Synthesis and Reactivity of Sulphinyldithioacetate and Sulphonyldithioacetate Esters and Some Related Compounds [1]

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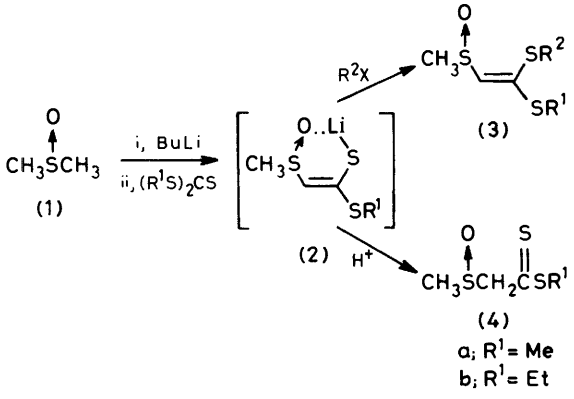
(Methylsulphinyl)ketene dithioacetals (3) or alkyl (methylsulphinyl)dithioacetates (4), and (methylsulphonyl)ketene dithioacetals (16) or alkyl (methylsulphonyl)dithioacetates (17) were prepared from dimethyl sulphoxide and dimethyl sulphone, respectively. Then, bis-[2,2-bis(ethylthio)vinyl]sulphide, bis-[2,2-bis(ethylthio)vinyl] sulphoxide, and bis-[2,2-bis(methylthio)vinyl] sulphone were derived from (4) or (17). The reactivity of these compounds was examined.

Several ketene dithioacetals conjugated with functional groups have recently been exploited in many synthetic procedures.[2] For their synthetic applications, we intended to synthesize ketene dithioacetals and related compounds of dimethyl sulphoxide (DMSO) (1) and dimethyl sulphone. The compounds thus obtained were found to be useful anion sources, and to be converted into the corresponding ketones and alcohols in moderate yield. Further, bis-[2,2-bis(ethylthio)vinyl] sulphoxide and bis-[2,2-bis(ethylthio)vinyl] sulphide were synthesized from dimethyl sulphoxide. In a similar way, bis-[2,2-bis(methylthio)vinyl] sulphone was synthesized starting from dimethyl sulphone. We present herein their preparations and an examination of their reactivity.



Results and Discussion

Preparation of (Methylsulphinyl)ketene Dithioacetals (3) *and Alkyl (Methylsulphinyl)dithioacetates* (4).—We could not obtain a satisfactory result by the reaction [3] of methylsulphinyl carbanion (dimsyl anion [4]) with carbon disulphide followed by alkylation perhaps because this reaction proceeds *via* a dithioacid intermediate which is easily oxidized. After several attempts compounds (3) were prepared in good yield by the reaction of lithiodimethyl sulphoxide (dimsyl-lithium) with trithiocarbonate esters, followed by alkylation.† The results are summarized in Table 1.

The structures of (3) were determined on the basis of elemental analyses and spectroscopic data, especially n.m.r. analyses. In the n.m.r. spectra of (3b) and (3d), the methylene protons of the group R^2, adjacent to the sulphur atom, were split owing to the effect of the chiral sulphinyl group,[5] *e.g.* two sets of quartet signals at δ 2.93 were observed for SCH_2Pr of (3d). This effect did not appear in the n.m.r. spectra of their corresponding isomers (3f) and (3h). This fact suggests that the methylsulphinyl and R^2S groups of (3) exist *cis* to one another. In addition, it was found that when the present reaction was performed using sodiodimethyl sulphoxide instead of lithiodimethyl sulphoxide, an equal mixture of the *Z*- and *E*-form of (3) was obtained. The reaction is considered to proceed *via* an intermediate (2) which has been reported to occur in a similar reaction.[6]

Table 1. Preparation of compounds (3)

Compd.	R^1	R^2	Properties	Yield (%)
(3a)	Me	Me	Oil, decomp. at 125 °C	74
(3b)	Me	Et	Crystals, m.p. 63—64 °C	41
(3c)	Me	Pr^i	Crystals, m.p. 50—51 °C	50
(3d)	Me	Bu^n	Oil, decomp. at 209 °C	44
(3e)	Me	$PhCH_2$	Crystals, m.p. 40—41 °C	63
(3f)	Et	Me	Oil, decomp. at 149 °C	82
(3g)	Et	Et	Crystals, m.p. 20—21 °C	80
(3h)	Bu^n	Me	Oil, decomp. at 155 °C	90

Although (3b) was stable in the crystalline state, *ca.* 20% isomerized to (3f) on being kept in chloroform solution at 0 °C for one week.

Alkyl (methylsulphinyl)dithioacetates (4) were isolated from the present reaction when dil. HCl was used in place of the alkyl halide. Compounds (4) decomposed slowly at ambient temperature and react with phenylhydrazine to give the corresponding phenylhydrazides; *e.g.* *N'*-phenyl(methylsulphinyl)thioacetohydrazide was isolated from methyl (methylsulphinyl)dithioacetate (4a; R^1 = Me).

Substitution of the Vinyl Proton of (3).—Compounds (3) reacted with 1 equiv. of BuLi, followed by addition of either

† As a synthetic application of this method, several dithiocarboxylic esters could be synthesized in high yield by the reaction of compounds containing active protons with trithiocarbonic esters using NaH or BuLi.

$$R^1CH_2R^2 \xrightarrow[\text{Base}]{(MeS)_2CS} R^1CH(CS_2Me)R^2$$

R^1	R^2	Base	Yield (%)
CN	$CONH_2$	NaH	65
CN	CO_2Et	NaH	56
CN	CN	NaH	95
CN	Ph	NaH	95
H	Ph	NaH	70
Ph	$CONH_2$	BuLi	52

an alkyl halide or *p*-nitrobenzaldehyde, to give (5) or (6), respectively, in moderate yield. The results are shown in Table 2.

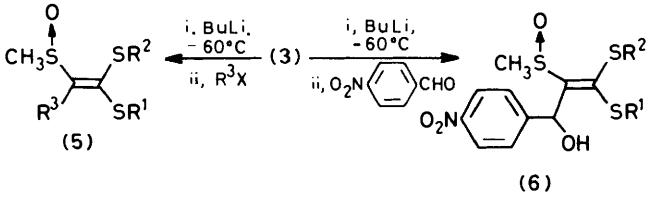


Table 2. Preparation of compounds (5) and (6)

Compd.	R^1	R^2	R^3	Properties	Yield (%)
(5a)	Et	Et	Me	Oil, decomp. at 150 °C/0.2 Torr	62
(5b)	Me	Et	$PhCH_2$	Needles, m.p. 57—58 °C	41
(6a)	Et	Et	—	Needles, m.p. 98—99 °C; 95—96 °C	43 *

* A 3 : 1 mixture of two diastereoisomers.

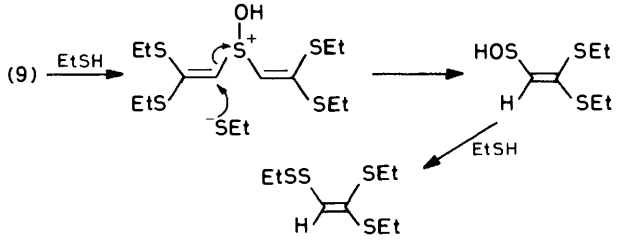
Substitution of the Methyl Proton of (4).—Compounds (4) were converted into the corresponding aldol-type adducts (7) or (8) by successive treatment with 2 equiv. of BuLi, addition of a carbonyl compound, and quenching with either an alkyl halide or mineral acid (see Table 3). Compound (8a) was easily converted into the corresponding phenylhydrazide, *N'*-phenyl-[(2-hydroxy 2-methylpropyl)sulphinyl]thioacetohydrazide, in the usual way.

Preparation of Bis-[2,2-*bis*(*ethylthio*)*vinyl*] *Sulphoxide* (9) *and Bis-*[2,2-*bis*(*ethylthio*)*vinyl*] *Sulphide* (10).—Compound (9) could not be prepared directly from the reaction of the dianion of dimethyl sulphoxide [7] with carbon disulphide followed by ethylation. When compound (4b) was subjected to successive treatment with NaH–BuLi, diethyl trithiocarbonate, and ethyl iodide, the expected product (9) was obtained as crystals, m.p. 25 °C in 56% yield. Next, the sulphoxide (9) was quantitatively converted into the sulphide (10) on refluxing in carbon tetrachloride containing triphenylphosphine.

Compound (9) was stable at <0 °C but decomposed completely at ambient temperature within 12 h. The decomposition products of (9) were confirmed as (11) * and (12) †

* The structure of this compound was determined by comparison of its i.r. spectrum with that of an authentic sample, which was prepared from the reaction of thiodiglycolic acid with ethanethiol in the presence of polyphosphonic ester.

† This compound was also synthesized from (9) and ethanethiol in refluxing ethanol in 63% yield. The reaction is considered to proceed as follows.



(main components), together with many by-products. Compound (13) was obtained by the reaction of 2 equiv. of BuLi, followed by alkylation.

Preparation of (Z)-2-*Benzylthio*-3,3-*dimethyl*-1-*methylsulphinylbut*-1-*ene* (14).—The dimsyl anion reacted with methyl dithiopivalate, which was prepared from Bu^{t}Li with dimethyl dithiocarbonate in the usual way, followed by benzylation to give (14) in 98% yield.

Preparation of the (*Methylsulphonyl*)*ketene Dithioacetal* (16), *Methyl* (*Methylsulphonyl*)*dithioacetate* (17), *and Bis-*[2,2-*bis*(*methylthio*)*vinyl*] *Sulphone* (18).—Dimethyl sulphone, when treated with NaH–$(MeS)_2CS$ and then acid or alkyl halide as described in the case of dimethyl sulphoxide, resulted in the formation of compounds (16) and (17) presumably *via* the intermediate (15).‡ Compound (17) was converted into (18) by a similar procedure to that described for the preparation of (9).

Substitution of the Methyl Proton of (17).—Compound (17) was treated with 2 equiv. of BuLi, and then with a carbonyl compound, followed by methyl iodide to give a vinyl sulphone (19). On treatment with dil. HCl, instead of alkyl halide, compound (17) was converted into a sulphonyl ester (20). The use of an ester afforded a keto ester (21). These results are summarized in Table 4.

Preparation of Ethyl (*Methylthio*)*dithioacetate* (22).—The reaction of methylthiomethanide anion [8] with diethyl trithiocarbonate afforded compound (22) in unsatisfactory yield. However, this compound could be obtained in moderate yield by deoxygenation of compound (4) using triphenylphosphine.

Experimental

Microanalyses were performed with a Perkin-Elmer 240 elemental analyser at the Chemical Analysis Center of Chiba University. I.r., u.v., mass, ^{1}H n.m.r., and ^{13}C n.m.r. spectra were measured with Japan Spectroscopic Co. DS 403G, Hitachi EPS-3T, RMU 6MC instruments, Japan Electron Optics Lab. Co. C-60HL, and FX-100 instruments, respectively. Silica gel used in column chromatography was Wakogel C-200, and silica gel used for t.l.c. was Wakogel B-5F.

General Procedure for Preparation of (*Methylsulphinyl*)*ketene Dithioacetals* (3).—To a solution of DMSO (1.56 g, 20 mmol) in THF (60 ml) was added a 15% solution of Bu^{n}Li in hexane (14 ml, 21 mmol) at −40 °C under nitrogen. After the mixture had been stirred for 30 min, a trithiocarbonate ester (10 mmol) was added and the mixture was stirred for an additional 30 min. After the addition of alkyl halide (22 mmol), the resulting mixture was stirred for 3 h at −10 °C, poured into water (50 ml), and then extracted with benzene. The extract was dried over sodium sulphate and evaporated to dryness (rotary evaporator). The yellow oil obtained was purified by column chromatography on silica gel using AcOEt–MeOH (20 : 1) as eluant to afford a dithioacetal (3). The following *new compounds* were thus prepared.

(3a), $\nu_{max.}$ (neat) 2 950, 2 800, 1 505, and 1 020 cm^{-1}; δ (CCl_4) 6.30 (1 H, s, CH), 2.64 (3 H, s, CH_3), and 2.49 (3 H, s, CH_3); *m/z* 182 (M^+) (Found: C, 32.9; H, 5.5. $C_5H_{10}OS_3$ requires C, 32.94; H, 5.53%).

‡ M.p.s of (16) and (17) reported in the literature were 97 and 82 °C, respectively; D. Laduree, P. Rioult, and J. Vialle, *Bull. Soc. Chim. Fr.*, 1973, 637.

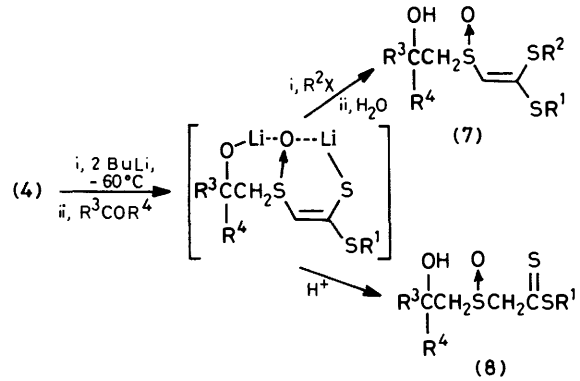
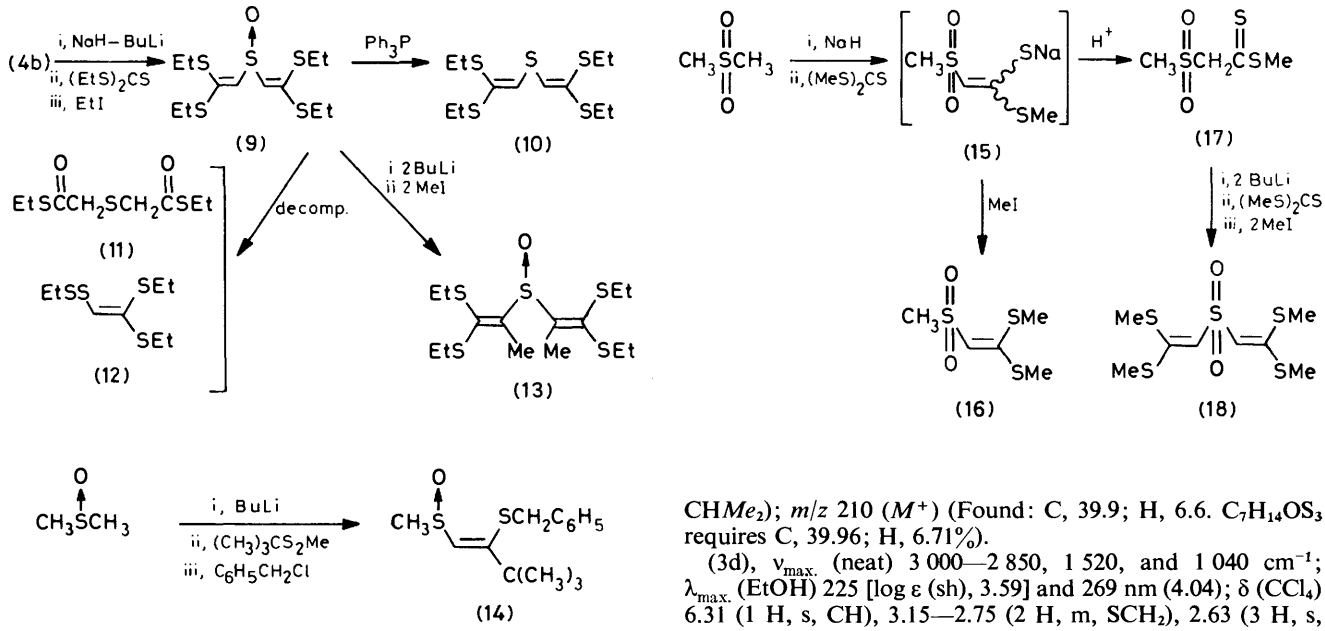


Table 3. Preparation of aldol-type adducts (7) and (8)

Compound	R^1	R^2	R^3	R^4	Properties	Yield (%)
(7a)	Et	Me	Me	Me	Oil, decomp. at 178 °C	80
(7b)	Et	Me	Ph	H	Crystals	73
(7c)	Et	Me	Ph	Me	Crystals, m.p. 122—123 °C	98
(7d)	Et	Me	Ph	Ph	Crystals, m.p. 113—114 °C	99
(7e)	Et	Me	Pr	H	Oil, decomp. on distillation	6
(8a)	Et	—	Me	Me	Oil, decomp. on distillation	64
(8b)	Et	—	Ph	H	Orange crystals, m.p. 100—101 °C	62
(8c)	Et	—	Ph	Me	Orange crystals, m.p. 66—67 °C	53
(8d)	Et	—	Ph	Ph	Orange crystals, m.p. 113—114 °C	68
(8e)	Et	—	*p*-$MeOC_6H_4$	H	Red crystals, m.p. 83—84 °C	43
(8f)	Et	—	*p*-MeC_6H_4	H	Red crystals, m.p. 79—80 °C	47
(8g)	Et	—	1-naphthyl	H	Red crystals, m.p. 99—100 °C	62



(3b), $\nu_{max.}$ (KBr) 3 000—2 900, 1 530, and 1 030 cm^{-1}; δ ($CDCl_3$) 6.20 (1 H, s, CH), 3.00 and 2.82 (2 H, dq, J_{gem} 16, J_{vic} 7.3 Hz, CH_2CH_3), 2.68 (3 H, s, CH_3), 2.41 (3 H, s, CH_3), and 1.32 (3 H, t, *J* 7.3 Hz, CH_2CH_3); *m/z* 196 (M^+) (Found: C, 36.75; H, 6.05. $C_6H_{12}OS_3$ requires C, 36.70; H, 6.16%).

(3c), $\nu_{max.}$ (KBr) 2 950—2 850, 1 510, and 1 040 cm^{-1}; $\lambda_{max.}$ (EtOH) 269 nm (log ε 4.06); δ (CCl_4) 6.31 (1 H, s, CH), 3.59 (1 H, sept, *J* 7 Hz, $CHMe_2$), 2.67 (3 H, s, CH_3), 2.45 (3 H, s, CH_3), and 1.36 and 1.32 (each 3 H, d, *J* 7 Hz, together $CHMe_2$); *m/z* 210 (M^+) (Found: C, 39.9; H, 6.6. $C_7H_{14}OS_3$ requires C, 39.96; H, 6.71%).

(3d), $\nu_{max.}$ (neat) 3 000—2 850, 1 520, and 1 040 cm^{-1}; $\lambda_{max.}$ (EtOH) 225 [log ε (sh), 3.59] and 269 nm (4.04); δ (CCl_4) 6.31 (1 H, s, CH), 3.15—2.75 (2 H, m, SCH_2), 2.63 (3 H, s, CH_3), 2.44 (3 H, s, CH_3), 1.80—1.35 (4 H, m, $CH_2CH_2CH_2$-CH_3), and 1.1—0.8 (3 H, m, CH_2CH_3); *m/z* 224 (M^+) (Found: C, 42.6; H, 7.45. $C_8H_{16}OS_3$ requires C, 42.82; H, 7.19%).

(3e), $\nu_{max.}$ (KBr) 2 950—2 850, 1 600, 1 520, and 1 030 cm^{-1}; $\lambda_{max.}$ (EtOH) 270 nm (log ε 4.13); δ (CCl_4) 7.17 (5 H, m, Ph), 6.31 (1 H, s, CH), 4.02 (2 H, s, CH_2), 2.31 (3 H, s, CH_3), and 2.28 (3 H, s, CH_3); *m/z* 258 (M^+) (Found: C, 51.2; H, 5.45. $C_{11}H_{14}OS_3$ requires C, 51.13; H, 5.46%).

(3f), $\nu_{max.}$ (neat) 2 940—2 760, 1 520, and 1 040 cm^{-1}; δ (CCl_4) 6.27 (1 H, s, CH), 2.88 (2 H, q, *J* 7 Hz, CH_2CH_3), 2.58 (3 H, s, CH_3), 2.45 (3 H, s, CH_3), and 1.36 (3 H, t, *J* 7 Hz,

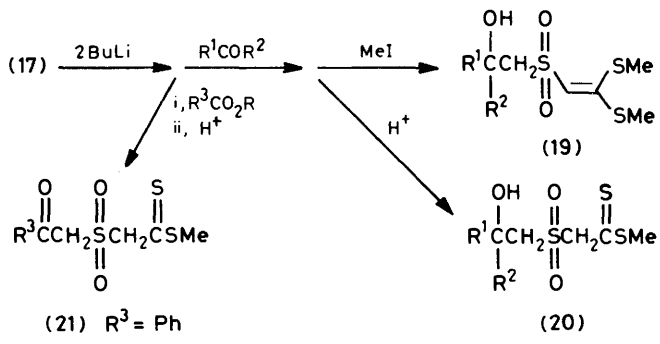
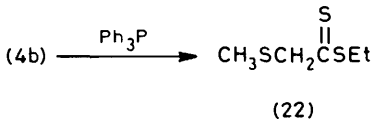


Table 4. Preparation of compounds (19)—(21)

Compds.	R^1	R^2	R^3	Properties	Yield (%)
(19a)	Me	Me	—	Needles, m.p. 91—92 °C	71
(19b)	Ph	Me	—	Plates, m.p. 121—122 °C	72
(19c)	Ph	Ph	—	Needles, m.p. 115—116 °C	29
(19d)	$-CH=CH[CH_2]_3-$		—	Oil, decomp. at 99—100 °C/0.3 Torr	20
(19e)	Pr^n	H	—	Oil, decomp. at 89—90 °C/0.07 Torr	51
(20a)	Me	Me	—	Oil, decomp. at 95—96 °C/0.07 Torr	70
(20b)	Ph	Ph	—	Orange plates, m.p. 122—123 °C	20
(20c)	Ph	H	—	Orange needles, m.p. 134—135 °C	33
(21)	—	—	Ph	Orange needles, m.p. 120—121 °C	58



CH_2CH_3); *m/z* 196 (M^+) (Found: C, 36.7; H, 6.1. $C_6H_{12}OS_3$ requires C, 36.70; H, 6.16%).

(3g), $\nu_{max.}$ (neat) 2 950—2 850, 1 510, and 1 040 cm^{-1}; $\lambda_{max.}$ (EtOH) 271 nm (log ε 4.05); δ (CCl_4) 6.45 (1 H, s, CH), 2.70—3.10 (4 H, m, 2 × CH_2CH_3), 2.60 (3 H, s, CH_3), and 1.15 1.50 (6 H, m, 2 × CH_2CH_3); *m/z* 210 (M^+) (Found: C, 39.7; H, 6.9. $C_7H_{14}OS_3$ requires C, 39.96; H, 6.71%).

(3h), δ (CCl_4) 6.43 (1 H, s, CH), 2.70—3.10 (2 H, m, SCH_2), 2.65 (3 H, s, CH_3), 2.47 (3 H, s, CH_3), 1.40—1.80 (4 H, m, $CH_2CH_2CH_2CH_3$), and 0.8—1.1 (3 H, m, CH_2CH_3); *m/z* 224 (M^+) (Found: C, 42.8; H, 7.1. $C_8H_{16}OS_3$ requires C, 42.82; H, 7.19%).

Methyl (Methylsulphinyl)dithioacetate (4a) *and Ethyl (Methylsulphinyl)dithioacetate* (4b).—These compounds were obtained by treatment with dil. HCl instead of alkyl halide described for the preparation of (3). The *new esters* had the following properties.

(4a), red oil; yield 71%; b.p. 148 °C (decomp.); $\nu_{max.}$ (neat) 3 000—2 900, 1 460, and 1 060 cm^{-1}; δ (CCl_4) 4.41 (2 H, s, CH_2), 2.71 (3 H, s, CH_3), and 2.66 (3 H, s, CH_3); *m/z* 168 (M^+) (Found: C, 28.45; H, 4.8. $C_4H_8OS_3$ requires C, 28.43; H, 4.80%).

(4b), red needles; yield 83%; m.p. 18—19 °C; $\nu_{max.}$ (neat) 2 950—2 900, 1 450, and 1 060 cm^{-1}; $\lambda_{max.}$ (EtOH) 316 nm (log ε 4.32); δ (CCl_4) 4.36 (2 H, s, CH_2), 3.26 (2 H, q, *J* 7 Hz, CH_2CH_3), 2.65 (3 H, s, CH_3), and 1.36 (3 H, t, *J* 7 Hz, CH_2CH_3); *m/z* 182 (M^+) (Found: C, 32.65; H, 5.45. $C_5H_{10}OS_3$ requires C, 32.94; H, 5.53%).

1,1-*Bis(ethylthio)*-2-*methylsulphinylprop*-1-*ene* (5a) *and* (Z)-1-*Ethylthio*-2-*methylsulphinyl*-1-*methylthio*-3-*phenylprop*-1-*ene* (5b).—To a mixture of (3g) (275 mg, 1.3 mmol) and THF (10 ml) was added a 15% solution of Bu^nLi in hexane (1.43 mmol) at −60 °C under nitrogen. After the mixture had been stirred for 20 min, methyl iodide (1.3 mmol) was added and the mixture was stirred for 1 h. The reaction mixture was quenched with water and extracted with ethyl acetate. The extract was washed with brine, dried over sodium sulphate, and evaporated under reduced pressure. The oil thus obtained was purified by t.l.c. on silica gel using ethyl acetate as eluant to give (5a). Similarly, (5b) was obtained from (3b) and benzyl chloride. The *new title compounds* were obtained.

(5a), $\nu_{max.}$ (neat) 2 950—2 850, 1 550, and 1 050 cm^{-1}; $\lambda_{max.}$ (EtOH) 275 nm (log ε 3.91); δ (CCl_4) 3.10—2.60 (4 H, m, 2 × CH_2), 2.47 (3 H, s, CH_3), 2.18 (3 H, s, CH_3), and 1.40—1.10 (6 H, m, 2 × CH_2CH_3); *m/z* 224 (M^+) (Found: C, 42.8; H, 7.12. $C_8H_{16}OS_3$ requires C, 42.82; H, 7.19%).

(5b), $\nu_{max.}$ (KBr) 3 050—2 850, 16 00, 1 540, and 1 030 cm^{-1}; $\lambda_{max.}$ (EtOH) 278 nm (log ε 4.03); *m/z* 286 (M^+) (Found: C, 54.5; H, 6.3. $C_{13}H_{18}OS_3$ requires C, 54.50; H, 6.33%).

3,3-*Bis(ethylthio)*-2-*methylsulphinyl*-1-(p-*nitrophenyl)prop*-2-*enol* (6a).—This compound was prepared as described for the preparation of (5) by using *p*-nitrobenzaldehyde instead of the alkyl halide. The product consisted of two diastereoisomers which were separated by t.l.c. on silica gel using AcOEt–benzene (1 : 2) as eluant. The minor component was isolated as yellow plates, m.p. 95—96 °C; yield 12%; $\nu_{max.}$ (KBr) 3 250, 3 000—2 850, 1 600, 1 520, and 1 020 cm^{-1}; δ ($CDCl_3$) 8.28 (2 H, d, *J* 8 Hz, ArH), 7.63 (2 H, d, *J* 8 Hz, ArH), 6.43 (1 H, d, *J* 10 Hz, CH), 5.85 (1 H, d, *J* 10 Hz, OH), 3.10 (3 H, s, CH_3), 2.88 (4 H, q, *J* 7 Hz, 2 × CH_2CH_3), and 1.30 (6 H, t, *J* 7 Hz, 2 × CH_2CH_3). The major component was isolated as needles, m.p. 97—99 °C; yield 31%; $\nu_{max.}$ (KBr) 3 250, 3 000—2 850, 1 600, 1 520, and 1 020 cm^{-1}; δ ($CDCl_3$) 8.23 (2 H, d, *J* 8 Hz, ArH), 7.70 (2 H, d, *J* 8 Hz, ArH), 6.50 (1 H, s, CH), 5.70 (1 H, s, OH), 2.95 (4 H, q, *J* 7 Hz, 2 × CH_2CH_3), 2.55 (3 H, s, CH_3), and 1.33 (6 H, t, *J* 7 Hz, 2 × CH_2CH_3) (Found: C, 46.7; H, 5.25; N, 3.85. $C_{14}H_{19}NO_4S_3$ requires C, 46.51; H, 5.31; N, 3.88%).

(E)-1-(2-*Hydroxy*-2-*methylpropylsulphinyl*)-2-*ethylthio*-2-*methylthioethene* (7a).*—To a solution of (4b) (255 mg, 1.4 mmol) in THF (100 ml) was added Bu^nLi (2.8 mmol) at −60 °C under nitrogen. After the mixture had been stirred for 20 min, acetone (0.2 ml) was added and the mixture was stirred for a further 20 min. The resulting mixture was treated with methyl iodide (0.3 ml) and extracted with ethyl acetate. The extract was worked up in the usual way to give *compound* (7a), $\nu_{max.}$ (neat) 3 330, 2 950—2 900, 1 510, and 1 020 cm^{-1}; δ (CCl_4) 6.47 (1 H, s, CH), 4.50 (1 H, br, OH), 3.12 and 2.97 [each 1 H, d, J_{gem} 14 Hz, together $C(OH)CH_2$], 2.97 (2 H, q, *J* 8 Hz, SCH_2CH_3), 2.50 (3 H, s, SCH_3), 1.42 and 1.43 [each 3 H, s, $C(CH_3)CH_3$], and 1.36 (3 H, t, *J* 8 Hz, CH_2CH_3); *m/z* 254 (M^+) (Found: C, 42.6; H, 7.2. $C_9H_{18}O_2S_3$ requires C, 42.49; H, 7.13%).

The following *new compounds* (7) were also obtained.

(7b), $\nu_{max.}$ (KBr) 3 300—3 150, 2 970—2 900, 1 600, 1 520, and 1 020 cm^{-1}; $\lambda_{max.}$ (EtOH) 273 nm (log ε 4.07); δ

* 1-[(*E*)-2-Ethylthio-2-methylthiovinylsulphinyl]-2-methylpropan-2-ol.

($CDCl_3$) 7.60—7.20 (5 H, m, Ph), 6.38 and 6.30 (together 1 H, 2 × s, CH), 5.50—5.10 (1 H, m, C*H*OH), 4.72 (1 H, br, OH), 3.30—2.70 [4 H, m, CH(OH)CH_2 and SCH_2CH$_3$], 2.47 (3 H, s, CH_3), and 1.35 (3 H, t, *J* 7 Hz, CH_2CH_3); *m/z* 302 (M^+) (Found: C, 51.45; H, 5.9. $C_{13}H_{18}O_2S_3$ requires C, 51.62; H, 6.00%).

(7c), $\nu_{max.}$ (KBr) 3 300—3 250, 3 040, 2 950—2 900, 1 600, 1 500, and 1 030 cm^{-1}; δ (CCl_4) 7.60—7.20 (5 H, m, Ph), 6.20 (0.4 H, s, CH), 5.93 (0.6 H, s, CH), 4.93 (1 H m, OH), 3.30—2.60 (4 H, m, 2 × CH_2), 2.45 (1.8 H, s, CH_3), 2.38 (1.2 H, s, CH_3), 1.85 (1.8 H, s, CH_3), 1.60 (1.2 H, s, CH_3), and 1.50—1.10 (3 H, m, CH_3); *m/z* 316 (M^+) (Found: C, 53.35; H, 6.35. $C_{14}H_{20}O_2S_3$ requires C, 53.13; H, 6.37%).

(7d), $\nu_{max.}$ (KBr) 3 250—3 200, 2 900, 1 510, and 1 060 cm^{-1}; δ (CCl_4) 7.80—7.20 (10 H, m, 2 × Ph), 6.20 (1 H, s, CH), 5.90 (1 H, s, OH), 3.70 (2 H, s, CH_2), 2.90 (2 H, q, *J* 7 Hz, CH_2CH$_3$), 2.50 (3 H, s, CH_3), and 1.40 (3 H, t, *J* 7 Hz, CH_2, CH_3); *m/z* 378 (M^+) (Found: C, 60.45; H, 5.9. $C_{19}H_{22}O_2S_3$ requires C, 60.28; H, 5.86%).

(7e), $\nu_{max.}$ (KBr) 3 350, 3 000—2 800, 1 510, and 1 050 cm^{-1}; δ (CCl_4) 6.31 (2 H, br, OH and CH), 3.60 [1 H, m, C(OH)*H*], 2.90 (4 H, m, 2 × CH_2), 2.50 (3 H, s, CH_3), 1.38 (7 H, m, $CH_3CH_2CH_2$ and CH_2CH_3), and 1.00 (3 H, t, *J* 7 Hz, CH_3-CH_2CH_2); *m/z* 268 (M^+) (Found: C, 44.7; H, 7.5. $C_{10}H_{20}O_2S_3$ requires C, 44.74; H, 7.51%).

General Procedure for the Preparation of 2-Hydroxy-2,2-disubstituted ethylsulphinyldithioacetate Esters (8).—Compounds (8) were obtained as described for the preparation of (7a) by using dil. HCl in place of the alkyl halide. The following *new compounds* were prepared.

(8a), δ (CCl_4) 4.48 (2 H, s, CH_2), 4.40 (1 H, br, OH), 3.34 (2 H, q, *J* 7 Hz, CH_2CH$_3$), 3.10 and 3.00 [each 1 H, d, J_{gem} 14 Hz, together C(OH)CH_2], 1.39 (6 H, s, 2 × CH_3), and 1.35 (3 H, t, *J* 7 Hz, CH_2CH_3); *m/z* 240 (M^+) (Found: C, 39.85; H, 6.7. $C_8H_{16}O_2S_3$ requires C, 39.97; H, 6.71%).

(8b), $\nu_{max.}$ (KBr) 3 300—3 150, 2 950—2 870, 1 600, 1 490, and 1 050 cm^{-1}; $\lambda_{max.}$ (EtOH) 316 nm (log ε 4.09); δ (CCl_4) 7.70—7.40 (5 H, m, Ph), 5.47 (1 H, m, CH), 4.61 (1 H, s, OH), 4.47 (2 H, s, CH_2), 3.50—3.10 [4 H, m, CH(OH)CH_2SO and SCH_2CH$_3$], and 1.32 (3 H, t, *J* 8 Hz, CH_2CH_3); *m/z* 288 (M^+) (Found: C, 49.9; H, 5.55. $C_{12}H_{16}O_2S_3$ requires C, 49.97; H, 5.59%).

(8c), $\nu_{max.}$ (KBr) 3 350—3 200, 2 950—2 900, 1 600, 1 500, and 1 020 cm^{-1}; $\lambda_{max.}$ (EtOH) 317 nm (log ε 4.04); δ (CCl_4) 7.80—7.40 (5 H, m, Ph), 4.50 (1 H, br, OH), 4.48 (2 H, s, $SOCH_2CS_2$), 3.55—3.10 [4 H, m, C(OH)CH_2SO and SCH_2-CH$_3$], 1.82 (1.9 H, s, CH_3), 1.70 (1.1 H, s, CH_3), and 1.36 (3 H, t, *J* 8 Hz, CH_2CH_3) (Found: C, 51.8; H, 6.0. $C_{13}H_{18}O_2S_3$ requires C, 51.62; H, 6.00%).

(8d), $\nu_{max.}$ (KBr) 3 400—3 300, 3 050, 2 950—2 900, 1 600, 1 500, and 1 060 cm^{-1}; $\lambda_{max.}$ (EtOH) 317 nm (log ε 4.09); δ (CCl_4) 7.70—7.20 (10 H, m, 2 × Ph), 5.36 (1 H, s, OH), 4.35 (2 H, s, $SOCH_2CS_2$), 4.00 and 3.60 [each 1 H, d, J_{gem} 15 Hz, together C(OH)CH_2] (Found: C, 59.25; H, 5.5. $C_{18}H_{20}O_2S_3$ requires C, 59.31; H, 5.53%).

(8e), $\nu_{max.}$ (KBr) 3 250, 3 000, 2 950—2 830, 1 615, 1 470, and 1 040 cm^{-1}; $\lambda_{max.}$ (EtOH) 226 (log ε 4.36), 276 (3.68), 283 (3.68), and 316 nm (4.11); δ (CCl_4) 7.40—6.70 (4 H, m, ArH), 5.30—5.00 [1 H, m, C*H*(OH)CH_2], 4.40 (1 H, br, OH), 4.30 (2 H, s, CH_2), 3.79 (3 H, s, OCH_3), 3.50—3.00 [4 H, m, CH-(OH)CH_2 and SCH_2CH$_3$], and 1.52 (3 H, t, *J* 7 Hz, SCH_2-CH_3); *m/z* 318 (M^+) (Found: C, 49.15; H, 5.65. $C_{13}H_{18}O_3S_3$ requires C, 49.03; H, 5.70%).

(8f), $\nu_{max.}$ (KBr) 3 350—3 250, 3 000, 2 950—2 850, 1 450, and 1 020 cm^{-1}; $\lambda_{max.}$ (EtOH) 317 nm (log ε 3.95); δ (CCl_4) 7.50—7.10 (4 H, m, ArH), 5.25 (1 H, m, CH), 4.50 (2 H, s, CH_2), 4.36 (1 H, s, OH), and 3.45—2.95 [4 H, m, CH(OH)-CH_2SO and SCH_2CH$_3$]; *m/z* 302 (M^+) (Found: C, 51.75; H, 5.95. $C_{13}H_{18}O_2S_3$ requires C, 51.62; H, 6.00%).

(8g), $\nu_{max.}$ (KBr) 3 300—3 200, 2 950—2 900, 1 600, 1 450, and 1 030 cm^{-1}; $\lambda_{max.}$ (EtOH) 273 (log ε 3.92), 283 (4.02), 294 (3.98), and 314 nm (4.00); *m/z* 338 (M^+) (Found: C, 56.85; H, 5.45. $C_{16}H_{18}O_2S_3$ requires C, 56.77; H, 5.36%).

Bis-[2,2-*bis*(*ethylthio*)*vinyl*] *Sulphoxide* (9).—To a solution of (4b) (180 mg, 0.99 mmol) in THF (10 ml) was added sodium hydride (50% oil dispersion; 70 mg, 1.4 mmol), Bu^{n}Li (1.2 mmol), and then, after the mixture had been stirred for 30 min, diethyl trithiocarbonate (327 mg, 1.9 mmol) at − 60 °C. The mixture was stirred for 1 h and treated with ethyl iodide (0.4 ml). The resulting solution was stirred for an additional 1 h at 0 °C, quenched with water (15 ml), and extracted with ethyl acetate. The extract was worked up in the usual way by using column chromatography on silica gel (eluant AcOEt) to give the *sulphoxide* (9) in 54% yield as crystals, m.p. 25 °C (from Et_2O); $\nu_{max.}$ (KBr) 2 950—2 850, 1 500, and 1 030 cm^{-1}; $\lambda_{max.}$ (EtOH) 270 (sh, log ε 4.14) and 308 nm (4.35); δ (CCl_4) 6.65 (2 H, s, 2 × CH), 2.95 (4 H, q, *J* 8 Hz, 2 × CH_2), 2.90 (4 H, q, *J* 8 Hz, 2 × CH_2), and 1.33 (12 H, t, *J* 8 Hz, 4 × CH_3); *m/z* 342 (M^+) (Found: C, 42.1; H, 6.4. $C_{12}H_{22}OS_5$ requires C, 42.07; H, 6.47%).

Bis-[2,2-*bis*(*ethylthio*)*vinyl*] *Sulphide* (10).—A mixture of (9) (339 mg, 0.99 mmol), CCl_4 (10 ml), and triphenylphosphine (400 mg, 1.5 mmol) was refluxed for 4 h. The reaction mixture was worked up by t.l.c. on silica gel using hexane–benzene (1 : 1) as eluant to give the sulphide (10) in 70% yield as an oil, b.p. 210 °C/0.1 Torr (Kugelrohr); $\nu_{max.}$ (neat) 2 950—2 850, 1 510, and 1 040 cm^{-1}; $\lambda_{max.}$ (EtOH) 306 nm (log ε 4.31); δ (CCl_4) 6.80 (2 H, s, 2 × CH), 2.77 (4 H, q, *J* 7 Hz, 2 × CH_2), 2.63 (4 H, q, *J* 7 Hz, 2 × CH_2), 1.20 (6 H, t, *J* 7 Hz, 2 × CH_3), and 1.15 (6 H, t, *J* 7 Hz, 2 × CH_3); *m/z* 326 (M^+) (Found: C, 44.05; H, 6.65. $C_{12}H_{22}S_5$ requires C, 44.13; H, 6.79%).

Bis[*ethylthio*(*carbonyl*)*methyl*] *Sulphide* (11) * *and Ethyl* 2,2-*Bis*(*ethylthio*)*vinyl Disulphide* (12).—When compound (9) was kept overnight at room temperature, it decomposed to give a black tarry material which was worked up in the usual way using t.l.c. on silica gel, eluant benzene–hexane (1 : 2), to give compounds (11) and (12) both in 6% yield: (12), an *oil*; $\nu_{max.}$ (neat) 2 950—2 850 and 1 515 cm^{-1}; $\lambda_{max.}$ (EtOH) 276 nm; δ ($CDCl_3$) 6.73 (1 H, s, CH), 2.82 (2 H, q, *J* 7 Hz, CH_2), 2.77 (2 H, q, *J* 7 Hz, CH_2), 2.73 (2 H, q, *J* 7 Hz, CH_2), 1.34 (3 H, t, *J* 7 Hz, CH_3), 1.26 (3 H, t, *J* 7 Hz, CH_3), and 1.24 (3 H, t, *J* 7 Hz, CH_3); *m/z* 240 (M^+) (Found: C, 39.95; H, 6.75. $C_8H_{16}S_4$ requires C, 39.96; H, 6.71%). Compound (12) was also prepared in 63% yield by stirring a solution of (9) and ethanethiol in THF for 12 h at room temperature.

Bis-[2,2-*bis*(*ethylthio*)-1-*methyl*] *Sulphoxide* (13).—To a solution of compound (9) (170 mg ,0.5 mmol) in THF (10 ml) was added a 15% solution of Bu^{n}Li in hexane (1 mmol) at −60 °C. After being stirred for 1 h the mixture was treated with methyl iodide (0.5 ml) and then stirred for an additional 1 h. The reaction mixture was worked up in the usual way to give *compound* (13), $\nu_{max.}$ (neat) 2 970—2 870, 1 550, and 1 020 cm^{-1}; $\lambda_{max.}$ (EtOH) 286 nm (log ε 4.13); δ (CCl_4) 3.20—2.50 (8 H, m, 4 × CH_2), 2.15 (6 H, s, 2 × CH_3), 1.31 (6 H, t, *J* 7 Hz, 2 × CH_3), and 1.23 (6 H, t, *J* 7 Hz, 2 × CH_3); *m/z* 370 (M^+) (Found: C, 45.25; H, 7.0. $C_{14}H_{26}OS_5$ requires C, 45.36; H, 7.07%).

* Di-*S*-ethyl 2,2′-thiodi(thioacetate).

(Z)-2-*Benzylthio*-3,3-*dimethyl*-1-*methylsulphinylbut*-1-*ene* (14).—The compound was prepared starting from dimethyl sulphoxide using methyl dithiopivalate and benzyl chloride. by the same method as described for the preparation of (3).

(14), needles, m.p. 72—73 °C (from Et_2O); yield 98%; $\nu_{max.}$ (KBr) 3 000—2 850, 1 600, 1 580, and 1 030 cm^{-1}; $\lambda_{max.}$ (EtOH) 280 nm (sh, log ε 3.57); δ (CCl_4) 7.23 (5 H, m, Ph), 6.65 (1 H, s, CH), 4.03 (2 H, s, CH_2), 2.58 (3 H, s, CH_3), and 1.13 [9 H, s, $C(Me)_3$]; *m/z* 268 (M^+) (Found: C, 62.65; H, 7.4. $C_{14}H_{20}OS_3$ requires C, 62.67; H, 7.51%).

2-*Methylsulphonyl*-1,1-*bis*(*methylthio*)*ethene* (16) *and Methyl* 2-(*Methylsulphonyl*)*dithioacetate* (17).—These compounds were prepared from dimethyl sulphone by the same method as described for the preparation of (3) and (4).

Bis-[2,2-*bis*(*methylthio*)*vinyl*] *Sulphone* (18).—This compound was prepared from dimethyl sulphone by the same method as described for the preparation of (9); *yellow prisms*, m.p. 144—145 °C [from CCl_4–$CHCl_3$] (1 : 1)]; yield 30%; $\nu_{max.}$ (KBr) 3 060, 2 990, 2 900, 1 495, 1 290, and 1 120 cm^{-1}; δ ($CDCl_3$) 6.30 (2 H, s, 2 × CH), 2.58 (6 H, s, 2 × CH_3), and 2.47 (6 H, s, 2 × CH_3) (Found: C, 31.8; H, 4.6. $C_8H_{14}O_2S_5$ requires C, 31.76; H, 4.67%).

2-(2-*Hydroxy*-2,2-*disubstituted ethylsulphonyl*)-1,1-*bis*-(*methylthio*)*ethenes* (19).—Compounds (19) were prepared from (17) by the same method as described for the preparation of (7). The following *new sulphonyl alcohols* were thus obtained.

(19a), $\nu_{max.}$ (KBr) 3 440, 3 000—2 800, 1 490, 1 280, and 1 120 cm^{-1}; $\lambda_{max.}$ (EtOH) 278 nm (log ε 3.69); δ ($CDCl_3$) 5.98 (1 H, s, CH), 3.80 (1 H, br, OH), 3.48 (2 H, s, CH_2), 2.58 (3 H, s, SCH_3), 2.45 (3 H, s, SCH_3), and 1.45 (6 H, s, 2 × CH_3) (Found: C, 37.65; H, 6.2. $C_8H_{16}O_3S_3$ requires C, 37.47; H, 6.30%).

(19b), $\nu_{max.}$ (KBr) 3 450, 3 060—2 950, 2 900, 1 500, 1 300, and 1 100 cm^{-1}; $\lambda_{max.}$ (EtOH) 211 (log ε 4.19) and 280 nm (4.15); δ ($CDCl_3$) 7.58 (5 H, m, Ph), 5.00 (1 H, s, OH), 4.93 (1 H, s, CH), 4.24 and 3.57 (together 2 H, d, J_{gem} 15 Hz, CH_2), 2.63 (3 H, s, SCH_3), 2.00 (3 H, s, SCH_3), and 1.68 (3 H, s, CH_3) (Found: C, 49.05; H, 5.65. $C_{13}H_{18}O_3S_3$ requires C, 49.02; H, 5.71%).

(19c), $\nu_{max.}$ (KBr) 3 400, 3 050—2 950, 1 470, 1 300, and 1 130 cm^{-1}; $\lambda_{max.}$ (EtOH) 211 (log ε 4.27) and 282 nm (4.12); δ ($CDCl_3$) 7.56 (10 H, m, 2 × Ph), 5.59 (1 H, s, CH), 4.91 (1 H, s, OH), 4.22 (2 H, s, CH_2), 2.56 (3 H, s, CH_3), and 1.92 (3 H, s, CH_3) (Found: C, 57.0; H, 5.3. $C_{18}H_{20}O_3S_3$ requires C, 56.81; H, 5.31%).

(19d), $\nu_{max.}$ (neat) 3 480, 2 920, 1 500, 1 300, and 1 150 cm^{-1}; $\lambda_{max.}$ (EtOH) 253 (log ε 3.68) and 276 nm (3.84); δ ($CDCl_3$) 5.95 (1 H, s, SO_2CH), 5.90 (2 H, d, CH=CH), 3.78 (1 H, br, OH), 3.53 (2 H, s, SO_2CH_2), 2.58 (3 H, s, CH_3), 2.45 (3 H, s, CH_3), and 2.00 (6 H, m, 3 × CH_2) (Found: C, 44.8; H, 6.1. $C_{11}H_{18}O_3S_3$ requires C, 44.87; H, 6.16%).

(19e), $\nu_{max.}$ (neat) 3 470, 3 010—2 800, 1 500, 1 300, and 1 120 cm^{-1}; $\lambda_{max.}$ (EtOH) 276 nm (log ε 3.97); δ (CCl_4) 6.00 (1 H, s, SO_2CH), 3.58 (1 H, br, OH), 3.25 (2 H, d, *J* 5 Hz, SO_2CH_2), 2.58 (3 H, s, SCH_3), 2.50 (3 H, s, SCH_3), 1.50 (5 H, m, 2 × CH_2, CH), and 0.98 (3 H, t, *J* 4 Hz, CH_3) (Found: C, 39.85; H, 6.67. $C_9H_{18}O_3S_3$ requires C, 39.97; H, 6.72%).

Methyl 2-(2-*Hydroxy*-2,2-*disubstituted ethylsulphonyl*)*dithioacetates* (20).—*Compounds* (20) were prepared from (17) by the same method as described for the preparation of (8).

(20a), $\nu_{max.}$ (neat) 3 470, 2 960, 2 900, 1 320, and 1 140 cm^{-1}; $\lambda_{max.}$ (EtOH) 235 (log ε 3.37) and 317 nm (3.99); δ ($CDCl_3$) 4.83 (2 H, s, SO_2CH_2S=S), 3.48 (2 H, s, CH_2), 3.40 (1 H, br, OH), 2.75 (3 H, s, SCH_3), and 1.45 (6 H, s, 2 × CH_3); *m/z* 242 (M^+) (Found: C, 34.65; H, 5.8. $C_7H_{14}O_3S_3$ requires C, 34.68; H, 5.83%).

(20b), $\nu_{max.}$ (KBr) 3 490, 2 900, 1 310, and 1 120 cm^{-1}; $\lambda_{max.}$ (EtOH) 211 (log ε 4.18) and 317 nm (3.97); δ ($CDCl_3$) 7.48 (10 H, m, 2 × Ph), 4.88 (1 H, br, OH), 4.48 (2 H, s, CH_2), 4.30 (2 H, s, SO_2CH_2C=S), and 2.68 (3 H, s, CH_3) (Found: C, 55.5; H, 5.05. $C_{17}H_{18}O_3S_3$ requires C, 55.70; H, 4.96%).

(20c), $\nu_{max.}$ (KBr) 3 480, 2 970, 1 290, and 1 140 cm^{-1}; $\lambda_{max.}$ (EtOH) 212 (log ε 4.06) and 317 nm (4.04); δ [$^2H_6$]DMSO) 7.40 (5 H, s, Ph), 5.15 (1 H, br, OH), 5.15 (2 H, s, SO_2CH_2-C=S), 3.43 (2 H, m, CH_2), and 2.70 (3 H, s, CH_3) (Found: C, 45.75; H, 4.85. $C_{11}H_{14}O_3S_3$ requires C, 45.49; H, 4.87%).

Methyl (2-*Phenacylsulphonyl*)*dithioacetate* (21).—This *compound* was prepared from (17) using ethyl benzoate by the same method as described for the preparation of (20), and had $\nu_{max.}$ (KBr) 3 000—2 900, 1 680, 1 310, and 1 140 cm^{-1}; δ ($CDCl_3$) 8.00 (2 H, dd, *J* 8 and 2 Hz, ArH), 7.65 (3 H, m, ArH), 5.02 (2 H, s, CH_2), 4.95 (2 H, s, CH_2), and 2.75 (3 H, s, CH_3) (Found: C, 45.6; H, 4.0. $C_{11}H_{12}O_3S_3$ requires C, 45.81; H, 4.20%).

Ethyl (2-*Methylthio*)*dithioacetate* (22).—This *compound* was prepared from (4) by the same method as described for the preparation of (10), and had $\nu_{max.}$ (neat) 2 950 and 2 900 cm^{-1}; δ (CCl_4) 3.90 (2 H, s, CH_2), 3.23 (2 H, q, *J* 8 Hz, CH_2CH_3), 2.20 (3 H, s, CH_3), and 1.37 (3 H, t, *J* 8 Hz, CH_2CH_3) (Found: C, 35.85; H, 5.9. $C_5H_{10}S_3$ requires C, 36.10; H, 6.07%).

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