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Highly Chemoselective Osmium-Mediated Dihydroxylation of 2-Vinyl and 2-Allyl-1,3-dithiane 1-Oxides

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Abstract: Chemoselective dihydroxylation of the double bonds of alkenyl-substituted 1,3-dithiane 1-oxide derivatives takes place without competing sulfur oxidation using osmium trichloride and potassium ferricyanide. © 1998 Elsevier Science Ltd. All rights reserved.

Introduction

The osmium mediated *cis*-dihydroxylation of olefins is an important and widely used synthetic tool. In either stoicheiometric ¹ or catalytic ² mode it is the reaction of choice for converting alkenes to *cis*-1,2-diols. The most synthetically useful asymmetric version is the Sharpless system using catalytic osmium tetroxide and chiral alkaloid ligands.³

1,3-Dithiane 1-oxide (DITOX) derivatives can act as combined chiral auxiliaries and asymmetric building blocks. Previously we have shown that 2-acyl substituted derivatives undergo a variety of transformations with up to excellent diastereoselectivities.⁴ Asymmetric sulfur oxidation allows access to both diastereoisomers of the acyl dithiane unit with excellent enantioselectivities.⁵ A chelation control model of these systems allows us to predict the stereochemical outcome of many of the reaction types studied to date. We are also interested in the potential degree of stereoselectivity attainable in reactions of non-acyl DITOX derivatives, and, as a result, in the problem of chemoselective alkene oxidation in the presence of sulfide and sulfoxide moieties in these thioacetal monosulfoxide systems.

We report here our investigations into the osmium-catalysed *cis*-dihydroxylation of 2-vinyl, 2allyl, and 2-alkenoyl 1,3-dithiane 1-oxide derivatives.

Substrate Preparation

A variety of 2-alkenyl and 2-alkenoyl-1,3-dithianes was prepared as described below.⁶

2-Allyl derivatives

Substrates **2a-e** and **3a-e** were constructed according to scheme 1. Generation of 2,2disubstituted dithianes **1a-d** was accomplished through a one-pot deprotonation, alkylation, deprotonation, allylation sequence at low temperature, using butyllithium as base, **1e** was prepared from 2-phenyl-1,3-dithiane by deprotonation and treatment with allyl bromide. Oxidation of each of **1a-e** with sodium metaperiodate proceeded smoothly to give syn **2a-e** and anti **3a-e** diastereoisomers (Table I), which were separable by flash column chromatography.



 i) *n*-BuLi (1.1 eq), THF, -20 °C, 1 h; RI, -20 °C to rt, 1 h; *n*-BuLi (1.1 eq), -20 °C, 1 h; R₂R₃C=C(R₁)CH₂Br, -20 °C to rt.
 ii) NalO₄ (1.1 eq), MeOH/H₂O, 0 °C, 16 h.
 Scheme 1

Table Pi	eparation	of 2-All	yl-1,	,3-dithiane	1-Oxides
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entry	R	R,	R ₂	R ₃	yield 1/%	yieid 2+3/%
a	Me	н	н	н		77
ь	Me	Me	н	н	53	81
с	Me	н	Me	Me	71	84
d	Et	н	н	н	89	78
e	Ph	н	Н	н	89 [†]	74

⁺ prepared from 2-phenyl-1,3-dithiane

2-Vinyl derivatives

Initial attempts to prepare 2-vinyl substrates by elimination from 2-(1-mesyloxy)-1,3-dithianes resulted in rearrangement giving 2-methylene-1,4-dithiepanes (Scheme 2).⁷

$$S \xrightarrow{(i)} S \xrightarrow{(i)} R \xrightarrow{(ii)} R \xrightarrow{(ii)} R \xrightarrow{(ii)} R = Me, n-Pr$$

(i) *n*-BuLi, (1.1 eq), THF, -20 °C, 1 h; Mel (1.1 eq), -20 °C to rt, 1 h; *n*-BuLi, (1.1 eq), -20 °C, 1 h; RCHO, (1.1 eq), -20 °C to rt, 1 h.
(ii) Et₃N (1.1 eq), THF, 0 °C, 0.5 h; MsCl (1.1 eq), 0 °C to rt, 1 h; Et₃N (1.1 eq), rt, 24-48 h. Scheme 2

The successful synthesis of potential substrates **6** and **7** is shown in scheme 3. Treatment of 2trimethylsilyl-1,3-dithiane with butyllithium at low temperature followed by condensation with acetone according to the method of Seebach gave ketene thioacetal **4** in excellent yield.⁸ Methylation at the 2-position of **4** wth deconjugation of the double bond by deprotonation and treatment with methyl iodide in the presence of HMPA gave vinyl dithiane **5**. Finally, oxidation with sodium metaperiodate gave a 1:6 ratio of the *syn* **6** and *anti* **7** diastereoisomers, which were separated by chromatography.



i) *n*-BuLi, (1.1 eq), THF, -78 °C to 0 °C, 5 h; (Me)₂CO, -78 °C to rt, 16 h; H₂O (91%).
ii) *n*-BuLi (1.1 eq), THF/HMPA, -78 °C to rt, 2.5 h; Mel (1.1 eq), -78 °C, 1 h (66%).
iii) NalO₄ (1.1 eq), MeOH/H₂O, 0 °C, 16 h (70%).
Scheme 3

2-Alkenoyl derivatives

Alkenoyl substrates syn 8 and anti 9 were prepared according to the literature procedure by deprotonation of the 2-alkyl dithiane and addition of the anion to crotonaldehyde. The resulting allylic alcohols were oxidized to the corresponding enones using manganese dioxide, and finally oxidized at sulfur with MMPP (Scheme 4). $^{\circ}$



 i) *n*-BuLi (1.1 eq), THF, -78° C, 1 h; RI, -78° C to rt, 2 h; *n*-BuLi (1.1 eq), -78°, 3 h; CH₃CH=CHCHO, -78° C to rt, 16 h;
 ii) MnO₂ (15 eq), CH₂Cl₂, rt; ii) MMPP (1.05 eq), MeOH/CH₂Cl₂, rt
 Scheme 4

Oxidation Reactions

Initially, *cis*-dihydroxylation reactions were attempted with **3a** as substrate using catalytic osmium tetroxide/NMO in aqueous acetone.² As we had feared, concomitant oxidation to disulfoxide and to sulfoxide/sulfone in addition to dihydroxylation was observed, leading to a complex mixture of products. Solladié and Hauser have both observed oxidation to sulfones in unsaturated systems containing sulfoxides using this method.¹⁰ More recently, catalytic osmium tetroxide/NMO has been used as a mild, selective method of conversion of sulfides to sulfones, even in the presence of alkenes.¹¹ It is therefore most interesting that osmium reagents are also among the very few oxidation at sulfur: Sharpless has found his asymmetric dihydroxylation process to be remarkably selective for alkene double bonds in the presence of sulfides.¹² Warren has published a non-enantioselective modification of the reaction using osmium trichloride hydrate and potassium ferricyanide, which induces dihydroxylation of a range of olefins chemoselectively without oxidation of sulfide units in the substrate molecules.¹³

2-Allyl derivatives

We first investigated oxidation of the allyl DITOX derivatives syn 2a-e and anti 3a-e. cis-Dihydroxylation under the conditions of Warren at room temperature gave diastereoisomeric mixtures of the 1,2-diols in excellent yields and with no trace of oxidation at either sulfide or sulfoxide units, albeit with low stereoselectivity (Scheme 5, Table II).



 (i) OsCl₃ (1 mol%), quinuclidine (4 mol%), K₃Fe(CN)₆ (3 eq), K₂CO₃ (3 eq), MeSO₂NH₂ (1 eq),[‡] BuOH/H₂O (1:1), rt, 2-24 h; Na₂S₂O₃
 [‡] Included only for non-terminal alkenes
 Scheme 5

Table II Dih	vdroxviation	of 2-Allyl-	1,3-dithiane	1-Oxides
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Entry	substrate	R	R ₁	R ₂	R ₃	Ratio (10:11) ¹⁴	yield (10+11)/%
1	syn 2a	Me	н	н	н	1.5:1	86
2	syn 2b	Me	Me	н	н	2.1:1	92
3	syn 2c	Me	н	Me	Me	2.2:1	89
4	syn 2d	Et	н	н	н	1.3:1	82
5	syn 2e	Ph	н	н	н	1.4:1	82
	5					Ratio (12:13) ¹⁴	yleld (12+13)/%
6	anti 3a	Me	н	н	н	1.5:1	85
7	anti 3b	Me	Me	н	н	1:1	88
8	anti 3c	Me	н	Me	Me	1.1:1	87
9	anti 3d	Et	н	н	н	1:1	80
10	anti 3e	Ph	Н	Н	н	1.7:1	80

Interestingly, reaction times in these systems were much shorter (<12 hours) than those reported by Warren for a variety of systems (96 hours).¹³ Attempts to increase diastereoselectivities by reducing reaction temperatures or altering reaction times were unsuccessful.

2-Vinyl derivatives

Dihydroxylation of 7 under identical conditions again gave a good yield of the diols, again with no trace of sufur oxidation; however, no diastereoselectivity was observed, 14 and 15 being formed in ca 1:1 ratio, as an inseparable mixture (Scheme 6). Attempted *cis*-dihydroxylation of the monosulfoxide derived from 4 was unsuccessful.



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2-Alkenoyl derivatives

Finally, dihydroxylation of α , β -unsaturated systems 8 and 9 was undertaken (Scheme 7). These reactions, with electron-deficient substrates, were considerably faster than the others investigated, with completion times as low as two hours. Although the yields of the major isomers and the chemoselectivities of the reactions remained consistently high, diastereoselectivities were again low. The structure of 19 was confirmed by single crystal X-ray analysis.



(I) OsCl₃ (1 mol%), quinuclidine (4 mol%), K₃Fe(CN)₆ (3 eq), K₂CO₃ (3 eq), MeSO₂NH₂ (1 eq), 'BuOH/H₂O (1:1), rt, 2-24 h; Na₂S₂O₃ Scheme 7

Conclusions

We have shown that osmium trichloride hydrate mediated dihydroxylation in alkenyl 1,3-dithlane systems proceeds in high yields and with remarkably high chemoselectivity, no concomitant sulfur oxidation being observed. Diastereocontrol in the reactions is low in all cases.

Acknowledgments

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Experimental Section

General experimental details have been previously reported.¹⁵ Additional details:

Purification of Solvents

Methanol was distilled from magnesium. Dichloromethane and butanol were used as supplied.

Procedures

2-Methyl-2-allyl-1,3-dithiane (1a)

A 2.4 M solution of ⁿbutyllithium in hexanes (1.1 eq, 38.2 mL, 91.7 mmol) was added to a stirring solution of 1,3 dithiane (10.0g, 83.3 mmol) in THF (200 mL) at -20 °C. After 1 hour methyl iodide (1.1 eq, 5.71 mL, 91.7 mmol) was added and the solution allowed to reach room temperature over

1 hour before recooling to -20 °C prior to further addition of a 2.4 M solution of "butyllithium in hexanes (1.1 eq, 38.2 mL, 91.7 mmol). The reaction mixture was stirred at this temperature for 1 hour, cooled to -20 °C and allyl bromide (1.1 eq, 7.93 mL, 91.6 mmol) added. The reaction mixture was allowed to reach room temperature over 2 hours. Normal work-up procedure gave 1a as a pale orange oil (14.2g, 98%), v_{max} (film) 3074 and 1637 cm⁻¹; $\delta_{\rm H}$ (270 MHz, CDCl₃) 1.66 (3H, s), 1.98-2.08 (2H, m), 2.76 (2H, d, *J* = 7.2 Hz), 2.85-3.02 (4H, m), 5.18-5.24 (2H, m), 5.90-6.02 (1H, m); *m/z* 175.06142 (M+H⁺); C₈H₁₅S₂ requires 175.06152.

2-Methyl-2-(3-(2-methyl-prop-1-ene))-1,3-dithiane (1b)

A 2.4 M solution of ⁿbutyllithium in hexanes (1.1 eq, 21.0 mL, 50.4 mmol) was added to a stirring solution of 1,3 dithiane (5.5g, 45.8 mmol) in THF (100 mL) at -20 °C. After 1 hour methyl iodide (1.1 eq, 3.14 mL, 50.4 mmol) was added and the solution allowed to reach room temperature over 1 hour before recooling to -20 °C prior to further addition of a 2.4 M solution of ⁿbutyllithium in hexanes (1.1 eq, 3.14 mL, 50.4 mmol). The reaction mixture was stirred at this temperature for 1 hour, cooled to -20 °C and 3-bromo-2-methyl propene (1.1 eq, 5.08 mL, 50.4 mmol) added. The reaction mixture was allowed to reach room temperature overnight. Normal work-up procedure and column chromatography using 10% ethyl acetate/ petroleum ether as eluent gave **1b** as a colourless, clear oil (4.60g, 53%), v_{max} (film) 3073 and 1640 cm⁻¹; δ_{H} (200 MHz, CDCl₃) 1.68 (3H, s), 1.92 (3H, s), 1.91-2.04 (2H, m), 2.69 (2H, s), 2.86-2.92 (4H, m), 4.82-4.85 (1H, m), 4.96-5.00 (1H, m); *m/z* 188.06928 (M⁺), C₉H₁₆S₂ requires 188.06934.

2-Methyl-2-(1-(3-methyl-but-2-ene))-1,3-dithlane (1c)

A 2.4 M solution of ⁿbutyllithium in hexanes (1.1 eq, 19.1 mL, 45.8 mmol) was added to a stirring solution of 1,3 dithiane (5g, 41.7 mmol) in THF (100 mL) at -20 °C. After 1 hour methyl iodide (1.1 eq, 2.85 mL, 45.8 mmol) was added and the solution allowed to reach room temperature over 1 hour before recooling to -20 °C prior to further addition of a 2.4 M solution of ⁿbutyllithium in hexanes (1.1 eq, 19.1 mL, 45.8 mmol). The reaction mixture was stirred at this temperature for 1 hour, cooled to -20 °C and 4-bromo-2-methyl-2-butene (1.1 eq, 5.28 mL, 45.8 mmol) added. The reaction mixture was allowed to reach room temperature overnight. Normal work-up procedure and column chromatography using 10% ethyl acetate/petroleum ether as eluent gave 1c as a colourless, clear oil (5.98g, 71%), v_{max} (film) 1673 cm⁻¹; $\delta_{\rm H}$ (200 MHz, CDCl₃) 1.60 (3H, s), 1.66 (3H, s), 1.76 (3H, s), 1.91-2.03 (2H, m), 2.60-2.64 (2H, s), 2.83-2.89 (4H, m), 5.23-5.32 (1H, m); *m/z* 202.08535 (M⁺), C₁₀H₁₈S₂ requires 202.08499.

2-Ethyl-2-allyl-1,3-dithiane (1d)

A 2.4 M solution of ⁿbutyllithium in hexanes (1.1 eq, 19.1 mL, 45.8 mmol) was added to a stirring solution of 1,3 dithiane (5g, 41.7 mmol) in THF (100 mL) at -20 °C. After 1 hour ethyl iodide (1.1 eq, 3.67 mL, 45.8 mmol) was added and the solution allowed to reach room temperature over 1 hour before recooling to -20 °C prior to further addition of a 2.4 M solution of ⁿbutyllithium in hexanes (1.1 eq, 19.1 mL, 45.8 mmol). The reaction mixture was stirred at this temperature for 1 hour, cooled to -20 °C and allyl bromide (1.1 eq, 3.97 mL, 45.8 mmol) added. The reaction mixture was allowed to reach room temperature over 4 hours. Normal work-up procedure and column chromatography using 10% ethyl acetate/ petroleum ether as eluent gave 1d as a colourless, clear oil (6.97g, 89%), v_{max} (film) 3076 and 1637 cm⁻¹; δ_{H} (200 MHz, CDCl₃) 1.01 (3H, t, J = 7.4 Hz), 1.92 (2H, q, J = 7.4 Hz), 1.89-2.05 (1H, m), 2.66 (2H, d, J = 7.1 Hz), 2.79-2.90 (5H, m), 5.11-5.19 (2H, m), 5.78-5.99 (1H, m); *m/z* 188.06946 (M⁺), C₉H₁₆S₂ requires 188.06934.

2-Phenyl-2-allyl-1,3-dithiane (1e)

A 2.4 M solution of ⁿbutyllithium in hexanes (1.1 eq, 11.7 mL, 28.1 mmol) was added to a stirring

solution of 2-phenyl-1,3 dithiane (5.0g, 25.5 mmol) in THF (100 mL) at -20 °C. After 1 hour allyl bromlde (1.1 eq, 2.49 mL, 28.1 mmol) was added and the solution allowed to reach room temperature over 2 hours. Normal work-up procedure and recrystallization from petroleum ether gave 1e as a yellow, crystalline solid (6.97g, 89%), m.p. 40-42 °C; v_{max} (Nujol) 3057 and 1638 cm⁻¹; δ_{H} (200 MHz, CDCl₃) 1.86-1.99 (2H, m), 2.66-2.76 (4H, m), 4.99-5.01 (1H, m), 5.07 (1H, s), 5.51-5.71 (1H, m), 7.22-7.42 (3H, m), 7.89-7.95 (2H, m); *m/z* 236.06962 (M⁺), C₁₃H₁₆S₂ requires 236.06934. Calc for C₁₃H₁₆S₂: C, 66.04; H, 6.82. Found: C, 65.85; H, 6.93%.

General procedure for sulfoxidation

An aqueous solution of sodium metaperiodate (1.1 eq) was added dropwise to a stirring solution of sulfide in methanol at 0 °C over 30 minutes. Stirring was continued overnight at 0 °C, and the solution allowed to reach room temperature over 30 minutes. The white precipitate was removed by filtration and washed with dichloromethane. The filtrate was reduced in volume by evaporation to approximately 10% of the original volume and partitioned between water and dichloromethane. The aqueous layer was washed twice with dichloromethane, the combined organic layers dried over MgSO₄ and the solvents removed under reduced pressure to yield a crude mixture of diastereoisomeric sulfoxides, separated by column chromatography using ethyl acetate as eluent.

Syn and anti-2-methyl-2-allyl-1,3-dithiane 1-oxides (2a & 3a)

Treatment of 1a (14.2g, 81.6 mmol) as described above with sodium metaperiodate (19.2g, 89.8 mmol) in water (200 mL) and methanol (300 mL) furnished the diastereoisomeric sulfoxides. Partial separation by column chromatography yielded both the less polar *syn* (2a) and more polar *anti* (3a) diastereoisomers as pale yellow oils (12.0g, 77%).

For syn **2a**: v_{max} (film) 3075, 1638 and 1034 cm⁻¹; δ_{H} (270 MHz, CDCl₃) 1.59 (3H, s), 2.22-2.36 (1H, m), 2.44-2.56 (2H, m), 2.70-2.95 (3H, m), 2.79 (1H, d, J = 7.2 Hz), 3.06-3.15 (1H, m), 5.30-5.38 (2H, m), 5.92-6.07 (1H, m); *m/z* 190.0486 (M⁺), C₈H₁₄OS₂ requires 190.0486.

For anti **3a**: v_{max} (film) 3081, 1638 and 1033 cm⁻¹; δ_{H} (270 MHz, CDCl₃) 1.67 (3H, s), 2.16-2.33 (1H, m), 2.38-2.51 (2H, m), 2.71 (2H, d, J = 7.2 Hz), 2.73-2.83 (2H, m), 3.06-3.14 (1H, m), 5.23-5.30 (2H, m), 5.86-6.01 (1H, m); δ_{L} (68 MHz, CDCl₃) 13.8, 24.7, 28.4, 42.1, 46.2, 61.2, 120.2, 130.4; *m/z* 190.0486 (M⁺), C₈H₁₄OS₂ requires 190.0486.

Syn and anti-2-methyl-2-(3-(2-methyl-prop-1-enyl))-1,3-dithiane 1-oxide (2b & 3b)

Treatment of **1b** (4.50g, 23.9 mmol) as described above with sodium metaperiodate (5.63g, 26.3 mmol) in water (20 mL) and methanol (150 mL) furnished the diastereoisomeric sulfoxides. Partial separation by column chromatography yielded the less polar *syn* (**2b**) diastereoisomer as a colourless crystalline solid and the more polar *anti* (**3b**) diastereoisomer as a colourless, clear oil (3.97g, 81%). For *syn* **2b**: m.p. 76-78 °C, v_{max} (Nujol) 3073, 1642 and 1034 cm⁻¹; δ_{H} (200 MHz, CDCl₃) 1.51 (3H, s) 1.96 (3H es) 2.21-2.46 (3H m) -2.96-3.03 (1H m) -4.92 (1H es) 5.02-5.04

s), 1.96 (3H, s), 2.21-2.46 (3H, m), 2.60-2.86 (4H, m), 2.96-3.03 (1H, m), 4.92 (1H, s), 5.02-5.04 (1H, m); m/z 204.06445 (M⁺); C₉H₁₆OS₂ requires 204.06425. Calc for C₉H₁₆OS₂: C, 52.90; H, 7.89. Found: C, 52.81; H, 7.92%.

For anti **3b**: v_{max} (film) 3074, 1642 and 1035 cm⁻¹; δ_{H} (200 MHz, CDCl₃) 1.64 (3H, s), 1.90 (3H, s), 2.09-2.46 (3H, m), 2.62-2.82 (4H, m), 3.01-3.11 (1H, m), 4.89-4.91 (1H, m), 5.01-5.04 (1H, m); *m/z* 204.06445 (M⁺); C₉H₁₆OS₂ requires 204.06425.

Syn and anti-2-methyl-2-(1-(3-methyl-but-2-enyl))-1,3-dithiane 1-oxide (2c & 3c)

Treatment of 1c (4.10g, 19.7 mmol) as described above with sodium metaperiodate (4.77g, 22.3 mmol) in water (50 mL) and methanol (300 mL) furnished the diastereoisomeric sulfoxides. Partial separation by column chromatography yielded the less polar *syn* (2c) diastereoisomer as a colourless, clear oil and the more polar *anti* (3c) diastereoisomer as a colourless crystalline solid

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(**3.74g, 84%**).

For syn 2c: v_{max} (film) 1672 and 1034 cm⁻¹; δ_{H} (200 MHz, CDCl₃) 1.49 (3H, s), 1.70 (3H, s), 1.79 (3H, s), 2.05-3.07 (8H, m), 5.24-5.33 (1H, m); *m/z* 218.08023 (M⁺), C₁₀H₁₈OS₂ requires 218.07991. For *anti* 3c: m.p. 62-64 °C; v_{max} (Nujol) 1672 and 1021 cm⁻¹; δ_{H} (200 MHz, CDCl₃) 1.61 (3H, s), 1.66 (3H, s), 1.76 (3H, s), 2.05-2.44 (3H, m), 2.50-2.78 (4H, m), 2.99-3.10 (1H, m), 5.02-5.31 (1H, m); *m/z* 204.06445 (M⁺), C₁₀H₁₈OS₂ requires 204.06425.

Syn and anti-2-ethyl-2-allyl-1,3-dithiane 1-oxide (2d & 3d)

Treatment of 1d (6.80g, 36.2 mmol) as described above with sodium metaperiodate (8.50g, 39.7 mmol) in water (50 mL) and methanol (200 mL) furnished the diastereoisomeric sulfoxides. Separation by column chromatography yielded both the less polar *syn* (2d) and more polar *anti* (3d) diastereoisomers as colourless, clear oils.

For syn 2d: (2.74g, 37%), v_{max} (film) 3077, 1636 and 1033 cm⁻¹; δ_{H} (200 MHz, CDCl₃) 1.11 (3H, t, J = 7.4 Hz), 1.75-2.27 (3H, m), 2.36-2.48 (2H, m), 2.60-2.91 (4H, m), 3.02-3.19 (1H, m), 5.23-5.32 (2H, m), 5.84-6.05 (1H, m); m/z 204.06445 (M⁺), C₉H₁₆OS₂ requires 204.06425.

For anti **3d**: (3.02g, 41%), v_{max} (film) 3078, 1638 and 1036 cm⁻¹; δ_{H} (200 MHz, CDCl₃) 1.11 (3H, t, J = 7.4 Hz), 1.88-2.23 (3H, m), 2.36-2.43 (2H, m), 2.49-2.92 (4H, m), 3.00-3.07 (1H, m), 5.19-5.32 (2H, m), 5.87-6.08 (1H, m); *m/z* 204.06426 (M⁺), C₉H₁₆OS₂ requires 204.06425.

Syn and anti-2-phenyl-2-allyl-1,3-dithiane 1-oxide (2e & 3e)

Treatment of 1e (5.40g, 22.9 mmol) as described above with sodium metaperiodate (5.38g, 25.2 mmol) in water (50 mL) and methanol (250 mL) furnished the diastereoisomeric sulfoxides. Separation by column chromatography yielded both the less polar *syn* (2e) and more polar *anti* (3e) diastereoisomers as colourless crystalline solids.

For syn 2e: (1.37g, 24%), m.p. 88-90 °C; v_{max} (Nujol) 1641 and 1042 cm⁻¹; δ_{H} (400 MHz, CDCl₃) 2.26-2.30 (1H, m), 2.35-2.45 (2H, m), 2.64-2.80 (2H, m), 2.89-2.96 (2H, m), 3.16-3.21 (1H, m), 5.08-5.12 (2H, m), 5.55-5.65 (1H, m), 7.35-7.39 (1H, m), 7.42-7.46 (2H, m), 7.99-8.01 (2H, m); δ_{C} (50 MHz, CDCl₃) 26.8, 29.7, 44.7, 47.0, 69.9, 119.9, 128.2, 128.6, 128.8, 130.0, 135.7; *m/z* 252.06430 (M⁺); C₁₃H₁₆OS₂ requires 252.06425. Calc for C₁₃H₁₆OS₂: C, 61.86; H, 6.39. Found: C, 62.06; H, 6.42%.

For anti **3e**: (2.86g, 50%), m.p. 62-64 °C; v_{max} (Nujol) 1639 and 1032 cm⁻¹; δ_{H} (400 MHz, CDCl₃) 1.70-1.74 (1H, m), 2.44-2.56 (3H, m), 2.72-2.78 (1H, m), 2.83-2.87 (2H, m), 2.94-2.99 (1H, m), 5.05-5.11 (2H, m), 5.40-5.50 (1H, m), 7.34-7.37 (1H, m), 7.43-7.47 (2H, m), 7.65-7.67 (2H, m); δ_{C} (50 MHz, CDCl₃) 16.1, 25.3, 41.3, 42.1, 69.1, 119.7, 127.8, 128.1, 128.9, 129.6, 135.8; *m/z* 252.06430 (M⁺); C₁₃H₁₆OS₂ requires 252.06425. Calc for C₁₃H₁₆OS₂: C, 61.86; H, 6.39. Found: C, 61.96; H, 6.39%.

2-(2-Propylidene)-1,3-dithiane (4)

A 2.4 M solution of ⁿbutyllithium in hexanes (1.1 eq, 4.76 mL, 11.4 mmol) was added to a stirring solution of 2-trimethylsilyl-1,3-dithiane (2.0 g, 10.4 mmol) in THF (20 mL) at -78 °C over 2 minutes. The solution was allowed to reach 0 °C over 5 hours, recooled to -78 °C, acetone (1.1 eq, 0.84 mL, 11.4 mmol) added, and the mixture allowed to reach room temperature overnight. The reaction mixture was poured onto water (40 mL), extracted with dichloromethane (3 x 30 mL), dried (Na₂SO₄) and evaporated under reduced pressure to give 4 as a pale yellow oil (1.52g, 91%); v_{max} (film) 2907 and 1422 cm⁻¹; δ_{H} (200 MHz, CDCl₃) 1.92 (6H, s), 2.05-2.17 (2H, m), 2.83-2.89 (4H, m); & (50 MHz, CDCl₃) 22.0, 24.8, 30.1, 91.0, 118.1; *m/z* 160.03822 (M⁺); C₇H₁₂S₂ requires 160.03806.

2-(2-Propylidene)-1,3-dithiane 1-Oxide

A solution of sodium metaperiodate (2.94 g, 13.7 mmol) in water (20 mL) was added dropwise to a stirring solution of 2-(2-propylidene)-1,3-dithiane (2.0 g, 12.5 mmol) in methanol (75 mL) at 0 °C. After 16 h the solution was allowed to reach room temperature over 0.5 hours, filtered, and the filtrate concentrated to 30 mL. Extraction with dichloromethane, drying (MgSO₄), evaporation under reduced pressure, and recrystallization from diethyl ether gave the title compound as a colourless solid (1.63g, 74%), m.p. 98-100 °C; v_{max} (Nujol) 2925 and 1041 cm⁻¹; δ_{H} (200 MHz, CDCl₃) 1.81-1.96 (1H, m), 2.07 (3H, s), 2.15 (3H, s), 2.54-2.71 (2H, m), 2.74-3.00 (2H, m), 3.08-3.18 (1H, m); δ_{C} (100 MHz, CDCl₃) 15.0, 21.2, 23.3, 30.2, 47.9, 130.2, 148.8; *m/z* 176.03311 (M⁺); C₇H₁₂S₂O requires 176.03297. Calc for C₇H₁₂S₂O: C, 47.69; H, 6.86. Found: C, 47.78; H, 6.88%.

2-Methyl-2-(2-propene)-1,3-dithiane (5)

A 2.4 M solution of ⁿbutyllithium in hexanes (1.1 eq, 4.30 mL, 10.3 mmol) was added to a stirring solution of 4 (1.5g, 9.4 mmol) in THF (20 mL) and HMPA (3 eq, 4.88 mL) at -78 °C. The solution was allowed to reach room temperature over 2.5 hours, recooled to -78 °C, methyl iodide (1.1 eq, 0.64 mL, 10.3 mmol) added, and the mixture allowed to reach room temperature over 1 hour. Normal work-up and column chromatography using 10% ethyl acetate/ petroleum ether as eluent gave **5** as a pale yellow oil (1.08g, 66%); v_{max} (film) 2971 and 1632 cm⁻¹; δ_{H} (200 MHz, CDCl₃) 1.63 (3H, s), 1.82-2.11 (2H, m), 1.93 (3H, s), 2.57-2.92 (4H, m), 5.14-5.17 (1H, m), 5.49 (1H, m); *m/z* 175.06111 (M⁺); C₈H₁₄S₂ requires 175.06152.

Syn & anti-2- methyl-2-(2-propene)-1,3-dithlane 1-oxide (6 & 7)

Treatment of 5 (1.00g, 5.7 mmol) as described above with sodium metaperiodate (1.35g, 6.3 mmol) in water (10 mL) and methanol (50 mL) furnished the diastereoisomeric sulfoxides. Separation by column chromatography yielded both the less polar *syn* (6) and more polar *anti* (7) diastereoisomers as pale yellow oils.

For syn 6: (0.11g, 10%); v_{max} (film) 3093, 1627 and 1039 cm⁻¹; δ_{H} (200 MHz, CDCl₃) 1.76 (3H, s), 2.00 (3H, d, J = 1.7 Hz), 2.11-2.33 (1H, m), 2.37-2.72 (3H, m), 2.88-3.00 (1H, m), 3.11-3.25 (1H, m), 5.31 (1H, t, J = 1.7 Hz), 5.69 (1H, s); & (50 MHz, CDCl₃) 20.4, 23.3, 25.3, 26.4, 45.5, 66.2, 117.8, 141.2; *m/z* 190.04876 (M⁺), C₈H₁₄OS₂ requires 190.04861.

For anti **7**: (0.66g, 60%); v_{max} (film) 1639 and 1032 cm⁻¹; δ_H (200 MHz, CDCl₃) 1.75 (3H, s), 1.97 (3H, d, J = 1.7 Hz), 2.02-2.24 (1H, m), 2.33-2.83 (4H, m), 3.01-3.13 (1H, m), 5.29 (1H, q, J = 1.7 Hz), 5.39 (1H, s); δ (50 MHz, CDCl₃) 14.7, 19.9, 25.1, 25.2, 45.5, 65.3, 117.3, 141.7; *m/z* 190.04876 (M⁺), C₈H₁₄OS₂ requires 190.04861.

General procedure for OsCl₃ mediated dihydroxylation

A round bottomed flask was charged with potassium ferricyanide (3.0 eq), potassium carbonate (3.0 eq), quinuclidine (4.0 mol%), osmium (III) chloride hydrate (1.0 mol%) and methanesulfonamide (1.0 eq)*. A 1:1 mixture of water and 'butanol (50 mL/g) was added and the solution stirred using a mechanical stirrer until all the solids had dissolved. Substrate was added and the solution stirred vigorously for an appropriate length of time at room temperature. Anhydrous sodium sulfite (12 eq) was added, stirring continued for one hour, and dichloromethane (50 mL/g) added. After a further 5 minutes of stirring the organic phase was separated, the aqueous phase extracted with dichloromethane (4 x 100 mL/g), and the combined organic extracts washed with 2 M potassium hydroxide* (10 ml). Drying (MgSO₄), evaporation under reduced pressure, and separation by column chromatography using 10% methanol/ ethyl acetate as eluent gave the diastereoisomeric 1,2-diols. * Only included for non-terminal alkenes.

Syn-2-methyl-2-(3-(propane-1,2-diol))-1,3-dithiane 1-oxides (10a & 11a)

Treatment of 2a (1.0g, 5.3 mmol) as described above with potassium ferricyanide (5.20g, 15.8

mmol), potassium carbonate (2.18g, 15.8 mmol), quinuclidine (23.4 mg, 0.2 mmol) and osmium (III) chloride hydrate (15.6 mg, 0.05 mmol) in water (25 mL) and ^tbutanol (25 mL) for 3 hours, followed by addition of sodium sulfite (7.96g, 63.2 mmol) and work up furnished the diastereoisomeric alcohols. Separation by column chromatography yielded both diastereoisomers as clear, colourless, semicrystalline oils.

For **10a** (less polar): (0.550g, 51%); ν_{max} (film) 3372 and 1015 cm⁻¹; δ_{H} (400 MHz, DMSO-d6) 1.53 (3H, s), 1.80-1.86 (1H, m), 1.99-2.08 (1H, m), 2.20-2.38 (3H, m), 2.63-2.80 (2H, m), 2.99-3.03 (1H, m), 3.23-3.31 (2H, m), 3.78-3.82 (1H, m), 4.74-4.78 (2H, m); δ_{c} (100 MHz, CDCl₃) 22.6, 25.0, 30.1, 39.6, 45.7, 60.3, 66.2, 66.6; *m/z* 225.06197 (M+H⁺); C₈H₁₇O₃S₂ requires 225.06191.

For **11a** (more polar): (0.376g, 35%); v_{max} (film) 3381 and 1017 cm⁻¹; δ_{H} (400 MHz, DMSO-d6) 1.49 (3H, s), 1.83-2.09 (3H, m), 2.23-2.29 (1H, m), 2.44-2.48 (2H, m), 2.72-2.80 (2H, m), 2.95-2.99 (1H, m), 3.21-3.27 (1H, m), 3.74-3.79 (1H, m), 4.60 (1H, d, J = 5.2 Hz), 4.68 (1H, t, J = 5.2 Hz); *m/z* 225.06197 (M+H⁺); C₈H₁₇O₃S₂ requires 225.06191.

Anti-2-methyl-2-(3-(propane-1,2-diol))-1,3-dithiane 1-oxides (12a & 13a)

Treatment of **3a** (1.0g, 5.3 mmol) as described above with potassium ferricyanide (5.20g, 15.8 mmol), potassium carbonate (2.18g, 15.8 mmol), quinuclidine (23.4 mg, 0.2 mmol) and osmlum (III) chloride hydrate (15.6 mg, 0.05 mmol) in water (25 mL) and ^tbutanol (25 mL) for 3 hours followed by addition of sodium sulfite (7.96g, 63.2 mmol) and work up furnished the diastereoisomeric alcohols. Separation by column chromatography yielded both diastereoisomers as clear, colourless, viscous oils.

For **12a** (less polar): (0.552g, 51%); v_{max} (film) 3372 and 1013 cm⁻¹; δ_{H} (270 MHz, DMSO-d6) 1.59 (3H, s), 1.79-2.03 (3H, m), 2.21-2.29 (1H, m), 2.42-2.51 (1H, m), 2.64-2.76 (2H, m), 2.97-3.05 (1H, m), 3.10-3.19 (1H, m), 3.27-3.35 (1H, m), 3.70-3.74 (1H, m), 4.66 (1H, t, J = 5.6 Hz), 4.74 (1H, d, J = 5.0 Hz); δ_{L} (68 MHz, CDCl₃) 12.7, 24.9, 28.7, 45.8, 46.1, 60.0, 66.3, 66.8; *m/z* 225 (M+H⁺).

For **13a** (more polar): (0.372g, 34%); v_{max} (film) 3380 and 1014 cm⁻¹; δ_{H} (270 MHz, DMSO-d6) 1.56 (3H, s), 1.58-1.66 (1H, m), 1.90-2.11 (2H, m), 2.19-2.28 (1H, m), 2.37-2.49 (1H, m), 2.63-2.76 (2H, m), 2.92-2.98 (1H, m), 3.09-3.18 (1H, m), 3.24-3.30 (1H, m), 3.72-3.79 (1H, m), 4.56 (1H, d, J = 5.8 Hz), 4.64 (1H, t, J = 5.8 Hz); δ_{c} (68 MHz, CDCl₃) 15.5, 24.9, 27.9, 42.2, 46.1, 60.4, 66.9, 68.6; m/z 225 (M+H⁺).

Syn-2-methyl-2-(3-(2-methyl-propane-1,2-diol))-1,3-dithiane 1-oxides (10b & 11b)

Treatment of **2b** (0.50g, 2.5 mmol) as described above with potassium ferricyanide (2.42g, 7.3 mmol), potassium carbonate (1.02g, 7.4 mmol), quinuclidine (11.0 mg, 0.1 mmol) and osmium (III) chloride hydrate (7.3 mg, 0.02 mmol) in water (12 mL) and ^tbutanol (12 mL) for 4 hours followed by addition of sodium sulfite (3.71g, 29.4 mmol) and work up furnished the diastereoisomeric alcohols. Separation by column chromatography yielded both diastereoisomers as clear, colourless, viscous oils.

For **10b** (less polar): (0.361g, 62%); v_{max} (film) 3391 and 1016 cm⁻¹; δ_{H} (400 MHz, DMSO-d6) 1.21 (3H, s), 1.61 (3H, s), 1.98-2.12 (3H, m), 2.24-2.28 (1H, m), 2.38-2.42 (1H, m), 2.75-2.93 (3H, m), 3.29-3.33 (1H, m), 3.49-3.53 (1H, m), 4.42 (1H, s), 4.71 (1H, t, J = 5.2 Hz); & (100 MHz, CDCl₃) 24.2, 25.5, 26.7, 28.5, 37.5, 45.4, 61.0, 70.1, 73.3; m/z 239.07782 (M+H⁺); $C_{9}H_{19}O_{3}S_{2}$ requires 239.07756.

For **11b** (more polar): (0.177g, 30%); v_{max} (film) 3372 and 1014 cm⁻¹; δ_{H} (400 MHz, DMSO-d6) 1.29 (3H, s), 1.62 (3H, s), 1.99-2.18 (3H, m), 2.26-2.30 (1H, m), 2.40-2.43 (1H, m), 2.66-2.81 (2H, m), 2.90-2.93 (1H, m), 3.14-3.24 (2H, m), 4.37 (1H, s), 4.81 (1H, m); *m/z* 239.07782 (M+H⁺); C₉H₁₉O₃S₂ requires 239.07756.

Anti-2-methyl-2-(3-(2-methyl-propane-1,2-diol))-1,3-dithiane 1-oxides (12b & 13b)

Treatment of **3b** (0.50g, 2.5 mmol) as described above with potassium ferricyanide (2.42g, 7.3 mmol), potassium carbonate (1.02g, 7.4 mmol), quinuclidine (11.0 mg, 0.1 mmol) and osmium (III) chloride hydrate (7.3 mg, 0.02 mmol) in water (12 mL) and ^tbutanol (12 mL) for 2.5 hours followed addition of sodium sulfite (3.71g, 29.4 mmol) and work up furnished the diastereolsomeric alcohols as an inseparable mixture of clear, colourless, viscous oils (0.512g, 88%).

Syn-2-methyl-2-(1-(3-methyl-butan-2,3-diol))-1,3-dithiane 1-oxides (10c & 11c)

Treatment of 2c (0.50g, 2.3 mmol) as described above with potassium ferricyanide (2.27g, 6.9 mmol), potassium carbonate (0.95g, 6.9 mmol), quinuclidine (10.2mg, 0.1 mmol), osmium (III) chloride hydrate (6.8 mg, 0.02 mmol) and methanesulfonamide (0.22g, 2.3 mmol) in water (12 mL) and ^tbutanol (12 mL) for 24 hours followed by addition of sodium sulfite (3.47g, 27.5 mmol) and work up furnished the diastereoisomeric alcohols. Separation by column chromatography yielded the diastereoisomers as a clear, colourless, viscous oil (10c) and a colourless crystalline solid (11c).

For **10c** (more polar): (0.352g, 61%); v_{max} (film) 3381 and 997 cm⁻¹; δ_{H} (400 MHz, DMSO-d6) 1.02 (3H, s), 1.09 (3H, s), 1.48 (3H, s), 1.81 (1H, dd, J = 13.0 and 8.4 Hz), 1.92-2.01 (1H, m), 2.19 (1H, d, J = 13.0 Hz), 2.25-2.28 (1H, m), 2.42-2.47 (1H, m), 2.74-2.83 (2H, m), 2.95-2.99 (1H, m), 3.44-3.48 (1H, m), 4.28 (1H, s), 4.57 (1H, d, J = 6.0 Hz); δ_{L} (100 MHz, CDCl₃) 22.9, 24.0, 25.2, 25.7, 26.1, 30.6, 44.9, 59.9, 72.7, 74.1; *m/z* 253.09319 (M+H⁺); C₁₀H₂₁O₃S₂ requires 253.09321.

For 11c (less polar): (0.164g, 28%), m.p. 133-135 °C; v_{max} (Nujol) 3376, and 1004 cm⁻¹; δ_{H} (400 MHz, DMSO-d6) 1.05 (3H, s), 1.14 (3H, s), 1.51 (3H, s), 1.77 (1H, dd, J = 14.8 and 9.2 Hz), 1.99-2.09 (1H, m), 2.27-2.33 (3H, m), 2.66-2.73 (1H, m), 2.76-2.83 (1H, m), 2.98-3.02 (1H, m), 3.52-3.56 (1H, m), 4.42 (1H, s), 4.70 (1H, d, J = 6.4 Hz); δ_{L} (100 MHz, CDCl₃) 22.7, 24.4, 25.0, 26.0, 30.2, 38.5, 45.9, 60.3, 72.0, 72.3. Calc for C₁₀H₂₀O₃S₂: C, 47.59; H, 7.99. Found: C, 47.43; H, 7.97%.

Anti-2-methyl-2-(1-(3-methyl-butan-2,3-diol))-1,3-dithiane 1-oxides (12c & 13c)

Treatment of 3c (0.50g, 2.3 mmol) as described above with potassium ferricyanide (2.27g, 6.9 mmol), potassium carbonate (0.95g, 6.9 mmol), quinuclidine (10.2 mg, 0.1 mmol), osmium (III) chloride hydrate (6.8 mg, 0.02 mmol) and methanesulfonamide (0.22g, 2.3 mmol) in water (12 mL) and 'butanol (12 mL) for 12 hours followed by addition of sodium sulfite (3.47g, 27.5 mmol) and work up furnished the diastereoisomeric alcohols. Separation by column chromatography yielded both diastereoisomers as colourless crystalline solids.

For **12c** (less polar): (0.264g, 46%), m.p. 151-152 °C; v_{max} (Nujol) 3395, 3327 and 993 cm⁻¹; δ_{H} (400 MHz, DMSO-d6) 0.97 (3H, s), 1.06 (3H, s), 1.57 (3H, s), 1.75 (1H, dd, J = 14.8 and 9.2 Hz), 1.90-1.96 (1H, m), 2.00 (1H, d, J = 14.8 Hz), 2.22-2.26 (1H, m), 2.44-2.49 (1H, m), 2.64-2.75 (2H, m), 2.99-3.04 (1H, m), 3.42-3.46 (1H, m), 4.31 (1H, s), 4.74 (1H, d, J = 5.6 Hz); & (50 MHz, CDCl₃) 12.7 24.0, 24.8, 25.5, 28.6, 44.4, 45.6, 60.1, 72.3; *m/z* 253.09319 (M+H⁺); C₁₀H₂₁O₃S₂ requires 253.09321. Calc for C₁₀H₂₀O₃S₂: C, 47.59; H, 7.99. Found: C, 47.63; H, 8.03%.

For **13c** (more polar): (0.236g, 41%), m.p. 118-120 °C; v_{max} (Nujol) 3409, 3367 and 1013 cm⁻¹; δ_{H} (200 MHz, DMSO-d6) 0.96 (3H, s), 1.05 (3H, s), 1.56 (3H, s), 1.55 (1H, dd, J = 14.8 and 9.3 Hz), 1.93-2.05 (1H, m), 2.19-2.26 (1H, m), 2.35-2.44 (1H, m), 2.62-2.75 (2H, m), 2.91-3.00 (2H, m), 3.45-3.53 (1H, m), 4.27 (1H, s), 4.58 (1H, d, J = 6.6 Hz); δ_{c} (50 MHz, CDCl₃) 15.1, 23.8, 24.7, 25.6, 27.9, 40.9, 45.8, 60.6, 72.6, 74.1; *m/z* 253.09344 (M+H⁺); C₁₀H₂₁O₃S₂ requires 253.09321. Calc for C₁₀H₂₀O₃S₂: C, 47.59; H, 7.99. Found: C, 47.55; H, 8.03%.

Syn-2-ethyl-2-(3-(propane-1,2-diol))-1,3-dithiane 1-oxides (10d & 11d)

Treatment of **2d** (0.50g, 5.3 mmol) as described above with potassium ferricyanide (2.42g, 7.3 mmol), potassium carbonate (1.01g, 7.3 mmol), quinuclidine (10.9 mg, 0.1 mmol) and osmium (III)

chloride hydrate (7.2 mg, 0.02 mmol) in water (12 mL) and ^tbutanol (12 mL) for 4 hours followed by addition of sodium sulfite (3.71g, 29.4 mmol) and work up furnished the diastereoisomeric alcohols. Separation by column chromatography yielded both diastereoisomers as clear, colourless, viscous oils.

For **10d** (more polar): (0.271g, 46%); v_{max} (film) 3381 and 1018 cm⁻¹; δ_{H} (200 MHz, DMSO-d6) 1.02 (3H, t, J = 7.4 Hz), 1.85-2.01 (4H, m), 2.10-2.28 (2H, m), 2.39-2.51 (2H, m), 2.70-2.89 (2H, m), 2.96-3.06 (1H, m), 3.16-3.40 (1H, m), 3.79-3.89 (1H, m), 4.61 (1H, t, J = 5.0 Hz), 4.72 (1H, d, J = 5.7 Hz); δ_{L} (50 MHz, CDCl₃) 8.2, 24.6, 26.1, 28.3, 31.3, 44.7, 64.4, 66.8, 68.1; *m/z* 239.07782 (M+H⁺); C₉H₁₉O₃S₂ requires 239.07756.

For **11d** (less polar): (0.210g, 36%); v_{max} (film) 3363 and 1010 cm⁻¹; δ_{H} (200 MHz, DMSO-d6) 1.00 (3H, t, J = 7.4 Hz), 1.89-2.09 (4H, m), 2.26-2.50 (3H, m), 2.66-2.92 (2H, m), 3.04-3.10 (1H, m), 3.18-3.47 (2H, m), 3.68-3.85 (1H, m), 4.81 (1H, t, J = 5.5 Hz), 4.88 (1H, d, J = 4.4 Hz); δ_{c} (50 MHz, CDCl₃) 6.9, 24.1, 27.2, 30.1, 37.3, 45.2, 65.2, 65.7, 66.5; *m/z* 239.07782 (M+H⁺); C₉H₁₉O₃S₂ requires 239.07756.

Anti-2-ethyl-2-(3-(propane-1,2-diol))-1,3-dithiane 1-oxides (12d & 13d)

Treatment of **3d** (0.50g, 5.3 mmol) as described above with potassium ferricyanide (2.42g, 7.3 mmol), potassium carbonate (1.01g, 7.3 mmol), quinuclidine (10.9 mg, 0.1 mmol) and osmium (III) chloride hydrate (7.2 mg, 0.02 mmol) in water (12 mL) and butanol (12 mL) for 3 hours followed by addition of sodium sulfite (3.71g, 29.4 mmol) and work up furnished the diastereoisomeric alcohols. Separation by column chromatography yielded both diastereoisomers as clear, colourless, viscous oils.

For **12d** (less polar): (0.236g, 40%); v_{max} (film) 3367 and 1036 cm⁻¹; δ_{H} (200 MHz, DMSO-d6) 0.99 (3H, t, j = 7.4 Hz), 1.54-1.66 (1H, m), 1.79-2.05 (3H, m), 2.09-2.31 (2H, m), 2.40-2.57 (2H, m), 2.79-2.93 (1H, m), 3.04-3.21 (2H, m), 3.32-3.42 (1H, m), 3.63-3.71 (1H, m), 4.74 (1H, t, J = 5.8 Hz), 4.93 (1H, d, J = 3.3 Hz); δ_{C} (50 MHz, CDCl₃) 6.2, 15.0, 24.1, 28.2, 41.4, 44.6, 64.0, 66.0, 66.2; *m/z* 239.07782 (M+H⁺); C₉H₁₉O₃S₂ requires 239.07756.

For **13d** (more polar): (0.232g, 40%); v_{max} (film) 3369 and 1022 cm⁻¹; δ_{H} (200 MHz, DMSO-d6) 1.02 (3H, t, J = 7.4 Hz), 1.69-1.81 (1H, m), 1.87-2.11 (4H, m), 2.15-2.25 (1H, m), 2.35-2.61 (2H, m), 2.74-2.88 (1H, m), 2.92-3.03 (1H, m), 3.07-3.31 (2H, m), 3.86-3.92 (1H, m), 4.57 (1H, d, J = 5.5 Hz), 4.68 (1H, t, J = 5.5 Hz); δ_{c} (50 MHz, CDCl₃) 6.7, 18.8, 24.3, 26.9, 37.6, 44.8, 64.6, 66.9, 68.2; *m/z* 239.07782 (M+H⁺); C₉H₁₉O₃S₂ requires 239.07756.

Syn-2-phenyl-2-(3-(propane-1,2-diol))-1,3-dithiane 1-oxides (10e & 11e)

Treatment of **2e** (0.50g, 2.0 mmol) as described above with potassium ferricyanide (1.96g, 6.0 mmol), potassium carbonate (0.82g, 6.0 mmol), quinuclidine (8.8 mg, 0.08 mmol) and osmium (III) chloride hydrate (5.9 mg, 0.02 mmol) in water (12 mL) and 'butanoi (12 mL) for 4 hours followed by addition of sodium sulfite (3.00g, 23.8 mmol) and work up furnished the diastereoisomeric alcohols. Separation by column chromatography yielded both diastereoisomers as clear, colourless, semicrystalline oils.

For **10e** (less polar): (0.286g, 50%); v_{max} (film) 3363 and 1021 cm⁻¹; δ_{H} (400 MHz, DMSO-d6) 2.10-2.16 (1H, m), 2.20-2.35 (3H, m), 2.44-2.48 (1H, m), 2.59-2.66 (2H, m), 3.01-3.05 (1H, m), 3.18-3.25 (2H, m), 3.43-3.47 (1H, m), 4.52 (1H, d, J = 4.4 Hz), 4.59 (1H, t, J = 5.8 Hz), 7.36 (1H, t, J = 7.2 Hz), 7.44 (2H, t, J = 7.6 Hz), 7.87 (2H, d, J = 7.6 Hz); δ_{L} (100 MHz, CDCl₃) 26.7, 30.2, 46.9, 48.6, 66.5, 66.7, 68.9, 128.7, 128.8, 129.3, 135.8; *m/z* 287.07714 (M+H⁺); C₁₃H₁₉O₃S₂ requires 287.07756.

For **11e** (more polar): (0.173g, 30%); v_{max} (film) 3374 and 1019 cm⁻¹; δ_{H} (400 MHz, DMSO-d6) 1.88-1.94 (1H, m), 2.19-2.22 (2H, m), 2.39-2.55 (3H, m), 2.66-2.69 (1H, m), 2.86-2.94 (2H, m), 2.99-3.05 (1H, m), 3.23-3.26 (1H, m), 4.50 (1H, t, J = 5.6 Hz), 4.54 (1H, d, J = 5.6 Hz), 7.37-7.40 (1H, t) = 5.6 Hz

m), 7.44-7.47 (2H, m), 7.89-7.92 (2H, m); δ_c (100 MHz, CDCl₃) 27.3, 29.1, 43.6, 46.9, 66.6, 68.8, 69.6, 128.7, 128.8, 129.1, 135.6; *m/z* 287.07714 (M+H⁺); C₁₃H₁₉O₃S₂ requires 287.07756.

Anti-2-phenyl-2-(3-(propane-1,2-diol))-1,3-dithiane 1-oxides (12e & 13e)

Treatment of **3e** (0.50g, 2.0 mmol) as described above with potassium ferricyanide (1.96g, 6.0 mmol), potassium carbonate (0.82g, 6.0 mmol), quinuclidine (8.8 mg, 0.08 mmol) and osmium (III) chioride hydrate (5.9 mg, 0.02 mmol) in water (12 mL) and ^tbutanol (12 mL) for 4 hours followed by addition of sodium sulfite (3.00g, 23.8 mmol) and work up furnished the diastereoisomeric alcohols. Separation by column chromatography yielded both diastereoisomers as clear, colourless, semicrystalline oils.

For 12e (less polar): (0.273g, 48%); v_{max} (film) 3350 and 1015 cm⁻¹; δ_{H} (400 MHz, DMSO-d6) 1.88-1.95 (1H, m), 2.28-2.34 (1H, m), 2.41-2.43 (2H, m), 2.57-2.63 (1H, m), 2.76-2.94 (3H, m), 3.26-3.43 (3H, m), 4.61 (1H, d, J = 4.4 Hz), 4.66 (1H, t, J = 4.4 Hz), 7.34-7.38 (1H, m), 7.42-7.45 (2H, m), 7.65-7.68 (2H, m); *m/z* 287.07794 (M+H⁺); C₁₃H₁₉O₃S₂ requires 287.07756.

For **13e** (more polar): (0.195g, 34%); v_{max} (film) 3362 and 1035 cm⁻¹; δ_{H} (400 MHz, DMSO-d6) 1.83-1.89 (1H, m), 2.14-2.20 (1H, m), 2.28-2.34 (1H, m), 2.51-2.69 (3H, m), 2.77-2.94 (2H, m), 3.01-3.15 (2H, m), 3.32-3.40 (1H, m), 4.53 (1H, d, J = 4.4 Hz), 4.62 (1H,bs), 7.35-7.39 (1H, m), 7.43-7.47 (2H, m), 7.61-7.67 (2H, m); *m/z* 287.07780 (M+H⁺); $C_{13}H_{19}O_3S_2$ requires 287.07756.

2-(1-Hydroxyethyl)-2-methyl-1,3-dithiane

A 2.4 molar solution of ⁿbutyllithium in hexanes (1.1 eq, 38.2 mL, 91.6 mmol) was added to a solution of 1,3-dithiane (10.0g, 83.3 mmol) in THF (250 mL) at -20 °C. After one hour methyl iodide (1.1 eq, 5.70 mL, 91.6 mmol) was added and the solution allowed to reach room temperature. After 1 hour the solution was recooled to -20 °C and ⁿbutyllithium (1.1 eq, 38.2 mL, 91.6 mmol) added. After a further hour acetaidehyde (1.1 eq, 5.11 mL 91.6 mmol) was added and the solution allowed to reach room temperature over 1 hour. Normal work-up, extraction with dichloromethane, drying over MgSO₄ and flash column chromatography with 10% ethyl acetate/petroleum ether as eluent yielded the title compound as a colourless oil (10.1g, 68%); v_{max} (film) 3490 cm⁻¹; δ_{H} (400MHz, CDCl₃) 1.34 (3H, d, J = 6.4 Hz), 1.40 (3H, s), 1.80-1.90 (1H, m), 2.07-2.13 (1H, m), 2.07-2.13 (1H, m), 2.59-2.65 (3H, m), 2.97-3.06 (2H, m), 4.25 (1H, q, J = 6.4 Hz); *m/z* (EI) 178.04882 (M⁺); C7H₁₄OS₂ requires 178.04861. Calc for C₇H₁₄OS₂: C, 47.15; H, 7.91. Found: C, 47.39; H, 8.00%.

2-(1-Hydroxybutyl)-2-methyl-1,3-dithiane

A 2.3 molar solution of ⁿbutyllithium in hexanes (1.1 eq, 23.9 mL, 55.0 mmol) was added to a solution of 1,3-dithiane (6.0g, 50.0 mmol) in THF (150 mL) at -20 °C. After 1 hour methyl iodide (1.1 eq, 3.42 mL, 55.0 mmol) was added and the solution allowed to reach room temperature. After 1 hour the solution was recooled to -20 °C and ⁿbutyllithium (1.1 eq, 23.9 mL, 55.0 mmol) added. After a further hour butyraldehyde (1.1 eq, 4.95 mL 55.0 mmol) was added and the solution allowed to reach room temperature over 1 hour. Normal work-up, extraction with dichloromethane, drying over MgSO₄ and flash column chromatography with 10% ethyl acetate/petroleum ether as eluent yielded the title compound as a colourless oil (9.01g, 87%); v_{max} (film) 3480 cm⁻¹; $\delta_{\rm H}$ (200MHz, CDCl₃) 1.34 (3H, t, J = 7.2 Hz), 1.29-1.51 (2H, m), 1.39 (3H, s), 1.57-2.17 (4H, m), 2.56-2.67 (2H, m), 2.79-2.86 (1H, m), 2.90-3.08 (2H, m), 3.93-3.98 (1H, m); *m/z* (EI) 206.07957 (M⁺); C₉H₁₈OS₂ requires 206.07991.

2-Methylene-3-methyl-1,4-dithlepane

Triethylamine (1.1 eq., 6.24 mL, 44.8 mmol) was added to a stirring solution of 2-(1-hydroxyethyl)-2-methyl-1,3-dithiane (7.25g, 40.7 mmol) in THF (250 mL) at 0 °C. After 30 minutes mesyl chloride (1.1 eq., 3.48 mL, 44.8 mmol) was added and the solution allowed to reach room temperature over 1 hour. After a further addition of triethylamine (1.5 eq., 9.36 mL, 61.1 mmol) the solution was stirred at room temperature for 2 days. Normal work-up, extraction with dichloromethane, drying over MgSO₄ and column chromatography with 10% ethyl acetate/ petroleum ether as eluent yielded the title compound as a colourless oil (5.70 g, 87%); v_{max} (film) 1596 cm⁻¹; δ_{H} (200MHz, CDCl₃) 1.48 (3H, d, J = 7.1 Hz), 1.95-2.30 (2H, m), 2.65-2.92 (2H, m), 2.98-3.12 (2H, m), 3.90 (1H, q, J = 7.1 Hz), 5.21 (1H, s), 5.36 (1H, s); *m/z* (Cl) 161.04602 (M+H⁺); C₇H₁₃S₂ requires 161.04587.

2-Methylene-3-propyl-1,4-dithlepane

Triethylamine (1.1 eq., 6.33 mL, 45.4 mmol) was added to a stirring solution of 2-(1-hydroxybutyl)-2-methyl-1,3-dithiane (8.5g, 41.3 mmol) in THF (150 mL) at 0 °C. After 30 minutes mesyl chloride (1.1 eq., 3.51 mL, 45.4 mmol) was added and the solution allowed to reach room temperature over 1 hour. After a further addition of triethylamine (1.5 eq., 8.63 mL, 62.0 mmol) the solution was stirred at room temperature for 24 hours. Normal work-up, extraction with dichloromethane, drying over MgSO₄ and column chromatography with 10% ethyl acetate/ petroleum ether as eluent yielded the title compound as a colourless oli (6.52 g, 87%); v_{max} (film) 3083 and 1595 cm⁻¹; δ_{H} (200MHz, CDCl₃) 0.94 (3H, t, J = 7.2 Hz), 1.32-1.52 (2H, m), 1.59-2.30 (4H, m), 2.63-2.76 (1H, m), 2.91-2.98 (2H, m), 2.97-3.08 (1H, m), 3.78 (1H, t, J = 7.1 Hz), 5.22 (1H, s), 5.44 (1H, s); δ_{c} (50MHz, CDCl₃) 1.3.7, 20.4, 28.7, 32.1, 33.3, 36.6, 50.2, 116.1, 146.2; *m/z* (Cl) 189.07738 (M+H⁺); C₉H₁₇S₂ requires 189.07717.

Anti-2-methyl-2-(2-(propan-1,2-diol))-1,3-dithiane 1-oxides (14 & 15)

Treatment of **7** (0.50g, 2.0 mmol) as described above with potassium ferricyanide (2.60g, 7.9 mmol), potassium carbonate (1.09g, 7.9 mmol), quinuclidine (11.7 mg, 0.1 mmol) and osmium (III) chloride hydrate (7.8 mg, 0.02 mmol) in water (12 mL) and butanol (12 mL) for 12 hours followed by addition of sodium sulfite (3.98g, 31.6 mmol) and work up furnished the diastereoisomeric alcohols as an inseparable mixture of clear, colourless, viscous oils (0.506g, 86%); m/z 225.06218 (M+H⁺); C₈H₁₇S₂O₃ requires 225.06191.

Syn-2-methyl-2-(1-(2,3-dihydroxybutanoyi))-1,3-dithiane 1 oxides (16 & 17)

Treatment of **8** (0.20g, 0.86 mmol) as described above with potassium ferricyanide (0.91g, 2.8 mmol), potassium carbonate (0.38g, 2.8 mmol), quinuclidine (4.1 mg, 0.04 mmol) and osmium (III) chloride hydrate (2.7 mg, 0.009 mmol) in water (6 mL) and ¹butanol (6 mL) for 2 hours followed by addition of sodium sulfite (1.39g, 11.0 mmol) and work up furnished the diastereoisomeric alcohols (16 and 17) as an inseparable mixture of clear, colourless, viscous oils (0.168g, 73%); m/z 253.05721 (M+H⁺); C9H₁₇S₂O₄ requires 253.05683.

Anti-2-ethyl-2-(1-(2,3-dihydroxybutanoyl))-1,3-dithiane 1 oxides (18 & 19)

Treatment of **9** (0.20g, 0.86 mmol) as described above with potassium ferricyanide (0.85g, 2.6 mmol), potassium carbonate (0.36g, 2.6 mmol), quinuclidine (3.8 mg, 0.03 mmol) and osmium (III) chloride hydrate (2.6 mg, 0.009 mmol) in water (6 mL) and ⁴butanol (6 mL) for 2 hours followed by addition of sodium sulfite (1.27g, 10.1 mmol) and work up furnished the diastereoisomeric alcohols (18 and 19). Partial separation by column chromatography yielded both diastereoisomers as colourless crystalline solids (0.180g, 79%).

For **18** (less polar): m.p. 116-118 °C; v_{max} (Nujol) 3408, 1697 and 1023 cm⁻¹; δ_{H} (400 MHz, DMSOd6) 0.93 (3H, t, J = 7.4 Hz), 1.12 (3H, d, J = 6.4 Hz), 1.66-1.72 (1H, m), 1.90-2.04 (2H, m), 2.09-2.18 (1H, m), 2.47-2.51 (1H, m), 2.64-2.70 (1H, m), 2.87-2.94 (1H, m), 3.02-3.06 (1H, m), 4.12-4.16 (1H, m), 4.33 (1H, dd, J = 8.0 and 4.0 Hz), 4.64 (1H, d, J = 6.4 Hz), 5.42 (1H, d, J = 8.0 Hz); *m/z* 267.07271 (M+H⁺); C₁₀H₁₉O₄S₂ requires 267.07248. Calc for C₁₀H₁₈O₄S₂: C, 45.10; H, 6.81. Found: C, 45.18; H, 6.84%. For **19** (more polar): m.p. 106-108 °C; v_{max} (Nujol) 3383, 1687 and 1025 cm⁻¹; δ_{H} (400 MHz, DMSOd6) 0.92 (3H, t, J = 7.4 Hz), 1.13 (3H, d, J = 6.4 Hz), 1.65-1.73 (1H, m), 1.88-2.07 (2H, m), 2.11-2.21 (1H, m), 2.71-2.78 (2H, m), 2.98-3.02 (1H, m), 3.31-3.33 (1H, m), 4.07-4.11 (1H, m), 4.53 (1H, dd, J = 6.0 and 3.6 Hz), 4.72 (1H, d, J = 6.8 Hz), 5.20 (1H, d, J = 8.0 Hz); δ_{c} (50 MHz, CDCl₃) 7.8, 14.3, 20.2, 25.8, 26.8, 43.2, 68.0, 74.6, 79.6, 209.5; *m/z* 267.07271 (M+H⁺); C₁₀H₁₉O₄S₂ requires 267.07248. Calc for C₁₀H₁₈O₄S₂: C, 45.10; H, 6.81. Found: C, 44.96; H 6.84%.

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of the products in all other cases is based on the assumption that this pattern holds for all cases, and must therefore be regarded as tentative.

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