Concerning the synthesis and enantioselective rearrangements of episulfoxides

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A novel synthesis of episulfoxides having the norbornane skeleton is possible by use of a rhodium catalyst to effect SO transfer from *trans*-stilbene episulfoxide to norbornene or norbornadiene. Analogous $Rh_2(OAc)_4$ catalysed sulfur transfer to these alkenes is also possible using propylene sulfide as the sulfur source. These methods did not give useful yields of products with alternative types of alkene substrate.

A novel type of chiral lithium amide base reaction, involving the rearrangement of certain types of symmetrical ring-fused episulfoxides, gives alkenyl sulfoxide products in up to 88% ee. The structures of the products, including absolute stereochemistry, were assigned based on X-ray crystal structure determinations.

Introduction

Some time ago we became interested in the possibility of applying our chiral lithium amide base methodology to the asymmetric synthesis of cyclic sulfoxides.[1] Although initial results using sulfoxides having 4–6-membered rings gave interesting results, the enantioselectivities in these novel symmetry-breaking reactions were somewhat modest (<70% ee).[2] More recently we recognised the possibility of employing 3-membered ring sulfoxides (episulfoxides) in similar asymmetric chemistry, and were able to attain somewhat better enantioselectivities for the chiral base mediated rearrangement of such systems.[3]

Realisation of a novel enantioselective transformation of episulfoxides highlighted the problems associated with the synthesis of these relatively rare types of heterocycle. We were prompted to examine new methods for the synthesis of episulfoxides (and the precursor episulfides) which would be more direct, and hopefully more efficient, than existing methods. This study led to the discovery of a new rhodium-catalysed S- and SO-transfer process, which was applied to the synthesis of norbornane episulfides and episulfoxides.[4]

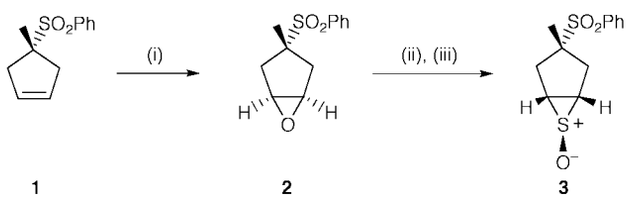
Since aspects of the synthesis and asymmetric rearrangement of episulfoxides are very intimately interrelated, we have chosen to describe full details of our studies in both of these areas in one full account.

Results and discussion

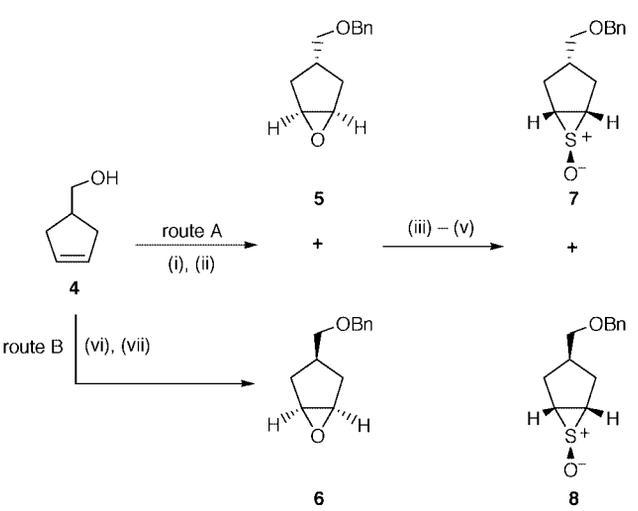
(i) Conventional synthesis of episulfoxides

For our chiral base studies we required prochiral ring-fused episulfoxides, which upon treatment with base and then an alkylating agent would furnish chiral alkenyl sulfoxides, *vide infra*. We chose to focus on episulfoxides having the norbornane skeleton, as well as episulfoxides derived from two different types of 4-substituted cyclopentene. The latter types were prepared as shown in Schemes 1 and 2 *via* the intermediacy of the corresponding epoxides.

Completely stereoselective epoxidation of the cyclopentenyl sulfone **1** gave the known epoxide **2**,[5] which was then converted into the desired episulfoxide **3** by treatment with triphenylphosphine sulfide in the presence of trifluoroacetic acid, and then oxidation with Oxone®.[6] In our hands, the use of potassium thiocyanate or thiourea for the conversion of epoxide **2** into the corresponding episulfide was not effective.[7,8] Also, a method which employs ammonium thiocyanate in the presence of ceric ammonium nitrate (CAN) gave only the product of epoxide opening by thiocyanate in 92% yield.[9] Although this intermediate could be converted into the desired episulfide by mesylation and treatment with base, this rather laborious sequence was barely more effective than the triphenylphosphine sulfide method (although purification was a little easier).[10] This



Scheme 1 *Reagents and conditions*: i, MCPBA, CH_2Cl_2, RT (86%); ii, Ph_3PS, TFA, PhH (49–60%); iii, Oxone®, MeOH, H_2O (81%).



Scheme 2 *Reagents and conditions*: i, NaH, BnBr (*ca.* 96%); ii, MCPBA, CH_2Cl_2, RT (96%); iii, NH_4SCN, CAN; iv, $MeSO_2Cl$, py, then $NaOH_{aq}$ (60% from **5/6**); v, Oxone®, MeOH, aq. $NaHCO_3$ (75–78%); vi, $VO(acac)_2$, TBHP, CH_2Cl_2 (58%); viii, NaH, BnBr.

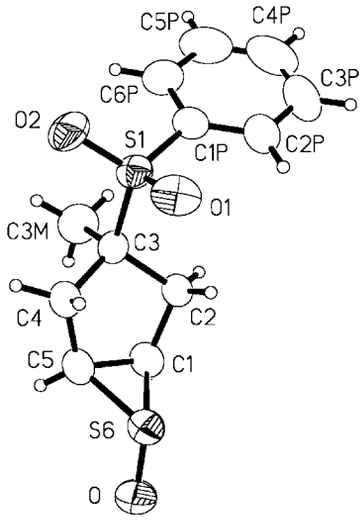


Fig. 1 A displacement ellipsoid plot of **3** showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level. Data were acquired at 298 K.

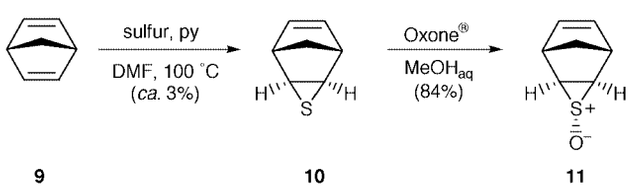
method was however adopted in the case of the epoxides shown in Scheme 2, *vide infra*.

Although the stereochemistry of the starting epoxide **2** was not in doubt, we chose to carry out an X-ray structure determination of the product episulfoxide **3** in order to be absolutely certain of the relative stereochemistry, Fig. 1. As can be seen, this structure confirmed that the epoxide to episulfide conversion had proceeded with inversion of configuration, and also that sulfoxidation had occurred on the less hindered convex face of the ring-fused episulfide.

In the case of episulfoxides **7** and **8**, we were content to employ a route which provided intermediate epoxides, and thence episulfides, in a non-stereoselective fashion, so as to allow screening of two diastereomeric series in subsequent chiral base reactions. Epoxidation of the benzyl ether derived from alcohol **4** gave a 3:2 mixture of the epoxides **5**:**6**. These could not be readily separated, but were best converted into the corresponding episulfides by the ammonium thiocyanate–CAN method described earlier. This gave the desired *syn* and *anti* episulfides in a 60% combined yield, and at this stage they were separated and oxidised to give the pure episulfoxides **7** and **8** as single stereoisomers.

The stereochemical assignments shown in Scheme 2 were made following an alternative stereocontrolled synthesis of **6**, which employed the known directed epoxidation of **4** using the Sharpless $VO(acac)_2$ protocol.[11] Conversion of **6** into the corresponding episulfide (not illustrated) then allowed us to assign the stereochemistry of the intermediate episulfides and the derived episulfoxides.

The synthesis of norbornane-derived episulfoxides presented special problems. We initially adopted a direct, although low-yielding, synthesis of the episulfide **10**, which involved reaction of norbornadiene **9** with sulfur in a mixture of DMF, NH_3 and pyridine at 100 °C, Scheme 3.[12] Although the reported yield of



9 10 11

Scheme 3

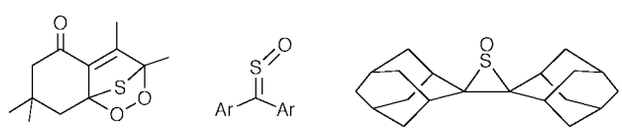
10 by this method is 19%, in our hands the reaction was somewhat less efficient, even in the presence of the free radical inhibitor 2,6-di-*tert*-butyl-4-methylphenol.[13] Oxidation of episulfide **10** using Oxone® gave the desired episulfoxide **11** as a single stereoisomer in good yield.

Although a range of alternative methods were then tested for the synthesis of episulfides from either norbornene or norbornadiene, none proved very effective. In the case of norbornadiene, standard approaches involving the intermediacy of an epoxide are fraught with problems due to neighbouring group participation from the remaining alkene.

The difficulties experienced in securing supplies of ring-fused episulfoxides prompted us to explore possible new, and more direct, avenues for their synthesis.

(ii) Synthesis of episulfoxides by rhodium catalysed SO-transfer

If direct transfer of sulfur monoxide to an alkene could be effected in a straightforward and efficient manner, then a more direct access to episulfoxides than the methods described above would clearly be possible. This problem has occupied several research groups, and although singlet SO has been added to allene and but-2-yne in an argon matrix at 12 K,[14] no practical and general procedure for episulfoxide preparation has emerged to date. In one significant report Adam and co-workers have described reactions employing thiophene endoperoxide **12** to



12 13 14

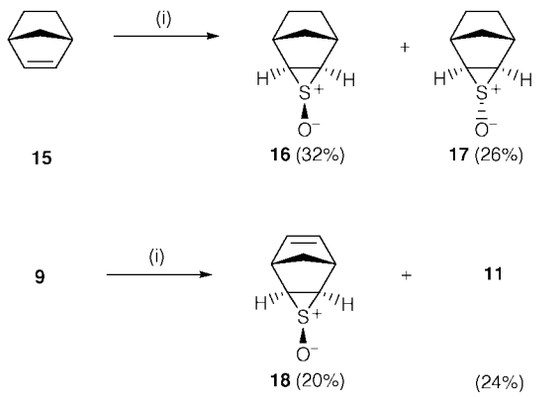
effect sulfur transfer to alkenes, thus resulting in episulfide formation.[15] More recently, the same research group has demonstrated an alternative thioepoxidation procedure which relies on photolytic sulfur atom transfer from aromatic sulfines **13**.[16] Neither of these methods appears to be fully developed as a general synthetic method and neither offered the convenience and high yields that we were aiming for.

In contrast to these sulfur transfer reactions, direct SO transfer to an alkene remains problematic because most sources of SO furnish the triplet ground state, which appears not to give episulfoxide products with alkenes (*vide infra*).[17] However, the thermolysis of certain episulfoxides, including **14**, can result in delivery of SO to *dienes* (resulting in the formation of dihydrothiophene *S*-oxides).[18] This type of process appeared to be worthy of further examination in the context of SO transfer to alkenes.

Our initial plans involved testing the idea that a thermally labile episulfoxide might effect SO transfer to an alkene to give an episulfoxide product. Aromatic episulfoxides are known to be especially thermally labile, for example *trans*-stilbene episulfoxide undergoes loss of SO on gentle heating in CH_2Cl_2. Under such conditions the ring-fused episulfoxide **3** illustrated in Scheme 1 appeared relatively stable. However, warming mixtures of (easily available) stilbene episulfoxide with alkene (or alkyne) substrates, ranging from electron rich vinyl ethers to electron poor α,β-unsaturated carbonyl compounds, resulted in no product episulfoxide formation (or any other sulfur-containing products). This was not too surprising in view of previous studies, but emphasized the complete failure of SO transfer, even under very mild conditions. Clearly a radically different approach to the SO-transfer problem was required.

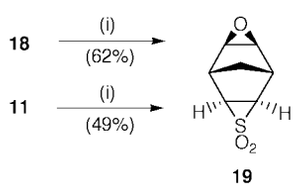
Further examination of the literature revealed that transition-metal complexes of SO have been described and, in the case of $(Ph_3P)_2Pd(SO)$, have been shown to effect SO transfer to a diene.[19] Consequently we repeated our attempts to transfer SO from stilbene episulfoxide to norbornadiene in the presence of various transition-metal catalysts. We were delighted to find that the use of either palladium catalysts, such as $Pd(dba)_2$ and $Pd(MeCN)_2Cl_2$, or rhodium catalysts, including $(Ph_3P)_3RhCl$ and $Rh_2(OAc)_4$, in CH_2Cl_2 resulted in the

formation of substantial amounts of the desired episulfoxide product. Optimum reaction conditions involved reaction of norbornene **15** or norbornadiene **9** with an excess (typically three equivalents) of stilbene episulfoxide and *ca.* 2–3 mol% of $Rh_2(OAc)_4$ in CH_2Cl_2 at room temperature, Scheme 4.



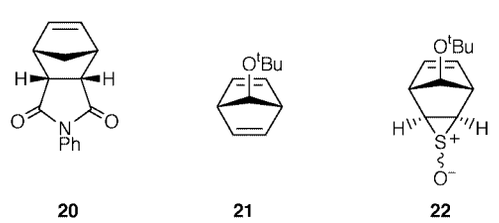
Scheme 4 *Reagents and conditions*: i, stilbene episulfoxide, $Rh_2(OAc)_4$ CH_2Cl_2, RT.

In both cases only the *exo*-orientated episulfoxide products were obtained, although in each case these were formed as easily separable mixtures of stereoisomers at sulfur. That this was indeed the case for the unsaturated products **11** and **18** was demonstrated by their independent oxidation, using the procedure very recently described by Taylor and co-workers,[20] to give the same epoxy-epi*sulfone* **19**, Scheme 5.



Scheme 5 *Reagents and conditions*: i, Oxone®, CF_3COCH_3.

Unfortunately, this unprecedented sulfoxidation procedure seems not to be of general utility. Even systems incorporating a reactive norbornene-type alkene, such as the readily available Diels–Alder adduct **20**, gave none of the desired episulfoxide

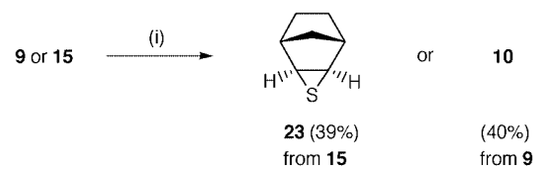


adduct. Perhaps in this case the imide functionality interferes with the catalyst. In the case of commercially available norbornadiene **21** we were able to isolate 16% of a mixture of products tentatively assigned as the epimeric episulfoxides **22**. A wide range of other alkenes were also tried, but only *cis*-cyclooctene and cyclopentadiene dimer gave traces of products, in quantities too small to fully characterise, but which appeared to be the desired episulfoxide products on the basis of IR or mass spectral evidence.

This observation, that only rather strained alkenes react well in sulfur transfer reactions seems to parallel similar findings of Adam,[16] but at present we have no convincing explanation for this result.

Since, in the absence of $Rh_2(OAc)_4$, stilbene episulfoxide is quite stable at room temperature, the metal catalyst must be involved in *both* the extrusion of SO from the starting episulfoxide and in its delivery to the alkene. One possible reaction mechanism, in line with findings by Schenk,[21] would involve coordination of the metal to the sulfur lone pair of the starting episulfoxide (both coordination to sulfur or oxygen appears possible) and generation of a M=SO complex, by loss of stilbene, which is then capable of sulfoxidation of a strained alkene.

During the course of these studies it was also found that *sulfur* transfer to norbornene and norbornadiene can also be catalysed by $Rh_2(OAc)_4$, Scheme 6. In this case we used the



Scheme 6 *Reagents and conditions*: i, propylene sulfide, $Rh_2(OAc)_4$ toluene, Δ.

commercially available propylene sulfide as a convenient sulfur source, the reaction requiring somewhat more vigorous reaction conditions compared with the SO transfer. Each of the product episulfides was isolated as a single *exo*-stereoisomer, the stereochemical assignments being made by comparison with literature data for **10**. Although the yields of episulfides are not high this new method appears to offer the most practical and operationally facile route to these compounds to date. As in the case of SO transfer, we were unable to apply this new process to other alkenes, and obtained only traces of product in reactions involving cyclopentadiene dimer.

(iii) Asymmetric rearrangement of episulfoxides using chiral lithium amide bases

Several groups have demonstrated that on treatment with a suitable base, especially LDA, episulfoxides undergo rearrangement to form intermediate alkenyl sulfenate anions, which can then be alkylated to give alkenyl sulfoxide products, *e.g.* Scheme 7.[22]

Scheme 7

We became interested in the possibility of employing chiral base reactions for the asymmetric transformation of episulfoxides on recognising that such a reaction might lead to synthetically useful non-racemic alkenyl sulfoxides. The substrates required are the types of systems described above, *i.e.* ring-fused episulfoxide derivatives incorporating at least one pro-stereogenic centre.

Chiral base reactions of **3**, involving treatment with lithium amide **28**, followed by addition of iodomethane, gave the desired alkenyl sulfoxide **24** in good chemical yield (79%) but in low ee (*ca.* 10%), Scheme 8. However, we were delighted to find that analogous reactions involving the bis-lithium amide **29** gave the sulfoxide **24** as a mixture of diastereomers (epimeric at sulfur, *ca.* 2 : 1 ratio) in 85% yield,[23] each of which was formed in 82% ee. As expected, the use of the enantiomeric base (*ent*-**29**) gave the opposite sense of asymmetric induction, leading to the enantiomer of **24** in similar chemical yield and ee.

Although the chiral product **24** was generated in good ee, the presence of two diastereomeric sulfoxides was an unwanted complication. Oxidation using Oxone® to give the corresponding sulfone **25** facilitated enantiomeric enrichment by recrystallisation, and also enabled an X-ray crystallographic

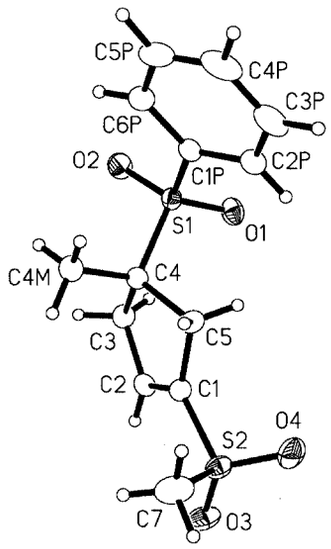


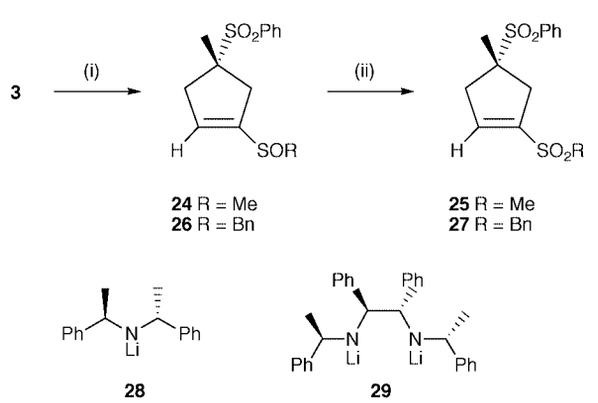
Fig. 2 A displacement ellipsoid plot of **25** showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level. Data were acquired at 150 K. The absolute configuration shown was established by refinement of the Flack parameter to a final value of −0.05(8).

determination, as shown in Fig. 2, which established the absolute configuration of this series of compounds.

The enantioselective transformation of **3** could also be carried out using benzyl bromide in place of iodomethane, which provided alkenyl sulfoxide **26** in 72% yield. Oxidation of this diastereomeric mixture to the corresponding sulfone **27** again enabled determination of the ee (85%) by HPLC, using an appropriate chiral stationary phase.

The transformation of episulfoxide **3** into alkenyl sulfoxide **26** proved more reliable if an *in situ* quench procedure was employed, involving addition of a *mixture* of episulfoxide and alkylating agent to the chiral base. It is possible that this method minimizes side reactions, or perhaps facilitates smooth alkylation by avoiding build up of insoluble sulfinate salts. In any case, we adopted this type of *in situ* quench procedure for all subsequent work. The use of chlorotrimethylsilane as electrophilic quench gave no isolable products, and alternative alkylating agents also proved unsatisfactory, for example allyl bromide gave very low yields of impure product.

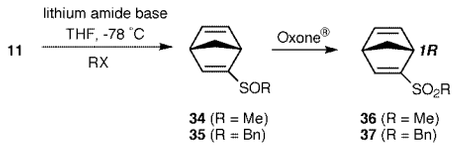
We went on to examine the analogous chiral base transformations of the two diastereomeric episulfoxides **7** and **8**, Scheme 9. In each case shown, the starting episulfoxide was converted



Scheme 8 *Reagents and conditions*: i, chiral base **28** or **29**, THF, −78 °C, MeI or $PhCH_2Br$; ii, Oxone®, MeOH, H_2O.

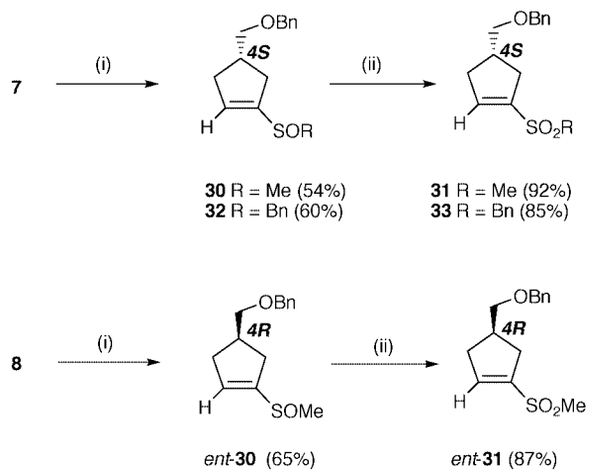
into the alkenyl sulfoxide product, **30** or **32** in 85–88% ee, as determined by HPLC analysis of the derived alkenyl sulfones **31** and **33**. It should be noted that the absolute configurations shown for the products in Scheme 9 are based solely on analogy

Table 1 Rearrangement of sulfoxide **11** [a]



Base	RX	Sulfoxide (%)	Sulfone (%)	Ee(%)([α]$_D$) sulfone	Configuration
28	MeI	**34** (73)	**36** (71)	43 (−19)	1*R*,4*S*
29	MeI	**34** (75)	**36** (70)	62 (+28)	1*S*,4*R*
29	$PhCH_2Br$	**35** (62)	**37** (70)	66 (+6)	1*S*,4*R*

[a] The absolute configurations shown above are for products obtained using base **28**.



Scheme 9 *Reagents and conditions*: i, chiral base **29**, THF, −78 °C, MeI or $PhCH_2Br$; ii, Oxone®, MeOH, H_2O.

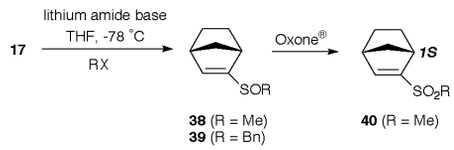
with the earlier results for episulfoxide **3**. Notably, the chiral base selectivity in this reaction results in the conversion of *diastereomeric* starting materials into *enantiomeric* products, *vide infra*. Finally, we conducted a study of the chiral base rearrangement to episulfoxides **11** and **17**, having the norbornane skeleton, the results of which are shown in Tables 1 and 2.

In the case of rearrangement of unsaturated episulfoxide **11** we found that the enantiomeric excess was somewhat lower than for the cyclopentene types, being typically around 65% using base **29**. The immediate sulfoxide products **34** and **35** were generated as mixtures of diastereomers at the sulfinyl centre (at most *ca.* 3 : 1 ratio) and enantiomeric excess determination was therefore best carried out after oxidation to the corresponding alkenyl sulfones. As in the previous examples the simpler base **28** gave inferior results in terms of asymmetric induction.

We then proceeded to examine analogous transformations of the corresponding saturated episulfoxide, the results of which are shown in Table 2.

Somewhat surprisingly, in this series of reactions the simpler base **28** gave better levels of enantioselectivity than the bis-lithium amide **29**, the latter base giving very poor results, even in the presence of added LiCl. As expected, these two bases gave products of opposite configuration.[24] In the reactions which employed MeI, the sulfoxide products proved difficult to separate by HPLC, and so again we carried out oxidation to the corresponding sulfone prior to assay for ee. However, all four stereoisomers in the mixture resulting from *S*-benzylation were separated by HPLC and so the ee assay could be carried out directly. A sample of the sulfone **40** of 76% ee was recrystallised from a petroleum ether–EtOAc–Et_2O mixture, to furnish crystals which were the subjected to X-ray crystallographic analysis.

Table 2 Rearrangement of sulfoxide **17**[a]



Base	RX	Sulfoxide (%)	Ee(%)([α]$_D$) sulfoxide	Sulfone (%)	Ee(%)([α]$_D$) sulfone	Configuration
29	MeI	**38** (63)	—	**40** (91)	<5	
29 + **LiCl**	MeI	**38** (59)	—	**40** (98)	27 (−24)	1*R*,4*S*
28	MeI	**38** (82)	—	**40** (99)	76 (+60)	1*S*,4*R*
29	$PhCH_2Br$	**39** (50)	<5	—	—	
29 + **LiCl**	$PhCH_2Br$	**39** (46)	17 (−10)	—	—	1*R*,4*S*
28	$PhCH_2Br$	**39** (82)	70 (+39)	—	—	1*S*,4*R*

[a] The absolute configurations shown above are for products obtained using base **28** (note the change in bridge priorities gives reveresed Cahn–Ingold–Prelog stereochemical descriptors compared to Table 1).

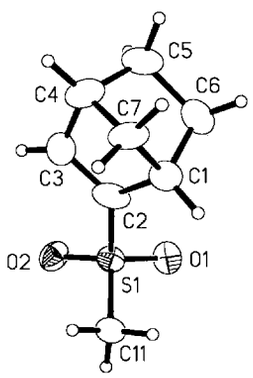
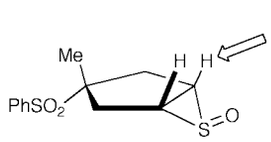


Fig. 3 A displacement ellipsoid plot of **40** showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level. Data were acquired at 150 K. The absolute configuration shown was established by refinement of the Flack parameter to a final value of 0.0(2).

The result of this structure determination, which establishes the absolute configuration of **40** (and therefore **38** and **39**), is shown in Fig. 3.

Comparison of the sense of asymmetric induction revealed by Fig. 2 and 3 shows that the chiral base is consistent in removing a particular enantiotopic hydrogen for each system—*i.e.* compare representations **41** and **42** for the selectivity proven



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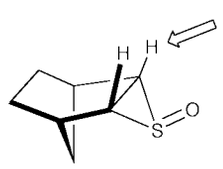

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for bis-lithium amide base **29**. Unfortunately, we have no comparison data for this base in reactions with other types of sulfoxide, which we carried out some time previously, which were most effective with camphor-derived bases.

Conclusion

Our initial interest in asymmetric transformation of episulfoxides, combined with the difficulty in preparing these compounds by existing routes, has led us to explore alternative methods for their synthesis. Unfortunately, a new transition-metal catalysed approach for direct SO transfer to alkenes has proved to be of very narrow application, and this has restricted the possibilities to explore the chiral base chemistry of a wide range of episulfoxides. Of the few systems explored, the chiral lithium amide base rearrangement appears to give only moderate selectivities, mainly in the range 65–85% ee. The change in the relative effectiveness of the two chiral bases **28** and **29** seen on swapping between the closely related norbornane episulfoxides **11** and **17** is puzzling. Unfortunately, the difficulty in accessing further episulfoxides, along with the likelihood of achieving only modest levels of induction, has deterred us from further study of these systems.

Experimental

General details

Except for the following additions, the general procedures used were as described previously.[25] In the present work all NMR spectra were run in $CDCl_3$ and all specific rotation measurements were taken at ambient temperature (20–25 °C). Enantiomeric excess determinations were carried out using the columns indicated, and using UV detection at either 254 nm, for the cyclopentene derivatives, or 210 nm for the norbornane systems. A Waters 600E System controller was employed, and the data were processed using an HP-3D DOS Chemstation.

[(1-Methylcyclopent-3-en-1-yl)sulfonyl]benzene 1

Butyllithium (38.5 ml of a 1.6 M solution in hexanes, 61.7 mmol) was added dropwise to a solution of ethyl phenyl sulfone (5.00 g, 29.4 mmol) in THF (50 ml) at −30 °C under nitrogen. The solution was warmed to 0 °C and *cis*-1,4-dichlorobut-2-ene (3.15 ml, 29.4 mmol) was added. The reaction mixture was stirred at 0 °C for 3 h, poured into water (50 ml) and extracted with EtOAc (3 × 100 ml). The combined extracts were dried ($MgSO_4$) and the solvents removed under reduced pressure. Chromatography (petroleum ether–EtOAc 7:3), followed by recrystallisation from petroleum ether–EtOAc gave **1** as a white crystalline solid (5.00 g, 77%), mp 66–67 °C; δ_H (250 MHz) 1.43 (3H, s, C*H*$_3$), 2.21 (2H, d, *J* 15.0 Hz, 2 × =CHC*H*H), 3.29 (2H, d, *J* 15.0 Hz, 2 × =CHCH*H*), 5.59 (2H, s, 2 × =C*H*), 7.53–7.68 (3H, m, Ph*H*) and 7.92 (2H, d, *J* 7.0 Hz, Ph*H*); δ_C (68 MHz) 23.7 (CH_3), 41.5 (CH_2), 67.8 (C), 127.5 (CH), 128.8 (CH), 129.9 (CH), 133.5 (CH) and 136.4 (C); *m*/*z* (EI) 223 (5%, MH^+), 143 (7), 125 (9), 82 (16), 81 (100), 80 (76) and 79 (39) (Found (CI): M + NH_4^+, 240.1060. $C_{12}H_{14}O_2S$ + NH_4 requires *M*, 240.1058).

(1α,3α,5α)-3-Methyl-3-(phenylsulfonyl)-6-oxabicyclo[3.1.0]-hexane 2

Solid 3-chloroperoxybenzoic acid (14.4 g, 50 mmol) was added to a solution of **1** (5.00 g, 22.5 mmol) in CH_2Cl_2 (50 ml) at 0 °C, and the reaction mixture stirred at room temperature for 18 h. The reaction mixture was washed with saturated aqueous Na_2SO_3 (100 ml), saturated aqueous $NaHCO_3$ (100 ml), dried ($MgSO_4$) and the solvent removed under reduced pressure.

Recrystallisation from petroleum ether–EtOAc gave **2** as a white crystalline solid (4.63 g, 86%), mp 96–98 °C (Found: C, 60.50; H, 6.21. $C_{12}H_{14}O_2S$ requires C, 60.50; H, 5.88%); δ_H (400 MHz) 1.39 (3H, s, CH_3), 1.92 (2H, d, *J* 15.0 Hz, 2 × OCHC*H*H), 2.73 (2H, d, *J* 15.0 Hz, 2 × OCHCH*H*), 3.63 (2H, s, 2 × OC*H*), 7.57 (2H, t, *J* 7.5 Hz, Ph*H*), 7.68 (1H, t, *J* 7.5 Hz, Ph*H*) and 7.86 (2H, d, *J* 7.5 Hz, Ar*H*); δ_C (68 MHz) 26.4 (CH_3), 35.6 (CH_2), 57.8 (CH), 66.3 (C), 128.9 (CH), 129.9 (CH), 133.8 (CH) and 135.9 (C); *m*/*z* (CI) 239 (6, MH^+), 183 (2), 143 (13), 125 (9), 97 (100), 79 (30), 77 (27), and 69 (53).

(1α,3β,5α)-3-Methyl-3-(phenylsulfonyl)-6-thiabicyclo[3.1.0]-hexane

Triphenylphosphine sulfide (4.94 g, 16.8 mmol) and trifluoroacetic acid (0.64 ml, 8.4 mmol) were added to a solution of **2** (2.00 g, 8.39 mmol) in dry benzene (25 ml) under nitrogen. The solution was heated to reflux for 3 h and then cooled to room temperature and the solvent removed under reduced pressure. The residue was taken up in Et_2O (2 × 100 ml), filtered and the filtrate evaporated under reduced pressure. Chromatography (petroleum ether–CH_2Cl_2 4:1) followed by recrystallisation from petroleum ether–EtOAc gave the title compound as a white crystalline solid (1.27 g, 60%); mp 114–115 °C (Found: C, 56.73; H, 5.61. $C_{12}H_{14}O_2S_2$ requires C, 56.66; H, 5.55%); ν_{max} ($CHCl_3$)/cm^{-1} 2942, 2862, 1586, 1462, 1448, 1303, 1152, 1126, 1086, 1069 and 980; δ_H (250 MHz) 1.51 (3H, s, CH_3), 2.23 (2H, dd, *J* 15.0, 4.0 Hz, 2 × SCHC*H*H), 2.73 (2H, d, *J* 15.0 Hz, 2 × SCHCH*H*), 3.36 (2H, d, *J* 4.0 Hz, 2 × SC*H*), 7.52–7.70 (3H, m, Ph*H*) and 7.84 (2H, m, Ph*H*); *m*/*z* (EI) 254 (2, M^+), 190 (23), 113 (47), 97 (12), 85 (13), 81 (65), 80 (55), 79 (100) and 77 (38) (Found M^+, 254.0432. $C_{12}H_{14}O_2S_2$ requires M, 254.0435).

Typical episulfide oxidation procedure: preparation of (1α,3β,5α,6α)-3-methyl-3-(phenylsulfonyl)-6-thiabicyclo[3.1.0]-hexane 6-oxide 3

A solution of Oxone® (2.20 g, 3.57 mmol) in water (10 ml) was added to a solution of the episulfide (909 mg, 3.57 mmol) in methanol (10 ml), and stirred for 5 min. The reaction mixture was diluted with water (10 ml), extracted with CH_2Cl_2 (3 × 20 ml), dried ($MgSO_4$) and the solvents removed under reduced pressure. Chromatography (EtOAc–MeOH 19:1) followed by recrystallisation from petroleum ether–EtOAc gave **3** as a white crystalline solid (785 mg, 81%); mp 128–129 °C (Found: C, 53.27; H, 5.48. $C_{12}H_{14}O_3S_2$ requires C, 53.31; H, 5.22%); ν_{max} ($CHCl_3$)/cm^{-1} 2934, 1586, 1462, 1448, 1306, 1154, 1120, 1084 and 972; δ_H (400 MHz) 1.36 (3H, s, CH_3), 2.26 (2H, m, 2 × SCHC*H*H), 2.40 (2H, d, *J* 15.5 Hz, 2 × SCHCH*H*), 3.35 (2H, m, 2 × SC*H*), 7.58 (2H, t, *J* 7.5 Hz, Ph*H*), 7.70 (1H, t, *J* 7.5 Hz, Ph*H*) and 7.81 (2H, d, *J* 7.5 Hz, Ph*H*); δ_C (68 MHz) 23.4 (CH_3), 36.0 (CH_2), 53.8 (CH), 70.5 (C), 129.3 (CH), 129.8 (CH), 134.3 (CH) and 135.8 (C); *m*/*z* (FAB) 271 (70, MH^+), 270 (4) and 129 (26) (Found MH^+, 271.0465. $C_{12}H_{14}O_3S_2$ + H requires M, 271.0463); *m*/*z* (EI) 143 (7), 128 (5), 110 (7), 97 (6), 81 (100), 80 (50) and 77 (29).

Synthesis of epoxides 5 and 6

(i) Benzylation of 4 to give 4-[(phenylmethoxy)methyl]cyclopentene. A solution of alcohol **4** (3.37 g, 34.4 mmol) in THF (20 ml) was added to a stirred suspension of sodium hydride (2.31 g, 60% dispersion in oil, 58 mmol, washed with petroleum ether) in THF (80 ml) under nitrogen, followed after 1.5 h by benzyl bromide (6.2 ml, 52 mmol). After the alcohol had been consumed by TLC (18 h), the mixture was quenched with MeOH (1 ml) and diluted with water (50 ml). The layers were separated and the aqueous layer extracted with CH_2Cl_2 (50 ml). The combined extracts were dried ($MgSO_4$) and the solvents removed under reduced pressure to afford a mixture of the title compound and benzyl bromide, used in the next reaction without purification (10.44 g, estimated to contain 6.24 g of the benzyl ether, 96%). A small portion was purified by chromatography (petroleum ether–Et_2O 19:1) and gave the title compound as a colourless oil; ν_{max} (film)/cm^{-1} 3053, 2926, 2848, 1615, 1496, 1453, 1362, 1272, 1100, 1028, 735 and 696; δ_H (400 MHz) 2.12 (2H, m, 3-*H*H, 5-*H*H), 2.48 (2H, m, 3-H*H*, 5-H*H*), 2.61 (1H, m, 4-*H*), 3.37 (2H, d, *J* 7.0 Hz, $PhCH_2OCH_2$), 4.52 (2H, s, $PhCH_2$), 5.65 (2H, s, 2 × =C*H*) and 7.27–7.45 (5H, m, Ph); δ_C (100 MHz) 36.0 (CH_2), 36.8 (CH), 72.9 (CH_2), 74.7 (CH_2), 127.4 (CH), 127.6 (CH), 128.3 (CH), 129.5 (CH) and 138.7 (C); *m*/*z* (EI) 188 (15, M^+), 157 (14), 97 (45), 91 (95), 79 (100) and 67 (71) (Found M^+, 188.1209. $C_{13}H_{16}O$ requires *M*, 188.1201).

(ii) Epoxidation to give (1α,3α,5α)- and (1α,3β,5α)-3-[(phenylmethoxy)methyl]-6-oxabicyclo[3.1.0]hexane 5 and 6. Solid 3-chloroperoxybenzoic acid (6.34 g, 18.4 mmol) was added to a solution of 4-[(phenylmethoxy)methyl]cyclopentene (1.73 g, 9.2 mmol) in CH_2Cl_2 (100 ml). After 40 min, the solution was washed with saturated aqueous Na_2SO_3 (50 ml), saturated aqueous $NaHCO_3$ (2 × 100 ml), dried ($MgSO_4$), and the solvent removed under reduced pressure. Chromatography (petroleum ether–EtOAc 9:1) gave a 3:2 (**5**:**6**) mixture of diastereoisomers of the title compound as a colourless liquid (1.81 g, 96%); ν_{max} (film)/cm^{-1} 3027, 2927, 2852, 1496, 1453, 1363, 1205, 1092, 835, 736 and 698; δ_H (400 MHz) 1.45–2.40 (5H + 5H, m, 2 × OCHCH_2, 3-*H*), 3.31 (2H, d, *J* 8.0 Hz, $PhCH_2OCH_2$, minor), 3.39 (2H, d, *J* 5.5 Hz, $PhCH_2OCH_2$, major), 3.46 (2H, s, 2 × OC*H*, major), 3.47 (2H, s, 2 × OC*H*, minor), 4.47 (2H, s, $PhCH_2$, minor), 4.49 (2H, s, $PhCH_2$, major) and 7.26–7.40 (5H + 5H, m, Ph); δ_C (68 MHz) 30.4 (CH_2), 31.0 (CH_2), 33.0 (CH), 35.2 (CH), 56.9 (CH), 58.4 (CH), 72.4 (CH_2), 72.7 (CH_2), 72.8 (CH_2), 76.7 (CH_2), 127.4 (2 × CH), 127.5 (2 × CH), 128.2 (2 × CH), 138.4 (C) and 138.5 (C); *m*/*z* (EI) 204 (1, M^+), 186 (2), 113 (22), 92 (35), 91 (100), 77 (13) and 67 (25) (Found M^+, 204.1155. $C_{13}H_{16}O_2$ requires *M*, 204.1150).

Synthesis of episulfoxides 7 and 8

(i) Conversion of epoxides 5 and 6 into the corresponding episulfides. A solution of the mixture of diastereoisomers **5** and **6** (5.44 g, 26.7 mmol), ammonium thiocyanate (6.09 g, 80.1 mmol) and ammonium cerium(IV) nitrate (2.93 g, 5.35 mmol) in ^{t}BuOH (70 ml) was heated to reflux for 1.5 h. The solvent was then removed and $CHCl_3$ (100 ml) was added to the residue which was then filtered through Kieselguhr and the solvent removed under reduced pressure to leave a 3:2 mixture of (1*R**,2*R**,4*R**)- and (1*R**,2*R**,4S*)-4-[(phenylmethoxy)-methyl]-2-hydroxycyclopentyl thiocyanate as a yellow oil (6.36 g, 91%); ν_{max} (film)/cm^{-1} 3420, 2934, 2861, 2153, 1454, 1364, 1094, 740 and 699; δ_H (400 MHz) 1.50–2.60 (6H + 6H, m), 3.26–3.57 (3H +3H, m), 4.17 (1H, m, C*H*OH, minor), 4.26 (1H, m, C*H*OH, major), 4.50 (2H, s, $PhCH_2$, major), 4.55 (2H, s, $PhCH_2$, minor) and 7.25–7.40 (5H + 5H, m, Ph); *m*/*z* (FAB) 264 (14, MH^+), 154 (33), 136 (29), 107 (26), 91 (100), 69 (38) and 55 (51) (Found MH^+, 264.1060. $C_{14}H_{17}NO_2S$ + H requires *M*, 264.1058).

Methanesulfonyl chloride (3.15 ml, 40.7 mmol) was added to a solution of the above thiocyanohydrins (6.36 g, 24.2 mmol) in pyridine (15 ml) at 0 °C. The reaction mixture was quenched with water (2 ml) after 2.5 h and then diluted with CH_2Cl_2 (30 ml). The organic layer was washed with 2 M HCl (3 × 50 ml), saturated aqueous $CuSO_4$ (2 × 50 ml), dried ($MgSO_4$), and the solvent removed under reduced pressure to leave a 3:2 mixture of (1*R**,2*R**,4*R**)- and (1*R**,2*R**,4S*)-2-[(methylsulfonyl)-oxy]-4-[(phenylmethoxy)methyl]cyclopentyl thiocyanate as a brown oil (7.44 g, 90%); ν_{max} (film)/cm^{-1} 3029, 2937, 2862, 2155, 1453, 1360, 1177, 1095, 969, 884, 742 and 700; δ_H (400 MHz) 1.60–2.62 (5H + 5H, m), 3.07 (3H, s, CH_3, major), 3.08 (3H, s,

CH_3, minor), 3.37–3.70 (3H + 3H, m), 4.51 (2H + 2H, s, PhCH_2), 4.93 (1H, app. q, *J* 7.0 Hz, C*H*OMs, minor), 5.04 (1H, app. q, *J* 5.5 Hz, C*H*OMs, major) and 7.25–7.40 (5H + 5H, m, Ph); *m*/*z* (FAB) 342 (22, MH^+), 154 (64), 136 (71), 107 (32), 91 (100), 73 (71) and 57 (57) (Found MH^+, 342.0829. $C_{15}H_{19}NO_4S_2$ + H requires *M*, 342.0834).

The above mixture of mesylates (7.44 g, 21.8 mmol) was stirred with sodium hydroxide (2.16 g, 54.0 mmol) in water (100 ml) for three days until reaction was complete by TLC analysis. 2 M HCl (30 ml) was then added, the reaction extracted with CH_2Cl_2 (3 × 100 ml), dried ($MgSO_4$), and the solvent removed under reduced pressure. Chromatography (petroleum ether–EtOAc 99:1) gave firstly (1α,3α,5α)-3-[(phenylmethoxy)methyl]-6-thiabicyclo[3.1.0]hexane as a colourless oil (1.48 g, 31%); ν_{max} (film)/cm^{-1} 3027, 2949, 2847, 1495, 1453, 1364, 1202, 1126, 1101, 1028, 736 and 697; δ_H (400 MHz) 1.74 (2H, ddd, *J* 13.5, 10.5, 2.5 Hz, 2 × SCHC*H*H), 2.20 (2H, dd, *J* 13.5, 7.0 Hz, 2 × SCHCH*H*), 2.36 (1H, m, 3-*H*), 3.31 (2H, d, *J* 2.5 Hz, 2 × SC*H*), 3.43 (2H, d, *J* 6.0 Hz, PhCH$_2$OCH_2), 4.48 (2H, s, PhCH_2) and 7.25–7.37 (5H, m, Ph); δ_C (68 MHz) 32.9 (CH_2), 33.1 (CH), 41.3 (CH), 72.2 (CH_2), 72.9 (CH_2), 127.5 (2 × CH), 128.3 (CH) and 138.3 (C); *m*/*z* (EI) 220 (2, M^+), 129 (3), 113 (32), 112 (23), 108 (24), 107 (5), 92 (10), 91 (100) and 78 (83) (Found M^+, 220.0928. $C_{13}H_{16}OS$ requires *M*, 220.0922); followed by (1α,3β,5α)-3-[(phenylmethoxy)methyl]-6-thiabicyclo[3.1.0]hexane as a pale yellow oil (2.03 g, 42%); ν_{max} (film)/cm^{-1} 3027, 2926, 2852, 1602, 1495, 1452, 1363, 1207, 1097, 1028, 938, 735 and 697; δ_H (400 MHz) 2.06 (2H, dd, *J* 15.0, 1.5 Hz, 2 × SCHC*H*H), 2.30 (2H, ddd, *J* 15.0, 10.0, 3.0 Hz, 2 × SCHCH*H*), 2.50 (1H, m, 3-*H*), 3.33 (2H, d, *J* 3.0 Hz, 2 × SC*H*), 3.43 (2H, d, *J* 8.0 Hz, PhCH$_2$OCH_2), 4.44 (2H, s, PhCH_2) and 7.23–7.38 (5H, m, Ph); δ_C (68 MHz) 32.7 (CH_2), 37.2 (CH), 42.6 (CH), 72.9 (CH_2), 77.5 (CH_2), 127.4 (CH), 127.6 (CH), 128.3 (CH) and 138.5 (C); *m*/*z* (EI) 220 (1, M^+), 188 (2), 187 (6), 129 (13), 113 (30), 107 (8) and 91 (100) (Found M^+, 220.0916. $C_{13}H_{16}OS$ requires *M*, 220.0922.

(ii) Oxidation of intermediate episulfides to give 7 and 8. *(1α,3β,5α,6α)-3-[(Phenylmethoxy)methyl]-6-thiabicyclo-[3.1.0]hexane 6-oxide* ***7***. The typical episulfide oxidation procedure was followed using (1α,3β,5α)-3-[(phenylmethoxy)-methyl]-6-thiabicyclo[3.1.0]hexane (1.65 g, 7.50 mmol) with the addition of $NaHCO_3$ (1.94 g, 23.1 mmol) to the reaction mixture. Purification by chromatography (EtOAc then EtOAc–MeOH 19:1) gave **7** as a colourless oil (1.34 g, 75%); ν_{max} (film)/cm^{-1} 3029, 2926, 2855, 1453, 1366, 1097, 1029, 969, 742 and 699; δ_H (400 MHz) 1.87 (2H, dd, *J* 15.5, 3.0 Hz, 2 × SCHC*H*H), 2.30–2.47 (3H, m, 2 × SCHCH*H*, 3-*H*), 2.83 (2H, d, *J* 7.5 Hz, PhCH$_2$OCH_2), 3.27 (2H, d, *J* 5.5 Hz, 2 × SC*H*), 4.42 (2H, s, PhCH_2) and 7.25–7.38 (5H, m, Ph); δ_C (68 MHz) 31.1 (CH_2), 37.5 (CH), 57.5 (CH), 72.3 (CH_2), 72.9 (CH_2), 127.5 (CH), 127.7 (CH), 128.3 (CH) and 137.7 (C); *m*/*z* (EI) 188 (1), 107 (1), 92 (10), 91 (100), 81 (3), 80 (3), 79 (14), 67 (10) and 65 (7) (Found MH^+, 237.0956. $C_{13}H_{16}O_2S$ + H requires *M*, 237.0916).

(1α,3α,5α,6α)-3-[(Phenylmethoxy)methyl]-6-thiabicyclo-[3.1.0]hexane 6-oxide ***8***. The typical episulfide oxidation procedure was followed using (1α,3α,5α)-3-[(phenylmethoxy)-methyl]-6-thiabicyclo[3.1.0]hexane (1.05 g, 4.76 mmol) with the addition of $NaHCO_3$ (1.94 g, 23.1 mmol) to the reaction mixture. Purification by chromatography (EtOAc then EtOAc–MeOH 19:1) gave **8** as an unstable colourless oil (875 mg, 78%); ν_{max} (film)/cm^{-1} 3029, 2915, 2853, 1453, 1367, 1093, 1074, 1044, 970, 742 and 699; δ_H (400 MHz) 1.44 (1H, m, 3-*H*), 1.89 (2H, ddd, *J* 14.5, 11.0, 3.5 Hz, 2 × SCHC*H*H), 2.36 (2H, dd, *J* 14.5, 7.5 Hz, 2 × SCHCH*H*), 3.25 (2H, d, *J* 6.0 Hz, PhCH$_2$OCH_2), 3.31 (2H, d, *J* 3.5 Hz, 2 × SC*H*), 4.44 (2H, s, PhCH_2) and 7.25–7.38 (5H, m, Ph); δ_C (68 MHz) 31.7 (CH_2), 36.5 (CH), 56.8 (CH), 71.9 (CH_2), 73.0 (CH_2), 127.5 (CH), 127.7 (CH), 128.4 (CH) and 137.8 (C); *m*/*z* (EI) 236 (1, M^+), 188 (1), 107 (3), 97 (10), 92 (25), 91 (100), 81 (5), 79 (27), 67 (21) and 65 (14) (Found MH^+, 237.0929. $C_{13}H_{16}O_2S$ + H requires *M*, 237.0916).

Alternative stereoselective access to epoxide 6[11]

A solution of *tert*-butyl hydroperoxide (3.88 mmol) in CH_2Cl_2 (2.5 ml) was added to a solution of **4** (188 mg, 1.92 mmol) and $VO(acac)_2$ (20 mg, 0.076 mmol) in CH_2Cl_2 (5 ml) under nitrogen. The reaction mixture was stirred for 19 h and then washed with saturated aqueous Na_2SO_3 (2 ml), dried ($MgSO_4$) and the solvent removed under reduced pressure. Chromatography (petroleum ether–EtOAc 1:1) gave *syn*-6-oxabicyclo[3.1.0]-hexane-3-methanol as a yellow oil (339 mg, 58%); δ_H (400 MHz) 1.98–2.05 (4H, m, 2-H_2, 4-H_2), 2.41 (1H, m, C*H*CH$_2$-OH), 2.91 (1H, br s, O*H*), 3.48 (2H, d, *J* 4.5 Hz, CH_2OH) and 3.53 (2H, s, 2 × OC*H*); *m*/*z* (EI) 114 (4, M^+), 96 (10), 95 (18), 83 (100), 67 (43), 55 (76) and 41 (61).

A solution of the above epoxide (200 mg, 1.75 mmol) in THF (2 ml) was added to a stirred suspension of sodium hydride (77 mg, 60% dispersion in mineral oil, 1.93 mmol) in THF (4 ml) at 0 °C under nitrogen. The mixture was stirred for 1 h before benzyl bromide (0.23 ml, 1.93 mmol) was added, then stirred for a further 22 h at room temperature. The reaction mixture was quenched with water (10 ml), extracted with EtOAc (3 × 10 ml), dried ($MgSO_4$) and the solvents removed under reduced pressure. Chromatography (petroleum ether–EtOAc 9:1) gave **6** as a yellow oil (114 mg, 40%).

(1α,2β,4β,5α)-3-Thiatricyclo[3.2.1.0^{2,4}]oct-6-ene 10[12]

A solution of diene **9** (11.7 ml, 109 mmol), sulfur (6.95 g, 217 mmol) and 2,6-di-*tert*-butyl-4-methoxyphenol (5.12 g, 21.7 mmol) in dry DMF (150 ml) was heated at 100 °C under nitrogen for 3.5 h. After cooling to room temperature, water (150 ml) was added and the mixture extracted with petroleum ether (3 × 150 ml). The combined extracts were washed with water (3 × 150 ml), dried ($MgSO_4$) and the solvent removed under reduced pressure. Chromatography (petroleum ether) and then Kugelrohr distillation (oven temperature 100 °C, 10 mmHg) gave **10** as a yellow oil (511 mg, 3.8%); ν_{max} (film)/cm^{-1} 2972, 2921, 1633, 1450, 1254, 1218, 1062, 919, 757 and 732; δ_H (250 MHz) 1.29 (1H, d, *J* 9.0 Hz, C*H*H), 1.84 (1H, d, *J* 9.0 Hz, CH*H*), 2.97 (2H, s, 2 × =CHC*H*), 3.03 (2H, s, 2 × SC*H*) and 6.38 (2H, s, 2 × =C*H*); *m*/*z* (EI) 124 (30 M^+), 123 (72), 97 (69), 91 (100), 79 (52) and 64 (32).

(1α,2β,3β,4β,5α)-3-Thiatricyclo[3.2.1.0^{2,4}]oct-6-ene 3-oxide 11

The typical procedure for episulfide oxidation was followed using episulfide **10** (450 mg, 3.63 mmol), and gave **11** as a colourless oil (425 mg, 84%); ν_{max} (film)/cm^{-1} 2996, 1458, 1311, 1078, 1054 and 708; δ_H (400 MHz) 1.51 (1H, d, *J* 9.0 Hz, C*H*H), 2.35 (2H, s, 2 × SC*H*), 2.78 (1H, d, *J* 9.0 Hz, CH*H*), 3.70 (2H, s, 2 × =CHC*H*) and 6.83 (2H, s, 2 × =C*H*); δ_C (68 MHz) 43.9 (CH_2), 47.1 (CH), 52.4 (CH) and 144.5 (CH); *m*/*z* (FAB) 141 (13, MH^+), 109 (27), 95 (36), 83 (43), 69 (68), 57 (100) and 55 (87) (Found MH^+, 141.0369. C_7H_8OS + H requires *M*, 141.0374).

Typical procedure for sulfur monoxide transfer to an alkene: (1α,2β,3α,4β,5α)- and (1α,2β,3β,4β,5α)-3-thiatricyclo[3.2.1.0^{2,4}]-octane 3-oxide 16 and 17

A solution of *trans*-2,3-diphenylthiirane 1-oxide (350 mg, 1.54 mmol),[26] alkene **15** (51 mg, 0.54 mmol) and rhodium(II) acetate (6.5 mg, 0.015 mmol) in CH_2Cl_2 (5 ml) was stirred for 3 h. The solvent was removed under reduced pressure, and then chromatography (petroleum ether–EtOAc 1:1, then EtOAc) afforded firstly **16** as a colourless oil (25 mg, 32%); ν_{max} (film)/cm^{-1} 2966, 2872, 1301, 1076, 1041 and 949; δ_H (250 MHz) 1.06 (1H, dt, *J* 10.5, 1.0 Hz, 8-*H*H), 1.37 (2H, m, 6-*H*H, 7-*H*H), 1.76 (2H, m,

6-H*H*, 7-H*H*), 2.15 (2H, d, *J* 1.0 Hz, 1-*H*, 5-*H*), 2.41 (1H, dm, *J* 10.5 Hz, 8-H*H*) and 3.27 (2H, br s, 2 × SC*H*); δ_C (68 MHz) 29.2 (CH_2), 32.8 (CH_2), 40.7 (CH) and 47.8 (CH); *m*/*z* (FAB) 143 (54, MH^+), 95 (42), 81 (61), 69 (77), 57 (92) and 55 (100) (Found MH^+, 143.0531. $C_7H_{10}OS$ + H requires *M*, 143.0531); followed by **17** as a colourless oil (20 mg, 26%); ν_{max} (film)/cm^{-1} 2967, 2872, 1307, 1064, 1026 and 965; δ_H (400 MHz) 0.61 (1H, d, *J* 11.0 Hz, 8-*H*H), 0.80 (1H, d, *J* 11.0 Hz, 8-H*H*), 1.45–1.65 (4H, m, 6-H_2, 7-H_2) and 2.86–2.91 (4H, m, 1-*H*, 2-*H*, 4-*H*, 5-*H*); δ_C (68 MHz) 27.7 (CH_2), 30.9 (CH_2), 38.3 (CH) and 53.6 (CH); *m*/*z* (FAB) 143 (14, MH^+), 95 (46), 81 (56), 69 (89), 57 (93) and 55 (100) (Found MH^+, 143.0531. $C_7H_{10}OS$ + H requires *M*, 143.0531).

(1α,2β,3α,4β,5α)- and (1α,2β,3β,4β,5α)-3-Thiatricyclo[3.2.1.0^{2,4}]-oct-6-ene 3-oxide 18 and 11

The above typical procedure was followed using diene **9** (0.13 ml, 1.2 mmol), and after chromatography (petroleum ether–EtOAc 1:1, then EtOAc) gave firstly **18** as a colourless oil (30 mg, 20%); ν_{max} (film)/cm^{-1} 2996, 1458, 1311, 1078, 1054 and 708; δ_H (400 MHz) 1.51 (1H, d, *J* 9.0 Hz, C*H*H), 2.35 (2H, s, 2 × SC*H*), 2.78 (1H, d, *J* 9.0 Hz, CH*H*), 3.70 (2H, s, 2 × =CHC*H*) and 6.83 (2H, s, 2 × =C*H*); δ_C (68 MHz) 43.9 (CH_2), 47.1 (CH), 52.4 (CH) and 144.5 (CH); *m*/*z* (FAB) 141 (13, MH^+), 109 (27), 95 (36), 83 (43), 69 (68), 57 (100) and 55 (87) (Found MH^+, 141.0369. C_7H_8OS + H requires *M*, 141.0374); followed by **11** as a colourless oil (36 mg, 24%); see above for full analytical data for this compound.

(1α,2β,4β,5α,6β,8β)-7-Oxa-3-thiatetracyclo[3.3.1.0^{2,4}.0^{6,8}]-nonane 3,3-dioxide 19

1,1,1-Trifluoroacetone (0.20 ml, 2.2 mmol) was added to a solution of episulfoxide **18** (25 mg, 0.18 mmol) in MeCN (2.7 ml) and aqueous Na_2EDTA (1.8 ml of a 0.4 mM solution, 0.72 μmol) at 0 °C. A mixture of Oxone® (573 mg, 0.93 mmol) and $NaHCO_3$ (236 mg, 2.81 mmol) was added in portions over 30 min. After a further 3 h, the reaction mixture was diluted with water (2 ml) and extracted with CH_2Cl_2 (3 × 5 ml) taking care to keep the temperature of the extracts at 0 °C. The combined organic layers were dried ($MgSO_4$) and the solvent removed under reduced pressure. Rapid chromatography (petroleum ether–EtOAc 2:1) gave **19** as an unstable white solid (19 mg, 62%), mp 80–90 °C (decomp.); ν_{max}/cm^{-1} 3035, 3001, 1293, 1224, 1129, 994, 915, 847, 796 and 754; δ_H (250 MHz) 1.47 (1H, d, *J* 12.0 Hz, 9-*H*H), 2.22 (1H, d, *J* 12.0 Hz, 9-H*H*), 3.20 (2H, br s), 3.31 (2H, br s) and 3.35 (2H, br s); δ_C (68 MHz) 17.2 (CH_2), 37.8 (CH), 49.4 (CH) and 50.6 (CH); *m*/*z* (CI) 173 (9, MH^+), 108 (25), 107 (22), 91 (18) and 79 (100) (Found MH^+, 173.0274. $C_7H_8O_3S$ + H requires *M*, 173.0272).

By the same method, episulfoxide **11** (30 mg, 0.21 mmol) gave the same product (18 mg, 49%).

(1α,2β,3α,4β,5α)- and (1α,2β,3β,4β,5α)-8-(1,1-Dimethylethoxy)-3-thiatricyclo[3.2.1.0^{2,4}]oct-6-ene 3-oxide 22

The above typical procedure for sulfur monoxide transfer was followed using diene **21** (44 mg, 0.27 mmol), and after chromatography (EtOAc) gave a 1:1 mixture of diastereoisomers of **22** as a colourless oil (9 mg, 16%); ν_{max} (film)/cm^{-1} 2974, 2931, 1365, 1238, 1194, 1112, 1073, 1033, 884 and 755; δ_H (400 MHz) 1.05 (9H, s, C(CH_3)$_3$), 1.17 (9H, s, C(CH_3)$_3$), 2.99 (2H, s), 3.18 (3H, m), 3.42 (4H, m), 3.54 (1H, s), 5.45 (2H, m, =C*H*) and 6.29 (2H, br s, =C*H*); δ_C (100 MHz) 28.2 (CH_3), 28.3 (CH_3), 45.6 (CH), 47.9 (CH), 51.0 (CH), 56.4 (CH), 74.4 (C), 74.5 (C), 79.9 (CH), 93.2 (CH), 126.0 (CH) and 134.8 (CH); *m*/*z* (FAB) 213 (4, MH^+), 107 (24), 95 (29), 81 (35), 69 (57), 57 (100) and 55 (86) (Found MH^+, 213.0951. $C_{11}H_{16}O_2S$ + H requires *M*, 213.0949).

Typical procedure for sulfur transfer to an alkene: preparation of (1α,2β,4β,5α)-3-thiatricyclo[3.2.1.0^{2,4}]octane 23

A solution of alkene **15** (53 mg, 0.56 mmol), 2-methylthiirane (0.10 ml, 1.3 mmol) and rhodium(II) acetate (2.3 mg, 0.0052 mmol) in toluene (1.5 ml) was heated to reflux for 22 h. After cooling to room temperature, the solvent was removed under reduced pressure. Chromatography (petroleum ether) gave **23** as a colourless oil (28 mg, 39%);[27] ν_{max} (film)/cm^{-1} 2954, 2869, 1448, 1326, 1300, 1138, 1068, 916, 765 and 649; δ_H (400 MHz) 0.65 (1H, d, *J* 10.5 Hz, 8-*H*H), 1.25 (2H, m, 6-*H*H, 7-*H*H), 1.53 (1H, dm, *J* 10.5 Hz, 8-H*H*), 1.63 (2H, m, 6-H*H*, 7-H*H*), 2.45 (2H, br s, 1-*H*, 5-*H*) and 2.74 (2H, s, 2 × SC*H*); δ_C (125 MHz) 27.6 (2 × CH_2), 37.5 (CH) and 37.7 (CH); *m*/*z* (EI) 126 (28, M^+), 95 (100), 93 (45) and 66 (35) (Found M^+, 126.0498. $C_7H_{10}S$ requires *M*, 126.0503).

(1α,2β,4β,5α)-3-Thiatricyclo[3.2.1.0^{2,4}]oct-6-ene 10

The above typical procedure for sulfur transfer was followed using diene **9** (88 mg, 0.96 mmol), and after chromatography (petroleum ether) gave **10** as a pale yellow oil (48 mg, 40%); see above for full analytical data for this compound.

Typical deprotonation procedure using base 29: preparation of (1*S*)-{[1-methyl-3-(methylsulfinyl)cyclopent-3-en-1-yl]-sulfonyl}benzene 24

A solution of base **29** was prepared by the addition of ^{n}BuLi (1.74 ml of a 1.4 M solution in hexanes, 2.44 mmol) to a solution of the corresponding diamine (555 mg, 1.32 mmol) in THF (3 ml) at −78 °C followed by warming to room temperature for 10 min. After cooling to −78 °C, a solution of episulfoxide **3** (300 mg, 1.11 mmol) and iodomethane (0.66 ml, 10.6 mmol) in THF (10 ml) was added. The reaction mixture was stirred for 1 h and then quenched with saturated aqueous NH_4Cl (20 ml), warmed to room temperature and extracted with CH_2Cl_2 (3 × 20 ml). The combined extracts were dried ($MgSO_4$), the solvents removed under reduced pressure, and the residue subjected to chromatography (EtOAc) to give a 2:1 mixture of diastereomers of **24** as a colourless oil (267 mg, 85%); ν_{max} ($CHCl_3$)/cm^{-1} 2933, 2851, 1621, 1586, 1459, 1378, 1308, 1142, 1122, 1089, 990 and 959; δ_H (250 MHz) 1.48 (3H, s, CCH_3), 1.49 (3H, s, CCH_3), 2.35–2.65 (5H + 5H, m, 2 × =CC*H*H, SCH_3), 3.40–3.52 (2H + 2H, m, 2 × =CCH*H*), 6.24 (1H + 1H, s, =C*H*), 7.54–7.75 (3H + 3H, m, Ph*H*) and 7.86–7.95 (2H + 2H, m, Ph*H*); *m*/*z* (EI) 284 (6, M^+), 188 (4), 159 (3), 143 (100), 142 (79), 127 (46), 95 (95), 79 (80) and 77 (80) (Found M^+, 284.0534. $C_{13}H_{16}O_3S_2$ requires M, 284.0541). The ee was determined as 82% by HPLC (OD column, 20% ^{i}PrOH in hexane), the retention times for the major diastereoisomer were 20.1 min (major) and 23.4 min (minor), and for the minor diastereoisomer 27.8 min (minor) and 29.3 min (major).

Typical sulfoxide oxidation procedure: (1*S*)-{[1-methyl-3-(methylsulfonyl)cyclopent-3-en-1-yl]sulfonyl}benzene 25

A solution of Oxone® (521 mg, 0.847 mmol) in water (5 ml) was added to a solution of sulfoxides **24** (241 mg, 0.847 mmol) in MeOH (5 ml) and stirred for 1 h. The reaction was diluted with water (5 ml), extracted with CH_2Cl_2 (3 × 15 ml), dried ($MgSO_4$) and the solvent removed under reduced pressure. Purification by chromatography (petroleum ether–EtOAc 2:3) gave **25** as a white solid (147 mg, 58%). Recrystallisation from ^{i}PrOH–hexane, and then ^{i}PrOH gave optically pure material for X-ray analysis; mp 124–125 °C (Found: C, 51.85; H, 5.48; S, 21.12. $C_{13}H_{16}O_4S_2$ requires C, 51.98; H, 5.37; S, 21.35%); ν_{max} ($CHCl_3$)/cm^{-1} 2929, 2853, 1629, 1586, 1318, 1140 and 958; δ_H (400 MHz) 1.51 (3H, s, CCH_3), 2.52 (1H, d, *J* 18.5 Hz, =CC*H*H), 2.63 (1H, d, *J* 17.0 Hz, =CC*H*H), 2.93 (3H, s, SCH_3), 3.49–3.61 (2H, m, 2 × =CCH*H*), 3.57 (1H, d, *J* 18.0 Hz, H*H*CCS), 6.60 (1H, s, =C*H*), 7.61 (2H, t, *J* 7.5 Hz, Ph*H*), 7.72 (1H, t, *J* 7.5 Hz, Ph*H*)

and 7.92 (2H, d, *J* 7.5 Hz, Ph*H*); *m*/*z* (CI) 301 (12, MH^+), 283 (10), 209 (13), 203 (11), 171 (15), 159 (100), 143 (37), 125 (77), 97 (57) and 79 (71) (Found MH^+, 301.0578. $C_{13}H_{16}O_4S_2$ + H requires M, 301.0568).

(1*S*)-({1-Methyl-3-[(phenylmethyl)sulfinyl]cyclopent-3-en-1-yl}-sulfonyl)benzene 26

The above typical deprotonation procedure with base **29** was followed using episulfoxide **3** (50 mg, 0.19 mmol) with benzyl bromide as the electrophile. Purification by chromatography (EtOAc) gave **26** as a mixture of diastereomers (1 : 1), as a colourless oil (48 mg, 72%); ν_{max} ($CHCl_3$)/cm^{-1} 2935, 2870, 1626, 1584, 1454, 1304, 1151 and 990; δ_H (400 MHz) 1.42 (3H, s, CH_3, major), 1.43 (3H, s, CH_3, minor), 2.25–2.55 (2H + 2H, m, 2 × =CCHH), 3.30–3.44 (2H + 2H, m, 2 × =CCHH), 3.98 (1H, d, H_A of AB system, *J* 13.0 Hz, PhCHH), 4.01–4.05 (1H + 1H, m, H_B of AB and $H_{A'}$ of A′B′ systems, 2 × PhCHH), 4.11 (1H, d, $H_{B'}$ of A′B′ system, *J* 12.5 Hz, PhCHH), 5.88 (1H, s, =CH, major), 6.00 (1H, s, =CH, minor), 7.17–7.37 (5H + 5H, m, PhH), 7.56–7.62 (2H + 2H, m, PhH), 7.65–7.72 (1H + 1H, m, PhH) and 7.86–7.93 (2H + 2H, m, PhH); *m*/*z* (FAB) 361 (61, MH^+), 219 (53) and 91 (100) (Found MH^+, 361.0936. $C_{19}H_{20}O_3S_2$ + H requires *M*, 361.0932).

(1*S*)-({1-Methyl-3-[(phenylmethyl)sulfonyl]cyclopent-3-en-1-yl}-sulfonyl)benzene 27

The typical oxidation procedure was followed using sulfoxide **26** (20 mg, 0.055 mmol), and gave **27** as a white solid (21 mg, 100%); mp 142–145 °C (Found: C, 60.59; H, 5.46; S, 16.86. $C_{19}H_{20}O_4S_2$ requires C, 60.62; H, 5.35; S, 17.03%); ν_{max} ($CHCl_3$)/cm^{-1} 2915, 2849, 1625, 1456, 1317, 1306, 1152, 1121 and 992; δ_H (250 MHz) 1.37 (3H, s, CH_3), 2.30 (1H, dm, *J* 16.5 Hz, =CCHH), 2.40 (1H, ddd, *J* 19.0, 2.5, 2.5 Hz, =CCHH), 3.26 (1H, app. dq, *J* 16.5, 2.5 Hz, =CCHH), 3.43 (1H, app. dq, *J* 19.0, 2.5 Hz, =CCHH), 4.25 (2H, s, PhCH_2), 6.39 (1H, s, =CH), 7.35–7.50 (5H, m, PhH), 7.58 (2H, t, *J* 7.5 Hz, PhH), 7.70 (1H, t, *J* 7.5 Hz, PhH) and 7.84 (2H, d, *J* 7.5 Hz, PhH); *m*/*z* (FAB) 377 (35, MH^+), 261 (12), 235 (9), 217 (16), 109 (26), 91 (70), 69 (76) and 55 (100) (Found MH^+, 377.0893. $C_{19}H_{20}O_4S_2$ + H requires M, 377.0881). The ee was determined as 85% by HPLC (OD column, 20% ^{i}PrOH in hexane), the retention times were 53.3 min (major) and 68.1 min (minor).

({[3-(Methylsulfinyl)cyclopent-3-en-1-yl]methoxy}methyl)-benzene 30 and ({[3-(methylsulfonyl)cyclopent-3-en-1-yl]-methoxy}methyl)benzene 31

A. From episulfoxide 7. The typical deprotonation procedure with base **29** was followed using episulfoxide **7** (49 mg, 0.21 mmol) with iodomethane as the electrophile. Purification by chromatography (EtOAc–MeOH 19 : 1) gave a 1 : 1 mixture of diastereoisomers of **30** as a colourless oil (38 mg, 73%); ν_{max} (film)/cm^{-1} 3029, 2932, 2851, 1453, 1364, 1100, 1063, 1028, 958, 741 and 700; δ_H (400 MHz) 2.28–2.90 (5H + 5H, m, 3-H_2, 4-H, 5-H_2), 2.60 (3H + 3H, s, CH_3), 3.43 (2H + 2H, m, PhCH_2-OCH_2), 4.52 (2H + 2H, m, PhCH_2), 6.33 (1H + 1H, m, =CH) and 7.27–7.39 (5H + 5H, m, Ph); δ_C (68 MHz) 32.2 (CH_2), 32.3 (CH_2), 36.4 (2 × CH_2), 38.0 (CH), 38.1 (CH), 38.9 (2 × CH_3), 73.5 (CH_2), 73.6 (CH_2), 73.7 (CH_2), 73.9 (CH_2), 128.1 (2 × CH), 128.8 (2 × CH), 135.8 (2 × CH), 136.0 (2 × CH), 138.6 (2 × C) and 146.6 (2 × C); *m*/*z* (EI) 250 (1, M^+), 233 (4), 143 (12), 113 (27), 91 (100), 79 (20) and 65 (22) (Found M^+, 250.1027. $C_{14}H_{18}O_2S$ requires *M*, 250.1028).

The sulfoxides (38 mg, 0.15 mmol) were oxidised by the typical oxidation procedure to give **31** as a colourless oil (40 mg, 98%); $[\alpha]_D$ +12 (*c*, 1.17, $CHCl_3$); ν_{max} (film)/cm^{-1} 3027, 2926, 2855, 1622, 1453, 1301, 1141, 1101, 955, 752 and 699; δ_H (400 MHz) 2.40–2.91 (8H, m, 3-H_2, 4-H, 5-H_2, CH_3), 3.43 (2H, d, *J* 5.0 Hz, PhCH_2OCH_2), 4.52 (2H, s, PhCH_2), 6.68 (1H, m, =CH) and 7.27–7.47 (5H, m, Ph); δ_C (100 MHz) 34.5 (CH_2), 36.1 (CH_2), 38.1 (CH), 41.2 (CH_3), 73.0 (CH_2), 73.1 (CH_2), 127.6 (CH), 127.7 (CH), 128.4 (CH), 138.1 (C), 142.5 (CH), 142.9 (C); *m*/*z* (EI) 266 (1, M^+), 187 (12), 169 (34), 145 (10), 107 (15), 91 (100), 81 (27), 77 (20) and 65 (23) (Found M^+, 266.0982. $C_{14}H_{18}O_3S$ requires *M*, 266.0977). The ee was determined as 85% by HPLC (OD column, 10% ^{i}PrOH in hexane), the retention times were 26.5 min (major) and 30.4 min (minor).

B. From episulfoxide 8. The typical deprotonation procedure with base **29** was followed using episulfoxide **8** (56 mg, 0.24 mmol) with iodomethane as the electrophile. Purification as above gave a 1 : 1 mixture of diastereoisomers of **30** as a colourless oil (20 mg, 34%).

The sulfoxides (6 mg, 0.024 mmol) were oxidised by the typical oxidation procedure to give **31** as a colourless oil (6 mg, 90%). The ee was determined as 85% by HPLC (OD column, 10% ^{i}PrOH in hexane), the retention times are given above, but the minor enantiomer eluted first.

4-[(Phenylmethoxy)methyl]-1-[(phenylmethyl)sulfinyl]cyclopent-1-ene 32 and 4-[(phenylmethoxy)methyl]-1-[(phenylmethyl)-sulfonyl]cyclopent-1-ene 33

The typical deprotonation procedure with base **29** was followed using episulfoxide **7** (46 mg, 0.19 mmol) with benzyl bromide as the electrophile. Purification by chromatography (EtOAc–petroleum ether 1 : 1 then EtOAc), gave a 1 : 1 mixture of diastereoisomers of **32** as a colourless oil (41 mg, 65%); ν_{max} (film)/cm^{-1} 3029, 2925, 2851, 1602, 1495, 1453, 1364, 1100, 1074, 1056, 1029, 766, 739 and 699; δ_H (400 MHz) 2.22–2.85 (5H + 5H, m, 3-H_2, 4-H, 5-H_2), 3.35–3.44 (2H + 2H, m, PhCH_2-OCH_2), 3.92–4.04 (2H + 2H, m, PhCH_2), 4.48–4.58 (2H + 2H, m, PhCH_2), 6.06 (1H + 1H, m, =CH) and 7.17–7.40 (10H + 10H, m, 2 × Ph); δ_C (68 MHz) 32.0 (CH_2), 32.2 (CH_2), 36.0 (2 × CH_2), 37.3 (CH), 37.5 (CH), 58.3 (2 × CH_2), 73.0 (CH_2), 73.1 (CH_2), 73.2 (CH_2), 73.4 (CH_2), 127.7 (CH), 128.2 (CH), 128.4 (CH), 128.6 (CH), 130.0 (CH), 137.2 (CH), 137.5 (CH), 138.2 (2 × C) and 143.6 (2 × C) (the remaining 7 × CH and 2 × C are underneath the other aromatic ^{13}C signals); *m*/*z* (FAB) 327 (99, MH^+), 235 (4), 181 (9), 123 (10), 107 (18), 92 (11) and 91 (100) (Found MH^+, 327.1400. $C_{20}H_{22}O_2S$ + H requires *M*, 327.1419).

The sulfoxides (41 mg, 0.13 mmol) were oxidised by the typical oxidation procedure to give **33** as a colourless oil (35 mg, 81%); $[\alpha]_D$ +1.5 (*c*, 1.01, $CHCl_3$); ν_{max} (film)/cm^{-1} 3030, 2923, 2854, 1619, 1495, 1454, 1309, 1150, 1121, 779, 740, 698 and 637; δ_H (400 MHz) 2.26–2.80 (5H, m, 3-H_2, 4-H, 5-H_2), 3.33 (2H, m, PhCH_2OCH_2), 4.19 (2H, s, PhCH_2), 4.50 (2H, s, PhCH_2), 6.45 (1H, dd, *J* 2.0, 2.0 Hz, =CH) and 7.25–7.48 (10H, m, 2 × Ph); δ_C (100 MHz) 35.0 (CH_2), 36.2 (CH_2), 38.0 (CH), 60.2 (CH_2), 73.0 (CH_2), 73.1 (CH_2), 127.6 (CH), 127.7 (CH), 128.2 (C), 128.4 (CH), 128.7 (CH), 128.8 (CH), 130.6 (CH), 138.1 (C), 140.9 (C) and 145.6 (CH); *m*/*z* (FAB) 343 (10, MH^+), 341 (6), 253 (4), 235 (4), 181 (17), 154 (15), 137 (13), 107 (13), 91 (100) and 81 (17) (Found MH^+, 343.1386. $C_{20}H_{22}O_3S$ + H requires *M*, 343.1368). The ee was determined as 88% by HPLC (OD column, 10% ^{i}PrOH in hexane), the retention times were 39.9 min (minor) and 42.3 min (major).

2-(Methylsulfinyl)bicyclo[2.2.1]hepta-2,5-diene 34 and 2-(methyl-sulfonyl)bicyclo[2.2.1]hepta-2,5-diene 36

A. Typical procedure for deprotonation using base 28. A solution of base **28** was prepared by the addition of ^{n}BuLi (0.71 ml of a 1.60 M solution in hexanes, 1.14 mmol) to a solution of the corresponding amine hydrochloride (157 mg, 0.60 mmol) in THF (5 ml) at −78 °C followed by warming to room temperature for 10 min. After cooling to −78 °C, a solution of episulfoxide **11** (70 mg, 0.50 mmol) and iodomethane (0.31 ml, 5.0 mmol) in THF (1 ml) was added. Work-up as for base **29** and

chromatography (EtOAc) gave a 3:2 mixture of diastereoisomers of **34** as a colourless oil (56 mg, 73%); ν_{max} (film)/cm^{-1} 2989, 2938, 1548, 1419, 1298, 1037 and 708; δ_H (400 MHz) 2.13–2.26 (2H + 2H, m, CH_2), 2.54 (3H, s, CH_3, minor), 2.61 (3H, s, CH_3, major), 3.81 (1H + 1H, br s), 3.87 (1H, br s, major), 4.02 (1H, br s, minor), 6.79 (1H + 1H, m), 6.89 (1H + 1H, m) and 7.22 (1H + 1H, m, 3-*H*); δ_C (68 MHz) 37.2 (CH_3), 37.9 (CH_3), 47.8 (CH), 48.9 (CH), 51.2 (CH), 51.3 (CH), 73.9 (CH_2), 74.0 (CH_2), 142.2 (CH), 142.5 (2 × CH), 142.7 (CH), 147.3 (CH), 147.9 (CH) and 159.8 (2 × C); *m*/*z* (EI) 154 (23, M$^+$), 138 (8), 123 (13), 107 (43), 106 (54), 91 (100), 79 (65), 77 (52), 66 (96) and 65 (77) (Found M$^+$, 154.0450. $C_8H_{10}OS$ requires *M*, 154.0452).

The sulfoxides (52 mg, 0.34 mmol) were oxidised by the typical oxidation procedure, and chromatography (petroleum ether–EtOAc 1:1) gave **36** as a colourless oil (41 mg, 71%); $[a]_D$ −19 (*c*, 1.46, $CHCl_3$); ν_{max} (film)/cm^{-1} 2997, 2940, 1551, 1299, 1162, 1134 and 762; δ_H (400 MHz) 2.22 (1H, d, *J* 6.5 Hz, 7-*H*H), 2.31 (1H, dt, *J* 6.5, 1.5 Hz, 7-H*H*), 2.88 (3H, s, CH_3), 3.86 (1H, br s, 1-*H* or 4-*H*), 3.91 (1H, br s, 1-*H* or 4-*H*), 6.81 (1H, dd, *J* 5.0, 3.0 Hz, 5-*H* or 6-*H*), 7.01 (1H, dd, *J* 5.0, 3.0 Hz, 5-*H* or 6-*H*) and 7.59 (1H, d, *J* 3.0 Hz, 3-*H*); δ_C (100 MHz) 41.2 (CH_3), 50.8 (CH), 51.7 (CH), 74.9 (CH_2), 142.1 (CH), 142.4 (CH), 154.5 (CH) and 157.1 (C); *m*/*z* (EI) 170 (12, M$^+$), 107 (6), 91 (100), 90 (24), 78 (4), 77 (9) and 65 (11) (Found M$^+$, 170.0397. $C_8H_{10}O_2S$ requires *M*, 170.0402). The ee was determined as 43% by HPLC (OD column, 2% ^{i}PrOH in hexane), the retention times were 33.4 min (major) and 35.3 min (minor).

B. Deprotonation using base 29. The typical deprotonation procedure with base **29** was followed using episulfoxide **11** (47 mg, 0.34 mmol) with iodomethane as the electrophile. Purification by chromatography (EtOAc) gave a 3:2 mixture of diastereoisomers of **34** as a colourless oil (39 mg, 75%).

The sulfoxides (36 mg, 0.23 mmol) were oxidised by the typical oxidation procedure, and chromatography (petroleum ether–EtOAc 1:1) gave **36** as a colourless oil (28 mg, 70%); $[a]_D$ +28 (*c*, 1.20, $CHCl_3$). The ee was determined as 62% by HPLC (OD column, 3% ^{i}PrOH in hexane), the retention times are given above but the minor enantiomer eluted first.

2-[(Phenylmethyl)sulfinyl]bicyclo[2.2.1]hepta-2,5-diene 35 and 2-[(phenylmethyl)sulfonyl]bicyclo[2.2.1]hepta-2,5-diene 37

The typical deprotonation procedure with base **29** was followed using episulfoxide **11** (50 mg, 0.36 mmol) with benzyl bromide as the electrophile. Purification by chromatography (EtOAc) gave a 3:1 mixture of diastereoisomers of **35** as a colourless oil (51 mg, 62%); $[a]_D$ −19 (*c*, 0.96, $CHCl_3$); ν_{max} (film)/cm^{-1} 3062, 2980, 2938, 1547, 1495, 1454, 1297, 1072, 1043, 766 and 700; δ_H (400 MHz) 2.07–2.18 (2H + 2H, m, 7-H_2), 3.72 (1H, br s, minor), 3.76 (1H, br s, major), 3.85 (1H, br s, minor), 3.88–4.06 (3H + 2H, m), 6.75 (1H, dd, *J* 5.0, 3.0 Hz, minor), 6.78 (1H, dd, *J* 5.0, 3.0 Hz, major), 6.86–6.92 (1H + 1H, m), 7.05 (1H, d, *J* 3.0 Hz, 3-*H*, major), 7.11 (1H, d, *J* 3.0 Hz, 3-*H*, minor), and 7.20–7.37 (5H + 5H, m, Ph); δ_C (100 MHz) 48.4 (CH), 49.1 (CH), 51.4 (CH), 51.5 (CH), 58.2 (CH_2), 58.7 (CH_2), 73.5 (CH_2), 74.0 (CH_2), 128.1 (CH), 128.5 (CH), 128.6 (CH), 130.1 (CH), 130.2 (CH), 142.2 (CH), 142.4 (CH), 142.7 (CH), 142.9 (CH), 148.8 (CH), 150.1 (CH), 157.6 (C) and 158.1 (C) (the additional quaternary and two methine carbon signals are coincident with the other signals); *m*/*z* (EI) 230 (1, M$^+$), 164 (3), 123 (2), 91 (100), 85 (19) and 83 (29) (Found M$^+$, 230.0756. $C_{14}H_{14}OS$ requires *M*, 230.0765).

The sulfoxides (48 mg, 0.21 mmol) were oxidised by the typical oxidation procedure, and chromatography (petroleum ether–EtOAc 3:1) gave **37** as a colourless oil (36 mg, 70%); $[a]_D$ +6 (*c*, 1.56, $CHCl_3$); ν_{max} (film)/cm^{-1} 2978, 2941, 1583, 1550, 1456, 1307, 1163, 1119, 778 and 698; δ_H (400 MHz) 2.09 (1H, d, *J* 6.5 Hz, 7-*H*H), 2.15 (1H, d, *J* 6.5 Hz, 7-H*H*), 3.57 (1H, br s, 1-*H* or 4-*H*), 3.74 (1H, br s, 1-*H* or 4-*H*), 4.18 (1H, d, J_{AB} 14.0 Hz, PhC*H*H), 4.24 (1H, d, J_{AB} 14.0 Hz, PhCH*H*), 6.72 (1H, dd, *J* 5.0, 3.0 Hz, 5-*H* or 6-*H*), 6.81 (1H, dd, *J* 5.0, 3.0 Hz, 5-*H* or 6-*H*), 7.28–7.45 (5H, m, Ph) and 7.47 (1H, d, *J* 3.0 Hz, 3-*H*); δ_C (100 MHz) 51.5 (CH), 51.9 (CH), 60.7 (CH_2), 74.7 (CH_2), 127.8 (C), 128.6 (CH), 128.8 (CH), 130.9 (CH), 141.8 (CH), 142.7 (CH), 155.4 (C) and 157.9 (CH); *m*/*z* (FAB) 247 (16, MH$^+$), 176 (13), 154 (100), 137 (69), 136 (72), 107 (25), 91 (44), 69 (29) and 57 (39) (Found MH$^+$, 247.0796. $C_{14}H_{14}O_2S$ + H requires *M*, 247.0793). The ee was determined as 66% by HPLC (OD column, 3% ^{i}PrOH in hexane), the retention times were 46.8 min (minor) and 51.3 min (major).

2-(Methylsulfinyl)bicyclo[2.2.1]hept-2-ene 38 and 2-(methylsulfonyl)bicyclo[2.2.1]hept-2-ene 40

A. Deprotonation using base 29. The typical deprotonation procedure with base **29** was followed using episulfoxide **17** (59 mg, 0.42 mmol), with iodomethane as the electrophile. Purification by chromatography (Et_2O–MeOH 49:1) gave a 3:1 mixture of diastereoisomers of **38** as a colourless oil (41 mg, 63%); ν_{max} (film)/cm^{-1} 2970, 2871, 1574, 1419, 1307, 1125, 1056, 1027, 952, 875 and 656; δ_H (400 MHz) 1.10–1.90 (6H + 6H, m, 3 × CH_2), 2.66 and 2.67 (3H + 3H, 2 × s, CH_3), 3.11 (1H + 1H, br s), 3.19 (1H, br s, major), 3.35 (1H, br s, minor), 6.57 (1H, d, *J* 3.0 Hz, =C*H*, minor) and 6.61 (1H, d, *J* 3.0 Hz, =C*H*, major); δ_C (100 MHz) 24.8 (CH_2), 24.9 (CH_2), 25.4 (CH_2), 25.5 (CH_2), 38.5 (CH_3), 39.3 (CH_3), 41.0 (CH), 41.1 (CH), 42.9 (CH), 43.5 (CH), 48.9 (CH_2), 49.4 (CH_2), 139.3 (CH), 139.9 (CH), 150.7 (C) and 151.5 (C); *m*/*z* (EI) 156 (16, M$^+$), 128 (46), 113 (43), 85 (63), 83 (100), 81 (63) and 65 (33) (Found M$^+$, 156.0611. $C_8H_{12}OS$ requires *M*, 156.0609).

The sulfoxides (36 mg, 0.23 mmol) were oxidised by the typical oxidation procedure and gave **40** as a white solid (36 mg, 91%) (Found: C, 55.69; H, 7.26. $C_8H_{12}O_2S$ requires C, 55.79; H, 7.02%); ν_{max} (film)/cm^{-1} 2976, 2875, 1581, 1294, 1174, 1136, 1060, 964 and 758; δ_H (400 MHz) 1.18–1.92 (6H, m, 3 × CH_2), 2.96 (3H, s, CH_3), 3.15 (1H, br s, 4-*H*), 3.32 (1H, br s, 1-*H*) and 6.95 (1H, d, *J* 3.0 Hz, =C*H*); δ_C (100 MHz) 24.3 (CH_2), 25.0 (CH_2), 42.1 (CH_3), 43.0 (CH), 43.6 (CH), 49.4 (CH_2), 146.3 (CH) and 147.4 (C); *m*/*z* (EI) 172 (11, M$^+$), 144 (36), 91 (12), 81 (100), 65 (29) and 53 (20) (Found M$^+$, 172.0565. $C_8H_{12}O_2S$ requires *M*, 172.0558). The sample was racemic by HPLC (OD column, 2.5% ^{i}PrOH in hexane).

B. Deprotonation with base 29 in the presence of LiCl. The typical deprotonation procedure with base **29** was followed using episulfoxide **17** (31 mg, 0.22 mmol) with iodomethane as the electrophile, except for the addition of a solution of lithium chloride (7.8 mg, 0.18 mmol) in THF (1 ml) to the solution of base **29** before **17** was added. Work-up and chromatography as before gave a 3:1 mixture of diastereoisomers of **38** as a colourless oil (20 mg, 59%).

The sulfoxides (20 mg, 0.13 mmol) were oxidised by the typical oxidation procedure and gave **40** as a white solid (21.5 mg, 98%); $[a]_D$ −24 (*c*, 1.20, $CHCl_3$). The ee was determined as 27% by HPLC (OD column, 2.5% ^{i}PrOH in hexane), the retention times were 26.6 min (minor) and 38.8 min (major).

C. Deprotonation with base 28. The typical deprotonation procedure with base **28** was followed using episulfoxide **17** (50 mg, 0.35 mmol), with iodomethane as the electrophile. Work-up and chromatography as before gave a 3:1 mixture of diastereoisomers of **38** as a colourless oil (45 mg, 82%).

The sulfoxides (45 mg, 0.29 mmol) were oxidised by the typical oxidation procedure and gave **40** as a white solid (49 mg, 99%); $[a]_D$ +60 (*c*, 1.13, $CHCl_3$). The ee was determined as 76% by HPLC (OD column, 2.5% ^{i}PrOH in hexane), the retention times were as above but the major enantiomer eluted first. Recrystallisation from petroleum ether–EtOAc–Et_2O afforded

colourless crystals for X-ray crystallographic analysis, mp 49–51 °C.

2-[(Phenylmethyl)sulfinyl]bicyclo[2.2.1]hept-2-ene 39

A. Deprotonation using base 29. The typical deprotonation procedure with base **29** was followed using episulfoxide **17** (53 mg, 0.37 mmol) with benzyl bromide as the electrophile. Purification by chromatography (EtOAc) gave a 9:1 mixture of diastereoisomers of **39** as a white solid (43 mg, 50%). A small portion was recrystallised from petroleum ether–CH_2Cl_2 to give colourless crystals; mp 91–93 °C (Found: C, 72.13; H, 7.01. $C_{14}H_{16}OS$ requires C, 72.37; H, 6.94%); ν_{max} (film)/cm^{-1} 2967, 2870, 1602, 1495, 1454, 1305, 1072, 1054, 1029, 764 and 699; δ_H (400 MHz) 1.05–1.84 (6H, m, 5-H_2, 6-H_2, 7-H_2), 2.77 (1H, br s, 1-*H*), 3.05 (1H, br s, 4-*H*), 4.02 (1H, d, J_{AB} 12.5 Hz, PhC*H*H), 4.10 (1H, d, J_{AB} 12.5 Hz, PhCH*H*), 6.49 (1H, d, *J* 3.0 Hz, =C*H*) and 7.25–7.43 (5H, m, Ph); δ_C (68 MHz) (major diastereoisomer) 24.9 (CH_2), 25.1 (CH_2), 42.1 (CH), 43.0 (CH), 47.8 (CH_2), 59.9 (CH_2), 128.2 (CH), 128.5 (CH), 130.1 (CH), 140.1 (CH) and 149.7 (C) (the additional quaternary carbon signal is coincident with one of the signals); *m*/*z* (EI) 232 (2, M^+), 183 (4), 125 (5), 91 (100) and 65 (8) (Found M^+, 232.0921. $C_{14}H_{16}OS$ requires *M*, 232.0922). The sample was racemic by HPLC (OD column, 2% ^{i}PrOH in hexane).

B. Deprotonation using base 29 in the presence of LiCl. The typical deprotonation procedure with base **29** was followed using episulfoxide **17** (29 mg, 0.20 mmol) with benzyl bromide as the electrophile, except for the addition of a solution of lithium chloride (5.8 mg, 0.14 mmol) in THF (1 ml) to the solution of base **29** before **17** was added. Work-up and chromatography as before gave a 9:1 mixture of diastereoisomers of **39** as a white solid (22 mg, 46%); $[a]_D$ −10 (*c*, 1.16, $CHCl_3$). The ee was determined as 17% by HPLC (OD column, 2% ^{i}PrOH in hexane), the retention times for the major diastereoisomer were 38.4 min (minor) and 45.8 min (major), and for the minor diastereoisomer 28.2 min (major) and 50.0 min (minor).

C. Deprotonation using base 28. The typical deprotonation procedure with base **28** was followed using episulfoxide **17** (49 mg, 0.35 mmol) with benzyl bromide as the electrophile (0.41 ml, 3.4 mmol). Purification as before gave the title compound as a white solid (65 mg, 82%); $[a]_D$ +39 (*c*, 0.70, $CHCl_3$). The ee was determined as 70% by HPLC (OD column, 2% ^{i}PrOH in hexane), the retention times are given above, and although the diastereoselectivity was the same, the opposite enantiomer was favoured.

Data for crystal structure determinations †

Compound 3. A crystal was attached to a glass fibre before transfer to the diffractometer. **Crystal data**. $C_{12}H_{14}O_3S_2$, *M* = 270.35, monoclinic, *a* = 6.2928(9), *b* = 19.505(3), *c* = 10.367(2) Å, *β* = 96.581(14)°, *U* = 1264.1(3) Å^3, *T* = 298(2) K, space group $P2_1/n$ (No. 14), *Z* = 4, D_c = 1.421 g cm^{-3}, *μ*(Mo-K*α*) = 0.414 mm^{-1}, 2221 unique reflections measured and used in all calculations. Final R_1 [1779 $F > 4\sigma(F)$] = 0.0447 and *wR*(all F^2) was 0.110.

Compound 25. A crystal was encapsulated in a film of RS3000 perfluoropolyether oil attached to a glass fibre before transfer into the cold stream of the low temperature device on the diffractometer. **Crystal data**. $C_{13}H_{16}O_4S_2$, *M* = 300.38, monoclinic, *a* = 9.907(7), *b* = 5.888(4), *c* = 12.317(6) Å, *β* = 103.06(5)°, *U* = 699.8(6) Å^3, *T* = 150(2) K, space group $P2_1$ (No. 4), *Z* = 2, D_c = 1.425 g cm^{-3}, *μ*(Mo-K*α*) = 0.387 mm^{-1}, 2458 unique reflections measured and used in all calculations. Final R_1 [2334 $F > 4\sigma(F)$] = 0.0264 and *wR*(all F^2) was 0.0641. The Flack parameter refined to −0.05(8), thereby establishing the absolute configuration.[28]

Compound 40. The crystal was handled as for that of compound **25**. **Crystal data**. $C_8H_{12}O_2S$, *M* = 172.24, monoclinic, *a* = 6.101(2), *b* = 8.826(4), *c* = 7.894(3) Å, *β* = 98.54(3)°, *U* = 420.3(3) Å^3, *T* = 150(2) K, space group $P2_1$ (No. 4), *Z* = 2, D_c = 1.361 g cm^{-3}, *μ*(Mo-K*α*) = 0.331 mm^{-1}, 1468 unique reflections measured and used in all calculations. Final R_1 [1359 $F > 4\sigma(F)$] = 0.0522 and *wR*(all F^2) was 0.142. The Flack parameter refined to 0.0(2), thereby establishing the absolute configuration.[28]

† CCDC reference number 207/383. See http://www.rsc.org/suppdata/p1/a9/a908391j/ for crystallographic files in .cif format.

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