General Method for the Preparation of Substituted Tetrathiafulvalenes and Directing Effects of Substituents

Dennis C. Green

IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

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A general method for the synthesis of substituted tetrathiafulvalenes is described in which tetrathiafulvalene (TTF) or a substituted derivative of TTF is metalated with butyllithium or lithium diisopropylamide and then reacted with appropriate reagents to give a wide variety of new substituted tetrathiafulvalenes. Electron-donating substituents were found to deactivate the adjacent proton, while electron-withdrawing substituents activated the adjacent proton; thus the sequence in which the substituents are introduced can be utilized to control the structure. Multilithiation, temperature effects, and mode of addition are also discussed in relation to their effects upon substitution patterns.

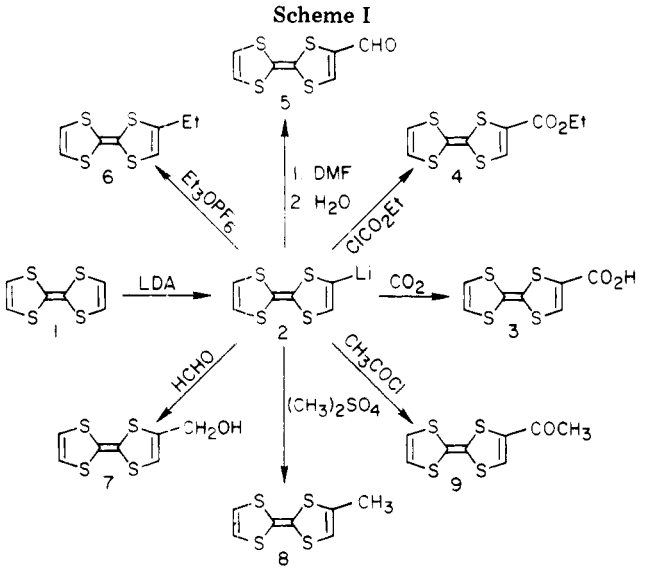
Recent interest in low ionization potential materials such as tetrathiafulvalene (TTF, **1**)[1] has spurred synthetic efforts to prepare various derivatives of **1** to effect modifications in the electron-donating properties of such molecules. The syntheses of symmetrical di- and tetrasubstituted TTF derivatives of **1** have been reviewed by Pittman.[2] Unsymmetrically substituted tetrathiafulvalenes, though, have been more difficult to obtain by the coupling techniques used, and only several have been reported utilizing mixed coupling procedures.[3] More recently a series of unsymmetrical TTF derivatives has been reported by reaction of dithiolium salts with dithiolium phosphoranes[4] and further unsymmetrical derivatives have been prepared by the Hurtley–Smiles synthesis.[5]

However the only derivatives obtained from reactions directly on TTF were radical cation salts[6] until the first monosubstituted TTF derivatives were prepared[7] by reaction of TTF with BuLi and subsequent reaction with CO_2 or $Et_3O^+PF_6^-$. A significant generalization of the lithiation procedure for the synthesis of mono- and multisubstituted tetrathiafulvalenes, as well as the directive effects of various substituents upon further substitution, is reported here.

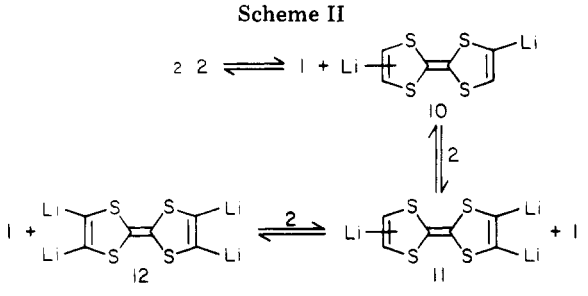
Results

The lithiation of **1**[8] with lithium diisopropylamide[9] (LDA) in ether at −70 °C gave **2**, which reacted with a variety of reagents to produce monosubstituted tetrathiafulvalenes in good yields (generally 30–70%; see Scheme I). Species **2** was found to be very reactive at −70 °C, and at higher temperatures redistribution occurred to give multilithiated products, TTF, and an unidentified product.

Scheme I



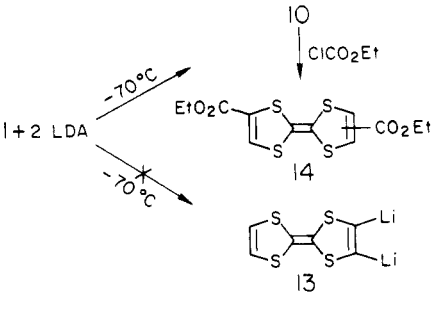
Scheme II



The multilithiated species were observed as their carboxylic acid derivatives when the reaction was carried out at −20 °C or when **2** was initially prepared at −70 °C and then warmed to −20 °C followed by addition to solid CO_2. However at −70 °C, **2** was stable and only a small amount (5%) of the dilithiated species **10** was formed, probably as a result of the reaction of LDA with **2** (Scheme II). Addition of 2 mol of LDA to **1** gave the 2,6(7)-disubstituted adduct **10** but none of the 2,3-disubstituted adduct **13** (Scheme III). However dilithiation of **8** yielded the 6,7 substitution adduct **16** upon addition to ethyl chloroformate (Scheme IV).

The presence of various substituents on **1** was found to exert directing effects that offer control over the position to be lithiated. Electron-donating substituents, such as the methyl group, decreased the acidity of the adjacent proton, and thereby directed substitution to the opposite ring. Conversely, electron-withdrawing groups such as the carboxylate group increased the acidity of the adjacent proton and substitution was then favored in that position on the same ring. Furthermore, variation of the temperature was found to extend the flexibility for the introduction of additional substituents. Protons deactivated by an adjacent methyl group failed to react with LDA at −70 °C, but at 25 °C the lithiation reaction indeed occurred. Thus 2,6(7)-dimethyltetrathiafulvalene **17** was inert to lithiation reagents at low temperature, although

Scheme III



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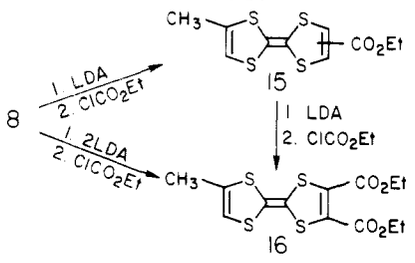
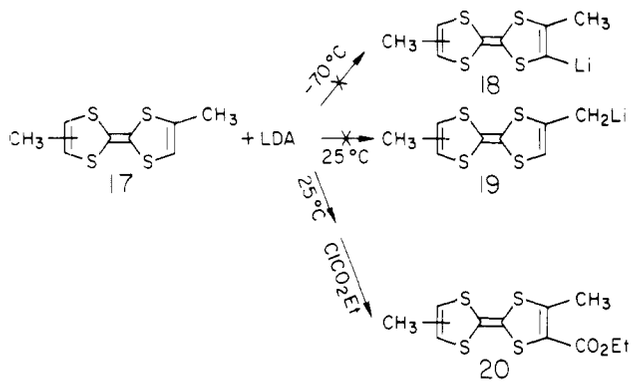
Scheme IV



Scheme V



substitution was effected at room temperature (Scheme V). The methyl protons were found to be unreactive toward the lithiation reagents and no substitution on the methyl group was observed at temperatures up to 25 °C.

The order of addition of reagents was found to be important in the preparation of some of the TTF derivatives. Normal addition of **2** to an excess of ethyl chloroformate gave the expected ester **4**. However, inverse addition of the ethyl chloroformate to **2** yielded 3-(ethoxycarbonyl)-2-tetrathiafulvalenyl 2′-tetrathiafulvalenyl ketone (**24**).

Discussion

The very property that makes TTF interesting as the donor component in charge-transfer salts (i.e., low ionization potential) also makes it difficult to substitute directly by most known methods. The common methods for introducing substituents onto thiophene, such as halogenation or chloromercuration, yield only the radical cation or dication salts when attempted on TTF.[6] This is due to the large difference in the oxidation potentials (thiophene +2.1 V; TTF +0.34 V).[10] Thus, substitution reactions can be effected only by utilizing nonoxidizing reagents such as butyllithium.

This direct substitution method has the advantage of increased versatility compared to the previously mentioned methods of the coupling of two substituted precursor moieties, where introduction of a functional group is limited by the incompatibility of many functional groups with the coupling reagents. As an example, the aldehyde or carboxylic acid functional groups would react with the phosphorus base used in the coupling reaction. It has the additional advantages that the starting material is commercially available and there are few separation problems, since most of the products are easily isolated by recrystallization or column chromatography. An exception, however, is found in the preparation of alkylated derivatives such as **6** and **8**. Because small amounts of **1** and the disubstituted derivative are inherent in the reaction mixtures, purification in such cases is difficult.

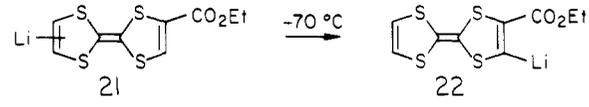
Further substitution of the TTF derivatives is sensitive to temperature/substituent effects. The temperature at which the exchange reaction of **2** to form **10** occurs is substituent dependent. For instance **18** failed to undergo exchange even

Table I. Oxidation Potentials[a] of Tetrathiafulvalene Derivatives

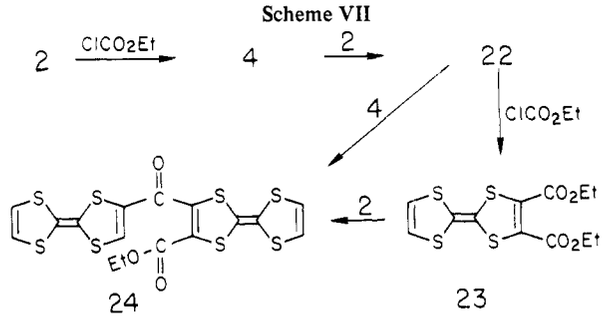
compd	registry no.	E_1	E_2
17		0.32	0.68
8	54397-94-3	0.33	0.70
6	63822-41-3	0.33	0.70
1	31366-25-3	0.34	0.71
7	68128-93-8	0.41	0.79
3	63822-38-8	0.47	0.83
9	67361-90-4	0.47	0.83
5	68128-94-9	0.53	0.89
20		0.43	0.79
15		0.45	0.81
4	63822-39-9	0.47	0.83
16	68128-95-0	0.54	0.87
23	68128-96-1	0.57	0.91
14		0.60	0.94
24	68128-97-2	0.52 and 0.60	0.92

[a] Peak potentials, volts vs. SCE, CH_3CH, 0.1 M tetraethylammonium perchlorate, 0.2 V/s sweep rate, Pt electrode.

Scheme VI



Scheme VII



at 25 °C, inhibited by the methyl group, while the parent system **2** exchanged at about −20 °C. Conversely, the presence of an electron-withdrawing group, such as in **4**, accelerated the exchange reaction so that it occurred even at −70 °C. This might explain why **23** was formed exclusive of the 2,6(7) adduct **14** when **4** was lithiated and added to ethyl chloroformate. Formation of **21** is possible to some extent in the addition of LDA to **4** since **1** reacts with LDA at −70 °C, although direct formation of **22** is most likely since the proton adjacent to the ester group is more acidic. If formed, **21** might undergo exchange to yield **22** (Scheme VI). However in the preparation of **14**, **21** should be an intermediate of the reaction of **10** with ethyl chloroformate, but no 2,3 product is observed; therefore metalation of **4** must form **22** directly.

The dilithiation of **1** gave an approximate 1:1 mixture of the 2,6 and 2,7 isomers as indicated in the NMR spectrum of **14**. The ring protons adjacent to the carboxyl groups appear as two equal singlets separated by 1 Hz, whereas the monosubstituted derivative **4** shows no splitting. The melting range is also broad, indicating a mixture of isomers. Reaction of **8**, however, with 2 mol of LDA gave **16** upon reaction with ethyl chloroformate. It is not known with certainty whether the 6,7-dilithio species is formed at −70 °C or if a stepwise reaction is involved. It appears, though, that the stepwise mechanism is favored since the same reaction with dimethyl sulfate showed mainly **17** and only a trace of 2,3,5-trimethyltetra-

thiafulvalene upon GC/MS analysis of the reaction mixture.

In regard to lithiation of substituted tetrathiafulvalenes, the temperature/substituent effects were particularly apparent upon inverse addition of ethyl chloroformate to **2**, which yielded **24** (Scheme VII). The mechanism of this reaction must first involve formation of **22**. The conditions of inverse addition favor such a pathway since the initially formed **4** is in the presence of a large excess of **2**. Once formed, **22** could then react with **4** to displace the ethoxy group and give **24**. No bis(2-tetrathiafulvalenyl) ketone was detected, indicating that reaction of **22** with **4** may be the preferred route, although a separate reaction of **23** with **2** also gave **24**. A stoichiometric reaction of **2** with **4** also failed to yield the bis(2-tetrathiafulvalenyl) ketone, but instead gave **24** and unreacted **4**.

Since the oxidation potentials of these materials are a measure of their donor strength, these values are listed in Table I. Alkyl substitution decreased the oxidation potential of TTF slightly as seen in the first four compounds listed, while the electron-withdrawing substituents increased the oxidation potentials to a greater and varying degree as in the next four entries. Methyl substitution had a greater effect though on compounds containing an electron-withdrawing substituent. Two methyl substituents decreased the E_1 value of TTF by only 20 mV, while two methyl groups decreased the E_1 values of compound **4** by 40 mV; and one methyl group lowered the E_1 value for the dicarboxylate **23** by 30 mV as in compound **16**. Thus the utility of functionalized TTF's as electron-donor systems is increased by alkyl substitution. Two electron-withdrawing groups on TTF increase the ionization potential sufficiently to preclude formation of charge-transfer salts with TCNQ, while the monofunctionalized derivatives have low enough ionization potentials to do so.[7] Alkyl substitution of derivatives such as **23** or **14** then tends to counteract this effect of increasing the ionization potential beyond the useful limits.

The cyclic voltammogram of **24** exhibits two reversible waves for the first oxidation and a two-electron wave for formation of the bis dication. This represents the first example of a system containing multiple TTF moieties and having multiple oxidation states.

The functionalized derivatives, particularly the monofunctional compounds, are of paramount importance in attaching TTF to other molecular systems such as polymers. Previous attempts at incorporating TTF into polymer systems[11-13] have been based on condensation polymers using difunctionalized TTF monomers such as the diisocyanate or dicarboxamide. These electron-withdrawing substituents raise the ionization potential sufficiently so that charge-transfer salts are no longer formed. Alkyl substitution at the vacant positions on TTF might help, but such polymers suffer from a further drawback in that the TTF is within the polymer backbone. It therefore lacks the necessary degree of freedom to arrange itself into a stacked structure,[13,14] which is required in the monomeric systems that display interesting solid-state electrical properties.

However derivatives **3** and **7** can be attached to functionalized polymers such as chloromethylated polystyrene to form TTF containing polymers with TTF *pendant* to the backbone. This provides for a well-characterized polymer and still allows TTF its necessary mobility. The properties of these polymers will be the subject of future publications.[14]

It can readily be seen from these initial results that considerable flexibility and substituent control are offered through this general method for the preparation of new TTF systems. Therefore, optimization of the unique electronic properties of these novel materials, through structure modification, can now be approached in a more systematic manner.

Experimental Section

All reactions were carried out under an atmosphere of argon or nitrogen. Diethyl ether was distilled from Na/Ph_2CO and stored under argon. TTF[8] and LDA (Ventron) were used as purchased without further purification. Melting points are uncorrected. Analyses were performed by Childers Laboratories and Galbraith Laboratories. Electrochemical data[10] were obtained by cyclic voltammetry using a Tacussel PRT-100-1X potentiostat driven by a Princeton Applied Research Model 175 Universal Programmer. NMR spectra were recorded on a Varian A60 spectrometer, and mass specta were obtained using a Hewlett Packard 5992A GC/MS system.

Tetrathiafulvalenyllithium (2). A solution of 5 mmol (0.535 g) of LDA in 20 mL of ether was added over 15 min to a solution of 5 mmol (1.02 g) of **1** in 100 mL of ether at −60 to −70 °C. A yellow precipitate formed near the end of the addition. The slurry was stirred for 15 min at −70 °C before utilization in further reactions.

2-Carboxytetrathiafulvalene (3). A slurry of 5 mmol of **2** at −70 °C was pressed (N_2 pressure) through a Teflon tube inserted through a septum cap into a flask containing solid CO_2 and ether. The mixture was warmed to 15 °C and the solvent was evaporated. H_2O (25 mL) was added and the mixture was filtered to remove unreacted **2** (0.535 g). The solution was then acidified with 1 M HCl and the red precipitate (0.88 g) was collected. Recrystallization from benzene gave 0.75 g (60% yield) of red needles: mp 182–184 °C dec; UV λ_{max} (0.1 M NaOH) 301 (ϵ 6900), 313 (7100), and 420 nm (100); IR (KBr) 1660 cm^{-1} (C=O); NMR [$(CD_3)_2CO$, Me_4Si reference] δ 7.6 (1 H, s, CH), 6.7 (2 H, s, CH), and 5.35 (1 H, s, CO_2H); mass spectrum *m/e* 248. Anal. Calcd for $C_7H_4O_2S_4$: C, 33.85; H, 1.62; O, 12.89; S, 51.64. Found: C, 34.03; H, 1.50; O, 13.03; S, 51.18.

The reaction was repeated and the solution of **2** was heated to −20 °C before addition to CO_2. TLC (cellulose, 99% EtOH) of the mixture showed the presence of the mono-, di-, tri-, and tetracarboxy derivatives of **1** compared to authentic samples of the mono-, di-, and tetracarboxytetrathiafulvalenes.

2-(Ethoxycarbonyl)tetrathiafulvalene (4). Method A. A slurry of 5 mmol of **2** was pressed (N_2 pressure) into a flask containing 25 mmol of ethyl chloroformate in 100 mL of ether at −70 °C and the solution was allowed to warm to 20 °C. The mixture was added to water and extracted with ether. The ether layer was dried over anhydrous $MgSO_4$ and the solvent was removed under vacuum. Dry column chromatography on grade III silica gel (4.5 × 10 cm column) yielded upon elution with 3:1 hexane/benzene 0.69 g of **4** (50% yield): red crystals from methanol; mp 79.5–80.5 °C; UV λ_{max} (CH_3CN) 292 sh (ϵ 11 800), 303 (12 900), 314 (13 600), 424 nm (1920); IR 1690 cm^{-1} (C=O); NMR (CCl_4, Me_4Si reference) δ 7.3 (1 H, s, CH), 6.3 (2 H, s, CH), 4.25 (2 H, q, CH_2, J = 7 Hz), 1.35 (3 H, t, CH_3, J = 7 Hz). Anal. Calcd for $C_9H_8O_2S_4$: C, 39.1; H, 2.89; O, 11.6; S, 46.4. Found: C, 39.50; H, 2.97; O, 11.81; S, 45.95.

Method B. A solution of 5 mmol of **2** in 50 mL of ether at −70 °C was prepared as above but the $ClCO_2Et$ (5 mmol) in 20 mL of ether was added dropwise over 15 min to the solution of **2**. The mixture was worked up and purified as in method A to give 0.7 g (51% yield) of **4** and 0.3 g (24% yield) of **24**, which was recrystallized from isooctane to give purple needles: mp 159–160 °C; UV λ_{max} (CH_3CN) 214 sh (ϵ 18 600), 253 sh (15 000), 290 sh (28 000), 304 (30 800), 314 (31 700), 475 (2700), 528 nm (3630); IR 1700 (C=O ester), 1625 cm^{-1} (C=O ketone); NMR ($CDCl_3$, Me_4Si reference) δ 7.45 (1 H, s, CH), 6.35 (4 H, s, CH), 4.25 (2 H, q, J = 7 Hz, CH_2), 1.27 (3 H, t, J = 7 Hz, CH_3); mass spectrum *m/e* 506. Anal. Calcd for $C_{16}H_{10}O_3S_8$: C, 37.99; H, 1.97. Found: C, 38.27; H, 2.28.

2-Formyltetrathiafulvalene (5). A solution of 5 mmol of **2** was pressed into a flask containing 50 mmol of dimethylformamide in 100 mL of ether at −70 °C. The mixture was warmed to 20 °C and added to H_2O, extracted with ether, and dried over $MgSO_4$. After purification on a silica gel column, the adduct was recrystallized from isooctane to yield 0.5 g (44% yield) of red needles: mp 110–111 °C; UV λ_{max} (CH_3CN) 238 (ϵ 1620), 285 (13 300), 298 (13 300), 312 (12 900), 462 nm (2260); IR 2810 and 1660 cm^{-1} (CHO); NMR (CD_3Cl, Me_4Si reference) δ 9.52 (1 H, s, CHO), 7.48 (1 H, s, CH), 6.38 (2 H, s, CH). Anal. Calcd for $C_7H_4OS_4$: C, 36.19; H, 1.72; O, 6.89; S, 55.20. Found: C, 35.97; H, 1.76; O, 7.19; S, 54.94.

2-Ethyltetrathiafulvalene (6). To a solution of 5 mmol of **2** at −70 °C was added 10 mmol of Et_3OPF_6 in ether. The yellow oil obtained (1.1 g of 50:50 TTF/EtTTF) was purified by dry column chromatography on grade III alumina using hexane as eluent. A narrow portion of the product band was shown to contain 5% TTF by mass spectrometry: IR 3080, 2980, 1490, 800, 780, and 650 cm^{-1}; NMR (CCl_4 relative to Me_4SI) δ 6.30 (2 H, s, CH), 5.85 (1 H, t, J = 1.5 Hz, CH), 2.45 (2 H, q, J = 7 Hz, CH_2), 1.25 (3 H, t, J = 7 Hz, CH_3).

2-(Hydroxymethyl)tetrathiafulvalene (7). Formaldehyde gas

(from 50 mmol of paraformaldehyde heated to 180 °C under a nitrogen stream) was passed through a solution of 5 mmol of **2** in ether at −70 °C. When the addition was complete, cooling was discontinued and the mixture was allowed to warm to 20 °C. H_2O containing 5 mL of 1 M HCl was added and the mixture was extracted with ether and purified on a silica gel column. Elution first with benzene removed the unreacted TTF and then with acetone gave the product, which was obtained as a yellow oil (0.4 g, 34% yield). Recrystallization from isooctane/toluene gave yellow crystals (mp 70–71 °C). This material decomposed on standing unless stored under an inert atmosphere: UV λ_{max} (CH_3CN) 309 (ϵ 13 200), 316 (13 400), 353 (2300), 452 nm (244); IR ($HCCl_3$) 3300, 3200, 3040, 3010, 3000, 2405, 1380, 1240, 1200, 1110, 1030, 800, and 650 cm^{-1}; NMR ($CDCl_3$, Me_4Si reference) δ 6.30 (2 H, s, CH), 6.23 (1 H, t, J = 1.5 Hz, CH), 4.40 (2 H, s, CH_2), 2.0 (1 H, s, OH). Anal. Calcd for $C_7H_6OS_4$: C, 35.85; H, 2.56; S, 54.60. Found: C, 35.97; H, 2.53; S, 54.62.

2-Methyltetrathiafulvalene (8). A 15-mmol solution of **2** (prepared using a 10% excess of LDA) was added to an ether solution of 150 mmol of Me_2SO_4 at −70 °C. The mixture was worked up as usual and dry column chromatographed using a nylon foil column on grade III basic alumina with hexane as the eluent. The first third of the yellow band was cut out and extracted to give 0.62 g of a yellow oil (80% **8** and 20% **16**). The remainder of the band contained **1**, **8**, and **16**: NMR (CCl_4, Me_4Si reference) δ 6.30 (2 H, s, CH), 5.85 (1 H, q, J = 1 Hz, CH), 2.05 (3 H, d, J = 1 Hz, CH_3); mass spectrum m/e (relative intensity) 218 (100), 173 (41), 146 (32), 116 (36), 102 (52), 88 (54), 76 (67), 45 (30).

2-Acetyltetrathiafulvalene (9). A solution of 5 mmol of **2** was pressed into a flask containing 25 mmol of acetyl chloride in ether at −70 °C. The mixture was warmed slowly to 20 °C and the ether and excess acetyl chloride were removed under vacuum. The residue was purified on a silica gel column using 3:1 hexane/benzene as eluent to give 0.8 g (67% yield) of red needles from isooctane: mp 152–153 °C; UV λ_{max} (CH_3CN) 235 (ϵ 5650), 285 (9600), 300 (9800), 312 (10 200), 455 nm (1940); IR 1635 cm^{-1} (C=O); NMR ($CDCl_3$, Me_4Si reference) δ 7.32 (1 H, s, CH), 6.35 (2 H, s, CH), 2.40 (3 H, s, CH_3). Anal. Calcd for $C_8H_6OS_4$: C, 39.10; H, 2.44; O, 6.51; S, 52.10. Found: C, 39.09; H, 2.42; O, 6.57; S, 51.90.

2,6(7)-Bis(ethoxycarbonyl)tetrathiafulvalene (14). To 5 mmol of TTF in 100 mL of ether at −70 °C was added 10 mmol of LDA in 10 mL of ether. This slurry was pressed into a flask containing 50 mmol of $ClCO_2Et$ in 50 mL of ether at −70 °C and slowly warmed to 25 °C. Purification on a grade III alumina column eluting with 1:1 chloroform/hexane gave 0.5 g of **4** and 0.1 g of red crystals: mp 140–160 °C (cis-trans mixture) (lit. 169–172 °C);[13] IR (KBr) 1700 cm^{-1} (C=O); NMR δ 7.27 (1 H, s, CH), 7.28 (1 H, s, CH), 4.25 (4 H, q, J = 7 Hz, CH_2), 1.33 (6 H, t, J = 7 Hz, CH_3).

2-Methyl-6(7)-(ethoxycarbonyl)tetrathiafulvalene (15). To an ether solution of 0.88 mmol of **8** at −70 °C was added 0.8 mmol of LDA in ether. The mixture was pressed into a flask containing excess $ClCO_2Et$ in ether at −70 °C. After normal workup, chromatography and recrystallization from isooctane gave a yellow solid (35% yield): mp 67–70 °C (mixture of isomers); UV λ_{max} (CH_3CN) 214 (ϵ 10 000), 294 (11 000), 303 (11 400), 313 (12 000), 432 nm (1500); IR (neat) 1695 cm^{-1} (C=O); NMR (CCl_4, Me_4Si reference) δ 7.30 (1 H, s, CH), 5.85 (1 H, q, J = 1 Hz, CH), 4.25 (2 H, q, J = 7 Hz, CH_2), 2.10 (3 H, d, J = 1 Hz, CH_3), 1.3 (3 H, t, J = 7 Hz, CH_3); mass spectrum m/e (relative intensity) 290 (62) 262 (100), 173 (28), 160 (69), 116 (30), 88 (30), 76 (37). Anal. Calcd for $C_{10}H_{10}O_2S_4$: C, 41.4; H, 3.5; S, 44.1. Found: C, 41.47; H, 3.66; S, 43.65.

2-Methyl-6,7-bis(ethoxycarbonyl)tetrathiafulvalene (16). Method A. **8** (0.5 mmol) was reacted with 1 mmol of LDA in ether at −70 °C. This mixture was added to 5 mmol of $ClCO_2Et$ in ether at −70 °C. The usual workup and chromatography gave a 30% yield of **15**. Recrystallization from hexane gave purple crystals: mp 33–34 °C; UV λ_{max} (CH_3CN) 293 (ϵ 13 700), 316 (13 800), 447 nm (1450); IR (neat) 1720 cm^{-1} (C=O); NMR (CCl_4, Me_4Si reference) δ 5.85 (1 H, q, J = 1 Hz, CH), 4.25 (4 H, q, J = 7 Hz, CH_2), 2.05 (3 H, d, J = 1 Hz, CH_3), 1.3 (6 H, t, J = 7 Hz, CH_3); mass spectrum m/e (relative intensity) 362 (70), 262 (100), 160 (86), 116 (22), 84 (20), 29 (24). Anal. Calcd for $C_{13}H_{14}O_4S_4$: C, 43.10; H, 3.90; O, 17.65; S, 35.35. Found: C, 42.94; H, 3.74; O, 17.71; S, 35.78.

Method B. Equimolar amounts of **15** and LDA were reacted in the usual manner. Reaction with $ClCO_2Et$ and workup and purification as for method A gave a 40% yield of **15**.

2,6(7)-Dimethyl-7(6)-(ethoxycarbonyl)tetrathiafulvalene (20). To 4.3 mmol of **17**[15,16] in 100 mL of ether at −70 °C was added 4.3 mmol of LDA in 10 mL of ether. No reaction was observed (TLC sample treated with $ClCO_2Et$) until the mixture was brought to 25 °C and stirred for 1 h. Then 21.5 mmol of $ClCO_2Et$ was added. Normal workup and chromatography yielded 50 mg (3.8% yield) of **20** which was recrystallized from hexane: mp 62–64 °C; UV λ_{max} (CH_3CN) 212 nm (ϵ 9700), 289 (8900), 310 (9200), 319 (9600), 415 (1300); IR (neat) 1701 cm^{-1} (C=O); NMR (CCl_4, Me_4Si reference) δ 5.85 (1 H, q, J = 1 Hz, CH), 4.2 (1 H, q, J = 7 Hz, CH_2), 2.40 (3 H, s, CH_3), 2.05 (3 H, d, J = 1 Hz, CH_3), 1.3 (3 H, t, J = 7 Hz, CH_3); mass spectrum m/e (relative intensity) 304 (75), 276 (80), 217 (45), 160 (100), 116 (56), 88 (23), 76 (33), 71 (31), 45 (27), 29 (24). Anal. Calcd for $C_{11}H_{12}O_2S_4$: C, 43.40; H, 4.0; O, 10.5; S, 42.10. Found: C, 43.19; H, 3.93; O, 10.74; S, 42.03.

2,3-Bis(ethoxycarbonyl)tetrathiafulvalene (23). To 2.6 mmol of **4** in 200 mL of ether at −75 °C was added 2.6 mmol of LDA in 20 mL of ether. This was stirred for 15 min at −75 °C and pressed into a flask containing an excess of $ClCO_2Et$ in ether at −75 °C. After normal workup and chromatography there was obtained 0.2 g of **4**, 0.13 g of **24**, and 0.30 g (33% yield) of **23**. Recrystallization of **23** from isooctane gave purple needles: mp 63 °C; UV λ_{max} (CH_3CN) 292 (ϵ 17 700), 302 (18 750), 314 (19 500), 460 nm (1060); NMR ($CDCl_3$, Me_4Si reference) δ 6.30 (2 H, s, CH), 4.25 (4 H, q, J = 7 Hz, CH_2), 1.30 (6 H, t, J = 7 Hz, CH_3); mass spectrum m/e (relative intensity) 348 (46), 248 (81), 203 (16), 146 (100), 102 (24), 88 (22), 76 (18), 70 (19), 29 (19). Anal. Calcd for $C_{12}H_{12}O_4S_4$: C, 41.40; H, 3.47. Found: C, 41.41; H, 3.59.

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Registry No.—**2**, 63822-37-7; **14** isomer 1, 42770-32-1; **14** isomer 2, 42770-33-2; **15** isomer 1, 68128-98-3; **15** isomer 2, 68128-99-4; **17** isomer 1, 54397-96-5; **17** isomer 2, 54397-97-6; **19** isomer 1, 68129-00-0; **20** isomer 1, 68129-01-1; ethyl chloroformate, 541-41-3.

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(8) TTF was purchased from the Aldrich Chemical Co.
(9) LDA was used in place of butyllithium because it is less nucleophilic and is therefore more suitable for use in the presence of substituents such as the ester group, since it does not attack the carbonyl of the ester.
(10) Peak potential, volts vs. SCE, 0.1 M tetraethylammonium perchlorate, CH_3CN, Pt electrode, 0.2 V/s.
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