415(3)	1.414(3)	1.402(2)	1.379(4)	1.371(3)
C(4A)−C(5)	1.429(4)	1.433(3)	1.459(2)	1.426(5)	1.436(3)
C(4A)−C(7A)	1.366(4)	1.371(3)	1.350(2)	1.400(5)	1.389(3)
C(5)−S(6)	1.726(3)	1.726(2)	1.790(2)	1.753(4)	1.798(2)
S(6)−S(7)	2.064(1)	2.064(1)	2.052(1)	2.081(1)	2.074(1)
S(7)−C(7A)	1.724(3)	1.725(2)	1.723(2)	1.724(3)	1.729(2)
C(7A)−S(8)	1.763(3)	1.755(2)	1.763(2)	–	–
C(7A)−C(7B)	–	–	–	1.409(5)	1.406(3)
S(8)−C(8A)	1.758(3)	1.749(2)	1.759(2)	–	–
S(8)···C(10)	3.74	3.87	4.11	–	–
A[a]	0.30	0.33	0.22	0.02	0.06

[a] **A** is the perpendicular distance (Å) of N(4) out of the C(3A)/C(4A)/C(9) plane.

The structure of **1** (Figure 1) shows the molecule to have a scorpion-like conformation with noncrystallographic C_s symmetry about a plane passing through N(4) and S(8) of the thiazine ring and including the ethyl substituent. The fused ring system is folded out of planarity by ca. 34° about the N(4)···S(8) vector. Inspection of the pattern of bonding reveals delocalization of the formal C=C double bonds of the thiazine ring into the adjacent C−S bonds of the dithiole rings; there is a similar delocalization into the thiocarbonyl groups from their adjacent C−S bonds (Table 1).

In this one-pot conversion of Hünig's base into **1** the 14 isopropyl C−H bonds have been replaced by 10 C−S bonds and two carbon−carbon double bonds, while the ethyl group has been untouched. This provides a striking example of high selectivity between primary and secondary *N*-alkyl groups in a competitive reaction that can be exploited in synthesis. Although compound **1** is poorly soluble in common solvents (except pyridine), which precludes the possibility of column chromatography on a large scale, it is easily extracted as its salt in concentrated sulfuric acid. Thus, the reaction is readily performed on the gram scale by extraction of the product with sulfuric acid and re-extraction with CH_2Cl_2 after dilution of the H_2SO_4 solution with ice.

By variation of the solvent, time of reflux, and addition of a source of oxygen, the reaction could be modified to give derivatives of the bis-dithiolothiazine ring system in which one or two exocyclic sulfur atoms are replaced by oxygen. We found that THF reacted with S_2Cl_2 under the reaction conditions to give 4-chlorobut-1-ene, detected by GC-MS, and could therefore act both as solvent and oxygen donor.[11] When the reaction was performed in THF instead of dichloroethane, the main product isolated was the red compound, **2**, mp 179−181 °C. Mass spectrometry and microanalysis showed **2** to be $C_8H_5NOS_6$ in which one sulfur in **1** had been replaced by an oxygen in compound **2**, which had a carbonyl absorption at 1660 cm^{-1} in the infrared spectrum. The ^1H NMR showed the presence of the *N*-ethyl group and ^{13}C NMR supported this, together with 6 quaternary carbon signals proving that the structure of **2** was no longer symmetrical, leading to the 3-oxo-5-thione structure, which was confirmed by X-ray crystallography.[19] The molecular structure of **2** shows that the replacement of one of the thiocarbonyls by carbonyl causes a desymmetrization in the molecule at both an atomic and an electronic level. Most noticeable is a 0.06 Å increase in the C(3)−S(2) bond length in the dithiole ring, and this is accompanied by a small reduction in the ring C=C double bond and a small increase in the C−C single bond distances. The remainder of the geometry is essentially unchanged, apart from a small reduction in the out-of-plane fold angle from 34° in **1** to 26° in **2**, a change probably due to packing differences (vide infra).

Despite a large number of experiments with the addition of oxygen donors, the mixture of S_2Cl_2 and DABCO was unsatisfactory for the selective synthesis of **2**, since it gave mixtures in which **2** was accompanied by **1** and **3**, making purification tedious. So we turned to Hünig's base as both reactant and base in the absence of DABCO. Thus, a mixture of Hünig's base (5 equiv), S_2Cl_2 (5 equiv), and cyclopenten-1-ylacetic acid[12] (1 equiv), as oxygen donor, in THF was stirred for 3 days and then refluxed for 3 h and extracted with concentrated sulfuric acid, to give **2** in 42% yield.[13] Other carboxylic acids gave more complex mixtures of products.

Furthermore, when Hünig's base was treated with 10 equiv of S_2Cl_2 in 1,2-dichloroethane in the presence of 9 equiv of DABCO for 3 days at room temperature, followed by addition of 20 equiv of formic acid and refluxing for 1 h, the orange product, $C_8H_5NO_2S_5$, **3**, mp 191−193 °C (42%) was selectively obtained, with two sulfur atoms in **1** being replaced by two oxygen atoms. The reaction may be scaled up by extraction of **3** from the reaction mixture with concentrated sulfuric acid. Again the *N*-ethyl group was intact, and ^{13}C NMR now showed three sp^2-tertiary carbon atoms, indicating the symmetrical 3,5-dione structure **3**, which was confirmed by X-ray crystallography.[19] Inspection of the molecular structure of **3** shows that the replacement of both thiocarbonyls by carbonyls restores the molecular C_s symmetry, and the changes in the pattern of bonding described above for **2** are now observed on both sides of the molecule. The fold angle in the thiazine ring is, at 34°, the same as observed in **1**.

The packing of the molecules of the two symmetrical species, **1** and **3**, reveals virtually isomorphous patterns. In both instances the arrangement is complex and is dominated by short intermolecular O···S (**3**) and S···S (**1**) contacts that extend through the crystal. Two distinctive patterns emerge, each of which involve head-to-tail, polar ribbons of molecules that are "cross-linked" to equivalent ribbons of both the same and opposite polarities (Figure 2, parts a and b, respectively). The packing of molecules of **2** is modified by the presence of included dichloromethane molecules, though there are still short contacts of 2.92 and 3.02 Å between the carbonyl oxygen of one molecule and the two sulfur atoms of the thiocarbonylsubstituted dithiole ring of the next.

We found that our 1,4-thiazines easily underwent a fast sulfur extrusion when boiled in higher boiling solvents, affording bis[1,2]dithiolo[4,5-*b*][5′,4′-*d*]pyrroles. Furthermore, the combined Hünig's base reaction and desulfurization allowed the one-pot preparation of these new pyrrole derivatives from Hünig's base. Refluxing **1** in xylene for 0.5 h produced a strongly purple-colored solution, from which compound **4**, mp 242−243 °C, was obtained quantitatively as black needles. The same compound **4** (42% after chromatographic purification) was obtained when Hünig's base (1 equiv) was treated with an excess of S_2Cl_2 (10 equiv) in chlorobenzene in the presence of DABCO (10 equiv) for 3 days at room temperature, followed by refluxing for 2 h. Mass spectrometry of **4** showed the presence of six sulfur atoms per molecule, in addition to eight carbons, five hydrogens, and one nitrogen, which was confirmed by high-resolution mass spectrometry and microanalysis. The ^1H NMR spectrum of **4** confirmed the presence of the ethyl group, and ^{13}C NMR showed three aromatic signals consistent with a symmetrical structure, in addition to the two aliphatic signals of the ethyl group. The only sulfur atom which can be lost from **1** to give a symmetrical structure is that of the 1,4-thiazine ring system, forming a new carbon−carbon bond, and affording the 4-ethylbis[1,2]-dithiolo[4,5-*b*][5′,4′-*d*]pyrrole-3,5-dithione **4**. It is remarkable that in this reaction, a carbon−carbon bond is formed between two distant and formally unreactive methyl groups from both isopropyl groups of Hünig's base; on the other hand, the ethyl group remains unchanged.

The related 1,4-thiazines **2** and **3** were also good substrates for desulfurization reactions. Thus, when the 3-oxo-5-thione **2** or the 3,5-dione **3** were heated under reflux in xylene for 1 and 3 h, respectively, the 4-ethyl-3-oxobis[1,2]dithiolo[4,5-*b*][5′,4′-*d*]pyrrole-5-thione (**5**), red crystals, mp 175−176 °C, and 4-ethylbis[1,2]dithiolo[4,5-*b*][5′,4′-*d*]pyrrole-3,5-dione (**6**), yellow crystals, mp 199−200 °C, respectively, were obtained in quantitative yield. The one-pot conversion of Hünig's base into the fused pyrrole **4** worked equally well for the pyrroles **5** and **6**. Thus, treating Hünig's base (1 equiv) with S_2Cl_2 (10 equiv) and DABCO (10 equiv) in chlorobenzene for 3 days at room temperature, followed by addition of formic acid (10 equiv) and refluxing for 2 h, afforded keto thione **5** (25%) as the main product, together with minor amounts of dithione **4** and dione **6**. Treating Hünig's base (1 equiv) with S_2Cl_2 (10 equiv) and DABCO (8 equiv) for 3 days at room temperature and then with formic acid (20 equiv) and refluxing for 7.5 h in chlorobenzene afforded **6** (42%)

(11) Some recent examples of THF ring opening reactions are: (a) Namy, J.-L.; Colomb, M.; Kagan, H. B. *Tetrahedron Lett.* **1994**, *35*, 1723. (b) Boisson, C.; Berthet, J. C.; Lance, M.; Nierlich, M.; Ephritikhine, M. *J. Chem. Soc., Chem. Commun.* **1996**, 2129.

(12) Masamune, T.; Sato, S.; Abiko, A.; Ono, M.; Murai, A. *Bull. Chem. Soc. Jpn*, **1980**, *53*, 2895.

(13) In the absence of DABCO, yields are calculated on the basis of 15 mol of Hünig's base giving 1 mol of product and 14 mol of Hünig's base hydrochloride (cf. Scheme 3).

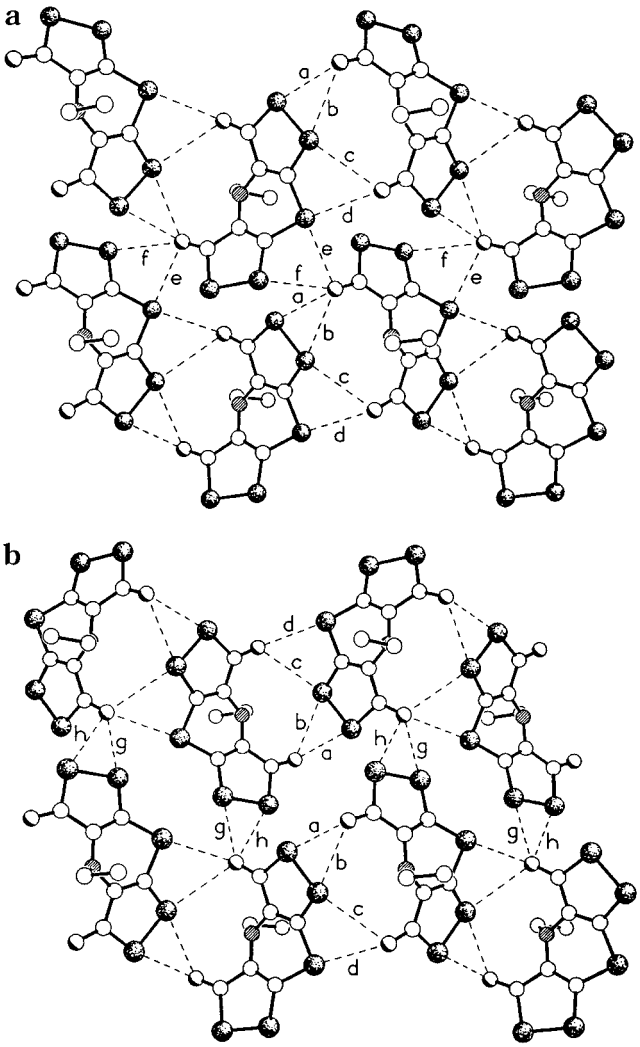


Figure 2. The two modes of cross-linking between polar ribbons (running from left to right) present in the structures of **1** and **3**. Intermolecular contacts S···S (**1**), O···S (**3**) Å; (a) 3.29, 3.06; (b) 3.31, 3.10; (c) 3.34, 3.30; (d) 3.34, 3.20; (e) 3.53, 3.14; (f) 3.36, 3.40; (g) 3.13, 2.86; and (h) 3.40, 3.24.

as the only significant reaction product. By monitoring the latter reaction by TLC, the initial formation of thiazine **3**, which slowly converted into pyrrole **6**, could be seen. According to the expected structure, compound **5** had both a carbonyl and a thione absorption at 1680 and 1291 cm^{-1} in the infrared spectrum. The ^1H NMR showed the *N*-ethyl group, and the ^{13}C NMR supported this, together with 6 sp^2-tertiary carbon atom signals showing that the structure of **5** was no longer symmetrical. The 3-keto-5-thione structure was confirmed by X-ray crystallography (Figure 3). In addition, the ^1H NMR of compound **6** showed the *N*-ethyl group was intact and ^{13}C NMR now showed 3 sp^2-tertiary carbon atoms, indicating the symmetrical 3,5-dione structure **6**, also confirmed by X-ray crystallography.[19]

The molecular structures of the two thermolysis products **5** and **6** have essentially coplanar ring systems with maximum deviations from planarity of 0.05 and 0.11 Å, respectively. The pattern of changes in bond lengths within the dithiole rings accompanying the replacement of thiocarbonyl by carbonyl described above for **2** and **3** with respect to **1** is also observed in these two compounds. The exception is in the formal C=C double bonds of the

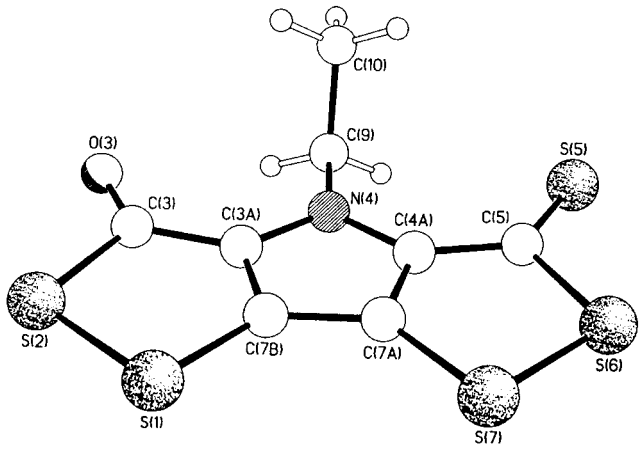


Figure 3. The molecular structure of **5**.

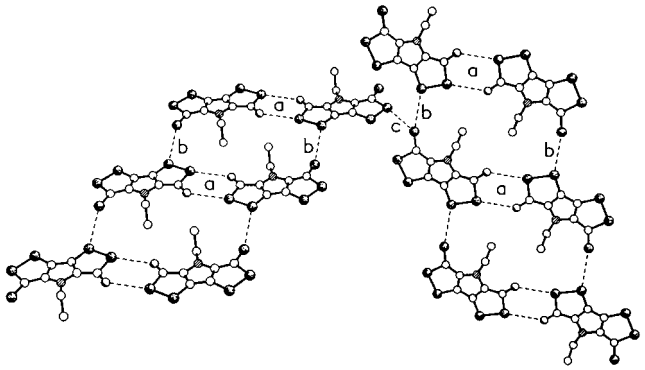


Figure 4. One of the pairs of orthogonally oriented ribbons present in the structure of **5**. Intermolecular S···O contact Å; (a) 3.14 and S···S contacts Å, (b) 3.31, and (c) 3.37.

central pyrrole rings, which have the normal pattern of delocalized bond lengths (Table 1).

As already seen for compounds **1** and **3**, the packing of the molecules of both **5** and **6** is dominated by O···S and S···S contacts. In **5** the packing consists of orthogonally oriented ribbons comprising O···S/S···O dimers connected by pairs of C=S···S linkages (Figure 4). Each ribbon is stacked parallel with its symmetry related counterpart (mean interplanar separation ca. 3.5 Å, though involving a short C=O···O=C of 3.16 Å). In contrast, molecules of **6** pack to form stacked sheets with a mean intersheet separation of ca. 3.6 Å. The interactions in one of these sheets are identified in Figure 5.

The interconversion of compounds **1** to **6** was also investigated (Scheme 1). Application of the nitrile oxide method for converting thiocarbonyl into carbonyl groups[14] readily gave the product **3** in 90% yield from **1** and in 95% from **2**, by treating them in THF at 0 °C for 15 min with excess of the nitrile oxide **7** generated in situ from ethyl chlorooximidoacetate and triethylamine. The reverse reactions, thiation of 3-keto-5-thione **2** and 3,5-dione **3**, were also readily achieved in about 70% by heating with Lawesson's reagent or phosphorus pentasulfide in THF for 5 h. In the pyrrole series, treating dithione **4** or oxothione **5** in THF at 0 °C for 15 min with excess of ethoxycarbonyl nitrile oxide **7** afforded, after chromatographic purification, dione **6** in 70−75% yield.

(14) Huisgen, R.; Mack, W.; Anneser, E. *Angew. Chem.*, **1961**, *73*, 656. Boberg, F.; Knoop, J. *Liebigs Ann. Chem.*, **1967**, *708*, 148. Kim, J. N.; Ryu, E. K. *Tetrahedron Lett.* **1993**, *34*, 8283.

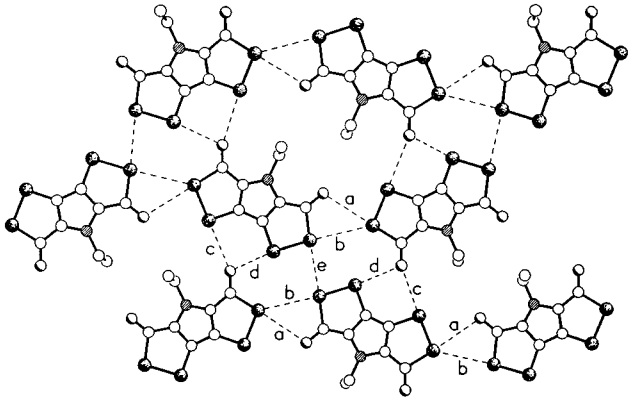
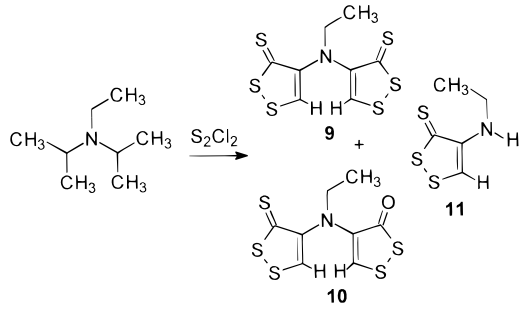


Figure 5. One of the sheets of molecules present in the structure of **6**. Intermolecular S···O and S···S contacts Å; (a) 3.21; (b) 3.51; (c) 3.33; (d) 3.13 and (e) 3.42.

Scheme 2

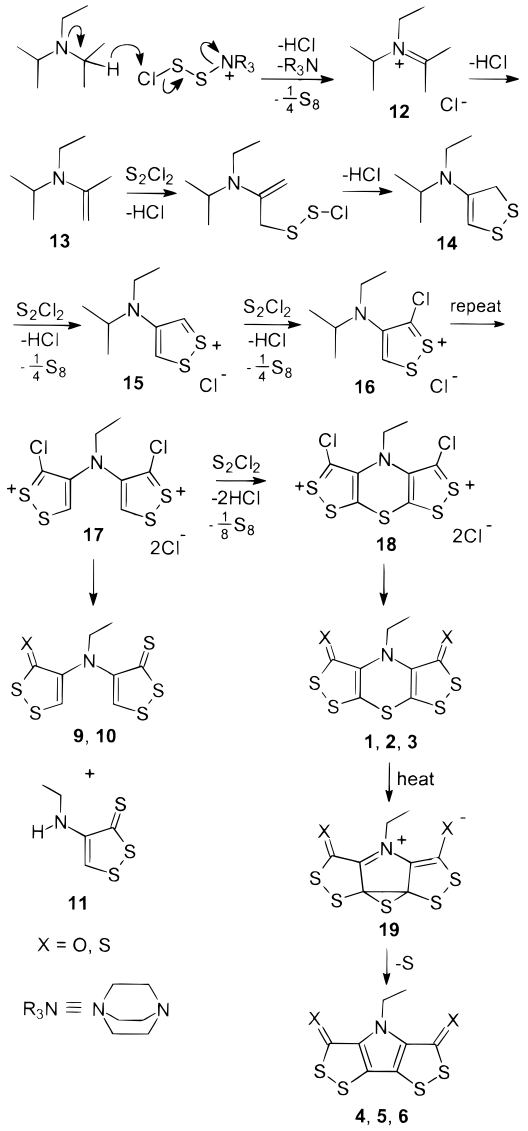


Oxidation of **4** with mercury(II) acetate in acetic acid/dichloromethane gave compound **6** (35%). Thiation of **5** or **6** by refluxing with excess of phosphorus pentasulfide in xylene for 1 h gave compound **4** in almost quantitative yield. Simultaneous thermal desulfurization and thiation of the 1,4-thiazines **2** or **3**, in the same conditions, also gave the pyrrole **4** in comparable yield.

Reaction Mechanisms

The transformation of Hünig's base into the bis[1,2]-dithiolo[1,4]thiazines requires some 15 or so separate reactions (see Scheme 3) which must therefore proceed in an average yield of about 94% (for a 40% yield of **1**). The primary question about this extensive reaction sequence is the order of formation of the 3 heterocyclic rings. The dithiole rings could be formed first, followed by the central 1,4-thiazine, or *vice versa*. With this in mind we performed the reaction under the simplest conditions in order to isolate any intermediate products. In some experiments, a green mixture of precipitated salts were filtered from the reaction mixture. By treating this mixture with methanol, three new compounds **9**, **10**, and **11** (relative proportions 4:15:1) were isolated in very low yield after column chromatography (Scheme 2). The presence of signals attributed to aromatic protons in the ^{1}H NMR spectra of **9**−**11**, also confirmed by DEPT experiments in the ^{13}C NMR, indicated that the complete tricyclic system had not been reached and that one or two dithiole ring had been formed. Again, as expected, the ethyl group was untouched in all three new compounds. Compound **9** was shown by mass spectrometry, high-resolution mass spectrometry, and microanalysis to be $C_8H_7NS_6$. It has a symmetrical structure in which signals corresponding to an aromatic proton and three

Scheme 3



carbon atoms, including the C═S group, could be assigned in the ^{1}H and ^{13}C NMR spectra. These facts suggested for **9** the structure *N*-ethyl-*N*-(3-thiono[1,2]-dithiol-4-yl)-4-amino[1,2]dithiole-3-thione. For compound **10**, mass spectrometry and microanalysis showed that one sulfur in **9** had been replaced by an oxygen; the structure was no longer symmetrical, as shown by the 6 aromatic carbon signals, two of which corresponded to C−H groups, leading to the *N*-ethyl-*N*-(3-oxo[1,2]dithiol-4-yl)-4-amino[1,2]dithiole-3-thione structure **10**. On the other hand, compound **11** had a molecular mass of 177, which implied the loss of a 1,2-dithiole-3-thione group from **9**, further supported by the appearance of an N−H group, seen as a broad signal at δ 4.5 in the ^{1}H NMR spectrum. All the spectral data indicated the structure 4-(ethylamino)-1,2-dithiole-3-thione for **11**. Formation of the mono and bicyclic products **9**−**11** strongly suggests a sequence in which the dithiole rings are formed first, followed by incorporation of the final bridging sulfur atom.

A mechanistic pathway for the formation of all the products is proposed in Scheme 3. The first step is oxidation of an isopropyl group in Hünig's base by S_2Cl_2 (or its reactive complex with DABCO) to give the more stable iminium ion **12**, as generally occurs in the oxida-

tion of tertiary amines.[15] In agreement with this, electron-withdrawing substituents on nitrogen (as in *N*,*N*-diisopropylacetamide or *N*,*N*-diisopropylcyanamide) suppress the reaction with S_2Cl_2 even under more vigorous conditions. Deprotonation of iminium ion **12** gives enamine **13** which reacts with S_2Cl_2 (or its DABCO complex) to give the 1,2-dithiole **14** which would be expected to react further with S_2Cl_2 to give the dithiolium salt **15**. Similar oxidation of this with S_2Cl_2 would give the 3-chlorodithiolium salt **16**. The dithiolium ring in this compound is expected to be stable and the whole sequence could then be repeated to transform the other isopropyl group similarly, to give the bis-dithiolium salt **17**. This could cyclize to the tricyclic species **18** by further reaction with S_2Cl_2, with loss of sulfur, or with any SCl_2 present.

The 3,5-dichloro-bis-dithiolium salt **18** is presumably the key intermediate in the formation of compounds **1**−**6**. It is expected to be stable, but highly reactive toward nucleophiles.[16] Sulfur nucleophiles generated during the reaction, including such possibilities as S_8 or ^-SSCl, would produce the 3,5-dithiole **1**; oxygen nucleophiles such as formic acid would similarly give the 3,5-dione **3**, and lower concentrations of the oxygen nucleophile would give the 3,5-ketothione **2**. The 1,4-thiazines **1**−**3** are perfectly stable in low boiling point solvents and are thus isolable from the reaction mixture, but sulfur extrusion in higher boiling solvents (xylene, chlorobenzene) gave the first examples of the bis[1,2]dithiolo[4,5-*b*][5′,4′-*d*]-pyrroles **4**−**6**. The sulfur extrusion reactions, which are highly selective, quantitative, and uncatalyzed, occur under significantly milder conditions than for other annelated 1,4-thiazines.[17] This can be attributed to stabilization of the key thiirane intermediate **19** by electron release from nitrogen and electron withdrawal by the carbonyl and thiocarbonyl groups, giving highly delocalized intermediate **19** on the way to the aromatic product. The ene-thiolate contribution, for X = S, will be more stable than the enolate contribution, for X = O, in agreement with the observed ease of sulfur extrusion (**1** > **2** > **3**).

The early steps in Scheme 3 appear to proceed at low temperature, while some of the later steps probably require the more vigorous refluxing conditions found necessary to complete the product formation. If the bis-thiolium salt **17** is not converted rapidly into **18**, it could itself react with the sulfur and oxygen nucleophiles to give **9** and **10** and could possibly be degraded to **11**.

Conclusions

Hünig's base is readily and extensively transformed by S_2Cl_2 and DABCO in a one-pot process to give the first bis[1,2]dithiolo[1,4]thiazine derivatives **1**−**3** and, at a slightly higher reaction temperature, the first bis[1,2]-dithiolopyrrole derivatives **4**−**6**. The latter are formed quantitatively by selective extrusion of one sulfur, from the 1,4-thiazine ring. Because of the high reactivity of S_2Cl_2 and its complex with DABCO the reaction conditions are very mild, in striking contrast to the very vigorous conditions required for the formation of 1,2-dithiolo-3-thiones by heating certain organic substrates with sulfur.[16] Surprisingly, S_2Cl_2 does not appear to have been used before for the synthesis of 1,2-dithioles. The interconversion of many of these products (Scheme 1) is described. While the bis-dithiolopyrrole rings **4**−**6** are planar, the bisdithiolothiazines **1**−**3** are bent with the *N*-ethyl group folded over the 1,4-thiazine ring in a scorpion like conformation, in the crystal lattice.

Experimental Section

Disulfur dichloride and Hünig's base were purchased from Aldrich and used without further purification. THF was distilled from sodium. 1,2-Dichloroethane and chlorobenzene were distilled from phosphorus pentoxide. Melting points were determined using a Kofler hot-stage apparatus and are uncorrected. 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. Table 3 shows the chemical shifts (δ) in ^1H and ^{13}C NMR spectra of compounds **1**−**6** and **9**−**11** at 400 and 100 MHz, respectively, taken in $CDCl_3$, except for compounds **1** and **4**, taken in pyridine-d_5. Methyl, methylene, and methine groups were assigned from DEPT experiments. sp^2-Tertiary carbon atoms were assigned by direct comparison of the chemical shifts in ^{13}C NMR spectra.

X-ray Crystallography. Table 2 provides a summary of the crystal data, data collection and refinement parameters for complexes **1**, **2**, **3**, **5** and **6**. Each of the structures was solved by direct methods and was refined by full matrix least-squares based on F^2. All of the non-hydrogen atoms in all the compounds were refined anisotropically. The hydrogen atoms in each of the five structures were placed in calculated positions, assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)$, [$U(H) = 1.5U_{eq}$(C-Me)], and allowed to ride on their parent atoms. Computations were carried out using the SHELXTL PC program system.[18]

4-Ethylbis[1,2]dithiolo[5,4-*b*][4′,5′-*e*][1,4]thiazine-3,5-dithione (1). Disulfur dichloride (4.6 mL, 57.5 mmol) was added dropwise under dry nitrogen to a solution of *N*-ethyldiisopropylamine (1.0 mL, 5.75 mmol) and 1,4-diazabicyclo-[2.2.2]octane (DABCO, 6.44 g, 57.5 mmol) in dichloroethane (100 mL) at −40 °C. The mixture was stirred under dry nitrogen for 15 min at −40 °C and then for 3 days at room temperature and then refluxed for 2 h. The reaction mixture was filtered through Celite, and the solvent was removed in the rotary evaporator. The residue was dissolved in dichloromethane (100 mL), filtered, washed with 70% v/v sulfuric acid (15 mL), and then extracted with concentrated sulfuric acid (95−98%, 20 mL). The concentrated sulfuric acid layer was poured into ice (200 g) and extracted with dichloromethane (3 × 50 mL). The combined organic extracts were washed with water (3 × 30 mL), dried with anhydrous magnesium sulfate, and evaporated. The crude was subjected to medium-pressure liquid chromatography (MPLC) (petroleum ether to CH_2Cl_2) to give **1** as black metallic needles (petroleum ether−CH_2Cl_2) (0.78 g, 40%); mp 202−203 °C dec. IR (CCl_4, cm^{-1}) ν 2964, 1551, 1314, 1254 (C=S), 1057, 1000; MS (EI, 70 eV, 240 °C) *m*/*z* 339 (M^+, 6), 307 (M − 32, 22), 274 (M − 65, 9), 247 (7), 174 (6), 160 (7), 126 (8), 112 (23), 100 (38), 76 (52); HRMS, M^+ = 338.8450 $C_8H_5NS_7$ requires 338.8467. Anal. Calcd for $C_8H_5NS_7$: C, 28.30; H, 1.48; N, 4.12. Found: C, 28.02; H, 1.18; N, 3.96.

4-Ethyl-3-oxobis[1,2]dithiolo[5,4-*b*][4′,5′-*e*][1,4]thiazine-5-thione (2). Disulfur dichloride (4 mL, 50 mmol) was added

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(17) Bohle, M.; Liebscher, J. *Adv. Heterocycl. Chem.* **1996**, *65*, 39.

(18) SHELXTL PC version 5.03, Siemens Analytical X-Ray Instruments, Inc., Madison, WI, 1994.

(19) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

Table 2. Crystal Data, Data Collection, and Refinement Parameters[a]

data	1	2	3	5	6
formula	$C_8H_5NS_7$	$C_8H_5NOS_6$	$C_8H_5NO_2S_5$	$C_8H_5NOS_5$	$C_8H_5NO_2S_4$
solvent	–	0.5 DCM	–	–	–
formula weight	339.6	366.0	307.4	291.4	275.4
color, habit	dark red needles	ruby red columnal needles	ruby red prisms	orange/red platy needles	orange/yellow blocks
crystal size/mm	0.78 × 0.23 × 0.17	0.68 × 0.16 × 0.16	0.63 × 0.53 × 0.37	0.93 × 0.08 × 0.05	0.67 × 0.67 × 0.27
lattice type	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group symbol, number	$P2_1/c$, 14	$I2/a$, 15[b]	$P2_1/c$, 14	$P2_1/c$, 14	$P2_1/c$, 14
T/K	153	293	293	293	293
cell dimensions					
a/Å	9.429(2)	13.930(1)	8.748(1)	5.471(1)	7.432(1)
b/Å	12.597(3)	14.307(1)	11.786(1)	7.745(1)	19.305(2)
c/Å	11.137(2)	13.943(2)	11.760(3)	26.673(3)	7.667(2)
α/deg	–	–	–	–	–
β/deg	103.18(1)	100.72(1)	104.52(1)	95.29(1)	110.87(1)
γ/deg	–	–	–	–	–
V/Å^3	1288.0(5)	2730.3(6)	1173.8(3)	1125.4(3)	1027.8(2)
Z	4	8	4	4	4
D_c/g cm^{-3}	1.751	1.781	1.740	1.720	1.780
$F(000)$	688	1480	624	592	560
μ/mm^{-1}	1.19	1.18	0.97	1.00	0.90
θ range/deg	2.2−25.0	2.1−30.0	2.4−30.0	2.7−30.0	2.1−30.0
no. of unique reflections					
measured	2263	3976	3432	3286	3001
observed, $\|F_o\| > 4\sigma(\|F_o\|)$	1973	3049	2962	2160	2442
absorption correction	–	face-indexed numerical	semiempirical	–	–
maximum, minimum transmission	–	0.84, 0.81	0.57, 0.52	–	–
no. of variables	145	160	146	136	137
R_1[c]	0.030	0.042	0.033	0.057	0.044
wR_2[d]	0.076	0.099	0.084	0.126	0.112
weighting factors a, b[e]	0.035, 0.785	0.038, 3.741	0.038, 0.564	0.060, 0.078	0.055, 0.376
largest difference peak, hole/eÅ^{-3}	0.39, −0.30	0.72, −0.50	0.33, −0.29	0.56, −0.32	0.55, −0.28

[a] Details in common: graphite monochromated radiation, ω-scans, Siemens P4/PC diffractometer, Mo Kα radiation, refinement based on F^2. [b] I-centered cell used since C-centered cell has $\beta = 123.7°$. [c] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [e] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

Table 3. Chemical Shifts (δ) in ^{1}H and ^{13}C NMR Spectra of Compounds 1−6 and 9−11

	CH_3	CH_2	C=C−CO	C=C−CS	C=O and C=S
1	δ_H 1.34(t)	δ_H 4.11(q)		δ_C 148.65	
	J = 7.4 Hz	J = 7.4 Hz		δ_C 158.75	$\delta_{C=S}$ 201.55
	δ_C 14.12	δ_C 44.07			
2	δ_H 1.33(t)	δ_H 3.96(q)	δ_C 137.46	δ_C 148.10	$\delta_{C=O}$ 182.29
	J = 7.2 Hz	J = 7.2 Hz	δ_C148.18	δ_C 155.24	$\delta_{C=S}$ 201.81
	δ_C 14.42	δ_C 42.97			
3	δ_H 1.32(t)	δ_H 3.80(q)	δ_C 136.83		$\delta_{C=O}$ 182.16
	J = 7.2 Hz	J = 7.2 Hz	δ_C 146.57		
	δ_C 14.57	δ_C 42.42			
4	δ_H 1.48(t)	δ_H 5.46(q)		δ_C 136.42	
	J = 7.0 Hz	J = 7.0 Hz		δ_C 145.21	$\delta_{C=S}$199.91
	δ_C 18.02	δ_C 35.65			
5	δ_H 1.42(t)	δ_H 4.99(q)	δ_C 129.74	δ_C 135.67	$\delta_{C=O}$ 181.43
	J = 7.1 Hz	J = 7.1 Hz	δ_C 135.18	δ_C 144.57	$\delta_{C=S}$ 198.17
	δ_C 17.37	δ_C 37.76			
6	δ_H 1.41(t)	δ_H 4.60(q)	δ_C 130.10		$\delta_{C=O}$ 181.22
	J = 7.1 Hz	J = 7.1 Hz	δ_C 135.20		
	δ_C 17.15	δ_C 39.74			
9	δ_H 1.24(t)	δ_H 3.74(q)		δ_H 8.13(s)	
	J = 7.1 Hz	J = 7.1 Hz		δ_{CH} 145.71	$\delta_{C=S}$ 201.55
	δ_C 13.68	δ_C 47.93		δ_{CC} 149.89	
10	δ_H 1.21(t)	δ_H 3.64(q)	δ_H 7.63(s)	δ_H 8.10(s)	$\delta_{C=O}$ 190.00
	J = 7.1 Hz	J = 7.1 Hz	δ_{CH} 135.61	δ_{CH} 146.10	$\delta_{C=S}$ 209.08
	δ_C 13.35	δ_C 47.90	δ_{CC} 138.22	δ_{CC} 150.13	
11	δ_H 1.33(t)	δ_H 3.20(m)		δ_H 6.91(s)	
[a]	J = 7.2 Hz	J_1 = 7.2 Hz		δ_{CH} 118.05	$\delta_{C=S}$ 202.54
	δ_C 14.72	J_2 = 1.4 Hz		δ_{CC} 151.52	
		δ_C 41.26			

[a] Other signal: N−H, δ_H = 4.86 (s, br).

dropwise under dry nitrogen to a solution of *N*-ethyldiisopropylamine (8.7 mL, 50 mmol) and cyclopenten-1-ylacetic acid[12] (**8**) (1.26 g, 10 mmol) in THF (50 mL) at −40 °C. The mixture was stirred for 15 min at −40 °C and then for 3 days at 5−10 °C and then refluxed for 3 h. The reaction mixture was filtered through Celite, and the solvent was removed in the rotary evaporator. The residue was extracted with concentrated sulfuric acid as in the previous experiment and then subjected to MPLC (petroleum ether to CH_2Cl_2−petroleum ether 1:1). The red fraction (0.95 g) was then washed with petroleum ether (3 × 10 mL) to give **2** as red needles (petroleum ether−CH_2Cl_2), (0.45 g, 42% based on 1/15 of the starting amine); mp 179−181 °C dec. IR (CCl_4, cm^{-1}) ν 2922, 1660 (C=O), 1633, 1287 (C=S), 1080, 1009; MS (EI, 70 eV, 210 °C) m/z 323 (M^+, 4), 291 (M − 32, 100), 276 (M − 47, 18), 263 (M − 60, 13), 231 (23), 198 (9), 160 (11), 126 (12), 112 (27), 100 (29); HRMS, found M^+ = 322.8671 $C_8H_5NOS_6$ requires 322.8695. Anal. Calcd for $C_8H_5NOS_6$: C, 29.72; H, 1.55; N, 4.33. Found: C, 29.78; H, 1.57; N, 4.31.

4-Ethylbis[1,2]dithiolo[5,4-*b*][4′,5′-*e*][1,4]thiazine-3,5-dione (3). Disulfur dichloride (4.6 mL, 57.5 mmol) was added dropwise under dry nitrogen to a solution of *N*-ethyldiisopropylamine (1.0 mL, 5.75 mmol) and DABCO (5.80 g, 51.8 mmol) in dichloroethane (100 mL) at −40 °C. The mixture was stirred under dry nitrogen for 15 min at −40 °C and then for 3 days at room temperature. Formic acid (4.3 mL, 115 mmol) was then added dropwise at 5 °C and the mixture refluxed for 1 h. The reaction mixture was filtered through Celite, and the solvent was removed in the rotary evaporator. The residue was extracted with concentrated sulfuric acid as in previous procedures and then subjected to MPLC (petroleum ether to CH_2Cl_2). Orange crystals; (petroleum ether−CH_2Cl_2) (0.74 g, 42%); mp 191−193 °C dec. IR (CCl_4, cm^{-1}) ν 2945, 1676 (C=O), 1626, 1553, 1145, 1024; MS (EI, 70 eV, 210 °C) m/z 307 (M^+, 75), 292 (M − 15, 25), 279 (M − 28, 62), 251 (M − 56, 32), 219 (39), 191 (27), 175 (59), 159 (48), 126 (45), 114 (80), 100 (65), 88 (100); HRMS, M^+ = 306.8926 $C_8H_5NO_2S_5$ requires 306.8924. Anal. Calcd for $C_8H_5NO_2S_5$: C, 31.27; H, 1.63; N, 4.56. Found: C, 31.07; H, 1.59; N, 4.51.

4-Ethylbis[1,2]dithiolo[4,5-*b*][5′,4′-*d*]pyrrole-3,5-dithione (4). Disulfur dichloride (4.6 mL, 57.5 mmol) was added dropwise under dry nitrogen to a solution of *N*-ethyldiisopropylamine (1.0 mL, 5.75 mmol) and DABCO (6.44 g, 57.5 mmol) in chlorobenzene (100 mL) at −40 °C. The mixture was stirred under dry nitrogen for 15 min at −40 °C and then for 3 days

at room temperature and then refluxed for 2 h. The reaction mixture was filtered through Celite, and the solvent was removed in the rotary evaporator. The residue was extracted with concentrated sulfuric acid as in previous procedures and then subjected to MPLC (petroleum ether to CH_2Cl_2). Black needles (petroleum ether−CH_2Cl_2) (0.75 g, 42%); mp 242−243 °C. IR (CCl_4, cm^{-1}) ν 1431, 1403, 1294, 1265 (C═S), 1049; MS (EI, 70 eV, 210 °C) *m/z* 309 ($M^+ + 2$, 39), 307 (M^+, 100), 274 (M − 33, 48), 247 (M − 60, 38), 210 (25), 203 (26), 138 (38), 126 (39), 112 (98), 100 (99); HRMS, M^+ = 306.8746 $C_8H_5NS_6$ requires 306.8746. Anal. Calcd for $C_8H_5NS_6$: C, 31.25; H, 1.64; N, 4.55. Found: C, 31.53; H, 1.67; N, 4.27.

4-Ethyl-3-oxobis[1,2]dithiolo[4,5-*b*][5′,4′-*d*]pyrrole-5-thione (5), Disulfur dichloride (4.6 mL, 57.5 mmol) was added dropwise under dry nitrogen to a solution of *N*-ethyldiisopropylamine (1.0 mL, 5.75 mmol) and DABCO (6.44 g, 57.5 mmol) in chlorobenzene (100 mL) at −40 °C. The mixture was stirred under dry nitrogen for 15 min at −40 °C and then for 3 days at room temperature. Formic acid (2.2 mL, 57.5 mmol) was then added dropwise and the mixture refluxed for 2 h. The reaction mixture was filtered through Celite, and the solvent was removed in the rotary evaporator. The residue was extracted with concentrated sulfuric acid as in previous procedures and then subjected to MPLC (petroleum ether to CH_2Cl_2). Red needles (petroleum ether−CH_2Cl_2) (0.42 g, 25%); mp 175−176 °C. IR (CCl_4, cm^{-1}) ν 1680 (C═O), 1442, 1429, 1370, 1350, 1291 (C═S), 1165, 1094, 1036; MS (EI, 70 eV, 210 °C) *m/z* 293 (M^++2, 28), 291 (M^+, 100), 276 (M − 15, 21), 263 (M − 28, 15), 258 (M − 33, 14), 231 (M − 60, 24), 112 (19), 100 (17); HRMS, M^+ = 290.8974 $C_8H_5NOS_5$ requires 290.8975. Anal. Calcd for $C_8H_5NOS_5$: C, 32.97; H, 1.73; N, 4.81. Found: C, 33.17; H, 2.03; N, 4.58.

4-Ethylbis[1,2]dithiolo[4,5-*b*][5′,4′-*d*]pyrrole-3,5-dione (6). Disulfur dichloride (4.6 mL, 57.5 mmol) was added dropwise under dry nitrogen to a solution of *N*-ethyldiisopropylamine (1.0 mL, 5.75 mmol) and DABCO (5.15 g, 46 mmol) in chlorobenzene (100 mL) at −40 °C. The mixture was stirred under dry nitrogen for 15 min at −40 °C and then for 3 days at room temperature. Formic acid (4.3 mL, 115 mmol) was then added dropwise and the mixture refluxed for 7.5 h. The reaction mixture was filtered through Celite, and the solvent was removed in the rotary evaporator. The residue was extracted with concentrated sulfuric acid as in previous procedures and then subjected to MPLC (petroleum ether to CH_2Cl_2). Yellow prisms (petroleum ether−CH_2Cl_2) (0.66 g, 42%); mp 199−200 °C. IR (CCl_4, cm^{-1}) ν 1694 and 1663 (C═O), 1454, 1437, 1343, 1285, 1203, 1159, 1073; MS (EI, 70 eV, 210 °C) *m/z* 277 ($M^+ + 2$, 21), 275 (M^+, 100), 260 (M − 15, 14), 247 (M − 28, 14), 215 (M − 60, 50), 123 (10), 100 (15); HRMS, M^+ = 274.9206 $C_8H_5NO_2S_4$ requires 274.9203. Anal. Calcd for $C_8H_5NO_2S_4$: C, 34.89; H, 1.83; N, 5.09. Found: C, 34.68; H, 2.10; N, 5.15.

Preparation of 9−11. Disulfur dichloride (6.9 mL, 86 mmol) was added dropwise under dry nitrogen to a solution of *N*-ethyldiisopropylamine (15 mL, 86 mmol) in dry THF (150 mL) at −40 °C. The mixture was stirred under dry nitrogen for 15 min at −40 °C then for 3 days at room temperature and then refluxed for 5 h until a dark precipitate appeared in the red solution. The reaction mixture was filtered through Celite, and the green solid on the Celite was washed with dichloromethane (4 × 50 mL). The combined dichloromethane solution was worked up separately, as in previous procedures. The green solid on the Celite was treated with absolute methanol (4 × 25 mL) to give an orange solution from which the solvent was removed in the rotary evaporator. MPLC (petroleum ether to CH_2Cl_2) of the residue afforded compounds **9**−**11**.

***N*-Ethyl-*N*-(3-thiono[1,2]dithiol-4-yl)-4-amino[1,2]dithiole-3-thione (9).** Brown solid (petroleum ether−CH_2Cl_2) (20 mg, 1% based on 1/15 of the starting amine); mp 164−165 °C. IR (CCl_4, cm^{-1}) ν 1545, 1495, 1260 (C═S), 1010; MS (EI, 70 eV, 200 °C) *m/z* 311 ($M^+ + 2$, 21), 309 (M^+, 82), 276 (M − 33, 14), 245 (M − 64, 100), 216 (64); HRMS, M^+ = 308.8899 $C_8H_7NS_6$ requires 308.8903.

***N*-Ethyl-*N*-(3-oxo[1,2]dithiol-4-yl)-4-amino[1,2]dithiole-3-thione (10).** Brown solid (petroleum ether−CH_2Cl_2) (73 mg, 4% based on 1/15 of the starting amine); mp 181−182 °C. IR (CCl_4, cm^{-1}) ν 1645 and 1635 (C═O), 1540, 1505, 1315 (C═S), 1187; MS (EI, 70 eV, 200 °C) *m/z* 295 ($M^+ + 2$, 22), 293 (M^+, 100), 278 (M − 15, 8), 260 (M − 33, 25), 204 (21), 173 (23); HRMS, M^+ = 292.9143 $C_8H_7NOS_5$ requires 292.9131.

4-Ethylamino[1,2]dithiole-3-thione (11). Brown solid (petroleum ether−CH_2Cl_2) (5 mg, 0.5% based on 1/15 of the starting amine); mp 137−138 °C. IR (CCl_4, cm^{-1}) ν 3340 (N−H), 2975, 1545, 1482, 1280 (C═S), 1220, 1110, 990; MS (EI, 70 eV, 200 °C) *m/z* 179 ($M^+ + 2$, 14), 177 (M^+, 100), 162 (M − 15, 26), 149 (M − 28, 17); HRMS, M^+ = 176.9747 $C_5H_7NS_3$ requires 176.9741.

General Procedures for the Interconversion of 1−6. Sulfur Extrusion from 1−3. A solution of 0.59 mmol of **1**, **2**, or **3** in xylene (50 mL) was refluxed for 0.5, 1, and 3 h, respectively. The solvent was removed in the rotary evaporator, and the residue was purified by MPLC, affording **4**, **5**, or **6** quantitatively.

Thiation of 2, 3, 5, and 6. A solution of **2** (0.19 g, 0.59 mmol) or **3** (0.18 g, 0.59 mmol) and phosphorus pentasulfide (1.1 g, 2.47 mmol) in dry THF (50 mL) was refluxed under N_2 for 5 h, following the transformation by TLC. The solvent was removed in the rotary evaporator, and the residue was purified by MPLC (petroleum ether to CH_2Cl_2), affording **1** (0.14 g, 70%). Alternatively, Lawesson's reagent (1 g, 2.47 mmol) may be used in place of P_4S_{10} giving **1** in similar yield. A mixture of **5** (0.17 g, 0.59 mmol) or **6** (0.16 g, 0.59 mmol) and phosphorus pentasulfide (1.1 g, 2.47 mmol) was refluxed in xylene for 1 h affording **4** (0.18 g) almost quantitatively after similar working-up.

Oxidation of 1, 2, 4, and 5. Triethylamine (0.42 mL, 3.0 mmol) was added dropwise to a solution of dithione **1** (0.2 g, 0.59 mmol) and ethyl chlorooximidoacetate (0.36 g, 2.4 mmol) in dry THF (10 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 subjected to MPLC (petroleum ether to CH_2Cl_2-petroleum ether, 5:1) to give **3** (163 mg, 90%). By a similar procedure, triethylamine (0.21 mL, 1.5 mmol), ketothione **2** (0.19 g, 0.59 mmol), and ethyl chlorooximidoacetate (0.18 g, 1.2 mmol) afforded **3** (172 mg, 95%). Analogously, triethylamine (0.23 mL, 1.6 mmol), dithione **4** (0.1 g, 0.33 mmol) or ketothione **5** (96 mg, 0.33 mmol), and ethyl chlorooximidoacetate (0.2 g, 1.4 mmol) afforded **6** (64 mg, 70% from **4**, 68 mg, 75% from **5**). Alternatively, **4** (60 mg, 0.20 mmol) and mercury(II) acetate (0.13 g, 0.4 mmol) were stirred at room temperature for 22 h in a mixture of dichloromethane (10 mL) and acetic acid (5 mL) to give **6** (20 mg, 35%).

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Supporting Information Available: Crystallographic data (excluding structure factors) for the structures reported in Table 2 (28 pages). This material is contained in 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.

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