Studies on the Asymmetric Oxidation of Ester Derivatives of 1,3-Dithiane-2-carboxylates. Asymmetric Synthesis of *trans*-1,3-Dithiane 1,3-Dioxide

Varinder K. Aggarwal,* Blanca N. Esquivel-Zamora, Graham R. Evans, and Elfyn Jones

Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK

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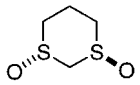
Asymmetric oxidation of a range of 1,3-dithianes was studied using the Kagan protocol [CHP (4 equiv), (+)-DET (2 equiv), $Ti(OiPr)_4$ (1 equiv), and H_2O (1 equiv) at −35 °C for 48 h]. 1,3-Dithiane itself gave monoxide (30% ee) and the trans bis-sulfoxide (59% ee) but with low enantioselectivity. In contrast, ester derivatives (Me, Et, *t*-Bu, Ph) of 1,3-dithiane-2-carboxylates gave monoxides (80−95% ee) and trans bis-sulfoxides (>97% ee) in high enantioselectivity. Optimum conditions for the oxidation of ethyl 1,3-dithiane-2-carboxylate required the Modena protocol [CHP (4 equiv), (+)-DET (2 equiv), and $Ti(OiPr)_4$ (0.5 equiv) at −22 °C for 24 h], and this gave the trans bis-sulfoxide in 60% yield and high enantioselectivity. The bis-sulfoxides were found to be acid sensitive and required rapid workup and purification for optimum yields. The differences between the Modena and Kagan oxidants are discussed together with a discussion on the origin of the high enantio- and diastereoselectivity of the reaction. Finally, hydrolysis and decarboxylation furnished *trans*-1,3-dithiane 1,3-dioxide.

The use of sulfoxides as chiral synthons for asymmetric synthesis is now well established.[1−3] There are now many examples in which sulfoxide-stabilized anions react with good diastereoselectivity with trigonal electrophiles.[4−12] Indeed, we have shown that the sodium anion of C_2 symmetric bis-sulfoxide **1** reacts with aromatic aldehydes with very high diastereocontrol.[13] We have also demonstrated that the dithiane dioxide moiety can be readily converted to a thiol ester, thus making **1** into a chiral activated acid anion equivalent.[14,15] To prepare enantiomerically pure material we needed to be able to prepare **1** in enantiopure form, and in this paper we describe our studies in this area in full.[16]



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For the preparation of **1**, we considered asymmetric oxidation of 1,3-dithiane or derivatives thereof. We were attracted by the possibility of carrying out oxidations of both sulfur groups in the same pot as this would obviously be more efficient and should also give products with enhanced enantioselectivity. This enhancement is a manifestation of the Horeau principle which was originally used to describe the stereochemical outcome in the dimerization of a nonracemic substrate.[17] The same principle applies to carrying out two enantioselective operations on the same substrate simultaneously.[18] In theory, if a reaction gives an *x*:*y* ratio of enantiomers in the first enantioselective operation, then, assuming there is no kinetic resolution (both enantiomers of the monofunctionalized product react at the same rate) or double stereo differentiation (the second step of the enantioselective reaction is not affected by the asymmetric center formed in the first step of the reaction), the ratio of enantiomers for the bisfunctionalized product will be x^2:y^2.[17] The enantiomeric excess of the C_2 symmetric substrate is therefore considerably higher than the monofunctionalized substrate. One can view this as the x^2, y^2 rule, and is much simpler to compute than considering ee values.[19] This bisfunctionalization process[20−23] also generates the diastereomeric meso compound (amount = 2*xy*) which has to be removed.

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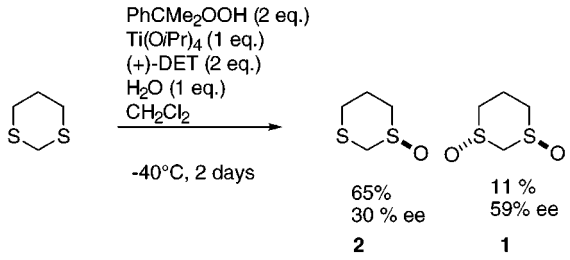
Scheme 1



Results

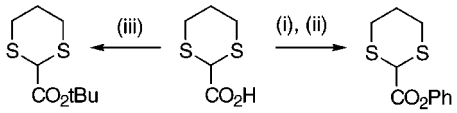
The asymmetric oxidation process we initially focused on was that developed by Kagan,[24−27] and we applied this to the oxidation of 1,3-dithiane (Scheme 1). However, this gave the monoxide **2** with very low enantioselectivity together with the dioxide **1** in low yield and in only moderate enantioselectivity. The ratio of enantiomers of the dioxide corresponded closely to the square of the ratio of the enantiomers of the monoxide, demonstrating the validity of the x^2, y^2 rule (Horeau principle) in the asymmetric oxidation of bis-sulfides. To enhance the enantioselectivity we considered the possibility of using enzymatic oxidations on 1,3-dithiane, but it has recently been shown that such processes lead only to the monosulfoxide; further oxidation gave the sulfone-sulfide not the bis-sulfoxide.[28]

To obtain the bis-sulfoxide with higher enantiomeric excess we needed higher enantioselectivity in the oxidation process. Kagan[29] had shown that oxidation of 2-carbethoxy-1,3-dithiane occurred with good selectivity, and during the course of our own work, Page[30−33] also showed that the same applied to 2-acyl-1,3-dithiane. These substrates were attractive for the preparation of **1**, as, following oxidation, the ester group could potentially be removed by base-catalyzed hydrolysis and decarboxylation.

A range of esters of 1,3-dithiane-2-carboxylic acid[34] were required for a study of the asymmetric oxidation process. The methyl ester **3** was prepared by a literature procedure,[35] and the ethyl ester **4** was commercially available. The phenyl ester was prepared from the corresponding acid chloride, and the *tert*-butyl ester was prepared by esterification of the acid using *N*,*N*-dimethylformamide di-*tert*-butyl acetal[36] (Scheme 2).

We initially tested the racemic oxidation of the commercially available 2-carbethoxy-1,3-dithiane **4** with a range of oxidants ($NaIO_4$, mCPBA, oxone, AcOOH, ozone)

Scheme 2[a]



[a] Reagents (i) $SOCl_2$, DCM, DMF (cat); (ii) PhOH, Et_3N; (iii) $Me_2NCH(OCMe_3)_2$, PhH, heat.

Table 1. Kagan Oxidation of 2-RO_2C-1,3-Dithianes[a]

entry	dithiane ester (R)	monoxide yield (ee, %[b])	*trans* dioxide yield (ee, %[b])
1	**3** (Me)	70 (80)	13 (>97)
2	**4** (Et)	85 (85)	10 (>97)
3	**5** (*t*-Bu)	79 (95)	11 (>97)
4	**6** (Ph)	63 (91)	8 (>97)

[a] Conditions used: CHP (2 equiv), (+)-DET (2 equiv), $Ti(OiPr)_4$ (1 equiv), and H_2O (1 equiv) at −35 °C for 48 h. Yields given are isolated yields. [b] The *R* sulfoxide(s) is preferentially formed (by analogy with the literature[29]). Ee's determined by NMR using TFAE as shift reagent.

and found that while the product was clearly visible by TLC it often decomposed upon isolation. We later discovered that the product was sensitive to acidic conditions presumably due to the very acidic C2 proton and the facility of the product to undergo an acid-catalyzed Pummerer reaction.[37] We therefore needed to rapidly separate the product from the acidic byproducts of the reaction. This was achieved by carrying out mCPBA oxidation in ether at 0 °C. Under these conditions the polar product **7** precipitated, leaving the acid byproduct in solution, and at the end of the reaction, the mixture was simply filtered and washed with cold ether. Even though the solid that was collected was essentially pure **7** by NMR, its stability was still limited until it had been passed through a silica gel column. These results indicated the need to *rapidly* isolate and purify the products from oxidations due to their sensitivity.

We tested all four esters under the Kagan oxidation conditions,[29,38,39] and the results are presented in Table 1. It was found that good asymmetric induction was obtained in the formation of the monoxide with all esters and that the enantioselectivity increased with increasing steric bulk of the ester substituent (entries 1−3).[40] The desired trans bis-sulfoxide was also obtained in these reactions, and in each case we were unable to detect the other enantiomer. However, attempts to increase the yield of the bis-sulfoxide by increasing the amount of oxidant, increasing temperature, and increasing reaction time were largely unsuccessful. We therefore studied the effect of different oxidation conditions, particularly the effect of water, and focused our attention on commercially available 2-carbethoxy-1,3-dithiane **4**. The results are presented in Table 2. The absolute stereochemistry of all esters has been assigned (1*R*) for the monoxides or (1*R*,3*R*) for the trans dioxides in accordance with literature precedent.[41]

We found that under the standard Kagan conditions but in the absence of water, a greater amount of the bis-

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(41) Kagan has reported the absolute configuration of **8** (see ref 29).

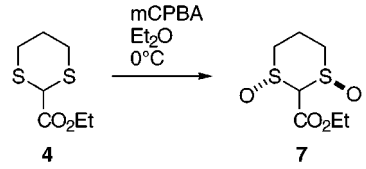
Table 2. Asymmetric Oxidation of 2-Carbethoxy-1,3-dithiane 4[a]

entry	equivalents of reagents CHP	(+)-DET	$Ti(OiPr)_4$	H_2O	time, h	temp °C	monoxide **8**, % yield (% ee)	dioxide **7**, % yield (% ee)	sulfoxide-sulfone **9**, % yield
1	2	2	1	1	48	−35	85% (85%)	10% (>97%)	0
2	2	2	1	0	48	−35	68% (84%)	28% (>97%)	0
3	4	2	1	0	48	−35	16% (85%)	57% (>97%)	20%
4	6	2	1	0	48	−35	−	55% (>97%)	20%
5	2	1	1	0	48	−35	95% (0%)	0	0
6	2	4	1	0	48	−35	58% (85%)	36% (>97%)	*b*
7	4	4	1	0	48	−35	26% (85%)	66% (>97%)	*b*
8	6	4	1	0	48	−35	*b*	20% (>97%)	38%
9	4	4	1	0	24	−22	28% (85%)	62% (>97%)	*b*
10	4	2	0.5	0	24	−22	37% (85%)	53% (>97%)	*b*
11[c]	4	2	0.5	0	24	−22	8%	60% (>97%)	19%
12[d]	4	0.8[e]	0.2	0	60	−35	*b*	44% (>97%)	18%
13[d]	4	0.8[e]	0.2	0	60	−25	*b*	32% (95%)	16%

[a] All reactions conducted at 0.08 M (dithiane concentration) unless otherwise stated with 1 equiv of **4**. Yields given are isolated yields. [b] Not determined. [c] Conducted at 0.17 M. [d] Conducted at 0.3 M. [e] 0.8 equiv of IPA were used in conjunction with 0.8 equiv of DET.

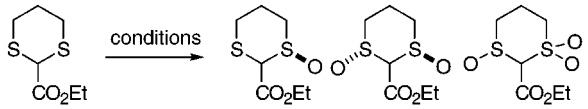
sulfoxide **7** was obtained (entry 2). This showed that the presence of water gives rise to a less active oxidant. Increasing quantities of oxidant led to increasing yields of the bis-sulfoxide and even formation of the sulfoxide-sulfone **9** (entries 3, 4). As these modified Kagan conditions were not very different from the Sharpless conditions for asymmetric epoxidation of allylic alcohols, we tested the Sharpless system but only obtained racemic monoxide **8** (entry 5). As can be seen, increasing the stoichiometry of (+)-DET from 1 to 2 equiv has a dramatic effect on the outcome of the asymmetric oxidation process (entry 2, 5). We therefore decided to increase the amount of DET further (4 equiv, Modena conditions[42]) and found that this gave rise to a slightly more active oxidant as more of the bis-sulfoxide was obtained when using 2 equiv of oxidant compared to the modified Kagan's conditions (entry 6). The enantiomeric excess of both the monoxide **8** and bis-sulfoxide **7** were the same under the Modena conditions as under the Kagan conditions (compare entries 1 and 6). Again, increasing the amount of oxidant increased the extent of oxidation (entries 7, 8), with optimum conditions requiring the use of 4 equiv of oxidant. The reaction could be conducted at higher temperature (entry 9) and with substoichiometric amounts of the titanium reagent (entry 10) without compromising enantioselectivity. While these latter conditions gave slightly reduced yields, the lower quantities of titanium salts aided workup and isolation. Increasing the concentration led to an improvement in yield and practicality for conducting the oxidation on significant scale (20 mmol, entry 11). The high yields with reduced quantities of catalyst (entries 10, 11) is noteworthy, as it has been previously reported that sulfoxides inhibit sulfide oxidation as they form good complexes with titanium, and so stoichiometric (or close to stoichiometric) amounts of catalyst are required.[25,43] Our β-sulfinyl esters should act as even stronger ligands to titanium but, nevertheless, do not significantly retard the reaction. This is almost certainly due to the large excess of DET present which complexes to titanium in preference and so prevents sulfoxide binding and poisoning. Thus, the Modena oxidation conditions have significant advantages over the Kagan protocol. Finally, we tested Kagan's recently reported catalytic conditions which require the use of molecular sieves and a combination of (+)-DET (catalytic quantities) and 2-propanol[44] and found that again high levels of enantioselectivity can

Scheme 3



4 **7**

Scheme 4



4 **8** **7** **9**

be achieved but the yield of the bis-sulfoxide **7** was not improved (entries 12, 13). Thus, the optimum conditions require the use of substoichiometric amounts of titanium reagent with an excess of oxidant (entry 11).

From the enantioselectivity found for the monoxide **8** (85%), the enantioselectivity expected for the bis-sulfoxide **7** according to the x^2, y^2 rule would be 98.7%. However, we were unable to detect the other enantiomer by chiral shift NMR using $Eu(hfc)_3$. Doping experiments with the racemate showed that we could detect 1.5% of the other enantiomer so all enantioselectivities are given as >97% ee. We were surprised not to find any of the meso isomer in the oxidation process, as according to the x^2, y^2 rule there should have been approximately 15% ($2xy$) of the cis product. The absence of the cis isomer could have been due to a difference in rate in further oxidation to the sulfoxide-sulfone if the cis dioxide oxidized faster than the trans isomer. If we regard the asymmetric oxidant as selectively oxidizing the pro *R* lone pair (i.e. the oxidant reacts faster with the pro *R* lone pair than the pro *S* lone pair) and assume this selectivity also applies to oxidation of sulfoxides then because the meso (*R*,*S*)-bis-sulfoxide has an *R* lone pair available for oxidation whereas the trans (*R*,*R*)-bis-sulfoxide has no *R* lone pairs available, the meso compound should be oxidized more rapidly (Scheme 5).[45,46] Unfortunately, we have been unable to prepare the cis (*R*,*S*)-bis-sulfoxide but nevertheless, were able to test whether the meso compound oxidized at a faster rate than the trans dioxide. The monoxide derived from (+)-DET was oxidized under the Modena condition but (−)-DET was used instead in order to prepare some of the meso dioxide (Scheme 6). How-

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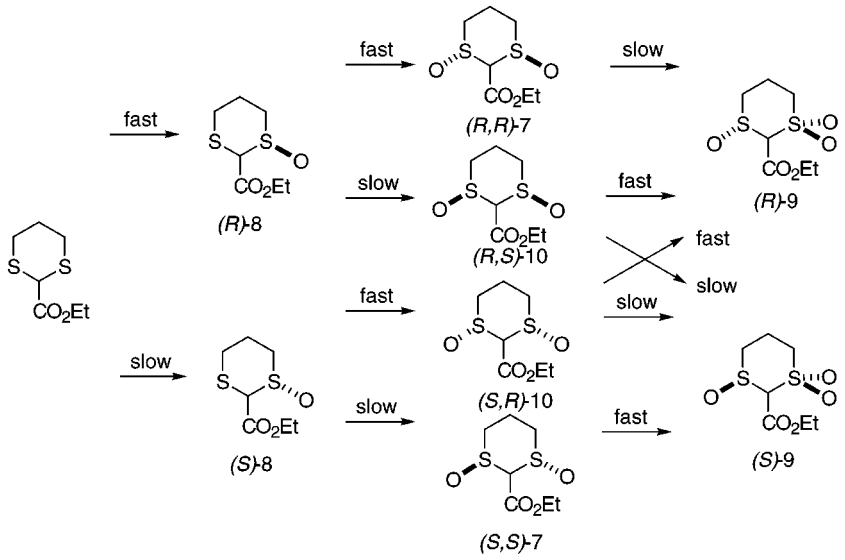
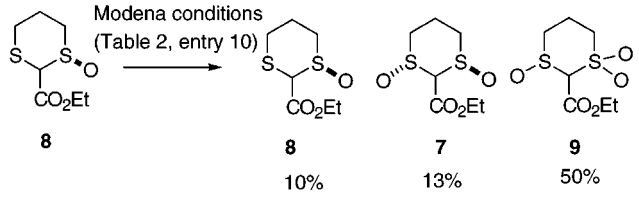
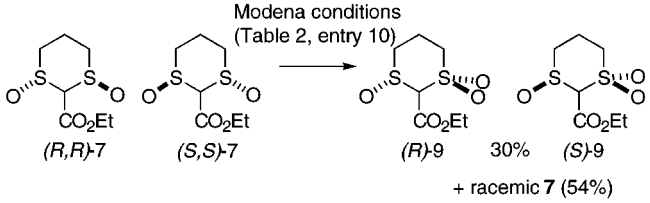
Scheme 5



Scheme 6



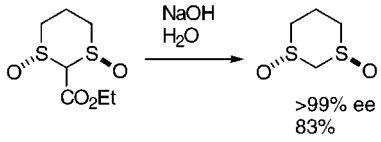
Scheme 7



ever, none was isolated; a small amount of the trans dioxide **7** and a large amount of the sulfoxide-sulfone **9** was obtained. This indicated that the meso dioxide was oxidized at a rate similar to, or even faster than, oxidation of the monoxide.[47]

We also wanted to test if any kinetic resolution was occurring, and this was achieved by carrying out an asymmetric oxidation on racemic **7** (Scheme 7). If the asymmetric oxidant preferred to oxidize the *R* lone pair, then one enantiomer (*S*,*S*) should oxidize more rapidly than the alternative (*R*,*R*)-enantiomer. If this was the case, this would result in an enhancement of the diastereoselectivity (already observed) and enantioselectivity of the process. This is an example of kinetic resolution of sulfoxides and has been observed with both binol-titanium reagents[48] as well as the Kagan system.[49,50] However, upon oxidation of the racemate, no change in enantioselectivity of the starting bis-sulfoxide was observed, indicating that the chiral oxidant did not selectively oxidize the (*R*)-lone pair of the sulfoxides.

Scheme 8



Finally, hydrolysis and decarboxylation occurred uneventfully and furnished the trans bis-sulfoxide **1** (Scheme 8). NMR analysis of **1** using the Pirkle shift reagent TFAE[51] showed that the enantiomeric excess was >99.5% and that no racemization had occurred during hydrolysis and decarboxylation. Measurement of the optical purity of the dioxide was initially problematic. While the enantiomeric excess of the dioxide ester **6** was determined using the chiral shift reagent, $Eu(hfc)_3$, in $CDCl_3$ this was not possible for dithiane dioxide **1** due to its insolubility. Unfortunately, very polar solvents that are required to solubilize **1** are not normally compatible with chiral shift reagents due to overwhelming chelation of the donor aprotic solvent to the metal. However, we were gratified to find that not only did acetonitrile-d_3 solubilize **1** but appreciable splitting of the C-2 protons for the individual enantiomers was observed in the experiments with TFAE. It was also possible, by carrying out doping experiments with a small amount of the racemate (1%), to detect the other enantiomer at very low levels of concentration (0.5%).

Conclusion

In summary, we have found that bis oxidation of ethyl 1,3-dithiane-2-carboxylate occurs in good yield (60%) and with high diastereo- and enantioselectivity using the Modena oxidation protocol [CHP (4 equiv), (+)-DET (2 equiv), and $Ti(OiPr)_4$ (0.5 equiv) at −22 °C for 24 h]. Indeed, the other diastereoisomer and enantiomer have not been observed. The very high enantioselectivity is a result of an intrinsically high enantioselective process coupled with an enhancement of enantioselectivity by carrying out two asymmetric transformations in one pot. The origin of the diastereoselectivity is probably a result

(47) It is possible that the preexisting stereocenter influenced the outcome of the second oxidation. However, we have never observed any reagent control in this process; the second oxidation does not seem to be affected by the first.

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of rapid oxidation of the meso dioxide to the sulfoxide-sulfone. No kinetic resolution is believed to be taking place to enhance the enantioselectivity of the oxidation process. The Modena oxidation allows reactions to be conducted at higher temperature without affecting the enantioselectivity and to be carried out using substoichiometric amounts of catalyst without significantly affecting the yield. These two features distinguish it from the Kagan oxidation protocol which is more sensitive to variation in temperature and to catalyst poisoning from the sulfoxide product. The trans dioxides are highly acid sensitive and require rapid workup and purification for optimum yields. Racemic oxidation was also achieved using mCPBA in diethyl ether at low temperature. Under these conditions the product precipitated out and was collected by filtration. Nevertheless, column chromatography was still required to remove traces of acid to prevent decomposition. Hydrolysis and decarboxylation occurred uneventfully and provided the trans bis-sulfoxide in high yield and very high enantiomeric excess.

Experimental Section

1,3-Dithiane and ethyl 1,3-dithiane-2-carboxylate were purchased from Aldrich and used without purification. Methyl 1,3-dithiane-2-carboxylate[35] and 1,3-dithiane-2-carboxylic acid[34] were prepared as described in the literature.

Preparation of (1*RS*,3*RS*)-*trans*-2-Carbethoxy-1,3-dithiane 1,3-Dioxide (7) Using mCPBA in Ether. Purified mCPBA (3.8 g, 11 mmol) in 25 mL of ether was added to 2-carbethoxy-1,3-dithiane **4** (1.0 g, 5.2 mmol) in 15 mL of ether at 0 °C. After 1 h stirring at this temperature the reaction was deemed complete by TLC (in addition to visual inspection—the product was evident as a white precipitate) and the mixture filtered through a sintered-glass funnel. The residue was washed with several aliquots of cold ether before being dissolved in dichloromethane, preadsorbed onto silica, and purified by column chromatography using EtOAc−10% EtOH in EtOAc as eluent. Recrystallization from *tert*-butyl acetate yielded the dioxide **7** as white crystals (0.66 g, 57%); mp 108−112 °C (from *tert*-BuOAc).

Preparation of (1*R*, 3*R*)-*trans*-2-Carbethoxy-1,3-dithiane 1,3-Dioxide (7) (Modena Oxidation). (+)-Diethyl tartrate (1.78 mL, 10.4 mmol) and titanium tetraisopropoxide (0.77 mL, 2.6 mmol) were dissolved in 31 mL of dry dichloromethane at room temperature and stirred for 20 min. 2-Carbethoxy-1,3-dithiane **4** (1.0 g, 5.2 mmol) was then added and the reaction mixture cooled to −40 °C and stirred for 1 h. Cumene hydroperoxide (3.84 mL, 20.8 mmol) was added, the mixture stirred for 10 min, and the flask then placed in the freezer at −22 °C for 24 h. Water (2 mL) was added and the reaction mixture allowed to attain room temperature with stirring. The resultant gel was filtered through Celite to remove titanium oxide (the filtration is difficult: we use a wide diameter Hirsch funnel and then filter paper and Celite and scrape the surface of the Celite to allow the reaction mixture to run through) and the residue washed copiously with dichloromethane. The combined organic extracts were dried over magnesium sulfate, and evaporation of solvent yielded an oil. Flash column chromatography (it is important to column-fractionate the crude material immediately after it has been worked up and not to store it, as it is not very stable) using 5% EtOH in EtOAc afforded the dioxide, **1** as a white crystalline solid (0.70 g, 60%); R_f 0.1 (5% EtOH/EtOAc) mp 132−133 °C (from EtOAc), $[\alpha]_D$ +240 (c = 3 in $CHCl_3$), ν_{max} (KBr) 1730, 1315, 1174, 1058 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 1.33 (3H, t, J = 7 Hz), 2.48−2.75 (2H, m), 2.97−3.23 (2H, m), 3.37−3.63 (2H, m), 4.34 (2H, q, J = 7 Hz), 4.87 (1H, s); δ_C (63 MHz, $CDCl_3$) 14.1, 14.4, 46.1, 46.3, 63.7, 73.5, 162.4. Anal. Calcd for $C_7H_{12}O_4S_2$: C, 37.5; H, 5.36; S, 28.57. Found: C, 37.34; H, 5.32; S, 28.52. EIMS m/z 224 (M^+, 32%), 208 (19), 175 (82), 106 (49), 90 (100), 73 (79).

Preparation of (+)-(*R*)-*trans/cis*-2-Carbethoxy-1,3-dithiane 1-Oxide (8) by Kagan Oxidation of Ethyl 1,3-Dithiane-2-carboxylate.[29] Titanium tetraisopropoxide (0.37 mL, 1.25 mmol) was added at room temperature to a stirred solution of (+)-(*R*,*R*)-diethyl tartrate (0.425 mL, 2.5 mmol) in dichloromethane (15 mL) under a nitrogen atmosphere. Water (22.5 μL, 1.25 mmol) was added dropwise into the vortex and the solution left stirring for 20 min. Ethyl 1,3-dithiane-2-carboxylate **4** (0.384 mL, 2.50 mmol) was added, the colorless/slightly yellow solution was cooled to −40 °C for 1 h, and cumene hydroperoxide (0.5 mL, 2.5 mmol) was added. The solution was kept at −40 °C for 60 h. Water (0.5 mL) was added, and the reaction mixture was stirred for 1 h at room temperature. The white gel was filtered through Celite which was thoroughly washed with dichloromethane (3 × 10 mL). The combined organic phases were dried ($MgSO_4$), and solvent was evaporated to afford a colorless oil which was preadsorbed onto silica and column-fractionated on silica, eluting with ethyl acetate:acetone 95:5 moving to 20:80. After the diethyl tartrate and 2-phenyl 2-propanol eluted, the monoxides **8** (440 mg, 85%) (*cis:trans* 40:60), followed.

***cis*-2-Carbethoxy-1,3-dithiane 1-oxide (*cis*-8)**,[29] white crystalline solid, (176 mg, 34%); R_f = 0.32 (5% acetone/EtOAc). δ_H (250 MHz, $CDCl_3$) 1.34 (3H, t J = 7 Hz), 2.26−2.42 (2H, m), 2.46−2.60 (1H, m), 3.03−3.09 (1H, m), 3.21−3.31 (1H, m), 3.55−3.65 (1H, m), 4.32 (2H, q J = 7 Hz), 4.61 (1H, s); δ_C (63 MHz, $CDCl_3$) 1.72, 24.10, 25.56, 46.25, 55.43, 62.21, 165.48; ee = 85% as determined by ^{1}H NMR using Eu(hfc)$_3$ (0.2 equiv) as chiral shift reagent

***trans*-2-Carbethoxy-1,3-dithiane 1-oxide (*trans*-8)**,[29] white crystalline solid, (264 mg, 51%); R_f = 0.24 (5% acetone/EtOAc). δ_H (250 MHz, $CDCl_3$) 1.34 (3H, t J = 7 Hz), 2.09−2.22 (1H, m), 2.50−2.62 (1H, m), 2.66−2.72 (1H, m), 2.80−2.90 (2H, m), 3.36−3.45 (1H, m), 4.31 (2H, q J = 7 Hz), 4.37 (1H, s); δ_C (63 MHz, $CDCl_3$) 13.88, 23.97, 27.89, 50.47, 62.79, 64.25, 165.65; ee = 88% as determined by ^{1}H NMR using Eu(hfc)$_3$ (0.2 equiv) as chiral shift reagent.

After the monoxides **8**, the ethyl 2-carboxylate-1,3-dithiane-*trans*-1,3-dioxide **7** came off as a white crystalline solid (60 mg, 10%).

(1*R*,3*R*)-Dithiane 1,3-Dioxide (1). Ester **7** (200 mg, 0.893 mmol) was dissolved in water (4 mL) and a solution of NaOH (70 mg, 1.786 mmol) in water (1 mL) added. The reaction mixture was stirred at 70 °C for 17 h. After cooling to room temperature 2.0 M HCl (1 mL) in ethanol (1 mL) was added and the solution stirred for 5 min. The solvents were removed under reduced pressure, and purification by column chromatography on silica gel using acetone−10% EtOH/acetone as eluent yielded **1** as a white solid (113 mg, 83%). R_f 0.15 (20% EtOH/EtOAc); mp 186.4−187 °C (MeOH); $[\alpha]_D$ +243 (c =1.0, H_2O); υ_{max} 1300, 1210, 1040−1000 cm^{-1}; δ_H (270 MHz, DMSO) 2.38 (2H, tt, J = 6.4, 5.3 Hz), 2.96 (2H, ddd, J = 12.9, 6.0, 5.1 Hz), 3.21 (2H, ddd, J = 12.9, 6.4, 5.9 Hz) 4.35 (2H, s); δ_C (68 MHz, DMSO) 14.9, 47.5, 61.6; δ_H (270 MHz, $CDCl_3$) 2.7 (2H, tt, J = 13.1, 5.6), 3.0 (2H, dt, J = 13.1, 5.6), 3.18 (2H, dt, J = 13.3, 6.7), 4.15 (2H, s); δ_C (68 MHz, $CDCl_3$) 14.9, 48.8, 63.5; EIMS m/z 152 (M^+ 86%), 103 (100), 90 (52), 73 (79), 63 (81). Anal. Calcd for $C_4H_8O_2S_2$: C, 31.58; H, 5.26; S, 42.11 Found: C, 31.59; H, 5.06; S, 42.24.

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Supporting Information Available: Experimental procedures, including data for the preparation of compounds not given below and method for ee determination (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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