Synthesis of cyclic ethers and allylic sulfides by rearrangement of phenylsulfanyl substituted 1,*n*-diols with toluene-*p*-sulfonic acid and with toluene-*p*-sulfonyl chloride

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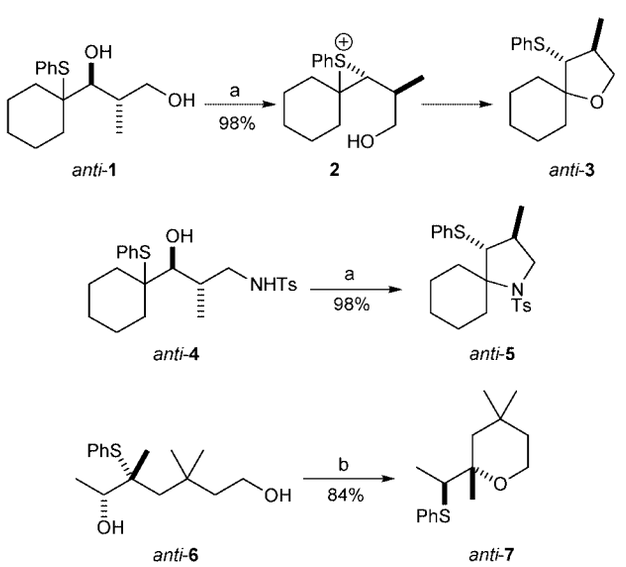
Rearrangement of a series of 1,*n*-diols ($n = 2$ to 12), with a PhS-group adjacent to one OH group, under two sets of conditions gives single compounds in excellent yield drawn for four possible classes of products. The effect of the chain length helps in the understanding of the different cyclisation modes and the mechanism of the rearrangements.

Treatment of a β-hydroxy sulfide, *e.g.* **1** with acid gives rise to the formation of an intermediate episulfonium ion *e.g.* **2**, by stereospecific loss of water.[1] This high energy episulfonium ion cannot be isolated and prefers to decompose by the loss of a proton to give an allylic sulfide.[2] Intramolecular capture of this episulfonium ion is possible with alcohols,[3] esters,[4] amides[5] and thiols[6] to give stereospecifically spirocyclic ethers *e.g.* **3**, lactones, amines and sulfides. Over the course of these studies we have elaborated rules for the regio- and stereocontrol (involving stereochemistry, Baldwin's rules[7] and the Thorpe–Ingold effect)[8] for such rearrangements.[9] We have always observed intramolecular cyclisation at the most substituted end of the episulfonium ion to give THFs like *anti*-**3**, amines *anti*-**5** and THP *anti*-**7**. In many cases the capture of an episulfonium ion does not obey Baldwin's rules due to the partially disfavoured *endo*-nature of some of these cyclisations. For example, addition of β-hydroxy sulfide *anti*-**1** with catalytic toluene-*p*-sulfonic acid (TsOH) gives the episulfonium ion **2** which is captured intramolecularly to give the spirocyclic ether *anti*-**3** in essentially quantitative yield *via* a disfavoured hybrid 6-*endo*–5-*exo*-*tet* cyclisation (Scheme 1).[3,4] This 1,2-PhS migration occurs stereospecifically with inversion of configuration at the migratory terminus.[10] Further studies have revealed that this rearrangement is under thermodynamic control, however the observed THF *anti*-**3** is the major kinetic product by far.[11]

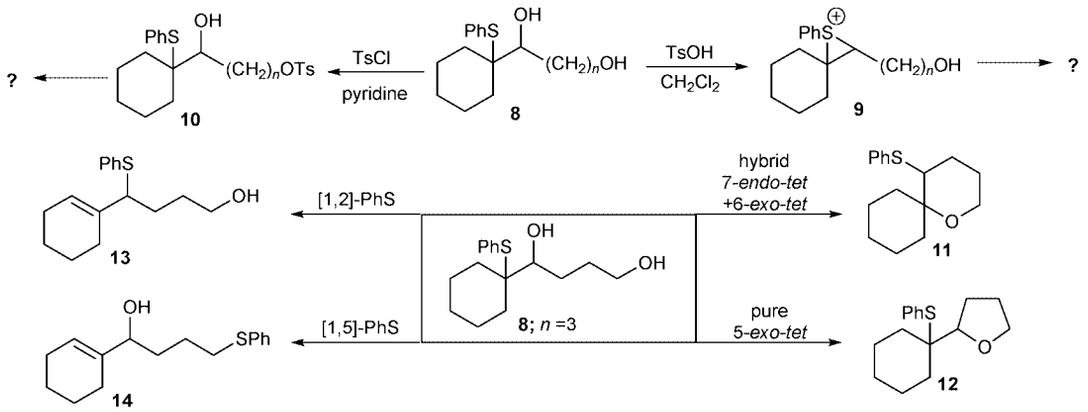


Scheme 1 *Reagents and conditions*: a, TsOH, CH_2Cl_2, reflux; b, TMSOTf, CH_2Cl_2, −78 °C.

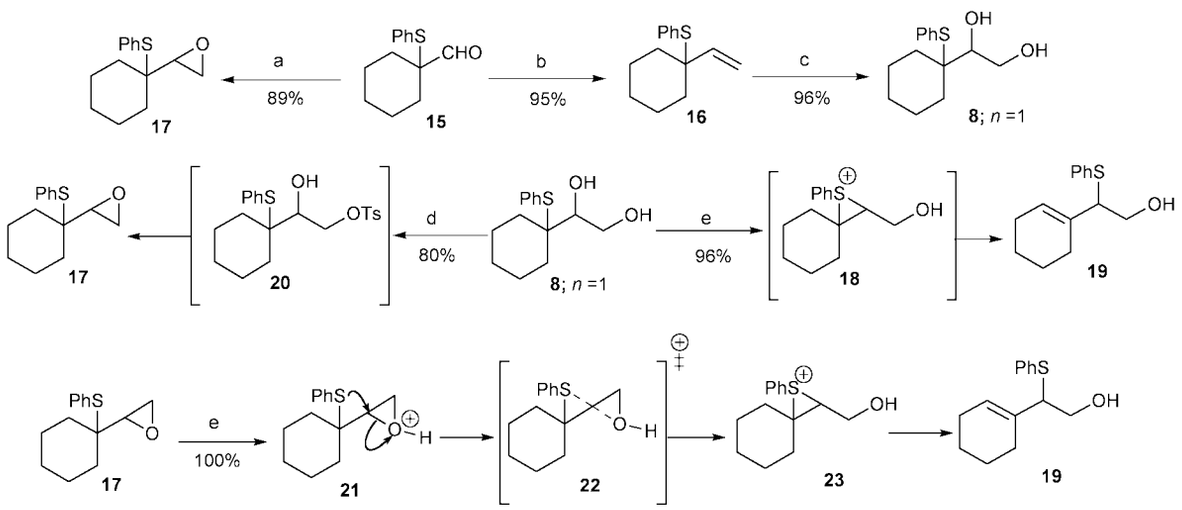
We were interested in extending this cyclisation procedure to the synthesis of less common larger ring size cyclic ethers and now report on our investigation into the different possible modes of cyclisations observed.[12] We comment on the effects of the chain length *n* between the two hydroxy groups in the diols **8** during acid-catalysed rearrangement and on an alternative reaction: the rearrangement of the same diols **8** with toluene-*p*-sulfonyl chloride (TsCl) in pyridine which give complementary products to that observed from the acid-catalysed rearrangement. The acid-catalysed rearrangement of these diols occurs *via* episulfonium ion formation, while the TsCl in pyridine reaction proceeds *via* primary toluene-*p*-sulfonate **10** as an intermediate, which is not usually isolated. The various products from the rearrangement of the diol **8**, $n = 3$ are illustrated in Scheme 2; the rearranged allylic sulfides **13**, formed by [1,2]-PhS shift, the allylic sulfide **14** formed by a less common [1,5]-PhS shift and the two cyclic ethers **11** formed with [1,2]-PhS migration by a hybrid 7-*endo*–6-*exo*-*tet* cyclisation and **12** formed without PhS migration by a pure 5-*exo*-*tet* cyclisation.

Synthesis and rearrangement of 1,2-diol 8, $n = 1$

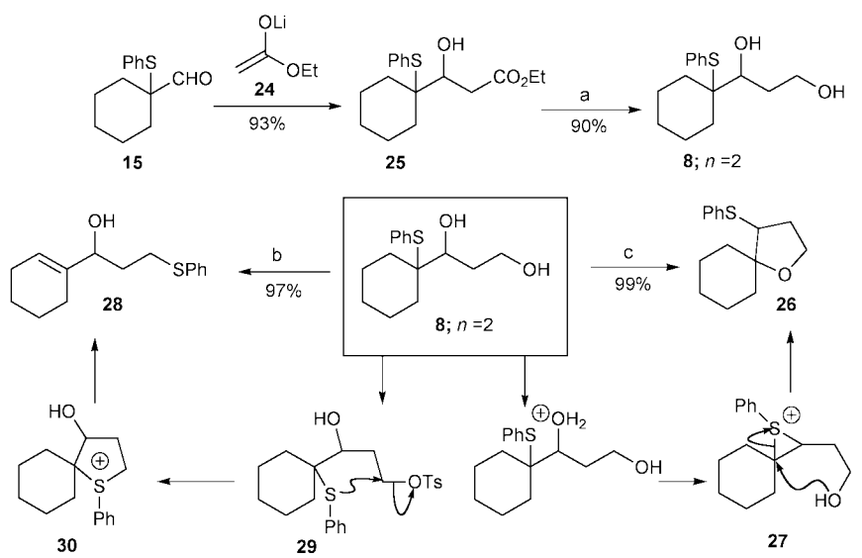
We chose to synthesise the diol **8**, $n = 1$ from the allylic sulfide **16**, using our modification of the Sharpless racemic dihydroxylation to introduce the 1,2-diol functionality.[13,14] This sulfide **16** was synthesised using the Wittig reaction; methyl triphenylphosphonium iodide was deprotonated with n-BuLi and quenched with the aldehyde **15**. This reaction had to be carried out in the absence of light because allylic sulfides like **16** are well known to rearrange (*via* the radical mechanism)[15] to the more thermodynamically stable allylic sulfide.[16] Treatment of the diol **8**, $n = 1$ under our usual toluene-*p*-sulfonic acid conditions[4] (TsOH in CH_2Cl_2) gave the allylic sulfide **19**, presumably *via* elimination of the episulfonium ion **18** (Scheme 3). In contrast, treatment of diol **8**, $n = 1$ with TsCl in pyridine gave the epoxide **17** in 80% yield by chemoselective tosylation (**20**) of the primary OH group in **8**, $n = 1$. The structure of this epoxide was independently confirmed by synthesis from the aldehyde **15** using sulfonium ylide chemistry.[17] However, submission of this epoxide **17** with TsOH causes rearrangement to give the allylic sulfide **19** by a [1,2]-SPh shift, presumably *via* the highly strained oxaspiro[2.2]cyclopentane transition state **22** and the



Scheme 2



Scheme 3 *Reagents and conditions*: a, $Me_2S{=}CH_2$, THF, −78 °C; b, $Ph_3P{=}CH_2$, THF, −78 °C; c, cat. $OsCl_3$, quinuclidine, $K_3Fe(CN)_6$, *t*-BuOH–H_2O; d, TsCl, pyridine; e, TsOH, CH_2Cl_2, reflux.



Scheme 4 *Reagents and conditions*: a, $LiAlH_4$, Et_2O; b, TsCl, pyridine; c, TsOH, CH_2Cl_2, reflux.

same episulfonium ion **23** in near quantitative yield. It is worthy of note that neither of the cyclised products such as an oxetane or the epoxide **17** have been observed in the acid-catalysed rearrangement, presumably because neither ring closure can compete with allylic sulfide formation. Under these reaction conditions the allylic sulfide **19** must be the thermodynamic product, but it may also be kinetically preferred.

Synthesis and rearrangement of 1,3-diol 8, $n = 2$

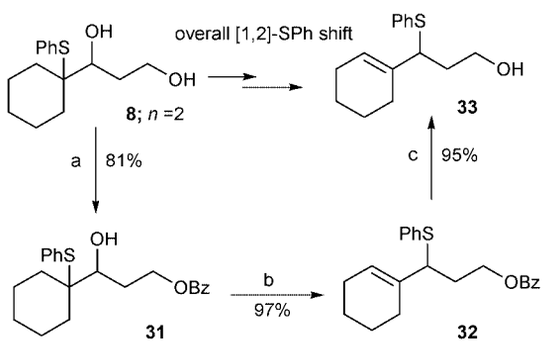
The homologous 1,3-diol **8**, $n = 2$ was synthesised using our previously developed aldol methodology.[4] Reaction of enolate **24** (derived from ethyl acetate and LDA) with aldehyde **15**, followed by reduction ($LiAlH_4$, ether, 2 h) gave the 1,3-diol **8**, $n = 2$ in excellent yield (Scheme 4). Acid-catalysed rearrangement of

Table 1 Yields in the synthesis of 1,*n*-diols **8**; *n* = 3–6, 8 and 11

Reactions ⟶ acetal formation			Organolithium	Addition to aldehyde **15**	Hydrolysis
Alcohols **34**	Acetal **35**		**36**	Acetals **37**	1,*n*-Diols **8**
n = 3; X = Br	*n* = 3; X = Br	92%	*n* = 3	*n* = 3; 99%	*n* = 3; 99%
n = 4; X = Cl	*n* = 4; X = Cl	90%	*n* = 4	*n* = 4; 85%	*n* = 4; 85%
n = 5; X = Br	*n* = 5; X = Br	94%	*n* = 5	*n* = 5; 94%	*n* = 5; 94%
n = 6; X = Br	*n* = 6; X = Br	95%	*n* = 6	*n* = 6 96%	*n* = 6; 88%
n = 8; X = Br	*n* = 8; X = Br	91%	*n* = 8	*n* = 8; 87%	*n* = 8; 100%
n = 11; X = Br	*n* = 11; X = Br	86%	*n* = 12	*n* = 11; 99%	*n* = 11; 89%

this diol gave the expected THF **26** (99%) *via* a hybrid 6-*endo*–5-*exo*-*tet* cyclisation—no oxetane by the competing (pure 5-*exo*-*tet*) pathway was observed. Under the TsCl–pyridine conditions, this 1,3-diol gave an unexpected allylic alcohol **28** (97%) by a [1,4]-SPh shift *via* the sulfonium ion **30**.[12,18] Both [1,2]- and [1,4]-SPh participation are well documented, and are known to occur at similar rates.[19] Presumably [1,4]-SPh rearrangement in this case is preferred over [1,2]-SPh participation because the initial chemoselective tosylation, which gives **29**, occurs on the primary alcohol in **8**, *n* = 2 (Scheme 4).

The structure of the allylic alcohol **28** was confirmed independently by synthesising the alternative allylic sulfide **33** derived from the alternative [1,2]-SPh shift. Chemoselective protection of the primary alcohol in diol **8**, *n* = 2 using benzoyl chloride gave **31**, rearrangement with TsOH gave the allylic sulfide **32** *via* a known [1,2]-SPh shift[1] and deprotection (HCl–EtOH) gave the allylic sulfide **33** (Scheme 5). The ^{1}H NMR



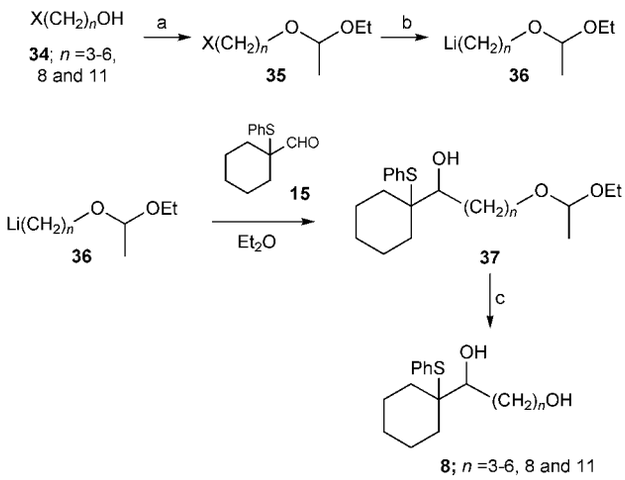
Scheme 5 *Reagents and conditions*: a, PhCOCl, Et_3N, CH_2Cl_2; b, TsOH, CH_2Cl_2, reflux; c, HCl, MeOH.

spectra of both **28** and **33** are clearly different, the allylic H in **28** (adjacent to oxygen) came at a much lower field (δ 4.11 ppm) than the allylic H in **33** (δ 3.65 ppm) which is next to sulfur, illustrating the difference in electronegativity (Scheme 5).

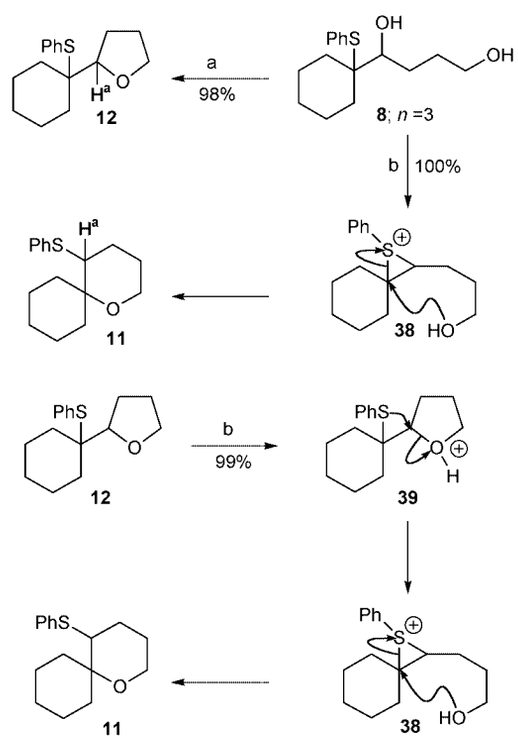
Synthesis and rearrangement of homologous 1,*n*-diols 8, *n* = 3–6, 8 and 11

These remaining homologous 1,*n*-diols **8**, *n* = 3–6, 8 and 11 were synthesised using a methodology developed by Eaton *et al.*[20] The required lithium derivatives **36** were synthesised by protecting the alcohols **34** as an acetal **35**, and a subsequent halogen–lithium exchange with a lithium (1% + Na) metal (Table 1). Addition of these organolithium reagents to the aldehydes **15** followed by deprotection (HCl–H_2O–EtOH) (which was easily achieved without rearrangement) gave the 1,*n*-diols **8**; *n* = 3–6, 8 and 11 in excellent yield as shown in Scheme 6 and Table 1.

Acid-catalysed rearrangement of the diols **8**, *n* = 3 gave exclusively the tetrahydropyrans (THP) **11** in quantitative yield. Rearrangement must occur *via* a hybrid 7-*endo*–6-*exo*-*tet* cyclisation onto the most substituted end of the episulfonium ion **38** as shown in Scheme 7. The alternative THF **12** from a pure 5-*exo*-*tet* cyclisation was not observed. However, treat-



Scheme 6 *Reagents and conditions*: a, Cl_2CHCO_2H, ethyl vinyl ether; b, Li, 1% Na, Et_2O, −20 °C; c, HCl, MeOH–H_2O (1 : 1).



Scheme 7 *Reagents and conditions*: a, TsCl, pyridine; b, TsOH, CH_2Cl_2, reflux.

ment of the 1,4-diol **8**, *n* = 3 with TsCl in pyridine gave this alternative THF **12** in excellent yield by simple ether formation. This THF **12** and THP **11** were easily characterised by both ^{1}H and ^{13}C NMR. In the ^{1}H NMR, the THP **11**[21] has a double doublet for **H**^{a} with typical six-membered ring axial–axial (11.2 Hz) and axial–equatorial (4.3 Hz) couplings, however for the

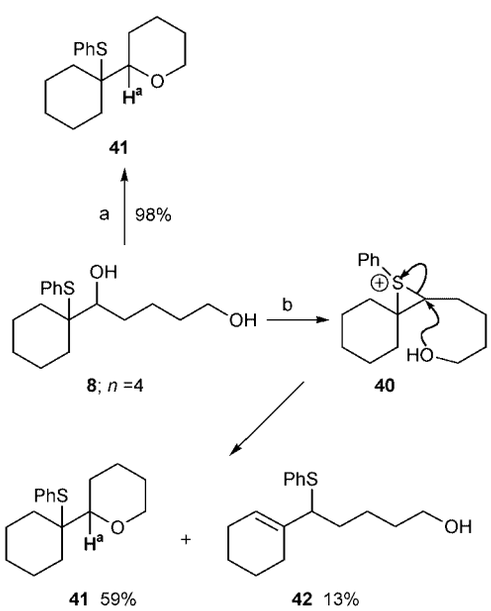
Table 2 Characterisation of pure-*exo* and hybrid *endo–exo* cyclic ethers by ^{13}C NMR and mass spectra

δ_c (ppm) or mass spectrum	Unrearranged heterocycle pure *exo*-cyclic ethers				Rearranged heterocycle hybrid *endo–exo*-cyclic ethers	
	Epoxide **17**	THF **12**	THP **41**	DHP **50**	THF **26**	THP **11**
Quaternary carbon (ppm)	(C–S) 59	(C–S) 55	(C–S) 57	(C–S) 57	(C–O) 84	(C–O) 75
Tertiary carbon (ppm)	(C–O) 74	(C–O) 80	(C–O) 82	(C–O) 80	(C–S) 55	(C–S) 55
191.1 ($PhSC_6H_{10}^+$)	40%	100%	70%	—	0%	0%
M − 191.1	5%	65%	100%	—	0%	0%
136.0 ($PhSC_2H_3^+$)	0%	0%	0%	—	60%	80%

THF **12** the H^a resonance overlapped with the other CH_2O protons. The most reliable method came from the ^{13}C NMR spectra; the THF has a quaternary carbon next to PhS (δ 55) and a CH group next to oxygen (δ 80), while the THP has a quaternary carbon next to oxygen (δ 75) and a CH group next to PhS (δ 55). Additionally, in the mass spectrum, the THF **12** fragments between the ring and the $C_6H_{10}SPh$ group and both fragments ($C_6H_{10}SPh$ and C_4H_7O) are observed. No such fragmentation is possible with the THP **11** which gives a $PhSC_2H_3$ fragment as the base peak (Table 2).

With this THF **12** now available (Scheme 7), we were able to demonstrate why we have never observed it in the acid-catalysed rearrangement of these types of diols such as **8**, $n = 3$. Submission of this THF under our usual TsOH–CH_2Cl_2 conditions for 5 min gave the THP **11** in quantitative yield. It is clear the THP **11** is the thermodynamic product from the acid-catalysed rearrangement. New evidence suggests that the THF **12** is the major kinetic product of cyclisation onto episulfonium ions like **38**.[21]

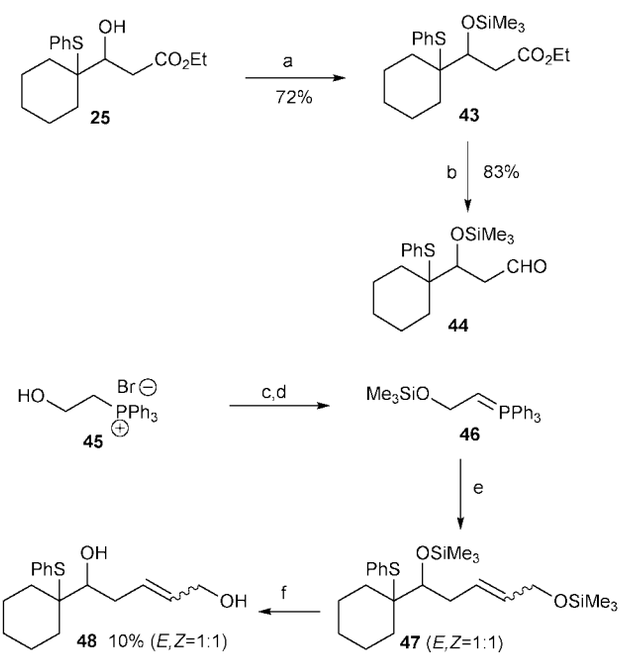
Acid-catalysed rearrangement of the homologous 1,5-diol **8**, $n = 4$ gave for the first time a mixture of products—the THP **41** (59%) and the allylic sulfide **42** (13%)—in a combined yield of only 72% as illustrated in Scheme 8. Presumably capture of the



Scheme 8 *Reagents and conditions*: a, TsCl, pyridine; b, TsOH, CH_2Cl_2, reflux.

episulfonium ion **40** by a pure 6-*exo-tet* cyclisation to give the THP **41** becomes less entropically favoured as the chain length *n* increases. Competing elimination of the episulfonium ion **40** gave the allylic sulfide **42** with an overall [1,2]-SPh shift. The alternative oxepine from a hybrid 8-*endo*–7-*exo-tet* in **40** was not observed. The THP **41** was assigned from the chemical shifts in the ^{13}C NMR spectrum and the mass fragmentation pattern, which was characteristic of this type of unrearranged heterocycle (Table 2). However, by ^1H NMR the THP **41** has an unusual double doublet for H^a with axial–axial (10.82 Hz) and axial–equatorial (1.65 Hz) couplings, which are untypical for a six membered ring. Resubmission of this THP **41** under prolonged heating with TsOH in toluene (12 hours) gave the more thermodynamic allylic sulfide **42** (92%) and clearly this allylic sulfide is the thermodynamic product from the cyclisation. In comparison TsCl–pyridine on diol **8**, $n = 4$ gave the same THP **41** but in 98% yield, by simple ether formation.

We were next interested in improving this 6-*exo-tet* cyclisation by increasing the effective concentration of the nucleophilic OH group in **40** by having a (*Z*)-alkene in the tethered chain. The synthesis of diol (*Z*)-**48** was achieved by trimethylsilyl protection of the OH group in the ester **25**, and DIBAL-H reduction gave the aldehyde **44** in good yield (Scheme 9). A



Scheme 9 *Reagents and conditions*: a, Me_3SiCl, Et_3N, CH_2Cl_2, 0 °C; b, DiBAL, THF, −78 °C; c, 2 eq. *n*-BuLi, THF, −78 °C; d, Me_3SiCl; e, 44, THF, −78 °C; e, TBAF, THF.

subsequent Wittig reaction with **46** gave a stereoisomeric mixture (ratio of 1 : 1) of alkenes (*E*) and (*Z*)-**47**, and deprotection with TBAF in THF gave a separable mixture of the (*E*)- and (*Z*)-alkene **48** in low yield. In contrast to the long chain diol **8**, $n = 4$, the rearrangement of the (*Z*)-alkene **48** gave quantitative formation of the dihydropyran (DHP) **50**, whereas unsurprisingly the (*E*)-alkene **48** preferred to eliminate to give the allylic sulfide (*E*,*E*)-**51**. Presumably the cyclisation of (*Z*)-**49** is more favourable than **40** and elimination cannot compete (Scheme 10).

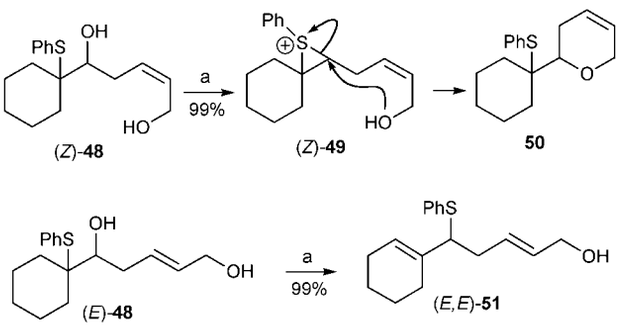
Rearrangement of the remaining diols **8**, $n = 5$, 6, 8 and 11 under acid catalysed conditions gave the allylic sulfides **53**–**56** in near quantitative yield (Table 3). For example, cyclisation of diol **8**, $n = 5$ no longer occurs (the chain length appears to be

too long and formation of the oxepine is disfavoured), and elimination of the episulfonium ion **52** is most preferred to give the allylic sulfide **53** in 95% yield. The TsCl–pyridine reaction finally gave the isolable primary toluene-*p*-sulfonate **10**, $n = 2$ (90%) from diol **8**, $n = 5$ as neither the cyclic ether formation nor a [1,7]-SPh shift is favourable (Scheme 11).

Conclusion

In the acid-catalysed rearrangement of 1,*n*-diols **8**, $n = 2$, 3, 4, 5, 6, 8 and 11, we have undoubtedly shown that the reaction is under thermodynamic control. By comparison of the products, we can deduce that allylic sulfides are formed when the chain length is too short (**8**, $n = 1$) or too long (**8**, $n > 4$) for efficient cyclisation. The rearranged heterocycles are formed only if the ring size is $n = 2$ (for THF's) and $n = 3$ and 4 (for THP's) but not otherwise—THP's are favoured over both THF's and oxepines (**8**, $n = 3$ and 4), and THF's are favoured only over oxetanes (**8**, $n = 2$). As a consequence of the increase of the chain length *n* pure *exo*-ring closure to give unrearranged cyclic ethers is favoured—this is purely a thermodynamic consequence. This acid-catalysed rearrangement predictably gives one compound in near quantitative yield (Table 3).

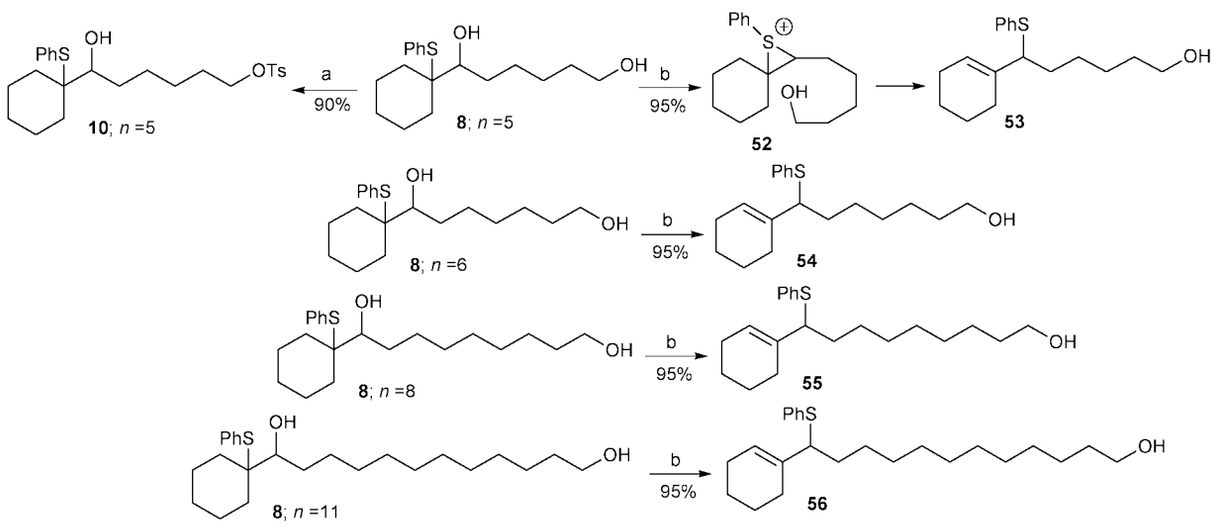
In the TsCl–pyridine reactions, all diols cyclise by simple ether formation, except when cyclisation is disfavoured by either ring strain (*e.g.*, **8**, $n = 2$ where the competitive [1,4]-SPh occurs) or when the chain length is too long (**8**, $n = 5$) and **10**, $n = 5$ is isolated. Furthermore, cyclisation onto the toluene-*p*-sulfonate proceeds under kinetic control. By comparison both reactions (TsCl–pyridine and TsOH–CH_2Cl_2) are very sensitive to ring strain, and disfavour four membered ring formation (**8**, $n = 2$ and 3).



Scheme 10 *Reagents and conditions*: a, TsOH, CH_2Cl_2, reflux.

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 or WM400 Fourier transform spectrometers using an internal deuterium lock. Chemical shifts are quoted in parts



Scheme 11 *Reagents and conditions*: a, TsCl, pyridine; b, TsOH, CH_2Cl_2, reflux.

Table 3 Products from the rearrangement of diols **8** and **48** with TsCl–pyridine and with TsOH–CH_2Cl_2

Starting material	Product from TsCl–pyridine		Product from TsOH–CH_2Cl_2	
	Product type	Yield	Product type	Yield
8; $n = 1$	Unrearranged heterocycle	17; 80%	Allylic sulfide	**19**; 98%
8; $n = 2$	[1,4]-SPh Shift	**28**; 97%	Rearranged heterocycle	**26**; 99%
8; $n = 3$	Unrearranged heterocycle	**12**; 98%	Rearranged heterocycle	**11**; 100%
8; $n = 4$	Unrearranged heterocycle	**41**; 98%	Unrearranged heterocycle	**41**; 59%
			Allylic sulfide	**42**; 13%
(*Z*)-**48**	—	—	Unrearranged heterocycle	**50**; 98%
(*E*)-**48**	—	—	Allylic sulfide	**51**; 95%
8; $n = 5$	Primary tosylate	**10**; $n = 5$; 90%	Allylic sulfide	**53**; 90%
8; $n = 6$	—	—	Allylic sulfide	**54**; 99%
8; $n = 8$	—	—	Allylic sulfide	**55**; 95%
8; $n = 11$	—	—	Allylic sulfide	**56**; 95%

per milllion downfield from tetramethylsilane. Carbon NMR spectra were recorded with broad proton decoupling and Attached Proton Test (ATP). 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 a AEI Kratos MS30 or MS890 machine using a DS503 data system for high resolution analysis. All compounds were isolated using flash column chromatography and were assumed to have a purity of greater than 98% (determined by NMR).

2-[1′-(Phenylsulfanyl)cyclohexyl]ethane-1,2-diol 8, $n = 1$

$OsCl_3 \cdot 6H_2O$ (84 μg, 14 mmol) was added to a stirred solution of allylic sulfide **16** (25 mg, 0.14 mmol), $K_3Fe(CN)_6$ (0.11 g, 0.42 mmol), K_2CO_3 (40 mg, 0.42 mmol), quinuclidine (0.9 mg, 14 μmol) and $OsCl_3 \cdot 6H_2O$ (84 μg, 14 mmol) in Bu^tOH–H_2O (1 ml, 1:1). The solution was stirred for 1 hour. 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) the *diol* **8**, $n = 1$ (27 mg, 96%) as an oil; R_f [light petroleum (40–60 °C)–ether (9:1)] 0.2; ν_{max} (film, $CDCl_3$)/cm^{-1} 3500–3200 (OH); δ_H(400 MHz, $CDCl_3$) 7.6–7.3 (5 H, m, SPh), 3.8 (1 H, dd, *J* 10.6 and 2.68, CHO), 3.65 (1 H, dd, *J* 10.8 and 7.8, CH_AH_BO), 3.45 (1 H, dt, *J* 7.8 and 3.1, CH_AH_BO), 3.3 (1 H, d, *J* 2.7 CHO*H*), 2.19 (1 H, dd, *J* 8.0 and 3.1, CH_2OH) and 2.04–1.20 (10H, m, 5 × CH_2); δ_C(100 MHz, $CDCl_3$) 137.2 (*m*-SPh), 130.0* (*i*-SPh), 129.1 (*p*-SPh), 128.9 (*o*-SPh), 75.2 (CHOH), 62.7* (CH_2O), 59.3* (*C*SPh), 30.9*, 30.7*, 26.0*, 21.7* and 21.6* (5 × CH_2) (Found M^+, 252.1181. $C_{14}H_{20}O_2S$ requires M, 252.1183); *m*/*z* 191.1 (60%, $C_6H_{10}SPh$), 109 (30, SPh), 81.1 (100, C_6H_9).

3-Hydroxy-3-[1′-(phenylsulfanyl)cyclohexyl]propanol 8, $n = 2$

$LiAlH_4$ (0.18 g, 4.7 mmol) was added to a stirred solution of the ester **37** (0.76 g, 2.36 mmol) in ether (100 ml) at 0 °C. The solution was stirred for 2 hours and poured onto an ice–brine solution. NaOH (20 ml, 10%) was added and the solution was 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 ether to give the diol **8**, $n = 2$ (0.56 g, 90%) as an oil; R_f [ether] 0.40; ν_{max} (film, $CDCl_3$)/cm^{-1} 3500–3200 (broad OH); δ_H(250 MHz, $CDCl_3$) 7.53–7.26 (5 H, m, SPh), 3.88–3.74 (2 H, m, C*H*OH and OH), 3.54–3.44 (2 H, m, CH_2OH), 2.77 (1 H, s, OH) and 1.96–1.2 (12 H, m, C_5H_{10} and CH_2CH_2OH); δ_C(100 MHz, $CDCl_3$) 137.2 (*m*-SPh), 130.0* (*i*-SPh), 129.1 (*p*-SPh), 128.9 (*o*-SPh), 75.1 (CHOH), 62.2* (CH_2O), 61.8* (*C*SPh), 32.1*, 30.4*, 29.5*, 26.2*, 21.8* and 21.7* (6 × CH_2) (Found: M^+, 266.1333. $C_{15}H_{22}O_2S$ requires M, 266.1340); *m*/*z* 157.1 (82%, M − SPh).

4-[1′-(Phenylsulfanyl)cyclohexyl]butane-1,4-diol 8, $n = 3$

HCl (2 ml, 3 M) was added to a stirred solution of the acetal **37**, $n = 3$ (0.14 g, 0.39 mmol) in EtOH–water (5 ml, 1:1). The solution was stirred for 1 hour. Na_2CO_3 (solid) was added (until the pH = 7). H_2O (50 ml) was added and the solution was 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 ether to give the *diol* **8**, $n = 3$ (0.12 g, 99%) as an oil; R_f [ether] 0.45; ν_{max} (film, $CDCl_3$)/cm^{-1} 3600–3200; δ_H(400 MHz, $CDCl_3$) 7.49–7.25 (5 H, m, SPh), 3.67–3.54 (3 H, m, OH and CH_2OH), 3.27–3.21 (1 H, d, *J* 10.2, C*H*OH), 2.96–2.88 (1 H, br s, OH) and 2.00–1.12 (14 H, m, 7 × CH_2); δ_C(100 MHz, $CDCl_3$) 137.22 (*m*-SPh), 130.0* (*i*-SPh), 129.0 (*p*-SPh), 128.8 (*o*-SPh), 74.9 (CHO), 62.8* (CH_2O), 61.7* (*C*SPh), 30.8*, 30.7*, 29.5*, 27.5*, 26.2*, 21.8* and 21.8* (7 × CH_2) (Found M^+, 280.1502. $C_{16}H_{24}O_2S$ requires M, 280.1496); *m*/*z* 280.2 (80%, M), 262.1 (M − H_2O), 191.1 (100, $C_6H_{10}SPh$), 171.1 (25, M − SPh), 110.0, (80, PhSH) and 81.1 (90, C_6H_9).

5-[1′-(Phenylsulfanyl)cyclohexyl]pentane-1,5-diol 8, $n = 4$

In the same way as diol **8**, $n = 3$, the acetal **37**, $n = 4$ (0.68 g, 1.85 mmol) and HCl (5 ml, 3 M) in EtOH–H_2O (10 ml, 1:1 ratio) gave, after flash column chromatography on silica gel eluting with ether, the *diol* **8**, $n = 4$ (0.52 g, 96%) as an oil; R_f [ether] 0.45; ν_{max} (film, $CDCl_3$)/cm^{-1} 3600–3250 (OH); δ_H(400 MHz, $CDCl_3$) 7.54–7.25 (5 H, m, SPh), 3.60 (2 H, t, *J* 6.2, CH_2O), 3.24 (1 H, d, *J* 9.8, C*H*OH), 3.19 (1 H, br s, OH) and 2.04–1.13 (16 H, m, 8 × CH_2); δ_C(100 MHz, $CDCl_3$) 137.2 (*m*-SPh), 130.1* (*i*-SPh), 129.0 (*p*-SPh), 128.8 (*o*-SPh), 74.7 (CHOH), 62.7* (CH_2O), 61.8* (*C*SPh), 32.7*, 30.6*, 30.1*, 29.6*, 26.3*, 23.6*, 21.9* and 21.8* (8 × CH_2) (Found M^+, 294.1651. $C_{17}H_{26}O_2S$ requires M, 294.1653); *m*/*z* 294.1 (40%, M), 191.1 (100, $C_6H_{10}SPh$), 185.2 (20, M − SPh), 109.0 (20, PhSH) and 81.1 (70, C_6H_9).

6-[1′-(Phenylsulfanyl)cyclohexyl]hexane-1,6-diol 8, $n = 5$

In the same way as diol **8**, $n = 3$, the acetal **37**, $n = 5$ (3.5 g, 9.21 mmol) and HCl (8 ml, 3 M) in EtOH–H_2O (40 ml, 1:1) gave, after flash column chromatography on silica gel eluting with ether, the *diol* **8**, $n = 5$ (2.6 g, 94%) as an oil; R_f [ether] 0.5; ν_{max} (film, $CDCl_3$)/cm^{-1} 3600–3300 (OH); δ_H(400 MHz, $CDCl_3$) 7.49–7.40 (5 H, m, SPh), 3.60 (2 H, t, *J* 6.6, CH_2O), 3.22 (1 H, dd, *J* 9.8 and 1.4, C*H*OH), 3.20 (1 H, br s, OH) and 2.01–1.19 (18 H, m, 8 × CH_2); δ_C(62.5 MHz, $CDCl_3$) 137.2 (*m*-SPh), 130.1* (*i*-SPh), 128.9 (*p*-SPh), 128.8 (*o*-SPh), 74.6 (CHOH), 62.8* (CH_2O), 61.9* (*C*SPh), 32.6*, 30.5*, 29.6*, 27.1*, 26.3*, 25.9*, 21.9* and 21.8* (8 × CH_2) (Found M^+, 308.1817. $C_{18}H_{28}O_2S$ requires M, 308.1809); *m*/*z* 308.2 (25%, M), 199.1 (25, M − SPh), 191.1 (90, $C_6H_{10}SPh$), 109.0 (40, PhS), 83.1 (100, C_6H_{11}) and 81.0 (90, C_6H_9).

7-[1′-(Phenylsulfanyl)cyclohexyl]heptane-1,7-diol 8, $n = 6$

In the same way as diol **8**, $n = 3$, the acetal **37**, $n = 6$ (74 mg, 0.23 mmol) and HCl (5 ml, 3 M) in EtOH–H_2O (10 ml, 1:1 ratio) gave, after flash column chromatography on silica gel eluting with ether, the *diol* **8**, $n = 6$ (67 mg, 88%) as an oil; R_f [ether] 0.45; ν_{max} (film, $CDCl_3$)/cm^{-1} 3600–3250 (OH); δ_H(250 MHz, $CDCl_3$) 7.52–7.24 (5 H, m, SPh), 3.60 (2 H, t, *J* 6.6, CH_2O), 3.21 (1 H, dd, *J* 9.4 and 2.0, C*H*OH) and 1.99–1.09 (21 H, m, 10 × CH_2 and OH); δ_C(62.5 MHz, $CDCl_3$) 137.2 (*m*-SPh), 130.2 (*i*-SPh), 129.0 (*p*-SPh), 128.8 (*o*-SPh), 74.7 (CHOH), 63.0 (CH_2O), 62.0 (*C*SPh), 32.7, 30.6, 30.5, 29.6, 29.5, 27.4, 26.3, 25.6, 21.9 and 21.8 (10 × CH_2).

9-[1′-(Phenylsulfanyl)cyclohexyl]nonane-1,9-diol 8, $n = 8$

In the same way as diol **8**, $n = 3$, the acetal **37**, $n = 8$ (80 mg, 0.23 mmol) and HCl (5 ml, 3 M) in EtOH–H_2O (10 ml, 1:1 ratio) gave, after flash column chromatography on silica gel eluting with ether, the *diol* **8**, $n = 8$ (78 mg, 100%) as an oil; R_f [ether] 0.4 ν_{max} (film, $CDCl_3$)/cm^{-1} 3600–3250 (OH); δ_H(250 MHz, $CDCl_3$) 7.50–7.25 (5 H, m, SPh), 3.60 (2 H, t, *J* 6.6, CH_2O), 3.22 (1 H, d, *J* 9.9 and 1.0, C*H*OH), 3.07 (1 H, s, OH) and 1.98–1.18 (24 H, m, 12 × CH_2); δ_C(62.5 MHz, $CDCl_3$) 137.3 (*m*-SPh), 130.2 (*i*-SPh), 129.0 (*p*-SPh), 128.8 (*o*-SPh), 74.7 (CHOH), 63.0 (CH_2O), 62.0 (*C*SPh), 32.8, 30.6, 29.7, 29.6, 29.5, 29.4, 27.4, 26.3, 25.7 and 21.9 (12 × CH_2).

12-[1′-(Phenylsulfanyl)cyclohexyl]dodecane-1,12-diol 8, $n = 11$

In the same way as diol **8**, $n = 3$, the acetal **37**, $n = 12$ (107 mg, 0.23 mmol) and HCl (5 ml, 3 M) in EtOH–H_2O (10 ml, 1:1 ratio) gave, after flash column chromatography on silica gel

eluting with ether, the *diol* **8**, $n = 8$ (80 mg, 89%) as an oil; R_f [ether] 0.50; ν_{max} (film, $CDCl_3$)/cm^{-1} 3600–3250 (OH); δ_H(250 MHz, $CDCl_3$) 7.54–7.25 (5 H, m, SPh), 3.60 (2 H, t, *J* 6.6, CH_2O), 3.22 (1 H, dd, *J* 11.2 and 1.9, C*H*OH) and 2.39–1.09 (32 H, m, 15 × CH_2 and 2 × OH); δ_C(62.5 MHz, $CDCl_3$) 137.2 (*o*-SPh), 130.1 (*i*-SPh), 128.9 (*p*-SPh), 128.6 (*m*-SPh), 74.6 (CHOH), 62.9 (*C*SPh), 61.8 (CH_2O), 32.6, 30.4, 29.7, 29.5, 29.3, 27.3, 26.1, 25.6, 21.8 and 21.7 (15 × CH_2).

6-Hydroxy-6-[1′-(phenylsulfanyl)cyclohexyl]hexyl toluene-*p*-sulfonate 10, *n* = 5

Toluene-*p*-sulfonyl chloride (72 mg, 3.25 mmol) was added to a stirred solution of diol **8**, $n = 5$ (0.1 g, 3.25 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 toluene-*p*-sulfonate **10**, $n = 5$ (0.135 g, 90%) as an oil; R_f [light petroleum (40–60 °C)–ether (1:1)] 0.3; ν_{max} (film, $CDCl_3$)/cm^{-1} 3200 (OH); δ_H(250 MHz, $CDCl_3$) 7.78 (2 H, d, *J* 8.3, *o*-SO_2Ar), 7.51–7.28 (7 H, m, SPh and *m*-SO_2Ar), 3.93 (2 H, t, *J* 6.5, CH_2O), 3.18 (1 H, dd, *J* 9.3 and 2.2, C*H*OH), 3.08 (1 H, br s, OH), 2.42 (3 H, s, CH_3, Ar) and 2.04–1.10 (20 H, m, 10 × CH_2); δ_C(62.5 MHz, $CDCl_3$) 144.6* (*i*-OAr), 137.2 (*m*-SPh), 133.2 (*i*-SPh), 130.1* (*i*-*C*CH_3, Ar), 129.8 (*o*-SPh), 129.0 (*p*-SPh), 128.8 (*o*-SO_2Ar), 127.8 (*m*-SO_2Ar), 74.5 (CHOH), 70.6* (CH_2O), 61.8* (*C*SPh), 30.6*, 30.3*, 29.6*, 28.8*, 26.7*, 26.2*, 25.5*, 21.8* and 21.8* (10 × CH_2) and 21.6 (CH_3, Ar) (Found M$^+$, 462.1887. $C_{25}H_{34}O_4S_2$ requires M, 462.1898); *m*/*z* 462.1 (2%, M), 353.2 (40, M − SPh), 191.1 (55, C_6H_{10}SPh), 91.1 (100, C_7H_7) and 81.1 (90, C_6H_9).

5-(Phenylsulfanyl)-1-oxaspiro[5.5]undecane 11

Toluene-*p*-sulfonic acid (3 mg, 17 μmol) was added to a stirred solution of diol **8**, $n = 3$ (25 mg, 89 μmol) in CH_2Cl_2 (2 ml). The solution was refluxed for 5 min. The solution was allowed to cool to room temperature and filtered through a silica plug. The solvent was removed 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 *tetrahydropyran* **11** (23.1 mg, 99%) as an oil; R_f [light petroleum (40–60 °C)–ether (9:1)] 0.4; ν_{max} (film, $CDCl_3$)/cm^{-1} 1600 (SPh); δ_H(400 MHz, $CDCl_3$) 7.49–7.17 (5 H, m, SPh), 3.66–3.56 (2 H, m, CH_2O), 3.03 (1 H, dd, *J* 11.2 and 4.3, C*H*SPh) and 2.22–1.05 (14 H, m, 7 × CH_2); δ_C(62.5 MHz, $CDCl_3$) 136.1* (*i*-SPh), 13.4 (*m*-SPh), 128.9 (*p*-SPh), 126.6 (*o*-SPh), 75.4* (CO), 60.0* (CH_2O), 55.5 (*C*HSPh), 36.3*, 27.2*, 26.4*, 25.9*, 21.3* and 20.6* (6 × CH_2) (Found M$^+$, 262.1395. $C_{16}H_{22}OS$ requires M, 262.1391); *m*/*z* 262.1 (25%, M), 165.1 (100, C_4H_8SPh), 136.0 (80, C_2H_3SPh) and 109.0 (5, PhS).

2-[1′-(Phenylsulfanyl)cyclohexyl]tetrahydrofuran 12

In the same way as toluene-*p*-sulfonate **10**, $n = 5$, the diol **8**, $n = 3$ (70 mg, 0.25 mmol) and toluene-*p*-sulfonyl chloride (52 mg, 0.25 mmol) gave, after flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (9:1), the *tetrahydrofuran* **12** (65 mg, 98%) as an oil; R_f [light petroleum (40–60 °C)–ether (9:1)] 0.2; ν_{max} (film, $CDCl_3$)/cm^{-1} 1600 (SPh); δ_H(400 MHz, $CDCl_3$) 7.56–7.24 (5 H, m, SPh), 3.89–3.82 (1 H, dt, *J* 6.6 and 6.7, OCH_AH_B), 3.72–3.70 (2 H, m, OCH_AH_B and CHO) and 2.08–1.18 (14 H, m, 7 × CH_2); δ_C(100 MHz, $CDCl_3$) 137.3 (*m*-SPh), 131.8* (*i*-SPh), 128.4 (*o*- and *p*-SPh), 84.4 (CHO), 68.7* (CH_2O), 56.6* (*C*SPh), 32.1*, 30.2*, 26.6*, 26.3*, 26.0*, 21.8* and 21.7* (7 × CH_2) (Found M$^+$, 262.1389. $C_{16}H_{22}OS$ requires M, 262.1391); *m*/*z* 262.1 (30%, M), 191.1 (100, C_6H_{10}SPh), 153.1 (90, M − SPh), 123.0 (20, CH_2SPh), 81.1 (65, C_6H_9) and 71.1 (65, M − C_6H_{10}SPh).

TsOH rearrangement of THF 12 to give the THP 11

In the same way as THP **11**, the tetrahydrofuran **12** (50 mg, 0.20 mmol) and toluene-*p*-sulfonic acid (37 mg, 0.20 mmol) in CH_2Cl_2 (3 ml) gave, after flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (9:1), the *tetrahydropyran* **11** (49.5 mg, 99%) as an oil; identical spectroscopically to that obtained previously.

[1-(Phenylsulfanyl)cyclohexyl]ethene 16

n-BuLi (3.63 ml, 1.3 M in hexanes, 4.73 mmol) was added to a solution of methyltriphenylphosphonium iodide (1.16 g, 4.51 mmol) in THF (50 ml) at −78 °C. The solution was stirred for 5 min. A solution of the aldehyde **15** (1.0 g, 4.51 mmol) in THF (10 ml) was added. The solution was stirred for 1 h. Saturated NH_4Cl (5 ml) was added and the solution was allowed to warm to room temperature and extracted with ether (3 × 50 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 *allylic sulfide* **16** (0.94 g, 95%) as an oil; R_f [light petroleum (40–60 °C)–ether (9:1)] 0.3; ν_{max} (film, $CDCl_3$)/cm^{-1} 1660 (C=C); δ_H(250 MHz, $CDCl_3$) 7.51–7.19 (5 H, m, SPh), 5.74 (1 H, dd, *J* 17.7 and 10.7, CH), 4.96 (1 H, dd, *J* 10.7 and 1.0, CH_AH_B), 4.57 (1 H, dd, *J* 17.7 and 1.0, CH_AH_B) and 1.75–1.20 (10 H, m, 5 × CH_2) (Found M$^+$, 218.1132. $C_{14}H_{18}S$ requires M, 218.1129); *m*/*z* 218.1 (20%, M), 109.1 (95, PhS and M − SPh) and 67.1 (100, C_5H_7).

2-[1′-(Phenylsulfanyl)cyclohexyl]epoxyethane 17

In the same way as toluene-*p*-sulfonate **10**, $n = 5$ the diol **8**, $n = 1$ (0.16 g, 0.62 mmol) and toluene-*p*-sulfonyl chloride (0.15 g, 0.68 mmol) in pyridine (2 ml) gave, after flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (1:1), the *epoxide* **17** (0.11 g, 80%) as an oil; R_f [light petroleum (40–60 °C)–ether (1:1)] 0.5; ν_{max} (film, $CDCl_3$)/cm^{-1} 1600 (SPh); δ_H(400 MHz, $CDCl_3$) 7.39–7.19 (5 H, m, SPh), 3.40 (1 H, dd, *J* 10.5 and 2.3, CH_AH_BO), 3.32 (1 H, dd, *J* 13.8 and 2.3, CH_AH_BO), 2.90 (1 H, dd, *J* 13.8 and 10.5, C*H*CH_2O) and 1.72–1.09 (10 H, m, 5 × CH_2); δ_C(100 MHz, $CDCl_3$) 137.2 (*m*-SPh), 130.6* (*i*-SPh), 128.7 (*p*-SPh), 128.7 (*o*-SPh), 73.6 (CHO), 62.6* (CH_2O), 59.1* (*C*SPh), 36.7*, 30.7*, 30.4*, 25.2* and 21.7* (5 × CH_2) (Found M$^+$, 234.1076. $C_{14}H_{18}OS$ requires M, 234.1078); *m*/*z* 282.1 (15%, M), 191.1 (40, C_6H_{10}SPh), 173.1 (5, M − SPh) and 81.1 (100, C_6H_9).

2-[1′-(Phenylsulfanyl)cyclohexyl]epoxyethane 17

n-BuLi (2.37 ml, 1.3 M in hexanes, 3.28 mmol) was added to a stirred solution of trimethylsulfonium iodide (0.64 g, 3.13 mmol) in THF (20 ml) at −30 °C. A solution of aldehyde **15** (0.69 g, 3.13 mmol) in THF (1 ml) was added. The solution was stirred for 1 hour. Saturated NH_4Cl (5 ml) was added and the solution was extracted with ether (3 × 50 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 *epoxide* **17** (0.64 g, 89%) as an oil; identical spectroscopically to that obtained previously.

2-Cyclohexenyl-2-(phenylsulfanyl)ethanol 19

In the same way as THP **11**, $n = 2$ the diol **8**, $n = 1$ (59 mg, 59 μmol) and toluene-*p*-sulfonic acid (2 mg, 11 μmol) in CH_2Cl_2 (1 ml) gave, after flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (1:1), the *allylic sulfide* **19** (13.7 mg, 96%) as an oil; R_f [light petroleum (40–60 °C)–ether (1:1)] 0.5; ν_{max} (film, $CDCl_3$)/cm^{-1} 3250 (OH); δ_H(400 MHz, $CDCl_3$) 7.40–7.22 (5 H, m, SPh), 5.46 (1 H, s, CH=C), 3.78–3.80 (1 H, m, CHSPh), 3.66 (1 H, q, *J* 6.9, CH_A-

H_BOH), 3.62 (1 H, q, *J* 6.9, CH_AH_BOH), 2.15–2.07 (2 H, m, CH_2=C), 1.98–1.93 (2 H, m, CH_2=C), 1.91 (1 H, t, *J* 6.9, OH) and 1.87–1.50 (4 H, m, 2 × CH_2); δ_C(100 MHz, $CDCl_3$) 133.1 (*m*-SPh), 128.7 (*p*-SPh), 127.4 (*o*-SPh), 126.3 (*C*H=C), 62.6* (CH_2OH), 58.5 (*C*HSPh), 26.0* and 25.2* (2 × CH_2), 22.6* and 22.2* (2 × CH_2) (Found M^+, 234.1075. $C_{14}H_{18}OS$ requires M, 234.1078); *m*/*z* 234.1 (15%, M), 203.1 (30, M − CH_2OH), 109.0 (30, SPh) and 81.1 (100, C_6H_9).

TsOH rearrangement of epoxide 17 to the allylic sulfide 19

In the same way as THP **11**, *n* = 2 the epoxide **17** (20 mg, 85 μmol) and toluene-*p*-sulfonic acid (4 mg, 17 μmol) in CH_2Cl_2 (1 ml) gave, after flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (1 : 1), the *allylic sulfide* **19** (19 mg, 100%) as an oil; identical spectroscopically to that obtained previously.

Ethyl 3-hydroxy-3-[1′-(phenylsulfanyl)cyclohexyl]propanoate 25

n-BuLi (8.46 ml, 1.3 M in hexanes, 11 mmol) was added to diisopropylamine (1.41 g, 1.90 ml, 14 mmol) in THF (50 ml) at −78 °C. The solution was stirred for 30 min. Ethyl acetate (0.88 g, 0.98 ml, 10 mmol) in THF (3 ml) was added slowly to this solution. The solution was stirred for 30 min. The aldehyde **15** (2 g, 9 mmol) in THF (10 ml) was added slowly. The solution was stirred for a further 30 min. Saturated NH_4Cl (20 ml) was added and the solution was allowed to warm to room temperature. The solution was 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* **25** (3.17 g, 93%) as a solid, mp 70–71 °C (from hexane); R_f [light petroleum (40–60 °C)–ether (1 : 1)] 0.40; ν_{max} (film, $CDCl_3$)/cm^{-1} 1730 (CO_2); δ_H(250 MHz, $CDCl_3$) 7.53–7.25 (5 H, m, SPh), 4.16 (2H, q, *J* 7.1, CH_2CH_3), 3.87 (1 H, d, *J* 10.2, OH), 3.08 (1 H, d, *J* 3.1, OH), 2.90 (1 H, dd, *J* 15.7 and 2.1, CH_AH_BC=O), 2.54 (1 H, dd, *J* 15.7 and 10.3, CH_AH_BC=O), 1.93–1.15 (10 H, m, 5 × CH_2) and 1.27 (3 H, t, *J* 7.1, CH_3); δ_C(100 MHz, $CDCl_3$) 173.2* (C=O), 137.3 (*m*-SPh), 131.9* (*i*-SPh), 129.0 (*p*-SPh), 128.8 (*m*-SPh), 72.7 (CHOH), 60.7 (CH_2O), 58.7* (*C*SPh), 36.4*, 30.3*, 30.1*, 25.9* and 21.7* (5 × CH_2) and 14.2 (CH_3) (Found M^+, 308.1435. $C_{17}H_{24}O_3S$ requires M, 308.1446); *m*/*z* 199.1 (18%, M − SPh).

4-(Phenylsulfanyl)-1-oxaspiro[4.5]decane 26

In the same way as THP **11**, the diol **8**, *n* = 2 (0.1 g, 0.37 mmol) and toluene-*p*-sulfonic acid (22 mg, 0.10 mmol) in THF (2 ml) gave, after flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (9 : 1), the *tetrahydrofuran* **26** (92 mg, 99%) as an oil; R_f [light petroleum (40–60 °C)–ether (1 : 1)] 0.78; ν_{max} (film, $CDCl_3$)/cm^{-1} 1600 (SPh); δ_H(250 MHz, $CDCl_3$) 7.47–7.17 (5 H, m, SPh), 3.97–3.86 (1 H, dt, *J* 9.0 and 5.0, OCH_AH_B), 3.86–3.77 (1 H, dt, *J* 8.8 and 6, OCH_AH_B), 3.40–3.32 (1 H, t, *J* 7.7, CHSPh), 2.50–2.36 (1 H, ddt, *J* 8.0, 7.0 and 2.4, $CH_CH_DCH_2O$), 2.10–1.96 (1 H, ddt, *J* 10.0, 9.9 and 8.0, $CH_CH_DCH_2O$) and 1.75–1.17 (10 H, m, 5 × CH_2) (Found M^+, 248.1234. $C_{15}H_{20}OS$ requires M, 248.1236); *m*/*z* 150.0 (100%, M − $C_6H_{10}O$), 135 (60, C_2H_2SPh), 117 (95, M − C_2H_2SPh) and 109.0 (35, SPh).

1-Cyclohexenyl-3-(phenylsulfanyl)propanol 28

In the same way as the toluene-*p*-sulfonate **10**, *n* = 5, the diol **8**, *n* = 2 (0.1 g, 0.36 mmol) and toluene-*p*-sulfonyl chloride (76 mg, 0.40 mmol) in pyridine (1 ml) gave, after column chromatography on silica eluting with light petroleum (40–60 °C)–ether (6 : 4) the *allylic alcohol* **28** (90.5 mg, 97%) as an oil; R_f [light petroleum (40–60 °C)–ether (6 : 4)] 0.42; ν_{max} (film, $CDCl_3$)/cm^{-1} 3400 (OH); δ_H(400 MHz, $CDCl_3$) 7.37–7.11 (5 H, m, SPh), 5.67 (1H, s, C=CH), 4.11 (1 H, t, *J* 7.0, C*H*OH), 3.02–2.92 (2 H, m, CH_2SPh), 2.01–1.51 (10 H, m, 5 × CH_2) and 1.64 (1 H, s, OH); δ_C(100 MHz, $CDCl_3$) 139.3* (*C*=CH), 136.5* (*i*-SPh), 129.1 (*m*-SPh), 128.9 (*o*-SPh), 125.8 (*p*-SPh), 123.4 (*C*H=C), 75.2 (CHOH), 34.2* (*C*H_2-SPh), 30.8*, 29.7*, 24.9*, 23.6* and 22.6* (5 × CH_2) (Found: M^+, 248.1237. $C_{15}H_{20}OS$ requires M, 248.1235); *m*/*z* 248.1 (100%, M), 139 (10, M − SPh) and 81 (40, M − C_3H_6OSPh).

3-Hydroxy-3-[1′-(phenylsulfanyl)cyclohexyl]propyl benzoate 31

Benzoyl chloride (0.4 g, 0.27 ml, 2.88 mmol) was added slowly to a stirred solution of diol **8**, *n* = 2 (0.9 g, 2.88 mmol), and Et_3N (0.29 g, 0.4 ml, 2.88 mmol) in CH_2Cl_2 (30 ml). The solution was stirred for 5 hours. Saturated NH_4Cl (10 ml) was added and the solution was 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 *benzoate* **31** (1.02 g, 81%) as an oil; R_f [light petroleum (40–60 °C)–ether (1 : 1)] 0.51; ν_{max} (film, $CDCl_3$)/cm^{-1} 1740 (CO_2Ph); δ_H(400 MHz, $CDCl_3$) 7.95–7.19 (10 H, m, Ph-C=O and SPh), 4.55–4.45 (2 H, m, CH_2O), 3.53–3.45 (1 H, dd, *J* 10.5 and 1.1, C*H*OH), 3.30–3.00 (1 H, s, OH), 2.25–1.95 (1 H, ddt, *J* 15.0, 9.0 and 1.1, CH_CH_D-CH_2O) and 2.03–1.07 (11 H, m, $CH_CH_DCH_2$ and 5 × CH_2); δ_C(100 MHz, $CDCl_3$) 166.6* (C=O), 137.3 (*m*-SPh), 132.9 (*m*-Ph-C=O), 130.4* (*i*-SPh), 130.2* (*i*-Ph-C=O), 129.6 (*o*-Ph-C=O), 129.0 (*p*-Ph-C=O), 128.6 (*p*-SPh), 128.3 (*o*-SPh), 71.5 (CHOH), 63.0* (CH_2O), 60.6* (*C*SPh), 30.3*, 30.0*, 29.8*, 26.2*, 21.8* and 21.8* (6 × CH_2) (Found M^+, 370.1594. $C_{22}H_{26}O_3S$ requires M, 370.1602); *m*/*z* 370.2 (75%, M), 352.2 (25, M − H_2O), 261.2 (40, M − SPh), 243.1 (75, M − SPh − H_2O), 191.1 (75, $C_6H_{11}SPh$), 139.1 (80, M − SPh − OH − Ph-C=O), 121.1 (80, $PhCO_2$), 105.0 (100, Ph-C=O) and 77.0 (75, Ph).

3-Cyclohexenyl-3-(phenylsulfanyl)propyl benzoate 32

In the same way as THP **11**, the benzoate **31** (0.4 g, 1 mmol) and toluene-*p*-sulfonic acid (41 mg, 0.2 mmol) in CH_2Cl_2 (2 ml) gave, after flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (1 : 1), the *allylic sulfide* **32** (0.37 g, 97%) as an oil; R_f [light petroleum (40–60 °C)–ether (1 : 1)] 0.5; ν_{max} (film, $CDCl_3$)/cm^{-1} 1750 (CO_2); δ_H(200 MHz, $CDCl_3$) 8.15–7.95 (2 H, m, *o*- to C=O, $PhCO_2$), 7.59–7.17 (8 H, m, SPh, *p*- and *m*- to C=O, $PhCO_2$) 5.45 (1 H, br s, CH=C), 4.99–4.27 (2 H, m, CH_2O), 3.76–3.69 (1 H, t, *J* 3.7, CHSPh) and 2.31–1.42 (10 H, m, 5 CH_2); δ_C(62.5 MHz, $CDCl_3$) 166.4* (C=O), 134.9* (*i*-$PhCO_2$), 133.2, 132.9, 130.2, 129.5, 128.5, 128.3, 127.2 and 126.0 (Ar, SPh and $PhCO_2$), 130.0* (*i*-SPh), 125.0* (CH=*C*), 109.0 (*C*H=C), 62.9* (CH_2O), 53.7 (CHSPh), 31.6* (*C*H_2CH=C), 25.1*, 24.2*, 22.6* and 22.5* (4 × CH_2) (Found M^+, 352.1473. $C_{22}H_{24}O_2S$ requires M, 352.1496); *m*/*z* 352.1 (20%, M), 243.1 (80, M − SPh), 191.1 (15, $C_6H_{10}SPh$), 121.1 (100, $PhCO_2$), 105.0 (55, PhCO) and 109 (25, SPh).

3-Cyclohexenyl-3-(phenylsulfanyl)propanol 33

NaOH (1 ml, 10%) was added to a stirred solution of benzoate **32** (1 g, 2.83 mmol) in MeOH–H_2O (10 ml, 1 : 1). The solution was stirred for 1 hour. HCl (2 ml, 3 M) was added (until pH = 7). H_2O (10 ml) was added and the solution was extracted with ether (3 × 50 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 *allylic sulfide* **33** (0.6 g, 85%) as an oil; R_f [light petroleum (40–60 °C)–ether (1 : 1)] 0.6; ν_{max} (film, $CDCl_3$)/cm^{-1} 3200 (OH); δ_H(400 MHz, $CDCl_3$) 7.36–7.18 (5 H, m, SPh), 5.30 (1 H, s, CH=C), 3.76–3.63 (3 H, m, CH_2O and C*H*SPh) and 2.21–1.12

(10 H, m, 5 × CH_2); δ_C(100 MHz, $CDCl_3$) 135.8* (*i*-SPh), 135.0* (*C*=CH), 133.2 (*m*-SPh), 128.5 (*p*-SPh), 127.1 (*o*-SPh), 125.5 (*C*H=C), 61.0* (CH_2OH), 54.0 (*C*HSPh), 35.3* (CH_2CH=C), 25.2*, 24.1*, 22.7* and 22.4* (4 × CH_2) (Found M^+, 248.1231. $C_{15}H_{20}OS$ requires M, 248.1234); *m*/*z* 248.1 (60%, M), 139.1 (75, M − SPh), 121.1 (100, CHSPh), 109.0 (55, SPh) and 58 (20, C_3H_6O).

5-Bromopentanol 34, *n* = 5, X = Br

In the same way as alcohol **33**, the 5-bromopentyl acetate (12 g, 9.56 ml, 57.4 mmol) and NaOH (20 ml, 10%) in EtOH–H_2O (100 ml, 1 : 1) gave, after flash column chromatography on silica gel eluting with ether, the *bromo alcohol* **34**, *n* = 5, X = Br (8.48 g, 89%) as a liquid; R_f [ether] 0.45; ν_{max} (film, $CDCl_3$)/cm^{-1} 3400–3200 (OH); δ_H(250 MHz, $CDCl_3$) 3.63 (2 H, t, *J* 6.3, CH_2O), 3.39 (2 H, t, *J* 6.7, CH_2Br) and 2.03–1.42 (7 H, m, 3 × CH_2 and OH); δ_C(62.5 MHz, $CDCl_3$) 62.53* (CH_2O), 33.73* (CH_2Br), 32.48*, 31.73* and 24.42* (3 × CH_2).

3-Bromo-1-(1′-ethoxyethoxy)propane 35, *n* = 3, X = Br

The bromo alcohol **34**, *n* = 3 (7.8 g, 5.07 ml, 56.1 mmol) was added to ethyl vinyl ether (20 ml) at 0 °C. Dichloroacetic acid (0.72 g, 0.46 ml, 5.61 mmol) was added and the solution was stirred for 12 hours. Na_2CO_3 (1 g, solid) was added. The solution was filtered through a cotton wool plug. The solvent was removed 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 *acetal* **35**, *n* = 3 (10.9 g, 92%) as a liquid; R_f [light petroleum (40–60 °C)–ether (9 : 1)] 0.45; ν_{max} (film, $CDCl_3$)/cm^{-1} 3100 (CH); δ_H(250 MHz, $CDCl_3$) 4.70 (1 H, m, OCHO), 3.78–3.42 (6 H, m, CH_2Br and 2 × CH_2O), 2.12–2.00 (2 H, m, CH_2), 1.29 (3 H, d, *J* 5.3, CH_3CH), 1.15 (3 H, t, *J* 7.3, CH_3) and 1.13 (3 H, t, *J* 7.0, CH_3); δ_C(62.5 MHz, $CDCl_3$) 99.9 (OCHO), 62.6* (CH_2O), 60.5* (CH_2O), 32.8* (CH_2Br), 30.6* (CH_2), 19.7 and 15.2 (2 × CH_3) (Found M^+, 210.0260. $C_7H_{15}O_2Br$ requires M, 210.0255); *m*/*z* 210.0 (100%, M).

4-Chloro-1-(1′-ethoxyethoxy)butane 35, *n* = 4, X = Cl

In the same way as acetal **35**, *n* = 3, the chloro alcohol **34**, *n* = 4 (7.8 g, 7.16 ml, 71.8 mmol) and dichloroacetic acid (0.92 g, 0.63 ml, 7.18 mmol) in ethyl vinyl ether (20 ml) gave, after flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (9 : 1), the *acetal* **35**, *n* = 4 (11.7 g, 90%) as a liquid; R_f [light petroleum (40–60 °C)–ether (9 : 1)] 0.35; ν_{max} (film, $CDCl_3$)/cm^{-1} 3100 (CH); δ_H(250 MHz, $CDCl_3$) 4.69 (1 H, m, OCHO), 3.64–3.37 (6 H, m, CH_2Cl and 2 × CH_2), 1.87–1.66 (4 H, m, 2 × CH_2), 1.28 (3 H, d, *J* 5.4, CH_3CH) and 1.18 (3 H, t, *J* 7.0, CH_3CH_2); δ_C(62.5 MHz, $CDCl_3$) 99.6 (OCHO), 62.5* (CH_2O), 60.8* (CH_2O), 32.8* (CH_2Cl), 30.5* and 30.5* (2 × CH_2), 19.8 and 15.4 (2 × CH_3) (Found $(M - CH_3)^+$, 165.0679. $C_7H_{14}O_2Cl$ requires M, 165.0682); *m*/*z* 165.1 (20%, M − CH_3), 91.1 (90, M − 1-ethoxyethoxy (OEE)) and 73 (100, M − C_4H_8Cl).

5-Bromo-1-(1′-ethoxyethoxy)pentane 35, *n* = 5, X = Br

In the same way as acetal **35**, *n* = 3, the bromo alcohol **34**, *n* = 5; X = Br (10 g, 60.2 mmol) and dichloroacetic acid (0.77 g, 0.49 ml, 6.02 mmol) in ethyl vinyl ether (20 ml) gave, after flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (9 : 1), the *acetal* **35**, *n* = 5, X = Br (13.47 g, 94%) as an oil; R_f [light petroleum (40–60 °C)–ether (9 : 1)] 0.4; δ_H(250 MHz, $CDCl_3$) 4.65 (1 H, q, *J* 5.3, OCHO), 3.70–3.35 (4 H, m, 2 × CH_2O), 3.26 (2 H, t, *J* 6.7, CH_2Br), 1.87 (2 H, m, CH_2), 1.65–1.43 (4 H, m, 2 × CH_2), 1.29 (3 H, d, *J* 5.4, CH_3CH) and 1.19 (3 H, t, *J* 7.1, CH_3CH_2); δ_C(62.5 MHz, $CDCl_3$) 99.6 (OCHO), 65.8* and 60.7* (2 × CH_2O), 33.8* (CH_2Br), 32.6*, 29.0* and 25.0* (3 × CH_2), 19.8 and 15.3 (2 × CH_3).

6-Bromo-1-(1′-ethoxyethoxy)hexane 35, *n* = 6, X = Br

In the same way as acetal **35**, *n* = 3, the bromo alcohol **34**, *n* = 6; X = Br (2.1 g, 11.6 mmol) and dichloroacetic acid (0.24 g, 0.16 ml, 1.93 mmol) in ethyl vinyl ether (10 ml) gave, after flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (9 : 1), the *acetal* **35**, *n* = 6, X = Br (2.7 g, 95%) as an oil; R_f [light petroleum (40–60 °C)–ether (9 : 1)] 0.36; δ_H(250 MHz, $CDCl_3$) 4.65 (1 H, q, *J* 5.4, OCHO), 3.68–3.34 (4 H, m, 2 × CH_2O), 3.39 (2 H, t, *J* 6.8, CH_2Br), 1.85 (2 H, q, *J* 6.6, CH_2CH_2Br), 1.56 (2 H, q, *J* 6.6, CH_2CH_2O), 1.52–1.30 (4 H, m, 2 × CH_2), 1.28 (3 H, d, *J* 5.3, CH_3CH) and 1.18 (3 H, t, *J* 7.1, CH_3CH_2); δ_C(62.5 MHz, $CDCl_3$) 99.5 (OCHO), 65.9 and 65.7 (2 × CH_2O), 33.8 (CH_2Br), 32.7, 29.0, 27.9 and 25.0 (4 × CH_2), 19.8 and 15.2 (2 × CH_3) (Found $(M - CH_3)^+$, 237.0488. $C_9H_{18}O_2Br$ requires M − CH_3, 237.0491); *m*/*z* 237.0 (85%, M − CH_3), 163.1 (75, M − OCH(Me)OEt), and 73.1 (100, M − $(CH_2)_6Br$).

8-Bromo-1-(1′-ethoxyethoxy)octane 35, *n* = 8, X = Br

In the same way as acetal **35**, *n* = 3, the bromo alcohol **35**, *n* = 8, X = Br (2.0 g, 9.6 mmol) and dichloroacetic acid (0.2 g, 0.13 ml, 1.6 mmol) in ethyl vinyl ether (10 ml) gave, after flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (9 : 1), the *acetal* **35**, *n* = 8, X = Br (2.43 g, 91%) as an oil; R_f [light petroleum (40–60 °C)–ether (9 : 1)] 0.38; δ_H(250 MHz, $CDCl_3$) 4.66 (1 H, q, *J* 5.3, OCHO), 3.68–3.30 (4 H, m, 2 × CH_2O), 3.39 (2 H, t, *J* 6.8, CH_2Br), 1.84 (2 H, q, *J* 6.7, CH_2-CH_2Br), 1.55 (2 H, q, *J* 6.7, CH_2CH_2O), 1.52–1.28 (4 H, m, 2 × CH_2), 1.29 (3 H, d, *J* 5.4, CH_3CH) and 1.18 (3 H, t, *J* 7.1, CH_3CH_2); δ_C(62.5 MHz, $CDCl_3$) 99.7 (OCHO), 65.4 and 60.8 (2 × CH_2O), 34.1 (CH_2Br), 32.9, 30.0, 29.4, 28.8, 28.2 and 26.3 (6 × CH_2), 20.0 and 15.5 (2 × CH_3) (Found $(M - CH_3)^+$, 265.0806. $C_{11}H_{20}O_2Br$ requires M − CH_3, 265.0806); *m*/*z* 291.2 (13%, M+), 237.0 (14, M − CH_3), 191.1 (75, M − OCH(Me)-OEt) and 73.1 (100, M − $(CH_2)_8Br$).

11-Bromo-1-(1′-ethoxyethoxy)undecane 35, *n* = 11, X = Br

In the same way as acetal **35**, *n* = 3, the bromo alcohol **35**, *n* = 11, X = Br (9 g, 36 mmol) and dichloroacetic acid (0.77 g, 0.49 ml, 6.02 mmol) in ethyl vinyl ether (20 ml) gave, after flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (9 : 1), the *acetal* **35**, *n* = 11, X = Br (10 g, 86%) as an oil; R_f [light petroleum (40–60 °C)–ether (9 : 1)] 0.31; δ_H(250 MHz, $CDCl_3$) 4.66 (1 H, q, *J* 5.3, OCHO), 3.70–3.38 (4 H, m, 2 × CH_2O), 3.34 (2 H, t, *J* 6.8, CH_2Br), 1.83 (2 H, q, *J* 6.8, CH_2CH_2Br), 1.52 (2 H, q, *J* 6.7, CH_2CH_2O), 1.43–1.26 (14 H, m, 7 × CH_2), 1.28 (3 H, d, *J* 5.4, CH_3CH) and 1.21 (3 H, t, *J* 6.9, CH_3CH_2); δ_C(62.5 MHz, $CDCl_3$) 99.6 (OCHO), 65.8 and 65.4 (2 × CH_2O), 34.7 (CH_2Br), 32.9, 30.0, 29.7, 29.6, 29.5, 28.9, 28.3 and 26.4 (8 × CH_2), 20.0 and 15.5 (2 × CH_3) (Found M^+, 322.1500. $C_{15}H_{31}O_2Br$ requires M, 322.1508); *m*/*z* 322.1 (11%, M+), 307.1 (50, M − CH_3), 233.1 (46, M − OCH(Me)-OEt), and 73.1 (100, M − $(CH_2)_{11}Br$).

4-(1″-Ethoxyethoxy)-1-[1′-(phenylsulfanyl)cyclohexyl]butanol 37, *n* = 3

Lithium (70 mg, lithium + 1% sodium wire, 10 mmol) was added to a stirred solution of acetal **35**, *n* = 3 (0.63 g, 3 mmol) in ether (2 ml) at −20°C. The solution was stirred for 3 hours. A solution of aldehyde **15** (0.22 g, 1 mmol) in ether (1 ml) was added. The solution was stirred for 1 hour. Saturated NH_4Cl (10 ml) was added and the solution was extracted with ether (3 × 50 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 *acetal* **37**; *n* = 3 (0.34 g, 99%) as an oil; R_f [light petroleum (40–60 °C)–ether (1 : 1)] 0.50; ν_{max} (film, $CDCl_3$)/cm^{-1} 3200 (OH); δ_H(250

MHz, $CDCl_3$) 7.56–7.21 (10 H, m, SPh^A and SPh^B), 4.64–4.56 (2 H, m, 2 × CHO), 3.62–3.48 (4 H, m, 2 × OCH_2CH_2), 3.48–3.31 (4 H, m, 2 × OCH_2CH_3), 3.28–3.22 (2 H, br s, 2 × OH), 2.03–1.30 (24 H, m, 12 × CH_2), 1.25–1.23 (3 H, d, *J* 1.9, $CHCH_3^A$), 1.23–1.20 (3 H, d, *J* 1.9, $CHCH_3^B$) and 1.20–1.10 (1 H, t, *J* 7.0, $CH_2CH_3^A$ and $CH_2CH_3^B$); δ_C(62.5 MHz, $CDCl_3$) 137.4 (*m*-SPh), 130.5* (*i*-SPh), 129.0 (*p*-SPh), 128.6 (*o*-SPh), 89.5 (OCHO), 74.9 (HCO), 65.0* (CH_2O), 60.7* (CH_2O), 55.4* (*C*SPh), 29.8*, 27.4*, 27.4*, 26.1* and 23.0* (5 × CH_2), 25.7, 22.2, 19.8 and 15.2 (2 × Me^A and 2 × Me^B) (Found M^+, 352.2070. $C_{20}H_{32}O_3S$ requires M, 352.2072); *m*/*z* 352.2 (20%, M), 335.0 (5, M − H_2O + H), 306.2 (80, M − CH_3CH_2OH), 278.2 (10, M − CH_3CHO − CH_3CH_2OH), 191.1 (100, $C_6H_{10}SPh$) and 110 (30, PhSH).

5-(1″-Ethoxyethoxy)-1-[(1′-phenylsulfanyl)cyclohexyl]pentanol 37, *n* = 4

In the same way as alcohol **37**, *n* = 3, the chloro acetal **35**, *n* = 4 (7.38 g, 40.8 mmol), lithium (0.68 g, lithium + 1% sodium wire, 136 mmol) and aldehyde **15** (3 g, 13.6 mmol) in ether (15 ml) gave, after flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (1 : 1), the *acetal* **37**, *n* = 4 (4.26 g, 85%) as an oil, R_f [light petroleum (40–60 °C)–ether (1 : 1)] 0. ν_{max} (film, $CDCl_3$)/cm^{-1} 3400–3200 (OH); δ_H(400 MHz, $CDCl_3$) 7.57–7.27 (5 H, m, SPh), 4.66 (1 H, q, *J* 5.34, OC*H*O), 3.64 (1 H, t, *J* 6.3, C*H*OH), 3.58–3.51 (2 H, m, CH_2O), 3.35 (1 H, m, CH_AH_BO), 3.23 (1 H, m, CH_AH_BO), 3.04 (1 H, s, OH), and 1.97–1.19 (16 H, m, 8 × CH_2); δ_C(100 MHz, $CDCl_3$) 137.2 (*m*-SPh), 130.2* (*i*-SPh), 128.9 (*p*-SPh), 128.8 (*o*-SPh), 99.7 (OCHO), 74.9 (CHOH), 65.3* (CH_2O), 62.0* (*C*SPh), 61.8* (CH_2O), 30.5*, 30.1*, 30.2*, 29.9*, 29.6*, 26.2*, 24.1* and 21.8* (8 × CH_2) and 19.8 (CH_3CH) (Found $(M - CH_2CH_3)^+$, 321.1884. $C_{19}H_{29}O_2S$ requires M − CH_2CH_3, 321.1888); *m*/*z* 321.2 (80%, M − CH_2CH_3), 191.1 (100, $C_6H_{10}SPh$), 109 (10, PhSH) and 81.0 (30, C_6H_9).

6-(1″-Ethoxyethoxy)-1-[(1′-phenylsulfanyl)cyclohexyl]hexanol 37, *n* = 5

In the same way as alcohol **37**, *n* = 3, the bromo acetal **35**, *n* = 5, X = Br (7.69 g, 34.08 mmol), lithium (0.79 g, lithium + 1% sodium wire, 113 mmol) and aldehyde **15** (2.5 g, 11.36 mmol) in ether (15 ml) gave, after flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (1 : 1), an inseparable diastereomeric mixture (50 : 50) of the *acetal* **37**, *n* = 5 (3.92 g, 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(250 MHz, $CDCl_3$) 7.53–7.27 (5 H, m, SPh), 4.65 (1 H, q, *J* 5.3, OCHO), 3.70–3.08 (4 H, m, 2 × CH_2), 3.22 (1 H, dt, *J* 9.2 and 2.3, C*H*OH), 3.08 (1 H, d, *J* 2.4, OH), 2.05–1.21 (18 H, m, 9 × CH_2), 1.29 (3 H, d, *J* 5.3, CH_3CH) and 1.19 (3 H, t, *J* 7.0, CH_3CH_2); δ_C(62.5 MHz, $CDCl_3$) 137.2 (*m*-SPh), 130.1* (*i*-SPh), 128.9 (*p*-SPh), 128.8 (*o*-SPh), 99.5 (OCHO), 74.6 (CHOH), 65.2* and 60.6* (2 × CH_2), 58.0* (*C*SPh), 30.6*, 30.5*, 29.8*, 29.6*, 27.2*, 26.4*, 26.2*, 25.8* and 21.8* (9 × CH_2), 19.8 and 15.3 (2 × CH_3) (Found $(M - OCH_2CH_3)^+$, 335.2036. $C_{20}H_{31}O_2S$ requires M − OCH_2CH_3, 335.2044); *m*/*z* 335.1 (10%, M − OCH_2CH_3), 308.2 (50, M − EE + H), 291.2 (20, M − OEE), 191.1 (100, $C_6H_{10}SPh$), 109.0 (25, PhS), 81.1 (85, C_6H_9) and 73.1 (55, EE).

7-(1″-Ethoxyethoxy)-1-[(1′-phenylsulfanyl)cyclohexyl]heptanol 37, *n* = 6

In the same way as alcohol **37**, *n* = 3, the chloro acetal **35**, *n* = 6 (0.76 g, 3 mmol), lithium (70 mg, lithium + 1% sodium wire, 10 mmol) and aldehyde **15** (0.22 g, 1 mmol) in ether (15 ml) gave, after flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (1 : 1), the *acetal* **37**, *n* = 6 (0.37 g, 96%) as an oil; R_f [light petroleum (40–60 °C)–ether (1 : 1)] 0.44; ν_{max} (film, $CDCl_3$)/cm^{-1} 3400–3200 (OH); δ_H(250 MHz, $CDCl_3$) 7.48–7.24 (5 H, m, SPh), 4.64 (1 H, q, *J* 5.2, OC*H*O), 3.70–3.35 (4 H, m, 2 × CH_2O), 3.25 (1 H, s, OH), 3.20 (1 H, dt, *J* 9.2 and 2.5, C*H*OH), 1.94–1.14 (20 H, m, 13 × CH_2), 1.28 (3 H, d, *J* 5.3, CH_3CH) and 1.20 (3 H, d, *J* 7.1, CH_3CH); δ_C(62.5 MHz, $CDCl_3$) 137.2 (*m*-SPh), 130.2 (*i*-SPh), 129.0 (*p*-SPh), 128.8 (*o*-SPh), 99.5 (OCHO), 74.7 (CHOH), 65.2 and 61.9 (2 × CH_2O), 60.6 (*C*SPh), 32.6, 30.5, 29.8, 29.6, 29.5, 27.4, 26.3, 26.2, 21.9 and 21.8 (10 × CH_2), 19.8 (CH_3CH) and 15.3 (CH_3CH) (Found M^+, 394.2510. $C_{23}H_{38}O_3S$ requires M, 394.2541); *m*/*z* 349.2 (68%, M − OEt) and 73.0 (100, M − $C_{19}H_{29}OS$).

9-(1″-Ethoxyethoxy)-1-[(1′-phenylsulfanyl)cyclohexyl]nonanol 37, *n* = 8

In the same way as alcohol **37**, *n* = 3, the chloro acetal **35**, *n* = 8 (0.84 g, 3 mmol), lithium (70 mg, lithium + 1% sodium wire, 10 mmol) and aldehyde **15** (0.22 g, 1 mmol) in ether (15 ml) gave, after flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (1 : 1), the *acetal* **37**, *n* = 8 (0.37 g, 87%) as an oil; R_f [light petroleum (40–60 °C)–ether (1 : 1)] 0.44; ν_{max} (film, $CDCl_3$)/cm^{-1} 3400–3200 (OH); δ_H(250 MHz, $CDCl_3$) 7.50–7.25 (5 H, m, SPh), 4.65 (1 H, q, *J* 5.4, OC*H*O), 3.71–3.36 (4 H, m, 2 × CH_2O), 3.22 (1 H, dd, *J* 8.7 and 1.1, C*H*OH), 1.80–1.16 (24 H, m, 12 × CH_2), 1.27 (3 H, d, *J* 5.1, CH_3CH) and 1.18 (3 H, t, *J* 7.1, CH_3CH_2); δ_C(62.5 MHz, $CDCl_3$) 137.3 (*m*-SPh), 130.2 (*i*-SPh), 129.0 (*p*-SPh), 128.8 (*o*-SPh), 99.5 (OCHO), 74.7 (CHOH), 65.3 and 62.0 (2 × CH_2O), 60.6 (*C*SPh), 32.8, 30.6, 30.0, 29.7, 29.6, 29.5, 29.4, 27.4, 26.3, 26.2, 25.7 and 21.9 (12 × CH_2), 19.9 (CH_3CH) and 15.3 (CH_3CH_2) (Found M^+, 422.0000. $C_{25}H_{42}O_3S$ requires M, 422.2800); *m*/*z* 422.0 (4%, M), 377.1 (75, M − OEt) and 73.0 (92, M − $C_{21}H_{33}OS$).

12-(1″-Ethoxyethoxy)-1-[(1′-phenylsulfanyl)cyclohexyl]-dodecan-1-ol 37, *n* = 11

In the same way as alcohol **37**, *n* = 3, the bromo acetal **35**, *n* = 11 (0.96 g, 3 mmol), lithium (70 mg, lithium + 1% sodium wire, 10 mmol) and aldehyde **15** (0.22 g, 1 mmol) in ether (15 ml) gave, after flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (9 : 1), the *acetal* **37**, *n* = 12 (0.46 g, 99%) as an oil; R_f [light petroleum (40–60 °C)–ether (9 : 1)] 0.14; δ_H(250 MHz, $CDCl_3$) 7.52–7.25 (5 H, m, SPh), 4.70 (1 H, q, *J* 5.4, OCHO), 3.67–3.34 (4 H, m, 2 × CH_2O), 3.22 (1 H, dt, *J* 9.3 and 2.1, C*H*OH), 3.06 (1 H, d, *J* 2.1, OH), 2.00–1.05 (32 H, m, 16 × CH_2), 1.28 (3 H, d, *J* 5.3, CH_3CH) and 1.18 (3 H, t, *J* 7.1, CH_3CH_2); δ_C(62.5 MHz, $CDCl_3$) 137.4 (*m*-SPh), 130.0 (*i*-SPh), 129.1 (*p*-SPh), 128.9 (*o*-SPh), 99.7 (OCHO), 74.8 (CHOH), 65.4 and 60.7 (2 × CH_2O), 62.2 (*C*SPh), 32.8, 30.7, 30.0, 29.9, 29.8, 29.7, 27.6, 26.4, 26.2, 22.0, 21.9 (15 × CH_2), 20.0 (CH_3CH) and 15.5 (CH_3CH_2) (Found $(M - Me)^+$, 447.3317. $C_{27}H_{45}O_3S$ requires (M − Me), 447.3296); *m*/*z* 447.3 (110%, M − Me), 419.1 (61, M − OEt) and 73.0 (92, M − $C_{24}H_{39}OS$).

2-[1′-(Phenylsulfanyl)cyclohexyl]tetrahydropyran 41

In the same way as the toluene-*p*-sulfonate **10**, *n* = 5, the diol **8**, *n* = 4 (75 mg, 0.26 mmol) and toluene-*p*-sulfonyl chloride (57 mg, 0.26 mmol) in pyridine (1 ml) gave, after flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (9 : 1), the *tetrahydropyran* **41** (69 mg, 98%) as an oil; R_f [light petroleum (40–60 °C)–ether (9 : 1)] 0.55; ν_{max} (film, $CDCl_3$)/cm^{-1} 1550 (SPh); δ_H(400 MHz, $CDCl_3$) 7.53–7.26 (5 H, m, SPh), 4.00 (1 H, dt, *J* 11.2 and 1.9, CH_AH_BO), 3.28 (1 H, td, *J* 11.2 and 2.7, CH_AH_BO), 3.07 (1 H, dd, *J* 10.8 and 1.6, C*H*SPh) and 2.04–1.21 (16 H, m, 8 × CH_2); δ_C(100 MHz, $CDCl_3$) 137.6 (*o*-SPh), 131.9* (*i*-SPh), 128.6 (*p*-SPh), 128.4 (*o*-SPh), 82.0 (CHOH), 69.1* (CH_2O), 57.2 (*C*SPh), 30.8*,

30.5*, 25.9*, 25.5*, 24.0*, 23.7*, 21.9* and 21.8* (8 × CH_2) (Found M^+, 276.1560. $C_{17}H_{24}OS$ requires M, 276.1548); *m/z* 276.1 (30%, M), 191.1 (70, $C_6H_{10}SPh$), 167.1 (63, M − SPh), 110.0 (10, PhSH) and 83.9 (100, M − $C_6H_{10}SPh$).

5-Cyclohexenyl-5-(phenylsulfanyl)pentan-1-ol 42

In the same way as THP **11**, the tetrahydropyran **41** (10 mg, 36.4 μmol) toluene-*p*-sulfonic acid (6.2 mg, 36.4 μmol) in toluene (1 ml) gave, after flash column chromatography on silica gel eluting with light petroleum (40–60 °C)–ether (9 : 1), the *allylic sulfide* **42** (9.2 mg, 92%) as an oil; R_f [light petroleum (40–60 °C)–ether (1 : 1)] 0.4; ν_{max} (film, $CDCl_3$)/cm^{-1} 3300–3100 (OH) and 1600 (SPh); δ_H(250 MHz, $CDCl_3$) 7.37–7.20 (5 H, m, SPh), 5.25 (1 H, br s, CH=C), 3.51 (1 H, t, *J* 7.6, C*H*SPh), 3.51 (2 H, t, *J* 7.2, CH_2O), 2.50 (1 H, br s, OH) and 2.15–1.20 (14 H, m, 7 × CH_2); δ_C(62.5 MHz, $CDCl_3$) 135.6* (*i*-SPh), 133.2 (*m*-SPh), 128.6 (*o*-SPh), 127.2 (*p*-SPh), 125.4 (*C*H=C), 57.2 (*C*HSPh), 70.7* (CH_2O), 31.9*, 27.1*, 25.1*, 24.6*, 23.9*, 22.8* and 22.2* (7 × CH_2); *m/z* 276.1 (100%, M) and 81.1 (30, C_6H_9).

Ethyl 3-trimethylsilyloxy-3-[1-(phenylsulfanyl)cyclohexyl]-propanoate 43

Me_3SiCl (0.21 ml, 3.5 mmol) was added to a stirred solution of the ester **25**, Et_3N (0.5 ml, 3.5 mmol) in THF (10 ml) at 0 °C. The solution was stirred for 2 days. Brine (saturated NaCl, 10 ml) was added and the solution was extracted with ether (2 × 10 ml). The combined organic layers were dried (Na_2SO_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 protected ester **43** (0.135 g, 72%) as an oil; R_f [light petroleum (40–60 °C)–ether (9 : 1)] 0.42; δ_H(400 MHz, $CDCl_3$) 7.56–7.27 (5 H, m, SPh), 4.17 (2 H, q, *J* 7.1, CH_3CH_2O), 4.10 (1 H, dd, *J* 9.3 and 1.6, CHOSi), 3.43 (1 H, dd, *J* 15.7 and 1.6, CH_AH_BCO), 2.52 (1 H, dd, *J* 15.7 and 9.3, CH_AH_BCO), 2.16–2.13 (10 H, m, 5 × CH_2); δ_C(100 MHz, $CDCl_3$) 173.2 (CO), 137.5 (*o*-SPh), 131.2 (*i*-SPh), 128.7 (*p*-SPh), 128.4 (*m*-SPh), 75.6 (CHOH), 60.4 (CH_2O), 57.7 (CSPh), 38.6, 31.2, 28.2, 25.9 and 21.8 (5 × CH_2), 14.3 (CH_3) and 0.2 (TMS) (Found M^+, 380.1864. $C_{20}H_{32}O_2SSi$ requires M, 380.1841); *m/z* 380.2 (24%, M), 291.1 (30, M − TMSO) and 271.2 (76, M − SPh).

3-Trimethylsilyloxy-3-[1-(phenylsulfanyl)cyclohexyl]propanal 44

DIBAL-H was slowly added to a stirred solution of ester **43** in CH_2Cl_2 at −78 °C. The solution was stirred for 30 min. Ether (50 ml), NaOH (20 ml, 10%) and K–Na tartrate (20 ml, 15%) was slowly added and the solution was allowed to stir for a further 30 min at room temperature. The solution was extracted with ether (3 × 30ml) 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 (9 : 1) to give the aldehyde **44** (2.54 g, 83%) as an oil; R_f [light petroleum (40–60 °C)–ether (9 : 1)] 0.41; δ_H(400 MHz, $CDCl_3$) 9.91 (1 H, dd, *J* 2.5 and 0.94, CHO), 7.52–7.26 (5 H, m, SPh), 4.13 (1 H, dd, *J* 7.8 and 2.7, C*H*OH), 3.34 (1 H, ddd, *J* 17.1, 2.7 and 0.9, CH_AH_BCHO), 2.88 (1 H, ddd, *J* 17.1, 7.8 and 2.5, CH_AH_BCHO), 2.12–1.10 (10 H, m, 5 × CH_2) and −0.05 (9 H, s, TMS); δ_C(100 MHz, $CDCl_3$) 209.9 (CHO), 137.2 (*o*-SPh), 131.3 (*i*-SPh), 128.7 (*p*-SPh), 128.5 (*m*-SPh), 73.4 (CHOSi), 57.7 (CSPh), 47.8 (CH_2CHO), 31.5, 29.8, 25.8, 21.8 and 21.7 (5 CH_2) and 0.3 (TMS) (Found M^+, 336.1578. $C_{18}H_{28}O_2SSi$ requires M, 336.1655); *m/z* 336.2 (9%, M), 247.1 (9, M − TMSO) and 271.2 (25, M − SPh).

(*E*)- and (*Z*)-1-[1-(Phenylsulfanyl)cyclohexyl]pent-3-ene-1,5-diol 48

n-BuLi (0.18 ml, 1.25 M in hexanes, 1.01 mmol) was added slowly to a stirred solution of 3-hydroxyethyl triphenylphosphonium bromide **45** (0.18 g, 0.46 mmol) in THF (10 ml) at 0 °C. The dark red solution was stirred for 30 min. The solution was then cooled to −30 °C and Me_3SiCl (63 μl, 0.5 mmol) was added and this solution was stirred for 15 min. A solution of aldehyde **44** (0.18 g, 0.46 mmol) in THF (10 ml) was slowly added and allowed to warm to room temperature over 2 hours. TBAF (0.54 ml, 1 M in THF, 0.54 mmol) was added and solution was stirred for a further 1 hour. Saturated NH_4Cl was added and the solution was extracted with ether (3 × 25 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 ether to give an separable stereoisomeric mixture of alkenes in a ratio of 1 : 1 of the (*Z*)-**48** (11.9 mg, 4.7%) as an oil; R_f [ether] 0.38; δ_H(250 MHz, $CDCl_3$) 7.51–7.25 (5 H, m, SPh), 5.88 (1 H, m, CH_A=CH_B), 5.63 (1 H, m, CH_A=CH_B), 4.24 (1 H, dd, *J* 12.0 and 7.9, CH_AH_BO), 3.97 (1 H, dd, *J* 12.0 and 6.6, CH_AH_BO), 3.43 (1 H, s, OH), 3.24 (1 H, dd, *J* 10.2 and 1.6, C*H*OH), 2.40 (1 H, dt, *J* 13.4 and 10.2, CH_AH_BCH=CH), 2.19 (1 H, dd, *J* 13.4 and 6.3, CH_AH_BCH=CH) and 2.01–1.19 (11 H, m, OH and 5 × CH_2); δ_C(100 MHz, $CDCl_3$) 137.2 (*m*-SPh), 131.1 (CH_A=CH_B), 130.1 (CH_A=CH_B), 130.0 (*o*-SPh), 129.9 (*i*-SPh), 129.2 (*p*-SPh), 73.4 (CHOH), 61.3 (CSPh), 30.4, 29.5, 28.6, 26.3 and 21.8 (5 × CH_2); and the (*E*)-**48** (12.4 mg, 5.3%) as an oil; R_f [ether] 0.28; δ_H(400 MHz, $CDCl_3$) 7.52–7.28 (5 H, m, SPh), 5.79–5.66 (2 H, m, CH_A=CH_B), 4.09 (2 H, d, *J* 4.9, CH_2O), 3.45 (1 H, dd, *J* 10.2 and 1.6, C*H*OH), 3.10 (1 H, s, OH), 2.38 (1 H, dd, *J* 5.1 and 4.9, CH_AH_BCH=CH), 2.19 (1 H, dd, *J* 10.3 and 6.0, CH_AH_BCH=CH) and 2.01–1.17 (11 H, m, OH and 5 × CH_2); δ_C(100 MHz, $CDCl_3$) 137.3 (*m*-SPh), 131.2 (CH_A=CH_B), 130.5 (CH_A=CH_B), 130.1 (*i*-SPh), 129.1 (*o*-SPh), 128.9 (*p*-SPh), 74.5 (CHOH), 63.6 (CH_2O), 61.1 (CSPh), 33.8, 30.6, 29.8, 26.2, 21.9 and 21.8 (6 × CH_2).

2-[1′-(Phenylsulfanyl)cyclohexyl]-3,6-dihydro-2*H*-pyran 50

In the same way as THP **11**, the (*Z*)-alkene **48** (11 mg, 37 μmol) and TsOH (1.4 mg, 7.5 μmol) in CH_2Cl_2 (5 ml) gave after flash column chromatography on silica gel, eluting with light petroleum (40–60 °C)–ether (9 : 1), the DHP **50** (11 mg, 99%) as an oil; R_f [light petroleum (40–60 °C)–ether (9 : 1)] 0.52; δ_H(400 MHz, $CDCl_3$) 7.55–7.18 (5 H, m, SPh), 5.85 (1 H, dd, *J* 10.1 and 1.0, CH_A=CH_B), 5.47 (1 H, br d, *J* 10.1, CH_A=CH_B), 4.22 (1 H, d, *J* 16.3, CH_AH_BO), 4.10 (1 H, d, *J* 16.3, CH_AH_BO), 3.38 (1 H, dd, *J* 10.7 and 3.1, CHSPh), 2.44 (1 H, m, CH_AH_BCH=CH), 2.22 (1 H, br d, *J* 17.3, CH_AH_BCH=CH) and 1.87–1.21 (10 H, m, 5 × CH_2); δ_c(100 MHz, $CDCl_3$) 135.5 (*m*-SPh), 131.9 (*i*-SPh), 128.4 (*o*-SPh), 128.1 (*p*-SPh), 126.1 (CH_A=CH_B), 124.8 (CH_A=CH_B), 77.9 (CHO), 66.9 (CH_2OH), 56.9 (CSPh), 31.1, 30.8, 25.9, 25.4, 21.9 and 21.8 (6 × CH_2).

(*E*,*E*)-5-(Cyclohex-1-enyl)-5-phenylsulfanylpent-2-en-1-ol 51

In the same way as THP **11**, the (*E*)-alkene **48** (12 mg, 41 μmol) and TsOH (1.5 mg, 8.2 mmol) in CH_2Cl_2 (5 ml) gave after flash column chromatography eluting with ether, the allylic sulfide (*E*,*E*)-**51** (12 mg, 99%) as an oil; R_f [ether] 0.5 δ_H(400 MHz, $CDCl_3$) 7.38–7.18 (5 H, m, SPh), 5.66 (2 H, m, CH=CH), 5.27 (1 H, s, CH=C), 4.08 (2 H, t, *J*, 4.5, CH_2OH), 3.53 (1 H, t, *J* 7.6, CHSPh), 2.40 (2 H, t, *J* 5.8, CH_2CH=CH), 21.6 (1 H, d, *J* 16.4, CH_AH_BCH=C) and 1.99–1.24 (8 H, m, 3 × CH_2, CH_AH_BCH=C and OH); δ_C(100 MHz, $CDCl_3$) 135.3 and 135.2 (*i*-SPh and *C*=CH), 133.3 (*m*-SPh), 131.0, 129.9 and 125.7 (CH=CH and *C*H=C), 128.5 (*o*-SPh), 127.1 (*m*-SPh), 63.6 (CH_2OH), 56.7 (CHSPh), 35.6, 25.2, 24.3, 22.7 and 22.4 (5 × CH_2).

6-Cyclohexenyl-6-(phenylsulfanyl)hexan-1-ol 53

In the same way as THP **11**, the alcohol **8**, *n* = 5 (62 mg, 0.2 mmol) toluene-*p*-sulfonic acid (10 mg, 50 μmol) in CH_2Cl_2

(1 ml) gave, after flash column chromatography on silica gel eluting with ether, the *allylic sulfide* **53** (55 mg, 95%) as an oil; R_f [ether] 0.51; δ_H(250 MHz, $CDCl_3$) 7.35–7.17 (5 H, m, SPh), 5.25 (1 H, br s, CH=C), 3.62 (2 H, t, *J* 6.6, CH_2O), 3.50 (1 H, t, *J* 7.6, C*H*SPh) and 2.17–1.33 (17 H, m, 8 × CH_2 and OH); δ_C(62.5 MHz, $CDCl_3$) 135.8 and 135.6 (*i*-SPh and CH=*C*), 133.2 (*o*-SPh), 128.4 (*m*-SPh), 126.9 (*p*-SPh), 125.4 (*C*H=C), 62.9 (CH_2O), 57.3 (*C*HSPh), 32.6, 32.5, 27.4, 25.5, 23.8, 22.7 and 22.5 (8 × CH_2).

7-Cyclohexenyl-7-(phenylsulfanyl)heptan-1-ol 54

In the same way as THP **11**, the alcohol **8**, *n* = 6 (65 mg, 0.2 mmol) toluene-*p*-sulfonic acid (10 mg, 50 μmol) in CH_2Cl_2 (1 ml) gave, after flash column chromatography on silica gel eluting with ether, the *allylic sulfide* **54** (60 mg, 99%) as an oil; R_f [ether] 0.50; δ_H(250 MHz, $CDCl_3$) 7.40–7.17 (5 H, m, SPh), 5.24 (1 H, br s, CH=C), 3.61 (2 H, t, *J* 6.6, CH_2O), 3.61 (1 H, t, *J* 7.6, C*H*SPh) and 2.16–1.24 (19 H, m, 9 × CH_2 and OH); δ_C(62.5 MHz, $CDCl_3$) 135.7 and 135.5 (*i*-SPh and CH=*C*), 133.1 (*m*-SPh), 128.4 (*o*-SPh), 126.8 (*p*-SPh), 125.4 (*C*H=C), 62.9 (CH_2O), 57.33 (*C*HSPh), 32.7, 32.4, 29.1, 27.6, 25.6, 25.2, 23.7, 22.7 and 22.5 (9 × CH_2) (Found M^+, 304.1860. $C_{19}H_{28}OS$ requires M, 304.1816); *m*/*z* 304.1 (79%, M) and 195.1 (42, M − SPh).

9-Cyclohexenyl-9-(phenylsulfanyl)nonan-1-ol 55

In the same way as THP **11**, the alcohol **8**, *n* = 8 (70 mg, 0.2 mmol) toluene-*p*-sulfonic acid (10 mg, 50 μmol) in CH_2Cl_2 (1 ml) gave, after flash column chromatography on silica gel eluting with ether, the *allylic sulfide* **55** (65 mg, 95%) as an oil; R_f [ether] 0.56; δ_H(250 MHz, $CDCl_3$) 7.47–7.16 (5 H, m, SPh), 5.24 (1 H, br s, CH=C), 3.62 (2 H, t, *J* 6.6, CH_2O), 3.49 (1 H, t, *J* 7.6, C*H*SPh) and 2.28–1.24 (23 H, m, 11 × CH_2 and OH); δ_C(62.5 MHz, $CDCl_3$) 135.8 and 135.7 (*i*-SPh and CH=*C*), 133.1 (*m*-SPh), 128.3 (*o*-SPh), 126.7 (*p*-SPh), 125.4 (*C*H=C), 63.0 (CH_2O), 57.4 (*C*HSPh), 32.8, 32.5, 29.5, 29.4, 29.3, 27.6, 25.7, 25.2, 23.7, 22.7 and 22.5 (11 × CH_2) (Found M^+, 322.2171. $C_{21}H_{32}OS$ requires M, 332.2174); *m*/*z* 332.2 (40%, M) and 233.1 (100, M − SPh).

13-Cyclohexenyl-13-(phenylsulfanyl)tridecan-1-ol 56

In the same way as THP **11**, the alcohol **8**, *n* = 12 (80 mg, 0.2 mmol) toluene-*p*-sulfonic acid (10 mg, 50 μmol) in CH_2Cl_2 (1 ml) gave, after flash column chromatography on silica gel eluting with ether, the *allylic sulfide* **56** (68 mg, 95%) as an oil; R_f [ether] 0.56; δ_H(250 MHz, $CDCl_3$) 7.35–7.17 (5 H, m, SPh), 5.24 (1 H, br s, CH=C), 3.62 (2 H, t, *J* 4.2, CH_2O), 3.50 (1 H, t, *J* 4.8, C*H*SPh) and 2.16–1.65 (29 H, m, 14 × CH_2 and OH); δ_C(62.5 MHz, $CDCl_3$) 136.0 and 135.9 (*i*-SPh and CH=*C*), 133.2 (*o*-SPh), 128.5 (*o*-SPh), 126.9 (*p*-SPh), 125.4 (*C*H=C), 63.2 (CH_2O), 57.5 (*C*HSPh), 32.9, 32.6, 29.6, 29.6, 29.5, 29.4, 27.7, 26.3, 25.8, 23.9, 22.8 and 22.7 (14 × CH_2) (Found M^+, 374.2632. $C_{24}H_{38}OS$ requires M, 374.2643); *m*/*z* 374.2 (24%, M) and 265.1 (100, M − SPh).

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