Reactions of 1,3-Dithiolane 1,3-Dioxides with Nucleophiles

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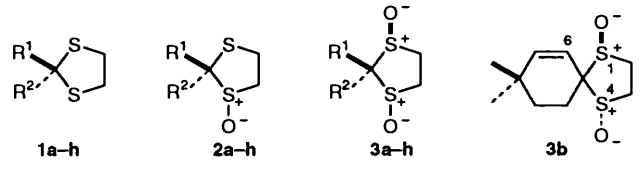
Reaction of benzenethiol with the 1,3-dithiolane 1,3-dioxides **3a–f** gave the 1,4-dithiane 1-oxides **4–5**, the α,β-unsaturated sulfoxides **6–9**, the ring-opening products **10–11** and various reduction products. Addition of benzenethiol, malononitrile, diethyl malonate or 2-mercapto-4,5-dihydrothiazole to the double bonds of the 2-alkenyl-1,3-dithiolane 1,3-dioxides **3g–h** was performed with methylmagnesium chloride in methanol. Addition of methanol or an allyl group to the dioxide **3h** occurred regioselectively to give the 1,3-dithiolane 1-oxide **19** or the 1,3-dithiolane **20**.

Sulfoxides are versatile reagents in organic synthesis,[1] being used as acyl nucleophile equivalents, in dehydrosulfinylation to give alkenes, in the Pummerer rearrangement to give carbonyl compounds and in [2,3] sigmatropic rearrangements to give allylic alcohols. Sulfoxides are intrinsically chiral reagents and their use in asymmetric control is well documented.[2] In contrast, there has been little work reported with disulfoxides,[3] although compounds such as the *trans*-1,3-dithiolane 1,3-dioxides, which have C_2-symmetry, are potential auxiliaries for enantioselective reactions. For example, Aggarwal and co-workers have shown both stereoselective addition reactions of *trans*-1,3-dithiane 1,3-dioxides with aromatic aldehydes and Diels–Alder reactions of *trans*-2-methylene-1,3-benzodithiole 1,3-dioxide with dienes. Khiar and his co-workers have demonstrated the use of C_2-symmetric disulfoxides as chiral ligands in asymmetric Diels–Alder reactions. We report herein the addition and ring-expansion of 1,3-dithiolane 1,3-dioxides **3a–h** in the presence of benzenethiol and other nucleophiles.



Results and Discussion

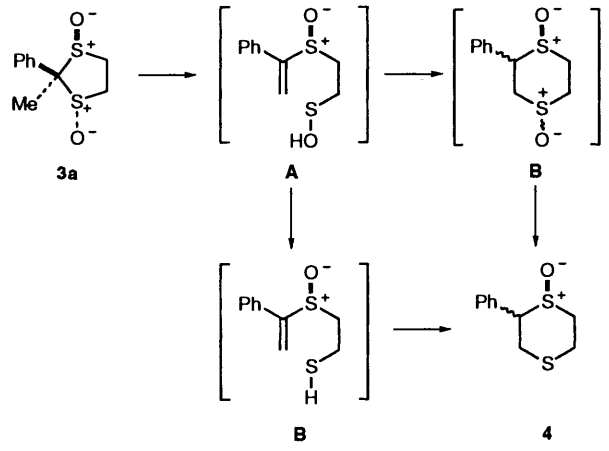
Preparation of Disulfoxides **3a–h**.—Although 1,3-dithiolanes can be oxidized directly to their corresponding 1,3-dioxides by use of 2 equiv. of $NaIO_4$,[4] we carried out this transformation in two successive oxidation steps, as shown in Table 1. This method provided an ambiguous assignment of the stereostructures of the disulfoxides **3a–h**. Oxidation of the 1,3-dithiolanes **1a–h** with 1 equiv. of $NaIO_4$ gave the corresponding monosulfoxdes **2a–h** in favour of the *trans*-isomers.[5] The dithiolane **1d** which had 2-methyl and 2-ethoxycarbonyl substituents afforded only the *trans*-isomer **2d**, where the sulfinyl oxygen and ethoxycarbonyl group were on opposite faces of the molecule.[6] In the ^1H NMR spectra of compounds **2**, the 2-H or 2-Me resonances of the *trans*-isomers usually occurred at lower field than those of the *cis*-isomers.[7] The monosulfoxides **2a–h** were then oxidized with 1 equiv. of *m*-chloroperbenzoic acid (*m*-CPBA)[8] to give the corresponding disulfoxides **3a–h**. The presence of C=C double bonds did not interfere with the oxidation process. Since the *trans*- and *cis*-isomers of **2b** were both converted into the disulfoxide **3b**, the product must have the *trans*-configuration. Similarly, the disulfoxides **3d–h** must also have the *trans*-configuration. The disulfoxides **3a** and **3c** exist as a mixture of two isomers, where the *cis*-isomers have the two oxygen atoms and the methyl group on the same face to form a C_s-symmetric molecule, as inferred by the coalescence of the C-4 and C-5 resonances. These results indicate that oxidation of the 1,3-dithiolane 1-oxides **2b** and **2d–h** occurred exclusively on the face opposite to the sulfinyl oxygen, whereas oxidation of the 1,3-dithiolane 1-oxides **2a** and **2c** were less selective, owing to the steric effect of the phenyl or the pentyl group.

Table 1 Conversion of the dithiolanes **1a–h** to the disulfoxides **3a–h** *via* the monosulfoxides **2a–h**

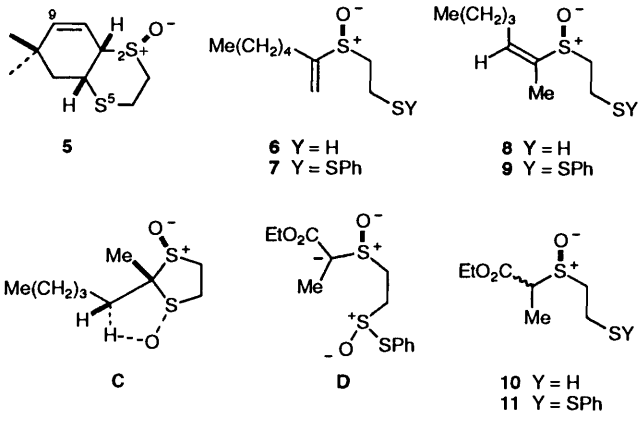
Dithiolane R^1, R^2	Monosulfoxide[a] (yield %; ratio of *trans*:*cis* isomers)	Disulfoxide[b] (yield %; ratio of *trans*:*cis* isomers)
1a Ph, Me	**2a** (66; 84:16)	**3a** (64; 25:75)[c]
1b CH=CHCMe$_2$CH$_2$CH$_2$	**2b** (54; 59:41)	**3b** (80; 100:0)
1c Me[CH$_2$]$_4$, Me	**2c** (76; 66:34)	**3c** (87; 80:20)[c]
1d EtO$_2$C, Me	**2d** (42; 100:0)	**3d** (84; 100:0)
1e MeCH$_2$CH$_2$, H	**2e** (37; 72:28)	**3e** (44; 100:0)
1f PhCH=CH, Me	**2f** (24; 63:27)	**3f** (60; 100:0)
1g PhCH=CH, H	**2g** (86; 75:25)	**3g** (55; 100:0)
1h MeCH=CH, H	**2h** (80; 75:25)	**3h** (100; 100:0)

[a] Oxidant, $NaIO_4$ (1 equiv.). [b] Oxidant *m*-CPBA (1 equiv.). [c] The *cis*-isomer of **3a** (or **3c**) had the two oxygen atoms and the methyl group on the same face.

Thermal Reactions of the Disulfoxides **3a–e** *in the Presence of Benzenethiol*.—A methanolic solution of dioxide **3a** and benzenethiol (1 equiv.) was heated at reflux to give the dithiane monooxide **4** in 72%, as a mixture of the *trans*- and *cis*-isomers (86:14). The 2-H and C-2 resonances in the *trans* isomer of **4** appeared at low field (δ 3.97 and 68.7), compared to the signals for the *cis* isomer (δ 3.85 and 61.3). The C-5 resonance occurs at δ 25.5 for the *trans* isomer, indicating an equatorial sulfinyl oxygen, whereas it resonates at δ 16.1 for the *cis* isomer, indicating an axial configuration.[9] Thermal ring expansion of the 2-methyl-1,3-dithiolane 1-oxide[10] has been shown to involve an H-shift from the methyl group to the sulfinyl oxygen, accompanied by a concurrent ring opening to give an intermediate vinylthioethylsulfenic acid. The product 5,6-dihydro-1,4-dithiine is subsequently obtained by a ring-closure process presumably *via* the sulfur-stabilized carbonium ion intermediate. Accordingly, ring-expansion of the dioxide **3a** to compound **4** was probably initiated by formation of the sulfenic acid intermediate **A** shown in Scheme 1. However, the intermediate **A** containing an electron deficient C=C double bond should act differently from the electrophilic vinyl sulfide species described above. The sulfenic acid **A** might undergo an intramolecular Michael addition[11] to give a disulfoxide **B**, in which the less hindered sulfoxide group is selectively reduced.



Scheme 1 *Reagents and conditions:* PhSH, MeOH, 70 °C, 36 h (72%)

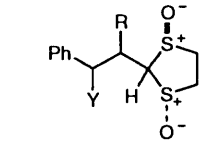


Alternatively, reduction of the sulfenic acid **A** to the thiol **B'**, followed by an intramolecular Michael addition would lead to the same product. The 1,3-dithiolane 1,3-dioxide **3b**, generated from 4,4-dimethylcyclohex-2-enone, underwent a similar ring expansion to afford the 1,4-dithiane 1-oxide **5** (73%). Since the ring-junction protons (1-H and 6-H) in compound **5** showed a small coupling constant (3.2 Hz), this bicyclic compound was determined to have a *cis* fused ring-junction and the resonance of C-4 at δ 21.7 was taken to indicate an equatorial sulfinyl oxygen.[9] The reaction of 2-methyl-2-pentyl-1,3-dithiolane 1,3-dioxide **3c** under similar conditions gave the a,β-unsaturated sulfoxides **6** and **8** accompanied by a significant amount of the disulfide **7**. This reaction was considered to involve the sulfenic acid intermediates generated from deprotonation of either the methyl or the pentyl group, similar to that shown in Scheme 1. Subsequent disproportionation of these sulfenic acid intermediates with benzenethiol would lead to the observed products. From the distribution of products, (**6** + **7**):**8** = 7:1, deprotonation of the methyl group appeared to be the more favoured process. In order to promote the ring closure of compounds **6** and **8**, the reaction temperature was raised to 110 °C for a prolonged period. However, such conditions yielded mainly the disulfides **7** and **9**, but no cyclization product. A 16% nuclear Overhauser enhancement of the vinyl proton (δ 6.18) in the sulfoxide **8** was observed by irradiation of the adjacent methyl group (δ 1.83), indicating the *Z*-configuration for compound **8**. Due to the deshielding effect of the sulfoxide group, the vinyl proton on the β-carbon of *E*-isomer usually resonates at lower field (about δ 6.4) than that of the *Z*-isomer.[12] The configuration of **9** was assigned as *Z*-, due to the vinyl resonance at δ 6.12 which was close to the value observed for compound **8**. The stereochemical outcome was in agreement with a concerted H-shift as shown in **C**.

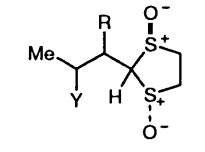
Treatment of the dithiolane dioxide **3d** with benzenethiol in refluxing methanol gave the thiol **10** and the corresponding phenyl disulfide **11**. These products were characterised by characteristic methyl doublets in the ^{1}H NMR spectra. The reaction sequence was presumably initiated by direct attack[13] of benzenethiol on one of the sulfoxide groups to give the intermediate anion **D**, stabilized by the other adjacent ester and the other sulfoxide group.

2-Propyl-1,3-dithiolane 1,3-dioxide **3e** was heated to 110 °C in a sealed tube in the presence of benzenethiol to give the partially reduced product **2e**. Partial deoxygenation of the disulfoxide **3f** gave the monosulfoxide **2f** on treatment with lithium ethanethiolate (1 equiv.) and complete deoxygenation gave the dithiolane **1f** on treatment with lithium dimethylcuprate (2 equiv.). These results were consistent with a previous report on the reduction of vinyl sulfoxides with EtMgBr–CuI.[12]

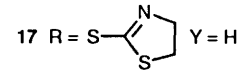
Addition to the C=C Double Bond of the Disulfoxides **3g** *and* **3h**.—Allyl sulfoxides are known to undergo [2,3] sigmatropic rearrangements to form intermediates, which can be reduced with benzenethiol to give allyl alcohols.[14] However, it was noted that benzenethiol adds to the C=C double bond of 2-styryl-1,3-dithiolane 1,3-dioxide **3g** in MeOH upon mediation with a Grignard reagent to give the disulfoxide **12** in 91% yield. Use of malonotrile as the nucleophile gave the addition product **13** as a diastereoisomeric mixture (67:33). Similar reactions of 2-prop-1-enyl-1,3-dithiolane 1,3-dioxide **3h** with the nucleophiles benzenethiol, malononitrile, diethyl malonate and 2-mercapto-4,5-dihydrothiazole in the presence of MeMgCl gave the addition products **14**, **15**, **16** and **17** respectively. In one case, addition of malononitrile to the disulfoxide **3h** was mediated by Al_2O_3.[15]



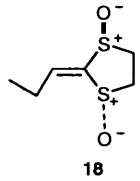
12 R = SPh, Y = H
[^{2}H]-**12** R = SPh, Y = D
13 R = CH(CN)$_2$, Y = H



14 R = SPh, Y = H
[^{2}H]-**14** R = SPh, Y = D
15 R = CH(CN)$_2$, Y = H
[^{2}H]-**15** R = CH(CN)$_2$, Y = D
16 R = CH(CO$_2$Et)$_2$, Y = H



17 R = S– Y = H



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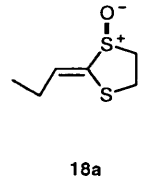

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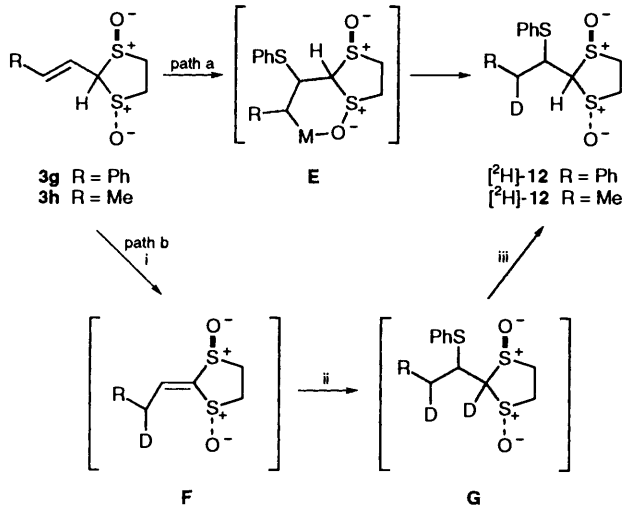
Two possible mechanisms were considered to account for the observed additions (Scheme 2). Path a evoked direct addition of the nucleophile to the C=C double bond; the intermediate might be stabilised by coordination to the sulfinyl oxygen as shown in **E**. Path b involved a primary isomerisation of compound **3g** (or **3h**) to the conjugated disulfoxide **F**, which then underwent a Michael-type reaction[16] with the nucleophile to give the observed product. Path a seemed less likely since the addition of EtSH to 2-methyl-2-styryl-1,3-dithiolane 1,3-dioxide **3f**, containing no hydrogen atom at C-2 failed (Table 2, entry 7). We thought the addition performed in MeOD would afford doubly deuteriated products **G** *via* path b. To our surprise, the monodeuteriated addition product [^{2}H]-**12** was obtained from

Table 2 Reactions of 1,3-dithiolane 1,3-dioxides **3a–h**

Entry	Disulfoxide	Reaction conditions	Products (yield, %; ratio of isomers)
1	**3a**	PhSH, MeOH, 70 °C, 36 h	**4** (72; 86:14)
2	**3b**	PhSH, MeOH, 70 °C, 22 h	**5** (73)
3	**3c**	PhSH, MeOH, 70 °C, 40 h	**6** (10) + **7** (10) + **8** (3)
4	**3c**	PhSH, MeOH, 110 °C (sealed), 12 h	**7** (22) + **9** (10)
5	**3d**	PhSH, MeOH, 70 °C, 3 h	**10** (14; 80:20) + **11** (41; 67:33)
6	**3e**	PhSH, MeOH, 110 °C (sealed), 18 h	**2e** (27) + **3e** (50)
7	**3f**	EtSH, BuLi, THF, room temp., 4 h	**2f** (43)
8	**3f**	Me_2CuLi, Et_2O, THF, 0 °C, 6 h	**1f** (36)
9	**3g**	PhSH, MeMgCl, MeOH, room temp., 24 h	**12** (91; 50:50)
10	**3g**	PhSH, MeMgCl, MeOD, room temp., 24 h	[^{2}H]-**12** (92)[a]
11	**3g**	$CH_2(CN)_2$, MeMgCl, MeOH, room temp., 19 h	**13** (42; 67:33)
12	**3h**	PhSH, MeMgCl, MeOH, room temp., 24 h	**14** (98; 57:43)
13	**3h**	PhSH, MeMgCl, MeOD, room temp., 24 h	[^{2}H]-**14** (100; 62:38)
14	**3h**	$CH_2(CN)_2$, MeMgCl, MeOH, room temp., 1 h	**15** (46; 67:33)
15	**3h**	$CH_2(CN)_2$, MeMgCl, MeOD, room temp., 1 h	[^{2}H]-**15** (11)[a,b]
16	**3h**	$CH_2(CN)_2$, Al_2O_3, room temp., 72 h	**15** (28; 56:44)[b]
17	**3h**	$CH_2(CO_2Et)_2$, MeMgCl, MeOH, room temp., 1 h	**16** (46; 71:29):
18	**3h**	2-mercapto-4,5-dihydro-thiazole, MeMgCl, MeOH, room temp., 0.5 h	**17** (83; 100:0)
19	**3h**	$MeCO_2H$, MeMgCl, MeOH, room temp., 1 h	**19** (55; 33:33:17:17)
20	**3h**	CH_2=$CHCH_2SiMe_3$, $(CF_3CO)_2O$, THF, room temp., 12 h	**20** (53)

[a] Ratio of isomers was not determined. [b] Starting material **3h** was recovered.



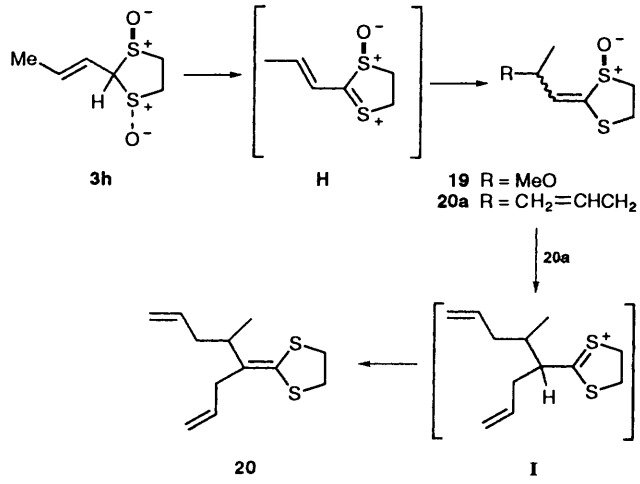
Scheme 2 *Reagents and conditions:* PhSH, MeMgCl, MeOD, room temp. 24 h. Path a: direct addition. Path b: i, isomerisation; ii, Michael addition; iii, work-up with aq. NH_4Cl.

the reaction of the disulfoxide **3g** with benzenethiolate ion in MeOD. Similarly, the monodeuteriated product [^{2}H]-**14** or [^{2}H]-**15** was also obtained from the reaction of the sulfoxide **3h** with either benzenethiol or malononitrile with the Grignard MeMgCl in MeOD. Since there was no deuterium atom incorporated at C-2 in the final product, we assumed a rapid exchange of the C_2-D, even in the presence of aqueous NH_4Cl. From literature,[4] the acidity of 2-H in 1,3-dithiane 1,3-dioxide has been measured to have a pK_a value of 25.0. To support our assumption, the addition of the conjugated disulfoxide **18** with PhSMgCl in MeOD, followed by work-up with aqueous NH_4Cl, gave the adduct **14** containing no deuterium atom.

Treatment of 2-prop-1-enyl-1,3-dithiolane 1,3-dioxide **3h** with chloromagnesium acetate in MeOH gave 2-(2-methoxypropylidene)-1,3-dithiolane 1-oxide **19** as a mixture of four diastereoisomers (**a**:**b**:**c**:**d** = 33:33:17:17). In the ^{1}H NMR spectrum, the vinyl resonances of the major *Z*-isomers (**a** + **b**) occurred at δ 5.94 and 5.99, respectively, whereas the minor *E*-isomers (**c** and **d**) resonated at lower field (δ 6.40 and 6.44 respectively). The reaction presumably proceeded with an intermediate α,β-unsaturated dithiolanium ion **H** (Scheme 3) derived from a Pummerer rearrangement similar to that proposed for the reactions of sulfoxides with Grignard reagents or allyltrimethylsilane.[17] Efficient trapping with methanol of the intermediate **H**, which presumably adopts the favourable *trans*-conformation at C(1′)–C(2), leads to the formation of the *Z*-isomers. Similarly, the reaction of the dioxide **3h** with allyltrimethylsilane in the presence of trifluoroacetic anhydride, gave the diallylated product **20**. In both reactions, the nucleophile added selectively at the γ-carbon (C-2′) of the α,β-unsaturated dithiolanium intermediate. The second allyl group was introduced by a subsequent Michael-type reaction to give the intermediate **I**, which then underwent isomerisation to furnish the final product **20**.

Experimental

General information concerning instrumentation and materials has been described previously.[18] *J* Values are given in Hz.



Scheme 3 *Reagents and conditions:* $MeCO_2H$, MeMgCl, MeOH, room temp., 1 h, giving **19** (55%), or CH_2=$CHCH_2SiMe_3$, $(CF_3CO_2)_2O$, THF, room temp., 12 h, giving **20** (53%)

1,3-Dithiolanes **1a–h** were prepared from the corresponding carbonyl compounds by literature methods.[19]

General Procedure for Oxidation of the Dithiolanes **1a–h** *to the Disulfoxides* **3a–h** via *the Monosulfoxides* **2a–h**.—A solution of 2-methyl-2-phenyl-1,3-dithiolane **1a** (1.26 g, 6.1 mmol) in MeOH (70 cm^3) was stirred with aqueous $NaIO_4$ (1.3 g, 6.1 mmol in 15 cm^3 water) at 0 °C for 12 h. The yellow solid was filtered off and the filtrate was concentrated and then extracted with EtOAc (3 × 30 cm^3). The extracts were combined, washed with brine (3 × 30 cm^3), dried (Na_2SO_4) and filtered. The filtrate was concentrated and chromatographed on silica gel with EtOAc–hexane (1:1) to give the monosulfoxide **2a** (0.85 g, 66%) as a mixture of the *trans*- and *cis*-isomers (84:16). The monosulfoxide **2a** in CH_2Cl_2 (40 cm^3) was treated with a solution of *m*-CPBA (0.68 g, 4 mmol) in CH_2Cl_2 (10 cm^3) at 0 °C for 2 h. The white solid was filtered off and the filtrate washed with aqueous NaOH (20%), dried (Na_2SO_4), concentrated and the residue chromatographed on silica gel with EtOAc to give the disulfoxide **3a** (0.58 g, 64%) as a white solid. This was obtained as a mixture of the *trans*- and *cis*-isomers (25:75), when the *cis*-sulfoxides are also *cis* to the methyl group.

2-*Methyl*-2-*phenyl*-1,3-*dithiolane* 1-*oxide* **2a**. A mixture of *trans*- and *cis*-isomers (66%; 84:16); oil: [R_f 0.49, hexane–EtOAc (1:4)]; *m/z* 212 (M^+, 78%), 136 (68) and 121 (100); $\delta_H(CDCl_3)$ 1.92 (s, Me *cis*), 1.98 (s, Me *trans*), 2.63–2.79 (1 H, m), 3.02–3.14 (1 H, m, dithiolane ring H), 3.21–3.33 (1 H, m), 3.61–3.75 (1 H, m), 7.21–7.38 (3 H, m) and 7.58–7.64 (2 H, m); $\delta_C(CDCl_3)$ 23.0 (q, Me *trans*)/25.0 (q, Me *cis*), 31.9 (t, C-4), 52.6 (t, C-5 *trans*)/52.0 (t), 82.9 (s, C-2 *trans*)/84.0 (s), 127.35 (d, 2 C), 128.1 (s), 128.4 (d) and 128.4 (d, 2 C) (Found: M^+, 212.0313. Calc. for $C_{10}H_{12}OS_2$: *M*, 212.0330).

8,8-*Dimethyl*-1,4-*dithiaspiro*[4.5]*dec*-6-*ene* 1-*oxide* **2b**. Two diastereoisomers (54%; 59:41) were separated by HPLC on a μ-Porsasil column with EtOAc as eluent. Major isomer: oil; HPLC(EtOAc) t_r 7.7 min; ν_{max}(neat)/cm^{-1} 1054; *m/z* 216 (M^+, 79%), 199 (38) and 140 (100); $\delta_H(CDCl_3)$ 1.04 (3 H, s), 1.05 (3 H, s), 1.68–1.76 (2 H, m), 1.94–2.08 (1 H, m), 2.44–2.54 (1 H, m), 3.10–3.22 (1 H, m), 3.28–3.41 (2 H, m), 3.62–3.76 (1 H, m), 5.27 (1 H, d, *J* 9.9) and 5.69 (1 H, d, *J* 9.9); $\delta_C(CDCl_3)$ 24.3 (t), 28.5 (q), 29.3 (1), 30.3 (t), 31.7 (s), 35.5 (t), 52.8 (t), 77.0 (s), 123.3 (d) and 143.5 (d) (Found: M^+, 216.0636. Calc. for $C_{10}H_{16}OS_2$: *M*, 216.0642). Minor isomer: white solid, m.p. 90–91 °C; HPLC (EtOAc) t_r 9.5 min; ν_{max}(KBr)/cm^{-1} 1054; *m/z* 216 (M^+, 75%), 199 (42) and 140 (100); $\delta_H(CDCl_3)$ 1.03 (3 H, s), 1.04 (3 H, s), 1.64–2.05 (4 H, m), 3.05–3.21 (1 H, m), 3.33–3.49 (2 H, m), 3.80–3.94 (1 H, m), 5.73 (1 H, d, *J* 10.0, H-b) and 5.88 (1 H, d, *J* 10.0); $\delta_C(CDCl_3)$ 28.3 (q), 29.1 (q), 31.35 (s), 31.65 (t), 32.7 (t), 34.3 (t), 54.8 (t), 76.4 (s), 119.5 (d) and 144.0 (d) (Found: M^+, 216.0642. Calc. for $C_{10}H_{16}OS_2$: *M*, 216.0642).

2-*Methyl*-2-*pentyl*-1,3-*dithiolane* 1-*oxide* **2c**. A mixture of *trans*- and *cis*-isomers (76%; 66:34); oil; TLC (hexane–EtOAc, 1:4) R_f 0.34; ν_{max}(neat)/cm^{-1} 1449 and 1052; *m/z* 206 (M^+, 76%) and 55 (100); $\delta_H(CDCl_3)$ 0.80 (3 H, t, *J* 6.9), 1.20–1.29 (4 H, m), 1.40 (s, Me *cis*), 1.55 (s, Me *trans*), 1.35–1.59 and 1.70–1.95 (4 H, m), 3.07–3.29 (3 H, m) and 3.45–3.64 (1 H, m); $\delta_C(CDCl_3)$ 13.75 (q), 19.0 (q, C-1″ *trans*)/24.3 (q), 22.1 (t)/22.2 (t), 24.95 (t)/25.95 (t), 29.6 (t)/30.9 (t), 31.7 (t)/31.8 (t), 38.8 (t)/34.3 (t), 54.1 (t)/53.6 (t) and 75.6 (s)/77.1 (s) (Found: M^+, 206.0811. Calc. for $C_9H_{18}OS_2$: *M*, 206.0799).

2-*Ethoxycarbonyl*-2-*methyl*-1,3-*dithiolane* 1-*oxide* **2d**. *trans*-Isomer: oil (42%); TLC (EtOAc) R_f 0.49; ν_{max}(neat)/cm^{-1} 1722, 1251 and 1052; *m/z* 209 (M^+ + 1, 41%) and 59 (100); $\delta_H(CDCl_3)$ 1.31 (3 H, t, *J* 7.1), 1.80 (3 H, s), 3.39–3.46 (2 H, m), 3.55–3.66 (1 H, m), 3.79–3.87 (1 H, m) and 4.22 (2 H, q, *J* 7.1); $\delta_C(CDCl_3)$ 13.9 (q), 17.6 (q), 34.6 (t), 53.3 (t), 62.6 (t), 79.5 (s) and 170.4 (s) (Found: M^+, 208.0230. Calc. for $C_7H_{12}O_3S_2$, *M*, 208.0228).

2-*Propyl*-1,3-*dithiolane* 1-*oxide* **2e**. A mixture of *trans*- and *cis*-isomers (37%; 72:28): oil; TLC (hexane–EtOAc, 1:4) R_f 0.20; ν_{max}(neat)/cm^{-1} 1458 and 1039; *m/z* 165 (M^+ + 1, 100%) and 164 (M^+, 97); $\delta_H(CDCl_3)$ 0.85 (t, *J* 7.3)/0.89 (t, *J* 7.3), 1.34–2.18 (4 H, m), 2.66–2.81 (1 H, m), 3.19–3.34 (2 H, m), 3.48–3.60 (1 H, m) and 4.02 (t, *J* 7.3, 2-H *trans*)/3.98 (t, *J* 7.3); $\delta_C(CDCl_3)$ 13.3 (q)/13.6 (q), 21.2 (t)/22.2 (t), 31.0 (t)/29.7 (t), 34.9 (t)/30.7 (t), 54.3 (t)/55.7 (t) and 73.1 (d)/68.3 (d) (Found: M^+, 164.0333. Calc. for $C_6H_{12}OS_2$: *M*, 164.0330).

2-*Methyl*-2-(2-*phenylvinyl*)-1,3-*dithiolane* 1-*oxide* **2f**. A mixture of *trans*- and *cis*-isomer (24%; 63:27): TLC (EtOAc–hexane, 1:1) R_f 0.2; ν_{max}(KBr)/cm^{-1} 2967, 1598, 1445, 1100 and 1053; *m/z* 238 (M^+, 73%) and 161 (100); $\delta_H(CDCl_3)$ 1.87 (s, Me *trans*)/1.78 (s), 3.14–3.86 (4 H, m), 6.24 (1 H, d, *J* 16)/6.53 (d, *J* 16), 6.88 (1 H, d, *J* 15.6)/6.85 (d, *J* 16) and 7.29–7.48 (5 H, m); $\delta_C(CDCl_3)$ 14.0 (q)/23.5 (q), 32.0 (t)/29.0 (t), 53.2 (t)/52.9 (t), 79.2 (s)/74.1 (s), 126.6 (d, 2 C)/127.6 (d), 126.7 (d)/124.1 (d), 128.3 (d), 128.5 (d, 2 C), 134.8 (d)/133.4 (d) and 135.2 (s)/135.6 (s) (Found: M^+, 238.0480. Calc. for $C_{12}H_{14}OS_2$: *M*, 238.0486).

2-(2-*Phenylvinyl*)-1,3-*dithiolane* 1-*oxide* **2g**. A mixture of *trans*- and *cis*-isomers (86%; 75:25): oily solid, TLC (EtOAc–hexane, 1:1) R_f 0.16; ν_{max}(neat)/cm^{-1} 2931, 1635, 1446, 1309 and 1049; *m/z* 224 (M^+, 11%) and 115 (100); $\delta_H(CDCl_3)$ 2.84–3.95 (4 H, m), 5.03 (d, *J* 8, 2-H)/4.96 (d, *J* 9), 6.05 (dd, *J* 14 and 8, 1-H)/6.33 (dd, *J* 16 and 9), 6.84 (d, *J* 14, 2′-H)/6.98 (d, *J* 16) and 7.29–7.46 (5 H, m); $\delta_C(CDCl_3)$ 31.9 (t, C-4)/32.2 (t), 53.7 (t, C-5)/56.4 (t), 75.2 (d, C-2)/70.1 (d), 121.5 (d, C-1′)/119.0 (d), 126.8 (d)/126.9 (d), 128.5 (d), 128.6 (d), 128.7 (d), 135.5 (s)/135.6 (s) and 136.4 (d, C-2′)/136.7 (d) (Found: M^+, 224.0323. Calc. for $C_{11}H_{12}OS_2$: *M*, 224.0339).

2-*Prop*-1-*enyl*-1,3-*dithiolane* 1-*oxide* **2h**. *trans*-Isomer: colourless crystals (80%), m.p. 108–109 °C, HPLC (EtOAc–hexane, 4:1) t_r 7.2 min; ν_{max}(KBr)/cm^{-1} 2993, 1655, 1035 and 926; *m/z* (M^+, 9%), 147 (5), 129 (8) and 108 (100); $\delta_H(CDCl_3)$ 1.70 (3 H, d, *J* 6, Me), 2.68–3.02 (4 H, m), 4.75 (d, *J* 9, 2-H), 5.32 (dd, *J* 15 and 9, 1′-H) and 6.04 (dq, *J* 15 and 6, 2′-H) (Found: M^+, 162.0182. Calc. for $C_6H_{10}OS_2$: *M*, 162.0173). *Cis*-isomer: liquid, HPLC (EtOAc–hexane, 4:1) t_r 8.4 min; ν_{max}(neat)/cm^{-1} 2912, 1656, 1423, 1036 and 926; $\delta_H(CDCl_3)$ 1.75 (d, *J* 6, Me), 2.80–3.90 (4 H, m), 4.70 (d, *J* 9, H-2), 5.50 (dd, *J* 15 and 9, 1′-H) and 5.90 (dq, *J* 6 and 15, 2′-H).

2-*Methyl*-2-*phenyl*-1,3-*dithiolane* 1,3-*dioxide* **3a**. A mixture of *trans*- and *cis*-isomers (64%; 25:75) inseparable by chromatography, m.p. 116–118 °C; TLC (MeOH–EtOAc, 1:9) R_f 0.25; ν_{max}(KBr)/cm^{-1} 1591, 1057 and 694; *m/z* 229 (M^+ + 1, 3%), 108 (92) and 84 (100); $\delta_H(CDCl_3)$ 1.77 (s, Me *trans*)/1.95 (s, Me *cis*), 3.46–3.72 (4 H, m) and 7.16–7.38 (5 H, m); $\delta_C(CDCl_3)$ 13.8 (q)/15.8 (q), 50.05 (t, C-4 and C-5, *cis*), 50.9 (t, C-5, *trans*), 53.9 (t, C-4, *trans*), 86.3 (s, C-2, *cis*), 91.1 (s, C-2, *trans*), 126.9 (d), 128.0 (d), 128.6 (d), 129.0 (d), 129.35 (d) and 135.35 (s), (Found: M^+, 228.0270. Calc. for $C_{10}H_{12}O_2S_2$: *M*, 228.0279).

8,8-*Dimethyl*-1,4-*dithiaspiro*[4.5]*dec*-6-*ene* 1,4-*dioxide* **3b**. White solid (80%), m.p. 131–132 °C; TLC (EtOAc) R_f 0.25; ν_{max}(KBr)/cm^{-1} 1043; *m/z* 232 (M^+, 5%) and 125 (100); $\delta_H(CDCl_3)$ 1.09 (3 H, s, Me), 1.10 (3 H, s, Me), 1.67–1.73 (2 H, m), 1.81–1.95 (1 H, m), 2.28–2.42 (1 H, m), 3.55–3.82 (4 H, m), 5.43 (1 H, d, *J* 10.1) and 6.09 (1 H, d, *J* 10.1); $\delta_C(CDCl_3)$ 20.6 (t), 28.4 (q), 28.7 (q), 31.6 (s), 34.8 (t), 50.9 (t), 51.9 (t), 88.5 (s), 114.2 (d) and 146.8 (d) (Found: M^+, 232.0597. Calc. for $C_{10}H_{16}O_2S_2$: *M*, 232.0592).

2-*Methyl*-2-*pentyl*-1,3-*dithiolane* 1,3-*dioxide* **3c**. A mixture of *trans*- and *cis*-isomers (87%; 80:20) were separated by chromatography on silica gel (MeOH–EtOAc, 1:9). *trans*-Isomer: white solid, m.p. 56–57 °C; TLC (MeOH–EtOAc, 1:9)

R_f 0.30; ν_{max}(KBr)/cm^{-1} 1460 and 1035; *m/z* 223 (M^+ + 1, 27%) and 108 (100); δ_H($CDCl_3$) 0.87 (3 H, t, *J* 6.8), 1.22–1.40 (4 H, m), 1.38 (3 H, s), 1.46–2.00 (4 H, m) and 3.44–3.81 (4 H, m); δ_C($CDCl_3$) 13.8 (q), 13.9 (q), 22.3 (t), 25.3 (t), 30.75 (t), 31.9 (t), 49.95 (t), 51.0 (t) and 90.0 (s) (Found: M^+, 222.0766. Calc. for $C_9H_{18}O_2S_2$: *M*, 222.0748). *cis*-Isomer: white solid, m.p. 60–61 °C; TLC (MeOH–EtOAc, 1:9) R_f 0.24; ν_{max}(KBr)/cm^{-1} 1438 and 1035; *m/z* 223 (M^+ + 1, 15%), 206 (40) and 108 (100); δ_H($CDCl_3$) 0.80 (3 H, t, *J* 6.7), 1.17–1.28 (4 H, m), 1.51 (3 H, s), 1.40–1.53 (4 H, m) and 3.34–3.64 (4 H, m); δ_C($CDCl_3$) 11.3 (q), 13.6 (q), 22.0 (t), 24.3 (t), 31.6 (t), 34.0 (t), 48.6 (t, 2 C) and 82.7 (s) (Found: M^+, 222.0738. Calc. for $C_9H_{18}O_2S_2$: *M*, 222.0748).

2-Ethoxycarbonyl-2-methyl-1,3-dithiolane 1,3-dioxide **3d**. White solid (84%), m.p. 91–92 °C; TLC (EtOAc) R_f 0.27; ν_{max}(KBr)/cm^{-1} 1733, 1246 and 1045; *m/z* 225 (M^+ + 1, 100%) and 211 (43); δ_H($CDCl_3$) 1.32 (3 H, t, *J* 7.2), 1.75 (3 H, s), 3.63–3.84 (3 H, m), 3.99–4.16 (1 H, m) and 4.29 (2 H, q, *J* 7.2); δ_C($CDCl_3$) 12.7 (q), 13.9 (q), 51.6 (t), 53.3 (t), 63.1 (t), 94.1 (s) and 163.9 (s) (Found: M^+, 224.0176. Calc. for $C_7H_{12}O_4S_2$: *M*, 224.0177).

2-Propyl-1,3-dithiolane 1,3-dioxide **3e**. White solid (44%), m.p. 95–96 °C; TLC (MeOH–EtOAc, 1:9) R_f 0.23; ν_{max}(KBr)/cm^{-1} 1455 and 1021; *m/z* 180 (M^+, 100%); δ_H($CDCl_3$) 1.07 (t, *J* 7.2, Me), 1.73 (2 H, sexet, *J* 7.2), 1.94–2.06 (2 H, m), 3.57–3.80 (4 H, m) and 3.84 (1 H, d, *J* 7); δ_C($CDCl_3$) 13.7 (t), 22.0 (t), 25.4 (t), 50.7 (t), 51.8 (t) and 91.0 (d) (Found: M^+, 180.0274. Calc. for $C_6H_{12}O_2S_2$: *M*, 180.0278).

2-Methyl-2-(2-phenylvinyl)-1,3-dithiolane 1,3-dioxide **3f**. White solid (60%), m.p. 109–110 °C; TLC (EtOAc) R_f 0.17; ν_{max}(KBr)/cm^{-1} 1636, 1492, 1400, 1089 and 1039; *m/z* 254 (M^+, 7%) and 129 (100); δ_H($CDCl_3$) 1.67 (3 H, s), 3.46–3.86 (4 H, m), 6.35 (d, *J* 16, 1′-H), 6.75 (d, *J* 16, 2′-H) and 7.30–7.43 (5 H, m); δ_C($CDCl_3$) 13.8 (q, 2 C), 50.5 (t), 51.3 (t), 88.2 (s), 118.9 (d), 126.3 (d, 2 C), 128.1 (d, 2 C), 128.2 (d), 134.8 (d) and 134.9 (s) (Found: M^+, 254.0436. Calc. for $C_{12}H_{14}O_2S_2$: *M*, 254.0435).

2-(2-Phenylvinyl)-1,3-dithiolane 1,3-dioxide **3g**. White crystal (55%), m.p. 155–157 °C (from EtOAc); TLC (EtOAc) R_f 0.17; ν_{max}(KBr)/cm^{-1} 2927, 1662, 1389, 1102 and 1031; *m/z* 240 (M^+, 14%) and 147 (100); δ_H($CDCl_3$) 3.68–3.92 (4 H, m), 4.72 (d, *J* 10, 2-H), 6.15 (dd, *J* 16 and 10, 1′-H), 6.98 (d, *J* 16, 2′-H) and 7.30–7.48 (5 H, m); δ_C($CDCl_3$) 52.0 (t), 52.7 (t), 93.1 (d), 112.5 (d), 127.1 (d, 2 C), 128.8 (d, 2 C), 129.2 (d), 135.1 (s) and 140.2 (d) (Found: C, 68.9; H, 5.0; S, 18.5. Calc. for $C_{11}H_{12}O_2S_2$: C, 68.84; H, 4.95; S, 18.50%).

2-Propenyl-1,3-dithiolane 1,3-dioxide **3h**. Oil (100%), TLC (MeOH-EtOAc, 1:9) R_f 0.25; ν_{max}(KBr)/cm^{-1} 2967, 1652, 1395, 1085 and 1027; *m/z* 179 (M^+ + 1, 1%) and 108 (100); δ_H($CDCl_3$) 1.85 (d, *J* 6, Me), 3.50–3.86 (4 H, m), 4.50 (d, *J* 9, 2-H), 5.44 (dd, *J* 15 and 9, 1′-H) and 6.10 (1 H, dq, *J* 15 and 6, 2′-H) (Found: M^+, 178.0119. Calc. for $C_6H_{10}O_2S_2$: *M*, 178.0122).

2-Phenyl-1,4-dithiane 1-Oxide **4**.—A mixture of the dithiolane disulfoxide **3a** (114 mg, 0.5 mmol) and benzenethiol (0.05 cm^3, 0.5 mmol) in MeOH (10 cm^3) was heated to 70 °C at reflux for 36 h. The mixture was cooled to room temperature, concentrated under reduced pressure and chromatographed on silica gel by elution with hexane–EtOAc (1:4) to give the *trans*- and *cis*-isomers of **4** in 62 and 10% yields, respectively. *trans*-Isomer: white solid, m.p. 180–181 °C; TLC (hexane–EtOAc, 1:4) R_f 0.16; ν_{max}(KBr)/cm^{-1} 1579, 1035 and 699; *m/z* 212 (M^+, 34%) and 104 (100); δ_H($CDCl_3$) 3.05–3.26 (5 H, m), 3.60–3.70 (1 H, m), 3.97 (dd, *J* 10.3 and 2.4. 2-H), 7.32–7.38 (5 H, m); δ_C($CDCl_3$) 25.5 (t, C-5), 31.4 (t, C-3), 52.6 (t, C-6), 68.7 (d, C-2), 128.5 (d, 2 C), 128.75 (d), 129.1 (d, 2 C) and 135.4 (s) (Found: M^+, 212.0315. Calc. for $C_{10}H_{12}OS_2$: *M*, 212.0330). *cis*-Isomer: white solid, m.p. 135–136 °C; TLC (hexane–EtOAc, 1:4) R_f 0.35; ν_{max}(KBr)/cm^{-1} 1597, 1026 and 696; *m/z* 212 (M^+, 65%) and 104 (100); δ_H($CDCl_3$) 2.43 (1 H, br d, *J* 12.9), 2.48 (1 H, br d, *J* 11.8), 3.01 (1 H, ddd, *J* 14.0, 12.7 and 2.8), 3.35 (1 H, ddd, *J* 14.0, 2.8 and 2.1), 3.73 (1 H, ddd, *J* 12.9, 12.7 and 2.1), 3.85 (1 H, dd, *J* 11.8 and 2.0), 4.02 (1 H, dd, *J* 11.8 and 11.8) and 7.25–7.38 (5 H, m); δ_C($CDCl_3$) 16.1 (t, C-5), 22.6 (t, C-3), 47.8 (t, C-6), 61.3 (d, C-2), 128.05 (d, 2 C), 128.6 (d), 129.0 (d, 2 C) and 135.4 (s) (Found: M^+, 212.0314. Calc. for $C_{10}H_{12}OS_2$: *M*, 212.0330).

8,8-Dimethyl-2,5-dithiabicyclo[4.4.0]*dec-9-ene 2-oxide* **5**.—Thermolysis of the disulfoxide **3b** by a procedure similar to that of **3a** described above gave 73% yield of the bicycle **5** as a white solid, m.p. 108–109 °C; *m/z* 216 (M^+, 50%) and 107 (100); δ_H($CDCl_3$) 1.08 (s, Me), 1.11 (s, Me), 1.74 (br d, *J* 13.4, 7β-H), 2.04 (dd, *J* 13.4 and 13.4, 7α-H), 2.83 (dd, *J* 4.1 and 4.1, 4-H), 3.02–3.18 (m, 3-H and 4-H), 3.39 (dt, *J* 13.4 and 3.2, 6-H), 3.47 (dd, *J* 5.2 and 3.2, 10-H), 3.60 (dd, *J* 9.2 and 4.5, 3-H), 5.82 (d, *J* 10.0, 9-H) and 6.01 (dd, *J* 10.0 and 5.2, 10-H); δ_C($CDCl_3$) 21.7 (t, C-4), 28.8 (q, Me), 30.3 (q, Me), 35.1 (s, C-8), 38.6 (t, C-7), 43.3 (d, C-6), 52.9 (t, C-3), 63.3 (d, C-1), 120.8 (d, C-9) and 143.0 (d, C-10) (Found: M^+, 216.0645. Calc. for $C_{10}H_{16}OS_2$: *M*, 216.0642).

Hept-1-en-2-yl 2-Mercaptoethyl Sulfoxide **6**, *Hept-1-en-2-yl 2-Phenylthioethyl Sulfoxide* **7**, *Hept-2-en-2-yl 2-Mercaptoethyl Sulfoxide* **8** *and Hept-2-en-2-yl 2-Phenylthioethyl Sulfoxide* **9**.—Compounds **6–9** were obtained by thermolysis of the disulfoxide **3c** at 70 °C or 110 °C (Table 2) by a procedure similar to that of **3a** described above. **6**: Oil, TLC (hexane–EtOAc, 1:1) R_f 0.34; ν_{max}(neat)/cm^{-1} 1622 and 1048; *m/z* 206 (M^+, 8%), 129 (48) and 61 (100); δ_H($CDCl_3$) 0.88 (t, *J* 6.7, 3, Me), 1.27–1.36 (4 H, m), 1.61–1.68 (2 H, m), 2.00–2.32 (2 H, m), 2.69–3.02 (4 H, m), 5.64 (1 H, d, *J* 1.8) and 5.83 (1 H, d, *J* 1.8); δ_C($CDCl_3$) 13.9 (q), 17.1 (t), 22.3 (t), 27.6 (t), 28.4 (t), 31.2 (t), 54.9 (t), 116.3 (t) and 152.0 (s) (Found: M^+, 206.0792. Calc. for $C_9H_{18}OS_2$: *M*, 206.0799). **7**: Oil, TLC (hexane–EtOAc, 1:1) R_f 0.54; ν_{max}(neat)/cm^{-1} 1623, 1434, 1052 and 740; *m/z* (20 eV) 315 (M^+ + 1, 9%), 168 (61) and 141 (100); δ_H($CDCl_3$) 0.90 (t, *J* 6.5, Me), 1.25–1.35 (4 H, m), 1.40–1.60 (2 H, m), 1.90–2.22 (2 H, m), 2.81–3.13 (4 H, m), 5.62 (1 H, s), 5.79 (1 H, s), 7.21–7.37 (3 H, m) and 7.50–7.56 (2 H, m); δ_C($CDCl_3$) 13.9 (q), 22.3 (t), 27.5 (t), 28.35 (t), 30.2 (t), 31.2 (t), 49.8 (t), 116.4 (t), 127.35 (d), 128.0 (d, 2 C), 129.2 (d, 2 C), 136.6 (s) and 151.8 (s) (Found: M^+, 314.0815. Calc. for $C_9H_{18}S_2$: *M*, 314.0832). **8**: Oil, TLC (hexane–EtOAc, 1:1) R_f 0.28; ν_{max}(neat)/cm^{-1} 1650 and 1048; *m/z* 206 (M^+, 10%) and 103 (100); δ_H($CDCl_3$) 0.89 (3 H, t, *J* 6.9), 1.24–1.48 (4 H, m), 1.83 (3 H, s), 2.13–2.25 (2 H, m), 2.72–2.96 (4 H, m) and 6.18 (1 H, t, *J* 7.5); δ_C($CDCl_3$) 9.2 (q), 13.8 (q), 17.5 (t), 22.3 (t), 27.8 (t), 30.8 (t), 54.6 (t), 135.2 (d) and 136.9 (s) (Found: M^+, 206.0793. Calc. for $C_9H_{18}OS_2$: *M*, 206.0799). **9**: Oil; TLC (30% EtOAc–hexane, 3:7) R_f 0.26; ν_{max}(neat)/cm^{-1} 1574 and 1048; *m/z* (20 eV) 315 (M^+ + 1, 16%), 169 (69) and 151 (100); δ_H($CDCl_3$) 0.90 (3 H, t, *J* 7.1), 1.25–1.42 (4 H, m), 1.77 (3 H, s), 2.12–2.19 (2 H, m), 2.88–3.05 (4 H, m), 6.12 (1 H, t, *J* 7.3), 7.22–7.36 (3 H, m) and 7.50–7.55 (2 H, m); δ_C($CDCl_3$) 9.2 (q), 13.8 (q), 22.3 (t), 27.7 (t), 30.5 (t), 30.7 (t), 49.5 (t), 127.3 (d), 128.05 (d, 2 C), 129.1 (d, 2 C), 135.2 (d) and 136.6 (s, 2 C) (Found: M^+, 314.0836. Calc. for $C_{15}H_{22}OS_3$: *M*, 314.0832).

1-Ethoxycarbonylethyl 2-Mercaptoethyl Sulfoxide **10** *and 1-Ethoxycarbonylethyl 2-Phenylthioethyl Sulfoxide* **11**.—Thermolysis of the disulfoxide **3d** by a procedure similar to that described for compound **3a**, gave the monosulfoxides **10** (14%) and **11** (41%). Either compound **10** or **11** existed as a mixture of diastereoisomers. **10**, a mixture of two isomers (80:20): oil, TLC (EtOAc) R_f 0.34; ν_{max}(neat)/cm^{-1} 1723 and 1020; *m/z* 211 (M^+ + 1, 11%) and 150 (100); δ_H($CDCl_3$) 1.32 (t, *J* 7.2, Me), 1.58 (d, *J* 7.3, Me major)/1.53 (d, *J* 7.3, minor), 2.92–3.12 (4 H, m), 3.62 (1 H, q, *J* 7.3)/3.78 (q, *J* 7.3) and 4.25 (q, *J* 7.2,

OCH_2)/4.26 (d, *J* 7.2); $\delta_C(CDCl_3)$ 10.9 (q), 14.1 (q), 17.9 (t), 55.0 (t, major)/52.6 (t, minor), 60.5 (d)/59.2 (d), 62.1 (t, OCH_2) and 168.65 (s) (Found: M^+, 210.0270. Calc. for $C_7H_{12}O_3S_2$: *M*, 210.0384). **11**, a mixture of two isomers (67:33): oil, TLC (EtOAc) R_f 0.53; ν_{max}(neat)/cm^{-1} 1723, 1049 and 1045; *m/z* 319 (M^+ + 1, 76%) and 168 (100); $\delta_H(CDCl_3)$ 1.28 (t, *J* 7.0, Me major)/1.32 (t, *J* 7.0, Me minor), 1.52 (d, *J* 7.3, Me)/1.59 (d, *J* 7.3, Me), 3.02–3.25 (4 H, m), 3.56 (q, *J* 7.3)/3.64 (q, *J* 7.3), 4.15–4.30 (2 H, m, OCH_2), 7.21–7.37 (3 H, m) and 7.47–7.56 (2 H, m); $\delta_C(CDCl_3)$ 10.7 (q, Me major)/10.8 (q), 14.1 (q), 30.8 (t)/31.2 (t), 50.1 (t)/50.3 (t), 60.45 (d), 62.0 (t), 127.1 (s), 127.4 (d), 128.1 (d), 129 (d, 2 C) and 168.5 (s) (Found: M^+, 318.0442. Calc. for $C_{13}H_{18}O_3S_3$: *M*, 318.0418).

2-(2-*Phenyl*-1-*phenylthioethyl*)-1,3-*dithiolane* 1,3-*Dioxide* **12**.—To a solution of benzenethiol (0.1 cm^3, 1 mmol) in MeOH (2 cm^3) was added dropwise a solution of MeMgCl (0.8 cm^3, 1.25 mol dm^{-3}, diethyl ether). The mixture was stirred for 20 min, after which a solution of the disulfoxide **3a** (228 mg, 1 mmol) in THF (2 cm^3) was added to it. The mixture was stirred at room temperature for a further 24 h to complete the addition (TLC analysis). Saturated aqueous NH_4Cl (1 cm^3) was then added to the mixutre and MeOH and THF removed by rotary evaporation. The residue was extracted with EtOAc (3 × 30 cm^3) and the combined extracts were dried (Na_2SO_4) and filtered. The filtrate was concentrated and the residue chromatographed on silica gel to give the title compound **12** (318 mg, 91%) containing two isomers (50:50). Isomer **a** was crystallised from EtOAc, m.p. 151.5–153.5 °C; ν_{max}(KBr)/cm^{-1} 2983, 1472, 1392, 1230, 1141 and 1026; *m/z* 350 (M^+, 36%), 223 (100) and 148 (21); $\delta_H(CDCl_3)$ 2.94–4.03 (8 H, m) and 7.28–7.36 (10 H, m); $\delta_C(CDCl_3)$ 40.4 (t), 48.7 (d), 51.2 (t), 52.1 (t), 96.0 (d, C-2), 127.0, 128.2, 129.1, 129.3, 129.7, 132.8 and 136.8 (Found: M^+, 350.0463. Calc. for $C_{17}H_{18}O_2S_3$: *M*, 350. 0469). Isomer **b** was isolated from the mother liquor by chromatography with EtOAc as eluent. $\delta_C(CDCl_3)$ 40.0 (t), 47.4 (d), 50.7 (t), 52.2 (t), 97.9 (d), 128.3, 128.4, 129.1, 129.3, 133.2, 133.4, 133.5 and 137.0. The reaction in MeOD gave 92% yield of [^{2}H]-**12**. $\delta_H(CDCl_3)$ 3.24–4.05 (7 H, m) and 7.26–7.42 (10 H, m); *m/z* 351 (M^+, 7%), 316 (11), 242 (19), 223 (39), 148 (40) and 110 (100) (Found: M^+, 351.0525. Calc. for $C_{17}H_{17}DO_2S_3$: *M*, 351.0531).

2-[1-(*Dicyanomethyl*)-2-*phenylethyl*]-1,3-*dithiolane* 1,3-*Dioxide* **13**.—Addition of **3g** with malononitrile by a procedure similar to that described for the dithiolane dioxide **12** gave compound **13** (42%) as a mixture of two diastereoisomers (67:23). The major isomer was crystallised from EtOAc, colourless crystals, m.p. 183–184.5 °C; ν_{max}(KBr)/cm^{-1} 2991, 2252, 1388, 1181 and 1021; *m/z* 306 (M^+, 1%), 241 (99) and 115 (100); $\delta_H(CDCl_3)$ 3.26–3.37 (3 H, m), 3.74–3.99 (5 H, m), 4.38 [d, *J* 5.1, $CH(CN)_2$] and 7.26–7.41 (5 H, m); $\delta_C(CDCl_3)$ 25.6 (d), 37.6 (t), 40.2 (d), 91.7 (d), 128.5 (d), 129.2 (d, 2 C), 129.6 (d, 2 C), 134.6 (s) and 167.0 (s, CN) (Found: M^+, 306.0481. Calc. for $C_{14}H_{14}O_2N_2S_2$: *M*, 306.0496). Minor isomer: $\delta_H(CDCl_3)$ 3.26–3.37 (3 H, m), 3.74–3.99 (5 H, m), 4.96 (1 H, d, *J* 4) and 7.29–7.43 (5 H, m).

2-(1-*Phenylthiopropyl*)-1,3-*dithiolane* 1,3-*Dioxide* **14**.—Addition of benzenethiol with the dithiolane dioxide **3h** in a similar manner to that described for compound **12** gave the title compound **14** (98%) containing two diastereoisomers (57:43). Two isomers were separated by HPLC on a μ-Porasil column by elution with EtOAc–Me_2CO (50:50). Major isomer: white solid, m.p. 118–120 °C; HPLC (EtOAc–acetone, 1:1) t_r 10.9 min; ν_{max}(KBr)/cm^{-1} 2966, 1436, 1393, 1088 and 1032; *m/z* 288 (M^+, 73%), 212 (56) and 180 (100); $\delta_H(CDCl_3)$ 1.26 (3 H, t, *J* 7.2, Me), 1.87–1.98, 2.11–2.20 (2 H, m), 3.42 (td, *J* 10, 3.5, 1′-H), 3.62–3.90 (5 H, m), 7.32–7.38 and 7.54–7.59 (5 H, m); $\delta_C(CDCl_3)$ 11.2 (q), 26.7 (t), 46.9 (d), 50.6 (t), 52.1 (t), 97.5 (d), 128.8 (d), 129.2 (d, 2 C), 131.5 (s) and 134.5 (d, 2 C) (Found: M^+, 288.0294. Calc. for $C_{12}H_{16}O_2S_3$: *M*, 288.0312). Minor isomer: oil, HPLC (EtOAc–acetone, 1:1) t_r 11.4 min; ν_{max}(neat)/cm^{-1} 2965, 1577, 1434, 1087, 1030 (s, S=O), 750 and 692; $\delta_H(CDCl_3)$ 1.24 (t, *J* 7.1, Me), 1.71–1.79, 1.90–2.02 (2 H, m), 3.38 (td, *J* 9.1 and 3.1, 1′-H), 3.54–3.94 (5 H, m), 7.30–7.38 and 7.54–7.60 (5 H, m); $\delta_C(CDCl_3)$ 11.2 (q), 26.6 (t), 47.0 (d), 50.4 (t), 52.3 (t), 98.6 (d), 128.5 (d), 129.2 (d) 131.8 (s) and 134.1 (d, 2 C) (Found: M^+, 288.0302. Calc. for $C_{12}H_{16}O_2S_3$: *M*, 288.0312).

2-[1-(*Dicyanomethyl*)]*propyl*-1,3-*dithiolane* 1,3-*Dioxide* **15**.—*Method A:* Addition of the dithiolane dioxide **3h** with malononitrile by a procedure similar to that described for compound **12** gave the title compound **15** (46%) containing two diastereoisomers (67:33). *Method B:* Neutral alumina (0.5 g) was activated by heating at 140 °C for 2 h, cooled and added to a solution of malononitrile (33 mg, 0.5 mmol) in THF (1 cm^3). The mixture was stirred for 0.5 h after which a solution of the dithiolane dioxide **3h** (89 mg, 0.5 mmol) in THF (1 cm^3) was added to it and the whole stirred for 72 h under an atmosphere of argon. After removal of the THF, the residue was extracted with EtOAc (2 × 10 cm^3). The combined extracts were washed with brine, dried (Na_2SO_4) and filtered. The filtrate was concentrated and the residue chromatographed on silica gel by elution with EtOAc to give the title compound **15** (34 mg, 28%) as a mixture of two isomers (56:44); colourless solid, m.p. 125–127 °C; TLC (EtOAc) R_f 0.25; ν_{max}(KBr)/cm^{-1} 2971, 2168 (CN), 1628, 1094 and 1026; *m/z* 244 (M^+, 4%) and 108 (100); $\delta_H(CDCl_3/CD_3OD)$ 1.21 (t, *J* 7.4, Me), 2.05–2.19 (2 H, m, 2′-H), 2.81–2.92 (1 H, m, 1′-H), 3.67–3.90 (5 H, m), 4.49 (d, *J* 5.8, $CH(CN)_2$ major)/4.99 (d, *J* 3.0, minor) (Found: M^+, 244.0341. Calc. for $C_9H_{12}N_2O_2S_2$: *M*, 244.0339). When the reaction was conducted in MeOD, [^{2}H]-**15** was obtained, accompanied by recovery of the starting material **3h**; *m/z* 245 (M^+, 1%) and 108 (100); $\delta_H(CDCl_3/CD_3OD)$ 1.28 (d, *J* 7.2, Me), 2.18–2.28 (1 H, m, 2′-H), 2.89–3.01 (1 H, m, 1′-H), 3.74–3.95 (5 H, m), 4.54 [d, *J* 5.9, $CH(CN)_2$, major] and 5.07 (d, *J* 3.0, minor) (Found: M^+, 245.0401. Calc. for $C_9H_{11}DN_2O_2S_2$: *M*, 245.0402).

2-{1-[*Bis*(*ethoxycarbonyl*)*methyl*]}propyl-1,3-*dithiolane* 1,3-*Dioxide* **16**.—Addition of the dithiolane dioxide **3h** with diethyl malonate by a procedure similar to that described for compound **12** gave the title compound **16** (46%) containing two diastereomers (71:29). Liquid, TLC (MeOH–EtOAc, 1:9) R_f 0.4; ν_{max}(neat)/cm^{-1} 2975, 1722 (s, C=O), 1231, 1093 and 1032; *m/z* 339 (M^+ + 1, 2%) and 108 (100); $\delta_H(CDCl_3)$ 1.02 (t, *J* 7.3, Me major)/1.05 (t, *J* 7.3, Me minor), 1.27–1.37 (6 H, m), 1.54–1.74 (2 H, m), 2.85–2.94 (1 H, m), 3.50–3.98 (7 H, m) and 4.19–4.39 (3 H, m) (Found: M^+, 338.0855. Calc. for $C_{13}H_{22}O_6S_2$: *M*, 338.0858).

2-{1-[(4,5-*Dihydro*-1,3-*thiazol*-2-*yl*)*thio*]}*propyl*-1,3-*dithiolane* 1,3-*Dioxide* **17**.—Addition reaction of the dithiolane dioxide **3h** with 2-mercapto-4,5-dihydrothiazole by a procedure similar to that described for compound **12** gave the title compound **17** (83%). Liquid, TLC (MeOH–EtOAc, 1:9); R_f 0.1; ν_{max}(neat)/cm^{-1} 1625 and 1030; *m/z* 297 (M^+, 1%) and 119 (100); $\delta_H(CDCl_3)$, 1.03 (t, *J* 7.2, Me), 1.82–1.94 (1 H, m), 2.02–2.15 (1 H, m), 3.35–3.49 (2 H, m), 3.60–3.99 (6 H, m) and 4.11–4.22 (2 H, m); $\delta_C(CDCl_3)$ 10.2 (q), 25.7 (t), 28.0 (t), 51.2 (t), 53.0 (t), 53.4 (t), 53.6 (t), 94.9 (d, C-2) and 199.4 (s) (Found: M^+, 296.9968. Calc. for $C_9H_{15}NO_2S_4$: *M*, 296.9986).

2-*Propylidene*-1,3-*dithiolane* 1,3-*Dioxide* **18**.—By a similar procedure to that described above for the dithiolane dioxide **3a**,

2-propylidene-1,3-dithiolane[20] was oxidized with $NaIO_4$ (1 equiv.) to give the 2-propylidene-1,3-dithiolane 1-oxide **18a** (59%) as a mixture of *E*- and *Z*-isomers (79:21); pale yellow oil, TLC (EtOAc–hexane, 1:1) R_f 0.13; ν_{max}(neat)/cm^{-1} 2965, 1676, 1397, 1171 and 1045; *m/z* 162 (M^+, 47%) and 145 (100); $\delta_H(CDCl_3)$ 1.06 (t, *J* 7.5, Me), 2.12–2.27 (2 H, m), 2.57–2.78, 3.40–3.64, 3.98–4.12 (4 H, m) and 6.46 (t, *J* 7.1, 1'-H *E*-isomer)/6.09 (t, *J* 7.8, 1'-H *Z*-isomer); $\delta_C(CDCl_3)$ 12.4 (q, C-3' *E*-isomer)/14.2 (q, C-3' *Z*-isomer), 25.6 (t, C-2')/26.5 (t), 31.9 (t, C-4)/31.4 (t), 54.9 (t, C-5)/55.6 (t), 135.3 (d, C-1')/134.6 (d) and 145.5 (s, C-2)/144.5 (s) (Found: M^+, 162.0176. Calc. for $C_6H_{10}OS_2$: *M*, 162.0173). Further oxidation of the monosulfoxide **18a** with *m*-CPBA (1 equiv.) gave 42% yield of the dioxide **18**: oil; ν_{max}(neat)/cm^{-1} 2973, 1607, 1459, 1327 and 1092; *m/z* 178 (M^+, 24%) and 135 (100); $\delta_H(CDCl_3)$ 1.17 (t, *J* 7.5, Me), 2.69 (2 H, qd, *J* 7.7 and 7.5), 3.58–3.86 (4 H, m) and 7.27 (t, *J* 7.7, 1'-H); $\delta_C(CDCl_3)$ 12.5 (q), 26.5 (t), 50.1 (t), 50.4 (t), 155.7 (s) and 156.7 (d) (Found: M^+, 178.0115. Calc. for $C_6H_{10}O_2S_2$: *M*, 178.0122).

2-(2-*Methoxypropylidene*)-1,3-*dithiolane* 1-*Oxide* **19**.—A methanolic solution of equivalent amounts of the dithiolane dioxide **3h**, acetic acid and MeMgCl (1.25 mol dm^{-3}, diethyl ether) were stirred at room temperature for 1 h to give the title compound **19** (55%), containing four diastereoisomers (**a**, **b**, **c** and **d**, 33:33:17:17). Isomers **a** and **b** had *Z*-configuration whereas **c** and **d** had *E*-configuration by analysis of the ^1H NMR spectrum. Oil, TLC (MeOH–EtOAc, 1:9) R_f 0.5; ν_{max}(neat)/cm^{-1} 2973, 1594, 1444, 1084 and 1042; *m/z* 192 (M^+, 7%) and 175 (86); $\delta_H(CDCl_3)$ 1.30 (d, *J* 6.5, *E*-isomer)/1.315 (d, *J* 6.3, *Z*-isomer)/1.32 (d, *J* 6.6, *E*-isomer)/1.38 (d, *J* 6.2, *Z*-isomer), 2.75 (1 H, m), 3.28 (s, OMe *Z*-isomer)/3.31 (s, *E*-isomer)/3.36 (s, *E*-isomer)/3.37 (s, *Z*-isomer), 3.49–3.86 (2 H, m), 3.90–4.13 (m, *Z*-isomer)/4.44–4.57 (m, *E*-isomer) and 5.94 (d, *J* 8.7, 1'-H, *Z*-isomer)/5.99 (d, *J* 8.7, *Z*-isomer)/6.40 (d, *J* 5.0, *E*-isomer)/6.44 (d, *J* 5.0, *E*-isomer) (Found: M^+, 192.0271. Calc. for $C_7H_{12}O_2S_2$: *M*, 192.0278).

1-*Allyl*-2-*methylpent*-4-*enylidene*-1,3-*dithiolane* **20**.—Under an atmosphere of argon, trifluoroacetic anhydride (0.15 cm^3, 1 mmol) was added dropwise to a solution of the dithiolane dioxide **3h** (89 mg, 0.5 mmol) in CH_2Cl_2 (2 cm^3) at 0 °C. The reddish mixture was stirred for 15 min and then allyltrimethylsilane (0.16 cm^3, 1 mmol) was added to it and the mixture stirred at room temperature for 12 h. After dilution with water (2 cm^3) the mixture was concentrated then extracted with EtOAc (2 × 10 cm^3). The combined extracts were washed with brine, dried (Na_2SO_4) and filtered. The filtrate was concentrated and the residue chromatographed on silica gel by elution with EtOAc–hexane (2:98) to give the title compound **20** (60 mg, 53%). Oil, TLC (EtOAc–hexane, 2:98) R_f 0.35; ν_{max}(neat)/cm^{-1} 1673; *m/z* 226 (M^+, 11%) and 185 (100); $\delta_H(CDCl_3)$ 1.03 (3 H, d, *J* 6.9), 2.02–2.27 (2 H, m), 2.61–2.78 (1 H, m), 2.86–2.91 (2 H, m), 2.32 (4 H, s, dithiolane ring H), 4.91–5.14 (4 H, m) and 5.63–5.86 (2 H, m); $\delta_C(CDCl_3)$ 18.25 (q, Me), 36.8 (t), 37.4 (t, dithiolane ring C), 39.45 (t), 42.3 (d), 115.6 (t, 2 C), 128.5 (s), 131.0 (s), 135.5 (d) and 137.25 (d) (Found: M^+, 226.0853. Calc. for $C_{12}H_{18}S_2$: *M*, 226.0850).

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