Stereochemical control in the synthesis of tetrahydrofurans by cyclisation of diols with [1,2]-phenylsulfanyl migration

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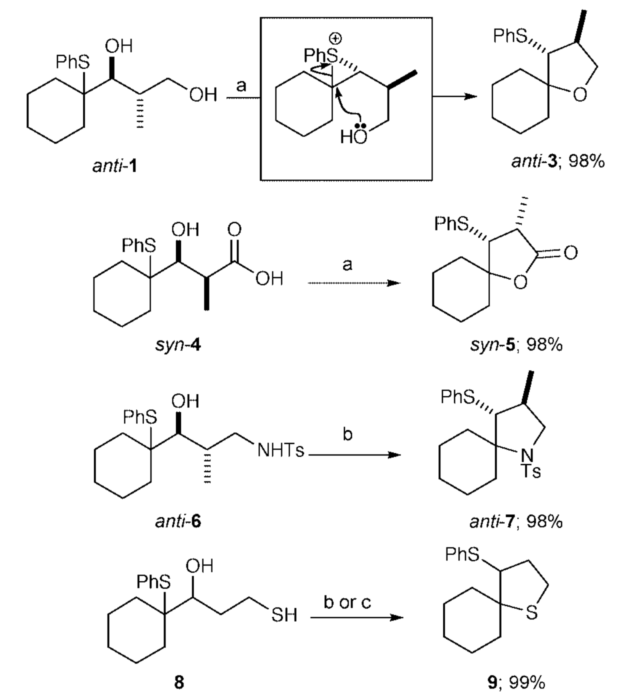
Received (in Cambridge, UK) 4th November 1999, Accepted 7th December 1999

Acid catalysed rearrangement of a series of 4-PhS-1,3-diols with toluene-*p*-sulfonic acid in benzene gives stereospecifically substituted 3-PhS-tetrahydrofurans in excellent yield *via* a [1,2]-SPh shift. We comment on the structural variation at both the migration origin and terminus on the outcome of the title reaction and define its limits.

In a series of papers, we have reported numerous rearrangements involving [1,2]-SPh migration giving spirocyclic compounds such as tetrahydrofurans *anti*-**3**,[1,2] tetrahydropyrans,[3] lactones *syn*-**5**,[1] pyrrolidines *anti*-**7**[4] and thiolanes **9**[5] in near quantitative yield. For example, treatment of diol *anti*-**1** with toluene-*p*-sulfonic acid (TsOH) in benzene generates the intermediate episulfonium ion *anti*-**2** by stereospecific loss of water.[1] This episulfonium ion is captured intramolecularly by the primary hydroxy group in *anti*-**2** giving the spirocyclic tetrahydrofuran *anti*-**3** in 98% yield (Scheme 1).[1] The observed [1,2]-SPh



Scheme 1 *Reagents and conditions*: a, TsOH, benzene, reflux; b, TMSOTf, CH_2Cl_2, −78 °C; c, TsOH, CH_2Cl_2, reflux.

migration is stereospecific with inversion at the migration terminus. We have used 1,3-diols like *anti*-**1** and related precursors such as *syn*-**4**, *anti*-**6** and **8** with a symmetrical migration origin primarily for ease of synthesis (from commercially available symmetrical ketones), but also because there was no further complication from the additional stereochemistry. We have observed stereospecific C–O,[1] C–N[4] and C–S[5] bond formation to give diastereoisomeric and enantiomerically[6] pure spirocyclic heterocycles and allylic derivatives.[7,8]

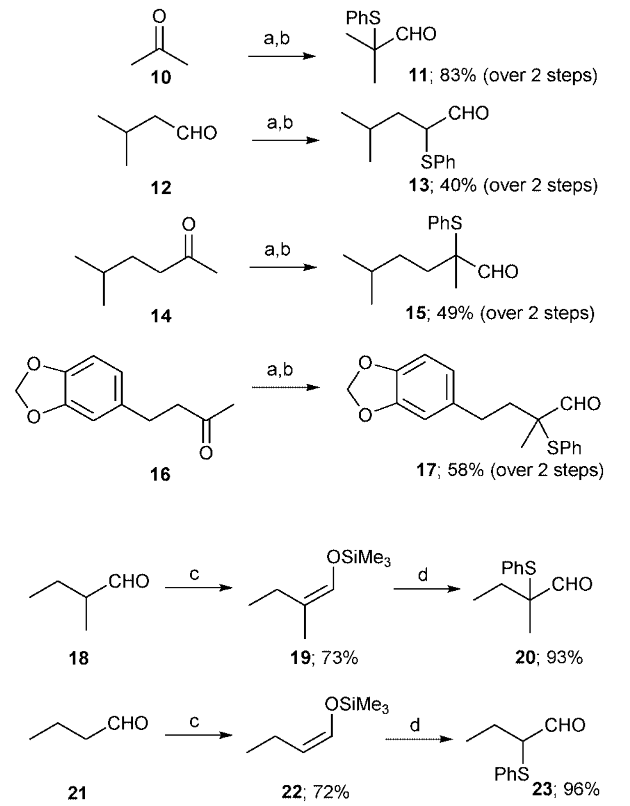
We now report on the cyclisation of a new acyclic class of diol with structural variation at both the migration origin and terminus. We discuss stereochemical features (relative stereochemistry, Baldwin's rules[9] and the Thorpe–Ingold effect[10,11]) which affect the observed mode and the efficiency of cyclisation of such [1,2]-SPh processes.

We required acyclic 2-PhS-aldehydes **11**, **13**, **15**, **17**, **20** and **23** for this study. We used two procedures for the introduction of the 2-PhS substituent. The de Groot and Jannsen method,[12,13]—addition of lithiated methoxymethyl phenyl sulfide[12] to the aldehyde **12** and ketones **10**, **14** and **16**, and subsequent rearrangement with $SOCl_2$ and Et_3N in CH_2Cl_2—gave the 2-PhS aldehydes **11**, **13**, **15** and **17**. We also used the reaction between silyl enol ethers **19** and **22** with freshly prepared PhSCl[14] to make the 2-PhS aldehydes **20** and **23**. All these methods were efficient giving the acyclic 2-PhS-aldehydes **11**, **13**, **15**, **17**, **20** and **23** in excellent overall yield and are essentially as good as those previously reported[1] for the cyclic 2-PhS aldehydes (Scheme 2).

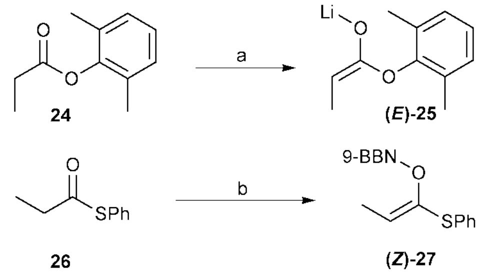
We synthesised the diol precursors using either the reliable *anti*-stereoselective aldol reaction of the lithium (*E*)-enolate **25**[15,16] of Heathcock's ester (2,6-dimethylphenyl propionate **24**) or the *syn*-stereoselective aldol from the boron (*Z*)-enolate **27**[16,17] of Masamune's ester (*S*-phenyl thiopropionate **26**) (Scheme 3) with 2-PhS acyclic aldehydes giving predictably single diastereoisomeric aldol adducts with greater than 98% stereocontrol.

The rearrangement of the simplest acyclic 1,3-diol *anti*-**29** with a symmetrical migration origin was studied, primarily to see whether there were any unusual effects on the rearrangement upon changing from a cyclic to an acyclic system (Scheme 4), since we have previously observed significant changes in the mechanistic pathway in related diols when investigating [1,4]-SPh shifts.[18] The diol *anti*-**29** was synthesised from the aldehyde **11** and the lithium enolate (*E*)-**25** of Heathcock's ester (2,6-dimethylphenyl propionate) giving the diastereoisomerically pure aldol *anti*-**28** in 94% yield. Subsequent reduction ($LiAlH_4$ in ether, 2 hours) gave the diol *anti*-**29**. Rearrangement of this diol under our usual conditions[1] (catalytic TsOH in refluxing CH_2Cl_2 for 5 minutes) gave stereospecifically the tetrahydrofuran *anti*-**31** in near quantitative yield, presumably *via* a

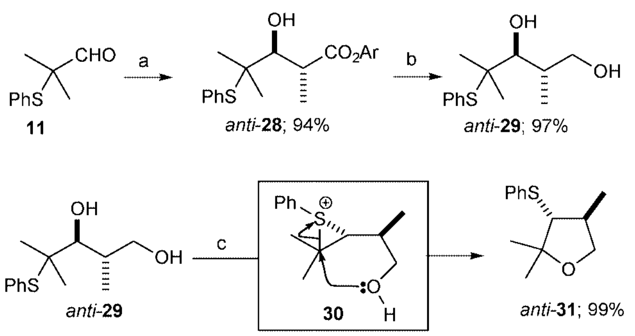
DOI: 10.1039/a908810e



Scheme 2 *Reagents and conditions*: a, n-BuLi, $PhSCH_2OMe$, THF, −78 °C; b, $SOCl_2$, Et_3N, CH_2Cl_2; c, Me_3SiCl, Et_3N, DMF; d, PhSCl, CH_2Cl_2.



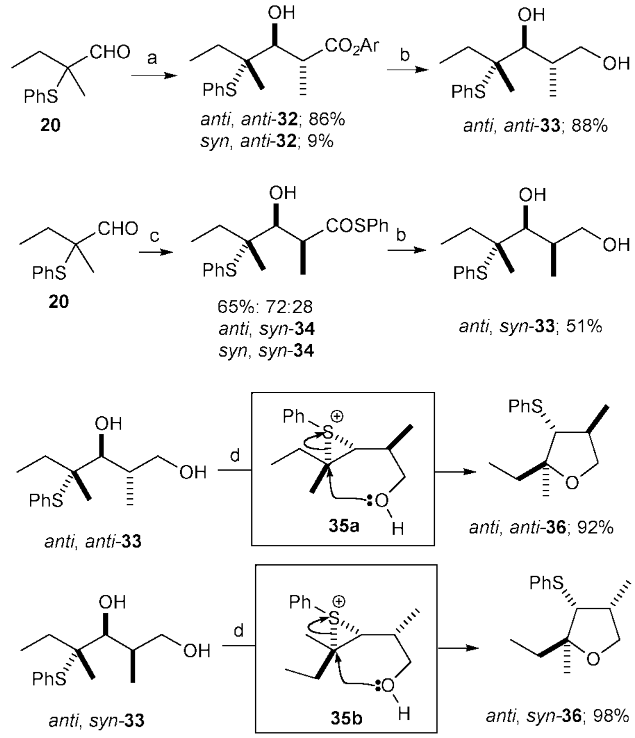
Scheme 3 *Reagents and conditions*: a, LDA, THF, −78 °C; b, 9-BBN-OTf, *i*-Pr_2NEt, toluene, −30 °C.



Scheme 4 *Reagents and conditions*: a, (*E*)-**25**, THF, −78 °C; b, $LiAlH_4$, ether, 2 hours; c, TsOH, CH_2Cl_2, 5 min.

hybrid 6-*endo*–5-*exo*-*tet* cyclisation[9] of the episulfonium ion **30** with an overall [1,2]-SPh shift. The aldol reaction, reduction and resulting cyclisation to give the tetrahydrofuran *anti*-**31** were essentially as good as those with the cyclic migration origin.[1]

The rearrangement of 4-PhS-1,3-diols with unsymmetrical acyclic tertiary migration origins was stereochemically important because the [1,2]-SPh shift might occur stereospecifically with inversion at both the migration origin and terminus. These diols were synthesised from the chiral (2*RS*)-aldehyde **20** by reaction with enolate (*E*)-**25**[15] or the *syn*-stereoselective boron (*Z*)-enolate **27**[17] of *S*-phenyl thiopropionate (Scheme 5). Both



Scheme 5 *Reagents and conditions*: a, (*E*)-**25**, THF, −78 °C; b, $LiAlH_4$, ether, 2 hours; c, (*Z*)-**27**, toluene, −30 °C; d, TsOH, benzene, 5 min.

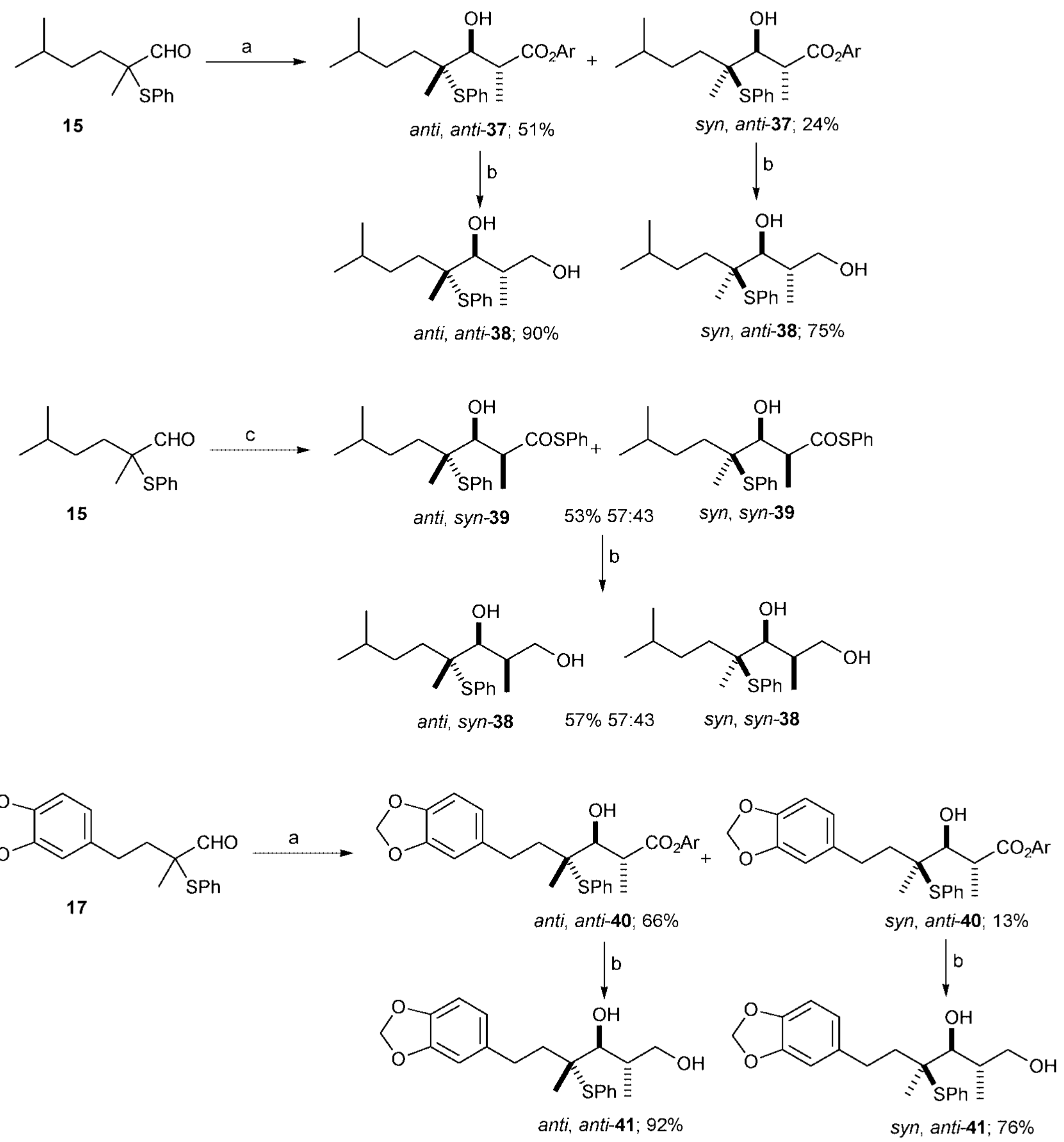
reactions gave excellent C(2,3)-stereocontrol (>98 : 2), but with opposite stereochemistry controlled by the enolate geometry. The C(3,4)-Felkin–Anh[19,20] selectivity was slightly better (Table 1) for the (*E*)-enolate **25**, than for the corresponding (*Z*)-**27**, presumably due to the skewed nature of the transition state.[21] Separation of diastereoisomers **32** and **34** by HPLC was required to give the diastereoisomerically pure aldol adducts *anti*, *anti*-**32** and *anti*, *syn*-**34**. Reduction ($LiAlH_4$ in ether) gave the 1,3-diols *anti*, *anti*- and *anti*, *syn*-**33**, which have the all-important stereochemistry at the migration origin and what would become the migration terminus in the tetrahydrofurans. Rearrangement of these diols (with TsOH in benzene) gave the corresponding tetrahydrofurans *anti*, *anti*- and *anti*, *syn*-**36** as single diastereoisomers with an overall [1,2]-SPh shift. Evidently, the cyclisation was stereospecific with inversion at both the migration origin and terminus (determined by NOE differences). Inversion at the tertiary migration origin is unusual and the cyclisation must be occurring *via* an S_N2 reaction involving the episulfonium ions **35a** and **35b**.

We next considered the relative C(3,4) stereochemistry in the cyclisation of the four diastereoisomeric diols *anti*, *anti*-, *anti*, *syn*-, *syn*, *anti*- and *syn*, *syn*-**38**, prepared by the addition of the lithium (*E*)-enolate **25** and the boron (*Z*)-enolate **27** to the aldehyde **15** (Scheme 6). The Felkin–Anh[19] selectivity with the aldehyde **15** was much lower than the previous case (Table 1), and thus we were able to obtain reasonable quantities of all possible diastereoisomeric aldol adducts **37** and **39**. Reduction ($LiAlH_4$ in ether, 2 hours) of **37** gave the diols *anti*, *anti*- and *anti*, *syn*-**38** required for the rearrangement study. Treatment of these diols **38** with toluene-*p*-sulfonic acid in benzene gave the tetrahydrofurans *anti*, *anti*- and *syn*, *anti*-**42** in excellent yield (Scheme 7). The efficient cyclisation of the *anti*, *syn*-stereoisomer of **33** (to give tetrahydrofuran **36**) and that of the *syn*, *anti*-stereoisomer of **38** showed that one *syn*-relationship did

Table 1 Stereoselectivity in aldol reactions

Entry	Aldehyde	Enolate	Aldol	C(2,3)-*anti*:*syn* (aldol)	C(3)–C(4)-*anti*:*syn* (Felkin–Anh)	Yield (%)
1	**11**	(*E*)-**25**	**28**	>98:2	—	94
2	**20**	(*E*)-**25**	**32**	>98:2	90:10	95
3	**20**	(*Z*)-**27**	**34**	2:>98	72:28	65
4	**15**	(*E*)-**25**	**37**	>98:2	78:22	75
5	**15**	(*Z*)-**27**	**39**	>98	57:43	53
6	**17**	(*E*)-**25**	**40**	>98:2	83:17	79
7	**13**	(*E*)-**25**	**44**	>98:2	67:33	26
8	**13**	(*Z*)-**27**	**46**	2:>98	>98:2	37
9	**23**	(*E*)-**25**	**47**	>98:2	71:29	69
10	**23**	(*Z*)-**27**	**49**	2:>98	90:10	72
11	**13**	[a]	**55**	—	93:7	33

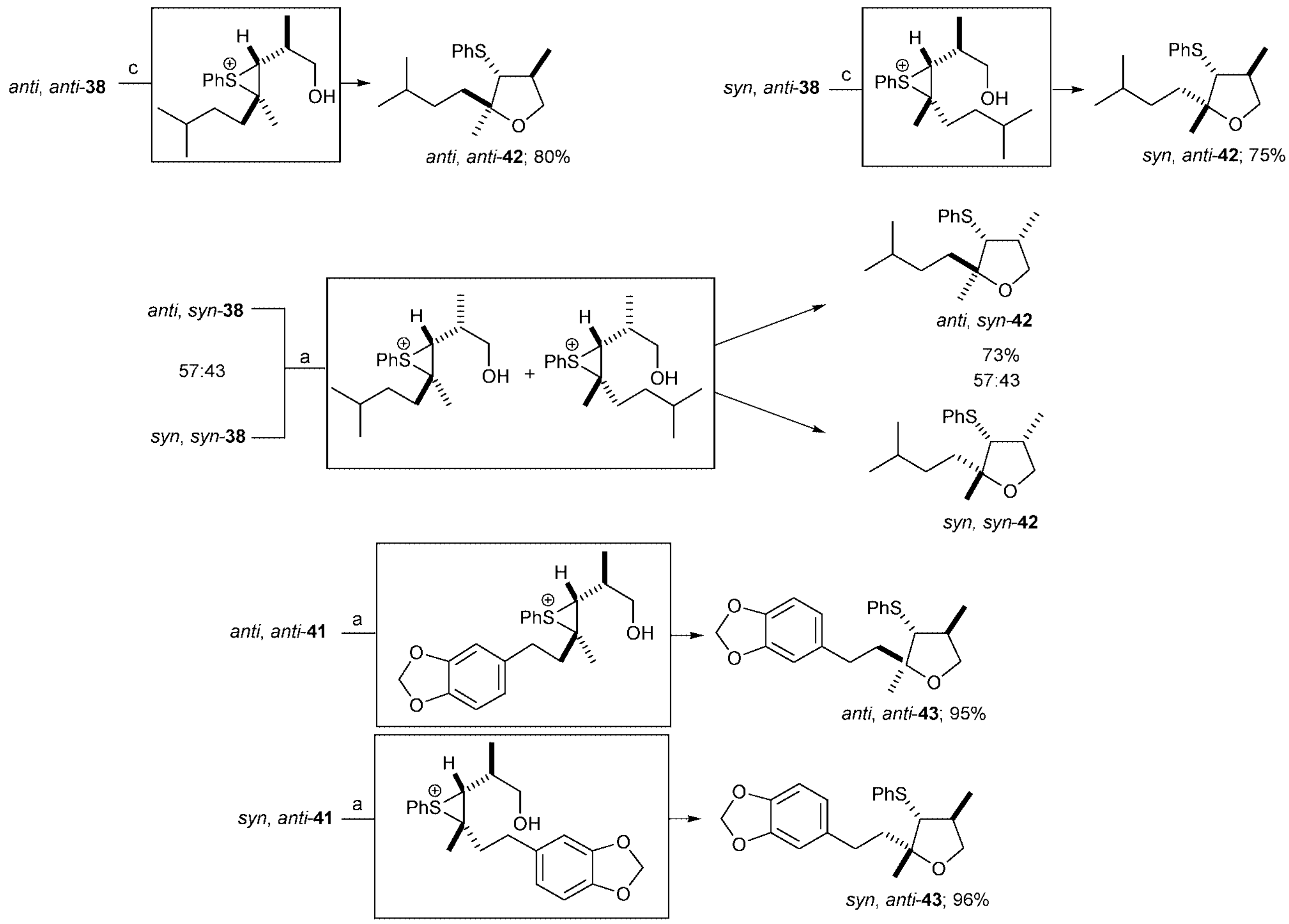
[a] Lithium enolate of methyl isobutyrate.



Scheme 6 *Reagents and conditions*: a, (*E*)-**25**, THF, −78 °C; b, $LiAlH_4$, ether, 2 hours; c, (*Z*)-**27**, toluene, −30 °C.

not hinder the cyclisation. The remaining *syn*, *syn*-relationship was explored only with an inseparable diastereoisomeric mixture (ratio 43:57) of *syn*, *syn*- and *anti*, *syn*-diols **38** (Scheme 6), but this cyclised stereospecifically to give the same diastereoisomeric mixture (ratio 43:57) of tetrahydrofurans *syn*, *syn* and *anti*, *syn*-**42** in excellent yield (Scheme 7). This was particularly important since formation of tetrahydrofuran *syn*, *syn*-**42** must occur *via* a cyclisation where all the larger substituents are on the same side of the developing tetrahydrofuran. Furthermore, rearrangement of some analogues diols *anti*, *anti*- and *syn*, *anti*-**41** gave the tetrahydrofurans *anti*, *anti*- and *syn*, *anti*-**43** in near perfect yield (Scheme 7).

Rearrangement of 4-PhS-1,3-diols *anti*-**29**, **33**, **38** and **41** with a tertiary migration origin occurs efficiently and cleanly giving tetrahydrofurans *anti*-**31**, **36**, **42** and **43** in near perfect yield. The cyclisation was independent of the developing stereochemistry at the positions C(2,3) and C(3,4) and was stereospecific with inversion at both the migration origin and



Scheme 7 *Reagents and conditions*: a, TsOH, benzene, 5 min.

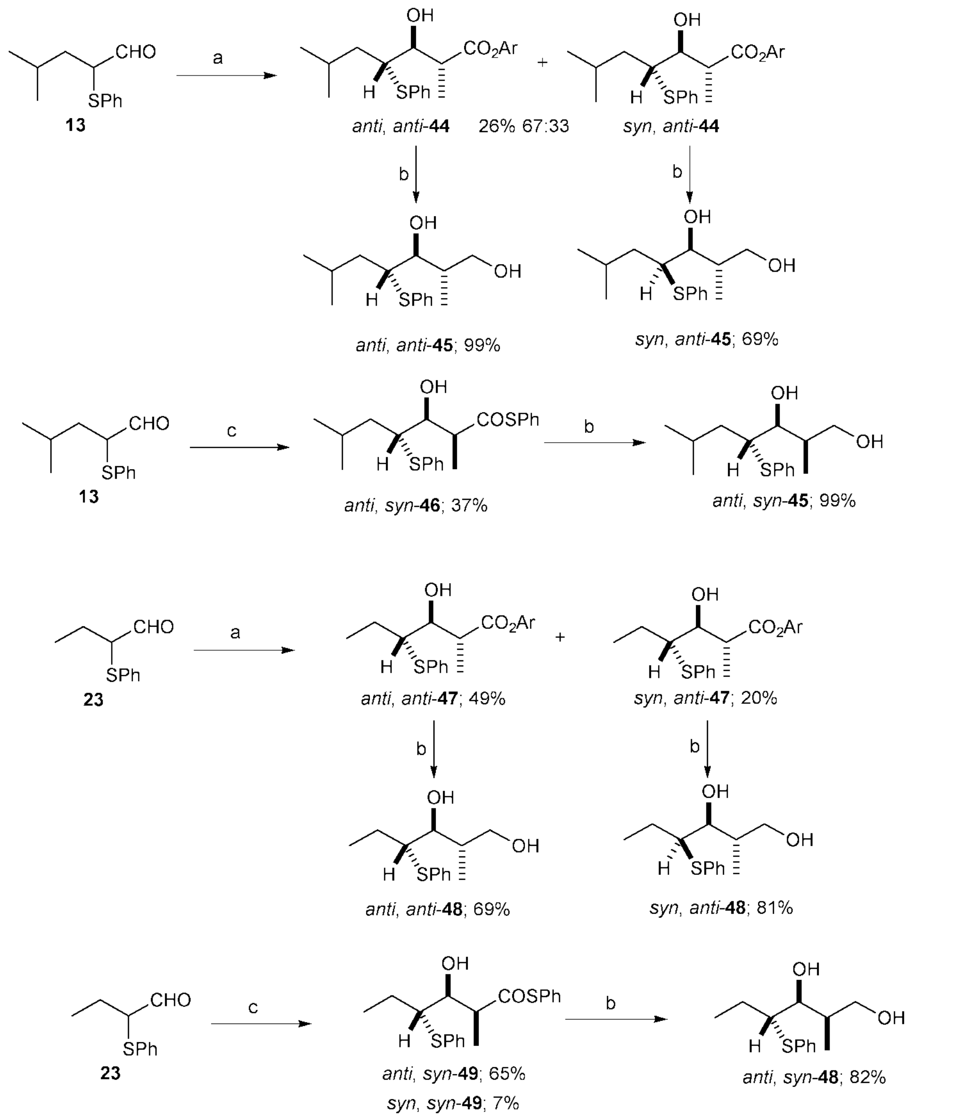
terminus. This is not unexpected since efficient cyclisation has been observed with the very similar symmetrical cyclic diols with a tertiary migration origin such as *anti*-**1**.[1]

We next chose to investigate the rearrangement of diols having a secondary migration origin. These 1,3-diols **45** and **48** were synthesised using the previously illustrated aldol and reduction procedure as shown in Scheme 8. The yields of the aldol adducts **44**, **46**, **47** and **49** from the addition of the enolates (*E*)-**25** and (*Z*)-**27** to the 2-PhS-aldehyde **13** and **23** were lower than those observed with the tertiary aldehydes **15**, **17** and **20**, presumably due to competitive enolisation of the aldehyde (*e.g.* **13**) under the reaction conditions. Reduction ($LiAlH_4$ in ether) of aldols **44**, **46**, **47** and **49** gave the corresponding diols **45** and **48** in excellent yield.

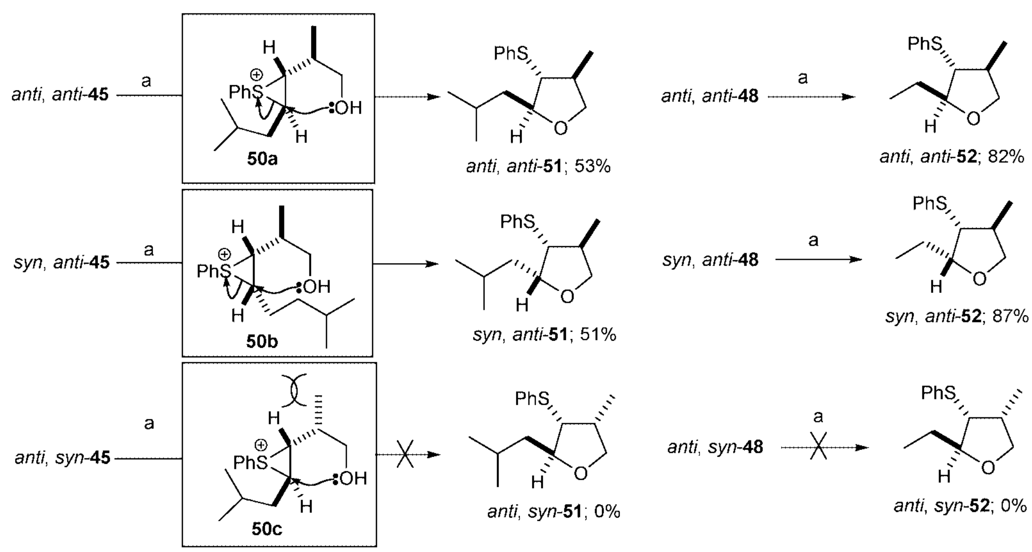
Cyclisation of these six 4-PhS-1,3-diols **45** and **48** with a secondary migration origin to form tetrahydrofurans under our usual acidic conditions (toluene-*p*-sulfonic acid in refluxing benzene) was more dependent on the stereochemistry of the original diol than in previous cases. For example, rearrangement of the diols *anti*, *anti*-**45**, *syn*, *anti*-**45**, *anti*, *anti*-**48** and *syn*, *anti*-**48** [the only change is in the C(3,4) stereochemistry] occurred to give the tetrahydrofurans *anti*, *anti*-**51**, *syn*, *anti*-**51**, *anti*, *anti*-**52** and *syn*, *anti*-**52** (Scheme 9). The yields were much lower than those of the corresponding diols with a tertiary migration origin, and the reaction times were at least one order of magnitude longer. Evidently, the rate determining formation of the intermediate episulfonium ion (such as **50a**) is slower and this is presumably due to the less substituted migration origin, a manifestation of the *exo*-component of the Thorpe–Ingold effect.[10,11] The efficiency of the cyclisation to form the tetrahydrofurans **51** and **52** as in previous cases was found to be independent of the C(3,4)-stereochemistry. The cyclisation was stereospecific with inversion at both the migration origin and terminus.

However, attempts to cyclise the remaining diols *anti*, *syn*-**45** and *anti*, *syn*-**48** which would have given the tetrahydrofurans *anti*, *syn*-**51** and *anti*, *syn*-**52** did not occur (Scheme 9). On prolonged heating these diols *anti*, *syn*-**45** and *anti*, *syn*-**48** slowly decomposed to give unidentifiable products. It appears that cyclisation to form *anti*, *syn*-**51** is no longer possible due to the (developing) unfavourable *syn*-stereochemistry between the PhS and the Me groups at the position C(2,3). This C(2,3)-stereochemistry is presumably more important than the C(3,4)-stereochemistry because the PhS group is *moving away* from the C-4 position in the transition state **50c**, while the C(2,3)-stereochemistry is established upon episulfonium ion formation, and during tetrahydrofuran formation this group is *moving towards* the C-2 position.[22] This observation is in sharp contrast to that observed with a similar diol with a tertiary migration origin (*e.g. anti*, *anti*-**33**) giving the tetrahydrofuran *anti*, *anti*-**36**. This case is different presumably because a secondary migration origin demands a much tighter S_N2 transition state such as **50a** and **50b** which is less favourable for an *endo*-type cyclisation.[9]

We chose to increase the efficiency of tetrahydrofuran formation of diols like *anti*, *syn*-**45** with a secondary migratory origin (Scheme 10) by using the *gem*-dimethyl Thorpe–Ingold effect.[10,11,23] The diol *anti*-**54** was synthesised by the addition of the lithium enolate derived from methyl isobutyrate and LDA to the aldehyde **13** giving the *anti*-ester **53** virtually as a single diastereoisomer. Subsequent reduction with $LiAlH_4$ in ether gave the corresponding diol *anti*-**54** in excellent yield. Rearrangement of the diol *anti*-**54** with toluene-*p*-sulfonic acid in benzene gave tetrahydrofuran *anti*-**56** in a moderate 44% yield which was as good as previous cases with a secondary migration origin. It appears that unfavourable developing C(2,3) *syn*-stereochemistry in **50c** which originally prevented cyclisation to the tetrahydrofuran *anti*, *syn*-**51** is now less



Scheme 8 *Reagents and conditions*: a, (*E*)-**25**, THF, −78 °C; b, $LiAlH_4$, ether, 2 hours; c, (*Z*)-**27**, toluene, −30 °C.



Scheme 9 *Reagents and conditions*: a, TsOH, benzene, 45 min.

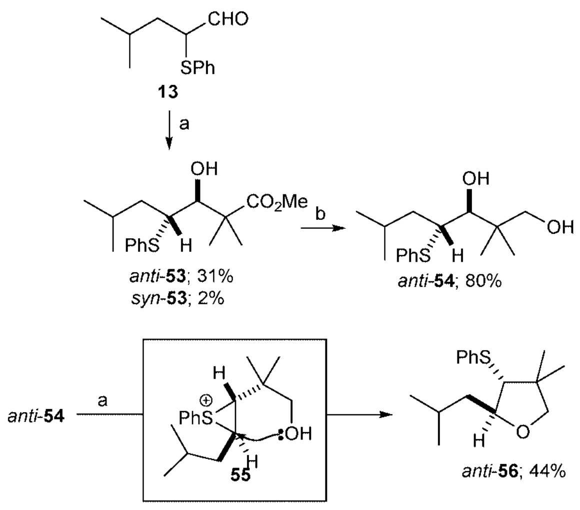
important for the capture of the episulfonium ion **55** because cyclisation to form the tetrahydrofuran *anti*-**56** is more efficient by at least two orders of magnitude due to the *endo*-component of the Thorpe–Ingold effect (angle and conformation effects)[23] resulting from the *gem*-dimethyl groups in *anti*-**54**.

Rearrangements of 1,3-diols **45**, **48** and *anti*-**54** with a secondary migration origin can occur, but it is less efficient and is much more dependent on the relative stereochemistry than those of the corresponding diols with a tertiary migration origin. The yields are lower and the reaction times are longer.

Table 2 Cyclisation of diols with [1,2]-PhS migration

Entry	Diol	THF	Yield (%)	Time[a]
1	*anti*-**29**	*anti*-**31**	99	5 min[c]
2	*anti*, *anti*-**33**	*anti*, *anti*-**36**	92	5 min
3	*anti*, *syn*-**33**	*anti*, *syn*-**36**	98	5 min
4	*anti*, *anti*-**38**	*anti*, *anti*-**42**	80	5 min
5	*syn*, *anti*-**38**	*syn*, *anti*-**42**	75	5 min
6	*anti*, *syn*-**38**	*anti*, *syn*-**42**	73[d]	5 min
	syn, *syn*-**38**	*syn*, *syn*-**42**		
7	*anti*, *anti*-**41**	*anti*, *anti*-**43**	95	5 min
8	*syn*, *anti*-**41**	*syn*, *anti*-**43**	96	5 min
9	*anti*, *anti*-**46**	*anti*, *anti*-**51**	53	35 min
10	*syn*, *anti*-**46**	*syn*, *anti*-**51**	51	45 min
11	*anti*, *syn*-**46**	*anti*, *syn*-**51**	[b]	45 min
12	*anti*, *anti*-**48**	*anti*, *anti*-**52**	82	45 min
13	*syn*, *anti*-**48**	*syn*, *anti*-**52**	87	45 min
14	*anti*, *syn*-**48**	*anti*, *syn*-**52**	[b]	45 min
15	*anti*-**54**	*anti*-**56**	44	45 min

[a] In refluxing benzene with 0.2 equiv. TsOH. [b] Decomposed slowly, no cyclic ether formed. [c] In refluxing CH_2Cl_2 with 0.2 equiv. TsOH. [d] Rearranged as a mixture (ratio 57 : 43) of diastereoisomers.



Scheme 10 *Reagents and conditions*: a, LDA and methyl isobutyrate, THF, −78 °C; b, $LiAlH_4$, ether, 2 hours; c, TsOH, benzene, 45 min.

When cyclisation to the tetrahydrofuran does occur, it is stereospecific with inversion at both the migration origin and terminus. The relative stereochemistry at C(2,3) is more important to the outcome of the cyclisation than that at C(3,4). For efficient cyclisation, a developing *anti*-stereochemistry within the transition state was necessary at C(2,3): without it no tetrahydrofuran formation occurs. The relative stereochemistry at C(3,4) is unimportant.

In conclusion, we have shown that rearrangement of a series of 4-PhS-1,3-diols *anti*-**29**, **33**, **38**, **41**, **45**, **48** and *anti*-**54** with toluene-*p*-sulfonic acid in benzene gave the tetrahydrofurans diols *anti*-**31**, **36**, **42**, **43**, **51**, **52** and *anti*-**56** with three contiguous stereogenic centres in good yield (Table 2). The cyclisation was stereospecific with inversion at both the migration origin and terminus and with retention at C(2). The following rules are observed. (1) Diols with a tertiary migration origin and a secondary terminus (like *anti*, *anti*-**33**) rearrange more efficiently than those with a secondary migration origin by at least one order of magnitude to give tetrahydrofurans such as *anti*, *anti*-**36**. (2) The relative stereochemistry at C(2,3) is more important than that at C(3,4) for efficient cyclisation. This can be overturned using the *gem*-dimethyl Thorpe–Ingold effect (*e.g.* *anti*-**54**).[10,11] (3) A developing *anti*-stereochemistry at C(2,3) is more favoured than *syn*. (4) A hybrid 6-*endo*–5-*exo-tet* cyclisation (disfavoured by Baldwin's rules)[9] is preferred to give tetrahydrofurans in all cases so far studied rather than a pure 5-*exo-tet* cyclisation to give oxetanes due to thermodynamic control.[24]

These acyclic 3-PhS-tetrahydrofurans derived from diols with a tertiary or secondary migration origin are useful precursors of tetrahydrofurans with 1,3-related stereogenic centres as Williams has already shown that the PhS-group can be removed efficiently and cleanly with Raney nickel.[25] The nearest analogue to our studies is that developed by Gruttadauria,[26] and he has also shown removal of the migrating PhSe substituent to give very similar compounds.

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 Bruker WM 200 or WM 250 Fourier transform spectrometers using an internal deuterium lock. Chemical shifts are quoted in parts per milllion 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. The symbols *i*-, *o*-, *m*- and *p*- denote the *ipso*-, *ortho*-, *meta*- and *para*-positions respectively for the phenyl ring (PhS group). Mass spectra were recorded on an AEI Kratos MS30 or MS890 machine using a DS503 data system for high resolution analysis. Melting points were measured on a Reichart hot stage microscope and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 297 grating spectrophotometer calibrated against polystyrene. All compounds were isolated using flash column chromatography and were assumed to have a purity of greater than 98% (determined by NMR).

2-(Phenylsulfanyl)-2-methylpropanal 11

n-BuLi (25.87 ml, 1.38 M in hexanes, 35.7 mmol) was added dropwise to a solution of methoxymethyl phenyl sulfide (5 g, 4.77 ml, 32.46 mmol) in THF (500 ml) at −78 °C and stirred for 30 min. Acetone **10** (5.64 g, 7 ml, 97.4 mmol) in THF (5 ml) was added dropwise and the solution was stirred for a further 20 min. A solution of brine (50 ml) was added and the mixture was allowed to warm to room temperature. The solution was extracted with ether (3 × 50 ml) and 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 the *1-methoxy-1-(phenylsulfanyl)-2-methylpropan-2-ol* (6.4 g, 93%) as an oil; R_f [light petroleum (bp 40–60 °C)–ether (9 : 1)] 0.1; ν_{max} (film, $CDCl_3$)/cm^{-1} 3200 (OH); δ_H(250 MHz, $CDCl_3$) 7.54–7.19 (5 H, m, SPh), 4.50 (1 H, s, C*H*SPh), 3.49 (3 H, s, OMe), 2.62 (1 H, s, OH) and 1.32 (6 H, s, 2 × Me); δ_C(62.5 MHz, $CDCl_3$) 135.82* (*i*-SPh), 132.73 (*m*-SPh), 129.15 (*p*-SPh), 127.45 (*o*-SPh), 103.52 (OC*H*SPh), 73.41* (COH), 57.69 (OMe), 25.30 and 25.14 (2 × Me) (Found M^+, 212.0884. $C_{11}H_{16}O_2S$ requires M, 212.0870); *m*/*z* 212.1 (15%, M), 165.0 (10, M − MeO − OH + H) and 103.1 (100, M − SPh).

Thionyl chloride (3.52 g, 2.22 ml, 30.7 mmol) was added dropwise to a solution of the above alcohol (2.2 g, 10.2 mmol) and Et_3N (10.3 g, 14 ml, 0.10 mol) in CH_2Cl_2 (200 ml) at 0 °C and stirred for 45 min. This solution was then poured into ice-cold hydrochloric acid (28 ml, 3 M) and extracted with CH_2Cl_2 (3 × 50 ml). The combined extracts 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 (9 : 1) the *aldehyde* **11** (1.65 g, 89%) as an oil; R_f [light petroleum (40–60 °C)–ether (9 : 1)] 0.6; ν_{max} (film, $CDCl_3$)/cm^{-1} 1730 (C=O); δ_H(250 MHz, $CDCl_3$) 9.33 (1 H, s, CHO), 7.41–7.25 (5 H, m, SPh) and 1.31 (2 × Me); δ_C(62.5 MHz, $CDCl_3$) 195.38* (CHO), 136.87 (*m*-SPh), 129.91* (*i*-SPh), 129.39 (*p*-SPh), 128.98 (*o*-SPh), 55.39* (CSPh) and 21.21 (Me) (Found M^+, 180.0617. $C_{10}H_{12}OS$ requires M, 180.0608); *m/z* 218.1 (10%, M), 151.1 (100, M − CHO) and 109.0 (10, SPh).

4-Methyl-2-(phenylsulfanyl)pentanal 13

In the same way as the aldehyde **11**, n-BuLi (8.25 ml, 1.55 M in hexanes, 12.8 mmol), methoxymethyl phenyl sulfide (1.8 g, 1.71 ml, 11.6 mmol) and the aldehyde **12** (1.24 ml, 11.16 mmol) gave, after flash chromatography on silica eluting with hexane–ether (4 : 1) the *1-methoxy-4-methyl-1-phenylsulfanylpentan-2-ol* (2.41 g, 87%) as an oil and as a mixture (ratio 65 : 35) of diastereoisomers; R_f [hexane–ether (4 : 1)] 0.14, ν_{max} (film, $CDCl_3$)/cm^{-1} 3440 (OH), 2870 (CH) and 1590 (SPh); δ_H(250 MHz, $CDCl_3$) 7.52–7.26 (5 H, m, SPh), 4.45 (1 H, d, *J* 6.2, C*H*(OMe)SPh minor) and 4.37 (1 H, d, *J* 7.1, C*H*(OMe)SPh major), 3.73–3.65 (1 H, m, C*H*OH), 3.53 (3 H, s, OMe major) and 3.49 (3 H, s, OMe, minor), 2.41 (1 H, br s, OH), 1.87–1.78 (1 H, m), 1.68 (1 H, dd, *J* 7.3 and 2.6, CH minor), 1.62 (1 H, dd, *J* 7.2 and 2.6, Me_2CHCH_2CHOH major) and 1.51–1.35 (1 H, m, Me_2CH-CH_2CHOH minor), 0.93 (3 H, d, *J* 6.7, CMe_AMe_B major), 0.93 (3 H, d, *J* 6.6, CMe_AMe_B, minor) and 0.87 (3 H, ds, *J* 6.6, CMe_AMe_B major) and 0.82 (3 H, d, *J* 6.5, CMe_AMe_B minor); δ_C(62.5 MHz, $CDCl_3$) (major diastereoisomer) 133.8, 132.7, 128.8, 127.8, 95.3, 71.1, 56.7, 41.6, 24.4, 23.8 and 21.4; (minor diastereoisomer) 133.5, 133.0, 129, 127.7, 98.0, 70.5, 57.0, 41.5, 24.6, 23.8 and 21.5 (Found M^+, 240.1195. $C_{13}H_{20}O_2S$ requires M, 240.1184); *m/z* 240.1 (16%, M), 153 (36), 131 (100), 110 (82, PhSH) and 57 (51).

A solution of the above alcohol (0.24 g, 1 mmol), MsCl (0.24 ml, 1.5 mmol) and Et_3N (0.15 g, 0.21 ml, 1.5 mmol) gave, after flash chromatography on silica gel, eluting with hexane–ether (10 : 1), the *aldehyde* **13** (0.1 g, 48%) as a liquid; R_f [hexane–ether (10 : 1)] 0.32; ν_{max} (film, $CDCl_3$)/cm^{-1} 4320 (OH), 2870 (CH), 1705 (CO) and 1580 (SPh); δ_H(250 MHz, $CDCl_3$) 9.32 (1 H, d, *J* 4.6, CHO), 7.60–7.26 (5 H, m, SPh), 3.59 (1 H, ddd, *J* 7.8, 7.4 and 4.5, CHSPh), 1.90–1.48 (3 H, m, CH_2CHMe_2), 0.96 (3 H, d, *J*, 6.6, CMe_AMe_B) and 0.94 (3 H, d, *J* 6.5, CMe_AMe_B); δ_C(62.5 MHz, $CDCl_3$) 195.0, 132.8, 129.1, 128.1, 131.8, 55.1, 36.5, 25.7, 22.4 and 22.3 (Found M^+, 208.0927. $C_{12}H_{16}OS$ requires M, 208.0922); *m/z* 208.1 (14%, M), 179 (24), 137 (12), 123 (100, CH_2SPh) and 110 (18, PhSH).

2,5-Dimethyl-2-phenylsulfanylhexanal 15

In the same way as the aldehyde **11**, n-BuLi (17.5 ml, 1.6 M in hexanes, 28 mmol), methoxymethyl phenyl sulfide (3.9 g, 25.8 mmol) and the aldehyde **14** (2.6 g, 22.7 mmol) gave, after flash chromatography on silica eluting with CH_2Cl_2, *1-methoxy-2,5-dimethyl-1-phenylsulfanylhexan-2-ol* (4.25 g, 70%) as an oil and as a mixture (ratio 67 : 33) of diastereoisomers; R_f [CH_2Cl_2] 0.50, ν_{max} (film, $CDCl_3$)/cm^{-1} 3500 (OH) and 1580 (SPh); δ_H(250 MHz, $CDCl_3$) 7.54–7.25 (5 H, m, SPh), 4.58 and 4.55 (1 H, s, C*H*OMe), 3.43 and 3.41 (3 H, s, OMe), 2.41 (1 H, br s, OH), 1.75–1.42 (5 H, m, $CHCH_2CH_2$), 1.27 (3 H, s, Me), 0.88 (3 H, d, *J* 6.5 and 6.3, Me_AMe_BCH) and 0.87 (3 H, d, *J* 6.5 and 6.3, Me_AMe_BCH) (Found M^+ 268.1491. $C_{15}H_{24}O_2S$ requires M^+, 268.1491); *m/z* 268 (4%, M), 159 (56, M − SPh), 154 (55, $PhSCH_2OMe$), 110 (100, PhSH) and 109 (43, SPh). Thionyl chloride (2.4 ml, 16.4 mmol) was added dropwise to a solution of the above alcohol (4.4 g, 16.4 mmol) and pyridine (16 ml) in CH_2Cl_2 (200 ml) at 0 °C and stirred for 45 min. This solution was then poured into ice-cold hydrochloric acid (28 ml, 3 M) and extracted with CH_2Cl_2 (3 × 50 ml). The combined extracts 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)–CH_2Cl_2 (6 : 4) to give the *2,5-dimethyl-2-phenylsulfanylhexanal* **15** (2.7 g, 70%) as an oil; R_f [light petroleum (40–60 °C)–CH_2Cl_2] 0.60; ν_{max} (film, $CDCl_3$)/cm^{-1} 3500 (OH) and 1580 (SPh); δ_H(250 MHz, $CDCl_3$) 9.32 (1 H, s, CHO), 7.40–7.28 (5 H, m, SPh), 1.76–1.59 (2 H, m, CH_2CMeSPh), 1.51–1.41 (2 H, m, $CHCH_2$), 1.22 (3 H, s, Me), 1.18–1.04 (1 H, m, $CHCH_2$), 0.89 (3 H, d, *J* 6.5, Me_AMe_BCH) and 0.88 (3 H, d, *J* 6.5, Me_A-Me_BCH); δ_C(67.5 MHz, $CDCl_3$) 195.2, 136.6, 129.4, 128.8, 59.42, 33.0, 31.8, 28.3, 22.4, 22.2 and 17.5 (Found M^+ 207.1203. $C_{13}H_{19}S$ requires M^+ − CHO, 207.1203); *m/z* 207 (29%, M − CHO), 169 (46, $C_9H_{13}OS$), 148 (29, C_9H_8S), 127 (18, M − SPh), 110 (23, PhSH), 109 (12, SPh), 97 (55, M − CHO − SPh) and 75 (100, C_5H_{15}).

2-Methyl-4-(3,4-methylenedioxyphenyl)-2-phenylsulfanylbutanal 17

In the same way as the aldehyde **11**, the ketone **16** (1.2 g, 6.25 mmol), n-BuLi (4.16 ml, 1.5 M in hexanes, 6.25 mmol) and methoxymethyl phenyl sulfide (0.96 g, 6.25 mmol) gave, after flash chromatography on silica eluting with hexane–ether (2 : 1) *1-methoxy-1-(phenylsulfanyl)-2-methyl-4-(3,4-methylenedioxyphenyl)butan-2-ol* (1.8 g, 83%) as an oil and as a mixture (ratio 1 : 1) of diastereoisomers; R_f [hexane–ether (2 : 1)] 0.34 and 0.28, ν_{max} (film, $CDCl_3$)/cm^{-1} 3575–3300 (OH); δ_H(250 MHz, $CDCl_3$) 7.55–7.26 (5 H, m, PhS), 6.72–6.58 (3 H, m, $CH_2O_2C_6H_3$), 5.90 (2 H, s, CH_2O_2), 4.60 and 4.59 (1 H, s and s, PhSC*H*OMe), 3.44 and 3.39 (3 H, s and s, OMe), 2.70–2.59 (2 H, m, $ArCH_2CH_2$), 1.35 and 1.33 (3 H, s and s, *Me*COH) (Found M^+ − SPh, 236.1040. $C_{19}H_{22}O_4S$ requires M − SPh, 236.1049); *m/z* 236.2 (2%, M − SPh), 219 (65) and 135 (100, $CH_2O_2C_6H_3CH_2$).

The above alcohol (1.7 g, 4.9 mmol), $SOCl_2$ (0.74 ml, 9.94 mmol) and pyridine (7 ml) gave, after crystallisation from hexane–CH_2Cl_2, the aldehyde **17** (1.08 g, 70%) as needles, mp 98–99.5 °C (Found C, 68.8; H, 5.8; S, 10.1%. $C_{18}H_{18}O_3S$ requires C, 68.8; H, 5.8; S, 10.2%); ν_{max} (film, $CHCl_3$)/cm^{-1} 1710 (CO); δ_H(250 MHz, $CDCl_3$) 9.33 (1 H, s, CHO), 7.42–7.26 (5 H, m, PhS), 6.70 (1 H, d, *J* 7.8, $CH_2O_2C_6H_3$, *m* to R), 6.62 (1 H, s, $CH_2O_2C_6H_3$, *o* to O and R), 6.59 (1 H, d, *J* 7.8, $CH_2O_2C_6H_3$, *p* to O), 5.91 (2 H, s, CH_2O_2), 2.81 (1 H, ddd, *J* 13.7, 11.1 and 5.6, $ArCH_AH_B$), 2.52 (1 H, ddd, *J* 13.7, 11.1 and 6.4, $ArCH_A$-H_B), 1.94 (2 H, m, $ArCH_2CH_2$) and 1.33 (3 H, s, $MeCR_2$SPh); δ_C(62.5 MHz, $CDCl_3$) 194.8, 147.7, 145.6, 136.9, 134.9, 129.6, 129.3, 129.0, 121.1, 108.8, 108.3, 100.8, 59.1, 36.1, 30.4 and 18.0; *m/z* 314.1 (3%, M) and 135 (100, $CH_2O_2C_6H_3CH_2$).

2-Methyl-2-phenylsulfanylbutanal 20

2-Methylbutanal (4.1 g, 47.6 mmol), Et_3N (10.6 g, 104 mmol) and Me_3SiCl (6.7 g, 61.9 mmol) were heated in DMF at 80 °C for 12 h. After cooling, pentane (300 ml) was added and quickly washed with ice-cold dilute hydrochloric acid (2 × 40 ml), $NaHCO_3$ (50 ml) and brine (50 ml) before being dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue was purified by distillation to give the silyl enol ether (5.49 g, 73%) as an oil; bp 125–130 °C (lit.,[27] bp 120–134 °C).

A solution of the silyl enol ether **19** (5.49 g, 34.7 mmol) in CH_2Cl_2 (100 ml) was cooled to −78 °C and PhSCl (38.2 mmol)[14] was added. After warming to room temperature, the solvent was reduced and the residue distilled to give the aldehyde **20**[28] (6.26 g, 93%) as an oil, bp 58–61 °C/0.04 mmHg; R_f [light petroleum (40–60 °C)–ether (9 : 1)] 0.6; δ_H(250 MHz, $CDCl_3$) 9.38 (1 H, s, CHO), 7.42–7.28 (5 H, m, SPh), 7.03 (3 H, s, OAr), 4.30 (1 H, d, *J* 7.56, OH), 3.65–3.53 (2 H, m, C*H*Me and C*H*OH), 1.82–1.60 (2 H, m, CH_2Me), 1.25 (3 H, s, MeC) and 1.00 (3 H, t, *J* 7.5, CH_2Me).

2-Phenylsulfanylbutanal 23

Butanal (5 g, 69.4 mmol), Et_3N (16.8 g, 167 mmol) and Me_3SiCl (9.05 g, 83.3 mmol) were heated in DMF at 80 °C for 12 h. After cooling, pentane (300 ml) was added and quickly washed with ice-cold dilute hydrochloric acid (2 × 40 ml), $NaHCO_3$ (50 ml) and brine (50 ml) before being dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue was purified by distillation to give the silyl enol ether (7.1 g, 72%), bp 76–82 °C/180 mmHg (lit.,[29] bp 56–62 °C/75 mmHg).

The silyl enol ether (7.1 g, 50 mmol) was cooled to −78 °C and PhSCl (26 ml, 2 M solution in CH_2Cl_2) was added. After warming to room temperature, the solvent was reduced and the residue distilled to give the aldehyde **23** (8.6 g, 96%) as an oil, bp 68–72 °C/2.5 mmHg (lit.,[30] bp 105 °C/0.1 Torr).

(2*SR*,3*RS*)-2,6-Dimethylphenyl 3-hydroxy-2,4-dimethyl-4-phenylsulfanylpentanoate *anti*-28

n-BuLi (10.66 ml, 1.35 M in hexane, 13.86 mmol) was added to a stirred solution of diisopropylamine (1.9 g, 2.57 ml, 18.9 mmol) in THF (100 ml) at −78 °C and the solution was stirred for 30 minutes. A solution of 2,6-dimethylphenyl propionate **24** (2.24 g, 12.6 mmol) in THF (20 ml) was slowly added and the solution was stirred for a further 30 minutes. The aldehyde **11** (2.5 g, 13.9 mmol) in THF (10 ml) was slowly added and stirred for 30 minutes. Saturated NH_4Cl (50 ml) was added and the solution allowed to warm to room temperature and extracted with ether (3 × 100 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 (9 : 1) to give the *ester anti*-**28** (4.63 g, 94%) as an oil; R_f [light petroleum (40–60 °C)–ether (9 : 1)] 0.18; ν_{max} (film, $CDCl_3$)/cm^{-1} 1750 (CO_2); δ_H(250 MHz, $CDCl_3$) 7.56–7.32 (5 H, m, SPh), 7.08 (3 H, s, 3 × ArH), 4.13 (1 H, d, *J* 7.37, OH), 3.54–3.44 (2 H, m, C*H*OH and C*H*Me), 2.19 (6 H, s, 2 × Me), 1.57 (3 H, d, *J* 7.11, MeCH), 1.38 (3 H, s, Me) and 1.29 (3 H, s, Me); δ_C(100 MHz, $CDCl_3$) 174.60* (C=O), 147.74* (*i*-CO, Ar), 137.53 (*m*-SPh), 130.72* (*i*-*C*Me, Ar), 130.26* (*i*-SPh), 129.23 (*p*-SPh), 128.78 (*o*-SPh), 126.06 (ArH), 79.44 (CHOH), 54.43* (*C*SPh), 39.34 (*C*HMe), 25.51, 24.88, 18.54 and 16.73 (5 × Me) (Found M^+, 358.1581. $C_{21}H_{26}O_3S$ requires M, 358.1602); *m*/*z* 358.2 (40%, M), 249.2 (M − SPh), 237.2 (100, M − OAr), 151.1 (70, C_3H_6SPh), 121.1 (55, ArOH) and 110.0 (25, PhSH).

(2*RS*,3*SR*)-3-Hydroxy-2,4-dimethyl-4-phenylsulfanylpentanol *anti*-29

Lithium aluminium hydride (0.16 g, 4.36 mmol) was added to a stirred solution of ester *anti*-**28** (0.5 g, 1.46 mmol) in ether (200 ml) at 0 °C. The solution was stirred for 3 hours and poured onto an ice–brine mixture. NaOH (20 ml) was added and the solution extracted with ether (3 × 100 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 the *diol anti*-**29** (0.34 g, 97%) as an oil; R_f [ether] 0.45; ν_{max} (film, $CDCl_3$)/cm^{-1} 3500–3200 (OH); δ_H(250 MHz, $CDCl_3$) 7.59–7.30 (5 H, m, SPh), 3.80 (3 H, m, CH_2O and OH), 3.29 (1 H, dd, *J* 7.29 and 1.57, C*H*OH), 3.11 (1 H, t, *J* 7.12, CH_2OH), 2.01–1.82 (1 H, m, C*H*Me), 1.31 (3 H, s, Me), 1.25 (3 H, Me) and 0.95 (3 H, d, *J* 7.27, *Me*CH); δ_C(100 MHz, $CDCl_3$) 137.3 (*m*-SPh), 130.0* (*i*-SPh), 129.3 (*p*-SPh), 128.8 (*o*-SPh), 79.8 (CHOH), 66.7* (CH_2O), 56.6* (*C*SPh), 35.0 (*C*HMe), 26.2, 22.0 and 18.1 (3 × Me) (Found M^+, 240.1172. $C_{13}H_{20}O_2S$ requires M, 240.1183); *m*/*z* 240.1 (65%, M), 181.1 (60, M − C_3H_7O), 151.1 (100, C_3H_6SPh), 131.1 (M − SPh) and 110.0 (60, PhSH).

(3*RS*,4*RS*)-3,5,5-Trimethyl-4-(phenylsulfanyl)tetrahydrofuran *anti*-31

Toluene-*p*-sulfonic acid (2 mg, 10 µmol) was added to a stirred solution of diol *anti*-**29** (12 mg, 50 µmol) in CH_2Cl_2 (3 ml). The solution was refluxed for 5 min. The solvent was removed under vacuum and the residue was purified by flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (9 : 1) to give the tetrahydrofuran *anti*-**31** (9.9 mg, 99%) as an oil; R_f [light petroleum (40–60 °C)–ether (9 : 1)] 0.5; ν_{max} (film, $CDCl_3$)/cm^{-1} 1580 (SPh); δ_H(200 MHz, $CDCl_3$) 7.48–7.22 (5 H, m, SPh), 3.95 (1 H, t, *J* 8.2, CH_AH_BO), 3.38 (1 H, t, *J* 8.2, CH_AH_BO), 2.80 (1 H, d, *J* 10.2, CHSPh), 2.30 (1 H, m, C*H*Me), 1.26 (3 H, s, Me), 1.20 (3 H, m, Me) and 1.10 (3 H, d, *J* 6.6, *Me*CH); δ_C(50 MHz, $CDCl_3$) 136.4* (*i*-SPh), 131.7 (*m*-SPh), 128.9 (*p*-SPh), 126.8 (*o*-SPh), 84.0* (CO), 71.1* (CH_2O), 64.5 (CHSPh), 40.7 (*C*HMe), 27.5, 23.6 and 16.7 (3 × Me); *m*/*z* 222 (10%, M), 150 (30, $PhSC_3H_6$) and 109 (100, SPh).

(2*RS*,3*RS*,4*RS*)-2,6-Dimethylphenyl 2,4-dimethyl-3-hydroxy-4-phenylsulfanylhexanoate *anti*, *anti*-32 and (2*SR*,3*RS*,4*SR*)-2,6-dimethylphenyl 2,4-dimethyl-3-hydroxy-4-phenylsulfanylhexanoate *syn*, *anti*-32

In the same way as the *anti*-ester **28**, n-BuLi (7.85 ml, 1.4 M in hexane, 11 mmol), diisopropylamine (1.06 g, 1.42 ml, 10.5 mmol), 2,6-dimethylphenyl propionate **24** (1.87 g, 10.5 mmol) and the aldehyde **20** (1.94 g, 10 mmol) gave, after flash chromatography on silica eluting with CH_2Cl_2, the *ester* **32** (3.52 g, 95%) as a (ratio 90 : 10) diastereoisomeric mixture. Further purification by flash chromatography eluting with hexane–CH_2Cl_2–methanol (60 : 40 : 1) gave the *anti*, *anti-ester* **32** (3.18 g, 86%) as an oil; R_f [CH_2Cl_2] 0.5; ν_{max} (film, $CHCl_3$)/cm^{-1} 3450 (sharp OH), 1740 (C=O), 1720 (C=O, H-bonded) and 1580 (SPh); δ_H(250 MHz, $CDCl_3$) 7.56–7.31 (5 H, m, SPh), 7.08 (3 H, s, OAr), 4.30 (1 H, d, *J* 7.7, CHO*H*), 3.61 (1 H, dq, *J* 2.9 and 7.2, C*H*Me), 3.56 (1 H, dd, *J* 2.9 and 7.7, C*H*OH), 2.21 (6 H, s, 2 × Me, OAr), 1.73 (2 H, m, CH_2Me), 1.60 (3 H, d, *J* 7.2, CHMe), 1.20 (3 H, s, CMeEt) and 1.1.5 (3 H, t, *J*, $MeCH_2$); δ_C(67.5 MHz, $CDCl_3$) 174.9, 147.7, 137.3, 130.9, 130.28, 129.0, 128.8, 126.0, 78.9, 58.8, 39.1, 29.3, 21.6, 18.7, 17.0 and 8.7 (Found $M^+ - C_6H_3(Me)_2$, 251.1115. $C_{14}H_{19}O_2S$ requires $M^+ - C_8H_9$, 251.1101); *m*/*z* 251 (15%, M − C_8H_9), 165 (28), 141 (20), 122 (100, $C_6H_3(Me)_2OH$) and 110 (50, PhSH), and the (2*SR*, 3*RS*, 4*RS*) *syn*, *anti-ester* **32** (320 mg, 9%) as an oil; R_f [CH_2Cl_2] 0.5; ν_{max} (film, $CHCl_3$)/cm^{-1} 3450 (sharp OH), 1740 (C=O), 1720 (C=O, H-bonded) and 1580 (SPh); δ_H(250 MHz, $CDCl_3$) 7.64–7.25 (5 H, m, SPh), 7.15 (3 H, s, OAr), 4.15 (1 H, d, *J* 7.0, CHO*H*), 3.51 (1 H, dd, *J* 3.0 and 7.0, C*H*OH), 3.45 (1 H, dq, *J* 7.5 and 3.0, C*H*Me), 2.20 (6 H, s, 2 × Me, OAr), 1.70 (2 H, m, CH_2Me), 1.50 (3 H, s, CMeEt), 1.10 (3 H, d, *J* 7.0, CHMe) and 1.10 (3 H, t, *J* 7.0, $MeCH_2$); δ_C(67.5 MHz, $CDCl_3$) 174.4, 137.3, 130.9, 130.3, 129.0, 128.7, 125.9, 79.1, 59.2, 39.5, 28.9, 21.3, 18.7, 18.6 and 8.8 (Found $M^+ - C_6H_3(Me)_2$, 251.1115. $C_{14}H_{19}O_2S$ requires $M^+ - C_8H_9$, 251.1101); *m*/*z* 251 (22%, M − C_8H_9), 165 (18), 141 (18), 122 (100, $C_6H_3(Me)_2OH$) and 110 (60, PhSH). It is easier to separate the (2*SR*,3*RS*,4*SR*) stereoisomer from the (2*SR*,3*RS*,4*RS*) stereoisomer at the diol stage **33** by chromatography or recrystallisation.

(2*RS*,3*RS*,4*SR*)-2,4-Dimethyl-3-hydroxy-4-phenylsulfanylhexane-1,3-diol *anti*, *anti*-33

In the same way as diol *anti*-**29**, the ester *anti*, *anti*-**32** (0.76 g, 2.1 mmol) and $LiAlH_4$ (0.15 g, 4.2 mmol) in ether (20 ml) gave, after flash column chromatography on silica gel eluting with CH_2Cl_2–MeOH (50 : 1) the *diol anti*, *anti*-**33** (0.46 g, 88%) as needles, mp 87–89 °C (recrystallised from ether–hexane); R_f [CH_2Cl_2–MeOH (50 : 1)] 0.17; ν_{max} (Nujol)/cm^{-1} 3350 and 3200 (OH); δ_H(250 MHz, $CDCl_3$) 7.51–7.29 (5 H, m, SPh), 3.72 (1 H, dd, *J* 3.4 and 11.2, CH_AH_BOH), 3.63 (1 H, dd, *J* 6.3 and 11.2,

CH_AH_BOH), 3.32 (1 H, d, *J* 5.2, C*H*OH), 1.95 (1 H, m, C*H*Me), 1.73 (2 H, m, CH_2Me), 1.12 (3 H, s, MeCSPh), 1.09 (3 H, t, *J* 6.5, CH_2Me) and 0.90 (3 H, d, *J* 7.0, CHMe); δ_C(67.5 MHz, $CDCl_3$) 137.4, 130.2, 129.2, 129.1, 128.9, 128.8, 80.4, 66.9, 60.8, 27.3, 25.1, 22.7, 18.2 and 9.0 (Found M^+, 254.1323. $C_{14}H_{22}O_2S$ requires $M^+ - SPh$, 254.1335); *m*/*z* 254 (10%, M), 165 (18), 165 (100, PhSC(Me)Et), 145 (20), 110 (80, PhSH), 85 (40) and 57 (48).

(2*RS*,3*RS*,4*RS*)-2,4-Dimethyl-3-hydroxy-4-phenylsulfanylhexane-1,3-diol *anti*, *syn*-33

In the same way as diol *anti*-**29**, the ester *anti*, *syn*-**34** (2.0 g, 5.5 mmol) and $LiAlH_4$ (0.41 g, 11 mmol) in ether (200 ml) gave, after flash column chromatography on silica gel eluting with CH_2Cl_2–MeOH (50:1) the *diol anti*, *syn*-**33** (1.41 g, 94%) initially as an oil and as a mixture (ratio 79:21 4*SR*:4*RS*) of diastereoisomers. Trituration with hexane allowed the major) *diol anti*, *syn*-**33** to be isolated (0.75 g, 51%) as needles, mp 91–92 °C (recrystallised from ether–hexane); R_f [CH_2Cl_2–MeOH (50:1)] 0.13; ν_{max} (Nujol)/cm^{-1} 3450 and 3200 (OH); δ_H(250 MHz, $CDCl_3$) 7.53–7.27 (5 H, m, SPh), 3.63 (1 H, d, *J* 1.4, C*H*OH), 3.59 (1 H, dd, *J* 4.6 and 10.4, CH_AH_BOH), 3.53 (1 H, dd, *J* 4.5 and 10.4, CH_AH_BOH), 1.99 (1 H, m, C*H*Me), 1.70 (2 H, m, CH_2Me), 1.11 (3 H, s, MeCEt), 1.08 (3 H, t, *J* 8.0, CH_2Me) and 1.06 (3 H, d, *J* 6.9, CHMe); δ_C(50 MHz, $CDCl_3$) 137.13 (*m*-SPh), 129.85 (*i*-SPh), 129.03 (*p*-SPh), 128.78 (*o*-SPh), 80.16 (CHOH), 66.75 (CH_2O), 60.56 (*C*SPh), 34.77 (*C*HMe), 26.96 (CH_2), 22.42 (*Me*C), 18.08 (*Me*CH) and 8.88 (*Me*CH_2) (Found M^+, 254.1336. $C_{14}H_{22}O_2S$ requires $M^+ -$ SPh, 254.1340); *m*/*z* 254 (2%, M), 2.36 (4, M $-H_2O$), 165 (76, PhSCMeEt) and 110 (100 PhSH).

(2*SR*,3*RS*,4*SR*)-*S*-Phenyl 2,4-dimethyl-3-hydroxy-4-phenylsulfanylhexanethioate 34

S-Phenyl thiopropionate **26** (0.66 g, 4 mmol) and diisopropylethylamine (0.77 ml, 4.4 mmol) in ether (6 ml) were added dropwise to a solution of 9-BBN–OTf (8.4 ml, 0.5 M in toluene, 4.2 mmol) at 0 °C and stirred for 10 min. The aldehyde **20** (0.38 g, 2 mmol) was added and the solution was stirred for a further 3 hours. Phosphate buffer (pH 7, 10 ml), MeOH (20 ml) and H_2O_2 (30%, 10 ml) were added and stirred for 5 min. Saturated NH_4Cl (10 ml) was added and the solution was extracted with ether (3 × 80 ml). The combined organic extracts were washed ($NaHCO_3$), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with light petroleum–CH_2Cl_2 (1:1) to give a (ratio 72:28) diastereoisomeric mixture of *thioester* **34**; R_f [hexane–CH_2Cl_2 (1:1)] 0.13; ν_{max} (film, $CHCl_3$)/cm^{-1} 3450 (sharp OH), 1695 (C=O) and 1580 (SPh); δ_H(250 MHz, $CDCl_3$) 7.55–7.28 (10 H, m, 2 × SPh), 3.87 (1 H, d, *J* 5.4, *CH*OH), 3.23 and 3.13* (1 H, dq, *J* 5.4 and 6.9, *CH*Me), 1.23* and 1.16 (3 H, s, EtCMe) and 1.11 (3 H, t, *J* 5.4, *Me*CH_2) (Found $M^+ -$ SPh, 251.1099 $C_{14}H_{19}O_2S$ requires $M^+ -$ SPh, 251.1106); *m*/*z* 251 (56%, M − SPh), 165 (18), 165 (71, PhSCOEt), 110 (90, PhSH) and 85 (100).

(2*RS*,3*SR*,4*RS*)-2,4-Dimethyl-2-ethyl-3-phenylsulfanyltetrahydrofuran *anti*, *anti*-36

In the same way as the tetrahydrofuran *anti*-**31**, the diol *anti*, *anti*-**33** (0.13 g, 0.47 mmol) and toluene-*p*-sulfonic acid (18 mg, 94 µmol) in benzene (5 ml) gave the *tetrahydrofuran anti*, *anti*-**36** (0.1 g, 92%) as an oil; R_f [CH_2Cl_2] 0.55; ν_{max} (film, $CHCl_3$)/cm^{-1} 1550 (SPh); δ_H(250 MHz, $CDCl_3$) 7.48–7.18 (5 H, m, SPh), 3.98 (1 H, t, *J* 8.3, CH_AH_BO), 3.31 (1 H, t, *J* 8.3, CH_AH_BO), 2.92 (1 H, d, *J* 10.6, C*H*SPh), 2.33 (1 H, m, C*H*Me), 1.50 (2 H, m, CH_2Me), 1.20 (3 H, s, MeCO), 1.10 (3 H, d, *J* 6.5, CHMe) and 0.83 (3 H, t, *J* 7.4, CH_2Me) (Found M^+, 236.1218. $C_{14}H_{22}O_2S$ requires $M^+ -$ SPh, 236.1235); *m*/*z* 236 (24%, M), 164 (100, M − EtCOMe), 149 (30) and 110 (40, PhSH).

(2*RS*,3*SR*,4*SR*)-2,4-Dimethyl-2-ethyl-3-phenylsulfanyltetrahydrofuran *anti*, *syn*-36

In the same way as the tetrahydrofuran *anti*-**31**, the diol *anti*, *syn*-**33** (57 mg, 0.22 mmol) and toluene-*p*-sulfonic acid (8 mg, 44 µmol) in benzene (5 ml) gave the *tetrahydrofuran anti*, *syn*-**36** (53 mg, 98%) as an oil; R_f [CH_2Cl_2] 0.55; ν_{max} (film, $CHCl_3$)/cm^{-1} 1580 (SPh); δ_H(250 MHz, $CDCl_3$) 7.39–7.15 (5 H, m, SPh), 3.96 (1 H, dd, *J* 8.8 and 6.6, CH_AH_BO), 3.56 (1 H, d, *J* 8.1, C*H*SPh), 3.55 (1 H, dd, *J* 8.8 and 4.8, CH_AH_BO), 2.62 (1 H, m, C*H*Me), 1.62 (2 H, m, CH_2Me), 1.25 (3 H, s, MeCO), 1.15 (3 H, d, *J* 7.1, C*H*Me) and 0.93 (3 H, t, *J* 7.4, CH_2Me) (Found M^+, 236.1230. $C_{14}H_{20}OS$ requires M^+, 236.1235); *m*/*z* 236 (12%, M), 164 (100, M − EtCOMe), 149 (25) and 110 (45, PhSH).

(2*RS*,3*SR*,4*RS*) 2,6-Dimethylphenyl 3-hydroxy-2,4,7-trimethyl-4-phenylsulfanyloctanoate *anti*, *anti*-37 and (2*RS*,3*SR*,4*SR*) 2,6-dimethylphenyl 3-hydroxy-2,4,7-trimethyl-4-phenylsulfanyloctanoate *syn*, *anti*-37

In the same way as the *anti*-ester **28**, n-BuLi (38 ml, 1.6 M in hexane, 6 mmol), diisopropylamine (0.9 g, 6.4 mmol), 2,6-dimethylphenyl propionate **24** (1 g, 5.66 mmol) and the aldehyde **15** (1.2 g, 5.1 mmol) gave, after flash chromatography on silica eluting with hexane–EtOAc (9:1) the *anti*, *anti*- and *syn*, *anti*-ester **37** (0.88 g, 66%) as an oil and as a mixture (ratio 75:25) of diastereoisomers. Further purification by flash chromatography eluting with hexane–EtOAc (9:1) gave the *anti*, *anti-ester* **37** (0.88 g, 42%) as an oil; R_f [hexane–EtOAc (9:1)] 0.4; ν_{max} (film, CH_2Cl_2)/cm^{-1} 3450 (sharp OH), 1740–1720 (C=O) and 1580 (SPh); δ_H(250 MHz, $CDCl_3$) 7.53–7.30 (5 H, m, SPh), 7.05 (3 H, s, OAr), 4.27 (1 H, d, *J* 7.4, C*H*OH), 3.55 (2 H, dq, *J* 7.4 and 7.0, *CH*Me), 3.55 (2 H, s, OH), 2.18 (6 H, s, 2 × Me, Ar), 1.67–1.42 (5 H, m, Me_2CH and CH_2CH_2), 1.57 (3 H, d, *J* 7, *Me*CH), 1.19 (3 H, s, *Me*CSPh) and 0.92 (6 H, d, *J* 6.2, Me_2CH); δ_C(67.5 MHz, $CDCl_3$) 174.6, 147.9, 137.2, 131.2, 130.3, 128.9, 128.8, 128.7, 125.9, 79.2, 58.7, 39.5, 34.8, 33.2, 28.7, 22.7, 22.6, 22.4, 18.6 and 16.6 (Found M^+ 293.1585. $C_{17}H_{25}O_2S$ requires $M^+ - C_8H_9O$, 293.1569); *m*/*z* 293 (7%, M − C_8H_9O), 208 (48, $Me_2CHCH_2CH_2CMeSPh$), 121 (100, C_8H_9), 107 (51, C_7H_7O) and 97 (65, $Me_2CHCH_2CH_2CHMe$), and the *syn*, *anti-ester* **37** (0.51 g, 24%) as an oil; R_f [hexane–EtOAc (9:1)] 0.3; ν_{max} (film, CH_2Cl_2)/cm^{-1} 3450 (sharp OH), 1740–1720 (C=O) and 1580 (SPh); δ_H(250 MHz, $CDCl_3$) 7.56–7.32 (5 H, m, SPh), 7.05 (3 H, s, OAr), 4.14 (1 H, d, *J* 7.0, C*H*OH), 3.50 (1 H, m, OH), 3.44 (1 H, dq, *J* 7.2 and 7.0, C*H*Me), 2.20 (6 H, s, 2 × Me, Ar), 1.67–1.40 (5 H, m, Me_2CH-CH_2CH_2), 1.55 (3 H, d, *J* 7.2, *Me*CH), 1.28 (3 H, s, *Me*CAr), 0.90 (3 H, d, *J* 6, Me_ACHMe_B) and 0.88 (3 H, d, *J* 6, Me_A-$CHMe_B$); δ_C(67.5 MHz, $CDCl_3$) 174.2, 147.8, 137.3, 130.8, 130.3, 129.0, 128.7, 125.9, 79.1, 59.0, 39.6, 34.2, 33.3, 28.6, 22.7, 22.6, 21.9, 16.8 and 16.7 (Found M^+ 293.1586. $C_{17}H_{25}O_2S$ requires $M^+ - C_8H_9O$, 293.1569); *m*/*z* 293 (5%, M − C_8H_9O), 207 (48, $Me_2CHCH_2CH_2CMeSPh$), 122 (100, C_8H_9O), 110 (45, PhSH) and 109 (40, SPh).

(2*SR*,3*SR*,4*RS*)-2,4,7-Trimethyl-4-phenylsulfanyloctane-1,3-diol *anti*, *anti*-38

In the same way as diol *anti*-**29**, the ester *anti*, *anti*-**37** (0.63 g, 1.53 mmol) and $LiAlH_4$ (0.16 g, 4.2 mmol) in ether (20 ml) gave, after flash column chromatography on silica gel eluting with CH_2Cl_2–EtOAc (4:1) the *diol anti*, *anti*-**38** (0.41 g, 90%) as an oil; R_f [CH_2Cl_2–EtOAc (4:1)] 0.69; ν_{max} (CH_2Cl_2)/cm^{-1} 3600 and 3450 (OH), 1580 (SPh) and 1100 (COH); δ_H(250 MHz, $CDCl_3$) 7.48–7.28 (5 H, m, SPh), 3.71 (1 H, dd, *J* 11.2 and 3.3, CH_AH_BOH), 3.62 (1 H, dd, *J* 11.2 and 6, CH_AH_BOH), 3.25 (1 H, d, *J* 4.5, C*H*OH), 1.89 (2 H, m, MeC*H* and OH), 1.70 (1 H, m, Me_2CH), 1.51–1.24 (4 H, m, $CHCH_2CH_2$), 1.20 (3 H, s, *Me*CSPh), 0.96 (3 H, d, *J* 7.0, *Me*CH), 0.94 (3 H, d, *J* 6.7, Me_AMe_BCH), 0.88 (3 H, d, *J* 6.7, Me_AMe_BCH) (Found M^+

207.1198. $C_{13}H_{19}S$ requires $M^+ - C_4H_9O_2$, 207.1203); *m*/*z* 209 (43%, $M - C_4H_9O_2$), 110 (100, PhSH), 109 (30, SPh) and 97 (78, $Me_2CHCH{=}CHMe$).

(2*RS*,3*SR*,4*RS*)-2,4,7-Trimethyl-4-phenylsulfanyloctane-1,3-diol *anti*, *syn*-38 and (2*RS*,3*SR*,4*SR*)-2,4,7-trimethyl-4-phenylsulfanyloctane-1,3-diol *syn*, *syn*-38

In the same way as diol *anti*-**29**, the ester **39** (0.25 g, 0.63 mmol) and $LiAlH_4$ (58 mg, 1.52 mmol) in ether (20 ml) gave, after flash column chromatography on silica gel eluting with CH_2Cl_2–EtOAc (4:1) the *diol anti*, *syn*- and *syn*, *syn*-**38** (0.14 g, 76%) initially as an oil and as a mixture (ratio 57:43 4*SR*:4*SR*) of diastereoisomers; R_f [CH_2Cl_2–EtOAc (4:1)] 0.40; ν_{max} (CH_2Cl_2)/cm^{-1} 3700 and 3450 (OH), and 1585 (SPh); δ_H(250 MHz, $CDCl_3$) 7.50–7.25 (5 H, m, SPh), 3.65–3.50 (3 H, m, C*H*$_2$OH and C*H*OH), 2.38–2.00 (2 H, br s, OH), 1.99–1.24 (5 H, m, $CHCH_2CH_2$), 1.20 (3 H, s, *Me*CSPh major), 1.12 (3 H, s, *Me*CSPh minor), 1.07 (3 H, d, *J* 8.0, *Me*CH minor), 1.07 (3 H, d, *J* 8.0, *Me*CH major), 0.91–0.88 (6 H, m, *Me*$_2$CH) (Found M^+ 296.1809. $C_{17}H_{28}O_2S$ requires M^+, 296.1803); *m*/*z* 296 (1%, M), 208 (30, $M - C_4H_8O_2$), 207 (98, $M - C_4H_9O_2$), 187 (60, M − SPh), 110 (100, PhSH), 109 (27, SPh), 97 (77, $Me_2CHCH{=}CHMe$).

(2*SR*,3*RS*,4*SR*)-*S*-Phenyl 3-hydroxy-2,4,7-trimethyl-4-phenylsulfanyloctanethioate *anti*, *syn*-39 and (2*SR*,3*RS*,4*RS*)-*S*-phenyl 3-hydroxy-2,4,7-trimethyl-4-phenylsulfanyloctanethioate *syn*, *syn*-39

In the same way as the thiolester *anti*, *syn*-**34**, 9-BBN-OTf (9 ml, 0.5 M in toluene, 4.5 mmol), diisopropylethylamine (0.6 g, 0.8 ml, 4.6 mmol), *S*-phenylsulfanyl propionate **26** (0.68 g, 4.1 mmol) and the aldehyde **15** (0.49 g, 2.1 mmol) in CH_2Cl_2 (5 ml) gave, after flash chromatography on silica eluting with hexane–EtOAc (9:1) the *thioester anti*, *syn*- and *syn*, *syn*-**39** (0.44 g, 53%) as an oil and as an inseparable (ratio 57:43) mixture of diastereoisomers; R_f [CH_2Cl_2] 0.34; ν_{max} (film, CH_2Cl_2)/cm^{-1} 3450 (OH), 1690 (C=O) and 1590 (SPh); δ_H(250 MHz, $CDCl_3$) 7.55–7.28 (10 H, m, 2 × SPh), 3.87–3.82 (1 H, m, C*H*OH), 3.24–3.08 (1 H, m, MeC*H*), 2.01 (1 H, s, OH), 1.67–1.43 (5 H, m, $CHCH_2CH_2$), 1.39 (3 H, d, *J* 7.0, *Me*CH), 1.23 (3 H, s, *Me*CSPh major), 1.16 (3 H, s, *Me*CSPh minor), 0.92 (6 H, d, *J* 6.0, *Me*$_2$CH minor), 0.88 (6 H, d, *J* 6.0, *Me*$_2$CH major) (Found M^+ 293.1576. $C_{17}H_{25}O_2S$ requires $M^+ - SPh$, 293.1569); *m*/*z* 293 (70%, M − SPh), 207 (55, $Me_2CHCH_2CH_2$-CMeSPh), 127 (72, C_8H_{15}), 110 (100, PhSH) and 109 (55, SPh).

(2*SR*,3*RS*,4*SR*)-2,6-Dimethylphenyl 2,4-dimethyl-3-hydroxy-6-(3,4-methylenedioxyphenyl)-4-phenysulfanylhexanoate *anti*, *anti*-40 and (2*SR*,3*RS*,4*RS*)-2,6-dimethylphenyl 2,4-dimethyl-3-hydroxy-6-(3,4-methylenedioxyphenyl)-4-phenysulfanylhexanoate *syn*, *anti*-40

In the same way as the *anti*-ester **28**, LDA (3 ml, 1 M in THF, 3.0 mmol), 2,6-dimethylphenyl propionate **24** (0.5 g, 2.8 mmol) and the aldehyde **17** (0.83 g, 1.6 mmol) gave, after flash chromatography on silica eluting with hexane–ether (3:1) and recrystallisation from hexane the *(2RS,3RS,4SR)-ester anti*, *anti*-**40** (0.71 g, 55%) as rosettes, mp 104–105 °C; R_f [hexane–ether (3:1)] 0.54 (Found C, 70.5; H, 6.5, S, 6.8. $C_{29}H_{32}O_5S$ requires C, 70.7, H, 6.5, S, 6.5); ν_{max} (film, $CHCl_3$)/cm^{-1} 3500–3300 (OH) and 1720 (C=O); δ_H(250 MHz, $CDCl_3$) 7.57–7.31 (5 H, m, SPh), 7.07 (3 H, s, OAr), 6.75–6.64 (3 H, m, $CH_2O_2C_6$*H*$_3$), 5.91 (2 H, s, CH_2O_2), 4.40 (1 H, d, *J* 7.9, OH), 3.65–3.56 (2 H, m, C*H*OH and C*H*Me), 2.94 (1 H, ddd, *J* 17.2, 13.5 and 8.6, ArC*H*$_A$H$_B$), 2.51 (1 H, ddd, *J* 17.2, 13.5 and 8.6, ArCH$_A$*H*$_B$), 2.12 (6 H, s, *Me*$_2C_6H_5$), 1.91 (2 H, dd, *J* 8.6 and 8.4, ArCH$_2$-C*H*$_2$), 1.62 (2 H, d, *J* 7.2, *Me*CH) and 1.25 (3 H, s, *Me*CSPh); δ_C(67.5 MHz, $CDCl_3$) 175.1, 147.7, 147.6, 145.6, 137.2, 136.2, 130.7, 130.2, 129.2, 128.9, 128.8, 126.1, 121.1, 108.9, 108.2, 100.7, 79.0, 58.1, 39.2, 38.8, 30.5, 22.2, 18.8 and 16.7; *m*/*z* 492.1 (2%, M) and 135 (100, $CH_2OC_6H_3CH_2$). Further flash chromatography gave the *(2SR,3RS,4RS)-ester syn*, *anti*-**40** (0.16 g, 13%) as an oil; R_f [hexane–ether (3:1)] 0.49; ν_{max} (film, $CDCl_3$)/cm^{-1} 3500–3300 (OH) and 1720 (C=O); δ_H(250 MHz, $CDCl_3$) 7.61–7.31 (5 H, m, SPh), 7.02 (3 H, s, OAr), 6.73–6.58 (3 H, m, $CH_2O_2C_6$*H*$_3$), 5.91 (2 H, s, CH_2O_2), 4.32 (1 H, d, *J* 6.9, OH), 3.58–3.48 (2 H, m, C*H*OH and C*H*Me), 2.93 (1 H, td, *J* 13.1 and 4.0, ArC*H*$_A$H$_B$), 2.72 (1 H, td, *J* 13.1 and 5.2, ArCH$_A$*H*$_B$), 2.07 (6 H, s, *Me*$_2C_6H_5$), 1.87 (2 H, dd, *J* 8.6 and 8.4, ArCH$_2$C*H*$_2$), 1.57 (2 H, d, *J* 7.1, *Me*CH) and 1.37 (3 H, s, *Me*CSPh) (Found M^+, 492.1953. $C_{29}H_{32}O_5S$ requires M, 492.1971); *m*/*z* 492.1 (2%, M) and 205 (100).

(2*RS*,3*RS*,4*SR*)-2,4-Dimethyl-6-(3,4-methylenedioxyphenyl)-4-phenylsulfanylhexane-1,3-diol *anti*, *anti*-41

In the same way as the diol *anti*-**29**, the ester *anti*, *anti*-**40** (0.37 g, 0.75 mmol) and $LiAlH_4$ (35 mg, 1.31 mmol) in ether (10 ml) gave, after flash column chromatography on silica gel eluting with CH_2Cl_2–MeOH (95:5) the *diol anti*, *anti*-**41** (0.26 g, 92%) as an oil; R_f [CH_2Cl_2–MeOH (95:5)] 0.55; ν_{max} (Nujol)/cm^{-1} 3450–3200 (OH) and 1220 (OCH_2OAr); δ_H(250 MHz, $CDCl_3$) 7.54–7.31 (5 H, m, SPh), 6.75–6.63 (3 H, m, $O_2C_6H_3R$), 5.91 (2 H, s, CH_2O_2), 3.71 (1 H, dd, *J* 11.2 and 3.3, C*H*$_A$H$_B$OH), 3.64 (1 H, td, *J* 11.2 and 6.3, ArC*H*$_A$H$_B$OH), 3.35 (1 H, d, *J* 5.2, C*H*OH), 2.88 (1 H, ddd, *J* 13.5, 11.0 and 7.6, ArC*H*$_A$H$_B$), 2.72 (1 H, ddd, *J* 13.5, 11.0 and 6.7, ArCH$_A$*H*$_B$), 2.02–1.85 (3 H, m, MeC*H* and ArCH$_2$C*H*$_2$), 1.20 (3 H, s, *Me*CSPh) and 0.93 (3 H, d, *J* 7.0, *Me*CH) (Found M^+, 374.1525. $C_{21}H_{26}O_4S$ requires M, 374.1552); *m*/*z* 374.1 (1%, M) and 135 (100, $CH_2O_2C_6H_3CH_2$).

(2*RS*,3*RS*,4*RS*)-2,4-Dimethyl-6-(3,4-methylenedioxyphenyl)-4-phenylsulfanylhexane-1,3-diol *syn*, *anti*-41

In the same way as the diol *anti*-**29**, the ester *syn*, *anti*-**40** (0.14 g, 0.28 mmol) and $LiAlH_4$ (35 mg, 1.31 mmol) in ether (10 ml) gave, after flash column chromatography on silica gel eluting with CH_2Cl_2–MeOH (95:5) the *diol syn*, *anti*-**41** (83 mg, 76%) as an oil; R_f [CH_2Cl_2–MeOH (95:5)] 0.55; ν_{max} (Nujol)/cm^{-1} 3450 and 3200 (OH) and 1220 (OCH_2OAr); δ_H(250 MHz, $CDCl_3$) 7.56–7.32 (5 H, m, SPh), 6.70 (1 H, d, *J* 8.4, $O_2C_6H_3R$, *m* to R), 6.60 (1 H, s, $O_2C_6H_3R$, *o* to O and R), 6.58 (1 H, d, *J* 8.4, $O_2C_6H_3R$, *m* to O), 5.91 (2 H, s, CH_2O_2), 3.76 (1 H, dd, *J* 11.2 and 3.1, C*H*$_A$H$_B$OH), 3.64 (1 H, td, *J* 13.0 and 4.1, ArC*H*$_A$H$_B$OH), 3.80 (1 H, br s, OH), 3.31 (1 H, d, *J* 4.4, C*H*OH), 3.06 (1 H, d, *J* 13.0 and 4.1, ArC*H*$_A$H$_B$), 2.71 (1 H, td, *J* 13.0 and 4.1, ArCH$_A$*H*$_B$), 1.96–1.88 (1 H, m, MeC*H*), 1.73 (1 H, td, *J* 13.3 and 4.1, ArCH$_2$C*H*$_A$H$_B$), 1.79–1.70 (1 H, br s, OH), 1.65 (1 H, td, *J* 13.3 and 4.1, ArCH$_2$CH$_A$*H*$_B$), 1.29 (3 H, s, *Me*CSPh), 0.95 (3 H, d, *J* 7.1, *Me*CH) (Found M^+, 374.1550. $C_{21}H_{26}O_4S$ requires M, 374.1552); *m*/*z* 374.1 (2%, M) and 135 (100, $CH_2O_2C_6H_3CH_2$).

(2*RS*,3*SR*,4*RS*)-2,4-Dimethyl-2-(3-methylbutyl)-3-phenylsulfanyltetrahydrofuran *anti*, *anti*-42

In the same way as the tetrahydrofuran *anti*-**31**, the diol *anti*, *anti*-**38** (83 mg, 0.28 mmol) and toluene-*p*-sulfonic acid (14 mg, 80 µmol) in benzene (4 ml) gave the *tetrahydrofuran anti*, *anti*-**42** (62 mg, 80%) as an oil; R_f [CH_2Cl_2] 0.72; ν_{max} (film, $CHCl_3$)/cm^{-1} 1550 (SPh); δ_H(250 MHz, $CDCl_3$) 7.47–7.21 (5 H, m, SPh), 3.97 (1 H, dd, *J* 8.7 and 8.2, C*H*$_A$H$_B$O), 3.32 (1 H, t, *J* 8.7, CH$_A$*H*$_B$O), 2.92 (1 H, d, *J* 10.6, C*H*SPh), 2.43 (1 H, m, C*H*Me), 1.52–1.25 (5 H, m, $CHCH_2CH_2$), 1.21 (3 H, s, MeCO), 1.10 (3 H, d, *J* 6.5, CHMe), 0.76 (3 H, d, *J* 6.5, *Me*$_A$Me$_B$CH) and 0.75 (3 H, d, *J* 6.5, Me$_A$*Me*$_B$CH); δ_C(67.5 MHz, $CDCl_3$) 135.8, 132.4, 128.9, 127.2, 85.3, 71.9, 62.5, 40.7, 38.2, 32.5, 28.4, 22.7, 22.5, 22.5 and 16.1 (Found M^+, 278.1699. $C_{17}H_{26}OS$ requires M^+, 278.1698); *m*/*z* 278 (5%, M), 164 (100, $M - C_7H_{14}O$) and 110 (45, PhSH).

(2*SR*,3*SR*,4*RS*)-2,4-Dimethyl-2-(3-methylbutyl)-3-phenylsulfanyltetrahydrofuran *syn*, *anti*-42

In the same way as the tetrahydrofuran *anti*-**31**, the diol *syn*, *anti*-**38** (44 mg, 0.15 mmol) and toluene-*p*-sulfonic acid (7.5 mg, 40 µmol) in benzene (3 ml) gave the *tetrahydrofuran anti*, *syn*-**42** (32 mg, 75%) as an oil; R_f [CH_2Cl_2] 0.67; ν_{max} (film, $CHCl_3$)/cm^{-1} 1550 (SPh); δ_H(250 MHz, $CDCl_3$) 7.47–7.21 (5 H, m, SPh), 3.92 (1 H, t, *J* 8.4, C$H_A$$H_B$O), 3.36 (1 H, t, *J* 8.4, CH_A-H_BO), 2.90 (1 H, d, *J* 9.6, C*H*SPh), 2.39–2.38 (1 H, m, C*H*Me), 1.62–1.42 (3 H, m, C*H*CH_2CH_2), 1.37–1.17 (3 H, m, CHC$H_2$$CH_2$), 1.14 (3 H, s, MeCO), 1.10 (3 H, d, *J* 6.5, CHMe), 0.90 (3 H, d, *J* 6.5, $Me_A$$Me_B$CH) and 0.89 (3 H, d, *J* 6.5, $Me_A$$Me_B$CH); δ_C(67.5 MHz, $CDCl_3$) 136.1, 132.0, 128.9, 127.0, 84.7, 27.4, 64.7, 41.07, 33.6, 32.5, 28.6, 25.1, 22.8, 22.7 and 16.7 (Found M^+, 278.1724. $C_{17}H_{26}OS$ requires M^+, 278.1698); *m*/*z* 278 (5%, M), 164 (100, M − $C_7H_{14}O$) and 110 (53, PhSH).

(2*RS*,3*SR*,4*SR*)-2,4-Dimethyl-2-(3-methylbutyl)-3-phenylsulfanyltetrahydrofuran *anti*, *syn*-42 and (2*SR*,3*SR*,4*SR*)-2,4-dimethyl-2-(3-methylbutyl)-3-phenylsulfanyltetrahydrofuran *syn*, *syn*-42

In the same way as the tetrahydrofuran *anti*-**31**, a diastereoisomeric mixture (57:43) of the diol *anti*, *syn*- and *syn*, *syn*-**38** (50 mg, 0.17 mmol) and toluene-*p*-sulfonic acid (7.5 mg, 40 µmol) in benzene (4 ml) gave the *tetrahydrofuran anti*, *syn*- and *syn*, *syn*-**42** (34 mg, 73%) as an oil and as a mixture (ratio 57:43) of diastereoisomers; R_f [CH_2Cl_2] 0.70; ν_{max} (film, $CHCl_3$)/cm^{-1} 1550 (SPh); δ_H(250 MHz, $CDCl_3$) 7.39–7.16 (10 H, m, SPh), 4.05 (1 H, dd, *J* 8.8 and 7.5, C$H_A$$H_B$O minor), 3.97 (1 H, dd, *J* 8.8 and 6.7, C$H_A$$H_B$O major), 3.56–3.50 (3 H, m, $CH_A$$H_B$O minor, $CH_A$$H_B$O major and C*H*SPh major), 3.42 (1 H, dd, *J* 8.8 and 6.7, C*H*SPh minor), 2.81–2.53 (2 H, m, C*H*Me major and C*H*Me minor), 1.61–1.30 (10 H, m, $CHCH_2CH_2$ major and $CHCH_2CH_2$ minor), 1.27 (3 H, s, MeCO minor), 1.24 (3 H, s, MeCO major), 1.15 (3 H, d, *J* 7.1, CHMe major), 1.12 (3 H, d, *J* 6.9, CHMe minor), 0.89 (3 H, d, *J* 6.5, $Me_A$$Me_B$CH minor), 0.88 (3 H, d, *J* 6.5, $Me_A$$Me_B$CH minor) and 0.84 (6 H, d, *J* 6.5, $Me_A$$Me_B$CH major and $Me_A$$Me_B$CH major) (Found M^+, 278.1698. $C_{17}H_{26}OS$ requires M^+, 278.1698); *m*/*z* 278 (8%, M), 164 (100, M − $C_7H_{14}O$) and 110 (45, PhSH).

(2*SR*,3*RS*,4*SR*)-2,4-Dimethyl-2-[2-(3,4-methylenedioxyphenyl)-ethyl]-3-phenylsulfanyltetrahydrofuran *anti*, *anti*-43

In the same way as the tetrahydrofuran *anti*-**31**, the diol *anti*, *anti*-**41** (20 mg, 0.53 µmol) and toluene-*p*-sulfonic acid (2 mg, 10.5 µmol) in benzene (5 ml) gave the *tetrahydrofuran anti*, *anti*-**43** (18 mg, 95%) as an oil; R_f [hexane–ether (1:1)] 0.26; ν_{max} (film, $CHCl_3$)/cm^{-1} 1250 (OCH_2OAr); δ_H(250 MHz, $CDCl_3$) 7.50–7.22 (5 H, m, SPh), 6.66 (1 H, d, *J* 8.4, $O_2C_6H_3R$, *m* to R), 6.46 (1 H, s, $O_2C_6H_3R$, *o* to O and R), 6.44 (1 H, d, *J* 8.4, $O_2C_6H_3R$, *m* to O), 5.88 (2 H, s, CH_2O_2), 4.02 (1 H, t, 8.7, C$H_A$$H_B$OR), 3.37 (1 H, t, *J* 8.7, $CH_A$$H_B$OR), 2.98 (1 H, d, *J* 10.7, PhSCH), 2.61–2.32 (3 H, m, $ArCH_2$ and MeC*H*CH-SPh), 1.82–1.57 (2 H, m, $ArCH_2CH_2$), 1.26 (3 H, s, *Me*CR_2OR), 1.14 (3 H, d, *J* 6.5, *Me*CH) (Found M^+, 356.1458. $C_{21}H_{24}O_3S$ requires M, 356.1446); *m*/*z* 356.1 (40%, M), 192 (100, M − $PhSCHCH_2CHMe$), 164 (80, $PhSCHCH_2CHMe$) and 135 (100, $CH_2O_2C_6H_3CH_2$).

(2*RS*,3*RS*,4*SR*)-2,4-Dimethyl-2-[2-(3,4-methylenedioxyphenyl)-ethyl]-3-phenylsulfanyltetrahydrofuran *syn*, *anti*-43

In the same way as the tetrahydrofuran *anti*-**31**, the diol *syn*, *anti*-**41** (68 mg, 0.18 mmol) and toluene-*p*-sulfonic acid (2 mg, 10.5 µmol) in benzene (5 ml) gave the *tetrahydrofuran syn*, *anti*-**43** (62 mg, 96%) as an oil; R_f [hexane–ether (2:1)] 0.45; ν_{max} (film, $CHCl_3$)/cm^{-1} 1250 (OCH_2OAr); δ_H(250 MHz, $CDCl_3$) 7.47–7.23 (5 H, m, SPh), 6.73 (1 H, d, *J* 7.9, $O_2C_6H_3R$, *m* to R), 6.72 (1 H, s, $O_2C_6H_3R$, *o* to O and R), 6.72 (1 H, dd, *J* 7.9 and 1.5, $O_2C_6H_3R$, *m* to O), 5.91 (2 H, s, CH_2O_2), 3.99 (1 H, t, *J* 8.5, C$H_A$$H_B$OR), 3.42 (1 H, t, *J* 8.5, $CH_A$$H_B$OR), 2.94 (1 H, d, *J* 10.8, PhSCH), 2.75–2.60 (2 H, m, $ArCH_2$), 2.46–2.42 (1 H, m, MeC*H*CHSPh), 1.95–1.73 (2 H, m, $ArCH_2CH_2$), 1.20 (3 H, s, *Me*CR_2OR), 1.13 (3 H, d, *J* 6.5, *Me*CH) (Found M^+, 356.1458. $C_{21}H_{24}O_3S$ requires M, 356.1450); *m*/*z* 356.1 (35%, M), 192 (100, M − $PhSCHCH_2CHMe$), 164 (80, $PhSCHCH_2CHMe$), 135 (60, $CH_2O_2C_6H_3CH_2$) and 110 (50, PhSH).

(2*RS*,3*SR*,4*RS*)-2,6-Dimethylphenyl 2,6-dimethyl-3-hydroxy-4-phenylsulfanylheptanoate *anti*, *anti*-44 and (2*RS*,3*SR*,4*SR*)-2,6-dimethylphenyl 2,6-dimethyl-3-hydroxy-4-phenylsulfanylheptanoate *syn*, *anti*-44

In the same way as the *anti*-ester **28**, n-BuLi (3.65 ml, 1.5 M in hexane, 5.5 mmol), diisopropylamine (0.77 g, 1.03 ml, 5.5 mmol), 2,6-dimethylphenyl propionate **24** (0.95 g, 5.3 mmol) and the aldehyde **13** (1.04 g, 5.0 mmol) gave, after flash chromatography on silica eluting with CH_2Cl_2, the *ester* **44** (3.52 g, 95%) as a mixture (ratio 67:33) of diastereoisomers. Further purification by flash chromatography eluting with hexane–ether (4:1) gave a mixture of diastereoisomers (ratio 70:30) of the *esters* **44** (0.51 g, 26%) as an oil. HPLC separation eluting with hexane–ether (6:1) gave the ester *anti*, *anti*-**44** (0.33 g, 17%) as crystals, mp 86–87 °C; R_f [hexane–ether (4:1)] 0.37; ν_{max} (film, CH_2Cl_2)/cm^{-1} 3550 (OH), 2930 (CH), 1745 (CO) and 1580 (SPh); δ_H(250 MHz, $CDCl_3$) 7.45–7.26 (5 H, m, SPh), 7.03 (3 H, s, OAr), 3.85 (1 H, dd, *J* 8.7 and 3.3, C*H*OH), 3.32 (1 H, dt, *J* 11.4 and 3.5, C*H*SPh), 3.10 (1 H, dq, *J* 8.7 and 7.2, C*H*Me), 2.12 (6 H, s, OAr, 2 × Me), 2.10–2.05 (1 H, m, C*H*Me_2), 1.64–1.43 (2 H, m, CH_2), 1.27 (3 H, d, *J* 7.2, *Me*CH-CO), 0.99 (3 H, d, *J* 6.4, C$Me_A$$Me_B$) and 0.97 (3 H, d, *J* 6.4, C$Me_A$$Me_B$); δ_C(62.5 MHz, $CDCl_3$) 173.2, 147.9, 133.7, 132.6, 130.2, 129.2, 128.5, 127, 125.8, 74.0, 51.3, 42.3, 36.2, 25.4, 23.8, 21.2, 16.3 and 14.2 (Found: C, 71.6; H, 8.1, S, 8.5%; M^+ 386.1927. $C_{23}H_{30}O_3S$ requires C, 71.5, H, 7.8, S, 8.3%; M, 386.1915); and the *ester syn*, *anti*-**44** (87.4 mg, 9%) as crystals, mp 67–68 °C; R_f [hexane–ether (4:1)] 0.37; ν_{max} (film, CH_2Cl_2)/cm^{-1} 3550 (OH), 2930 (CH), 1745 (CO) and 1580 (SPh); δ_H(250 MHz, $CDCl_3$) 7.49–7.23 (5 H, m, SPh), 7.05 (3 H, s, OAr), 3.98 (1 H, dd, *J* 6.5 and 5.2, C*H*OH), 3.43 (1 H, quintet, *J* 5.0, C*H*SPh), 3.29 (1 H, quintet, *J* 7.0, C*H*Me), 2.78 (1 H, br s, OH), 2.11 (6 H, s, OAr, 2 × Me), 2.09–2.03 (1 H, m, C*H*Me_2), 1.63–1.54 (2 H, m, CH_2), 1.43 (3 H, d, *J* 7.1, *Me*CHCO), 0.98 (3 H, d, *J* 6.6, C$Me_A$$Me_B$) and 0.94 (3 H, d, *J* 6.6, C$Me_A$$Me_B$); δ_C(62.5 MHz, $CDCl_3$) 173.1, 147.9, 133.4, 132.4, 130.0, 129.1, 128.7, 127.4, 126.0, 72.6, 50.7, 41.7, 37.2, 25.5, 23.8, 21.2, 16.5 and 13.4 (Found M^+, 386.1906. $C_{23}H_{30}O_3S$ requires M, 386.1916); *m*/*z* 386.1 (5%, M), 265 (100), 209 (22), 155 (41), 122 (72) and 109 (43).

(2*RS*,3*RS*,4*RS*)-2,6-Dimethyl-3-hydroxy-4-phenylsulfanylheptane-1,3-diol *anti*, *anti*-45

In the same way as the diol *anti*-**29**, the ester *anti*, *anti*-**44** (0.1 g, 0.26 mmol) and $LiAlH_4$ (18 mg, 0.48 mmol) in ether (10 ml) gave, after flash column chromatography on silica gel eluting with ether–hexane (5:2), the *diol anti*, *anti*-**45** (69 mg, 99%) as a solid at or very near room temperature; R_f [ether–hexane (5:2)] 0.32; ν_{max} (CH_2Cl_2)/cm^{-1} 3520 (OH), 2930 (CH) and 1590 (SPh); δ_H(250 MHz, $CDCl_3$) 7.41–7.27 (5 H, m, SPh), 3.50 (2 H, d, *J* 5.8, CH_2OH), 3.41 (1 H, dd, *J* 9.6 and 2.1, C*H*OH), 3.34 (1 H, ddd, *J* 8.8, 3.4 and 2.2, CHSPh), 2.65 (2 H, br s, 2 × OH), 1.89 (2 H, m, C*H*MeCH_2OH and C*H*Me_2), 1.57–1.34 (2 H, m, CH_2CHMe_2), 0.98 (3 H, d, *J* 6.7, C$Me_A$$Me_B$), 0.97 (1 H, d, *J* 6.5, C$Me_A$$Me_B$) and 0.70 (3 H, d, *J* 7.0, CH*Me*CH_2OH); δ_C(62.5 MHz, $CDCl_3$) 134.8, 132.0, 129.1, 127.3, 77.2, 68.4, 52.0, 36.5, 35.4, 25.5, 23.8, 21.1 and 12.9 (Found M^+, 268.1499. $C_{15}H_{24}O_2S$ requires M, 268.1498); *m*/*z* 268.1 (16%, M), 180 (84), 137 (35), 123 (100, $PhSCH_2$) and 110 (79, PhSH).

(2*RS*,3*RS*,4*SR*)-2,6-Dimethyl-3-hydroxy-4-phenylsulfanylheptane-1,3-diol *anti*, *syn*-45

In the same way as the diol *anti*-**29**, the ester *anti*, *syn*-**46** (0.13 g, 0.34 mmol) and $LiAlH_4$ (37 mg, 0.98 mmol) in ether (10 ml) gave, after flash column chromatography on silica gel eluting with CH_2Cl_2–ether (6:1), the *diol anti*, *syn*-**45** (92 mg, 99%) as prisms, mp 67–70 °C; R_f [CH_2Cl_2–ether (6:1)] 0.30; ν_{max} (CH_2Cl_2)/cm^{-1} 3610 and 3460 (OH), 2850 (CH) and 1590 (SPh); δ_H(250 MHz, $CDCl_3$) 7.48–7.27 (5 H, m, SPh), 3.74 (1 H, dd, *J* 10.8 and 4.0, CH_AH_BOH), 3.64 (1 H, dd, *J* 10.8 and 5.9, CH_AH_BOH), 3.54 (1 H, dd, *J* 9.5 and 2.8, C*H*OH), 3.04 (1 H, dt, *J* 5.2 and 9.5, CHSPh), 2.22–2.11 (1 H, m) and 1.89–1.81 (1 H, m) (C*H*MeCH$_2$OH and C*H*Me$_2$), 1.33–1.16 (2 H, m, C*H*$_2$CHMe$_2$), 0.98 (3 H, d, *J* 7.0, CMe_AMe_B), 0.91 (1 H, d, *J* 6.7, CMe_AMe_B) and 0.95 (3 H, d, *J* 6.6, CH*Me*CH$_2$OH); δ_C(62.5 MHz, $CDCl_3$) 133.8, 132.2, 128.9, 127.9, 74.2, 67.5, 54.5, 39.3, 36.6, 25.3, 23.6, 21.1 and 8.8 (Found M^+, 268.1518. $C_{15}H_{24}O_2S$ requires M, 268.1498); *m*/*z* 268.1 (15%, M), 180 (75), 137 (41), 123 (100, PhSCH$_2$) and 110 (67, PhSH).

(2*SR*,3*SR*,4*SR*)-2,6-Dimethyl-3-hydroxy-4-phenylsulfanylheptane-1,3-diol *syn*, *anti*-45

In the same way as the diol *anti*-**29**, the ester *syn*, *anti*-**44** (0.1 g, 0.26 mmol) and $LiAlH_4$ (18 mg, 0.48 mmol) in ether (10 ml) gave, after flash column chromatography on silica gel eluting with ether–hexane (2:1), the *diol syn*, *anti*-**45** (48 mg, 69%) as prisms, mp 55–57 °C; R_f [ether–hexane (2:1)] 0.33; ν_{max} (CH_2Cl_2)/cm^{-1} 3730 (OH), 3600 (OH), 2900 (CH) and 1585 (SPh); δ_H(250 MHz, $CDCl_3$) 7.44–7.19 (5 H, m, SPh), 3.68 (1 H, t, *J* 5.3, C*H*OH), 3.62 (2 H, d, *J* 4.7, C*H*$_2$OH), 3.34 (1 H, quintet, *J* 4.9, CHSPh), 2.10–1.98 (2 H, m, C*H*MeCH$_2$OH and C*H*Me$_2$), 1.57–1.34 (4 H, m, C*H*$_2$CHMe$_2$ and 2 × OH), 0.96 (3 H, d, *J* 7.0, CMe_AMe_B), 0.95 (3 H, d, *J* 6.6, CMe_AMe_B) and 0.91 (3 H, d, *J* 6.7, CH*Me*CH$_2$OH); δ_C(62.5 MHz, $CDCl_3$) 134.8, 132.0, 129.0, 127.0, 74.9, 66.6, 56.8, 52.0, 38.4, 25.4, 23.7, 21.3 and 11.6 (Found M^+, 268.1511. $C_{15}H_{24}O_2S$ requires M, 268.1498); *m*/*z* 268.1 (11%, M), 180 (53), 137 (37), 123 (100, PhSCH$_2$) and 110 (69, PhSH).

(2*RS*,3*RS*,4*SR*)-*S*-Phenyl 2,6-dimethyl-3-hydroxy-4-phenylsulfanylheptanethioate *anti*, *syn*-46

In the same way as the thioester *anti*, *syn*-**34**, 9-BBN–OTf (21 ml, 0.5 M in toluene, 10.5 mmol), diisopropylethylamine (1.42 g, 1.95 ml, 11 mmol), *S*-phenyl thiopropionate **26** (1.67 g, 10 mmol) and the aldehyde **13** (1.04 g, 5 mmol) in CH_2Cl_2 (25 ml) gave, after flash chromatography on silica eluting with CH_2Cl_2, the *thioester anti*, *syn*-**46** (0.6 g, 37%) as crystals, mp 86–87 °C; R_f [CH_2Cl_2] 0.34; ν_{max} (film, CH_2Cl_2)/cm^{-1} 3610 (OH), 2910 (CH), 1690 (C=O) and 1585 (SPh); δ_H(250 MHz, $CDCl_3$) 7.52–7.23 (10 H, m, 2 × SPh), 3.92 (1 H, dd, *J* 6.3 and 5.0, C*H*OH), 3.23 (1 H, dt, *J* 4.8 and 7.5, CHSPh), 3.07 (1 H, quintet, *J* 6.9, C*H*Me), 2.59 (1 H, br s, OH), 1.99 (1 H, m, *J* 6.7, C*H*Me$_2$), 1.49 (1 H, d, *J* 7.4, CH_AH_B), 1.46 (1 H, d, *J* 7.0, CH_AH_B), 1.35 (3 H, d, *J* 7.0, *Me*CH), 0.89 (3 H, d, *J* 6.7, CMe_AMe_B) and 0.88 (3 H, d, *J* 6.5, CMe_AMe_B); δ_C(67.5 MHz, $CDCl_3$) 200.3, 134.4, 133.0, 132.9, 129.3, 129.1, 127.6, 127.4, 73.7, 53.4, 51.3, 41.6, 25.3, 22.7, 22.0 and 13.5 (Found $M^+ - SPh$, 265.1256. $C_{15}H_{21}O_2S$ requires $M^+ - SPh$, 265.1262); *m*/*z* 265.1 (100%, M − SPh), 209 (32), 123 (64), 110 (67, PhSH) and 109 (56, PhS) (Found: C, 67.2, H, 7.2, S, 17.3%. $C_{21}H_{26}O_2S_2$ requires C, 67.3, H, 7.9, S, 17.1%).

(2*SR*,3*RS*,4*SR*) 2,6-Dimethylphenyl 3-hydroxy-2-methyl-4-phenylsulfanylhexanoate *anti*, *anti*-47 and (2*SR*,3*RS*,4*RS*) 2,6-dimethylphenyl 3-hydroxy-2-methyl-4-phenylsulfanylhexanoate *syn*, *anti*-47

In the same way as the ester *anti*-**28**, n-BuLi (7.85 ml, 1.4 M in hexane, 11 mmol), diisopropylamine (1.06 g, 1.42 ml, 10.5 mmol), 2,6-dimethylphenyl propionate **24** (1.87 g, 10.5 mmol) and the aldehyde **23** (1.8 g, 10 mmol) gave, after flash chromatography on silica eluting with CH_2Cl_2–MeOH (200:1), a mixture (ratio 71:29) of diastereoisomeric *esters* **47** (2.87 g, 80%). Further purification by HPLC eluting with CH_2Cl_2–MeOH (200:1) gave the major (2*SR*,3*RS*,4*SR*) ester *anti*, *anti*-**47** (1.72 g, 49%) as an oil; t_R [CH_2Cl_2–MeOH (200:1)] 8.8 min; ν_{max} (film, $CDCl_3$)/cm^{-1} 3500 (OH), 1740 (C=O), 1710 (C=O, H-bonded) and 1580 (SPh); δ_H(250 MHz, $CDCl_3$) 7.47–7.26 (5 H, m, SPh), 7.05 (3 H, s, OAr), 3.84 (1 H, dd, *J* 7.1 and 5.1, C*H*OH), 3.27 (1 H, quintet, *J* 7.2, C*H*Me), 3.23 (1 H, m, C*H*SPh), 2.12 (6 H, s, 2 × Me; OAr), 1.89 (1 H, ddq, *J* 14.6, 3.3 and 7.3, C*H*Me), 1.65 (1 H, ddq, *J* 14.6, 9.6 and 7.3, C*H*Me), 1.38 (3 H, d, *J* 7.2, C*H*Me) and 1.19 (3 H, t, *J* 7.3, CH$_2$Me); δ_C(67.5 MHz, $CDCl_3$) 173.4, 147.9, 134.2, 132.4, 130.2, 129.1, 128.6, 127.4, 125.8, 74.6, 55.32, 42.2, 21.5, 16.3, 14.9 and 11.8 (Found M^+ 358.1609. $C_{21}H_{26}O_3S$ requires M^+, 358.1596); *m*/*z* 358 (2%, M), 237 (73, M − OAr), 191 (18), 181 (16, M − MeCHCO$_2$Ar), 127 (100) and 122 (80, ArOH). The (2*SR*,3*RS*,4*RS*)-*syn*, *anti*-ester **47** was isolated (0.77 g, 20%) as an oil; t_R [CH_2Cl_2–MeOH (200:1)] 10.6 min; ν_{max} (film, $CDCl_3$)/cm^{-1} 3450 (OH), 1740 (C=O), 1710 (C=O, H-bonded) and 1580 (SPh); δ_H(250 MHz, $CDCl_3$) 7.49–7.07 (8 H, m, SPh and OAr), 4.06 (1 H, t, *J* 6.1, C*H*OH), 3.40 (1 H, dq, *J* 6.0 and 7.1, C*H*Me), 3.27 (1 H, ddd, *J* 6.1, 3.3 and 9.8, C*H*SPh), 2.15 (6 H, s, 2 × Me; OAr), 2.02 (1 H, ddq, *J* 14.6, 7.3 and 3.3, CH_AH_B-Me), 1.62 (1 H, ddq, *J* 14.6, 9.8 and 7.3, CH_AH_BMe), 1.41 (3 H, d, *J* 7.1, C*H*Me) and 1.19 (3 H, t, *J* 7.3, CH$_2$Me); δ_C(67.5 MHz, $CDCl_3$) 173.5, 147.8, 133.9, 131.9, 129.8, 129.0, 128.6, 127.1, 125.9, 72.43, 54.0, 41.78, 21.9, 16.3, 12.5 and 11.6 (Found M^+ 358.1602. $C_{21}H_{26}O_3S$ requires M^+, 358.1596); *m*/*z* 358 (5%, M), 237 (73, M − OAr), 191 (12), 181 (26, M − MeCHCO$_2$Ar), 127 (100) and 122 (70, ArOH).

(2*RS*,3*RS*,4*SR*)-2-Methyl-4-phenylsulfanylhexane-1,3-diol *anti*, *anti*-48

In the same way as diol *anti*-**29**, the ester *anti*, *anti*-**47** (0.7 g, 1.94 mmol) and $LiAlH_4$ (0.14 g, 3.88 mmol) in ether (200 ml) gave, after flash column chromatography on silica gel eluting with CH_2Cl_2–MeOH (100:1), the *diol anti*, *anti*-**48** (0.32 g, 96%) initially as an oil and after recrystallisation from ether–hexane as needles, mp 63–63.5 °C; R_f [CH_2Cl_2–MeOH (50:1)] 0.14; ν_{max} (Nujol)/cm^{-1} 3370, 3310 (OH) and 1580 (SPh) (Found C, 64.8; H, 8.2; S 13.4. $C_{13}H_{20}O_2S$ requires C, 65.0, H, 8.3; S 13.3); δ_H(250 MHz, $CDCl_3$) 7.42–7.24 (5 H, m, SPh), 3.55 (2 H, distorted ABX system, *J* 4.5, 6.9 and 10.9, CH_AH_BO), 3.45 (1 H, dd, *J* 9.2 and 2.6, C*H*OH), 3.20 (1 H, dt, *J* 10.4 and 2.6, C*H*SPh), 1.97 (1 H, m, C*H*Me), 1.82 (1 H, ddq, *J* 14.8, 10.4 and 7.4, CH_AH_BMe), 1.52 (1 H, ddq, *J* 14.8, 10.4 and 7.4, CH_AH_B-Me), 1.16 (3 H, t, *J* 7.4, MeCH$_2$) and 0.74 (3 H, d, *J* 7.0, CH*Me*); δ_C(67.5 MHz, $CDCl_3$) 134.3, 132.0, 129.1, 127.3, 77.42, 68.2, 56.3, 36.8, 20.4, 13.3 and 12.5 (Found M^+ 240.1175. $C_{13}H_{20}O_2S$ requires M^+, 240.1179); *m*/*z* 240 (20%, M), 152 (100, n-PrSPh), 123 (40) and 110 (75, PhSH).

(2*SR*,3*RS*,4*SR*)-2-Methyl-4-phenylsulfanylhexane-1,3-diol *anti*, *syn*-48

In the same way as diol *anti*-**29**, the ester *anti*, *syn*-**49** (0.26 g, 0.76 mmol) and $LiAlH_4$ (57 mg, 1.52 mmol) in ether (200 ml) gave, after flash column chromatography on silica gel eluting with CH_2Cl_2–MeOH (50:1), the diol *anti*, *syn*-**48** (0.15 g, 87%) as an oil; R_f [CH_2Cl_2–MeOH (50:1)] 0.11; ν_{max} (film)/cm^{-1} 3400 (OH) and 1580 (SPh); δ_H(250 MHz, $CDCl_3$) 7.49–7.23 (5 H, m, SPh), 3.73 (1 H, dd, *J* 10.8 and 4.0, CH_AH_BOH), 3.67 (1 H, dd, *J* 10.8 and 5.4, CH_AH_BOH), 3.63 (1 H, dd, *J* 9.5 and 3.5, C*H*OH), 2.96 (1 H, dt, *J* 3.5 and 9.4, C*H*SPh), 1.91–1.62 (2 H, m, C*H*$_2$Me), 1.39 (1 H, m, C*H*Me), 1.11 (3 H, t, *J* 7.2, CH$_2$Me) and 0.98 (3 H, d, *J* 7.0, CHMe) (Found M^+ 240.12201.

$C_{13}H_{20}O_2S$ requires M^+, 240.1184); *m*/*z* 240 (23%, M), 152 (100, PhSPr), 151 (54, PhSCHEt), 123 (44) and 110 (75, PhSH).

(2*RS*,3*RS*,4*RS*)-2-Methyl-4-phenylsulfanylhexane-1,3-diol *syn*, *anti*-48

In the same way as diol *anti*-**29**, the ester *syn*, *anti*-**47** (66 mg, 0.18 mmol) and $LiAlH_4$ (13.5 mg, 0.36 mmol) in ether (200 ml) gave, after flash column chromatography on silica gel eluting with ether–CH_2Cl_2–MeOH (30:70:1), the *diol syn*, *anti*-**48** (36 mg, 81%) as needles, mp 76–79 °C (recrystallised from ether–hexane); R_f [ether–CH_2Cl_2–MeOH (30:70:1)] 0.37; ν_{max} (Nujol)/cm^{-1} 3400 (OH) and 1580 (SPh); δ_H(250 MHz, $CDCl_3$) 7.44–7.19 (5 H, m, SPh), 3.78 (1 H, dd, *J* 7.1 and 4.0, C*H*OH), 3.72 (1 H, dd, *J* 10.6 and 4.2, C$H_A$$H_B$OH), 3.64 (1 H, dd, *J* 10.6 and 5.1, $CH_A$$H_B$OH), 3.16 (1 H, dd, *J* 9.0, 7.1 and 3.4, CHSPh), 2.18 (1 H, m, C$H_A$$H_B$Me), 1.89 (1 H, ddq, *J* 14.6, 3.4 and 7.3, $CH_A$$H_B$Me), 1.56 (1 H, m, C*H*Me), 1.12 (3 H, t, *J* 7.3, CH_AH_B-Me) and 0.92 (3 H, d, *J* 7.0, CHMe) (Found M^+ 2440.1192. $C_{13}H_{20}O_2S$ requires M^+, 240.1184); *m*/*z* 240 (13%, M), 152 (100, $PhSCH_2Et$), 151 (58, PhSCHEt), 123 (44) and 110 (77, PhSH).

(2*RS*,3*RS*,3*SR*) *S*-Phenyl 3-hydroxy-2-methyl-4-phenylsulfanylhexanethioate *anti*, *syn*-49

In the same way as the thioester *anti*, *syn*-**34**, 9-BBN-OTf (21 ml, 0.5 M in toluene, 10.5 mmol), diisopropylethylamine (1.42 g, 1.95 ml, 11 mmol), *S*-phenyl thiopropionate **26** (1.67 g, 10 mmol) and the aldehyde **23** (0.90 g, 5 mmol) in CH_2Cl_2 (25 ml) gave, after flash chromatography on silica eluting with hexane–ethyl acetate–diisopropylethylamine (18:1:1), a diastereoisomeric mixture (ratio 90:10) of *thioesters* **49** (1.23 g, 72%) as an oil. Separation of the diastereoisomers by HPLC eluting with hexane–ethylacetate–diisopropylethylamine (18:1:1) gave the *(2RS,3RS,4SR)-thioester anti*, *syn*-**49** (1.12 g, 65%) as an oil; t_R [hexane–CH_2Cl_2 (1:1)] 5.7 min; ν_{max} (film, $CHCl_3$)/cm^{-1} 3450 (OH), 1690 (C=O) and 1580 (SPh); δ_H(250 MHz, $CDCl_3$) 7.51–7.22 (10 H, m, 2 × SPh), 3.98 (1 H, dd, *J* 6.8 and 4.8, C*H*OH), 3.10 (2 H, m, C*H*SPh and C*H*Me), 1.82–1.57 (2 H, m, CH_2Me), 1.36 (3 H, d, *J* 7, C*H*Me) and 1.10 (3 H, t, *J* 7.3, CH_2Me); δ_C(67.5 MHz, $CDCl_3$) 200.3, 134.7, 134.4, 132.6, 129.3, 129.1, 127.5, 127.4, 73.7, 57.4, 51.52, 26.0, 13.6 and 11.7 (Found M^+ 346.1066. $C_{19}H_{22}O_2S$ requires M^+, 346.1061); *m*/*z* 346 (1%, M), 237 (100, M − SPh), 181 (50), 163 (20), 151 (28), 110 (52, PhSH) and 109 (41).

(2*SR*,3*SR*,4*RS*)-4-Methyl-2-(2-methylpropyl)-3-phenylsulfanyltetrahydrofuran *syn*, *anti*-51

In the same way as the tetrahydrofuran *anti*-**31**, the diol *syn*, *anti*-**45** (13.1 mg, 48.9 mmol) and toluene-*p*-sulfonic acid (1 mg, 5.26 µmol) in benzene (5 ml) gave the *tetrahydrofuran syn*, *anti*-**51** (6.2 mg, 51%) as an oil; R_f [CH_2Cl_2–hexane (3:1)] 0.33; ν_{max} (film, $CHCl_3$)/cm^{-1} 2930 (CH) and 1580 (SPh); δ_H(250 MHz, $CDCl_3$) 7.36–7.27 (5 H, m, SPh), 4.03 (1 H, dd, *J* 8.5 and 6.5, C$H_A$$H_B$O), 3.79 (1 H, dt, *J* 8.1 and 3.6, CHO), 3.49 (1 H, dd, *J* 8.5 and 6.5, $CH_A$$H_B$O), 3.37 (1 H, t, *J* 7.6, CHS), 2.57 (1 H, d, *J* 6.9, C*H*Me), 1.75 (1 H, n, *J* 6.9, C*H*Me_2), 1.49–1.37 (2 H, m, CH_2CHMe_2), 1.09 (3 H, d, *J* 7.0, CH*Me*) and 0.87 (6 H, d, *J* 6.6, CMe_2); δ_C(62.5 MHz, $CDCl_3$) 136.2, 130.2, 129.0, 126.3, 81.7, 74.0, 56.1, 44.2, 37.0, 25.5, 23.5, 21.7 and 14.1 (Found M^+, 250.1377. $C_{15}H_{22}O_2S$ requires M, 250.1392); *m*/*z* 250.1 (48%, M), 175 (17), 164 (100, $PhSCHCHMeCH_2$), 149 (34), 110 (65, SPh) and 55 (48).

(2*RS*,3*SR*,4*RS*)-4-Methyl-2-(2-methylpropyl)-3-phenylsulfanyltetrahydrofuran *anti*, *anti*-51

In the same way as the tetrahydrofuran *anti*-**31**, the diol *anti*, *anti*-**45** (42.8 mg, 0.16 mmol) and toluene-*p*-sulfonic acid (1 mg, 5.26 µmol) in benzene (5 ml) gave the *tetrahydrofuran anti*, *anti*-**51** (21 mg, 53%) as an oil; R_f [CH_2Cl_2–hexane (3:1)] 0.38; ν_{max} (film, $CHCl_3$)/cm^{-1} 2940 (CH) and 1580 (SPh); δ_H(250 MHz, $CDCl_3$) 7.48–7.22 (5 H, m, SPh), 3.91 (1 H, dd, *J* 8.5 and 7.3, C$H_A$$H_B$O), 3.72 (1 H, dt, *J* 4.8 and 7.8, CHO), 3.45 (1 H, dd, *J* 8.6 and 6.7, $CH_A$$H_B$O), 2.56 (1 H, t, *J* 7.8, CHS), 2.20 (1 H, quintet, *J* 7.0, C*H*Me), 1.75 (1 H, n, *J* 6.8, C*H*Me_2), 1.43–1.37 (2 H, m, CH_2CHMe_2), 1.10 (3 H, d, *J* 6.8, CH*Me*), 0.88 (3 H, d, *J* 6.7, C$Me_A$$Me_B$) and 0.87 (3 H, d, *J* 6.7, C$Me_A$$Me_B$); δ_C(62.5 MHz, $CDCl_3$) 133.6, 133.0, 128.6, 127.5, 82.9, 72.1, 58.7, 43.7, 41.1, 25.4, 23.6, 21.7 and 17.1 (Found M^+, 250.1370. $C_{15}H_{22}O_2S$ requires M, 250.1392); *m*/*z* 250.1 (54%, M), 175 (18), 164 (100, $PhSCHCHMeCH_2$), 149 (39), 110 (74, SPh) and 55 (53).

(2*SR*,3*SR*,4*RS*)-2-Ethyl-4-methyl-3-phenylsulfanyltetrahydrofuran *syn*, *anti*-52

In the same way as the tetrahydrofuran *anti*-**31**, the diol *syn*, *anti*-**48** (7.5 mg, 31 µmol) and toluene-*p*-sulfonic acid (1.2 mg, 6.2 µmol) in benzene (5 ml) gave the *tetrahydrofuran syn*, *anti*-**52** (6 mg, 87%) as an oil; R_f [CH_2Cl_2] 0.35; ν_{max} (film, $CHCl_3$)/cm^{-1} 1580 (SPh); δ_H(250 MHz, $CDCl_3$) 7.39–7.16 (5 H, m, SPh), 4.01 (1 H, dd, *J* 8.5 and 6.3, C$H_A$$H_B$O), 3.69 (1 H, dt, 6.3 and 8.5, CHO), 3.51 (1 H, dd, *J* 7.4 and 4.2, $CH_A$$H_B$O), 3.42 (1 H, d, *J* 7.4, CHSPh), 2.27 (1 H, septet, *J* 6.8, C*H*Me), 1.75–1.44 (2 H, m, CH_2Me), 1.10 (3 H, d, *J* 7.0, CHMe) and 0.94 (3 H, t, *J* 7.4, CH_2Me) (Found M^+ 222.1076. $C_{13}H_{18}O_2S$ requires M^+, 222.1078); *m*/*z* 222 (54%, M), 164 (57, M − EtCHO), 149 (40) and 110 (100, PhSH).

(2*RS*,3*SR*,4*RS*)-Ethyl-4-methyl-3-phenylsulfanyltetrahydrofuran *anti*, *anti*-52

In the same way as the tetrahydrofuran *anti*-**31**, the diol *anti*, *anti*-**48** (60 mg, 0.25 mmol) and toluene-*p*-sulfonic acid (9.5 mg, 50 µmol) in benzene (5 ml) gave the *tetrahydrofuran anti*, *anti*-**52** (45 mg, 82%) as an oil; R_f [CH_2Cl_2] 0.54; ν_{max} (film, $CHCl_3$)/cm^{-1} 1580 (SPh); δ_H(250 MHz, $CDCl_3$) 7.45–7.21 (5 H, m, SPh), 3.93 (1 H, dd, *J* 8.5 and 7.3, C$H_A$$H_B$O), 3.62 (1 H, dt, 4.0 and 7.8, CHO), 3.45 (1 H, dd, *J* 8.5 and 6.8, $CH_A$$H_B$O), 2.74 (1 H, t, *J* 7.8, CHSPh), 2.22 (1 H, septet, *J* 7.8, C*H*Me), 1.66 (1 H, ddq, *J* 15.0, 7.8 and 4.0, C$H_A$$H_B$Me), 1.47 (1 H, septet, *J* 7.8, $CH_A$$H_B$Me), 1.10 (3 H, d, *J* 6.8, C*H*Me) and 0.94 (3 H, t, *J* 7.5, CH_AH_BMe) (Found M^+ 222.1076. $C_{13}H_{18}O_2S$ requires M^+, 222.1078); *m*/*z* 222 (80%, M), 164 (70, M − EtCHO), 149 (50), 112 (55), 111 (78) and 110 (100, PhSH).

(3*RS*,4*SR*)-Methyl 2,2,6-trimethyl-3-hydroxy-4-phenylsulfanylheptanoate *anti*-53 and (3*RS*,4*RS*)-methyl 2,2,6-trimethyl-3-hydroxy-4-phenylsulfanylheptanoate *syn*-53

In the same way as the *anti*-ester **28**, n-BuLi (1.8 ml, 1.5 M in hexane, 1.75 mmol), diisopropylamine (0.27 g, 0.38 ml, 2.75 mmol), methyl isobutyrate (0.27 g, 0.30 ml, 1.65 mmol) and the aldehyde **13** (0.52 g, 2.5 mmol) gave, after flash chromatography on silica eluting with hexane–ether (2:1), the *ester anti*-**53** (0.24 g, 31%) as an oil; R_f [hexane–ether (2:1)] 0.24; ν_{max} (film, $CHCl_3$)/cm^{-1} 3450 (OH), 2960 (CH) and 1725 (CO); δ_H(250 MHz, $CDCl_3$) 7.45–7.20 (5 H, m, SPh), 3.86 (1 H, m, C*H*OH), 3.62 (3 H, s, OMe), 3.28 (1 H, td, *J* 2.4 and 9.0, CHSPh), 2.97 (1 H, br s, OH), 2.06–1.96 (1 H, m, C*H*Me_2), 1.49 (1 H, ddd, *J* 14.8, 11.5 and 3.5, C$H_A$$H_BCHMe_2$), 1.27 (1 H, ddd, *J* 11.5, 11.0 and 3.0, $CH_A$$H_BCHMe_2$), 1.17 (3 H, s, C$Me_A$$Me_B$), 1.13 (3 H, s, $CMe_A$$Me_B$), 0.93 (3 H, d, *J* 6.7, CH$Me_A$$Me_B$) and 0.89 (3 H, d, *J* 6.7, $CMe_A$$Me_B$); δ_C(62.5 MHz, $CDCl_3$) 177.5, 135.2, 132.5, 128.9, 127.2, 78.9, 77.3, 77.0, 76.7, 51.9, 51.0, 42.3, 37.5, 25.7, 23.8, 23.2, 22.5 and 21.1 (Found M^+, 310.1612. $C_{17}H_{26}O_3S$ requires M, 310.1602); *m*/*z* 310.1 (10%, M), 131 (100) and 123 (80, $PhSCH_2$). Chromatography also gave the *ester syn*-**53** (13 mg, 2%) as an oil; R_f [hexane–ether (4:1)] 0.18; ν_{max} (film, $CHCl_3$)/cm^{-1} 2930 (CH) and 1725 (CO); δ_H(250 MHz, $CDCl_3$) 7.42–7.21 (5 H, m, SPh), 3.68 (3 H, s, OMe), 3.66 (1 H, m, C*H*OH), 3.23 (1 H, td, *J* 7.4 and 2.8, CHSPh), 1.87–1.75 (1 H, m, C*H*Me_2), 1.71–1.60 (1 H, m, C$H_A$$H_B$CHMe$_2$), 1.51–1.42 (1 H, m, CH$_A$$H_B$CHMe$_2$), 1.30 (3 H, s, C$Me_AMe_B$), 1.24 (3 H, s, CMe$_A$$Me_B$), 0.82 (3 H, d, *J* 6.5, CHMe_AMe$_B$) and 0.79 (3 H, d, *J* 6.6, CMe$_A$$Me_B$); δ_C(62.5 MHz, $CDCl_3$) 177.8, 134.5, 132.0, 128.9, 127.0, 78.3, 52.1, 51.0, 45.6, 43.5, 25.3, 23.4, 22.8, 22.4 and 22.1 (Found M^+, 310.1622. $C_{17}H_{26}O_3S$ requires M, 310.1602); *m*/*z* 310.1 (7%, M), 131 (90) and 123 (100, $PhSCH_2$).

(3*RS*,4*SR*)-2,2,6-Trimethyl-4-phenylsulfanylheptane-1,3-diol *anti*-54

In the same way as the diol *anti*-**29**, the ester *anti*-**53** (0.22 g, 0.70 mmol) and $LiAlH_4$ (71 mg, 1.9 mmol) in ether (10 ml) gave, after flash column chromatography on silica gel eluting with ether–hexane (2:1), the *diol anti*-**54** (0.16 g, 80%) as an oil; R_f [ether–hexane (2:1)] 0.36; ν_{max} (film)/cm^{-1} 3360 (OH) and 2960 (CH); δ_H(250 MHz, $CDCl_3$) 7.42–7.23 (5 H, m, SPh), 3.64 (1 H, d, *J* 1.2, C*H*OH), 3.40 (1 H, d, *J* 10.9, CH_AH$_B$OH), 3.40 (1 H, m, SPh), 3.32 (1 H, d, *J* 10.9, CH$_A$$H_B$OH), 2.05–1.98 (1 H, m, C*H*Me_2), 1.62 (1 H, ddd, *J* 14.9, 10.1 and 2.7, CH_AH$_B$CH$_2$SPh), 1.48 (1 H, ddd, *J* 14.9, 11.2 and 3.8, CH$_A$$H_BCH_2$SPh), 1.00 (3 H, d, *J* 6.5, CHMe_AMe$_B$), 0.99 (3 H, d, *J* 6.7, CHMe$_A$$Me_B$), 0.92 (3 H, s, C$Me_AMe_B$) and 0.77 (3 H, s, CMe$_A$$Me_B$); δ_C(67.5 MHz, $CDCl_3$) 134.8, 132.5, 129.1, 127.4, 80.0, 73.5, 51.4, 38.9, 37.2, 26.2, 23.8, 23.0, 21.3 and 20.3 (Found M^+, 282.1644. $C_{16}H_{26}O_2S$ requires M^+, 282.1653); *m*/*z* 282.1 (10%, M − SPh), 180 (90), 123 (90, $PhSCH_2$) and 110 (100, PhSH).

(2*RS*,3*SR*)-4,4-Dimethyl-2-(2-methylpropyl)-3-phenylsulfanyltetrahydrofuran *anti*-56

In the same way as the tetrahydrofuran *anti*-**31**, the diol *anti*-**54** (0.12 g, 0.42 mmol) and toluene-*p*-sulfonic acid (2.8 mg, 14.7 µmol) in benzene (5 ml) gave the *tetrahydrofuran anti*-**56** (42 mg, 44%) as an oil; R_f [CH_2Cl_2–hexane (3:2)] 0.50; ν_{max} (film)/cm^{-1} 2960 (CH); δ_H(250 MHz, $CDCl_3$) 7.46–7.18 (5 H, m, SPh), 3.85 (1 H, dt, *J* 4.0 and 8.7, CHO), 3.57 (2 H, s, CH_2O), 2.90 (1 H, d, *J* 9.2, CHSPh), 1.83–1.73 (1 H, m, C*H*Me_2), 1.41–1.35 (2 H, m, CH_2CHMe$_2$), 1.13 (3 H, s, CMe_AMe$_B$), 1.07 (3 H, s, CMe$_A$$Me_B$) and 0.87 (6 H, d, *J* 6.5, CHMe_2); δ_C(62.5 MHz, $CDCl_3$) 135.9, 131.8, 128.9, 126.9, 82.7, 72.9, 44.1, 44.0, 42.8, 25.5, 25.3, 23.8, 22.3 and 21.7 (Found M^+, 264.1556. $C_{16}H_{24}OS$ requires M, 264.1548); *m*/*z* 264.1 (30%, M), 178 (35), 163 (40), 110 (50, PhSH) and 59 (100, CMe_2CHCH_2).

Acknowledgements

We thank the EPSRC for grants (to V. K. A., J. E., S. M. and F. H. S.), Ray V. H. Jones (Zeneca Process Technology Department, Grangemouth) for a CASE award (to J. E.) and the British Council for a Fleming Fellowship (to M.-J. V.).

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Paper a908810e