Asymmetric oxidation of 1,3-dithianes to 1,3-dithiane 1-oxides

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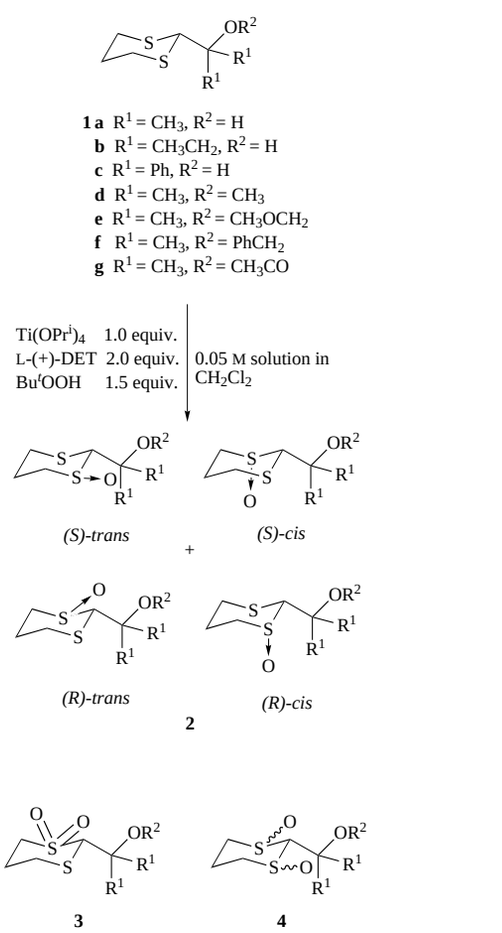
Oxidation of 2-(1-hydroxy-1-methylethyl)-1,3-dithiane with the Sharpless reagent has been examined under various reaction conditions. Oxidation of 2-(1-hydroxy-1-methylethyl)-1,3-dithiane with $Ti(OPr^i)_4$–diethyl L-(+)-tartrate–*tert*-butyl hydroperoxide (1:2:1.5) in CH_2Cl_2 in the presence of 4 Å molecular sieves gives (1*S*,2*S*)-2-(1-hydroxy-1-methylethyl)-1,3-dithiane 1-oxide with high *trans* selectivity and with moderate enantioselectivity. The enantioselectivity depends upon the substituent at the 2-position of the 1,3-dithiane. Oxidation of 2-(1-methoxy-1-methylethyl)- and 2-(1-acetoxy-1-methylethyl)-1,3-dithiane gives (1*S*,2*S*)-2-(1-methoxy-1-methylethyl)- and (1*R*,2*S*)-2-(1-acetoxy-1-methylethyl)-1,3-dithiane 1-oxides, respectively in >99% ee.

Introduction

Chiral sulfoxides are important synthetic intermediates for enantioselective carbon–carbon bond formation,[1] and a number of methods for the preparation of chiral sulfoxides have been reported.[2] Particularly, successful asymmetric oxidations of prochiral sulfides to chiral sulfoxides have been demonstrated by using a modified Sharpless reagent,[3a] salen-Mn complexes,[3b] and microbial enzymes.[3c] Recently, 1,3-dithiane 1-oxide and its derivatives were used as precursors of chiral acyl anions as well as chiral auxiliaries in an asymmetric synthesis.[4] Page and co-workers have reported that enantioselective oxidation of 2-acyl-1,3-dithiane by Kagan's method gives the monooxide in good yield with excellent optical purity.[5] Enantioselectivity in the asymmetric oxidation of 2-substituted 1,3-dithianes depends upon the substituents at the 2-position, whereas the asymmetric oxidation of 1,3-dithiane gives 1,3-dithiane 1-oxide with low stereoselectivity together with the inevitable formation of the 1,3-disulfoxide and the sulfone. In contrast, original Sharpless asymmetric epoxidation of allylic alcohols gives high enantioselectivity through a catalytic pathway under rigorously anhydrous conditions, showing that highly enantioselective epoxidation requires the coordination of the hydroxy group in allylic alcohols with the titanium reagent.[6] We have recently reported highly stereoselective oxidation of the adducts of 1,3-dithiane with camphor which can be most effectively achieved by the Sharpless reagent under anhydrous reaction conditions, giving the optically pure 1,3-dithiane 1-oxide derivative which leads to the formation of optically pure 1,3-dithiane 1-oxide.[7] We examined oxidation of 1,3-dithiane derivatives bearing a polar substituent at the 2-position such as an hydroxy or alkoxy group, expecting to induce some interaction with the titanium reagent. We describe herein an asymmetric oxidation of 2-hydroxymethyl- and 2-alkoxymethyl-1,3-dithianes with $Ti(OPr^i)_4$–L-tartrate–Bu^{t}OOH under various reaction conditions including anhydrous conditions.

Results and discussion

Hydroxymethyl- and alkoxymethyl-1,3-dithianes **1a**–**g** were readily prepared as follows: a THF solution of 1,3-dithiane was treated with 1.1 equiv. of BuLi at −78 °C and reacted with ketones at −78 °C to afford 2-hydroxymethyl-1,3-dithianes **1a**, **1b** and **1c** in 67–98% yield. Preparation of 2-alkoxymethyl-1,3-dithianes **1d-f** was accomplished by treatment of 2-(1-hydroxy-1-methylethyl)-1,3-dithiane **1a** with sodium hydride and subsequently with the corresponding alkyl halides (61–82% yield). The acetoxyethyl-1,3-dithiane **1g** was prepared by treatment of 2-(1-hydroxy-1-methylethyl)-1,3-dithiane **1a** with sodium hydride and subsequently with acetic anhydride (61% yield). First, oxidation of **1a** was examined according to Kagan's method[8] using $Ti(OPr^i)_4$–diethyl L-(+)-tartrate (DET)–Bu^{t}OOH–H_2O (1:2:1:1) in CH_2Cl_2 at −30 °C for 11 h to give 2-(1-hydroxy-1-methylethyl)-1,3-dithiane 1-oxide **2a** in 58% yield with high *trans* selectivity (*trans*:*cis* = 97:3, entry 1, Table 1) (Scheme 1). In this reaction, no formation of over-oxidized products such as sulfone **3a** or 1,3-dioxide **4a** were observed. However, the optical purity of *trans*-**2a** was estimated



Scheme 1

to be at best 20% ee and was difficult to reproduce. The monooxide **2a** was found to form with high diastereoselectivity in a *trans*:*cis* ratio of 98:2 when oxidation of **1a** with $Ti(OPr^i)_4$–L-(+)-DET–Bu^{t}OOH (1:2:1.5) in CH_2Cl_2 was carried out under anhydrous conditions (entry 2). The reaction was significantly accelerated in comparison with the reaction in the presence of water (entry 1) and was complete within 2 h. It should be noted that no formation of the sulfone or other over-oxidized products was observed in the oxidation of the sulfide in the 1,3-dithiane ring under anhydrous conditions, although Kagan's oxidation of sulfides needs water to suppress the over-oxidation.[3a] In addition, we observed good reproducibility of the $[\alpha]_D$ value of *trans*-**2a** in the oxidation under anhydrous conditions, although the enantioselectivity was still low under these conditions. In order to improve the enantioselectivity, oxidation of **1a** was examined under various reaction conditions. Changing the solvent did not have any significant influence on the reaction time, yield and *trans* selectivity, but it had a considerable influence on enantioselectivity. The $[\alpha]_D$ value of *trans*-**2a** was −6.8 when chloroform was used as solvent (entry 3), whereas the oxidation in dichloromethane improved the $[\alpha]_D$ value to −11.4 (entry 6). These reactions were carried out in the presence of powdered 4 Å molecular sieves (10 wt%) to remove the residual water.[7] In addition, *trans*-**2a** showed positive values of $[\alpha]_D$ 2.9 and 6.8 in reactions in 1,2-dichloroethane and carbon tetrachloride, respectively (entries 4 and 5). The concentration of the reagents was also found to have an influence on enantioselectivity. When the reaction was carried out at a sufficiently high concentration of the titanium reagent to form the polymeric titanium complex (see ref. 9), enantioselectivity was lowered; the $[\alpha]_D$ values of *trans*-**2a** obtained in the reaction in 0.5 M solution were only −1.5 (entry 7), in 0.1 M solution −7.7 (entry 8) and in 0.05 M solution −10.8 (entry 9). The enantioselectivity was also improved at low temperature. The $[\alpha]_D$ value of *trans*-**2a** was −15.7 in dichloromethane at −78 °C, although it took a longer reaction time to complete the reaction (entry 12). Oxidation of the hydroxymethyl-1,3-dithiane **1a** by cumenyl hydroperoxide resulted in a lowering of the enantioselectivity (entry 13). High *trans*-selectivity (>97:3) was obtained throughout the reactions performed under anhydrous conditions.

Reactions using various amounts of L-(+)-DET were next examined and the results are summarized in Table 2. Oxidation without L-(+)-DET proceeded rapidly but gave a complex mixture of oxidation products such as monooxide **2a**, sulfone **3a** and 1,3-dioxide **4a** (entry 1). In the absence of both $Ti(OPr^i)_4$ and L-(+)-DET, no oxidation occurred at −30 °C with *tert*-butyl hydroperoxide. On the other hand, the 1,3-dioxide **4** was predominantly obtained together with a trace amount of **2a** in the reaction with one equivalent of $Ti(OPr^i)_4$ and 0.5 equivalents of L-(+)-DET (entry 2). When more than one equivalent of L-(+)-DET was used, only **2a** was produced in 61–98% yields with high *trans* selectivity in a ratio of 99:1 (entries 3, 4, 5 and 6). The highest $[\alpha]_D$ value (−10.8) of *trans*-**2a** was obtained when 2 equiv. of L-(+)-DET were used (entry 4). Oxidation of **1a** using diisopropyl L-(+)-tartrate (DIPT) or dimethyl L-(+)-tartrate (DMT) in place of L-(+)-DET gave **2a** also with high *trans* selectivity, but with low $[\alpha]_D$ values of *trans*-**2a** (entries 7 and 8). These results show that oxidation with $Ti(OPr^i)_4$–L-(+)-DET–Bu^{t}OOH (1:2:1.5) as oxidant in 0.05 M dichloromethane solution in the presence of powdered 4 Å molecular sieves are the conditions of choice.

Table 3 shows the results obtained from the oxidation of 1,3-dithiane derivatives bearing various substituents at the 2-position under appropriate reaction conditions. Oxidation of 2-(1-ethyl-1-hydroxypropyl)-1,3-dithiane (**1b**) gave 1-oxide **2b** in 86% yield in a *trans*:*cis* ratio of 87:13, and the optical purity of the isolated *trans*-**2b** was 24% ee (entry 2). Oxidation of 2-(1-hydroxy-1,1-diphenylmethyl)-1,3-dithiane (**1c**) afforded 1-oxide **2c** in 81% yield in a *trans*:*cis* ratio of 61:39 (entry 3). The optical purity was not determined in this case because neither the pure *trans* nor *cis* isomer could be isolated. Oxidation of 2-(1-alkoxy-1-methylethyl)-1,3-dithianes **1d**–**g** proceeded slower than that of **1a**–**c**. Oxidation of the methyl ether **1d** gave the 1,3-dithiane 1-oxide **2d** in 58% yield with high *trans* selectivity (*trans*:*cis* = 98:2) (entry 4). The optical purity of *trans*-**2d** obtained in this reaction was extremely high (>99% ee). The methoxymethyl ether **1e** and the benzyl ether **1f** gave 1,3-dithiane 1-oxides **2e** and **2f** in 87 and 84% yields, respectively, with high *trans* selectivity (*trans*:*cis* = 92:8), but with moderate enantioselectivity (entries 5 and 6). Oxidation of 2-(1-acetoxy-1-methylethyl)-1,3-dithiane **1g** gave the monooxide **2g** in a *trans*:*cis* ratio of 73:27, where the optical purity of the isolated *trans* isomer, *trans*-**2g**, was only 14% ee. In contrast, the isolated *cis* isomer, *cis*-**2g**, was found to be optically pure (>99% ee) (entry 7). These results show that the enantioselectivity depends upon the substituents, but a reasonable rationalization remains to be proposed at this moment.

Stereochemistry

The diastereomeric ratio, the enantiomeric excess, and stereochemistry of monooxides **2a**–**g** were determined as follows. The diastereomeric ratios of monooxides **2a**–**g** were determined by integration of the diastereomeric methine protons on the 1,3-dithiane ring of monooxides **2** in the ^1H NMR spectra of the crude products. The ^1H NMR chemical shifts of the methine proton on the C(2) carbon in the major isomer appeared at lower field than the minor isomer, *e.g.* in the case of **2a**, the

Table 1 Oxidation of **1a** with $Ti(OPr^i)_4$–L-(+)-DET–Bu^{t}OOH under various conditions[a]

Entry	Solvent	Concentration (mol dm^{-3})	Reaction conditions *T*/°C	*t*/h	Yield of **2a** (%)	Diastereoselectivity *trans*:*cis*	$[\alpha]_D$ of the *trans* isomer	ee (%)
1	CH_2Cl_2	0.5[b]	−30	11	58	97:3	—	—
2	CH_2Cl_2	0.5	−30	2	77	98:2	−2.7 (*c* 1.60, 20 °C)	8
3	$CHCl_3$	0.05[c]	−20	2	60	98:2	−6.8 (*c* 0.65, 22 °C)	20
4	$ClCH_2CH_2Cl$	0.05[c]	−20	3	68	98:2	+2.9 (*c* 1.00, 21 °C)	8
5	CCl_4	0.05[c]	−20	2	69	99:1	+6.8 (*c* 1.07, 27 °C)	20
6	CH_2Cl_2	0.05[c]	−20	2	70	99:1	−11.4 (*c* 0.95, 22 °C)	33
7	CH_2Cl_2	0.5	−20	2	68	97:3	−1.5 (*c* 0.50, 21 °C)	4
8	CH_2Cl_2	0.1	−20	3	65	97:3	−7.7 (*c* 0.70, 25 °C)	23
9	CH_2Cl_2	0.05	−20	2	74	99:1	−10.8 (*c* 0.80, 24 °C)	32
10	CH_2Cl_2	0.01	−20	5	91	96:4	−7.5 (*c* 0.70, 25 °C)	22
11	CH_2Cl_2	0.05	−30	15	62[d]	99:1	−11.1 (*c* 0.85, 27 °C)	33
12	CH_2Cl_2	0.05[c]	−78	8	61[d]	97:3	−15.7 (*c* 1.53, 25 °C)	46
13	CH_2Cl_2	0.05[c,e]	−20	6	89	98:2	−1.4 (*c* 1.00, 23 °C)	4

[a] All reactions were carried out using $Ti(OPr^i)_4$–L-(+)-DET–Bu^{t}OOH (1:2:1.5) under anhydrous conditions unless otherwise noted. [b] Water (1 equiv.) was added. [c] Powdered 4 Å molecular sieves were added. [d] The reaction was stopped before completion. [e] Cumenyl hydroperoxide was used as oxidant.

Table 2 Oxidation of **1a** with various amounts of L-(+)-DET[a]

Entry	L-(+)-tartrate	Equiv.	Reaction time *t*/h	Yield of **2a** (%)	Diastereoselectivity *trans*:*cis*	$[\alpha]_D$ of the *trans*-isomer	ee (%)
1	—	0	3	—[b]	—	—	—
2	L-(+)-DET	0.5	3	—[c]	—[d]	—	—
3	L-(+)-DET	1.0	2	61	99:1	−10.2 (*c* 0.5, 24 °C)	30
4	L-(+)-DET	2.0	2	74	99:1	−10.8 (*c* 0.8, 24 °C)	32
5	L-(+)-DET	3.0	3	79	99:1	−7.9 (*c* 1.0, 20 °C)	23
6	L-(+)-DET	4.0	3	98	99:1	−8.3 (*c* 0.8, 25 °C)	24
7	L-(+)-DIPT	2.0	5	78	99:1	−4.4 (*c* 1.0, 23 °C)	13
8	L-(+)-DMT	2.0	3	70	98:2	−4.6 (*c* 1.1, 21 °C)	13

[a] All reactions were carried out in CH_2Cl_2 (0.05 mol dm^{-3}) at −20 °C using 1 equiv. of $Ti(OPr^i)_4$, 1.5 equiv. of Bu^tOOH, and L-(+)-tartrate in the presence of 4 Å molecular sieves. [b] Complex oxidation products were formed. [c] Formation of a trace amount of the monooxide was observed. [d] Not determined.

Table 3 Oxidation of 2-substituted 1,3-dithianes **1** with $Ti(OPr^i)_4$–L-(+)-DET–Bu^tOOH[a]

Entry	Compound	R^1	R^2	Reaction conditions *T*/°C	*t*/h	Yield of **2** (%)	Diastereoselectivity *trans*:*cis*	$[\alpha]_D$ of the *trans* isomer	Major enantiomer	ee[b] (%)
1	**1a**	CH_3	H	−78	8 h	61	97:3	−15.7 (*c* 1.53, 25 °C)	*S*	46
2	**1b**	C_2H_5	H	−78	10 h	86	87:13		*S*	24
3	**1c**	Ph	H	−20	2 h	81	61:39		—	—
4	**1d**	CH_3	CH_3	−78	10 h	58	98:2	−35.2 (*c* 0.65, 27 °C)	*S*	>99
5	**1e**	CH_3	CH_2OCH_3	−40	40 h	87	92:8	−13.4 (*c* 0.95, 18 °C)	*S*	51
6	**1f**	CH_3	CH_2Ph	−20	3 h	84	92:8	−9.1 (*c* 0.98, 25 °C)	*S*	44
7	**1g**	CH_3	$COCH_3$	−78	10 h	84	73:27	+4.9 (*c* 1.4, 22 °C)	*R*	14
								+71.7[c] (*c* 0.3, 22 °C)	*R*	>99

[a] All reactions were carried out with solutions of **1** in CH_2Cl_2 (0.05 mol dm^{-3}) using $Ti(OPr^i)_4$–L-(+)-DET–Bu^tOOH (1:2:1.5) in the presence of powdered 4 Å molecular sieves. [b] Determined by ^1H NMR spectroscopy using the chiral shift reagent (*R*)-TFAE. [c] The $[\alpha]_D$ value for the *cis* isomer.

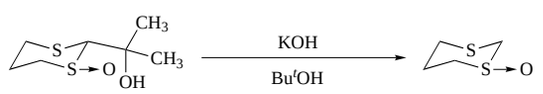
Table 4 ^{13}C NMR chemical shifts (δ) of 2-substituted 1,3-dithiane 1-oxides

1,3-Dithianes	C(2)	C(4)	C(5)	$\Delta\delta$	C(6)
1a	60.8	30.7	25.7		30.7
2a (major isomer)	73.3	30.9	25.9	+0.2	54.3
2a (minor isomer)	71.4	29.1	14.9	−10.8	47.2
1b	58.7	31.1	26.0		31.1
2b (major isomer)	71.1	31.1	29.9	+3.9	54.6
1c[a]	58.5	30.4	25.1		30.4
2c (*trans*)[a]	74.1	29.4	31.9	+6.8	54.4
2c (*cis*)[a]	68.0	28.5	14.4	−10.7	47.0
1d	57.7	30.7	25.7		30.7
2d (major isomer)	74.5	30.1	29.2	+3.5	55.0
1e	58.9	30.2	25.2		30.2
2e (major isomer)	75.6	30.1	29.3	+4.1	54.8
1f	58.0	30.9	26.0		30.9
2f (major isomer)	64.0	30.0	29.0	+3.0	54.9
1g	56.4	30.7	25.7		30.7
2g (major isomer)	71.8	30.5	30.2	+4.5	55.4
2g (minor isomer)	68.3	29.7	14.3	−11.4	47.6

[a] The data for **1c**, *trans*-**2c** and *cis*-**2c** were cited from the literature (ref. 10).

methine proton on C(2) appeared at δ 3.75 in the major isomer and at δ 3.64 in the minor isomer, respectively. The major diastereomer of **2a** was assigned to be *trans* by comparison of the ^{13}C NMR chemical shifts of the 1,3-dithiane ring with those reported by Carey *et al.*;[10] they have reported that the chemical shifts of C(5) and C(6) in the *trans* isomers of various corresponding 2-substituted-1,3-dithiane 1-oxides appear at lower field than those of the *cis* isomers, and the differential chemical shifts ($\Delta\delta$ values) between ^{13}C NMR chemical shifts of the monooxides and the corresponding 1,3-dithianes are also stereochemically diagnostic. In particular, the ^{13}C NMR chemical shifts of C(5) in *cis* isomers appear at significantly higher field than those of the *trans* isomers, and patterns of $\Delta\delta$ values of the C(5) and C(6) carbons in *cis* isomers are completely different from *trans* isomers. The ^{13}C NMR chemical shifts of the 1,3-dithiane ring of monooxides **2a**–**g** are shown in Table 4. The chemical shifts of C(5) and C(6) were δ 25.7 and 30.7 in the 1,3-dithiane **1a**. After column chromatography and subsequent recrystallization the ^{13}C NMR spectrum of the pure diastereoisomer of **2a** showed δ 25.9 and 54.3 in the major isomer, and δ 14.9 and 47.2 in the minor isomer, respectively. Thus the $\Delta\delta$ value of C(5) was +0.2 in the major isomer and −10.8 in the minor isomer, showing that the major isomer is in the *trans* form. Similarly, the major isomers of monooxides **2b**–**g** were determined to have the *trans* configuration from the pattern of $\Delta\delta$ values of the ^{13}C NMR chemical shifts, although the minor isomers were not isolated in the cases of **2b**–**f**.

The absolute configuration of *trans*-**2a** was determined by conversion to 1,3-dithiane 1-oxide **5** by base-catalyzed hydrolysis (Scheme 2). Thus, hydrolytic cleavage of an enantio-



2a **5**

Scheme 2

meric mixture of *trans*-**2a**, whose $[\alpha]_D^{20}$ was −15.7 (*c* 1.5, CH_2Cl_2), was carried out by treatment with potassium hydroxide in Bu^tOH at 50 °C for 1 h, giving 1,3-dithiane 1-oxide **5** in 78% yield. The $[\alpha]_D^{20}$ of the enantiomeric mixture of the monooxide **5** was −93.5 (*c* 0.16, ethanol), showing that the *S* conformer is enriched with 42% ee in comparison with $[\alpha]_D^{20}$ −224 (*c* 1.0, ethanol) for (*S*)-**5** in the literature.[11] From these results, the major enantiomer of *trans*-**2a** was assigned to be (1*S*,2*S*)-2-(1-hydroxy-1-methylethyl)-1,3-dithiane 1-oxide.

The absolute configuration of **2d** was determined by X-ray crystallographic analysis to be (1*S*,2*S*)-2-(1-methoxy-1-methylethyl)-1,3-dithiane 1-oxide as shown in Fig. 1. Optical purities of the *trans* isomer of **2a**–**g** and the *cis* isomer of **2g** were determined by analysis of the ^1H NMR spectra using the chiral shift reagent (*R*)-2,2,2-trifluoro-1-(9-anthryl)ethanol [(*R*)-TFAE],[12] which caused splitting of the C(2) methine

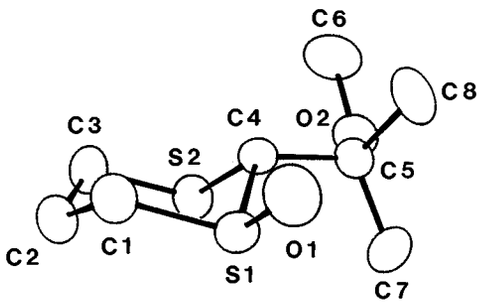
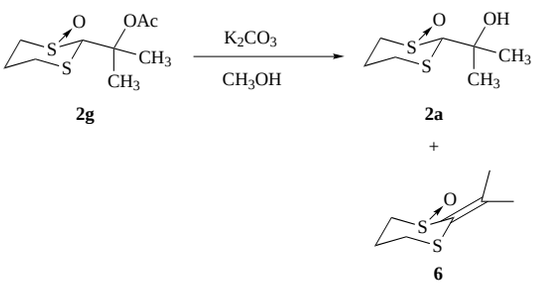


Fig. 1 ORTEP drawing of (1*S*,2*S*)-**2d**

proton. In the case of **2a**, for example, the C(2) methine proton at δ 3.75 in the *trans* isomer was split into two singlets by the addition of (*R*)-TFAE, where the major (1*S*,2*S*) enantiomer appeared at lower field than the minor (1*R*,2*R*) isomer. Similarly, the major (1*S*,2*S*) isomer of the *trans* oxide **2d** appeared at lower field than the minor. Enantiomeric excesses of *trans*-**2b** and **2d**–**g** are shown in Table 3. Stereochemical assignment of the absolute configuration of the major enantiomer of *trans* oxides **2b**, **2e** and **2f** was carried out using (*R*)-TFAE. Thus, absolute configurations of the major enantiomer of **2b**, **2e** and **2f** were assigned to be (1*S*,2*S*) in accord with those of *trans*-**2a** and **2d**, and were determined as described above; all these compounds showed the C(2) methine proton at lower field in the major enantiomer than in the minor one in the ^{1}H NMR spectra. On the other hand, the major isomer of *trans*-**2g** appeared at higher field than the minor, showing the major isomer to be (1*R*,2*R*). These correlations are compatible with the results reported by Pirkle and co-workers which showed correlations of the absolute configurations of some sulfoxides and their chemical shifts using a chiral shift reagent.[12] Furthermore, the signs of the $[\alpha]_D$ values in the enantiomers seem to correlate with the absolute stereochemistry. The (1*S*,2*S*) oxides **2a**–**f** showed negative rotations, whereas both the *trans* and *cis* diastereomers of **2g** showed positive $[\alpha]_D$ values. From these results the absolute configuration of the *cis* oxide *cis*-**2g** was tentatively assigned to be (1*R*,2*S*). This assignment of *trans*-**2g** was further confirmed by conversion of *trans*-**2g** to **2a** as shown in Scheme 3. Deacylation of *trans*-**2g** was carried out with potassium



Scheme 3

methoxide to give 2-isopropylidene-1,3-dithiane 1-oxide **6** in 57% yield and monooxide **2a** in 34% yield. This deacylated product **2a** showed a positive $[\alpha]_D$, showing that the major enantiomer of *trans*-**2g** was the (1*R*,2*R*) isomer.

Experimental

General

^{1}H NMR spectra were recorded on a Varian Gemini-200 instrument operating at 200 MHz, and chemical shifts (δ) are expressed in parts per million downfield from tetramethylsilane in $CDCl_3$. ^{13}C NMR spectra were recorded on a Varian Gemini-200 machine operating at 54.29 MHz. IR spectra were recorded on a JASCO A-102 spectrometer or JASCO FT200 spectrometer; absorptions are given in reciprocal centimetres. Optical rotations were measured on a JASCO DIP-4 instrument (100 mm, 1 cm^3 cell) in the indicated solvent, and concentrations are given in units of grams solute per 100 cm^3. Mass spectra (70 eV) were determined on a Hitachi M-2000 spectrometer. Microanalyses were performed with a Perkin-Elmer 240 instrument. Reactions involving air- or moisture-sensitive compounds were carried out in appropriate round-bottomed flasks under argon. All reactions were monitored by thin layer chromatography on 0.25 mm Merck silica gel plates (60F-254), with UV light and 7% phosphomolybdic acid or *p*-anisaldehyde in ethanol with heating. Column chromatography was carried out on columns packed with Fujii Silysia silica gel BW-200. A *tert*-butyl hydroperoxide solution in dichloromethane was prepared according to the literature[13] and stored over 4 Å molecular sieves under argon in a refrigerator. Diethyl L-(+)-tartrate was purified by distillation before use. Powdered 4 Å molecular sieves were dried under reduced pressure with heating before use.

2-(1-Hydroxy-1-methylethyl)-1,3-dithiane 1a

To a solution of 1,3-dithiane (4.08 g, 34.00 mmol) in THF (80 cm^3) was added BuLi (1.47 mol dm^{-3}, 25.4 cm^3, 37.40 mmol) at −78 °C. The mixture was allowed to warm to 0 °C and stirred for 30 min. Then the mixture was cooled to −78 °C and a solution of pre-distilled acetone (3.74 cm^3, 50.94 mmol) in THF (50 cm^3) was added. After the mixture was stirred for 5 min, the reaction mixture was quenched with aqueous NH_4Cl (10 cm^3) and the organic layer was separated. The aqueous layer was extracted with ether (4 × 10 cm^3) and the combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. Purification by column chromatography (85:15 and then 70:30 hexane–ethyl acetate) gave **1a** (5.92 g, 98%) (Found: C, 47.50; H, 7.14. Calc. for $C_7H_{14}OS_2$: C, 47.25; H, 7.19%); ν_{max}(KBr)/cm^{-1} 3400, 2900, 1720, 1420, 1370, 1240, 1150, 920 and 790; δ_H 1.36 (6H, s, 2 × CH_3), 1.75–1.97 (1H, m, 5-H), 2.04–2.19 (1H, m, 5-H), 2.27 (1H, s, OH), 2.78–3.00 (4H, m, 4-H and 6-H) and 4.14 (1H, s, 2-H); δ_C 25.65, 27.18, 30.66, 60.80 and 73.16.

2-(1-Ethyl-1-hydroxypropyl)-1,3-dithiane 1b

The reaction was carried out as described above except using 1,3-dithiane (601 mg, 5.00 mmol), BuLi (1.0 equiv.) and diethyl ketone (0.56 cm^3, 5.50 mmol). Purification by column chromatography (95:5 and then 80:20 hexane–ethyl acetate) afforded **1b** (852 mg, 83%) (Found: C, 52.45; H, 8.98. Calc. for $C_9H_{18}OS_2$: C, 52.38; H, 8.79%); ν_{max}(KBr)/cm^{-1} 3500, 2975, 2900, 1460, 1420, 1370, 1320, 1280, 1250, 1150, 950, 910 and 800; δ_H 0.91 (6H, t, *J* 7.3, 2 × CH_3CH$_2$),† 1.67 (2H, q, *J* 7.3, CH$_3$CH_2), 1.68 (2H, q, *J* 7.3, CH$_3$CH_2), 1.72–1.93 (1H, m, 5-H), 2.01–2.17 (1H, m, 5-H), 2.78–2.97 (4H, m, 4-H and 6-H), 2.90 (1H, s, OH) and 4.25 (1H, s, 2-H); δ_C 7.4, 26.0, 28.9, 31.1, 58.7 and 76.4.

2-(1,1-Diphenyl-1-hydroxymethyl)-1,3-dithiane[10] 1c

The reaction was carried out as described above except using 1,3-dithiane (601 mg, 5.00 mmol), BuLi (1.1 equiv.) and benzophenone (911 mg, 5.00 mmol). Purification by column chromatography (95:5 and then 80:20 hexane–ethyl acetate) afforded **1c** (1.02 g, 67%); ν_{max}(KBr)/cm^{-1} 3550, 3400, 3025, 2900, 1490, 1450, 1420, 1330, 1280, 1160, 1060, 1030, 970, 900, 750 and 700; δ_H 1.70–2.16 (2H, m, 5-H), 2.15 (1H, s, OH), 2.74–2.97 (4H, m, 4-H and 6-H), 3.30 (1H, s, 2-H), 7.12–7.29 (6H, m, Ph) and 7.52–7.11 (4H, m, Ph).

2-(1-Methyl-1-methoxyethyl)-1,3-dithiane 1d

To a suspension of sodium hydride (60% dispersion in mineral oil, 190 mg, 4.75 mmol) in THF (3.0 cm^3) was added portionwise a solution of **1a** (564 mg, 3.17 mmol) in THF (2.0 cm^3) at

† *J* Values are given in units of Hz.

0 °C. After stirring for 1 h, methyl iodide (0.22 cm^3, 3.48 mmol) was added and the mixture was stirred for an additional 6 h. The reaction mixture was then quenched with water (10 cm^3). The aqueous layer was extracted with diethyl ether (4 × 10 cm^3) and the combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure to give a crude oil, which was purified by column chromatography (90:10 and then 80:20 hexane–ethyl acetate) to give **1d** (500 mg, 82%) (Found: C, 49.71; H, 8.64. Calc. for $C_8H_{16}OS_2$: C, 49.96; H, 8.38%); ν_{max}(KBr)/cm^{-1} 2950, 2900, 1410, 1380, 1360, 1250, 1210, 1170, 1130, 1040, 960, 880, 840 and 750; δ_H 1.35 (6H, s, 2 × CH_3), 1.67–2.17 (2H, m, 5-H), 2.78–2.97 (4H, m, 4-H and 6-H), 3.27 (3H, s, CH_3O) and 4.29 (1H, s, 2-H); δ_C 23.0, 25.7, 30.7, 49.2, 57.7 and 76.7.

2-[1-Methyl-1-(methoxymethoxy)ethyl]-1,3-dithiane 1e

The reaction was carried out as described above except using **1a** (712 mg, 3.99 mmol), sodium hydride (60% dispersion in mineral oil, 240 mg, 5.99 mmol) and chloromethyl methyl ether (0.425 cm^3, 5.59 mmol). Purification by column chromatography (95:5 and then 80:20 hexane–ethyl acetate) afforded **1e** (584 mg, 67%) (Found: C, 48.87; H, 8.40. Calc. for $C_9H_{18}O_2S_2$: C, 48.61; H, 8.16%); ν_{max}(KBr)/cm^{-1} 2900, 2850, 1450, 1410, 1380, 1360, 1240, 1200, 1140, 1120, 1080, 1030 and 910; δ_H 1.43 (6H, s, 2 × CH_3), 1.70–2.17 (2H, m, 5-H), 2.79–2.96 (4H, m, 4-H and 6-H), 3.42 (3H, s, CH_3O), 4.26 (1H, s, 2-H) and 4.78 (2H, s, OCH_2O); δ_C 24.0, 25.2, 30.2, 54.8, 58.9, 75.7 and 90.5.

2-[1-Methyl-1-(benzyloxy)ethyl]-1,3-dithiane 1f

The reaction was carried out as described above except using **1a** (427 mg, 2.40 mmol), sodium hydride (60% dispersion in mineral oil, 144 mg, 3.60 mmol) and benzyl bromide (0.383 cm^3, 2.64 mmol). Purification by column chromatography (95:5 and then 70:30 hexane–ethyl acetate) afforded **1f** (392 mg, 61%), which was found to decompose gradually on standing at room temperature (Found: C, 62.49; H, 7.88. Calc. for $C_{14}H_{20}OS_2$: C, 62.64; H, 7.51%); ν_{max}(KBr)/cm^{-1} 3000, 2950, 2900, 1500, 1460, 1420, 1380, 1360, 1280, 1260, 1220, 1180, 1160, 1130, 1090, 1050, 1030, 740 and 700; δ_H 1.43 (6H, s, 2 × CH_3), 1.70–2.17 (2H, m, 5-H), 2.78–2.95 (4H, m, 4-H and 6-H), 4.41 (1H, s, 2-H), 4.52 (2H, s, OCH_2Ph) and 7.22–7.42 (5H, m, Ph); δ_C 24.2, 26.0, 30.9, 58.0, 63.9, 77.5, 127.1, 127.4, 128.3 and 139.0.

2-(1-Methyl-1-acetoxyethyl)-1,3-dithiane 1g

The reaction was carried out as described above except using **1a** (687 mg, 3.85 mmol), sodium hydride (60% dispersion in mineral oil, 251 mg, 5.78 mmol) and acetic anhydride (0.856 cm^3, 7.70 mmol). Purification by column chromatography (95:5 and then 80:20 hexane–ethyl acetate) afforded **1g** (558 mg, 61%) (Found: C, 48.76; H, 7.54. Calc. for $C_9H_{16}O_2S_2$: C, 49.06; H, 7.32%); ν_{max}(KBr)/cm^{-1} 3000, 2950, 1740, 1420, 1390, 1370, 1250, 1160, 1120, 1020 and 800; δ_H 1.56 (6H, s, 2 × CH_3), 1.99 (3H, s, CH_3CO), 1.67–2.15 (2H, m, 5-H), 2.79–2.97 (4H, m, 4-H and 6-H) and 5.03 (1H, s, 2-H); δ_C 21.9, 24.4, 25.7, 30.7, 56.4, 82.8 and 169.9.

Typical procedure: asymmetric oxidation of 1a

A solution of $Ti(OPr^i)_4$ (0.141 cm^3, 0.474 mmol) and diethyl L-(+)-tartrate (0.163 cm^3, 0.949 mmol) in (9.5 cm^3) was stirred at 0 °C for 1 h. Then the mixture was cooled to −20 °C and powdered 4 Å molecular sieves (8.0 mg, 10 wt%) were added. After stirring for 1 h, a solution of **1a** (84.6 mg, 0.475 mmol) in CH_2Cl_2 (1.2 cm^3) was added and the mixture was stirred for 1 h at −20 °C. Then a solution of *tert*-butyl hydroperoxide (5.114 M solution in CH_2Cl_2, 0.139 cm^3, 0.711 mmol) was added dropwise over a period of 15 min. After stirring for 2 h, water (0.35 cm^3) was added, and then the mixture was allowed to warm to room temperature. The mixture was filtered through Celite 500 and the precipitates were rinsed with CH_2Cl_2. The filtrate was washed successively with 5% aqueous $Na_2S_2O_3$ and 5% aqueous NaOH. The organic solution was dried over Na_2SO_4, and the solvent was evaporated to give a crude oil, which was purified by column chromatography (99:1 and then 90:10 CH_2Cl_2–methanol) to afford 2-(1-hydroxy-1-methylethyl)-1,3-dithiane 1-oxide **2a** (56 mg, 61%). *trans*-**2a** (Found: C, 43.37; H, 7.51. Calc. for $C_7H_{14}O_2S_2$: C, 43.27; H, 7.26%); ν_{max}(KBr)/cm^{-1} 3400, 2925, 1420, 1340, 1170, 1140, 1000, 920 and 879; δ_H 1.36 (3H, s, CH_3), 1.47 (3H, s, CH_3), 2.11–2.79 (5H, m, 5-H, 4-H and 6-H), 2.81 (1H, ddd, *J* 13.0, 13.0, 3.6, 6-H), 3.75 (1H, s, OH) and 4.61 (1H, s, 2-H); δ_C 25.93, 28.95, 30.00, 30.92, 54.33, 73.32 and 74.33; *m*/*z* 194 (M^+, 17%), 122 (100) and 75 (39).

cis-**2a**; ν_{max}(KBr)/cm^{-1} 3300, 2925, 1400, 1380, 1360, 1220, 1190, 1150, 1120, 1030, 1000, 920, 860 and 800; δ_H 1.34 (3H, s, CH_3), 1.43 (3H, s, CH_3), 1.65–1.72 (2H, m, 5-H), 2.33–2.92 (3H, m, 4-H and 6-H), 3.07–3.19 (1H, m, 6-H), 3.64 (1H, s, 2-H) and 2.87 (1H, s, OH); δ_C 14.85, 27.9, 29.0, 29.1, 47.20, 71.37 and 73.30; *m*/*z* 194 (M^+, 25%), 119 (100) and 75 (100).

2-(1-Ethyl-1-hydroxypropyl)-1,3-dithiane 1-oxide 2b

Oxidation was carried out as described above except using **1b** (134 mg, 0.649 mmol) to give **2b** (120 mg, 83%). *trans*-**2b** (Found: C, 48.54; H, 8.30. Calc. for $C_9H_{18}O_2S_2$: C, 48.61; H, 8.16%); ν_{max}(KBr)/cm^{-1} 3400, 2970, 2925, 2880, 1460, 1420, 1390, 1340, 1280, 1260, 1145, 1015, 985, 940 and 870; δ_H 0.99 (3H, t, *J* 7.3, CH_3CH_2), 1.01 (3H, t, *J* 7.3, CH_3CH_2), 1.39–1.77 (4H, m, 5-H and CH_3CH_2), 1.93 (2H, dq, *J* 7.3, 14.1, CH_3CH_2), 2.11–2.75 (2H, m, 4-H), 2.79 (1H, ddd, *J* 3.0, 14.1, 14.1, 6-H), 3.44 (1H, ddd, *J* 3.0, 3.0, 14.1, 6-H), 3.85 (1H, s, 2-H) and 4.25 (1H, br s, OH); δ_C 6.7, 7.4, 29.1, 29.9, 31.0, 31.1, 54.6, 71.1 and 77.6. *cis*-**2b**; δ_H 0.87 (3H, t, *J* 7.3, CH_3CH_2), 0.94 (3H, t, *J* 7.3, CH_3CH_2), 1.40–2.27 (4H, m, 5-H and CH_3CH_2), 2.12–3.02 (5H, m, 4-H, CH_3CH_2 and 6-H), 3.10–3.24 (1H, m, 6-H), 3.78 (1H, s, 2-H) and 4.24 (1H, br s, OH).

2-(1,1-Diphenyl-1-hydroxymethyl)-1,3-dithiane 1-oxide[10] 2c

Oxidation was carried out as described above using **1c** (87 mg, 0.288 mmol) to give **2c** (74 mg, 81%). *trans*-**2c**; ν_{max}(KBr)/cm^{-1} 3300, 3050, 2900, 1620, 1490, 1440, 1410, 1230, 1160, 1010, 990, 900, 750 and 700; δ_H 2.12–2.73 (4H, m, 5-H and 4-H), 2.88 (1H, ddd, *J* 3.0, 12.6, 12.6, 6-H), 3.43 (1H, ddd, *J* 3.0, 3.0, 12.6, 6-H), 4.40 (1H, s, OH), 5.86 (1H, s, 2-H) and 7.19–7.80 (10H, m, 2 × Ph); *m*/*z* 316 (M^+, 10%), 284 (43), 210 (100). *cis*-**2c**; δ_H 1.64–1.90 (1H, m, 5-H), 2.10–2.72 (4H, m, 5-H, 4-H and 6-H), 2.94–3.16 (1H, m, 6-H), 4.70 (1H, s, OH), 4.84 (1H, s, 2-H) and 7.19–7.80 (10H, m, Ph).

2-(1-Methyl-1-methoxyethyl)-1,3-dithiane 1-oxide 2d

Oxidation was carried out as described above using **1d** (78 mg, 0.404 mmol) to give **2d** (49 mg, 58%). *trans*-**2d** (Found: C, 46.24; H, 7.71. Calc. for $C_8H_{16}O_2S_2$: C, 46.12; H, 7.74%); $[\alpha]_D^{27}$ −35.2; (*c* 0.65 in CH_2Cl_2); ν_{max}(KBr)/cm^{-1} 3450, 2900, 2850, 1420, 1360, 1300, 1250, 1200, 1140, 1110, 1060, 1010, 910, 890, 850 and 720; δ_H 1.49 (3H, s, CH_3), 1.50 (3H, s, CH_3), 2.12–2.51 (2H, m, 5-H), 2.55–2.69 (2H, m, 4-H), 2.71 (1H, ddd, *J* 6.0, 14.1, 14.1, 6-H), 3.29 (3H, s, CH_3O), 3.42 (1H, ddd, *J* 6.0, 6.0, 14.1, 6-H) and 3.76 (1H, s, 2-H); δ_C 23.8, 25.2, 29.2, 30.1, 49.5, 55.0, 74.5 and 76.5; *m*/*z* 208 (M^+, 19%), 86 (100) and 71 (79). *cis*-**2d**; δ_H 1.35 (3H, s, CH_3), 1.36 (3H, s, CH_3), 2.00–2.80 (5H, m, 5-H, 4-H and 6-H), 3.09–3.21 (1H, m, 6-H), 3.28 (3H, s, CH_3O) and 3.73 (1H, s, 2-H).

2-[1-Methyl-1-(methoxymethoxy)ethyl]-1,3-dithiane 1-oxide 2e

Oxidation was carried out as described above using **1e** (108 mg, 0.486 mmol) to give **2e** (101 mg, 87%). *trans*-**2e** (Found: C, 45.51; H, 7.69. Calc. for $C_9H_{18}O_3S_2$: C, 45.35; H, 7.61%); $[\alpha]_D^{18}$ −13.4 (*c* 0.95 in CH_2Cl_2); ν_{max}(KBr)/cm^{-1} 2900, 1460, 1420, 1380, 1140, 1080, 1020, 910 and 720; δ_H 1.56 (3H, s, CH_3), 1.57

(3H, s, CH_3), 2.00–2.79 (4H, m, 5-H and 4-H), 2.72 (1H, ddd, *J* 6.2, 14.1, 14.1, 6-H), 3.39 (1H, ddd, *J* 6.2, 6.2, 14.1, 6-H), 3.41 (3H, s, CH_3O), 3.73 (1H, s, 2-H), 4.76 (1H, d, *J* 7.5, OCH_2O) and 4.83 (1H, d, *J* 7.5, OCH_2O); δ_C 25.2, 26.8, 29.3, 30.1, 54.8, 55.6, 75.6, 77.0 and 91.2; *m/z* 238 (M^+, 32%), 177 (100) and 86 (100). *cis*-**2e**; δ_H 1.43 (6H, s, 2 × CH_3), 1.70–2.92 (5H, m, 5-H, 4-H and 6-H), 3.05–3.18 (1H, m, 6-H), 3.41 (3H, s, CH_3O), 3.82 (1H, s, 2-H), 4.76 (1H, d, *J* 7.6, OCH_2O) and 4.85 (1H, d, *J* 7.6, OCH_2O).

2-(1-Methyl-1-benzyloxyethyl)-1,3-dithiane 1-oxide 2f

The reaction was carried out as described above using **1f** (55 mg, 0.205 mmol) to give **2f** (49 mg, 84%). *trans*-**2f** (Found: C, 59.01; H, 6.99. Calc. for $C_{14}H_{20}O_2S_2$: C, 59.12; H, 7.09%); $[\alpha]_D^{25}$ −9.1 (*c* 0.98 in CH_2Cl_2); ν_{max}(KBr)/cm^{-1} 3095, 3075, 3040, 3010, 2980, 2920, 2910, 1500, 1460, 1415, 1405, 1365, 1300, 1235, 1215, 1195, 1150, 1060, 1035, 915, 900, 875, 840, 740 and 700; δ_H 1.52 (3H, s, CH_3), 1.55 (3H, s, CH_3), 2.02–2.60 (4H, m, 5-H and 4-H), 2.65 (1H, ddd, *J* 3.2, 12.8, 12.8, 6-H), 3.35 (1H, ddd, *J* 3.2, 3.2, 12.8, 6-H), 4.50 (2H, s, OCH_2Ph) and 7.17–7.36 (5H, m, Ph); δ_C 24.5, 26.2, 29.0, 30.0, 54.9, 64.0, 74.6, 76.9, 127.3, 127.7, 128.2 and 136.8; *m/z* 284 (M^+, 37%), 193 (68) and 123 (100). *cis*-**2f**; δ_H 1.39 (3H, s, CH_3), 1.40 (3H, s, CH_3), 2.04–2.92 (5H, m, 5-H, 4-H and 6-H), 2.98–3.11 (1H, m, 6-H), 3.75 (1H, s, 2-H), 4.44 (1H, d, *J* 12.0, OCH_2Ph), 4.54 (1H, d, *J* 12.0, OCH_2Ph) and 7.12–7.38 (m, 5H).

2-(1-Acetoxy-1-methylethyl)-1,3-dithiane 1-oxide 2g

The reaction was carried out as described above using **1g** (81 mg, 0.368 mmol) to give **2g** (73 mg, 84%). *trans*-**2g** (Found: C, 45.43; H, 6.94. Calc. for $C_9H_{16}O_3S_2$: C, 45.73; H, 6.82%); $[\alpha]_D^{22}$ 4.9 (*c* 1.40 in CH_2Cl_2); ν_{max}(KBr)/cm^{-1} 3450, 3000, 2950, 1740, 1420, 1370, 1250, 1180, 1160, 1120, 1040, 930 and 730; δ_H 1.59 (3H, s, CH_3), 1.73 (3H, s, CH_3), 2.00 (3H, s, CH_3CO), 2.10–2.68 (4H, m, 5-H and 4-H), 2.73 (1H, ddd, *J* 3.2, 13.1, 13.1, 6-H), 3.38 (1H, ddd, *J* 3.2, 3.2, 13.1, 6-H) and 4.75 (1H, s, 2-H); δ_C 22.2, 25.0, 26.3, 30.2, 30.5, 55.4, 71.8, 81.9 and 170.2; *m/z* 236 (M^+, 13%), 177 (31) and 123 (100). *cis*-**2g**; $[\alpha]_D^{22}$ 71.7 (*c* 0.30, CH_2Cl_2); δ_H 1.54 (3H, s, CH_3), 1.56 (3H, s, CH_3), 2.03 (3H, s, CH_3CO), 2.00–2.98 (5H, m, 5-H, 4-H and 6-H), 3.04–3.16 (1H, m, 6-H) and 4.76 (1H, s, 2-H); δ_C 14.3, 22.2, 24.8, 25.5, 29.7, 47.60, 68.3, 82.8 and 170.6.

Base-catalyzed hydrolysis of 2a: formation of 1,3-dithiane 1-oxide 5

A solution of **2a** {$[\alpha]_D^{20}$ −15.7 (*c* 1.5, CH_2Cl_2), 46 mg, 0.237 mmol} and potassium hydroxide (1.0 equiv.) in *tert*-butyl alcohol (3 cm^3) was stirred at 50 °C for 1 h. The mixture was then neutralized by aqueous NH_4Cl and extracted with $CHCl_3$ (5 × 5 cm^3). The combined organic extracts were washed, dried over Na_2SO_4, and concentrated under reduced pressure to give a crude product **5** (25 mg, 78%); ν_{max}(KBr)/cm^{-1} 2900, 1430, 1170, 1040, 1020, 920, 890, 830 and 730; δ_H 2.01–2.27 (1H, m, 5-H), 2.38–2.68 (4H, m, 5-H, 4-H and 6-H), 3.20–3.34 (1H, m, 6-H), 3.58 (1H, d, *J* 12.6, 2-H) and 3.95 (1H, dd, *J* 2.5, 12.6, 2-H). The crude product was recrystallized from a mixed solvent system of CH_2Cl_2 and cyclohexane to give the pure product, $[\alpha]_D^{24}$ −70.6 (*c* 0.22, ethanol) [lit.,[13] $[\alpha]_D^{20}$ −224 (*c* 0.85 in ethanol)].

Deprotection of 2g

A mixture of **2g** (47 mg, 0.199 mmol) and a catalytic amount of potassium carbonate (5 mg, 0.036 mmol) in dry methanol (3 cm^3) was stirred at room temperature for 5 h. The mixture was poured into water and extracted with CH_2Cl_2 (3 × 10 cm^3). The combined organic extracts were dried over Na_2SO_4, and concentrated under reduced pressure to give a crude product, which was purified by column chromatography to give the deprotected oxide **2a** (13.3 mg, 34%) and 2-isopropylidene-1,3-dithiane 1-oxide **6** (19.9 mg, 57%). **6** (Found: C, 47.53; H, 6.94. Calc. for $C_7H_{12}OS_2$: C, 47.69; H, 6.86%); ν_{max}(KBr)/cm^{-1} 2900, 1605, 1430, 1170, 1040, 1020, 920, 890, 830 and 730; δ_H 1.73–1.94 (1H, m, 5-H), 2.05 (3H, s, CH_3), 2.14 (3H, s, CH_3), 2.52–2.71 (2H, m, 5-H and 4-H), 2.80–2.94 (2H, m, 4-H and 6-H) and 3.04–3.17 (1H, m, 6-H).

Crystal data for (1*S*,2*S*)-2d

$C_8H_{16}O_2S_2$, $M = 208.34$. Orthorhombic, $a = 6.822(1)$, $b = 8.991(1)$, $c = 16.968(3)$ Å, $V = 1041.2$ Å,^{3} space group $P2_12_12_1$, $Z = 4$, $D_x = 1.227$ g cm^{-3}. Colorless, crystal dimensions: 0.30 × 0.40 × 0.40 mm, μ(Mo-Kα) = 0.710 73 Å.

Data collection and processing

Diffraction data for *trans*-**2d** were obtained with an Enraf-Nonius CAD4 four-circle automated diffractometer. The reflection intensities were monitored by three standard reflections at every 2 h, and these showed less than 2% decay over the period of the data collection. Reflection data were corrected for Lorentz and polarization effects. Absorption corrections for the crystals were applied according to the DIFABS procedure in both the cases.[14]

Structure analysis and refinement

The structure was solved by the heavy-atom method and refined anisotropically for non-hydrogen atoms by full-matrix least-squares calculations. Refinement was continued until all shifts were smaller than one third of the standard deviations of the parameters involved. Atomic scattering factors and anomalous dispersion terms were taken from the literature.[15] All hydrogen atoms were located from difference Fourier maps, and their parameters were isotropically refined. The absolute configuration of the monooxide **2d** was determined by the anomalous dispersion method. The final R and R_w values were 0.034 and 0.046 for (1*S*,2*S*)-**2d**, which indicated that the monooxide **2d** has the absolute configuration as illustrated in Fig 1. The weighting scheme $w^{-1} = \{\sigma^2(|F_o| + (0.02|F_o|)^2\}$ was employed for the crystal. The final difference Fourier map did not show any significant features. The calculations were performed on a VAX-3100 computer by using the program system SDP-MolEN.[16] Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans 1*, available *via* the RSC Web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/190.

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