The scope and limitation of the [1,4]-Sbenzyl participation and debenzylation in the stereochemically controlled synthesis of substituted thiolanes

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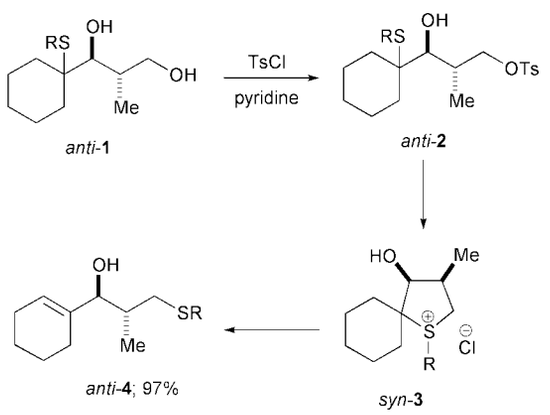
Treatment of a series of 4-benzylsulfanyl-1,3-diols with toluene-*p*-sulfonyl chloride in pyridine gave substituted thiolanes in high yield by [1,4]-SBn participation and debenzylation with the chloride anion. The reaction is stereospecific giving up to three contiguous stereogenic centres and occurs efficiently irrespective of the stereochemistry.

We have recently reported[1] that the synthesis of allylic alcohols (*e.g.*, *anti*-**4**) can occur in high yield by [1,4]-SPh migration on simple treatment of 4-PhS-1,3-diols, such as *anti*-**1** with toluene-*p*-sulfonyl chloride (TsCl) in pyridine. The intermediate tosylate *anti*-**2** and the sulfonium salt *syn*-**3** cannot be isolated, and the allylic alcohol **4** is formed in 97% yield with an overall [1,4]-SPh shift, presumably *via* elimination of the intermediate sulfonium salt *syn*-**3** (Scheme 1). We have usually used the SPh



Scheme 1

group[2] in such rearrangements as the starting materials (PhSCl and $PhSCH_2OMe$) are commercially available. In fact, the SPh group is stable during the course of a numerous [1,2]-,[2,3] and [1,4]-SPh[1,4] rearrangements, and no loss of the Ph group has been observed.[1,2]

We now report an extension to this reaction in the rearrangement of a series of 4-benzylsulfanyl-1,3-diols such as *anti*-**1** with TsCl in pyridine, when R is benzyl,[5] as a general method for the synthesis of substituted thiolanes (Scheme 1). We comment on the effects of stereochemistry and structural variation at the migration origin on the outcome of the reaction, all of which help to elucidate the mechanism of the reaction (Scheme 2).

The five possible products from the spirocyclic sulfonium salt *syn*-**3** are the allylic alcohol **4** (by elimination *exo* to the sulfonium ring with [1,4]-SR shift), the ketone **5** (by *endo*-elimination with [1,4]-SR shift), the rearranged chloride **6** (substitution at the migration origin with [1,4]-SR shift), the unrearranged chloride **7** (substitution at what would be the migration terminus, but with no SR migration) and the thiolane *anti*-**8** (by *exo*-substitution at the R group in **3**).[6] The required 4-benzylsulfanyl-1,3-diols, *anti*-**1** (R = Bn), *anti*- and *syn*-**9**, **12**, **14**, *anti*,*anti*-**16**, *syn*- and *anti*-**19**, **22**, *syn*-**25**, *syn*- and *anti*-**28**, **31** and **33**, for this study were derived using known stereoselective aldol methodology[2] with α-BnS substituted aldehydes and all have been previously reported.[7]

Table 1 Thiolanes from the rearrangement of 4-benzylsulfanyl-1,3-diols with TsCl in pyridine

Diol	Thiolane	Yield (%)
anti-**1** (R = Bn)	*syn*-**8**[a]	52
anti-**9**	*syn*-**11**	92
syn-**9**	*anti*-**11**	93
12	**13**	95
14	**15**	94
anti,*anti*-**16**	*anti*,*syn*-**18**	96
syn-**19**	*syn*-**21**	91
anti-**19**	*anti*-**21**	94
syn,*anti*-**22**	*syn*,*syn*-**24**	96
anti,*anti*-**22**	*anti*,*syn*-**24**	96
anti-**25**	*anti*-**27**	90
anti-**28**	*syn*-**30**	89
syn-**28**	*anti*-**30**	89
31	**32**	90
33	**34**	92

[a] Allylic alcohol *anti*-**4** was also formed in 48%.

The rearrangement of simple cyclic 1,3-diols *anti*-**1** (R = Me, Et and Bn) with a symmetrical migration origin was studied to see whether there were any unusual effects from changing the PhS migrating substituent. Treatment of *anti*-**1** (R = Bn) with TsCl in pyridine gave an inseparable mixture (52 : 48) of the spirocyclic thiolane *syn*-**8** and the sulfide *anti*-**4** (R = Bn) in quantitative yield (Table 1). It appears that competitive *exo*-debenzylation of the sulfonium salt *syn*-**3** (R = Bn) (presumably by simple S_N2 substitution)[8–10] to give the thiolane *syn*-**8** and E2 elimination of **3** to give the allylic alcohol *anti*-**4** (R = Bn) occur at similar rates. The other side product, benzyl chloride (BnCl) is not isolated under the reaction conditions. The choice of the migrating substituent RS in **3** to promote *exo*-dealkylation is

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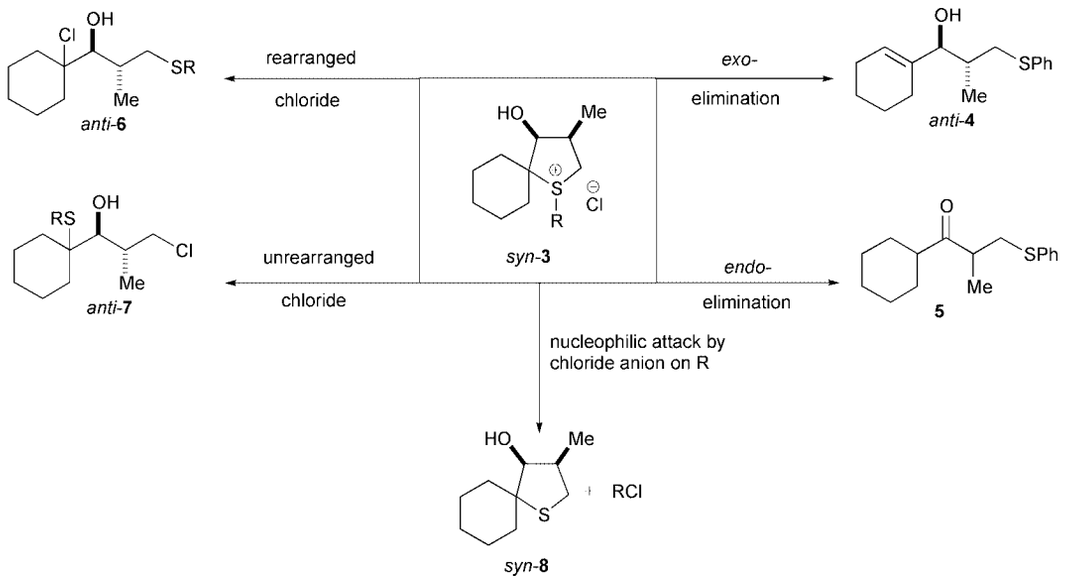
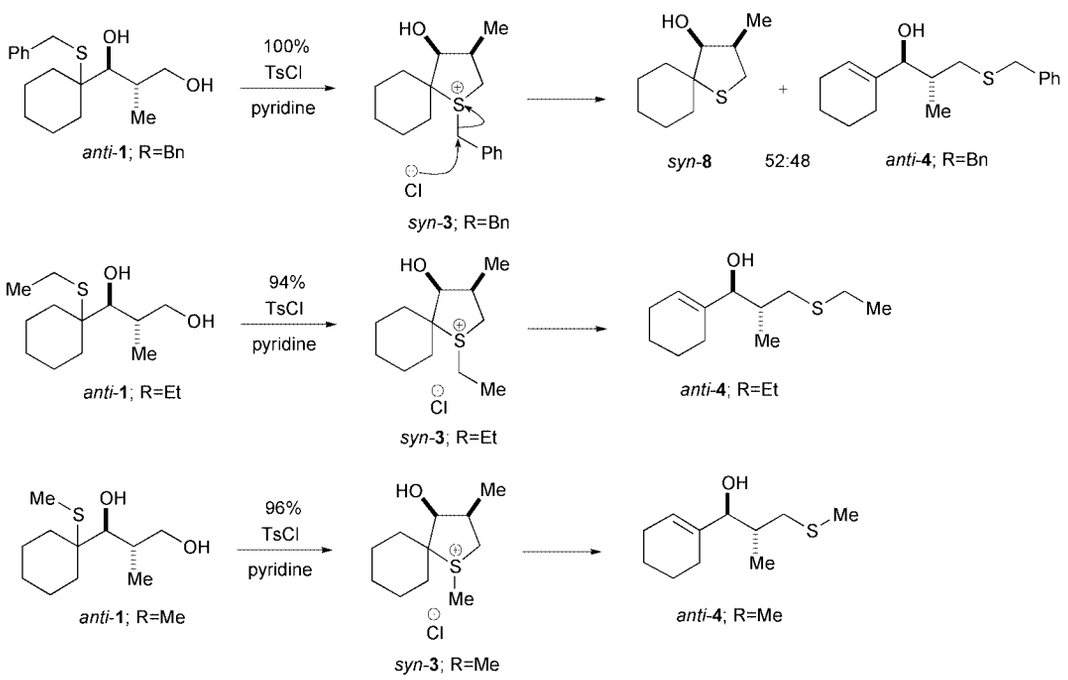


Scheme 2 Five possible products from the rearrangement of the diol *anti*-**1** *via* the sulfonium ion *syn*-**3**.

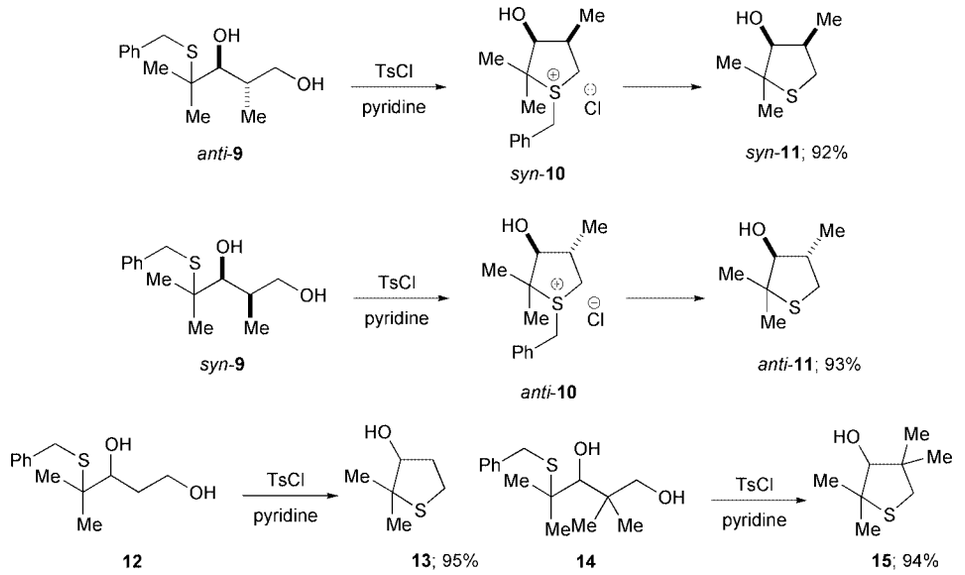


Scheme 3

important and it occurs only when R is benzyl. For simple alkyl substituents like R = Me and Et[7] *anti*-**1** gives only allylic alcohols in near perfect yield by the usual E2 elimination of the sulfonium salt *anti*-**3** (R = Me and Et) (Scheme 3). This is not that surprising as S_N2 displacements are at least two orders of magnitude faster at a benzyl group than at a comparable ethyl group.[11] Attempts to enhance the rate of dealkylation by *exo*-cleavage of **3** (R = Bn) by the addition of a better nucleophile (iodide as NaI)[12] or performing the reaction in the presence of one equivalent of base (such as n-BuLi) proved unsuccessful; there was no change in the chemical yield or ratio of products. Further attempts to isolate the intermediate sulfonium salt *syn*-**3** by precipitation of the chloride anion as the AgCl and NaCl (with $AgBF_4$ and $NaClO_4$) also proved unsuccessful. However, these changes did have the effect of lowering the overall yield, but the ratio of thiolane *syn*-**8** and the allylic alcohol *anti*-**4** remained unchanged. The dealkylation of similar sulfonium salts is known,[10] and has previously been used in the synthesis of cyclic[12] and acyclic sulfides.[13–16]

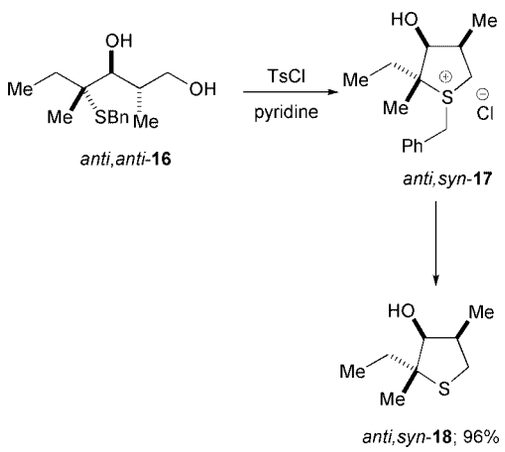
The remainder of this study involved the use of the more reactive benzylsulfanyl (BnS) group. To promote thiolane formation further and to broaden the scope of the reaction, we rearranged a series of acyclic 4-BnS-1,3-diols such as **9** since *exo*-elimination of the axial proton in spirocyclic sulfonium salt **3** is likely to be more favourable than in open chain compounds.[1] Treatment of the 4-BnS-1,3-diols *anti*- and *syn*-**9**, **12**, and **14** with TsCl in pyridine gave the substituted thiolanes *syn*- and *anti*-**11**, **13** and **15** as single products in near quantitative yield (Scheme 4). No subsequent E2 elimination of the sulfonium salt occurred and the allylic alcohol was not observed. This [1,4]-SBn participation appears to be insensitive to the developing stereochemistry within the sulfonium salt since *anti*-diol **9** gives the *syn*-thiolane **11** stereospecifically *via* the sulfonium salt *syn*-**10**, while the *syn*-diol **10** gives the *anti*-thiolane **11** *via* the sulfonium salt *syn*-**10**. This cyclisation occurred irrespective of the substitution pattern: **9** has one substituent (Me), **12** has none, and **14** has a *gem*-dimethyl group (Scheme 4).

Rearrangement of the related 1,3-diol *anti*,*anti*-**16** with a stereogenic tertiary migration origin gave valuable information on the effect of substitution and stereochemistry at such a centre in an open chain compound. The symmetrical cyclohexyl



Scheme 4

grouping in **1** (R = Bn) gave a mixture of both the allylic alcohol **4** and thiolane **6**, whereas the compounds with the much simpler dimethyl group in **9**, **12** and **14** gave exclusively the thiolane. An ethyl group has been shown to be somewhere between the two and we chose to use the diol *anti*,*anti*-**16** to explore this and the stereochemistry in the same compound.[1] Treatment of diol *anti*,*anti*-**16** under our usual conditions gave the thiolane *anti*,*syn*-**18** as the sole product in near quantitative yield (Scheme 5). Retention of all the three contiguous stereogenic centres was observed (by a 500 MHz NOESY spectrum). No elimination into the ethyl group at the migration origin occurred, even though this was the major route in an elimination pathway in an analogous [1,4]-SPh shift.[1]



Scheme 5

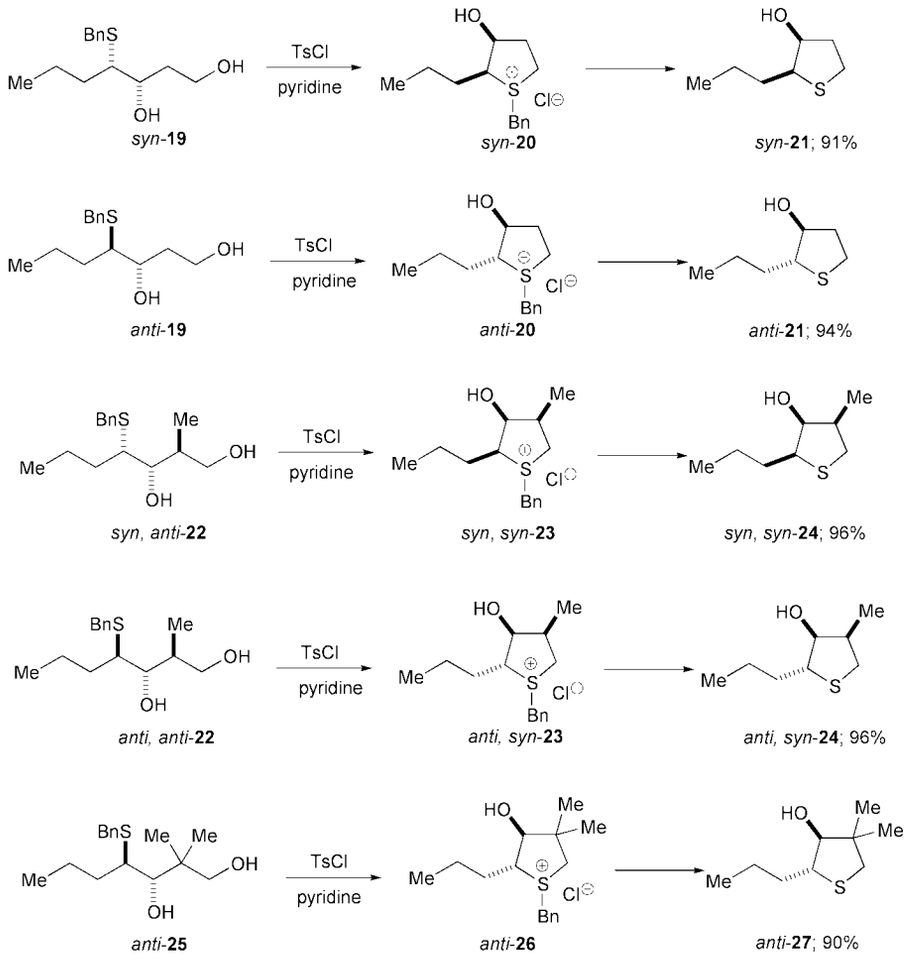
An alternative way of reducing the likelihood of elimination is to have a secondary migration origin[1] and this has been shown in related systems using the SPh group; a less substituted migration origin presumably means less positive charge on this carbon in the transition state and disfavours a loose E2 elimination. Treatment of the 4-BnS-1,3-diols *syn*- and *anti*-**19**, *syn*,*anti*- and *anti*,*anti*-**22** and *anti*-**25** having two or three contiguous stereogenic centres gave stereospecifically the corresponding thiolanes *syn*- and *anti*-**21**, *syn*,*syn*- and *anti*,*syn*-**24** and *anti*-**27** in excellent yield, regardless of the stereochemistry of the substituents (Scheme 6). In fact, the successful formation of the thiolane *syn*,*syn*-**24** was particularly remarkable as the all-*syn*-stereochemistry is already present in the sulfonium salt *syn*,*syn*-**23**. This is in sharp contrast to our previous experience in the formation of THF's using an acid-catalysed [1,2]-SPh shift by rearrangement of compounds with a secondary migration origin.[2c] In those cases the cyclisation was shown to be more dependent on stereochemistry than those with a tertiary migration origin.[2] A developing *anti*-stereochemistry at C(2,3) is more favoured than *syn*, presumably because a secondary migration origin demands a much tighter S_N2 transition state, which is less favourable for an *endo*-type cyclisation.

Even with a primary migration origin the diols *anti*- and *syn*-**28**, **31** and **33** rearranged efficiently giving the corresponding thiolanes *syn*- and *anti*-**30**, **32** and **34** as single products in excellent yield. *exo*-Debenzylation of the intermediate sulfonium salts such as *syn*-**29** occurs with complete regioselectivity even though there are three attractive primary centres for S_N2 attack by the chloride ion (Scheme 7). The reaction is again independent of the developing stereochemistry within the sulfonium ring. This reaction is yet still more remarkable since it relies on three separate steps: initial tosylation, [1,4]-SBn participation and debenzylation, occurring sequentially in an efficient manner within a single reaction vessel. No intermediate tosylate (*e.g.*, *anti*-**2**) or sulfonium salt (*e.g.*, *syn*-**3**) was isolated. The nearest analogy to this work is the cyclisation and debenzylation of benzylsulfanyl sugar derivatives[10] in low yield with PPh_3 and I_2 or of the preformed tosylates with NaI and $BaCO_3$ in refluxing acetone.[12] Other methods for constructing the thiolane ring have included S_N2 displacements involving thiolates,[17] intramolecular SH addition to alkenes,[18] cycloadditions,[19] reduction of thiophenes[20] and desulfurisation of substituted 1,2-dithianes.[21]

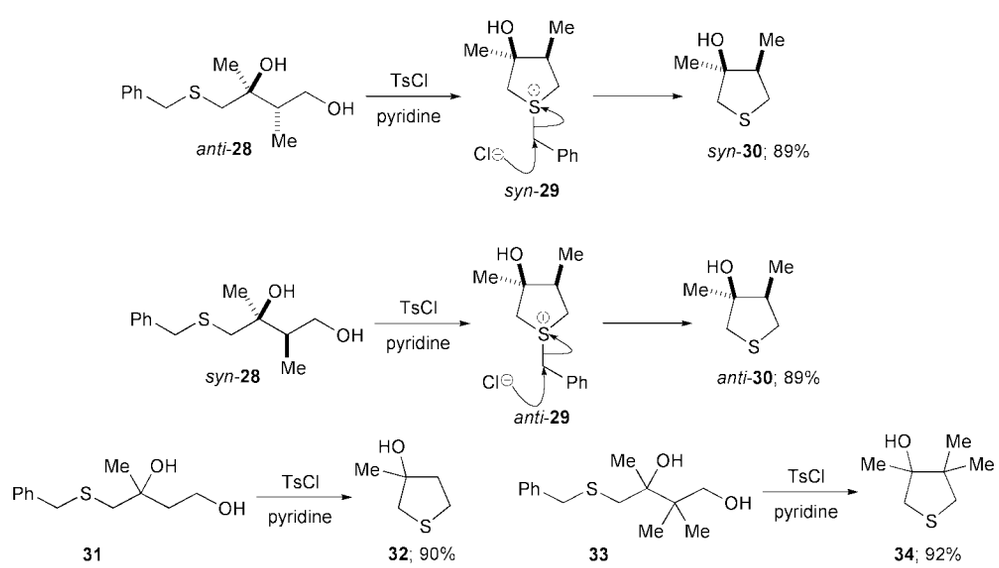
In the course of this study, a noticeable feature of all these substituted thiolanes (*e.g. syn*-**30**) is that in the ^{1}H NMR there is a characteristic geminal coupling constant within the CH_2S grouping (*J* 10.5 Hz); this geminal coupling is substantially larger than that of a corresponding tetrahydrofuran, which is typically[2] 8.5 Hz. Presumably this is because the sulfur is less electronegative and the C–S bond longer.

In conclusion, we have shown that the synthesis of thiolanes using a [1,4]-benzylsulfanyl participation and debenzylation sequence is insensitive to both the substitution pattern at the migration origin and, more importantly, the developing stereochemistry within the thiolane ring. The only exception was the cyclohexane *anti*-**1** (R = Bn) where competitive elimination occurred to give some allylic alcohol *anti*-**4** (R = Bn). In summary, the rearrangement of 4-RS-1,3-diols with TsCl in pyridine fall into four categories.

1. Debenzylation of *S*-benzylsulfonium salts is preferred to either *exo*- or *endo*-eliminations.



Scheme 6



Scheme 7

2. *exo*-Elimination to give allylic alcohols like *anti*-**4** is favoured when PhS is the migrating group and when there is a tertiary migration origin.[1,5,22]

3. *endo*-Elimination to give ketones is very rare, and occurs only to a small extent when PhS is the migrating group and when there is a tertiary acyclic migration origin.[1,22]

4. *endo*-Substitution is favoured when PhS is the migrating group and when there is a secondary migration origin.[1]

Experimental

All solvents were distilled before use. Tetrahydrofuran (THF) and ether were freshly distilled from $LiAlH_4$, whilst dichloromethane (CH_2Cl_2) and toluene were freshly distilled from CaH_2. Triphenylmethane was used as the indicator for THF. n-BuLi was titrated against diphenylacetic acid before use. All reactions were carried out under nitrogen using oven-dried glassware. Flash column chromatography was carried out using Merck Kieselgel 60 (230–400 mesh). Thin layer chromatography (TLC) was carried out on commercially available pre-coated plates (Merck Kieselgel $60F_{254}$ silica). Proton and carbon NMR spectra were recorded on a Bruker WM 200, WM 250, WM400 or WM500 Fourier transform spectrometers using an internal deuterium lock. Chemical shifts are quoted in parts

per million downfield from tetramethylsilane. Carbon NMR spectra were recorded with broad proton decoupling and Attached Proton Test (APT). The symbol * after the carbon shift indicates an even number of attached protons; *i.e*. CH_2 or quaternary carbons. Mass spectra were recorded on a AEI Kratos MS30 or MS890 machine using a DS503 data system for high resolution analysis.

(2*RS*,3*SR*)-1-Cyclohexenyl-2-methyl-3-methylsulfanylpropanol *anti*-4 (R = Me)

Toluene-*p*-sulfonyl chloride (0.14 g, 0.68 mmol) was added to a stirred solution of the diol *anti*-**1** (R = Me, 0.15 g, 0.68 mmol) in pyridine (1 ml). The solution was stirred for 12 hours. Ether (20 ml) was added and the solution was extracted with HCl (10 ml, 3 M) and evaporated under reduced pressure. The residue was purified by flash chromatography on a silica gel column with light petroleum (40–60 °C)–ether (1 : 1) to give the *allylic alcohol anti*-**4** (R = Me, 0.13 g, 96%) as an oil; R_f [light petroleum (40–60 °C)–ether (9 : 1)] 0.5; ν_{max}(film, $CDCl_3$)/cm^{-1} 3300 (OH); δ_H(400 MHz, $CDCl_3$) 5.62 (1 H, br s, CH=C), 3.73 (1 H, d, *J* 8.3, C*H*OH), 2.81 (1 H, dd, *J* 13.0 and 7.1, CH_AH$_B$S), 2.44 (1 H, dd, *J* 13.0 and 7.9, CH$_A$*H*$_B$S), 2.10 (3 H, s, MeS), 2.08–1.49 (10 H, m, 4 × CH_2, C*H*Me and OH) and 0.88 (3 H, d, *J* 6.8, MeCH); δ_C(100 MHz, $CDCl_3$) 138.6* (*C*=CH), 124.9 (*C*H=C), 81.1 (CHOH), 38.5* (CH_2S), 35.9 (*C*HMe), 25.0*, 23.2*, 22.6* and 22.6* (4 × CH_2), 16.4 and 16.4 (*Me*CH and MeS) (Found M$^+$, 200.1233. $C_{11}H_{20}OS$ requires M, 200.1234); *m*/*z* 200.1 (20%, M), 182.1 (15, M − H_2O), 153.1 (10, M − SMe), 111.1 (100, M − C_3H_6SMe), 89.0 (30, C_3H_6SMe), 61.0 (20, CH_2SMe) and 47.0 (5, SMe).

(2*RS*,3*SR*)-1-Cyclohexenyl-2-methyl-3-ethylsulfanylpropanol *anti*-4 (R = Et)

In the same way, the diol *anti*-**1** (R = Et, 40 mg, 0.17 mmol) and toluene-*p*-sulfonyl chloride (36 mg, 0.17 mmol) in pyridine (1 ml) gave, after flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (1 : 1), the *allylic alcohol anti*-**4** (R = Et, 34 mg, 94%) as an oil; R_f [light petroleum (40–60 °C)–ether (1 : 1)] 0.45; ν_{max}(film, $CDCl_3$)/cm^{-1} 3300 (OH); δ_H(400 MHz, $CDCl_3$) 5.61 (1 H, br s, CH=C), 3.74 (1 H, br d, *J* 8.2, C*H*OH), 2.84 (1 H, dd, *J* 12.6 and 4.0, CH_AH$_B$S), 2.55 (2 H, q, *J* 7.4, CH_2Me), 2.45 (1 H, dd, *J* 12.6 and 7.8, CH$_A$*H*$_B$S), 2.12–1.96 (3 H, m, CH_2C=C and C*H*Me), 1.92–1.78 (3 H, m, CH_2C=C and OH), 1.70–1.48 (4 H, m, 2 × CH_2), 1.24 (3 H, t, *J* 7.4, MeCH_2) and 0.88 (3 H, d, *J* 6.8, MeCH); δ_C(100 MHz, $CDCl_3$) 138.7* (*C*=CH), 124.9 (*C*H=C), 81.1 (CHOH), 36.3 (*C*HMe), 35.7* (CH_2S), 26.8* (CH_2S), 25.0*, 23.3*, 22.6* and 22.6* (4 × CH_2), 16.5 and 14.8 (2 × Me) (Found M$^+$, 214.1386. $C_{12}H_{22}OS$ requires M, 214.1391); *m*/*z* 214.1 (20%, M) and 153.0 (50, M − SEt).

(2*RS*,3*SR*)-1-Cyclohexenyl-2-methyl-3-benzylsulfanylpropanol *anti*-4 (R = Bn) and (3*RS*,4*SR*)-3-methyl-4-hydroxy-1-thiaspiro-[4.5]decane *syn*-8

In the same way, the diol *anti*-**1** (R = Bn, 0.1 g, 0.34 mmol) and toluene-*p*-sulfonyl chloride (77 mg, 0.37 mmol) in pyridine (1 ml) gave, after flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (1 : 1), an inseparable mixture (48 : 52) of the *allylic alcohol anti*-**4** (R = Bn^A) and the *thiolane syn*-**8** (signals labelled with ^{B}) (93 mg, 100%) as an oil; R_f [light petroleum (40–60 °C)–ether (1 : 1)] 0.45; ν_{max}(film, $CDCl_3$)/cm^{-1} 3300 (OH); δ_H(400 MHz, $CDCl_3$) 7.31–7.18 (10 H, m, Ph^A), 5.58 (1 H, br s, CH=C^A), 3.70–3.64 (4 H, m, C*H*OH^A, CH_2Ph^A and C*H*OH^B), 2.82 (1 H, dd, *J* 10.9 and 7.3, CH_AH$_B$S^B), 2.75 (1 H, dd, *J* 12.7 and 3.9, CH_AH$_B$S^A), 2.62 (1 H, t, *J* 10.9, CH$_A$*H*$_B$S^B), 2.58–2.48 (1 H, m, C*H*Me^B), 2.36 (1 H, dd, *J* 12.7 and 7.8, CH$_A$*H*$_B$S^A), 2.05–1.15 (21 H, m, 4 × CH_2^A, 5 × CH_2^B, OH^A, OH^B and C*H*Me^A), 1.13 (3 H, d, *J* 6.5, MeCH^B) and 0.84 (3 H, d, *J* 6.8, MeCH^A); δ_C(100 MHz, $CDCl_3$) 138.6* (*C*=CH^A), 138.5* (*i*-Ph^A), 128.9* (*i*-Ph^A), 128.4 (*m*-Ph^A), 126.9 (*p*-Ph^A), 124.9 (*C*H=C^A), 83.7 (CHOH^A), 80.8 (CHO^B), 63.9* (CS^B), 40.3 (C*H*Me^A), 39.7*, 37.1*, 35.4*, 34.4* and 34.2* (2 × *C*H$_2$C=C^A, 2 × CH$_2$S^A and CH$_2$S^B), 36.1 (*C*HMe^B), 25.6*, 25.0*, 24.7*, 23.2*, 23.1* and 22.6* (2 × CH_2^A and 5 × CH_2^B), 16.4 (*Me*CH^A) and 14.1 (*Me*CH) (Found M$^+$, 276.1541. $C_{17}H_{24}OS$ requires M, 276.1547); *m*/*z* 276.2 (30%, M), 185.1 (60, M − Bn) and 91.1 (100, Bn).

TsCl rearrangement of diol *anti*-1 (R = Bn) with n-BuLi

n-BuLi (0.42 ml, 1.3 M in hexanes, 0.53 mmol) was added slowly to a stirred solution of diol *anti*-**1** (R = Bn, 0.12 g, 0.51 mmol) in THF (5 ml) at −78 °C. The solution was stirred for 10 min. Toluene-*p*-sulfonyl chloride (0.1 g, 0.51 mmol) was then added and the solution was stirred for 3 hours. Saturated NH_4Cl (10 ml) was added and the solution was extracted with ether (3 × 20 ml). The combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (1 : 1) to give an inseparable mixture (50 : 50) of the *allylic alcohol anti*-**4** (R = Bn) and thiolane *syn*-**8** (0.1 g, 95%) as an oil; identical spectroscopically to that obtained previously.

Attempted *in situ*-debenzylation of diol *anti*-1 (R = Bn) with NaI

MeLi (0.25 ml, 1.4 M in ether, 0.36 mmol) was added slowly to a stirred solution of diol *anti*-**1** (R = Bn, 85 mg, 0.36 mmol) in THF (5 ml) at −78 °C. The solution was stirred for 10 min. Toluene-*p*-sulfonyl chloride (76 mg, 0.36 mmol) and NaI (53 mg, 0.36 mmol) were then added and the solution was stirred for 2 hours. Saturated NH_4Cl (10 ml) was added and the solution was extracted with ether (3 × 20 ml). The combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (1 : 1) to give an inseparable mixture (50 : 50) of the *allylic alcohol anti*-**4** (R = Bn) and thiolane *syn*-**8** (73 mg, 94%) as an oil; identical spectroscopically to that obtained previously.

(2*SR*,3*RS*)-3-Hydroxy-2,2,4-trimethylthiolane *syn*-11

In the same way, the diol *anti*-**9** (0.12 g, 0.46 mmol) and toluene-*p*-sulfonyl chloride (88 mg, 0.46 mmol) in pyridine (1 ml) gave, after flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (1 : 1), the *thiolane syn*-**11** (69 mg, 92%) as an oil; R_f [light petroleum (40–60 °C)–ether (1 : 1)] 0.5; ν_{max}(film, $CDCl_3$)/cm^{-1} 3300 (OH); δ_H(500 MHz, $CDCl_3$) 3.55 (1 H, dd, *J* 8.4 and 2.6, C*H*OH), 2.94 (1 H, dd, *J* 10.5 and 7.1, CH_AH$_B$S), 2.67 (1 H, t, *J* 10.5, CH$_A$*H*$_B$S), 2.65–2.56 (1 H, m, C*H*Me), 1.65 (1 H, d, *J* 8.4, OH), 1.38 (6 H, s, 2 × Me) and 1.18 (3 H, d, *J* 6.4, MeCH); δ_C(100 MHz, $CDCl_3$) 84.6 (CHOH), 57.9* (CS), 40.8 (*C*HMe), 35.6* (CH_2S), 32.1 (Me), 24.8 (Me) and 14.3 (*Me*CH); *m*/*z* 145.0 (15%, M − H), 113.0 (100, M − SH) and 101.0 (5, M − CH_2S + H).

(2*SR*,3*SR*)-3-Hydroxy-2,2,4-trimethylthiolane *anti*-11

In the same way, the diol *syn*-**9** (75 mg, 0.29 mmol) and toluene-*p*-sulfonyl chloride (61 mg, 0.29 mmol) in pyridine (1 ml) gave, after flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (1 : 1), the *thiolane anti*-**11** (43 mg, 93%) as an oil; R_f [light petroleum (40–60 °C)–ether (1 : 1)] 0.5; ν_{max}(film, $CDCl_3$)/cm^{-1} 3300 (OH); δ_H(400 MHz, $CDCl_3$) 3.35 (1 H, d, *J* 10.3, C*H*OH), 2.84 (1 H, dd, *J* 10.5 and 7.9, CH_AH$_B$S), 2.44 (1 H, t, *J* 10.5, CH$_A$*H*$_B$S), 2.24–2.13 (1 H, m, C*H*Me), 1.78–1.75 (1 H, br s, OH), 1.37 (3 H, s, Me), 1.29 (3 H, s, Me) and 1.13 (3 H, d, *J* 6.4, MeCH); δ_C(100 MHz, $CDCl_3$) 86.8 (CHOH), 51.7* (CS), 40.4 (*C*HMe), 31.1* (CH_2S), 28.7

(Me), 25.8 (Me) and 17.6 (*Me*CH); *m*/*z* 145.0 (15%, M − H) and 128.1 (50, M − H_2O).

2,2-Dimethyl-3-hydroxythiolane 13

In the same way, the diol **12** (0.1 g, 0.41 mmol) and toluene-*p*-sulfonyl chloride (86 mg, 0.41 mmol) in pyridine (1 ml) gave, after flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (1 : 1), the *thiolane* **13** (57 mg, 95%) as an oil; R_f [light petroleum (40–60 °C)–ether (1 : 1)] 0.6; ν_{max}(film, $CDCl_3$)/cm^{-1} 3300 (OH); δ_H(400 MHz, $CDCl_3$) 3.87 (1 H, t, *J* 4.4, C*H*OH), 2.98–2.87 (2 H, m, CH_2S), 2.30–2.22 (1 H, m, CH_AH_B), 2.11–2.06 (1 H, m, CH_AH_B), 1.98–1.90 (1 H, br s, OH) and 1.35 (3 H, s, Me) and 1.33 (3 H, s, Me); δ_C(100 MHz, $CDCl_3$) 81.9 (CHOH), 56.0* (CS), 35.3* (CH_2S), 30.2 (Me), 26.9 (CH_2) and 24.0 (Me) (Found M^+, 132.0698. $C_6H_{12}OS$ requires M, 132.0689); *m*/*z* 132.1 (100%, M) and 74.1 (5, C_3H_6S).

3-Hydroxy-2,2,4,4-tetramethylthiolane 15

In the same way, the diol **14** (0.1 g, 0.37 mmol) and toluene-*p*-sulfonyl chloride (77 mg, 0.37 mmol) in pyridine (1 ml) gave, after flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (1 : 1), the *thiolane* **15** (61 mg, 94%) as an oil; R_f [light petroleum (40–60 °C)–ether (1 : 1)] 0.5; ν_{max}(film, $CDCl_3$)/cm^{-1} 3300 (OH); δ_H(400 MHz, $CDCl_3$) 3.43 (1 H, s, C*H*OH), 2.69 (1 H, AB quartet, *J* 11.1, CH_AH_BS), 2.57 (1 H, AB quartet, *J* 11.1, CH_AH_BS), 1.78–1.62 (1 H, br s, OH), 1.42, 1.33, 1.14 and 1.09 (4 × Me); δ_C(100 MHz, $CDCl_3$) 88.6 (CHOH), 52.7* (*C*SCH_2), 45.3 (*C*Me), 40.4* (CH_2S), 32.4, 28.7, 25.5 and 20.9 (4 × Me) (Found M^+, 160.0911. $C_8H_{16}OS$ requires M, 160.0921); *m*/*z* 159.1 (100%, M − H), 142.1 (20, M − H_2O + H) and 127.1 (20, M − SH).

(2*RS*,3*SR*,4*SR*)-2,4-Dimethyl-2-ethyl-3-hydroxythiolane *anti,syn*-18

In the same way, the diol *anti*,*anti*-**16** (85 mg, 0.32 mmol) and toluene-*p*-sulfonyl chloride (60 mg, 0.32 mmol) in pyridine (1 ml) gave, after column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (1 : 1) the *thiolane anti,syn*-**18** (49 mg, 96%) as an oil; R_f [light petroleum (40–60 °C)–ether (1 : 1)] 0.45; ν_{max}(film, $CDCl_3$)/cm^{-1} 3440 (OH); δ_H(400 MHz, $CDCl_3$) 3.69 (1 H, d, *J* 3.1, C*H*OH), 2.82 (1 H, dd, *J* 10.3 and 7.7, CH_AH_BS), 2.66 (1 H, t, *J* 10.3, CH_AH_BS), 2.52–2.63 (1 H, m, C*H*CH_3), 1.58–1.66 (2 H, m, CH_2CH_3), 1.35 (3 H, s, CH_3), 1.15 (3 H, d, *J* 6.5, $CHCH_3$), 0.97 (3 H, t, *J* 7.3, CH_3CH_2); δ_C(100 MHz, $CDCl_3$) 83.1 (CHOH), 57.8 (CS), 40.8 (*C*HCH_3), 36.1 (CH_2S), 29.7 (CH_2), 22.7, 14.3 and 9.5 (3 × CH_3) (Found M^+, 160.1321. $C_8H_{16}OS$ requires M, 160.0922); *m*/*z* 159 (20%, M^+ − H), 127 (100, M − SH).

(2*RS*,3*SR*)-3-Hydroxy-2-propylthiolane *anti*-21

In the same way, the diol *anti*-**19** (0.1 g, 0.39 mmol) and toluene-*p*-sulfonyl chloride (81.7 mg, 0.39 mmol) in pyridine (1 ml) gave, after flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (1 : 1), the *thiolane anti*-**21** (53 mg, 94%) as an oil; R_f [light petroleum (40–60 °C)–ether (1 : 1)] 0.5; ν_{max}(film, $CDCl_3$)/cm^{-1} 3300 (OH); δ_H(400 MHz, $CDCl_3$) 4.15 (1 H, q, *J* 3.7, C*H*OH), 3.16–3.10 (1 H, m, CHS), 2.95–2.83 (2 H, m, CH_2S), 2.10–1.96 (2 H, m, CH_2), 2.00 (1 H, br s, OH), 1.69–1.58 (1 H, m, CH_AH_B), 1.50–1.38 (1 H, m, CH_AH_B), 1.36–1.23 (2 H, m, CH_2) and 0.88 (3 H, t, *J* 7.1, Me); δ_C(100 MHz, $CDCl_3$) 79.4 (CHOH), 56.1 (CHS), 38.5* (CH_2S), 36.1*, 27.3* and 21.5* (3 × CH_2) and 13.90 (Me); *m*/*z* 145.1 (10%, M − H), 129.1 (10, M − H_2O + H), 115.1 (100, M − S + H) and 102.1 (10, M − C_3H_7 − H).

(2*SR*,3*SR*)-3-Hydroxy-2-propylthiolane *syn*-21

In the same way, the diol *syn*-**19** (45 mg, 0.17 mmol) and toluene-*p*-sulfonyl chloride (36.8 mg, 0.17 mmol) in pyridine (1 ml) gave, after flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (1 : 1), the *thiolane syn*-**21** (23 mg, 91%); R_f [light petroleum (40–60 °C)–ether (1 : 1)] 0.5; ν_{max}(film, $CDCl_3$)/cm^{-1} 3300 (OH); δ_H(400 MHz, $CDCl_3$) 4.29 (1 H, q, *J* 2.9, C*H*OH), 3.42–3.35 (1 H, m, CHS), 3.00 (1 H, td, *J* 10.5 and 6.9, CH_AH_BS), 2.90 (1 H, td, *J* 10.5 and 1.9, CH_AH_BS), 2.24–2.16 (1 H, m, CH_AH_B), 1.95–1.85 (1 H, m, CH_AH_B), 1.81–1.71 (2 H, m, CH_CH_D and OH), 1.62–1.52 (1 H, m, CH_CH_D), 1.46–1.36 (2 H, m, CH_2) and 0.94 (3 H, t, *J* 7.29, Me); δ_C(100 MHz, $CDCl_3$) 75.2 (CHOH), 54.4 (CHS), 37.7* (CH_2S), 32.3*, 27.9* and 22.3* (3 × CH_2) and 14.1 (Me); *m*/*z* 145.1 (5%, M − H), 115.1 (100, M − S + H) and 102.1 (10, M − C_3H_7 − H).

(2*SR*,3*SR*,4*RS*)-3-Hydroxy-4-methyl-2-propylthiolane *syn*,*syn*-24

In the same way, the diol *syn*,*anti*-**22** (50 mg, 0.18 mmol) and toluene-*p*-sulfonyl chloride (41 mg, 0.19 mmol) in pyridine (1 ml) gave, after flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (1 : 1), *thiolane syn*,*syn*-**24** (28 mg, 96%) as an oil; R_f [light petroleum (40–60 °C)–ether (1 : 1)] 0.5; ν_{max}(film, $CDCl_3$)/cm^{-1} 3300 (OH); δ_H(400 MHz, $CDCl_3$) 3.34–3.24 (1 H, m, C*H*OH), 3.10 (1 H, td, *J* 8.9 and 3.1, C*H*SCH_2), 2.85 (1 H, dd, *J* 10.5 and 7.4, CH_AH_BS), 2.48 (1 H, t, *J* 10.5, CH_AH_BS), 2.13–2.03 (1 H, m, C*H*Me), 1.97–1.90 (1 H, m, CH_AH_B), 1.82 (1 H, d, *J* 5.2, OH), 1.48–1.28 (3 H, m, CH_AH_B and CH_2), 1.11 (3 H, d, *J* 6.5, MeCH) and 0.92 (3 H, t, *J* 7.1, $MeCH_2$); δ_C(100 MHz, $CDCl_3$) 84.1 (CHOH), 52.7 (CHS), 43.8 (*C*HMe), 37.1* (CH_2S), 32.5* (CH_2), 22.7* (CH_2), 16.9 (*Me*CH) and 14.0 (*Me*CH_2) (Found M^+, 160.0920. $C_8H_{16}OS$ requires M, 160.0922); *m*/*z* 160.1 (20%, M), 127.1 (100, M − SH), 114.1 (55, M − CH_2S) and 71.0 (90, M − C_4H_8 S− H).

(2*RS*,3*SR*,4*RS*)-3-Hydroxy-4-methyl-2-propylthiolane *anti*,*syn*-24

In the same way, the diol *anti*,*anti*-**22** (92 mg, 0.34 mmol) and toluene-*p*-sulfonyl chloride (75 mg, 0.36 mmol) in pyridine (1 ml) gave, after flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (1 : 1), *thiolane anti*,*syn*-**24** (52.7 mg, 96%) as an oil; R_f [light petroleum (40–60 °C)–ether (1 : 1)] 0.5; ν_{max}(film, $CDCl_3$)/cm^{-1} 3300 (OH); δ_H(400 MHz, $CDCl_3$) 3.92 (1 H, br s, C*H*OH), 3.18–3.12 (1 H, m, CHS), 2.86 (1 H, dd, *J* 10.4 and 7.2, CH_AH_BS), 2.56 (1 H, t, *J* 10.4, CH_AH_BS), 2.34–2.24 (1 H, m, C*H*Me), 1.80–1.72 (1 H, br s, OH), 1.67–1.25 (4 H, m, 2 × CH_2), 1.12 (3 H, d, *J* 6.7, MeCH) and 0.88 (3 H, t, *J* 7.1, $MeCH_2$); δ_C(100 MHz, $CDCl_3$) 81.9 (CHOH), 55.8 (CHS), 40.4 (*C*HMe), 39.1* (CH_2S), 33.9* (CH_2), 21.4* (CH_2), 13.8 (*Me*CH) and 13.1 (*Me*CH_2) (Found M^+, 160.0925. $C_8H_{16}OS$ requires M, 160.0922); *m*/*z* 160.1 (20%, M), 127.1 (100, M − SH), 114.1 (60, M − CH_2S) and 71.0 (50, M − C_4H_8S − H). There was an NOE enhancement (by a 500 MHz NOESY) between the Me (δ_H 1.12) and Me (δ_H0.88) for the thiolane *anti*,*syn*-**24** signifying an *anti,syn*-relationship.

(2*RS*,3*SR*)-4,4-Dimethyl-3-hydroxy-2-propylthiolane *anti*-27

In the same way, the diol *syn*-**25** (60 mg, 0.21 mmol) and toluene-*p*-sulfonyl chloride (44.2 mg, 0.21 mmol) in pyridine (1 ml) gave, after flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (1 : 1), the *thiolane anti*-**27** (33 mg, 90%) as an oil; R_f [light petroleum (40–60 °C)–ether (1 : 1)] 0.5; ν_{max}(film, $CDCl_3$)/cm^{-1} 3300 (OH); δ_H(400 MHz, $CDCl_3$) 3.32 (1 H, d, *J* 9.1, C*H*OH), 3.09–2.99 (1 H, br s, C*H*SCH_2), 2.76–2.66 (1 H, AB quartet, CH_AH_BS), 2.58–2.48 (1 H, AB quartet, CH_AH_BS), 1.98–1.88 (1 H, m, CH_AH_B), 1.75–1.68 (1 H, br s, OH), 1.48–1.28 (3 H, m, CH_2 and CH_AH_B), 1.09 (3 H, s, Me), 1.01 (3 H, s, Me) and 0.91 (3 H,

t, J 7.2, $MeCH_2$); δ_C(100 MHz, $CDCl_3$) 85.7 (CHOH), 50.3 ($CHSCH_2$), 43.5* (CMe), 39.4* (CH_2S), 37.5* (CH_2), 26.10 (Me), 22.2* (CH_2), 19.0 (Me) and 14.1 ($MeCH_2$); *m*/*z* 174.1 (100%, M) and 128.1 (20, M − CH_2S).

(2*SR*,3*RS*)-3,4-Dimethyl-3-hydroxythiolane *syn*-30

In the same way, the diol *anti*-**28** (0.1 g, 0.42 mmol) and toluene-*p*-sulfonyl chloride (86.6 mg, 0.42 mmol) in pyridine (1 ml) gave, after flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (1 : 1) the *thiolane syn*-**30** (50 mg, 89%) as an oil; R_f [light petroleum (40–60 °C)–ether (1 : 1)] 0.5; ν_{max}(film, $CDCl_3$)/cm^{-1} 3300 (OH); δ_H(400 MHz, $CDCl_3$) 2.95 (2 H, t, J 9.8, CH_AH_BS), 2.79 (2 H, AB quartet, J 11.2, CH_2S), 2.60 (1 H, t, J 9.8, CH_AH_BS), 1.93–1.84 (1 H, m, CHMe), 1.66–1.58 (1 H, br s, OH), 1.32 (3 H, s, Me) and 1.01 (3 H, d, J 6.7, MeCH); δ_C(100 MHz, $CDCl_3$) 80.1* (COH), 46.0 (CHMe), 45.5* (CH_2S), 35.7* (CH_2S), 23.2 (MeC) and 12.01 (MeCH) (Found M^+, 132.0612. $C_6H_{12}OS$ requires M, 132.0609); *m*/*z* 132.1 (5%, M), 99.0 (5, M − SH) and 85.1 (15, M − CH_2S − H).

(2*RS*,3*SR*)-3,4-Dimethyl-3-hydroxythiolane *anti*-30

In the same way, the diol *syn*-**28** (0.1 g, 0.42 mmol) and toluene-*p*-sulfonyl chloride (86.6 mg, 0.42 mmol) in pyridine (1 ml) gave, after flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (1 : 1) the *thiolane anti*-**30** (49 mg, 89%) as an oil; R_f [light petroleum (40–60 °C)–ether (1 : 1)] 0.45; ν_{max}(film, $CDCl_3$)/cm^{-1} 3300 (OH); δ_H(400 MHz, $CDCl_3$) 3.15 (1 H, dd, J 10.5 and 6.1, CH_AH_BS), 2.84 (1 H, AB quartet, J 11.0, CH_CH_DS), 2.75 (1 H, AB quartet, J 11.0, CH_CH_DS), 2.48 (1 H, dd, J 10.5 and 4.6, CH_AH_BS), 2.22–2.13 (1 H, m, CHMe), 1.96–1.92 (1 H, br s, OH), 1.32 (3 H, s, Me) and 0.97 (3 H, d, J 6.9, MeCH); δ_C(100 MHz, $CDCl_3$) 82.5* (COH), 46.8 (CHMe), 42.2* (CH_2S), 35.9* (CH_2S), 21.3 (MeC) and 15.9 (MeCH) (Found M^+, 132.0610. $C_6H_{12}OS$ requires M, 132.0609); *m*/*z* 132.1 (15%, M), 99.0 (20, M − SH) and 85.1 (30, M − CH_2S − H).

3-Hydroxy-3-methylthiolane 32

In the same way, the diol **31** (0.11 g, 0.48 mmol) and toluene-*p*-sulfonyl chloride (0.1 g, 0.48 mmol) in pyridine (1 ml) gave, after flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (1 : 1) the *thiolane* **32** (51 mg, 90%) as an oil; R_f [light petroleum (40–60 °C)–ether (1 : 1)] 0.6; ν_{max}(film, $CDCl_3$)/cm^{-1} 3300 (OH); δ_H(400 MHz, $CDCl_3$) 2.99 (1 H, td, J 10.5 and 6.8, CH_AH_BS), 2.96 (1 H, AB quartet, J 11.7, CH_CH_DS), 2.93–2.86 (1 H, m, CH_AH_BS), 2.73 (1 H, dd, J 11.7 and 1.6, CH_CH_DS), 2.20–2.16 (1 H, m, CH_AH_B), 1.85–1.76 (1 H, m, CH_AH_B) and 1.46 (3 H, s, Me); δ_C(100 MHz, $CDCl_3$) 80.8* (COH), 44.6* (CH_2S), 43.1* (CH_2S), 28.9* (CH_2) and 24.7 (CH_2); *m*/*z* 118.1 (100%, M).

3,4,4-Trimethyl-3-hydroxythiolane 34

In the same way, the diol **33** (0.1 g, 0.39 mmol) and toluene-*p*-sulfonyl chloride (82 mg, 0.39 mmol) in pyridine (1 ml) gave, after flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (1 : 1), the *thiolane* **34** (52.8 mg, 92%) as an oil; R_f [light petroleum (40–60 °C)–ether (1 : 1)] 0.5; ν_{max}(film, $CDCl_3$)/cm^{-1} 3300 (OH); δ_H(400 MHz, $CDCl_3$) 3.02 (1 H, AB quartet, J 11.3, CH_AH_BS), 2.90 (1 H, AB quartet, J 10.4, CH_CH_DS), 2.78 (1 H, AB quartet, J 11.3, CH_AH_BS), 2.55 (1 H, AB quartet, J 10.4, CH_CH_DS), 1.92–1.87 (1 H, br s, OH), 1.22 (3 H, s, Me), 1.06 (3 H, s, Me) and 0.96 (3 H, s, Me); δ_C(100 MHz, $CDCl_3$) 82.8 (CHOH), 47.6* (CMe), 43.4* (CH_2Ph), 42.6* (CH_2S), 24.7, 20.6 and 20.3 (3 × Me) (Found M^+, 146.0763. $C_7H_{14}OS$ requires M, 146.0765); *m*/*z* 146.1 (100%, M), 129.1 (20, M − H_2O + H) and 100 (10, M − CH_2S).

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