

Preparation and Cycloaddition Reactions of Some  $\alpha\beta$ -Unsaturated Dithioesters

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$\beta$ -Hydroxydithioesters (**5**) are obtained *via* treatment of mixtures of methyl dithioacetate and the appropriate carbonyl compound with sodium hydride in tetrahydrofuran.  $\alpha\beta$ -Unsaturated dithioesters (**1**) can be prepared from (**5**) by way of suitable elimination reactions. Cycloadducts are formed by the reaction of (**1**) with a number of dienophiles and one diene.

Although dithioesters have been known for many years,<sup>1</sup> it is only recently that  $\alpha\beta$ -unsaturated dithioesters have attracted attention. Preparative approaches to these compounds (**1**) which have been investigated include: (a) reaction of a vinyl cuprate with carbon disulphide followed by methyl iodide;<sup>2</sup> this is successful for compounds (**1a**–**c**), but attempts to make the dithioester (**1d**) in this way gave its dimer; (b) sulphhydrolysis at  $-75^\circ\text{C}$  of the immonium salt derived by *S*-methylation of the thioamide (**2**) gave the phenyl derivative (**1e**)<sup>3</sup> which dimerised above  $-30^\circ\text{C}$ ; (c) base-catalysed isomerisation of  $\beta\gamma$ -unsaturated dithioesters,<sup>4</sup> in turn prepared from *N*-phenyliminothioesters, gave (**1a**) and, at  $-40^\circ\text{C}$ , (**1f**) which dimerised at room temperature; and (d) flash pyrolysis of the bridged anthracene (**3**) and trapping of the product in a matrix at  $-196^\circ\text{C}$  gave the parent dithioacrylate (**1g**).<sup>4</sup>

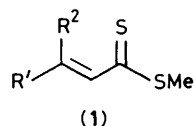
We were interested in  $\alpha\beta$ -unsaturated dithioesters as potential heterodienes or heterodienophiles in cycloaddition reactions,<sup>5</sup> and we describe in this paper their preparation from  $\beta$ -hydroxydithioesters and some cycloadditions in which they are involved. Subsequent to the completion of our work it was reported that addition of Grignard reagents to  $\beta$ -ketodithioesters gave 3,3-disubstituted  $\beta$ -hydroxydithioesters, and the latter were dehydrated to 3,3-disubstituted  $\alpha\beta$ -unsaturated dithioesters on treatment with toluene-*p*-sulphonic acid in benzene at reflux.<sup>6</sup>

In 1978 a preparation of the  $\beta$ -hydroxydithioester (**4**) was described<sup>7</sup> involving treatment of ethyl dithioacetate with lithium di-isopropylamide (LDA) in tetrahydrofuran (THF) followed by isobutyraldehyde at  $-78^\circ\text{C}$ .

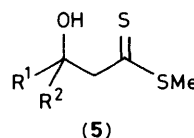
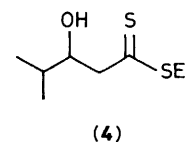
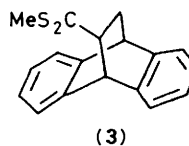
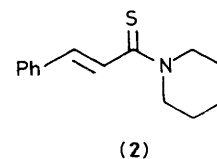
We find that the  $\beta$ -hydroxydithioesters (**5a**–**c**) are obtained in about 60% yield after addition of a solution of methyl dithioacetate and the appropriate carbonyl compound in THF to a suspension of sodium hydride in THF at  $-20^\circ\text{C}$ . In the case of the propanedithioate (**5d**) only poor yields (10–15%) were obtained, using gaseous formaldehyde with LDA as base at  $-45^\circ\text{C}$ .

Thus the reaction of a metallated dithioacetate with an aldehyde or a ketone appears to be a generally useful method for the preparation of  $\beta$ -hydroxydithioesters. The efficient attack at carbon may be contrasted with the reaction with an alkyl halide which leads, *via* attack at sulphur, to a ketene dithioacetate.<sup>8</sup>

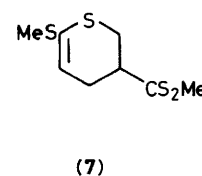
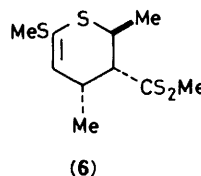
A number of elimination reactions were performed on the  $\beta$ -hydroxydithioester (**5**) or its derivatives in order to establish the conditions for the formation of the corresponding  $\alpha\beta$ -unsaturated dithioesters. In the case of compound (**5a**), treatment with phosphorus oxychloride in pyridine (0  $\rightarrow$   $20^\circ\text{C}$ ) gave the stable dithioester (**1a**) which showed no tendency to dimerise. Treatment of compound (**5b**) with phosphorus oxychloride in pyridine at  $-45^\circ\text{C}$  or of the trifluoroacetate of (**5b**) with pyridine (1 equiv.) or 2,6-dimethylpyridine (1 equiv.) in toluene gave methyl dithiocrotonate (**1f**) which readily dimerised to the [4 + 2]-adduct (**6**) at room temperature in



- a;  $R^1 = R^2 = \text{Me}$       e;  $R^1 = \text{Ph}, R^2 = \text{H}$   
 b;  $R^1 = R^2 = \text{Bu}^n$     f;  $R^1 = \text{Me}, R^2 = \text{H}$   
 c;  $R^1 = \text{Bu}^t, R^2 = \text{H}$     g;  $R^1 = R^2 = \text{H}$   
 d;  $R^1 = \text{Bu}^n, R^2 = \text{H}$



- a;  $R^1 = R^2 = \text{Me}$   
 b;  $R^1 = \text{Me}, R^2 = \text{H}$   
 c;  $R^1 = \text{Ph}, R^2 = \text{H}$   
 d;  $R^1 = R^2 = \text{H}$



agreement with the findings of other workers.<sup>4</sup> Methyl dithioacrylate (**1g**) was not isolable, and treatment of the trifluoroacetate of (**5d**) with pyridine (1 equiv.) in toluene gave the dimer (**7**)<sup>4</sup> together with some polymer and unchanged starting material.

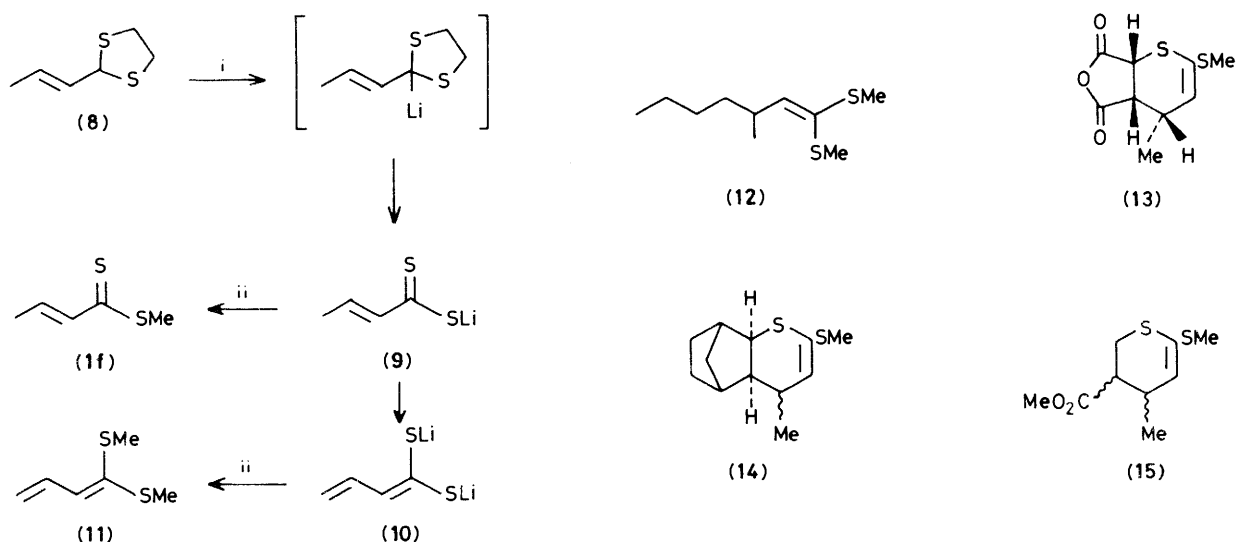
Clearly the elimination reactions of  $\beta$ -hydroxydithioester derivatives provide a convenient route to  $\alpha\beta$ -unsaturated dithioesters. The stability of the latter compounds is highly dependent on the degree of substitution at the  $\beta$ -carbon, and unless they are disubstituted ready dimerisation occurs.

An attempt was also made to prepare the  $\alpha\beta$ -unsaturated dithioester (**1f**) *via* metallation–cycloelimination<sup>9</sup> involving the

Table. Reaction of methyl dithiocrotonate (**1f**) with some dienophiles

Entry	Dienophile	Source of ( <b>1f</b> )	Product	Yield (%)
1	Maleic anhydride	( <b>5b</b> )-POCl <sub>3</sub> -pyridine <sup>a</sup>	( <b>13</b> )	20
2	Maleic anhydride	Trifluoroacetate of ( <b>5b</b> )- 2,6-dimethylpyridine <sup>b</sup>	( <b>13</b> )	80
3	Norbornene	Acetate of ( <b>5b</b> )- di-isopropylamine <sup>b</sup>	( <b>14</b> )	59
4	Methyl acrylate	Acetate of ( <b>5b</b> )- di-isopropylamine <sup>b</sup>	( <b>15</b> )	58
5	1-Piperidinopropene	Acetate of ( <b>5b</b> ) <sup>b</sup>	( <b>16</b> )	96 <sup>c</sup>
6	1-Morpholinocyclohexene	Acetate of ( <b>5b</b> ) <sup>b</sup>	( <b>17</b> )	100 <sup>c</sup>

<sup>a</sup> (**1f**) generated *ex situ*. <sup>b</sup> (**1f**) generated *in situ*. <sup>c</sup> Crude yield.

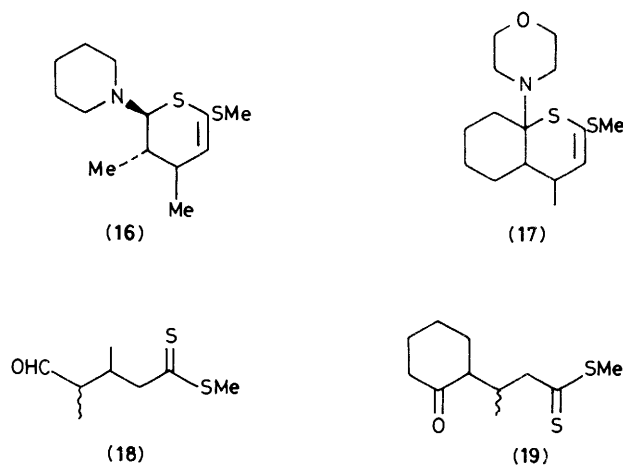


Scheme. Reagents: i, LDA-THF, -70 °C; ii, MeI

crotonaldehyde dithioacetal (**8**)<sup>10</sup> as shown in the Scheme. In practice, after treatment with methyl iodide, a mixture of the dithioester (**1f**), the ketene dithioacetal (**11**), and unchanged starting material (**8**) was obtained, the ratio depending on the conditions. Presumably, the first formed elimination product (**9**) underwent further deprotonation giving the derivative (**10**) and hence the ketene dithioacetal (**11**) after methylation. Treatment of the dithioacetal (**8**) in light petroleum-THF (4:1) with Bu<sup>n</sup>Li followed after 1 h by addition of methyl iodide gave, as the major product isolated, the ketene dithioacetal (**12**); this is considered to have been formed *via* conjugate addition of Bu<sup>n</sup>Li to compound (**9**).

Products were obtained from the reaction of some dienophiles with methyl dithiocrotonate (**1f**) and the results are summarised in the Table. The enamine adducts (entries 5 and 6) appeared to be single diastereoisomers; they were rather sensitive to hydrolysis, the former being hydrolysed on attempted chromatography on silica gel to give a compound considered to be the formyl dithioester (**18**), and the latter with aqueous HCl giving what is presumably the analogue (**19**).\*

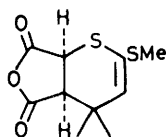
Thus, the dithioester (**1f**) acts effectively as a diene towards electron deficient and electron rich dienophiles. Although the strained olefin norbornene (8,9,10-trinorborn-2-ene) is sufficiently reactive to give an adduct with (**1f**), the simple olefin



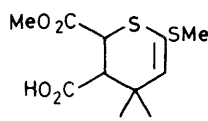
cyclopentene is not. Assuming that the HOMO and LUMO energies and coefficients can be approximated by those calculated for methyl vinyl thioester,<sup>11</sup> the orientation found for the addition of (**1f**) to methyl acrylate, Table (entry 4), is that expected on the basis of frontier orbital considerations.<sup>12</sup> However, the orientation assigned to the enamine adducts (**16**) and (**17**) is the opposite of that expected by such considerations. This may imply that the enamine addition occurs in a stepwise fashion through a zwitterionic intermediate.<sup>13</sup>

For comparison purposes, the addition of maleic anhydride to the stable dithioester (**1a**) was investigated, and found to occur under somewhat more vigorous conditions (toluene

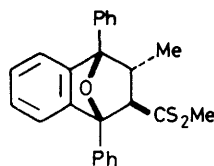
\* In the formation of both (**18**) and (**19**), epimerisation occurred so they were obtained as mixtures of diastereoisomers.



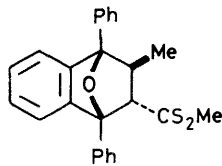
(20)



(21)



(22a)



(22b)

reflux; 15 h) to give the adduct (20), characterised as the half ester (21)\* obtained on treatment of (20) with potassium hydroxide in methanol.

It was also of interest to find out whether methyl dithiocrotonate (1f) would be forced to react as a dienophile with a suitably reactive diene and whether addition would occur to C=S or C=C. In fact, compound (1f) turns out to be a reluctant dienophile and it did not give an adduct with furan or with 2,3-dimethylbuta-1,3-diene. Towards cyclopentadiene it behaved as a diene, as described in the following paper,<sup>14</sup> and only with 1,3-diphenylisobenzofuran was an adduct of the desired type obtained. Spectroscopic data indicated that the adduct was a mixture of the stereoisomers (22a) and (22b), and hence that addition had occurred to C=C.

### Experimental

<sup>1</sup>H N.m.r. spectra were recorded with a Perkin-Elmer R 24 (60 MHz) or R 32 (90 MHz) (Me<sub>4</sub>Si as internal standard), or a Bruker WH 300 (300 MHz) (CHCl<sub>3</sub> as internal standard) instrument. <sup>13</sup>C N.m.r. spectra were recorded with Bruker WH 90 spectrometer operating at 22.63 MHz or a Bruker WH 300 instrument operating at 75.57 MHz for solutions in CDCl<sub>3</sub>. Chemical shifts are quoted in p.p.m. downfield of internal Me<sub>4</sub>Si. Ether refers to diethyl ether. Light petroleum refers to the fraction with b.p. 40–60 °C.

**Methyl 3-Hydroxy-3-phenylpropanedithioate.**—To a stirred suspension of sodium hydride (0.5 g, 10.4 mmol) in dry THF (10 ml) under nitrogen at –40 °C was added during 20 min, a solution of methyl dithioacetate<sup>15</sup> (0.91 g, 8.6 mmol) and benzaldehyde (0.96 g, 9.1 mmol) in dry THF (10 ml). After a further 2 h at –40 to –45 °C, ice-cold saturated ammonium chloride solution (100 ml) was added and the product was extracted into ether. The ethereal solution was washed with aqueous sodium metabisulphite, dried (MgSO<sub>4</sub>), and evaporated. Chromatography on silica gel (20 g) using dichloromethane as eluant followed by concentration of the appropriate fractions under reduced pressure gave *methyl 3-hydroxy-3-phenylpropanedithioate* as an orange oil (1.04 g, 57%) (Found: C, 57.05; H, 5.6; S, 29.7. C<sub>10</sub>H<sub>12</sub>OS<sub>2</sub> requires C, 56.6; H, 5.7; S, 30.2%); δ(CCl<sub>4</sub>) 2.55 (3 H, s, SMe), 3.25 (2 H, d, J<sub>2,3</sub> 6 Hz, 2-H), 5.15 (1 H, t, J<sub>2,3</sub> 6 Hz, 3-H), and 7.0–7.5 (5 H, br, Ph).

**Methyl 3-Hydroxybutanedithioate.**—To a stirred suspension of sodium hydride (10.0 g, 0.21 mol) in dry THF (120 ml) at –20 °C under nitrogen was added, during 1 h, a solution of

methyl dithioacetate (20 g, 0.19 mol) and acetaldehyde (9.7 g, 0.22 mol) in dry THF (150 ml). After a further 20 min at –20 °C, work-up as above gave crude methyl 3-hydroxybutanedithioate. Column chromatography on silica gel (300 g) using dichloromethane as eluant gave the *dithioester* as an orange liquid (15.56 g, 55%), b.p. 108–110 °C at 10 mmHg (Found: C, 40.4; H, 6.5; S, 42.1. C<sub>5</sub>H<sub>10</sub>OS<sub>2</sub> requires C, 40.0; H, 6.7; S, 42.65%); δ(CCl<sub>4</sub>) 1.15 (3 H, d, Me), 2.6 (3 H, s, SMe), 3.05 (2 H, d, 2-H), and 4.25 (1 H, sextet, 3-H).

**Methyl 3-Hydroxy-3-methylbutanedithioate.**—To a stirred suspension of sodium hydride (5.5 g, 0.11 mol) in dry THF (150 ml) at –20 °C under nitrogen was added, during 30 min, a solution of methyl dithioacetate (10.7 g, 0.1 mol) and AnalaR acetone (33.3 g, 0.57 mol) in dry THF (50 ml). After a further 65 min at –20 °C, work-up as above gave a red oil. Column chromatography (silica gel; 180 g) using dichloromethane as eluant gave a red liquid (1.38 g) which was shown by n.m.r. to contain unchanged methyl dithioacetate and 4-hydroxy-4-methylpentan-2-one (by comparison with authentic spectra), and an orange oil, *methyl 3-hydroxy-3-methylbutanedithioate* (10.04 g, 60%). A sample was further purified by short-path distillation (0.1 mmHg, bath temp. 50–65 °C) for microanalysis (Found: C, 44.1; H, 7.5; S, 38.9. C<sub>6</sub>H<sub>12</sub>OS<sub>2</sub> requires C, 43.85; H, 7.35; S, 39.05%); δ(CCl<sub>4</sub>) 1.2 (6 H, s, Me<sub>2</sub>), 2.6 (3 H, s, SMe), 3.15 (2 H, s, CH<sub>2</sub>), and 3.5 (1 H, s, OH); λ<sub>max</sub>(EtOH) 308 (ε, 16 100) and 454 nm (18).

**Methyl 3-Hydroxypropanedithioate.**—n-Butyl-lithium solution (1.55M in hexane; 61.0 ml, 95 mmol) was added, with stirring, to a solution of di-isopropylamine (9.5 g, 94.3 mmol) in dry THF (160 ml) under nitrogen, at –48 °C. Methyl dithioacetate was added at such a rate that the temperature of the solution did not rise above –38 °C. When the addition was complete, formaldehyde gas (generated by thermal depolymerisation of 11.5 g paraformaldehyde) was passed into the solution, using a slow stream of nitrogen, for 75 min. Stirring at –40 to –43 °C for a further 30 min was followed by the addition of saturated aqueous ammonium chloride (100 ml). Isolation with ether gave a dark red liquid, which was chromatographed on silica gel (100 g) using dichloromethane–light petroleum (3:1) through to dichloromethane as eluant, to give unchanged methyl dithioacetate (3.02 g, 30% recovery), some unidentified material (0.08 g), and *methyl 3-hydroxypropanedithioate* (1.07 g, 8.3%). Further elution with ether gave impure product (0.87 g, total yield 15%). The material was further purified by distillation to give an orange liquid, b.p. 51–53 °C at 0.2 mmHg (Found: C, 35.75; H, 6.05; S, 47.25. C<sub>4</sub>H<sub>8</sub>OS<sub>2</sub> requires C, 35.25; H, 5.9; S, 47.05%); δ(CCl<sub>4</sub>) 2.45 (1 H, br s, OH), 2.6 (3 H, s, SMe), 3.15 (2 H, t, J 6 Hz, 2-H), and 3.9 (2 H, br t, J 6 Hz, 3-H); m/z (e.i.) 136 (M<sup>+</sup>, 27%), 118 (–H<sub>2</sub>O, 18), 89 (–SMe, 26), 71 (C<sub>3</sub>H<sub>3</sub>S<sup>+</sup>, 58), 59 (C<sub>2</sub>H<sub>3</sub>S<sup>+</sup>, 100), and 45 (C<sub>2</sub>H<sub>5</sub>O<sup>+</sup>, 70); λ<sub>max</sub>(EtOH) 305 (ε, 15 000) and 454 nm (15).

**Methyl 3-Acetoxybutanedithioate.**—A solution of methyl 3-hydroxybutanedithioate (5.0 g, 0.033 mol), acetic anhydride (10.2 g, 0.1 mol), and pyridine (8.04 g, 0.1 mol) in dry toluene (100 ml) was stirred at 16 °C for 24 h. Water (50 ml) was then added and after 5 min the layers were separated. The aqueous phase was extracted with ether and the combined organic extracts were washed with dilute aq. HCl, water, and brine, dried (MgSO<sub>4</sub>) and the solvent removed under reduced pressure. Distillation gave *methyl 3-acetoxybutanedithioate* (5.25 g, 83%), b.p. 73–74 °C at 0.8 mmHg (Found: C, 44.0; H, 6.2; S, 33.4. C<sub>7</sub>H<sub>12</sub>O<sub>2</sub>S<sub>2</sub> requires C, 43.7; H, 6.3; S, 33.35%); δ(CCl<sub>4</sub>) 1.1 (3 H, d, J 6 Hz, Me), 1.85 (3 H, s, COMe), 2.55 (3 H, s, SMe), 3.1 (2 H, octet, J 13, 7 Hz, 2-H), and 5.25 (1 H, sextet, J 6 Hz, 3-H); λ<sub>max</sub>(EtOH) 306 (ε, 17 000) and 455 nm (15).

\* The structure was assigned on the basis that the carbonyl group at C-2 in (20) would be the less hindered.

**Methyl 3-Trifluoroacetoxybutanedithioate.**—A solution of methyl 3-hydroxybutanedithioate (5.05 g, 0.034 mol) and trifluoroacetic anhydride (10.5 g, 0.05 mol) in dry toluene (150 ml) was kept at 16 °C for 25 h and then added to water (100 ml). The layers were separated and the aqueous phase was extracted with ether. The combined organic extracts were washed with water, dilute aq. NaHCO<sub>3</sub>, and brine, dried (MgSO<sub>4</sub>) and concentrated under reduced pressure to leave an orange liquid. Column chromatography (silica gel; 100 g) using light petroleum–dichloromethane (9:1) as eluant gave methyl 3-trifluoroacetoxybutanedithioate (6.7 g, 81%). This compound could also be purified by distillation (b.p. 37 °C at 0.3 mmHg);  $\delta$ (CDCl<sub>3</sub>) 1.42 (3 H, d, *J* 7 Hz, Me), 2.6 (3 H, s, SMe), 2.94–3.65 (2 H, septet, *J* 15, 8, 6 Hz, 2-H), and 5.65 (1 H, sextet, 3-H); *m/z* (e.i.) 246 (*M*<sup>+</sup>, 28%), 91 (–CS<sub>2</sub>Me, 30), 85 (C<sub>4</sub>H<sub>5</sub>O<sub>2</sub><sup>+</sup>, 100), and 69 (CF<sub>3</sub><sup>+</sup>, 38).

**Methyl 3-Trifluoroacetoxypropanedithioate.**—To a stirred solution of methyl 3-hydroxypropanedithioate (238 mg, 1.75 mmol) in dry benzene (6 ml) at 3 °C was added trifluoroacetic anhydride (370 mg, 1.77 mmol). After 20 min, the product was partitioned between water and light petroleum. The organic solution was washed with saturated aq. NaHCO<sub>3</sub>, water, and brine, dried (MgSO<sub>4</sub>), and concentrated under reduced pressure, leaving methyl 3-trifluoroacetoxypropanedithioate, as an orange liquid (364 mg, 90%). N.m.r. and t.l.c. showed that this material was pure enough for further use. It could be purified by chromatography on silica gel, using light petroleum–dichloromethane (9:1) as eluant;  $\delta$ (CCl<sub>4</sub>) 2.5 (3 H, s, SMe), 3.15 (2 H, t, *J* 6 Hz, 2-H), and 4.45 (2 H, t, *J* 6 Hz, 3-H);  $\lambda_{\text{max}}$ (Et<sub>2</sub>O) 304.5 ( $\epsilon$ , 19 500) and 454 nm (14);  $\nu_{\text{max}}$ (liq. film) 1 790 (s, C=O), 1 150–1 175 cm<sup>–1</sup> (br, s, C=S). This compound darkened after several days and n.m.r. showed that extensive decomposition had taken place, and so it was stored in solution in light petroleum at 4 °C.

**Methyl 3-Methylbut-2-enedithioate.**—A stirred solution of methyl 3-hydroxy-3-methylbutanedithioate (3.95 g, 24.1 mmol) in dry pyridine (35 ml) at 0 °C was treated with phosphorus oxychloride (7.7 g, 47.4 mmol). After 5 h at 0–10 °C, then 1 h at 16 °C, the solution was added to ice–water, and extracted with ether. The ethereal layer was washed with dilute aq. HCl, water, and brine, dried (MgSO<sub>4</sub>) and the solvent removed under reduced pressure, leaving crude methyl 3-methylbut-2-enedithioate (3.17 g, 90%). Distillation gave a red liquid (2.38 g, 68%, one spot on t.l.c.), b.p. 88–91 °C at 11 mmHg (lit.<sup>2</sup> 46–48 °C at 0.5 mmHg). A sample was further purified by short-path distillation (Found: C, 49.15; H, 6.8; S, 43.5. Calc. for C<sub>6</sub>H<sub>12</sub>S<sub>2</sub>: C, 49.25; H, 6.9; S, 43.85%);  $\delta$ (CCl<sub>4</sub>) 1.9 (3 H, s, Me), 2.15 (3 H, s, Me), 2.55 (3 H, s, SMe), and 6.5–6.65 (1 H, m, =CH);  $\lambda_{\text{max}}$ (EtOH) 300 ( $\epsilon$  16 500), 322sh (7 150), and 495 nm (60).

**Methyl trans-But-2-enedithioate.**—A stirred solution of methyl 3-hydroxybutanedithioate (0.27 g, 1.8 mmol) in dry pyridine (2 ml) at –45 °C was treated with phosphorus oxychloride (0.55 g, 3.6 mmol). After 30 min, the solution was allowed to warm slowly, until t.l.c. showed that the starting material had been consumed (1½ h). The solution was diluted with ice-cold carbon tetrachloride (5 ml), washed with dilute aq. HCl and dilute aq. NaHCO<sub>3</sub>, and dried (MgSO<sub>4</sub>). Filtration gave a bright red solution containing methyl *trans*-but-2-enedithioate;  $\delta$ (CCl<sub>4</sub>) 1.77 (3 H, d, *J* 6 Hz, Me), 2.5 (3 H, s, SMe), and 6.6–6.8 (2 H, m, *J*  $\approx$  15, 7 Hz, 2-H and 3-H) [lit.<sup>4</sup>  $\delta$ (CCl<sub>4</sub>) 2.60 (3 H, s), ABX<sub>3</sub> system  $\delta_A$  6.79 (1 H);  $\delta_B$  7.00 (1 H);  $\delta_X$  1.83 (3 H); *J*<sub>AB</sub> 15, *J*<sub>AX</sub> –1.3, *J*<sub>BX</sub> 6.8 Hz];  $\lambda_{\text{max}}$ (CCl<sub>4</sub>) 286 and 336 nm.

In a control reaction carried out as above, using 250 mg (1.65 mmol) of  $\beta$ -hydroxydithioester, work-up after 2 min at –5 °C employed a solution of anisole (106.6 mg, 0.99 mmol) in carbon

tetrachloride (5 ml). From the integrals of the anisole OMe resonance and the dithioester SMe resonance, the ratio of anisole:dithioester was estimated to be 2:1; hence the yield of the unsaturated dithioester was *ca.* 0.5 mmol (30%). There was also some dimer (6) present (*ca.* 0.1 mmol, 15%).

**Reaction of 2-Prop-1-enyl-1,3-dithiolane with Bases.**—(a) **With lithium di-isopropylamide.** A solution of LDA in THF (2 ml) at –70 °C was prepared from di-isopropylamine (2.1 mmol) and Bu<sup>n</sup>Li (1.55M in hexane; 2.2 mmol). After addition of the dithiolane (2.1 mmol) in THF (1 ml) the mixture was stirred for 1 h at –70 °C and methyl iodide (2.4 mmol) was added. After a further 30 min aq. NH<sub>4</sub>Cl was added and the product was isolated with ether. Chromatography on silica gel using light petroleum through to benzene as eluant gave a red liquid (72 mg) shown by comparison of the n.m.r. data with lit. data<sup>16</sup> to be mainly 1,1-bismethylthiobuta-1,3-diene;  $\delta$ (CCl<sub>4</sub>) 2.27 (6 H, s) 5.05 (1 H, dd, *J* 9, 2 Hz, 4-H), 5.15 (1 H, dd, *J* 17, 2 Hz, 4-H<sup>1</sup>), 6.3 (1 H, d, *J* 11 Hz, 2-H), and 6.9 (1 H, dt, *J* 17, 10 Hz, 3-H), together with some methyl but-2-enedithioate. This mixture deteriorated on standing. The later column fractions were complex mixtures containing some unchanged dithiolane.

(b) **With *n*-butyl-lithium.** The reaction was carried out in light petroleum–dry THF (4:1 v/v) at –70 °C using *n*-butyl-lithium (1.55M soln. in hexane). The product was isolated as before and chromatographed on silica gel using light petroleum as eluant to give unchanged dithiolane (32%) and 1,1-bismethylthio-3-methylhept-1-ene (48%) (Found: C, 59.0; H, 9.9; S, 30.9. C<sub>10</sub>H<sub>20</sub>S<sub>2</sub> requires C, 58.75; H, 9.85; S, 31.35%);  $\delta$  (300 MHz; CDCl<sub>3</sub>) 0.88 (3 H, t, *J* 7 Hz, CH<sub>2</sub>Me), 0.97 (3 H, d, *J* 6.7 Hz, CHMe), 1.21–1.36 (6 H, m), 2.27 (3 H, s, SMe), 2.29 (3 H, s, SMe), 2.87 (1 H, m, 3-H), and 5.69 (1 H, d, *J* 9.8 Hz, 2-H); *m/z* (c.i.) 205 (*M*<sup>+</sup> + 1, 66%), 189 (–MeH, 24), 157 (–MeSH, 65), 147 (–BuH, 100), 109 (43), and 99 (42).

**4-Methyl-6-methylthio-3,4-dihydro-2H-thiopyran-2,3-dicarboxylic Anhydride (13).**—(a) Methyl 3-hydroxybutanedithioate (1.53 g, 10.2 mmol) was used to generate a solution of methyl but-2-enedithioate in chloroform (30 ml), as previously described (reaction time 2 min at –5 °C). Maleic anhydride (0.98 g, 10.0 mmol) was then added and the solution kept at 18 °C, until n.m.r. showed the reaction to be complete (3¼ h). After the mixture had been washed thoroughly with water (6 × 20 ml), the solvent was removed under reduced pressure, leaving an orange oil (0.77 g), which on trituration with light petroleum yielded the crude anhydride (13) as a yellowish solid (0.5 g, 20%). Concentration of the supernatant solution under reduced pressure gave the dimer methyl 2,4-dimethyl-6-methylthio-3,4-dihydro-2H-thiopyran-3-carbodithioate (6) (0.19 g, 14%). The solid was recrystallised from carbon tetrachloride and then light petroleum–carbon tetrachloride to give the *anhydride* (13), as white plates (0.17 g, 7%), m.p. 81.5–82.5 °C (Found: C, 46.85; H, 4.65; S, 27.5. C<sub>9</sub>H<sub>10</sub>O<sub>3</sub>S<sub>2</sub> requires C, 46.95; H, 4.40; S, 27.85%);  $\delta$ (CDCl<sub>3</sub>) 1.5 (3 H, d, *J* 7 Hz, Me), 2.3 (3 H, s, SMe), 2.4–3.0 (1 H, m, 4-H), 3.65 (1 H, dd, *J* 10, 5 Hz, 3-H), 4.25 (1 H, d, *J* 10 Hz, 2-H), and 5.95 (1 H, d, *J* 5 Hz, 5-H);  $\nu_{\text{max}}$ (CCl<sub>4</sub>) 1 865 (m, C=O), 1 775 cm<sup>–1</sup> (s, C=O).

(b) A solution of methyl 3-trifluoroacetoxybutanedithioate (174 mg, 0.7 mmol), maleic anhydride (137 mg, 1.4 mmol), and dry 2,6-dimethylpyridine (740 mg, 6.9 mmol) in dry toluene (7 ml) was heated to 40 °C for 2 h. After cooling, the solution was added to water (10 ml) and the phases separated. The aqueous phase was extracted with ether and the combined organic solutions were washed with dilute aq. HCl, water, and brine, dried (MgSO<sub>4</sub>), and concentrated under reduced pressure leaving an orange-brown oil (180 mg). Trituration with light petroleum gave the anhydride (13) as a pale brown solid (130 mg, 80%), m.p. 70–75 °C. N.m.r. indicated that this material

was pure enough for further use. Recrystallisation from light petroleum-carbon tetrachloride was unsuccessful.

**Reaction of Methyl 3-Methylbut-2-enedithioate with Maleic Anhydride.**—(a) Methyl 3-methylbut-2-enedithioate (1.22 g, 8.35 mmol) and maleic anhydride (0.82 g, 8.37 mmol) were refluxed in dry toluene (20 ml) for 15 h. After being cooled to room temperature, the toluene was removed under reduced pressure. All attempts to crystallise the residue failed. Column chromatography (silica gel; 20 g) using chloroform as eluant gave a little unchanged unsaturated dithioester and 4,4-dimethyl-6-methylthio-3,4-dihydro-2H-thiopyran-2,3-dicarboxylic anhydride (1.17 g, 57%);  $\delta$ (CDCl<sub>3</sub>) 1.37 (6 H, s, Me, scale expansion showed 2 peaks), 2.3 (3 H, s, SMe), 3.35 (1 H, d, *J* 10 Hz, 3-H), 4.45 (1 H, d, *J* 10 Hz, 2-H), and 6.0 (1 H, s, 5-H). Distillation at reduced pressure gave impure material, b.p. 132–133 °C at 0.05 mmHg.

(b) The reaction was carried out as above, using 1.16 g (7.9 mmol) of the unsaturated dithioester. The crude product was treated with methanolic potassium hydroxide (1.13 g, 20 mmol in 75 ml) at 16 °C for 15 h. Water was then added and the alkaline solution washed with ether. The aqueous phase was acidified (dilute aq. HCl) and the product taken into ether. The combined organic extracts were washed with brine, dried (MgSO<sub>4</sub>), and concentrated under reduced pressure. The residue was triturated with light petroleum to give 2-methoxycarbonyl-4,4-dimethyl-6-methylthio-3,4-dihydro-2H-thiopyran-3-carboxylic acid (**21**) as a pale yellow powder (1.79 g, 82% based on unsaturated dithioester), m.p. 79.5–82 °C. Recrystallisation from light petroleum-benzene, then methanol-water gave white crystals, which were dried *in vacuo* over phosphorus pentoxide for several days, m.p. 94.5–95.5 °C (Found: C, 47.45; H, 5.95; S, 23.35. C<sub>11</sub>H<sub>16</sub>O<sub>4</sub>S<sub>2</sub> requires C, 47.8; H, 5.85; S, 23.2%);  $\delta$ (CDCl<sub>3</sub>) 1.03 (3 H, s, Me), 1.25 (3 H, s, Me), 2.3 (3 H, s, SMe), 2.87 (1 H, d, *J* 12 Hz, 3-H), 3.7 (3 H, s, OMe), 4.2 (1 H, d, *J* 12 Hz, 2-H), 5.77 (1 H, s, 5-H), and 7.55 (1 H, br s, CO<sub>2</sub>H).

**Methyl 4-Methyl-6-methylthio-3,4-dihydro-2H-thiopyran-3-carboxylate (15).**—To a stirred solution of methyl 3-acetoxybutanedithioate (480 mg, 2.55 mmol) in methyl acrylate (5 ml, 55 mmol) at 60 °C was added di-isopropylethylamine (330 mg, 2.58 mmol). After 1½ h at 45–70 °C, water was added and the phases separated. The aqueous layer was extracted with ether and the combined organic solutions were washed with dilute aq. HCl, water, and brine, dried (MgSO<sub>4</sub>) and the solvent removed under reduced pressure to give the crude adduct (466 mg, 84%), as a mixture of stereoisomers. Column chromatography (silica gel) using light petroleum-dichloromethane (1:1) as eluant gave the dimer (**6**) (23.5 mg, 7%) and the thiopyran (**15**) (320 mg, 58%). Satisfactory analytical data have not been obtained;  $\delta$  (300 MHz; CDCl<sub>3</sub>) 0.95 (d, *J* 7 Hz, Me<sub>major</sub>), 1.08 (d, *J* 7 Hz, Me<sub>minor</sub>), 2.34 (2, SMe<sub>major</sub>), 2.35 (s, SMe<sub>minor</sub>), 2.81–3.19 (4 H, m), 3.74 (s, OMe<sub>major</sub>), 3.75 (s, OMe<sub>minor</sub>), 5.85 (d, *J* 4 Hz 5-H<sub>minor</sub>), and 5.97 (d, 6 Hz, 5-H<sub>major</sub>); minor: major isomer = 1:4 from integrals of vinyl proton resonances; *m/z* (e.i.) 219 (*M* + 1<sup>+</sup>, 85%), 159 (–HCO<sub>2</sub>Me, 18), 111 (20), 99 (27), 87 (C<sub>4</sub>H<sub>7</sub>O<sub>2</sub><sup>+</sup>, 23), 85 (C<sub>4</sub>H<sub>5</sub>O<sub>2</sub><sup>+</sup>, 100), 69 (27), 55 (27), 45 (29), and 41 (29);  $\nu_{\max}$  (liq. film) 1 730 (s, C=O) cm<sup>-1</sup>. This material was shown by n.m.r. to have almost completely deteriorated on standing at 4 °C for 12 days. T.l.c. (light petroleum-ether, 1:1) then showed at least four mobile components.

**6-Methyl-4-methylthio-3-thiatricyclo[6.2.1.0<sup>2,7</sup>]undec-4-ene (14).**—A stirred solution of methyl 3-acetoxybutanedithioate (273 mg, 1.42 mmol), norbornene (700 mg, 7.43 mmol), and a little hydroquinone in dry toluene (3 ml) was treated with diisopropylethylamine (185 mg, 1.43 mmol) and left for 45 h at 16 °C. The product was then partitioned between water and

light petroleum and the combined organic extracts were washed with water and brine, dried (MgSO<sub>4</sub>), and concentrated under reduced pressure to give a yellow oil (345 mg). Column chromatography (silica gel; 5 g) using light petroleum through to light petroleum-dichloromethane (4:1) as eluant gave the dimer (**6**) (32.3 mg, 17%) and an almost colourless oil, 6-methyl-4-methylthio-3-thiatricyclo[6.2.1.0<sup>2,7</sup>]undec-4-ene (**14**) as a mixture of stereoisomers (188 mg, 59%). Satisfactory analytical data have not been obtained;  $\delta$  \* (300 MHz; CDCl<sub>3</sub>) 1.15 (octet, *J*<sub>9,10</sub> 9.75 Hz, *J*<sub>9,11</sub> 1.5 Hz) and *ca.* 1.25 (obscured) (9-H and 10-H), 1.21 (d, *J* 7.2 Hz, Me<sub>major</sub>), 1.25 (?d, Me<sub>minor</sub>) (the multiplet at  $\delta$  1.15–1.25 integrates as 7 H), 1.45 (1 H, br t, *J*<sub>2,7</sub> 8.2 Hz, *J*<sub>6,7</sub> *ca.* *J* Hz, 7-H), *ca.* 1.6 (partly obscured by impurity, 11-H<sub>a</sub>), 1.98 (1 H, septet, *J*<sub>5,6</sub> 3.6 Hz, 6-H) 2.07 (1 H, dt, *J*<sub>11s,a</sub> 10.2 Hz, *J*<sub>11s,9,10n</sub> *ca.* 2.0 Hz, 11-H<sub>s</sub>), 2.17 (1 H, br, s, 1-H or 8-H), 2.30 (br s, partly obscured, 1-H or 8-H), 2.31 (s, SMe<sub>major</sub>), 2.34 (s, SMe<sub>minor</sub>) (the resonances at  $\delta$  2.30–2.34 integrate as 4 H), 3.09 (1 H, dd, *J*<sub>2,11a</sub> *ca.* 1.5 Hz, 2-H), 5.75 (d, *J*<sub>5,6</sub> *ca.* 6 Hz, 5-H<sub>minor</sub>), and 5.77 (d, *J*<sub>5,6</sub> 3.6 Hz, 5-H<sub>major</sub>) (the resonances at  $\delta$  5.75–5.77 integrate as 1 H);  $\delta_c$  (75.57 MHz): (major isomer) 16.11 (q, Me), 19.73 (q, Me), 28.99 (t, CH<sub>2</sub>), 30.00 (t, CH<sub>2</sub>), 34.38 (t, bridge CH<sub>2</sub>), 36.56 (d, CH), 41.42 (d, CH), 42.79 (d, CH), 52.83 (d, CH), 58.16 (d, CH), 131.72 (d, CH=), and 133.34 p.p.m. (s, =C-4); (minor isomer) 19.08, 29.41, 31.41, 35.81, 37.31, 49.80, 52.35, 53.46, 130.20, and 133.85 (multiplicity undetermined); *m/z* (e.i.) 266 (*M*<sup>+</sup>, 58%), 211 (–Me, 69), 117 (C<sub>4</sub>H<sub>5</sub>S<sup>+</sup>, 87), 93 (46), 85 (100), and 41 (48). After standing at 16 °C for 2 days, n.m.r. indicated considerable deterioration. The compound was therefore stored in solution in light petroleum at 4 °C.

**Reaction of Methyl 3-Acetoxybutanedithioate with *N*-Prop-1-enylpiperidine.**—Solutions of methyl 3-acetoxybutanedithioate (0.5 g, 2.6 mmol) in dry toluene (3 ml) and freshly distilled *N*-prop-1-enylpiperidine<sup>17</sup> (0.65 g, 5.2 mmol) in dry toluene (3 ml) were mixed under nitrogen and stirred at 18 °C for 1 h. Light petroleum (30 ml) was added and after 2 days at 4 °C the resulting solid was filtered off and the filtrate evaporated under reduced pressure. The residue was dissolved in ether and the solution washed with water and brine, dried (Na<sub>2</sub>SO<sub>4</sub>), and the solvent removed under reduced pressure, leaving 3,4-dimethyl-6-methylthio-2-piperidino-3,4-dihydro-2H-thiopyran (**16**), as a yellow oil (0.64 g, 96%);  $\delta$  (90 MHz; CDCl<sub>3</sub>) 1.02 (3 H, d, *J* 6 Hz, Me), 1.07 (3 H, d, *J* 7 Hz, Me), 1.35–1.8 (m, CH<sub>2</sub>), 1.9–2.15 (m), 2.3 (3 H, s, SMe), 2.4–2.8 (m, NCH<sub>2</sub>), 4.23 (1 H, d, *J* 10 Hz, 2-H), and 5.6 (1 H, d, *J* 3 Hz, 5-H);  $\delta_c$  16.71 (q), 16.89 (q), 20.43 (q), 24.53 (t, CH<sub>2</sub>N), 26.06 (t, CH<sub>2</sub>), 40.05 (d, C-4), 49.96 (t, CH<sub>2</sub>N), 79.32 (d, C-2), 127.81 (d, 5-C), and 128.5 p.p.m. (s, C-6); also peaks at  $\delta$  23.21 and 44.36 p.p.m. (t); *m/z* (f.i.) 257 (*M*<sup>+</sup>, e.i.) 257 (*M*<sup>+</sup>, 3%), 166 (–CS<sub>2</sub>Me, 22), 152 (–CH<sub>2</sub>CS<sub>2</sub>Me, 16), 125 (C<sub>8</sub>H<sub>15</sub>N<sup>+</sup>, 100), 110 (44), 85 (C<sub>5</sub>H<sub>11</sub>N<sup>+</sup>, 30), and 41 (36). Distillation at reduced pressure (b.p. 108–110 °C at 0.1 mmHg) was not a successful means of purification.

Some of the crude adduct (**16**) (80 mg) was adsorbed onto a small column of silica gel and, after 1 h, the product was eluted with light petroleum-dichloromethane (9:1) through to dichloromethane, giving a yellow liquid, methyl 4-formyl-3-methylpentanedithioate (50 mg, 85% based on adduct);  $\delta$ (CCl<sub>4</sub>) 0.85–1.2 (6 H, m, Me), 2.05–2.50 (2 H, m), 2.52 (3 H, s, SMe), 2.9–3.1 (2 H, m), and 9.6 (1 H, d, *J* 5 Hz, CHO);  $\lambda_{\max}$  (EtOH) 306 (strong) and 454 nm (weak);  $\nu_{\max}$  (liq. film) 2 700 (w, CHO), 1 725 (s, C=O), and 1 175 cm<sup>-1</sup> (m, C=S).

**Reaction of Methyl 3-Acetoxybutanedithioate with 1-Morpholinocyclohexene.**—Methyl 3-acetoxybutanedithioate (0.3 g, 1.56 mmol) and 1-morpholinocyclohexene<sup>18</sup> (0.56 g, 3.35

\* In the n.m.r. assignments, the subscripts *a* and *s* refer to *anti* and *syn*, and *x* and *n* to *exo* and *endo*, respectively.

mmol) were mixed at 18 °C. After 24 h, the product was partitioned between water and ether as above, giving a yellow liquid (0.49 g), which had n.m.r. data consistent with 5-methyl-3-methylthio-1-morpholino-2-thiabicyclo[4.4.0]dec-3-ene;  $\delta(\text{CDCl}_3)$  1.1 (d,  $J$  7 Hz, Me), 1.1—2.2 (m,  $\text{CH}_2$ ), 2.3 (s, SMe), 2.65—2.9 (m, morph.  $\text{CH}_2$ ), 3.6—3.85 (m, morph.  $\text{CH}_2$ ), 5.67 and (d,  $J$  3 Hz, =CH). Column chromatography (silica gel) using light petroleum-ether (10—20%) as eluant gave the impure adduct (17). A sample of the crude material (280 mg) was suspended in dilute aq. HCl (3M; 5 ml) at 18 °C for 2.5 h. The product was then taken into ether and the combined ether extracts were washed with water and brine, dried ( $\text{MgSO}_4$ ), and evaporated under reduced pressure. P.l.c. using light petroleum-ether (9:1) as eluant gave a yellow liquid (41 mg), which was shown by n.m.r., i.r., and u.v. to be methyl 3-methyl-3-(2-oxocyclohexyl)propanedithioate;  $\delta(\text{CCl}_4)$  0.9 and 0.95 (3 H, d,  $J$  6 Hz, Me), 1.25 (1 H, m, 3-H), 1.4—2.5 (9 H, m,  $\text{CH}_2$ ), and 2.9 (2 H, m, 2-H);  $\lambda_{\text{max.}}(\text{EtOH})$  306 ( $\epsilon$  18 400) and 455 nm (13);  $\nu_{\text{max.}}(\text{liq. film})$  1 705 (s, C=O), and 1 165  $\text{cm}^{-1}$  (m, C=S).

*Methyl 2-Methyl-1,4-diphenyl-1,2,3,4-tetrahydro-1,4-epoxy-naphthalene-3-carbodithioate (22).*—A stirred solution of methyl 3-hydroxybutanedithioate (0.63 g, 4.2 mmol) and 1,3-diphenylisobenzofuran (1.13 g, 4.2 mmol) in dry pyridine (5 ml) was treated with acetic anhydride (0.97 g, 9.5 mmol) and heated to 60 °C for 2 h. Water (1 ml) was then added and after a further 5 min the product was partitioned between ether and water. The ethereal solution (50 ml) was washed with dilute aq. HCl, water, and brine, dried ( $\text{MgSO}_4$ ), and concentrated under reduced pressure to give the adduct as a mixture of stereoisomers. Column chromatography (silica gel) using light petroleum-dichloromethane (9:1) through to light petroleum-dichloromethane (7:3) as eluant gave recovered diphenylisobenzofuran (0.08 g, 7%), a viscous oil (0.27 g) which was shown by n.m.r. to contain some of the dimer (6), and a sticky yellow solid (1.11 g), a mixture of stereoisomers (22) by n.m.r. Recrystallisation from light petroleum or ethanol-water gave the adduct (22) as a single stereoisomer. A second recrystallisation from light petroleum produced yellow prisms, m.p. 122—124 °C (Found: C, 74.4; H, 5.4; S, 16.0.  $\text{C}_{25}\text{H}_{22}\text{OS}_2$  requires C, 74.6; H, 5.5; S, 19.95%);  $\delta(\text{CCl}_4-\text{CDCl}_3)$  0.95 (3 H, d,  $J$  7 Hz, Me), 2.3 (3 H, s, SMe), 3.3 (1 H, dq,  $J$  5, 7 Hz, 2-H), 3.75 (1 H, d,  $J$  5 Hz, 3-H), and 6.95—7.8 (14 H, m, Ar);  $\lambda_{\text{max.}}(\text{CHCl}_3)$  315 ( $\epsilon$  14 600) and 455 nm (27);  $\nu_{\text{max.}}(\text{CCl}_4)$  1 190  $\text{cm}^{-1}$  (br s, C=S).

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