Episulfone substitution and ring-opening reactions *via* α-sulfonyl carbanion intermediates

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Three-membered cyclic sulfones undergo substitution on treatment with base–electrophile mixtures, such as LDA–Me_3SiCl and Bu^t–P_4 phosphazene base–PhCHO, to give either substituted episulfones or the corresponding alkenes following loss of SO_2. The structure of a trisilylated episulfone product, 2a, was determined by X-ray crystallography. In the absence of Me_3SiCl, reaction of episulfones with lithium diisopropylamide results in ring-opening to give alkenyl sulfinate intermediates, which can be alkylated to give (*E*)-alkenyl sulfone products in stereoselective fashion.

Introduction

Three-membered cyclic sulfones (thiirane 1,1-dioxides or episulfones) **1** can be prepared by several long-established procedures, including the treatment of alkanesulfonyl chlorides with a tertiary amine base, and the reaction of alkanesulfonyl chlorides or SO_2 with diazoalkanes, especially diazomethane.[1] Episulfones are also well established as intermediates in the classical Ramberg–Bäcklund reaction and quite recently it has been established that certain types of episulfone can be isolated from Ramberg–Bäcklund reactions, provided that modified, mild conditions are used.[2] Considering the widespread interest in sulfones as synthetic intermediates, especially in C–C bond-forming reactions involving α-sulfonyl carbanions, there is a dearth of synthetic methodology involving episulfones. At the outset of our studies described below, the documented chemistry of episulfones was limited mainly to studies of their SO_2 extrusions to give alkenes,[3] and a few reports on their ring-opening reactions with nucleophiles.[4]

We recently reported the first examples of episulfone substitutions involving α-sulfonyl carbanion intermediates,[5] similar transformations being also described by Taylor and co-workers,[6] and herein give full details of our results in this area.

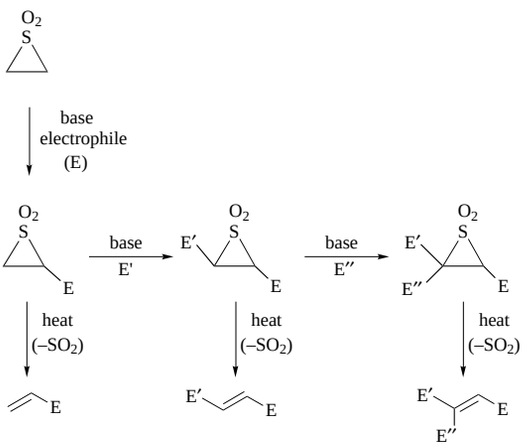
Results and discussion

We were intrigued by the possibility of carrying out substitutions of episulfones *via* their derived α-sulfonyl carbanions, since this should lead to useful substituted alkenes following thermal, stereospecific SO_2 extrusion, and would constitute a new approach to unsaturated products, *e.g.* Scheme 1.

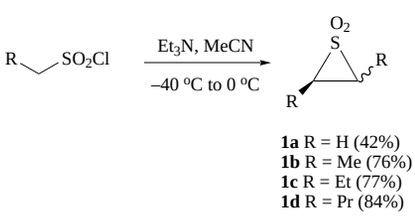
Thus, in principle, a simple episulfone might undergo sequential substitution to give a range of substituted episulfones (which in turn would furnish the corresponding alkenes) provided that both the regio- and stereo-chemistry could be controlled. The only precedent to indicate that such episulfone substitution might be possible is the observation that, in the presence of D_2O, base-mediated desulfonylation of certain episulfones, particularly 2,3-diphenylepisulfone (stilbene episulfone), occurs with deuterium incorporation, implicating an intermediate episulfone-derived carbanion.[7]

Preparation of starting episulfones

Initially, we prepared a range of simple, symmetrically-substituted episulfones **1a–d** by the method of Opitz, involving treatment of alkanesulfonyl chlorides with Et_3N in MeCN.[1a,b] Products **1b–d** were obtained as mixtures of *cis*- and *trans*-isomers, mostly in the form of colourless oils, which can be stored under refrigeration, Scheme 2. It proved possible to separate the stereoisomeric mixtures by flash chromatography, enabling isolation of samples of pure *cis*- and *trans*-isomers, although in much of the work described below mixtures of stereoisomeric episulfones were employed. Stilbene episulfone, available by this method, proved much more unstable than the aliphatic episulfones, and was not used in the subsequent work.[8]



Scheme 1

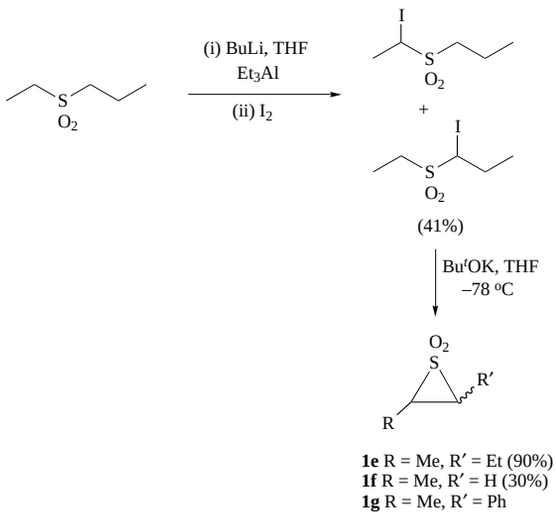


1a R = H (42%)
1b R = Me (76%)
1c R = Et (77%)
1d R = Pr (84%)

Scheme 2

Although most of our studies utilised simple episulfones **1a–d**, we also sought unsymmetrically substituted systems, which would be of interest in addressing aspects of regioselectivity in subsequent reactions. Established routes to such compounds

include the reaction of diazoalkanes with sulfenes (generated *in situ* from the appropriate alkanesulfonyl halides as indicated in Scheme 2),[1] or the modified Ramberg–Bäcklund protocol introduced by Taylor's group.[3] In our hands, the former type of reaction, employing either diazomethane or trimethylsilyldiazomethane, proved fruitless, whilst the success of the latter procedure appears highly substrate-dependent. Thus, metallation of ethyl propyl sulfone, reaction with iodine and base treatment of the resulting mixture of α-iodo sulfones gave the desired methyl ethyl episulfone **1e** in 37% overall yield, Scheme 3.[9]



Scheme 3

Unfortunately, application of this synthetic sequence to sulfones which would lead to episulfones with a more clearly defined regiochemical bias, such as **1f** and **1g**, gave very low yields, and was not pursued further.

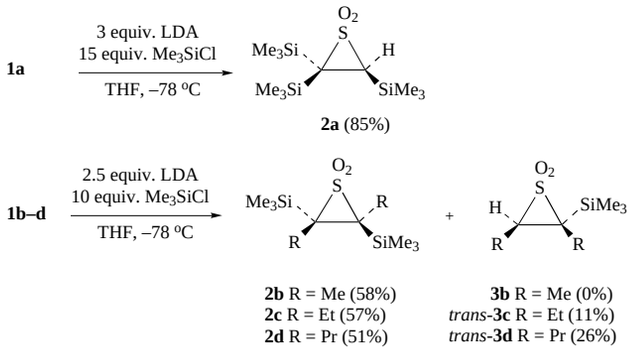
Episulfone silylation using LDA–Me_3SiCl

Treatment of episulfones **1** with a range of bases, including lithium diisopropylamide (LDA) and various alkyllithiums, in THF at low temperature, followed by quenching with typical electrophiles, such as Me_3SiCl or PhCHO, proved unrewarding. Although these conventional, external quench (EQ) type of reactions did not furnish the desired substituted episulfones, we were to find later that useful transformation of episulfones into vinyl sulfinate salts was possible this way (see below).

Since it quickly became clear that the difficulty in obtaining substituted episulfones from the EQ reactions was associated with the instability of the intermediate α-sulfonyl carbanion, we next turned to *in situ* quench (ISQ) reactions using Me_3SiCl as the electrophile.[10] Pleasingly, reaction of each of the episulfones **1a–d** with an excess of LDA in the presence of Me_3SiCl resulted in clean conversion into the silylated episulfone products shown, Scheme 4.

The parent episulfone **1a** is an exceptional case, being efficiently converted into the trisilylated episulfone **2a** on treatment with 3 equiv. of LDA in the presence of a good excess of Me_3SiCl. Efforts to introduce fewer silicon groups, by using less base, resulted in the formation of rather complex mixtures, whilst we also failed to prepare the fully silylated episulfone by use of more base or by exposing **2a** to LDA–Me_3SiCl. The vicinally-disubstituted episulfones **1b–d** behaved similarly on exposure to mixtures of LDA–Me_3SiCl, each producing only one stereoisomeric disilylated episulfone **2b–d** together with minor amounts of monosilylated products **3c** and **3d** (no **3b** was obtained under these conditions, *vide infra*).

The *trans*-stereochemistry was assigned to the disilylated episulfones **2b–d**, since the highly selective formation of a *cis*-bis(trimethylsilyl)episulfone appeared unreasonable on steric



Scheme 4

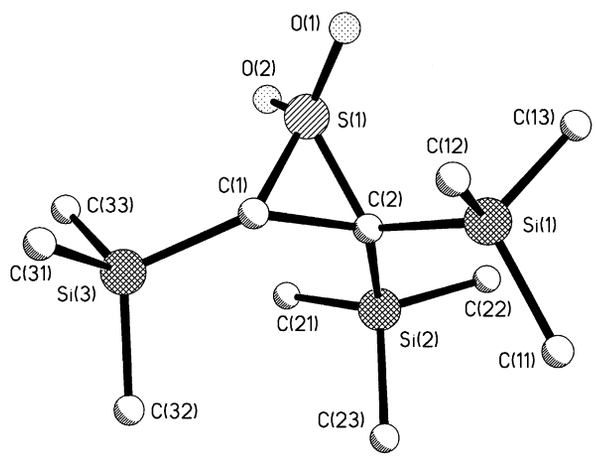


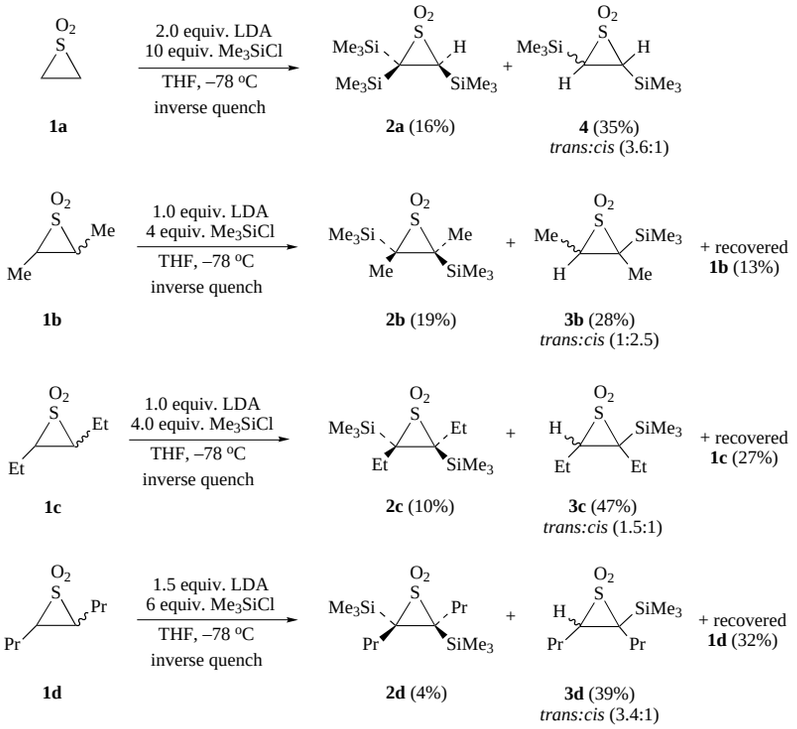
Fig. 1 X-Ray structure of episulfone **2a**

grounds. This assignment appeared even more incontestable following the finding that individual isomers of starting episulfone **1b** both gave the same disilylated product. This result indicated that rapid equilibration of the intermediate stereoisomeric α-sulfonyl carbanions must be taking place, even over the lifetime allowed by the powerful *in situ* electrophilic quench.

The crystalline trisilylated episulfone **2a** proved stable enough for an X-ray structure determination, shown in Fig. 1. This fully confirmed the structure anticipated for this remarkable product, and revealed some notable features, such as the long C–C bond length of 1.678(3) Å present in the three-membered ring, which is in accord with related structures described by other groups.[6]

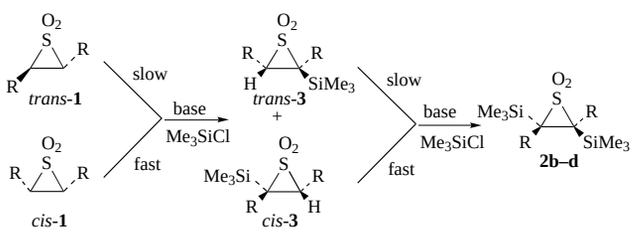
Interestingly, the monosilylated episulfones **3c** and **3d** were obtained as single stereoisomers, the *trans*-stereochemistry shown being assigned following conversion into the corresponding vinylsilane products, obtained after thermal extrusion of SO_2. Since unsymmetrically-substituted episulfones such as **3** were attractive, because of the possibility of further regioselective substitution, we attempted to increase the yield of such products by conducting silylation reactions with fewer equivalents of LDA, and also by using an inverse quench procedure, whereby LDA was added to a mixture of starting episulfone and Me_3SiCl, *e.g.* Scheme 5. Employing this method allowed the isolation of the disilylated derivative **4**, which had not been observed in earlier reactions of the parent episulfone **1a**. Also, it was possible to obtain the monosilylated derivative **3b** for the first time, albeit in a modest 28% yield, and to achieve increased yields of monosilylated episulfones **3c** and **3d**.

For starting episulfones **1b–d**, the inverse quench reactions provided increased yields of monosilylated derivatives **3**, compared to the standard ISQ conditions, but compounds prepared by this method were isolated as stereoisomeric mixtures. This contrasted with the earlier ISQ reactions which had provided products **3** as single diastereoisomers, assigned the *trans*-



Scheme 5

stereochemistry. We have ascribed this result to a kind of kinetic resolution effect, whereby compounds **3** are initially formed as a mixture of diastereoisomers, but the second deprotonation–silylation consumes the *cis*-isomer more rapidly than the *trans*-isomer, leaving the latter compound as the eventual observed product, Scheme 6. This effect presumably also



Scheme 6

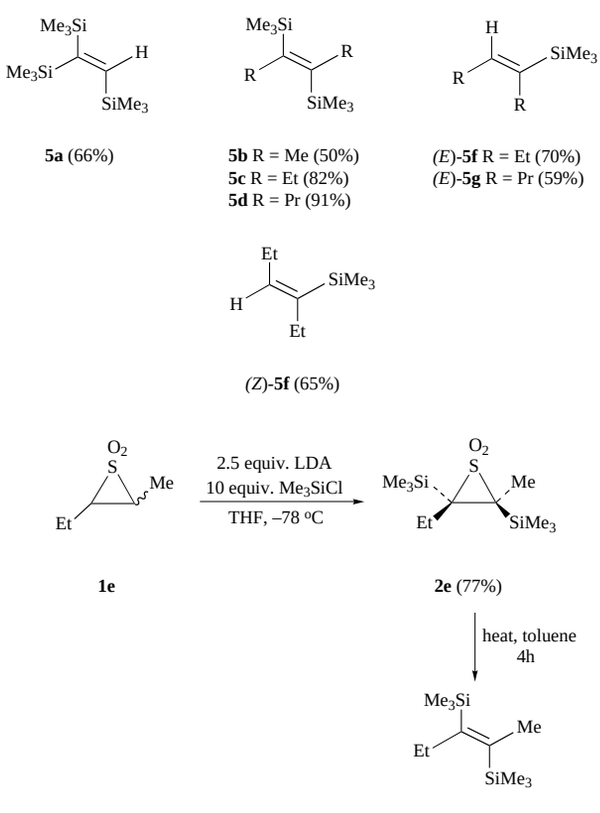
accounted for the fact that the small amounts of starting episulfone **1** (initially a mixture of stereoisomers) recovered from the silylation reactions were often enriched in the *trans*-isomer. In both the reactions of **1** and of **3**, the LDA base must react more rapidly with the stereoisomer in which one face of the episulfone is sterically more accessible, this being the face opposite to the alkyl substituents in *cis*-**1**, and the face opposite to the bulky $SiMe_3$ group in *cis*-**3**.

Synthesis of silylated alkenes by thermal extrusion of SO_2

Although the silylated episulfone products obtained using the LDA–Me_3SiCl procedure proved quite stable, and could be subjected to flash column chromatography without serious loss, they were, as expected, converted cleanly into the corresponding alkenes **5** following brief thermolysis in toluene at reflux.

As expected, stereoisomerically pure episulfones furnished a single alkene product, whilst mixtures of isomeric episulfones gave products having similar isomeric ratios. At this point it became possible to assign the stereochemistry of the monosilylated alkenes **5f**–**g** (and therefore the episulfone precursors) as indicated, based on assignments made previously.[11]

In addition, we examined the silylation–SO_2 extrusion chemistry of the unsymmetrical episulfone **1e**, but were unable to achieve any regioselectivity in the substitution reactions. However, this episulfone underwent the same stereoselective double silylation reaction, to give **2e**, followed by conversion to the corresponding vinyl disilane **5e**, as was observed with the symmetrical systems **1b**–**d**, Scheme 7.



Scheme 7

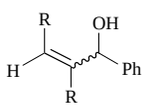
The episulfone silylation–SO_2 extrusion protocol can be seen to enable a short access to certain types of vinyl silane, bissilane, and the tris-silane **5a**, in good overall yield.

Fluoride-mediated substitution of silylated episulfones

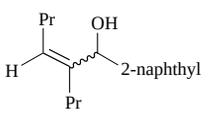
Naturally, we were very interested in the prospect of introducing substituents other than silicon into the episulfones, which would ultimately allow the synthesis of other types of alkenyl products. Since we had available a range of silylated episulfones, we first examined the possible conversion of such compounds into carbon-substituted derivatives, by reaction with electrophiles in the presence of fluoride. This approach was prompted by a report by Fuchs and co-workers,[12] which described the use of CsF in benzene in the presence of 18-crown-6 to enable reaction of α-silylated sulfones with certain electrophiles such as aromatic aldehydes. We examined various modifications of this method, and initially found that reaction of episulfones **3b–d** with excess CsF in THF in the presence of 18-crown-6 and PhCHO allowed the preparation of the allylic alcohols **6b–d** in moderate yield.

Mixtures of stereoisomeric starting materials were used in all cases, giving directly the allylic alcohols as (*E*):(*Z*)-mixtures, in which the (*Z*)-isomer predominated, with no trace of the corresponding hydroxyalkyl-substituted episulfones, which are the presumed intermediates.

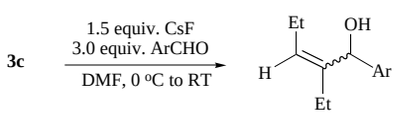
Subsequently, we preferred a slightly different procedure, involving reaction of the silylated episulfone with CsF in DMF, based on a method utilised for elimination from a silylated aziridine.[13] This method allowed the use of lesser amounts of CsF, and avoided the use of 18-crown-6. The method was used for the conversion of **3d** into allylic alcohol **6e**, and for the reaction of **3c** with a range of aromatic aldehydes to give allylic alcohols, including **6c** and **6f–h**, Scheme 8.[14] In every case the



6b R = Me (41%) (*Z*):(*E*) (3:1)
6c R = Et (62%) (*Z*):(*E*) (5:1)
6d R = Pr (40%) (*Z*):(*E*) (1.2:1)



6e (54%) (*Z*):(*E*) (2.2:1)



6c, f–h

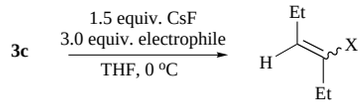
6c Ar = Ph (63%) (*Z*):(*E*) (3.4:1)
6f Ar = 1-naphthyl (59%) (*Z*):(*E*) (4.8:1)
6g Ar = 2-naphthyl (54%) (*Z*):(*E*) (6.0:1)
6h Ar = 2-furyl (43%) (*Z*):(*E*) (1.3:1)

Scheme 8

starting episulfone was used as a mixture of stereoisomers, furnishing the products as (*E*):(*Z*) mixtures in which the (*Z*)-isomer (in which the alkyl groups R are *trans*-disposed) predominated (ratios ranging from 1.3:1 to 6:1). In these products the stereochemistry was unambiguously assigned following NOE experiments. For example, irradiation of the signal corresponding to the benzylic methine proton in **6c** and **6d** resulted in enhancement of the signal corresponding to the vinylic signal in the minor (*E*)-isomer only, showing in these isomers a *syn* disposition of C*H*(OH)Ph and C=C*H* groups.

Although we were confident that this substitution process involves a nucleophilic episulfone intermediate, we eliminated an alternative possibility, involving a fluoride-mediated substitution of a vinyl silane intermediate, by showing that vinylsilanes **5** did not give allylic alcohol products on mixing with CsF and aromatic aldehydes under our typical reaction conditions.

We also found that a limited range of other electrophiles could be employed in this type of reaction (using the CsF–THF–18-crown-6 method) including $PhCOCF_3$, $PhSO_2F$, PhCOF, Ph_2Se_2 and Ph_2S_2, Scheme 9. The substituted alkenyl



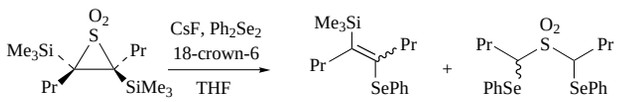
7a–e

7a X = C(OH)CF_3Ph (35%) (*Z*):(*E*) (2.8:1)
7b X = SO_2Ph (25%) (*Z*):(*E*) (1:1.6)
7c X = COPh (40%) (*Z*):(*E*) (6:1)
7d X = SePh (43%) (5.6:1)
7e X = SPh (40%) (1:1)

Scheme 9

products **7a–e** were isolated in modest yields and as mixtures of stereoisomers. The stereochemical assignments shown are tentative, and have been made by analogy with literature compounds.[15] In no case were we able to observe intermediate episulfones, even when the reactions with Ph_2Se_2 and Ph_2S_2, were started at low temperature and monitored closely by TLC.

Attempts to extend the application of the fluoride-mediated substitution methods to reactions involving *disilylated* episulfone starting materials gave less satisfactory results. For example, reaction of *trans*-**2d** with CsF, 18-crown-6 and PhSeSePh resulted in the formation of alkene **8** and the α,α′-bisphenylseleno sulfone **9** in low yields, Scheme 10. The latter



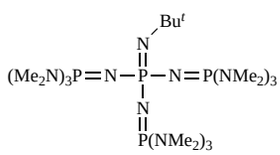
2d **8** (14%) (1.5:1) **9** (16%) (1.3:1)

Scheme 10

compound presumably arises by an initial replacement of one silicon group by a PhSe group, followed by nucleophilic attack of the released $PhSe^-$ on the intermediate episulfone, and finally loss of the remaining silicon substitutent. This mode of episulfone cleavage has been observed previously in reactions of stilbene episulfones with reducing agents.[16]

Substitution of episulfones using a phosphazene base

In searching for basic conditions which would extend the repertoire of substitution chemistry available to episulfones, we briefly examined the use of Schwesinger's Bu^t–P_4 phosphazene base **10**.[17] This base can be used in the presence of certain



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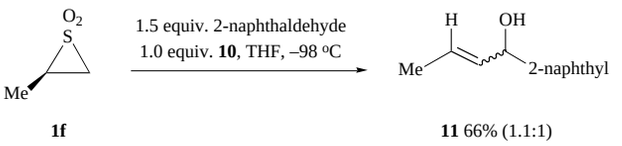
electrophiles, including PhCHO and some alkyl halides, and has been utilised in enolate alkylation reactions in which conventional lithium amide bases proved ineffectual.[18]

We quickly established that addition of a solution of **10** to a mixture of either **1c** or **1d** and benzaldehyde, at −98 °C in THF, gave the allylic alcohols **6c** and **6d**, identical to those prepared by the fluoride-mediated reaction. If the starting episulfones were used as stereoisomeric mixtures, or as single *cis*-isomers, then the allylic alcohols were obtained as (*E*):(*Z*) mixtures with little or no selectivity. However, we were pleased to find that the use of *trans*-episulfones in such phosphazene base subsitution reactions led to the formation of allylic alcohols with very good selectivity. For example, reaction of *trans*-**1c** with benzaldehyde gave **6c** in 76% yield with an (*E*):(*Z*) ratio of 1:28, and reaction with 2-naphthaldehyde gave **6g** in 71% yield with an (*E*):(*Z*) ratio of 1:25.

A single reaction was tried with the mono-substituted episulfone **1f**, involving reaction with 2-naphthaldehyde, which gave the product of deprotonation at the unsubstituted position on the ring, **11**, as the only observed product, as *ca.* 1:1 mixture of stereoisomers, Scheme 11.

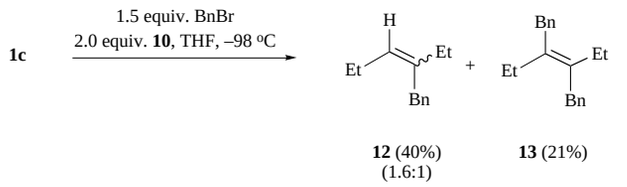


1f **11** 66% (1.1:1)

Scheme 11

These are promising results, indicating that *trans*-disubstituted episulfones can be substituted with good stereocontrol, and that good regiocontrol in substitution of mono-substituted episulfones seems likely.

Unfortunately, reactions involving other types of electrophile appeared less promising. For example, alkylation of **1c** with benzyl bromide gave a mixture of alkene products **12** and **13**, Scheme 12. Such alkylations contrast with the reactions involv-



12 (40%) (1.6:1) **13** (21%)

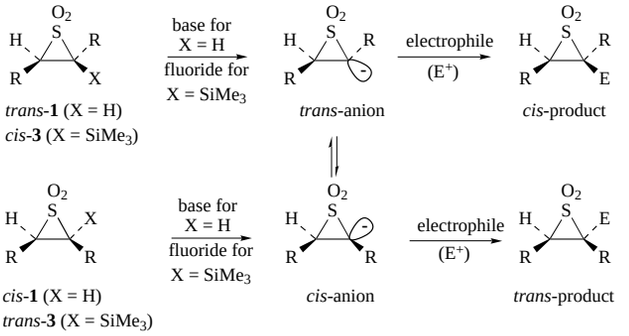
Scheme 12

ing aromatic aldehydes in that double alkylation is observed. This implies that a monobenzylated episulfone survives long enough for a second substitution reaction to occur, indeed on several occasions we were able to observe presumed substituted episulfone intermediates by TLC, although these could not be isolated.

Stereochemical aspects of episulfone substitution

The selectivities observed in the formation of silylated episulfones under the LDA–Me_3SiCl (ISQ) conditions can be understood by invoking a configurationally unstable intermediate episulfone α-sulfonyl carbanion, which gives monosilylated products **3** as stereoisomeric mixtures (Scheme 5). The formation of disilylated products **2** as single stereoisomers (Scheme 4) is presumably dictated by the severe steric interactions which would result from the formation of the alternative isomers having a *cis*-disposition of trimethylsilyl groups.

The stereoselective formation of monosilylated products as minor components in reactions involving 2.5 equiv. of LDA, *i.e.* **3c** and **3d** in Scheme 4, can be attributed to kinetically controlled isomer separations, as indicated in Scheme 6. The fluoride-mediated substitutions of the monosilylated episulfones were tested mainly on *cis*:*trans* mixtures, with aromatic aldehydes as the electrophiles, resulting in the formation of allylic alcohols with poor selectivity favouring the (*Z*)-isomer (usually *ca.* 2:1). Even when single isomers were employed in this type of reaction, a similar lack of selectivity was observed. These results indicate a lack of stereocontrol in the carbonyl addition reactions of the intermediate, configurationally unstable, α-sulfonyl carbanions, generated under these conditions, Scheme 13. Since single isomers of starting material give products **6** as (*E*):(*Z*) mixtures the presumed α-sulfonyl carbanion is configurationally unstable even during the short lifetime available in the presence of an excess of aromatic aldehyde. The stereochemical results with some of the other electrophiles (*i.e.* leading to **7a**–**e**) are probably not worth detailed consideration since the chemical yields and selectivities were often low. In the case of phosphazene base-mediated substitution the equi-



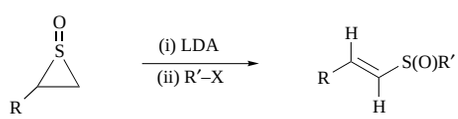
Scheme 13

libration between the intermediate metallated episulfones (Scheme 13) is again apparent since starting with *cis*-**1** leads to mixtures of stereoisomeric periods.

Presumably, partial equilibration towards the more energetically favourable *trans*-anion is observed, leading to a predominance of (*Z*)-product in most cases. In the case of the highly selective reactions, involving *trans*-**1** as the starting materials, the good (*Z*)-selectivity presumably reflects the higher stability of the *trans*-anion intermediate over the corresponding *cis*-anion. Unfortunately, when starting with mixtures of isomers, the necessity for an *in situ* quench does not allow anion equilibration to take place to an extent that leads to high isomer ratios in the products.

Base-mediated conversion of episulfones into alkenyl sulfones

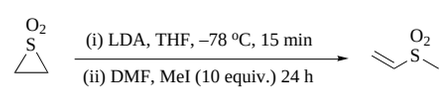
We were prompted to re-examine the reactions of episulfones with strong bases, in the absence of an ISQ, on examining reports from the group of Schwan concerning the conversion of episulfoxides into alkenyl sulfoxides, *e.g.* Scheme 14.[19,20] This



Scheme 14

reaction proceeds *via* initial deprotonation to form an intermediate episulfoxide carbanion, which then undergoes a ring-opening rearrangement to give an alkenylsulfenic acid salt, which is alkylated on sulfur with an appropriate alkyl halide to give the observed alkenyl sulfoxide product. Although a few earlier reports give some indication that the analogous transformation of episulfones could also be achieved, this process had not been described in any detail.[21,22]

Our preliminary experiments quickly established that reaction of an episulfone with LDA in THF, followed by addition of MeI, indeed results in the formation of the anticipated alkenyl sulfone product, but in very low yields. Since the high-yielding alkylation of sulfinate salts is known to require the use of solvents such as DMSO, or the generation of the corresponding tetraalkylammonium sulfinates,[23] we decided that the poor yields that we observed were due to the failure of the alkylation step in the THF solvent. By addition of an equivalent volume of DMF to the THF solution resulting from the LDA-mediated ring-opening of parent episulfone **1a**, and by employing a large excess of methyl iodide (4–10 equiv.), we were able to improve the yield of alkenyl sulfone product **14** to 41%, Scheme 15.



1a **14** (41%)

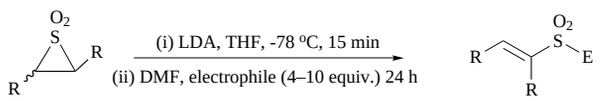
Scheme 15

Table 1 Preparation of vinyl sulfones **15**[a] by reaction of episulfones **1** with alkyl halides

	Alkyl halide			
Episulfone	MeI	$PhCH_2Br$	$H_2C{=}CHCH_2Br$	$ClCH_2CO_2Et$
1b (R = Me)	**15a** (40)	**15b** (62)	**15c** (47)	**15d** (41)
1c (R = Et)	**15e** (56)	**15f** (51)	**15g** (65)	**15h** (68)

[a] Yields given in parentheses.

Presumably, our very earliest attempts at episulfone substitution had resulted in conversion of the episulfones into vinylsulfinate salts, but these had not been isolated. By following the above procedure we were able to convert either **1b** or **1c** into vinyl sulfone products **15** in quite respectable yields, Scheme 16 and Table 1.



1b R = Me
1c R = Et

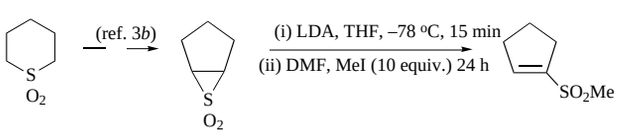
15a–h
(*E*):(*Z*) ≥ 20:1

Scheme 16

Notably, the vinyl sulfone products **15** are formed in highly stereoselective fashion, irrespective of the stereochemistry of the starting episulfone, the thermodynamically favoured (*E*)-isomer predominating in every case. The (*E*):(*Z*) ratio of 20:1 indicated in Scheme 16 represents the lowest levels of selectivity seen, indeed, in several cases we were unable to unequivocally identify any of the minor alkenyl sulfone isomer, although some of the ^{1}H NMR spectra of the crude products showed minor contaminants, including very small amounts of *O*-alkylated product (*i.e.* sulfinate ester).

We also tried to apply the new method to trisubstituted episulfones, in particular, substrates such as **3c** and **3d**, bearing a silicon substituent, but these compounds gave disappointingly low yields of vinyl sulfone products, accompanied by sulfinate ester by-products.

Finally, we were able to apply the rearrangement to the bicyclic episulfone **16**, the methyl sulfone **17** being isolated in modest yield, Scheme 17. This new method should prove a useful route to certain types of vinyl sulfone, since it proceeds straightforwardly, in two steps, from commercially available alkanesulfonyl chlorides.



16

17 (28%)

Scheme 17

Conclusion

The carbanion chemistry of episulfones has been examined in detail for the first time. Substitution of episulfones, *via* intermediate α-sulfonyl carbanions, does not appear to be possible unless an ISQ procedure is adopted, the two such methods we have developed involving either lithium amide or phosphazene bases. The scope and limitations of these methods have been defined using a small number of episulfone substrates. It remains to be seen if the chemistry can be made more general and more accessible, by the development of improved routes to episulfone starting materials.

It is clear that under ISQ conditions, episulfone substitution can compete with alternative reaction modes, such as desulfonylation and ring-opening. However, this latter type of process can also be employed to provide a useful new route to vinyl sulfones.

Experimental

Melting points were determined using a Reichert Microscope apparatus and are uncorrected. Solvents were purified using standard techniques before use. Phosphazene Bu^t–P_4 was purchased from Fluka Chemicals and was used without purification. Analytical TLC was performed on Merck precoated silica gel F_{254} glass-backed plates. Flash column chromatography was carried out under slight positive pressure using Merck Kieselgel 60 (230–400 mesh). Microanalyses were performed in the University of Nottingham microanalytical laboratory using a Perkin-Elmer 240B elemental analyser. Infrared spectra were recorded on a Perkin-Elmer 1720 FTIR machine. NMR spectra were recorded on a Bruker WP250, JEOL FX270 or Bruker AM400 machine with Me_4Si as internal standard. *J* Values are recorded in Hz and multiplicities indicated for ^{13}C NMR were obtained using a DEPT sequence. Mass spectra were obtained using an AE1 902 or VG micromass 70E spectrometer. Light petroleum refers to the fraction with bp 40–60 °C.

Crystallographic data for episulfone 2a

A large crystal, selected to offset the expected decay due to irradiation, was mounted on a glass fibre and transferred to the diffractometer.

Crystal data. $C_{11}H_{28}O_2SSi_3$, $M = 308.7$. Monoclinic, $a = 6.5954(9)$, $b = 17.476(3)$, $c = 16.015(4)$ Å, $\beta = 101.68(2)°$, $V = 1808$ Å^3 (by least squares refinement on the diffractometer angles for 25 automatically centred reflections, $\lambda = 1.541\,84$ Å), space group $P2_1/n$ (alt. $P2_1/c$, No. 14), $Z = 4$, $D_x = 1.130$ g cm^{-3}, colourless tablet, 1.00 × 0.75 × 0.5 mm, μ(Cu-Kα) = 3.452 mm^{-1}.

Data collection and processing. Enraf-Nonius CAD4 diffractometer, ω–2θ scans, graphite monochromated Cu-Kα X-radiation; 4306 reflections measured (θ_{max} 72°, $-8 \le h \le 8$, $-1 \le k \le 21$, $-1 \le l \le 18$), of which 3547 were unique [merging $R = 0.108$ after correcting for absorption using Ψ scans] and 2779 with $F_o \ge 4\sigma(F_o)$ were used in all calculations. A correction for linear isotropic decay (17%) was applied as part of the data collection procedure.

Structure solution and refinement. Automatic direct methods and Fourier synthesis (all non-H atoms). Full-matrix least-squares refinement with all non-H atoms anisotropic. (At isotropic convergence a final correction for absorption was applied empirically [24]). The hydrogen atoms were initially placed in calculated positions and thereafter allowed to ride on their parent carbon atoms with C–H = 0.96 Å and $U_{iso}(H) = xU_{eq}(C)$, where $x = 1.2$ for the H atom on C(1) and 1.5 for the methyl H atoms. A three-term Chebyshev weighting scheme [25] was applied and gave satisfactory agreement analyses. At convergence, $R = 0.0524$, $R_w = 0.0605$, goodness-of-fit = 1.05 for 154 refined parameters (R indices are defined in Ref. 26). The final difference Fourier synthesis showed no feature above 0.42 or below −0.34 e Å^{-3}. All calculations were performed using the CRYSTALS [26] program package. Fractional atomic coordinates, thermal parameters, bond lengths and bond angles have all been deposited with the Cambridge Crystallographic Data Centre (CCDC). See 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 207/69.

Episulfone 1a [1a]

A stirred solution of methanesulfonyl chloride (1.00 ml, 12.9 mmol) in THF (100 ml) at −40 °C under a nitrogen atmosphere was treated dropwise with NEt_3 (5.4 ml, 38.7 mmol). The resulting white suspension was stirred for 1 h before addition of light petroleum (150 ml), then filtered under vacuum to remove the

NEt_3·HCl. The filtrate was evaporated at room temperature to give a crude brown oil which was washed with diethyl ether (3 × 100 ml). The organic extracts were combined and evaporated to give a yellow oil (1.131 g). Flash column chromatography (30% CH_2Cl_2 in light petroleum) yielded episulfone **1a** (250 mg, 42%) as a colourless oil, ν_{max}(film)/cm^{-1} 3852, 3626, 3426, 3103, 3006, 1310, 1181, 1768 and 1630; δ_H(250 MHz; $CDCl_3$) 3.13 (4 H, s, 2 × CH_2); δ_C(68 MHz; $CDCl_3$) 31.43 (CH_2).

Typical procedure for preparation of episulfones 1b–d[1a]

A solution of ethanesulfonyl chloride (2.90 ml, 30.6 mmol) in acetonitrile (200 ml) at −40 °C under a nitrogen atmosphere, was treated dropwise with NEt_3 (6.40 ml, 45.9 mmol) and the resulting white suspension was stirred for 4 h. The mixture was then warmed to room temperature and filtered under reduced pressure to remove the NEt_3·HCl. The filtrate was evaporated at room temperature to give an orange oil–solid mixture. This residue was washed with Et_2O (3 × 100 ml) and the extracts were combined and evaporated at room temperature to yield 2,3-dimethylthiirane 1,1-dioxide **1b** as a 1.2:1 *cis*:*trans* mixture as a mobile oil (1.403 g, 76%). In this case **1b** could be used without the need for further purification, although samples of pure *cis* and *trans* isomers could be obtained by flash column chromatography if desired; ν_{max}(film)/cm^{-1} 2984, 2935, 1453, 1306, 1161, 1106 and 1037; δ_H(400 MHz; $CDCl_3$) *cis*: 1.45 (6 H, d, *J* 6.4, 2 × CH_3) and 3.36 (2 H, m, 2-H and 3-H); *trans*: 1.61 (6 H, d, *J* 6.4, 2 × CH_3) and 2.80 (2 H, m, 2-H and 3-H); δ_C(68 MHz; $CDCl_3$) *cis*: 6.81 (CH_3) and 42.30 (CH, C-2 and C-3); *trans*: 12.10 (CH_3) and 46.90 (CH, C-2 and C-3); *m/z* (EI) 97 (47%), 85 (48), 83 (53), 71 (67) and 57 ($M^+ - SO_2$, 100).

Following the above general procedure, and after purification by flash column chromatography (15% ethyl acetate in light petroleum) was obtained 2,3-diethylthiirane 1,1-dioxide **1c** (2.201 g, 77%) as a 1:2.2 *cis*:*trans* mixture as a mobile oil. Samples of pure *cis* and *trans* isomers could be obtained by flash column chromatography if desired; ν_{max}(film)/cm^{-1} 2970, 2937, 2878, 1461, 1346, 1303 and 1164; δ_H(250 MHz; $CDCl_3$) *cis*: 1.13 (6 H, t, *J* 7.2, 2 × CH_3), 1.75–2.08 (4 H, m, 2 × CH_2) and 3.28 (2 H, m, 2-H and 3-H); *trans*: 1.10 (6 H, t, *J* 7.3, 2 × CH_3), 1.77–2.12 (4 H, m, 2 × CH_2) and 2.75 (2 H, m, 2-H and 3-H); δ_C(68 MHz; $CDCl_3$) *cis*: 13.25 (CH_3), 16.66 (CH_2) and 49.54 (CH, C-2 and C-3); *trans*: 12.08 (CH_3), 21.44 (CH_2) and 52.58 (CH, C-2 and C-3); *m/z* (EI) 149 (MH^+, 68%), 99 (100), 84 ($MH^+ - SO_2$, 44), 71 (66) and 43 (100).

Following the above general procedure, and after purification by flash column chromatography was obtained 2,3-dipropylthiirane 1,1-dioxide **1d** (2.566 g, 84%) as a 1:2.5 *cis*:*trans* mixture as a mobile oil. In this case **1d** could be used without further purification, but samples of pure *cis* and *trans* isomers could be obtained by flash column chromatography if desired; ν_{max}(film)/cm^{-1} 2962, 2874, 2736, 1458, 1301, 1242 and 1162; δ_H(250 MHz; $CDCl_3$) *cis*: 0.98 (6 H, t, *J* 7.3, 2 × CH_3), 1.39–1.58 (4 H, m, 2 × CH_2CH$_3$), 1.68–1.95 (4 H, m, 2 × SO_2CHCH_2) and 3.22–3.35 (2 H, m, 2-H and 3-H); *trans*: 0.93 (6 H, t, *J* 7.4, 2 × CH_3), 1.39–1.50 (4 H, m, 2 × CH_2CH$_3$), 1.81–1.88 (4 H, m, 2 × SO_2CHCH_2) and 2.72–2.76 (2 H, m, 2-H and 3-H); δ_C(68 MHz; $CDCl_3$) *cis*: 13.32 (CH_3), 21.93 (CH_2, CH_2CH_3), 25.02 (CH_2, CHCH_2) and 47.80 (CH, C-2 and C-3); *trans*: 13.08 (CH_3), 20.88 (CH_2, CH_2CH_3), 29.81 (CH_2, CHCH_2) and 51.02 (CH, C-2 and C-3); *m/z* (EI) 112 ($M^+ - SO_2$, 48%), 83 (37), 70 (59), 64 (59), 56 (58), 55 (100) and 41 (87).

2-Ethyl-3-methylthiirane 1,1-dioxide 1e

To a solution of ethyl propyl sulfone (4.51 g, 34 mmol) in THF (150 ml) at 0 °C was added BuLi (21.3 ml of a 1.6 M solution in hexanes, 34 mmol), the mixture stirred for 30 min and then treated with a solution of Et_3Al (37 ml of a 1 M solution in hexanes, 37 mmol). Solid iodine (9.4 g, 37 mmol) was then added and the mixture stirred for a further 30 min before quenching by addition of saturated aqueous $Na_2S_2O_3$ (130 ml). The organic product was extracted into CH_2Cl_2 (4 × 130 ml), the combined organic extract washed with water (100 ml) and dried ($MgSO_4$). Evaporation of the solvent under reduced pressure and flash column chromatography of the residue (20% ethyl acetate in light petroleum) gave the desired mixture of α-iodosulfones, predominantly α-iodoethyl propyl sulfone (3.67 g, 41%) mp 56–57 °C (Found: C, 22.84; H, 4.39; S, 12.26. $C_5H_{11}IO_2S$ requires C, 22.91; H, 4.23; S, 12.23%); ν_{max}(KBr)/cm^{-1} 2962, 2874, 1440, 1310, 1279 and 1130; δ_H(400 MHz; $CDCl_3$) 1.12 (3 H, t, *J* 7.5, CH_2CH_3), 1.92 (2 H, m, CH_2CH$_3$), 2.20 (3 H, d, *J* 7.0, CHICH_3), 3.19–3.36 (2 H, m, SO_2CH_2) and 4.88 (1 H, q, *J* 7.0, C*H*ICH$_3$); *m/z* (EI) 262 (M^+, 13%), 169 (13) and 155 (100).

A solution of the product iodo sulfone (0.861 g, 3.3 mmol) in THF (45 ml) at −78 °C was treated dropwise with a solution of Bu^{t}OK (3.8 ml of a 1.0 M solution in THF, 3.8 mmol). After 10 min the reaction was quenched by addition of water (30 ml) and the product extracted into CH_2Cl_2 (3 × 20 ml), the combined organic extracts washed with water (10 ml), dried ($MgSO_4$) and evaporated under reduced pressure to give episulfone **1e** (397 mg, 90%) which was used without further purification; ν_{max}(film)/cm^{-1} 2970, 1435, 1302 and 1162; δ_H(400 MHz; $CDCl_3$) *trans*: 1.09 (3 H, t, *J* 7.5, CH_2CH_3), 1.59 (3 H, d, *J* 6.5, CH_3), 1.85–2.05 (2 H, m, CH_2CH$_3$), 2.71 [1 H, q, 6.5, C*H*-(SO_2)CH$_3$] and 2.85 [1 H, m, C*H*(SO_2)CH$_2$CH$_3$]; *cis*: 1.08 (3 H, t, *J* 7.5, CH_2CH_3), 1.47 (3 H, d, *J* 6.5, CH_3), 1.73–1.99 (2 H, m, CH_2CH$_3$), 3.23 [1 H, ddd, *J* 6.5, 9.0 and 11.0, C*H*(SO_2)-CH$_2$CH$_3$] and 3.39 [1 H, dq, *J* 6.5 and 11.0, C*H*(SO_2)CH$_3$]; δ_C(68 MHz; $CDCl_3$) *cis*: 6.87 (CH_3), 12.80 (CH_3), 16.19 (CH_2), 42.73 (CH) and 48.61 (CH); *trans*: 11.90 (CH_3), 12.64 (CH_3), 21.31 (CH_2), 46.24 (CH) and 53.21 (CH); *m/z* (EI) 70 ($C_5H_{10}^+$, 48%), 64 (37) and 55 (100).

2-Methylthiirane 1,1-dioxide 1f

This episulfone was prepared analogously to **1e** (30%), by treatment of chloromethyl ethyl sulfone with Bu^{t}OK in THF at −78 °C; ν_{max}(KBr)/cm^{-1} 1318, 1285 and 1165; δ_H(250 MHz; $CDCl_3$) 1.62 (3 H, d, *J* 6.5, CH_3), 2.60 (1 H, dd, *J* 6.5 and 7.5, C*H*H), 3.21 (1 H, dd, *J* 11 and 7.5, CH*H*) and 3.29–3.46 (1 H, m, C*H*CH$_3$); δ_C(68 MHz; $CDCl_3$) 12.83 (CH_3), 38.17 (CH_2) and 39.98 (CH).

2,2,3-Tris(trimethylsilyl)thiirane 1,1-dioxide 2a

A solution of episulfone **1a** (150 mg, 1.63 mmol) in THF (2 ml) was added dropwise to a stirred solution of LDA [generated from butyllithium (3.06 ml) of a 1.6 M solution in hexanes, 4.89 mmol] and diisopropylamine (0.68 ml, 4.89 mmol) and Me_3SiCl (3.10 ml, 24.43 mmol) in THF (20 ml) at −78 °C under a nitrogen atmosphere. After being stirred for 50 min the reaction was quenched at −78 °C with saturated aqueous NH_4Cl (150 ml) and the mixture was then washed with CH_2Cl_2 (2 × 100 ml). The organic phases were separated, dried ($MgSO_4$) and solvents removed under reduced pressure to yield episulfone **2a** (429 mg, 85%) as a colourless solid, which may be crystallised by dissolving in methanol and cooling to −20 °C, mp 69 °C (Found: C, 42.81; H, 9.29. $C_{11}H_{28}O_2SSi_3$ requires C, 42.81; H, 9.14%); ν_{max}($CHCl_3$ solution)/cm^{-1} 1411, 1281, 1249, 1149, 897 and 892; δ_H(250 MHz; $CDCl_3$) 0.32, 0.36 and 0.38 (3 × 9 H, s, $SiMe_3$) and 2.45 (1 H, s, CH); δ_C(68 MHz; $CDCl_3$) −0.21, 0.22 and 1.87 (3 × CH_3, $SiMe_3$), 38.80 (CH) and 40.43 (C); *m/z* (CI) 244 ($M^+ - SO_2$, 14%), 156 (46), 155 (40), 141 (30) and 73 (100) [Found (FAB): 326.1462. M + NH_4^+. $C_{11}H_{32}O_2NSi_2$ requires *M* + NH_4, 326.1462].

Typical procedure for silylation of episulfones 1b–e using LDA–Me_3SiCl

A solution of episulfone **1b** (365 mg, 3.04 mmol) in THF (1 ml) was added to a stirred solution of LDA (generated from butyllithium and diisopropylamine) (7.59 mmol) and Me_3SiCl (3.85 ml, 30.37 mmol) in THF (10 ml) at −78 °C under a nitrogen

atmosphere. After being stirred for 4 h, the reaction was quenched at −78 °C with saturated aqueous NH_4Cl (40 ml) and the mixture extracted with CH_2Cl_2 (2 × 60 ml). The organic phases were combined, dried ($MgSO_4$) and evaporated under reduced pressure to furnish a yellow oil–solid mixture (708 mg). Purification by flash column chromatography (10% ethyl acetate in light petroleum) yielded 2,3-dimethyl-2,3-bis(trimethylsilyl)thiirane 1,1-dioxide **2b** (469 mg, 58%) as a colourless solid, mp 71 °C; ν_{max}($CHCl_3$ solution)/cm^{-1} 2957, 1448, 1406, 1248, 1056, 1036 and 836; δ_H(250 MHz; $CDCl_3$) 0.26 (18 H, s, 2 × $SiMe_3$) and 1.66 (6 H, s, 2 × Me); δ_C(68 MHz; $CDCl_3$) 0.07 (CH_3, $SiMe_3$), 16.35 (CH_3, Me) and 48.43 (C, C-2 and C-3); *m/z* (EI) 200 ($M^+ - SO_2$, 63%), 185 (19), 127 (76), 97 (88) and 73 (100) [Found (FAB): 265.1107. M + H^+. $C_{10}H_{25}O_2SSi_2$ requires *M* + H, 265.1113].

Following the above general procedure, starting with episulfone **1c** (500 mg) and after flash column chromatography (5% then 10% ethyl acetate in light petroleum) was obtained firstly 2,3-diethyl-2,3-bis(trimethylsilyl)thiirane 1,1-dioxide **2c** (567 mg, 57%) as a colourless solid, mp 73 °C; ν_{max}($CHCl_3$ solution)/cm^{-1} 1319, 1250, 1175 and 850; δ_H(250 MHz; $CDCl_3$) 0.24 (18 H, s, 2 × $SiMe_3$), 0.96 (6 H, t, *J* 7.4, 2 × CH_3), 2.04 (2 × 1 H, dq, *J* 7.4 and 16.0, C*H*HCH$_3$) and 2.13 (2 × 1 H, dq, *J* 7.4 and 16.0, CH*H*CH$_3$); δ_C(68 MHz; $CDCl_3$) 1.19 (CH_3, $SiMe_3$), 12.92 (CH_3), 22.81 (CH_2) and 54.55 (C, C-2 and C-3); *m/z* (FAB) 585 (2 M + H^+, 9%), 365 (9), 315 (M + Na^+, 4), 293 (MH^+, 8), 228 ($M^+ - SO_2$, 100), 213 (26) and 140 (99), followed by 2,3-diethyl-2-trimethylsilylthiirane 1,1-dioxide **3c** (80 mg, 11%) as a colourless oil, ν_{max}(film)/cm^{-1} 2970, 1460, 1291, 1253, 1171, 1113, 1089 and 842; δ_H(250 MHz; $CDCl_3$) 0.26 (9 H, s, $SiMe_3$), 1.06 and 1.15 (3 H, t, *J* 7.1, 2 × CH_3), 1.82–2.17 (4 H, m, 2 × CH_2) and 2.94 (1 H, t, *J* 7.3, 3-H); δ_C(68 MHz; $CDCl_3$) −1.33 (CH_3, $SiMe_3$), 13.37 and 13.93 (2 × CH_3), 16.64 and 21.08 (2 × CH_2), 49.64 (C, C-2) and 50.66 (CH, C-3); *m/z* (EI) 156 ($M^+ - SO_2$, 4%), 141 (9), 83 (45) and 73 (100) [Found (EI) 156.1331. $M^+ - SO_2$. $C_9H_{20}Si_2$ requires $M - SO_2$, 156.1334].

Following the above general procedure, starting with episulfone **1d** (750 mg), and after flash column chromatography (5% then 10% ethyl acetate in light petroleum) was obtained firstly 2,3-dipropyl-2,3-bis(trimethylsilyl)thiirane 1,1-dioxide **2d** (690 mg, 51%) as a colourless solid, mp 99 °C (decomp.) (Found: C, 52.59; H, 10.41. $C_{14}H_{32}O_2SSi_2$ requires C, 52.44; H, 10.06%); ν_{max}(film)/cm^{-1} 3097, 3086, 1450, 1377, 1186 and 1081; δ_H(250 MHz; $CDCl_3$) 0.29 (18 H, s, $SiMe_3$), 0.94 (6 H, t, *J* 7.2, CH_3), 1.24–1.32 and 1.42–1.50 (2 × 2 H, m, CH_2CH$_3$), 1.81–1.88 and 1.99–2.07 (2 × 2 H, ddd, *J* 2.5, 4.2 and 14.5, SO_2CHCH_2); δ_C(68 MHz; $CDCl_3$) 1.15 (CH_3, $SiMe_3$), 13.88 (CH_3), 21.44 (CH_2, *C*H_2CH$_3$), 32.31 (CH_2, SO_2CHCH_2) and 53.70 (C, C-2 and C-3); *m/z* (FAB) 321 (MH^+, 6%), 305 (5), 256 ($M^+ - SO_2$, 100), 183 (48), 168 (46) and 125 (48) [Found (EI): M^+, 321.1740. $C_{14}H_{33}O_2SSi_2$ requires *M*, 321.1701], followed by 2,3-dipropyl-2-trimethylsilylthiirane 1,1-dioxide **3d** (270 mg, 26%) as a colourless oil, δ_H(250 MHz; $CDCl_3$) 0.26 (9 H, s, $SiMe_3$), 1.06 (2 × 3 H, t, *J* 7.0, 2 × CH_3), 1.20–2.00 (8 H, m, 4 × CH_2) and 2.95 (1 H, dd, *J* 6.3 and 8.3, SO_2CH); δ_C(68 MHz; $CDCl_3$) −1.33 (CH_3, $SiMe_3$), 13.41 and 14.20 (2 × CH_3), 21.98, 22.45, 24.80 and 29.83 (4 × CH_2), 48.91 (C, C-2) and 49.00 (CH, C-3); *m/z* (EI) 278 (7%), 264 (23), 250 (7) and 73 (100).

Following the above general procedure, starting with episulfone **1e** (276 mg), and after flash column chromatography (5% ethyl acetate in light petroleum) was obtained 2-ethyl-3-methyl-2,3-bis(trimethylsilyl)thiirane 1,1-dioxide **2e** (426 mg, 77%) as a colourless oil, ν_{max}(KBr)/cm^{-1} 2961, 1287, 1254, 1171 and 843; δ_H(250 MHz; $CDCl_3$) 0.29 (9 H, s, $SiMe_3$), 0.31 (9 H, s, $SiMe_3$), 1.06 (3 H, t, *J* 7.5, CH_2CH_3), 1.68 (3 H, s, CH_3) and 1.97–2.31 (2 H, m, CH_2CH$_3$); δ_C(68 MHz; $CDCl_3$) 0.00 (CH_3, $SiMe_3$), 1.94 (CH_3, $SiMe_3$), 12.83 (CH_3),16.86 (CH_3), 23.83 (CH_2), 48.21 (C) and 54.57 (C); *m/z* (EI) 214 (M − SO_2, 17%), 126 (60) and 73 (100).

***cis*- and *trans*-2,3-Bis(trimethylsilyl)thiirane 1,1-dioxide 4**

A solution of episulfone **1a** (266 mg, 2.89 mmol) and Me_3SiCl (3.66 ml, 28.88 mmol) in THF (15 ml) at −78 °C under a nitrogen atmosphere, was treated dropwise with LDA [generated from butyllithium (3.61 ml of a 1.6 M solution in hexanes, 5.78 mmol) and diisopropylamine (0.82 ml, 5.78 mmol)] in THF (5 ml). After stirring for 70 min, saturated aqueous sodium hydrogen carbonate (100 ml) was added to the yellow reaction mixture, and this was then poured onto water (50 ml) and extracted with CH_2Cl_2 (2 × 100 ml). The organic phases were combined, dried ($MgSO_4$) and evaporated under reduced pressure to yield a crude yellow oil (1.565 g). Flash column chromatography (10% ethyl acetate in light petroleum) yielded firstly trisilylated episulfone **2a** (145 mg, 16%), followed by *trans*-episulfone **4** (112 mg, 16%), and then a mixture of episulfones *trans*-**4**:*cis*-**4** in a 1.5:1 ratio (130 mg, 19%) as a colourless solid, mp 61 °C; ν_{max}($CHCl_3$ solution)/cm^{-1} 3120, 2450, 1540, 1430, 1200 and 1120; δ_H(250 MHz; $CDCl_3$) 0.17 (18 H, s, $SiMe_3$, *trans*), 0.28 (18 H, s, $SiMe_3$, *cis*), 2.35 (2 H, s, CH, *trans*) and 2.78 (2 H, s, CH, *cis*); δ_C(68 MHz; $CDCl_3$) −2.40 (CH_3, $SiMe_3$, *trans*), −0.55 (CH_3, $SiMe_3$, *cis*), 33.98 (CH, *trans*) and 36.43 (CH, *cis*); *m/z* (CI) 172 ($M^+ - SO_2$, 18%), 157 (63), 99 (20), 74 (23), 73 (100) (Found: M + NH_4^+, 254.1066. $C_8H_{24}O_2NSSi_2$ requires *M* + NH_4, 254.1066).

***cis*- and *trans*-2,3-Dimethyl-2-trimethylsilylthiirane 1,1-dioxide 3b**

A solution of episulfone **1b** (600 mg, 4.99 mmol) and Me_3SiCl (2.53 ml, 19.96 mmol) in THF (7 ml) under a nitrogen atmosphere, was treated with LDA [generated from butyllithium (0.32 ml, 4.99 mmol) and diisopropylamine (0.70 ml, 4.99 mmol)] in THF (7 ml). The reaction mixture was stirred for 4 h before addition of saturated aqueous NH_4Cl (15 ml). The mixture was poured onto CH_2Cl_2 (100 ml) and washed with water (100 ml). The organic phase was then separated, dried ($MgSO_4$) and evaporated under reduced pressure to yield a yellow oil (1.002 g). Flash column chromatography (5%, 10% then 20% ethyl acetate in light petroleum) yielded firstly disilylated episulfone **2b** (250 mg, 19%), followed by a 2.5:1 mixture of *cis*-**3b**:*trans*-**3b** (252 mg, 28%) as a colourless oil, ν_{max}(film)/cm^{-1} 2962, 2930, 2900, 2870, 1455, 1290, 1253, 1172, 1145, 1103, 1066, 1052 and 844; δ_H(250 MHz; $CDCl_3$) 0.20 (9 H, s, $SiMe_3$, *trans*), 0.26 (9 H, s, $SiMe_3$, *cis*), 1.42 (3 H, d, *J* 6.7, CHC*H*$_3$, *trans*), 1.45 (3 H, s, CH_3, *trans*), 1.58 (3 H, d, *J* 6.7, CHC*H*$_3$ *cis*), 1.63 (3 H, s, CH_3 *cis*), 2.75 (1 H, q, *J* 6.7, SO_2CH, *cis*) and 3.09 (1 H, q, *J* 6.7, SO_2CH, *trans*); δ_C(68 MHz; $CDCl_3$) −2.93 (CH_3, $SiMe_3$, *trans*), −0.88 (CH_3, $SiMe_3$, *cis*), 7.18 (CH_3, *trans*), 10.39 (CH_3, *trans*), 10.69 (CH_3, *cis*), 19.37 (CH_3, *cis*), 42.82 (C, C-2, *cis*), 42.88 (CH, C-3, *cis*), 46.50 (C, C-2, *trans*) and 51.04 (CH, C-3, *trans*); *m/z* (EI) 128 ($M^+ - SO_2$, 13%), 113 (54), 73 (100), 64 (13) and 59 (12). Finally, unreacted starting material **1b** was isolated (75 mg, 13%).

***cis*- and *trans*-2,3-Diethyl-2-trimethylsilylthiirane 1,1-dioxide 3c**

A solution of episulfone **1c** (200 mg, 1.35 mmol) and Me_3SiCl (0.69 ml, 5.40 mmol) in THF (5 ml) at −78 °C under a nitrogen atmosphere, was treated dropwise with LDA (generated from butyllithium and diisopropylamine) (1.35 mmol) in THF (5 ml) over approximately 15 s. The reaction was stirred at −78 °C for 2 h then saturated aqueous NH_4Cl (20 ml) was added and the mixture was allowed to warm to room temperature. The mixture was poured onto water (100 ml) and extracted with CH_2Cl_2 (100 ml). The organic phase was separated, dried ($MgSO_4$) and evaporated to yield a yellow oil (244 mg). Flash column chromatography (2% ethyl acetate in light petroleum) yielded firstly disilylated episulfone **2c** (75 mg, 10%) then a 1:1.5 mixture of *cis*-**3c**:*trans*-**3c** (140 mg, 47%) as a colourless oil; ν_{max}(film)/cm^{-1} 2968, 2878, 1461, 1292, 1252, 1170 and 1112; δ_H(250 MHz; $CDCl_3$) (for *cis*-**3c** only) 0.27 (9 H, s, $SiMe_3$), 1.08 and 1.10 (2 × 3 H, t, *J* 6.9, 2 × CH_3), 1.72–2.18 (4 H, m, 2 × CH_2)

and 2.66 (1 H, dd, *J* 6.8, 7.0, 3-H); δ_C(68 MHz; $CDCl_3$) (*cis* and *trans*) −1.38 and 0.27 (CH_3, $SiMe_3$), 10.47 (CH_3, C-5 or C-7, *trans*), 12.78 and 13.35 (2 × CH_3, C-5 or C-7, *cis*), 13.55 (CH_3, C-5 or C-7, *trans*), 16.05 (CH_2, C-4 or C-6, *cis*), 18.87 and 20.27 (2 × CH_2, C-4 or C-6, *trans*), 25.55 (CH_2, C-4 or C-6, *cis*), 48.82 (C, C-2, *cis*), 50.04 (CH, C-3, *cis*), 51.12 (C, C-2, *trans*) and 54.36 (CH, C-3, *trans*). Finally, starting material **1c** was isolated (53 mg, 27%).

cis- and *trans*-2,3-Dipropyl-2-trimethylsilylthiirane 1,1-dioxide 3d

A stirred solution of episulfone **1d** (870 mg, 4.94 mmol) and Me_3SiCl (3.76 ml, 29.66 mmol) in THF (10 ml) at −78 °C under a nitrogen atmosphere, was treated with a solution of LDA (generated from butyllithium and diisopropylamine) (7.41 mmol) in THF (10 ml) under a nitrogen atmosphere. After being stirred for 2 h, the reaction was quenched with saturated aqueous NH_4Cl (10 ml), poured into water (200 ml) and extracted with CH_2Cl_2 (200 ml). The organic phase was separated, dried ($MgSO_4$) and evaporated to give a yellow oil (2.011 g). Flash column chromatography (5% ethyl acetate in hexanes) yielded firstly the disilylated episulfone **2d** (40 mg, 4%), followed by the monosilylated episulfone **3d** (476 mg, 39%) as a 1:3.4 mixture of *cis*:*trans* isomers as a colourless oil, ν_{max}(film)/cm^{-1} 2960, 2870, 1291, 1252, 1169 and 1091; δ_H(250 MHz; $CDCl_3$) (for *cis*-**3d** only) 0.22 (9 H, s, $SiMe_3$), 0.94 (2 × 3 H, t, *J* 7.3, 2 × CH_3), 1.47 (8 H, m, 4 × CH_2) and 2.44 (1 H, dd, *J* 5.9 and 8.9, 3-H); δ_C(68 MHz; $CDCl_3$) (for *cis*-**3d** only) 0.00 (CH_3, $SiMe_3$), 13.28 and 14.08 (2 × CH_3), 21.85, 22.32, 24.69 and 29.72 (4 × CH_2), 47.96 (C, C-2) and 48.82 (CH, C-3). Finally, unreacted starting material **1d** was also isolated (238 mg, 32%).

General procedure for conversion of episulfones into vinylsilanes

A solution of the episulfone in a small volume of toluene (or in one case $CHCl_3$) was heated to reflux for 1–4.5 h and monitored by TLC (5–10% ethyl acetate in light petroleum). After being cooled to room temperature the solvent was evaporated under reduced pressure to give a yellow oil, which was purified either by flash column chromatography (pentane or light petroleum) or distillation (*ca.* 100 °C, 10 mmHg), which yielded the corresponding vinylsilanes as colourless mobile oils.

1,1,2-Tris(trimethylsilyl)ethene 5a.[11a] Following the above general procedure with episulfone **2a** (200 mg, 0.65 mmol), and heating in toluene (10 ml) for 4 h followed by flash column chromatography yielded the vinyl tris-silane **5a** (105 mg, 66%) (Found: C, 54.04; H, 11.95. $C_{11}H_{28}Si_3$ requires C, 54.02; H, 11.54%); ν_{max}(film)/cm^{-1} 2955, 2897, 1448, 1406, 1248 and 1036; δ_H(250 MHz; $CDCl_3$) 0.12, 0.89 and 0.91 (3 × 9 H, s, 3 × $SiMe_3$) and 7.37 (1 H, s, CH); δ_C(68 MHz; $CDCl_3$) 0.25, 0.90 and 2.02 (3 × CH_3, $SiMe_3$), 163.51 (CH) and 169.00 (C); *m/z* (EI) 244 (M^+, 15%), 156 (38) and 73 (100).

(*E*)-2,3-Bis(trimethylsilyl)but-2-ene 5b. Following the above general procedure with episulfone **2b** (2.66 g, 10 mmol), and heating in $CHCl_3$ for 2.5 h (40 ml) followed by distillation (115 °C at 3 mmHg) yielded the vinyl bis-silane **5b** (1.00 g, 50%), ν_{max}(film)/cm^{-1} 2954, 2897, 1448, 1406, 1370, 1248, 1073 and 1035; δ_H(250 MHz; $CDCl_3$) 0.13 (18 H, s, 2 × $SiMe_3$) and 1.81 (6 H, s, 2 × CH_3); δ_C(68 MHz; $CDCl_3$) 0.39 (CH_3, $SiMe_3$), 23.16 (CH_3) and 174.92 (C); *m/z* (EI) 200 (M^+, 7%), 182 (21), 149 (20), 105 (42) and 73 (100) (Found: M^+, 200.1418. $C_{10}H_{24}Si_2$ requires *M*, 200.1417).

(*E*)-3,4-Bis(trimethylsilyl)hex-3-ene 5c.[11b] Following the above general procedure with episulfone **2c** (87 mg, 0.30 mmol), and heating in toluene (6 ml) for 1.5 h, followed by flash column chromatography yielded the vinyl bis-silane **5c** (56 mg, 82%), ν_{max}(film)/cm^{-1} 2950, 1490, 1395 and 1270; δ_H(250 MHz; $CDCl_3$) 0.14 (18 H, s, 2 × $SiMe_3$), 0.93 (6 H, t, *J* 7.2, 2 × CH_3) and 1.60 (4 H, q, *J* 7.2, 2 × CH_2); δ_C(68 MHz; $CDCl_3$) 1.60 (CH_3, $SiMe_3$), 16.25 (CH_3), 30.21 (CH_2) and 155.04 (C); *m/z* (EI) 228 (M^+, 10%), 140 (23) and 73 (100) (Found: M^+, 228.1736. $C_{12}H_{28}Si_2$ requires *M*, 228.1730).

(*E*)-4,5-Bis(trimethylsilyl)oct-4-ene 5d. Following the above general procedure with episulfone **2d** (81 mg, 0.25 mmol), and heating in toluene (6 ml) for 1.5 h, followed by flash column chromatography yielded the vinyl bis-silane **5d** (59 mg, 91%), ν_{max}(film)/cm^{-1} 2956, 2898, 2872, 1260 and 1248; δ_H(250 MHz; $CDCl_3$) 0.14 (18 H, s, $SiMe_3$), 0.89 (6 H, t, *J* 7.1, 1-H), 1.19–1.34 (4 H, m, 2-H) and 2.11–2.18 (4 H, m, 3-H); δ_C(68 MHz; $CDCl_3$) 1.45 (CH_3, $SiMe_3$), 14.23 (CH_3, C-1), 25.10 (CH_2, C-2), 40.12 (CH_2, C-3), 153.90 (C, C-4); *m/z* (EI) 256 (M^+, 10%), 125 (15) and 73 (100) (Found: M^+, 256.2044. $C_{14}H_{32}Si_2$ requires *M*, 256.2043).

(*E*)-2,3-Bis(trimethylsilyl)pent-2-ene 5e. Following the above general procedure with episulfone **2e** (114 mg) and heating in toluene (1 ml) for 4 h, followed by bulb to bulb distillation (*ca.* 80 °C at 1 mmHg) yielded the vinylsilane **5e** as a colourless oil (58 mg, 68%), ν_{max}(KBr)/cm^{-1} 2962, 1248 and 836; δ_H(250 MHz; $CDCl_3$) 0.14 (9 H, s, $SiMe_3$), 0.17 (9 H, s, $SiMe_3$), 0.92 (3 H, t, *J* 7.5, CH_3), 1.87 (3 H, s, CH_3) and 2.24 (2 H, q, *J* 7.5, CH_2); δ_C(68 MHz; $CDCl_3$) 1.44 (CH_3, 2 × $SiMe_3$), 16.80 (CH_3), 23.85 (CH_3), 30.35 (CH_2), 147.98 (C) and 155.92 (C); *m/z* (EI) 214 (M^+, 18%), 141 (13), 126 (60) and 73 (100) (Found: M^+, 214.1581. $C_{11}H_{26}Si_2$ requires *M*, 214.1573).

(*E*)-3-(Trimethylsilyl)hex-3-ene 5f. Following the above general procedure with episulfone *trans*-**3c** (323 mg, 1.47 mmol), and heating in toluene (6 ml) for 1.5 h, followed by flash column chromatography yielded the vinyl silane (*E*)-**5f** (160 mg, 70%), ν_{max}(film)/cm^{-1} 2971, 2935, 2878, 2361, 1463, 1324, 1290, 1195, 1158, 1133 and 1051; δ_H(250 MHz; $CDCl_3$) 0.10 (9 H, s, $SiMe_3$), 0.91 and 0.98 (2 × 3 H, t, *J* 7.0, 2 × CH_3), 2.05–2.16 (4 H, m, 2 × CH_2) and 5.69 (1 H, t, *J* 7.0, 4-H); δ_C(68 MHz; $CDCl_3$) −1.26 (CH_3, $SiMe_3$), 14.17 and 14.89 (2 × CH_3, C-1 and C-6), 21.41 and 22.36 (2 × CH_2, C-2 and C-5), 141.54 (CH, C-4) and 141.76 (C, C-3).

(*Z*)-3-(Trimethylsilyl)hex-3-ene 5f.[11c] Following the above general procedure with episulfone *cis*-**3c** (20 mg, 0.09 mmol), and heating in toluene (2 ml) for 2 h, followed by flash column chromatography yielded the vinylsilane (*Z*)-**5f** (9.2 mg, 65%), δ_H(250 MHz; $CDCl_3$) 0.17 (9 H, s, $SiMe_3$), 0.98 and 0.99 (2 × 3 H, t, *J* 7.0, 2 × CH_3), 1.98–2.12 (4 H, m, 2 × CH_2) and 5.91 (1 H, t, *J* 7.0, 4-H); δ_C(68 MHz; $CDCl_3$) 0.31 (CH_3, $SiMe_3$), 14.56, 15.40 (2 × CH_3, C-1 and C-6), 25.23, 30.86 (2 × CH_2, C-2 and C-5), 141.81 (CH, C-4) and 143.22 (C, C-3).

(*E*)-4-(Trimethylsilyl)oct-4-ene 5g.[11d,e] Following the above general procedure with episulfone *trans*-**3d** (249 mg, 1 mmol), and heating in toluene (10 ml) for 2 h, followed by flash column chromatography yielded the vinylsilane (*E*)-**5g** (109 mg, 59%), ν_{max}(film)/cm^{-1} 2958, 2925, 2853, 1463, 1250, 1144, 1042 and 843; δ_H(400 MHz; $CDCl_3$) −0.02 (9 H, s, $SiMe_3$), 0.85 (3 H, t, *J* 7.0, CH_3), 0.86 (3 H, t, *J* 7.0, CH_3), 1.21–1.39 (4 H, m, 2-H and 7-H), 1.99–2.06 (4 H, m, 3-H and 6-H) and 5.67 (1 H, t, *J* 7.0, 5-H); δ_C(68 MHz; $CDCl_3$) 0.90 (CH_3, $SiMe_3$), 14.43 and 14.68 (2 × CH_3), 22.99 and 23.65 (2 × CH_2, C-2 and C-7), 30.71 and 32.17 (2 × CH_2, C-3 and C-6), 141.40 (CH, C-5) and 141.97 (C, C-4); *m/z* (EI) 184 (M^+, 12%), 169 (44), 110 (23) and 73 (100) (Found: M^+, 184.1617. $C_{11}H_{24}Si$ requires *M*, 184.1647).

Typical procedure for reactions of silylated episulfones with PhCHO using CsF–18-crown-6 in THF

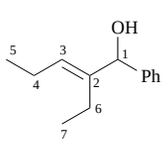
(*E*)- and (*Z*)-2-Methyl-1-phenylbut-2-en-1-ol 6b. A solution of episulfone **3b** (120 mg, 0.62 mmol) in THF (4 ml) was added to a rapidly stirred suspension of caesium fluoride (660 mg, 4.37 mmol), 18-crown-6 (82 mg, 0.31 mmol) and benzaldehyde (0.19 ml, 0.31 mmol) in THF (4 ml) at −78 °C under a nitrogen atmosphere. The temperature was raised to 0 °C and after stirring for 4.5 h the reaction mixture was quenched with saturated aqueous NH_4Cl (30 ml). The mixture was added to CH_2Cl_2 (100 ml) and the organic extract washed with water (2 × 100 ml) and brine (100 ml), then the organic phase was separated, dried

($MgSO_4$) and evaporated under reduced pressure. Flash column chromatography (5% ethyl acetate in light petroleum) of the resulting oil gave the allylic alcohol **6b** (41 mg, 41%) as a 3:1 mixture of (*Z*):(*E*) isomers as a colourless oil, ν_{max}(film)/cm^{-1} 3332 (br), 2922, 1450, 1229, 1069, 1020 and 895; δ_H(400 MHz; $CDCl_3$) 1.42 (3 H, q, *J* 0.5, C=CCH_3, *E*), 1.50 (3 H, q, *J* 0.5, C=CCH_3, *Z*), 1.59 (3 H, dq, *J* 0.5, 6.9, 4-H, *E*), 1.73 (3 H, dq, *J* 0.5, 6.9, 4-H, *Z*), 1.84 (2 H, br, OH, *E* and *Z*), 5.06 (1 H, s, 1-H, *E*), 5.38 (1 H, q, *J* 6.7, 3-H, *Z*), 5.64 (1 H, q, *J* 6.7, 3-H, *E*), 5.72 (1 H, s, 1-H, *Z*), 7.15–7.20 (2 H, m, Ar, *E* and *Z*) and 7.24–7.31 (8 H, m, Ar, *E* and *Z*); δ_C(68 MHz; $CDCl_3$) 11.63 and 13.10 (2 × CH_3, C-4 and C-5, *E*), 13.28 and 17.36 (2 × CH_3, C-4 and C-5, *Z*), 70.55 (CH, C-1, *Z*), 79.30 (CH, C-1, *E*), 121.22 (CH, C-3, *E*), 122.43 and 125.45 (2 × CH, C-3 and Ar, *Z*), 126.15 and 126.88 (2 × CH, Ar, *E*), 127.17 (CH, Ar, *Z*), 128.16 (CH, Ar, *Z*), 137.14 (C, C-2, *Z*), 137.56 (C, C-2, *E*), 142.46 (C, Ar, *Z*) and 142.55 (C, Ar, *E*).

(*E*)- and (*Z*)-2-Ethyl-1-phenylpent-2-en-1-ol 6c.† Following the above general procedure using episulfone **3c** (200 mg) was obtained allylic alcohol **6c** (107 mg, 62%) as a colourless oil as a 5:1 mixture of (*Z*):(*E*) isomers (Found: C, 82.00; H, 9.60. $C_{13}H_{18}O$ requires C, 82.10; H, 9.53%); ν_{max}(film)/cm^{-1} 3350 (br), 2960, 2910, 2860, 1495, 1450, 1030, 1100, 715 and 690; δ_H(250 MHz; $CDCl_3$) 0.85 (3 H, t, *J* 7.0, 5-H or 7-H, *E*), 0.93 (3 H, t, *J* 7.0, 5-H or 7-H, *Z*), 1.00 (3 H, t, *J* 7.0, 5-H or 7-H, *E*) 1.06 (3 H, t, *J* 7.0, 5-H or 7-H, *Z*), 1.70–1.92 (3 H, m, 4-H and 6-H, *E* and *Z*), 1.93–2.18 and 2.19–2.38 (2 × 2.5 H, m, 4-H and 6-H, *E* and *Z*), 5.18 (1 H, s, 1-H, *E*), 5.37 (1 H, t, *J* 7.0, 3-H, *Z*), 5.58 (1 H, t, *J* 7.0, 3-H, *E*), 5.79 (1 H, s, 1-H, *Z*) and 7.19–7.39 (10 H, m, Ar, *E* and *Z*); δ_C(68 MHz; $CDCl_3$) 12.94 (CH_3, C-5 or C-7, *Z*), 14.19 and 14.34 (2 × CH_3, C-5 and C-7, *E*), 14.74 (CH_3, C-5 or C-7, *Z*), 20.56 and 20.76 (2 × CH_2, C-4 and C-6, *E*), 20.99 and 22.92 (2 × CH_2, C-4 and C-6, *Z*), 71.34 (CH, C-1, *Z*), 78.10 (CH, C-1, *E*), 125.57 (CH, C-3, *Z*), 126.53 (CH, C-3, *E*), 126.80 (CH, Ar, *Z*), 127.29 (CH, Ar, *E*), 128.12 (CH, Ar, *Z*) 128.17 (CH, Ar, *E*), 141.21 and 142.21 (2 × C, C-2 and Ar, *Z*), 142.84 and 142.88 (2 × C, C-2 and Ar, *E*); *m/z* (CI) 191 (MH^+, 35%), 190 (M^+, 55), 173 ($MH^+ - H_2O$, 100) and 113 (32).

(*E*)- and (*Z*)-2-Propyl-1-phenylhex-2-en-1-ol 6d. Following the above general procedure using episulfone **3d** (130 mg) was obtained allylic alcohol **6d** (46 mg, 40%) as a colourless oil as a 1.2:1 mixture of (*Z*):(*E*) isomers (Found: C, 82.27; H, 10.40. $C_{15}H_{22}O$ requires C, 82.52; H, 10.16%); ν_{max}(film)/cm^{-1} 3391 (br), 1604, 1322, 1243, 1172 and 1079; δ_H(400 MHz; $CDCl_3$) 0.73 (3 H, t, *J* 6.2, 6-H or 9-H, *E*), 0.74 (3H, t, *J* 6.2, 6-H or 9-H, *Z*), 0.86 (3 H, t, *J* 6.2, 6-H or 9-H, *E*), 0.88 (3 H, t, *J* 6.2, 6-H or 9-H, *Z*), 1.07–1.42 (8 H, m, 5-H and 8-H, *E* and *Z*), 1.65–2.09 (8 H, m, 4-H and 7-H, *E* and *Z*), 5.08 (1 H, s, 1-H, *E*), 5.32 (1 H, t, *J* 6.2, 3-H, *Z*), 5.55 (1 H, t, *J* 6.2, 3-H, *E*), 5.71 (1 H, s, 1-H, *Z*) and 7.14–7.46 (10 H, m, Ar, *E* and *Z*); δ_C(68 MHz; $CDCl_3$) 13.93, 14.04, 14.27 and 14.41 (4 × CH_3, C-6 and C-9, *E* and *Z*), 21.98 (CH_2, C-5 or C-8, *Z*), 22.70 (CH_2, C-5 or C-8, *E*), 22.93 (CH_2, C-5 or C-8, *E*), 23.29 (CH_2, C-5 or C-8, *Z*), 29.69 (CH_2, C-4 or C-7, *E*), 29.80 (CH_2, C-4 or C-7, *Z*), 29.94 (CH_2, C-4 or C-7, *E*), 32.67 (CH_2, C-4 or C-7, *Z*), 71.25 (CH, C-1, *Z*), 78.11 (CH, C-1, *E*), 125.54, 126.54, 126.76, 127.24, 127.28, 128.00, 128.09 and 128.16 (8 × CH, C-3 and Ar, *E* and *Z*), 140.23, 141.20 and 142.79 (3 × C, C-2 and Ar, *E* and *Z*); *m/z* (EI) 218 (M^+, 19%), 175 (94), 133 (71), 105 (98) and 79 (100).

† The numbering system used in the NMR assignments for compound **6c** is shown below. A similar system is used for compounds **6d**–**6h**, **7a** and **7c**.



Typical procedure for reactions of silylated episulfones with aromatic aldehydes using CsF in DMF

(*E*)- and (*Z*)-1-(2′-Naphthyl)-2-propylhex-2-en-1-ol 6e. A solution of episulfone *trans*-**3d** (493 mg, 2.0 mmol) in DMF (2 ml) was added to a rapidly stirred suspension of caesium fluoride (456 mg, 1.5 mmol) and 2-naphthaldehyde (937 mg, 6.0 mmol) in DMF (2 ml) under a nitrogen atmosphere at 0 °C. The mixture was stirred and allowed to warm to room temperature. After 2.5 h water (20 ml) was added and the mixture was then partitioned between CH_2Cl_2 (200 ml) and additional water (200 ml), the organic phase was then separated, dried ($MgSO_4$) and evaporated under reduced pressure. The DMF was removed by adding tetrachloroethylene (50 ml) and evaporating under reduced pressure (exceptionally, in this case the residual 2-naphthaldehyde in the crude oil–solid mixture was then partially removed by crystallisation in hexane at −20 °C); evaporation of the mother liquor and subsequent flash column chromatography (5% ethyl acetate in hexane) yielded the allylic alcohol **6e** (130 mg, 54%) as a 2.2:1 ratio of (*Z*):(*E*) isomers, as a colourless oil, ν_{max}(film)/cm^{-1} 3387 (br), 3056, 2958, 2929, 2869, 1508, 1464, 1377, 1358, 1269, 1119 and 1028; δ_H(250 MHz; $CDCl_3$) 0.79 (3 H, t, *J* 7.0, 6-H or 9-H, *Z*), 0.82 (3 H, t, *J* 7.0, 6-H or 9-H, *E*), 0.95 (3 H, t, *J* 7.0, 6-H or 9-H, *E*), 0.99 (3 H, t, *J* 7.0, 6-H or 9-H, *Z*), 1.20–1.58 (8 H, m, 5-H and 8-H, *E* and *Z*), 1.70–2.15 (6 H, m, 4-H and 7-H, *E* and *Z*), 2.22–2.36 (2 H, m, 4-H and 7-H, *E* and *Z*), 5.31 (1 H, s, 1- H, *E*), 5.45 (1 H, t, *J* 7, 3-H, *Z*), 5.68 (1 H, t, *J* 7, 3-H, *E*), 5.93 (1 H, s, 1-H, *Z*), 7.35–7.50 (6 H, m, Ar, *E* and *Z*) and 7.75–7.90 (8 H, m, Ar, *E* and *Z*); δ_C(68 MHz; $CDCl_3$) 14.01 (CH_3, C-6 or C-9, *E*), 14.02 and 14.02 (2 × CH_3, C-6 and C-9, *Z*), 14.04 (CH_3, C-6 or C-9, *E*), 22.04 (CH_2, C-5 or C-8, *Z*), 22.55 and 22.69 (2 × CH_2, C-5 and C-8, *E*), 23.36 (CH_2, C-5 or C-8, *Z*), 29.80 (CH_2, C-4 or C-7, *E*), 29.90 (CH_2, C-4 or C-7, *Z*), 30.01 (CH_2, C-4 or C-7, *E*), 32.85 (CH_2, C-4 or C-7, *Z*), 71.47 (CH, C-1, *Z*), 77.90 (CH, C-1, *E*), 123.91 and 124.27 (2 × CH, C-3 and Ar, *Z*), 124.92 and 124.97 (2 × CH, C-3 and Ar, *E*), 125.56 (CH, Ar, *Z*), 125.73 (CH, Ar, *E*), 125.96 (CH, Ar, *Z*), 127.66 and 127.68 (2 × CH, Ar, *E*), 127.76 (CH, Ar, *Z*), 127.96 (CH, Ar, *E*), 128.08 and 128.46 (2 × CH, Ar, *Z*), 132.47, 132.85, 139.54, 139.84, 139.90 and 140.82 (6 × C, C-2 and Ar, *E* and *Z*); *m/z* (CI) 268 (M^+, 75%), 251 ($M^+ - H_2O$, 100), 225 ($M^+ - C_2H_7$, 50), 155 (31) and 129 (34) (Found: M^+, 268.1853. $C_{19}H_{24}O$ requires *M*, 268.1827).

(*E*)- and (*Z*)-2-Ethyl-1-phenylpent-2-en-1-ol 6c. Following the above general procedure using episulfone **3c** (220 mg) and benzaldehyde (0.30 ml), and following purification by flash column chromatography (10% ethyl acetate in hexane), was obtained the allylic alcohol **6c** (152 mg, 63%) as a 3.4:1 mixture of (*Z*):(*E*) isomers with spectral data as described above for the reaction in THF.

(*E*)- and (*Z*)-1-(1′-Naphthyl)-2-ethylpent-2-en-1-ol 6f. Following the above general procedure using episulfone **3c** (440 mg) and 1-naphthaldehyde (0.78 ml), and following purification by flash column chromatography (5% ethyl acetate in hexane), was obtained the allylic alcohol **6f** (223 mg, 59%) as a 4.8:1 ratio of (*Z*):(*E*) isomers, as a colourless oil, ν_{max}(film)/cm^{-1} 3550 (br), 3049, 2961, 2931, 2872, 1510, 1450, 1040 and 770; δ_H(250 MHz; $CDCl_3$) 0.82 (3 H, t, *J* 6.9, 5-H or 7-H, *E*), 0.85 (3 H, t, *J* 6.9, 5-H or 7-H, *Z*), 1.00 (3 H, t, *J* 6.9, 5-H or 7-H, *E*), 1.15 (3 H, t, *J* 6.9, 5-H, or 7-H, *Z*), 1.48–2.22 (6 H, m, 4-H and 6-H, *E*, 6-H, *Z*), 2.25–2.57 (2 H, dq, *J* 7.1, 7.1, 4-H, *Z*), 5.46 (1 H, t, *J* 7.1, 3-H, *Z*), 5.65 (1 H, t, *J* 7.1, 3-H, *E*), 5.90 (1 H, s, 1-H, *E*), 6.36 (1 H, s, 1-H, *Z*), 7.41–7.56 (6 H, m, Ar, *Z* and *E*) and 7.77–7.97 (8 H, m, Ar, *Z* and *E*); δ_C(68 MHz; $CDCl_3$) 12.97 (CH_3, C-5 or C-7, *Z*) 13.90 (CH_3, C-5 or C-7, *E*), 14.03 (CH_3, C-5 or C-7, *E*), 14.53 (CH_3, C-5 or C-7, *Z*), 21.10 (CH_2, C-4 or C-6, *E*), 21.11 and 24.46 (2 × CH_2, C-4 and C-6, *Z*), 29.30 (CH_2, C-4 or C-6, *E*), 69.25 (CH, C-1, *Z*), 75.00 (CH, C-1, *E*), 123.18, 123.49, 123.90, 124.50, 125.31, 125.40, 125.79, 127.72, 128.00, 128.72, 129.62 and 129.90 (12 × CH, C-3 and Ar, *Z* or *E*), 130.90, 133.30, 137.50 and 141.11 (4 × C, C-2 and Ar, *Z* or *E*); *m/z* (CI)

240 (M^+, 100%), 222 ($M^+ - H_2O$, 13), 211 (84), 193 (59), 155 (74) and 129 (89) (Found: M^+, 240.1503. $C_{17}H_{20}O$ requires *M*, 240.1514).

(*E*)- and (*Z*)-1-(2′-Naphthyl)-2-ethylpent-2-en-1-ol 6g. Following the above general procedure using episulfone **3c** (220 mg) and 2-naphthaldehyde (470 mg), and following purification by flash column chromatography (5% ethyl acetate in hexane), was obtained the allylic alcohol **6g** (130 mg, 54%) as a 6.0:1 ratio of (*Z*):(*E*) isomers, as a colourless oil (Found: C, 84.70; H, 8.40. $C_{17}H_{20}O$ requires C, 85.00; H, 8.39%); ν_{max}(film)/cm^{-1} 3429 (br), 3039, 2903, 2850, 1590, 1500, 1450, 1110, 1040 and 740; δ_H(250 MHz; $CDCl_3$) 0.87 (3 H, t, *J* 7.0, 5-H or 7-H, *E*), 0.95 (3 H, t, *J* 7.0, 5-H or 7-H, *Z*), 1.05 (3 H, t, *J* 7.0, 5-H or 7-H, *E*), 1.11 (3 H, t, *J* 7.0, 5-H or 7-H, *Z*), 1.74–2.22 (5 H, m, 4-H, 6-H and OH, *E* and *Z*), 2.27–2.43 (4 H, m, 4-H and 6-H, *E* and *Z*), 5.35 (1 H, s, 1-H, *E*), 5.45 (1 H, t, *J* 7.0, 3-H, *Z*), 5.68 (1 H, t, *J* 7.0, 3-H, *E*), 5.96 (1 H, s, 1-H, *Z*), 7.48–7.52 (6 H, m, Ar, *E* and *Z*) and 7.76–7.92 (8 H, m, Ar, *E* and *Z*); δ_C(68 MHz; $CDCl_3$) (*Z* only) 13.02 and 14.84 (2 × CH_3, C-5 and C-7), 21.12 and 23.05 (2 × CH_2, C-4 and C-6), 71.49 (CH, C-1), 123.92, 124.27, 125.60, 126.00, 127.62, 127.80, 127.93 and 128.96 (8 × CH, C-3 and Ar), 132.62, 133.35, 140.35 and 141.14 (4 × C, C-2 and Ar); *m/z* (CI) 241 (MH^+, 20%), 223 ($MH^+ - H_2O$, 85) and 133 (100).

(*E*)- and (*Z*)-1-(2′-Furyl)-2-ethylpent-2-en-1-ol 6h. Following the above general procedure using episulfone **3c** (220 mg) and furan-2-carbaldehyde (0.25 ml), and following purification by flash column chromatography (10% ethyl acetate in hexane), was obtained the allylic alcohol **6h** (178 mg, 43%) as a 1.3:1 ratio of (*Z*):(*E*) isomers, as a colourless oil, ν_{max}(film)/cm^{-1} 3420 (br), 2830, 2950, 1450 and 1365; δ_H(250 MHz; $CDCl_3$) 0.88 (3 H, t, *J* 7.0, 5-H or 7-H, *Z*), 1.00 and 1.01 (2 × 3 H, t, *J* 7.0, 5-H and 7-H, *E*), 1.02 (3 H, t, *J* 7.0, 5-H or 7-H, *Z*), 1.83–2.25 (8 H, m, 4-H and 6-H, *E* and *Z*), 5.15 (1 H, s, 1-H, *E*), 5.38 (1 H, t, *J* 7, 3-H, *Z*), 5.56 (1 H, t, *J* 7, 3-H, *E*), 5.66 (1 H, s, 1-H, *Z*), 6.18 (1 H, d, *J* 9.2, 4′-H, *Z*), 6.20 (1 H, d, *J* 9.2, 4′-H, *E*), 6.29 (2 × 1 H, m, 3′-H, *E* and *Z*) and 7.37 (2 × 1 H, s, 5′-H, *E* and *Z*); δ_C(68 MHz; $CDCl_3$) 13.05 (CH_3, C-5 or C-7, *Z*), 13.90 and 14.23 (2 × CH_3, C-5 and C-7, *E*), 14.48 (CH_3, C-5 or C-7, *Z*), 20.79 (CH_2, C-4 or C-6, *E*), 20.90 (CH_2, C-4 or C-6, *Z*), 23.97 (CH_2, C-4 or C-6, *Z*), 29.69 (CH_2, C-4 or C-6, *E*), 67.04 (CH, C-1, *Z*), 71.94 (CH, C-1, *E*), 105.96 (CH, C-3, *Z*), 106.61 (CH, C-3, *E*), 110.20 (CH, Ar, *Z*), 129.34 (CH, Ar, *E*), 129.44 (CH, Ar, *Z*), 138.97 and 139.82 (2 × C, C-2, *E* and *Z*), 141.83 (CH, Ar, *Z*), 141.84 (CH, Ar, *Z*) and 155.40 (C, Ar, *Z*); *m/z* (CI) 163 ($MH^+ - H_2O$, 100%) (Found: M^+, 180.11504. $C_{11}H_{16}O_2$ requires *M*, 180.11504).

Typical procedure for fluoride-mediated reactions of silylated episulfone 3c to give products 7a–e

(*E*)- and (*Z*)-3-Ethyl-1,1,1-trifluoro-2-phenylhex-3-en-2-ol 7a. A solution of episulfone **3c** (220 mg, 1.0 mmol) in THF (1 ml) was added dropwise to a stirred suspension of caesium fluoride (228 mg, 1.5 mmol), 18-crown-6 (26 mg, 0.1 mmol) and α,α,α-trifluoroacetophenone (0.42 ml, 3.0 mmol) in THF (1 ml) at 0 °C under a nitrogen atmosphere. The suspension was stirred at 0 °C for 10 h, then saturated aqueous NH_4Cl (10 ml) was added. The mixture was then poured onto CH_2Cl_2 (200 ml) and washed with water (200 ml) and then with brine (200 ml). The organic phase was separated, dried ($MgSO_4$) and evaporated at reduced pressure to give the crude product as a slightly yellow oil (509 mg). Purification by column chromatography (2% ethyl acetate in light petroleum) yielded the allylic alcohol **7a** (92 mg, 35%) as a 2.8:1 mixture of (*Z*):(*E*) isomers as a colourless oil (Found: C, 65.29; H, 6.95. $C_{14}H_{17}OF_3$ requires C, 65.10; H, 6.63%); ν_{max}(film)/cm^{-1} 3436 (br), 2967, 1450, 1264, 1168, 1124 and 1032; δ_H(250 MHz; $CDCl_3$) 0.65 (3 H, t, *J* 8.0, 6-H or 8-H, *E*), 0.86 and 1.06 (2 × 3 H, t, *J* 8.0, 6-H and 8-H, *Z*), 1.15 (3 H, t, *J* 8.0, 6-H or 8-H, *E*), 1.69–2.22 (8 H, m, 5-H, and 7-H, *E* and *Z*), 2.40 and 2.45 (2 × 1 H, OH, *E* and *Z*), 5.45 (1 H, t, *J* 8.0, 4-H, *Z*), 5.82 (1 H, t, *J* 8.0, 4-H, *E*), 7.32–7.43 (6 H, m, Ar, *E* and *Z*) and 7.50–7.61 (4 H, m, Ar, *E* and *Z*); δ_C(68 MHz; $CDCl_3$) 13.48 (CH_3, C-6 or C-8, *E*), 13.91 (CH_3, C-6 or C-8, *Z*), 14.18 (CH_3, C-6 or C-8, *E*), 14.88 (CH_3, C-6 or C-8, *Z*), 21.04 and 21.42 (2 × CH_2, C-5 and C-7, *Z*), 22.32 and 26.94 (2 × CH_2, C-5 and C-7, *E*), 80.72 (C, C-1, *E*), 81.11 (C, C-1, *Z*), 123.10 (C, C-2, *Z*), 124.00 (C, C-2, *E*), 127.17 (CH, C-4, *Z*), 128.01 and 128.10 (2 × CH, Ar, *Z*), 128.30 (CH, C-4, *E*), 128.39 (CH, Ar, *Z*), 132.45, 132.49 and 135.26 (3 × CH, Ar, *E*), 136.95 (C, C-3 or Ar, *Z*), 137.61 (C, C-3 or Ar, *E*), 138.87 (C, C-3 or Ar, *Z*) and 140.25 (C, C-3 or Ar, *E*); *m/z* (EI) 258 (34%), 229 (32), 211 (48), 189 (93), 105 (100), 91 (27), 83, (37), 77 (39) and 55 (92).

(*E*)- and (*Z*)-Phenyl hex-3-en-3-yl sulfone 7b. Following the above general procedure using episulfone **3c** (220 mg, 1.0 mmol) and benzenesulfonyl fluoride (0.36 ml, 3.0 mmol) in THF (2 ml), and following purification by flash column chromatography (7% ethyl acetate in light petroleum) was obtained the vinyl sulfone **7b** (55 mg, 25%) as a 1.6:1 mixture of (*E*):(*Z*) isomers as a colourless oil (Found: C, 64.50; H, 7.37. $C_{12}H_{16}O_2S$ requires C, 64.25; H, 7.19%); ν_{max}(film)/cm^{-1} 2960, 2935, 2876, 1446, 1303, 1170, 1137 and 1087; δ_H(250 MHz; $CDCl_3$) 0.92 (3 H, t, *J* 7.6, 1-H or 6-H, *E*), 0.99 and 1.08 (2 × 3 H, t, *J* 7.6, 1-H and 6-H, *Z*), 1.10 (3 H, t, *J* 7.6, 1-H or 6-H, *E*), 2.16–2.38 (6 H, m, 2-H and 5-H, *E* and *Z*), 2.64 (2 H, q, *J* 7.6, 5-H, *Z*), 5.99 (1 H, t, *J* 7.7, 4-H, *Z*), 6.88 (1 H, t, *J* 7.7, 4-H, *E*), 7.15–7.27 (2 H, m, Ar, *E* and *Z*), 7.49–7.63 (5 H, m, Ar, *E* and *Z*) and 7.84–7.89 (3 H, m, Ar, *E* and *Z*); δ_C(68 MHz; $CDCl_3$) 12.96 (CH_3, C-1 or C-6, *E*), 13.44 and 13.55 (2 × CH_3, C-1 and C-6, *Z*), 13.73 (CH_3, C-1 or C-6, *E*), 19.68 and 21.58 (2 × CH_2, C-2 and C-5, *E*), 21.91 and 25.90 (2 × CH_2, C-2 and C-5, *Z*), 125.00 (CH, C-4, *Z*) 127.10 and 127.94 (2 × CH, Ar, *E*), 128.12 (CH, Ar, *Z*), 129.00, 132.97 (2 × CH, Ar, *E*), 139.96, 141.60, 141.70, 143.09 and 143.34 (5 × C or CH, C-3, C-4 and Ar, *E* and *Z*).

(*E*)- and (*Z*)-2-Ethyl-1-phenylpent-2-en-1-one-7c. Following the above general procedure using episulfone **3c** (220 mg, 1.0 mmol) and benzoyl fluoride (0.33 ml, 3.0 mmol) in THF (2 ml), and following purification by flash column chromatography (2% ethyl acetate in light petroleum), was obtained the ketone **7c** (75 mg, 40%) as a 6.0:1 mixture of (*Z*):(*E*) isomers as a colourless oil (Found: C, 82.69; H, 8.80. $C_{13}H_{16}O$ requires C, 82.94; H, 8.57%); ν_{max}(film)/cm^{-1} 2949, 2870, 1685, 1388, 1211 and 1122; δ_H(250 MHz; $CDCl_3$) 0.90 (3 H, t, *J* 7.0, 5-H or 7-H, *Z*), 1.05 (3 × 3 H, t, *J* 7.0, 5-H and 7-H, *E* and *Z*), 1.83–1.92 (2 H, m, 4-H or 6-H, *E*), 2.29–2.37 (4 H, m, 4-H and 6-H, *E* and *Z*), 2.44–2.50 (2 H, m, 4-H or 6-H, *Z*), 5.64 (1 H, t, *J* 8.0, 3-H, *Z*), 6.17 (1 H, t, *J* 8.0, 3-H, *E*), 7.39–7.88 (7 H, m, Ar, *E* and *Z*), 7.88–7.99 (2 H, m, Ar, *E* and *Z*) and 8.02–8.11 (1 H, m, Ar, *E* and *Z*); δ_C(68 MHz; $CDCl_3$) 12.57 (CH_3, C-5 or C-6, *E*), 13.39 and 13.57 (2 × CH_3, C-5 and C-6, *Z*). 13.82 (CH_3, C-5 or C-6, *E*), 19.87 and 21.92 (2 × CH_2, C-4 and C-7, *Z*), 22.95 and 27.92 (2 × CH_2, C-4 and C-7, *E*), 127.89 (CH, C-3 or Ar, *Z*), 128.52 (CH, C-3 or Ar, *E*), 128.95 (CH, C-3 or Ar, *Z*), 129.09 (CH, C-3 or Ar, *E*), 129.18 (CH, C-3 or Ar, *Z*), 131.59 and 133.10 (2 × CH, C-3 or Ar, *E*), 135.20 (CH, C-3 or Ar, *Z*), 137.03 (C, C-2 or Ar, *E*), 139.43 (C, C-2 or Ar, *Z*), 140.81 (C, C-2 or Ar, *E*), 141.87 (C, C-2 or Ar, *Z*), 198.03 (C, C-1, *Z*) and 200.72 (C, C-1, *E*); *m/z* (EI) 188 (M^+, 23%), 173 (11), 159 (56), 105 (100), 77 (61), 55 (21) and 51 (17).

(*E*)- and (*Z*)-3-Phenylselenohex-3-ene 7d. Following the above general procedure using episulfone **3c** (220 mg, 1.0 mmol) and diphenyl diselenide (936 mg, 3.0 mmol) in THF (3 ml), and following purification by flash column chromatography (pentane), was obtained the selenide **7d** (101 mg, 43%) as a 5.6:1 mixture of isomers **a**:**b** as a colourless oil (Found: C, 60.50; H, 6.80. $C_{12}H_{16}Se$ requires C, 60.30; H, 6.74%); ν_{max}(film)/cm^{-1} 2950, 2860, 1570, 1470, 1450, 720 and 680; δ_H(250 MHz; $CDCl_3$) (**a** denotes major isomer) 0.92 (3 H, t, *J* 7.0, 1-H or 6-H, **a**), 0.93 and 0.95 (2 × 3 H, t, *J* 7.0, 1-H and 6-H, **b**), 0.96 (3 H, t, *J* 7.0, 1-H or 6-H, **a**), 1.99–2.31 (8 H, m, 2-H and 5-H, **a** and **b**), 5.77 (1 H, t, *J* 7.0, 4-H, **a**), 5.85 (1 H, t, *J* 7.0, 4-H, **b**), 7.09–7.20

(6 H, m, Ar, **a** and **b**) and 7.30–7.42 (4 H, m, Ar, **a** and **b**); δ_C(68 MHz; $CDCl_3$) 13.92 (CH_3, C-1 or C-6, **b**), 14.03 (CH_3, C-1 or C-6, **a**), 14.09 (CH_3, C-1 or C-6, **b**), 14.09 (CH_3, C-1 or C-6, **a**), 22.64 (CH_2, C-2 or C-5, **b**), 25.31 (CH_2, C-2 or C-5, **a**), 26.26 (CH_2, C-2 or C-5, **b**), 32.77 (CH_2, C-2 or C-5, **a**), 126.40 (CH, C-4, **a**), 126.66 (CH, C-4, **b**), 128.93 and 132.04 (2 × CH, Ar, **a**), 132.05 (CH, Ar, **b**), 130.65 (C, C-3 or Ar, **a**), 132.38 (CH, Ar, **b**), 133.78 (C, C-3 or Ar, **b**), 138.13 (CH, Ar, **a**) and 139.15 (CH, Ar, **b**).

(*E*)- and (*Z*)-3-Phenylthiohex-3-ene 7e. Following the above general procedure using episulfone **3c** (330 mg, 1.5 mmol) and diphenyldisulfide (983 mg, 4.5 mmol) in THF (3 ml), and following purification by flash column chromatography (pentane), was obtained the sulfide **7e** (115 mg, 40%) as a *ca.* 1:1 mixture of isomers **a** and **b** as a colourless oil (Found: C, 74.77; H, 8.58. $C_{12}H_{16}S$ requires C, 74.94; H, 8.39%); ν_{max}(film)/cm^{-1} 2940, 2900, 2840, 1640, 1470, 730 and 680; δ_H(250 MHz; $CDCl_3$) 1.01 (3 H, t, *J* 7.0, 1-H or 6-H, **a**), 1.03 and 1.05 (2 × 3 H, t, *J* 7.0, 1-H and 6-H, **b**), 1.05 (3 H, t, *J* 7.0, 1-H or 6-H, **a**), 2.13–2.26 (2 H, m, 2-H and 5-H, **a** and **b**), 2.28–2.42 (2 H, m, 2-H and 5-H, **a** and **b**), 5.82 (1 H, t, *J* 7.0, 4-H, **b**), 5.92 (1 H, t, *J* 7.0, 4-H, **a**) and 7.10–7.35 (10 H, m, Ar, **a** and **b**); δ_C(68 MHz; $CDCl_3$) 13.49 (CH_3, C-1 or C-6, **a**), 13.49 (CH_3, C-1 or C-6, **b**), 13.95 (CH_3, C-1 or C-6, **a**), 14.08 (CH_3, C-1 or C-6, **b**), 22.35 (CH_2, C-2 or C-5, **b**), 23.28 (CH_2, C-2 or C-5, **a**), 24.48 (CH_2, C-2 or C-5, **b**), 30.82 (CH_2, C-2 or C-5, **a**), 125.67 (CH, C-4, **a**), 126.13 (CH, C-4, **b**), 128.75 (CH, Ar, **a**), 129.16 (CH, Ar, **b**), 129.17 (CH, Ar, **a**), 129.92 (CH, Ar, **b**), 134.18 (C, C-3 or Ar, **a**), 135.83 (C, C-3 or Ar, **b**), 137.15 (C, C-3 or Ar, **a**) and 137.91 (C, C-3 or Ar, **b**); *m/z* (CI) 193 (MH^+, 100%) and 192 (M^+, 15).

(*E*)- and (*Z*)-4-(Phenylseleno)-5-(trimethylsilyl)oct-4-ene 8 and bis[1-(phenylseleno)butyl] sulfone 9

A solution of episulfone **2d** (321 mg, 1 mmol) in THF (2 ml) was slowly added to a stirred suspension of caesium fluoride (152 mg, 1.0 mmol), 18-crown-6 (26 mg, 0.1 mmol) and diphenyl diselenide (935 mg, 3 mmol) in THF (2 ml) at −78 °C under a nitrogen atmosphere. The temperature was raised to 0 °C and the reaction mixture stirred vigorously for 4 h. The reaction was quenched with saturated aqueous NH_4Cl (10 ml). The mixture was then poured onto CH_2Cl_2 (200 ml) and washed with water (200 ml). The organic phase was separated, dried ($MgSO_4$) and solvents removed under reduced pressure to yield a crude yellow solid. Purification by flash column chromatography (5% ethyl acetate in light petroleum, then 10% ethyl acetate in light petroleum) yielded firstly compound **8** (47 mg, 14%) as a 1.5:1 mixture of isomers **a**:**b** as a colourless oil, ν_{max}(film)/cm^{-1} 2957, 2927, 2870, 1564, 1475, 1464, 1437, 1375, 1248, 1150, 1068, 1022 and 998; δ_H(250 MHz; $CDCl_3$) (**a** denotes major isomer) 0.22 (9 H, s, $SiMe_3$, **a**), 0.23 (9 H, s, $SiMe_3$, **b**), 0.73 (3 H, t, *J* 7.0, 1-H or 8-H, **a**), 0.81 (3 H, t, *J* 7.0, 1-H or 8-H, **b**), 0.90 (3 H, t, *J* 7.0, 1-H or 8-H, **a**), 0.95 (3 H, t, *J* 7.0, 1-H or 8-H, **b**), 1.22–1.61 (8 H, m, 2-H and 7-H, **a** and **b**), 2.16–2.32 and 2.33–2.44 (8 H, m, 3-H and 6-H, **a** and **b**), 7.17–7.40 and 7.40–7.50 (10 H, m, Ar, **a** and **b**); δ_C(68 MHz; $CDCl_3$) 0.99 (CH_3, $SiMe_3$, **a**), 1.26 (CH_3, $SiMe_3$, **b**), 13.46 (CH_3, C-1 or C-8, **a**), 13.70 (CH_3, C-1 or C-8, **b**), 14.16 (CH_3, C-1 or C-8, **a**), 14.36 (CH_3, C-1 or C-8, **b**), 22.90 (CH_2, C-2 or C-7, **b**), 23.87 and 23.87 (2 × CH_2, C-2 and C-7, **a**), 23.98 (CH_2, C-2 or C-7, **b**), 35.96 and 37.13 (2 × CH_2, C-3 and C-6, **b**), 39.62 and 40.06 (2 × CH_2, C-3 and C-6, **a**), 126.09, 126.65, 128.90, 128.95, 130.94 and 131.03 (6 × CH, Ar, **a** and **b**), 133.19 (C, C-4, C-5 or Ar, **a** or **b**), 133.24 (CH, Ar, **a** or **b**), 143.02, 144.13, 144.74 and 150.93 (4 × C, C-4, C-5 or Ar, **a** and **b**); *m/z* (EI) 340 (5%), 215 (12), 183 (70), 156 (5), 125 (9), 109 (24) and 73 (100) (Found: M^+, 340.1126. $C_{17}H_{28}SiSe$ requires *M*, 340.1125).

This was followed by **9**, which consisted of two diastereomers in a ratio of 1.3:1 (16%) which were separated by flash chromatography. The least polar diastereomer of **9** was isolated as a viscous oil (46 mg, 9%) (Found: C, 49.41; H, 5.58. $C_{20}H_{26}O_2SSe_2$ requires C, 49.18; H, 5.37%); ν_{max}(film)/cm^{-1} 2931, 2919, 2880, 1574, 1463, 1438, 1377, 1307, 1282, 1154, 1120, 1096, 1072, 1020 and 997; δ_H(250 MHz; $CDCl_3$) 0.95 (6 H, t, *J* 6.3, 4-H), 1.51–1.91 (6 H, m, 2-H and 3-H), 2.18–2.36 (2 H, m, 2-H), 4.93 (2 H, dd, *J* 3.3 and 9.6, 1-H), 7.23–7.42 (6 H, m, Ar) and 7.57–7.67 (4 H, m, Ar); δ_C(68 MHz; $CDCl_3$) 13.41 (CH_3, C-4), 20.66 (CH_2, C-3), 28.64 (CH_2, C-2), 60.12 (CH, C-1), 125.92 (C, Ar), 129.08 and 129.30 and 135.98 (3 × CH, Ar); *m/z* (CI) 490 (M^+, 30%), 440 (45), 365 (36), 171 (44), 157 (44), 314 (88), 213 (65) and 55 (100). The more polar diastereomer of **9** was eluted next, also as a viscous oil (35 mg, 7%) (Found: C, 49.25; H, 5.52. $C_{20}H_{26}O_2SSe_2$ requires C, 49.18; H, 5.37%); ν_{max}(film)/cm^{-1} 2958, 2926, 2871, 1577, 1476, 1438, 1379, 1314, 1123, 1096, 1021 and 999; δ_H(250 MHz; $CDCl_3$) 0.88 (6 H, t, *J* 6.7, 4-H), 1.22–1.49 and 1.65–2.08 (8 H, 2 × m, 2-H and 3-H), 4.56 (2 H, dd, *J* 3.3 and 10.8, 1-H), 7.25–7.42 (6 H, m, Ar) and 7.62–7.68 (4 H, m, Ar); δ_C(68 MHz; $CDCl_3$) 13.44 (CH_3, C-4), 20.77 (CH_2, C-3), 30.76 (CH_2, C-2), 62.46 (CH, C-1), 127.30 (C, Ar), 128.89, 129.33 and 135.43 (CH, Ar); *m/z* (CI) 508 ($M + NH_4^+$, 85%), 423 (68), 261 (53), 213 (100) and 78 (82).

Episulfone substitution using phosphazene base Bu^t–P_4

(*E*)- and (*Z*)-2-Propyl-1-phenylhex-2-en-1-ol 6d. A solution of episulfone **1d** (17.6 mg, 0.1 mmol) and benzaldehyde (30 μl, 0.3 mmol) in THF (0.2 ml) at −98 °C under an argon atmosphere was treated dropwise with phosphazene base Bu^t–P_4 **10** (0.2 ml of a 1.0 M solution in hexanes, 0.2 mmol). After 30 min, the reaction was judged not to be complete (TLC) and another 0.5 equiv. of Bu^t–P_4 **10** was added (50 μl, 0.5 mmol). TLC then indicated that the reaction was complete, and so after a total of 2 h at −98 °C the reaction was warmed to room temperature and the solvent evaporated at reduced pressure. The resulting oil was washed with diethyl ether (3 × 2 ml) and the organic extracts were combined, dried ($MgSO_4$) and evaporated (including 3 h at 1 mmHg) to give a crude, golden oil (71 mg). Flash column chromatography (10% ethyl acetate in light petroleum) yielded the allylic alcohol **6d** (16 mg, 73%) with the same physical data as previously reported.

(*E*)- and (*Z*)-2-Ethyl-1-phenylpent-2-en-1-ol 6c. A solution of *trans*-episulfone **1c** (30 mg, 0.2 mmol) and benzaldehyde (30 μl, 0.3 mmol) in THF (0.02 ml) at −98 °C under an argon atmosphere was treated dropwise with phosphazene base Bu^t–P_4 **10** (0.2 ml of a 1.0 M solution in hexanes, 0.2 mmol). After 1.5 h at −98 °C the reaction was diluted with Et_2O (2.5 ml), warmed to room temperature and partitioned between CH_2Cl_2 (70 ml) and brine (70 ml). The organic phase was separated, dried ($MgSO_4$) and evaporated under reduced pressure to yield the crude product. Flash column chromatography (10% ethyl acetate in light petroleum) yielded the allylic alcohol **6c** (29 mg, 76%) as a 28:1 mixture of (*Z*):(*E*) isomers, with the same physical data as reported earlier.

(*E*)- and (*Z*)-2-Ethyl-1-(2′-naphthyl)pent-2-en-1-ol 6g. A solution of *trans*-episulfone **1c** (30 mg, 0.2 mmol) and 2-naphthaldehyde (47 mg, 0.3 mmol) in THF (0.2 ml) at −98 °C under an argon atmosphere was treated dropwise with phosphazene base Bu^t–P_4 (0.2 ml of a 1.0 M solution in hexanes, 0.2 mmol). After 1.5 h at −98 °C the reaction was diluted with diethyl ether (2.5 ml), warmed to room temperature, and partitioned between CH_2Cl_2 (70 ml) and brine (70 ml). The organic phase was separated, dried ($MgSO_4$), and evaporated under reduced pressure to yield the crude product. Flash column chromatography (10% ethyl acetate in light petroleum) yielded the allylic alcohol **6g** (34 mg, 71%) as a 25:1 mixture of (*Z*):(*E*) isomers with the same physical data as previously reported.

(*E*)- and (*Z*)-1-(2′-naphthyl)but-2-en-1-ol 11. Phosphazene base Bu^t–P_4 **10** (20 μl of a 1.0 M solution in hexanes, 0.20 mmol) was added over approximately 10 s to a stirred solution of episulfone **1f** (22 mg, 0.2 mmol) and 2-naphthaldehyde (47 mg, 0.3 mmol) in THF (0.2 ml) at −98 °C under a nitrogen atmosphere. The reaction was worked up after 2.5 h by diluting with diethyl

ether (2.5 ml) at −98 °C and then partitioning between diethyl ether (100 ml) and brine (100 ml). The organic phase was then separated, dried ($MgSO_4$) and evaporated to yield a brown oil. Purification by column chromatography (20% ethyl acetate in light petroleum) yielded the alcohol **11** (26 mg, 66%) as a colourless oil as a 1.1:1 mixture of isomers **a**:**b**, ν_{max}($CHCl_3$ solution)/cm^{-1} 3401 (br), 3055, 3016, 2972, 2919, 1507, 1442, 1370, 1271, 1216, 1124 and 1036; δ_H(250 MHz; $CDCl_3$) (**a** denotes major isomer) 1.75 (3 H, d, *J* 5.5, 4-H, **b**), 1.84 (3 H, d, *J* 5.5, 4-H, **a**), 5.34 (1 H, d, *J* 6.0, 1-H), 5.71–5.82 (5 H, m, 1-H **b**, 2-H **a** and **b**, 3-H **a** and **b**), 7.45–7.52 (6 H, m, Ar, **a** and **b**) and 7.83–7.85 (8 H, m, Ar, **a** and **b**); δ_C(101 MHz; $CDCl_3$) 13.42 (C-4, **b**), 17.71 (C-4, **a**), 69.57 (C-1, **b**), 75.28 (C-1, **a**), 124.27, 124.49, 125.80, 126.08, 126.67, 127.63, 127.76, 127.96, 128.18, 128.31, 132.78, 132.85, 133.33 and 133.49 (14 × C-2, C-3 and Ar, **a** or **b**), 140.69 and 141.03 (2 × C, Ar, **a** or **b**); *m/z* (EI) 198 (M^+, 100%), 173 (94), 155 (92), 141 (50), 129 (85), 128 (73) and 127 (72) (Found: M^+, 198.1045. $C_{14}H_{14}O$ requires *M*, 198.1045).

(*E*)- and (*Z*)-3-Benzylhex-3-ene 12 and (*E*)-3,4-dibenzylhex-3-ene 13. A solution of episulfone **1c** (30 mg, 0.2 mmol) and benzyl bromide (0.036 ml, 0.3 mmol) in THF (0.2 ml) at −98 °C under an argon atmosphere was treated dropwise with phosphazene base Bu^t–P_4 **10** (0.2 ml of a 1.0 M solution in hexanes, 0.2 mmol) and monitored by TLC. After 1.5 h the reaction was judged not to be complete and so a further 1.0 equiv. of phosphazene base Bu^t–P_4 **10** (0.2 ml, 0.2 mmol) was added. After 3 h at −98 °C, the reaction was diluted with diethyl ether (2.5 ml), warmed to room temperature, poured onto brine (70 ml) and then extracted with CH_2Cl_2 (70 ml). The organic phase was separated, dried ($MgSO_4$), evaporated under reduced pressure and then subjected to flash column chromatography (100% pentane) to give firstly **12** (14 mg, 40%) as a 1.6:1 mixture of (*Z*):(*E*) isomers as a colourless oil, ν_{max}($CHCl_3$ solution)/cm^{-1} 3085, 3060, 3026, 2919, 1495, 1460, 1080, 1030, 727 and 694; δ_H(400 MHz; $CDCl_3$) 0.95 (3 H, t, *J* 7.5, 1-H or 6-H, *E*), 0.96 (3 H, t, *J* 7.5, 1-H or 6-H, *Z*), 0.98 (3 H, t, *J* 7.5, 1-H or 6-H, *E*), 1.02 (3 H, t, *J* 7.5, 1-H or 6-H, *Z*), 1.88–2.25 (8 H, m, 2-H and 5-H, *E* and *Z*), 3.29 (2 H, s, 7-H, *E*), 3.40 (2 H, s, 7-H, *Z*), 5.18 (1 H, t, *J* 6.7, 4-H, *E*), 5.31 (1 H, t, *J* 6.7, 4-H, *Z*) and 7.12–7.49 (10 H, m, Ar, *E* and *Z*) (Found: M^+, 174.1405. $C_{13}H_{18}$ requires *M*, 174.1408).

This was followed by **13** (11 mg, 21%) as a single isomer as a colourless oil, ν_{max}($CHCl_3$ solution)/cm^{-1} 2909, 2840, 2793, 1659, 1492, 1460, 1380, 1082, 903 and 862; δ_H(400 MHz; $CDCl_3$) 0.98 (6 H, t, *J* 7.2, 1-H), 2.12 (4-H, q, *J* 7.4, 2-H), 3.55 (4 H, s, 4-H), 7.18–7.39 (10 H, m, Ar); δ_C(101 MHz; $CDCl_3$) 13.40 (C-1), 24.86 (C-2), 36.55 (C-3), 125.73, 128.26 and 128.58 (3 × Ar), 134.68 and 141.04 (C-3 and Ar); *m/z* (EI) 264 (M^+, 63%), 173 (94), 131 (85), 117 (63) and 91 (100) (Found: M^+, 264.1878. $C_{18}H_{24}$ requires *M*, 264.1878).

Typical procedure for the conversion of episulfones into alkenyl sulfones

Methyl vinyl sulfone 14.[27] A solution of episulfone **1a** (368 mg, 4 mmol) in THF (1 ml) was added to a stirred solution of LDA (generated from butyllithium and diisopropylamine) (4 mmol) in THF (4 ml) at −78 °C. After 10 min, MeI (1.00 ml, 16 mmol) and then DMF (4 ml) were added and the mixture was stirred at −78 °C for 1 h, and then at room temperature for 24 h. The white suspension was quenched with saturated aqueous NH_4Cl (1 ml), poured onto brine (150 ml) and washed with diethyl ether (150 ml). The organic phase was separated, dried ($MgSO_4$) and evaporated under reduced pressure to give a yellow oil. Purification by flash column chromatography (10% then 30% ethyl acetate in light petroleum) yielded methyl vinyl sulfone **14** (172 mg, 41%) as a colourless oil, ν_{max}(film)/cm^{-1} 3018, 2927, 1299, 1132 and 960; δ_H(250 MHz; $CDCl_3$) 2.96 (3 H, s, CH_3), 6.14 (1 H, d, *J* 9.8, 3-*Z*-H), 6.46 (1 H, d, *J* 16.6, 3-*E*-H) and 6.73 (1 H, dd, *J* 9.8, 16.6, 2-H); δ_C(68 MHz; $CDCl_3$) 42.25 (CH_3), 129.42 (CH_2) and 137.52 (CH); *m/z* (EI) 107 (MH^+, 100%), 65 (15), 63 (12) and 47 (52) (Found: MH^+, 107.0153. $C_3H_7O_2S$ requires *M*H, 107.0167).

(*E*)-But-2-en-2-yl methyl sulfone 15a. Following the above general procedure using episulfone **1b** (240 mg, 2 mmol) and MeI (0.50 ml, 8 mmol), and following flash column chromatography (diethyl ether then 60% ethyl acetate in light petroleum), was obtained the alkenyl sulfone **15a** (107 mg, 40%) as a colourless oil, ν_{max}(film)/cm^{-1} 2929, 1293, 1171, 1181 and 761; δ_H(400 MHz; $CDCl_3$) 1.83 (3 H, d, *J* 7.0, 4-H), 2.02 (3 H, s, 1-H), 2.84 (3 H, s, CH_3), 6.79 (1 H, 1, *J* 7.0, 3-H); δ_C(68 MHz; $CDCl_3$) 11.66 and 14.18 (2 × CH_3, C-1 and C-4), 40.43 (CH_3, SO_2CH_3), 136.95 (CH, C-3), 137.41 (C, C-2); *m/z* (EI) 134 (M^+, 12%), 91 (34), 71 (100) and 55 (91) (Found: M^+, 134.0414. $C_5H_{10}O_2S$ requires *M*, 134.0402).

Benzyl (*E*)-but-2-en-2-yl sulfone 15b. Following the above general procedure using episulfone **1b** (270 mg, 2.25 mmol) and benzyl bromide (3.85 g, 22.5 mmol), and following purification by flash column chromatography (20%, 30% then 40% ethyl acetate in light petroleum), was obtained the alkenyl sulfone **15b** (290 mg, 62%) as a colourless oil (Found: C, 62.83; H, 6.79. $C_{11}H_{14}O_2S$ requires C, 63.14; H, 6.71%); ν_{max}(film)/cm^{-1} 1652, 1309 and 1112; δ_H(400 MHz; $CDCl_3$) 1.71 (3 H, d, *J* 6.3, 4-H), 1.91 (3 H, s, 1-H), 4.16 (2 H, s, CH_2Ar), 6.50 (1 H, q, *J* 6.3, 3-H) and 7.27–7.40 (5 H, m, Ar); δ_C(68 MHz; $CDCl_3$) 11.95 and 14.02 (2 × CH_3, C-1 and C-4), 59.01 (CH_2, *C*H_2Ar), 128.32 (C, C-2), 128.57 (CH, C-3), 128.61 and 130.51 (2 × CH, Ar), 135.04 (C, Ar); *m/z* (EI) 210 (M^+, 15%), 131 (24), 119 (11), 92 (56), 91 (100) and 55 (36) (Found: M^+, 210.0692. $C_{11}H_{14}O_2S$ requires *M*, 210.0715).

Allyl (*E*)-but-2-en-2-yl sulfone 15. Following the above general procedure using episulfone **1b** (280 mg, 2.3 mmol) and allyl bromide (2.82 g, 23 mmol), and following purification by flash column chromatography (20% ethyl acetate in light petroleum), was obtained the alkenyl sulfone **15c** (170 mg, 47%) as a colourless oil, ν_{max}(KBr)/cm^{-1} 1305, 1167, 1115 and 937; δ_H(250 MHz; $CDCl_3$) 1.82 (3 H, dd, *J* 7 and 1, 4-H), 1.96 (3 H, d, *J* 1, 1-H), 3.64 (2 H, d, *J* 7.5, SO_2CH_2), 5.30 (1 H, dd, *J* 17.5 and 1, =CH_ZH), 5.36 (1 H, dd, *J* 10.5 and 1, =CHH_E), 5.77 (1 H, ddt, *J* 17.5, 10.5 and 7.5, C*H*=CH_2) and 6.71 (1 H, dq, *J* 7 and 1, 3-H); δ_C(68 MHz; $CDCl_3$) 11.68 (CH_3), 13.84 (CH_3), 56.66 (CH_2), 123.70 (CH_2), 124.70 (CH), 138.63 (CH) and 135.3 (C); *m/z* (EI) 119 (18%) and 55 (100).

(*E*)-But-2-en-2-yl ethoxycarbonylmethyl sulfone 15d. Following the above general procedure using episulfone **1b** (270 mg, 2.25 mmol) and ethyl bromoacetate (3.85 g, 22.5 mmol), and following purification by flash column chromatography (20% ethyl acetate in light petroleum) was obtained the alkenyl sulfone **15d** (130 mg, 41%) as a colourless oil (Found: C, 46.74; H, 7.06. $C_8H_{14}O_4S$ requires C, 46.58; H, 6.85%); ν_{max}(KBr)/cm^{-1} 1738, 1313, 1173, 1119 and 1026; δ_H(250 MHz; $CDCl_3$) 1.28 (3 H, t, *J* 7, OCH_2CH_3), 1.88 (3 H, dq, *J* 7 and 1, H-4), 2.06 (3 H, m, H-1), 3.94 (2 H, s, SO_2CH_2), 4.22 (2 H, q, *J* 7, OCH_2CH_3) and 6.86 (1 H, qq, *J* 7 and 1, H-3); δ_C(68 MHz; $CDCl_3$) 11.50, 13.80 and 14.07 (3 × CH_3), 57.22 and 62.12 (2 × CH_2), 135.78 (C), 139.46 (CH) and 162.44 (C=O); *m/z* (EI) 161 (M − OEt^+, 71%), 119 (62) and 113 (100).

Methyl (*E*)-hex-3-en-3-yl sulfone 15e. Following the above general procedure using episulfone **1c** (296 mg, 2.0 mmol) and MeI (0.50 ml, 8 mmol), and after purification by flash column chromatography (20% then 30% ethyl acetate in light petroleum), was obtained the alkenyl sulfone **15e** (183 mg, 56%) as a colourless oil (Found: C, 51.44; H, 8.81. $C_7H_{14}O_2S$ requires C, 51.82; H, 8.70%); ν_{max}(film)/cm^{-1} 2971, 1303, 1170, 1126 and 763; δ_H(400 MHz; $CDCl_3$) 1.10 and 1.19 (2 × 3 H, t, *J* 7.5, 1-H and 6-H), 2.25 (2 H, dq, *J* 7.5 and 7.5, 5-H), 2.46 (2 H, q, *J* 7.5, 2-H), 2.88 (3 H, s, SO_2CH_3) and 6.71 (1 H, t, *J* 7.5, 4-H); δ_C(68 MHz; $CDCl_3$) 13.03 and 14.18 (2 × CH_3, C-1 and C-6), 19.98 and 21.64 (2 × CH_2, C-2 and C-5), 41.62 (CH_3, SO_2CH_3), 141.76 (C, C-3) and 143.75 (CH, C-4);

m/z (EI) 210 (M^+, 15%), 131 (24), 119 (11), 92 (56), 91 (100) and 55 (36) (Found: M^+, 162.0684. $C_7H_{14}O_2S$ requires *M*, 162.0715).

Benzyl (*E*)-hex-3-en-3-yl sulfone 15f. Following the above general procedure using episulfone **1c** (296 mg, 2.0 mmol) and benzyl bromide (0.95 ml, 8 mmol) and after purification by flash column chromatography (20% then 30% ethyl acetate in light petroleum), was obtained the alkenyl sulfone **15f** (240 mg, 51%) as a colourless oil (Found: C, 65.73; H, 7.71. $C_{13}H_{18}O_2S$ requires C, 65.51; H, 7.61%); ν_{max}(film)/cm^{-1} 2970, 1455, 1306 and 1101; δ_H(250 MHz; $CDCl_3$) 0.92 and 1.15 (2 × 3 H, t, *J* 7.5, 1-H and 6-H), 2.12 (2 H, dq, *J* 7.5 and 7.5, 5-H), 2.31 (2 H, q, *J* 7.5, 2-H), 4.18 (2 H, s, CH_2Ph), 6.31 (1 H, t, *J* 7.5, 4-H) and 7.27–7.36 (5 H, m, Ar); δ_C(68 MHz; $CDCl_3$) 12.51 and 13.95 (2 × CH_3, C-1 and C-6), 20.24 and 21.44 (2 × CH_2, C-2 and C-5), 59.79 (CH_2, CH_2Ph), 128.33 and 130.51 (2 × CH, C-4 or Ar), 130.67 and 139.03 (2 × C, C-3 and Ar), 146.31 (CH, C-4 or Ar); *m/z* 238 (M^+, 3%), 181 (29), 92 (38), 91 (100), 27 (65) and 55 (32).

Allyl (*E*)-hex-3-en-3-yl sulfone 15g. Following the above general procedure using episulfone **1c** (296 mg, 2.0 mmol) and allyl bromide (0.69 ml, 8 mmol), and after purification by flash column chromatography (15% then 25% ethyl acetate in light petroleum), was obtained the alkenyl sulfone **15g** (245 mg, 65%) as a colourless oil, ν_{max}(film)/cm^{-1} 2971, 2938, 2877, 1309, 1290 and 1123; δ_H(250 MHz; $CDCl_3$) 1.08 and 1.16 (2 × 3 H, t, *J* 7.6, 1-H and 6-H), 2.24 (2 H, dq, *J* 7.5, 7.5, 5-H), 2.37 (2 H, q, *J* 7.5, 2-H), 3.66 (2 H, d, *J* 7.3, SO_2CH_2), 5.29 (1 H, dd, *J* 1.2, 16.9, =CH_E), 5.38 (1 H, dd, *J* 1.0, 10.2, =CH_ZH), 5.71–5.88 (1 H, m, C*H*=CH_2) and 6.62 (1 H, t, *J* 7.5, 4-H); δ_C(68 MHz; $CDCl_3$) 12.90 and 13.84 (2 × CH_3, C-1 and C-6), 19.98 and 21.56 (2 × CH_2, C-2 and C-5), 57.77 (CH_2), 123.76 (CH_2=CH_2), 124.96 (CH, *C*H=CH_2), 139.35 (C, C-3) and 145.88 (CH, C-4); *m/z* (EI) 189 (MH^+, 100%), 83 (75), 55 (98) and 41 (98) (Found: M^+, 188.0898. $C_{13}H_{18}O_2S$ requires *M*, 188.0871).

Ethoxycarbonylmethyl (*E*)-hex-3-en-3-yl sulfone 15h. Following the above general procedure using episulfone **1c** (250 mg, 1.67 mmol) and ethyl chloroacetate (2.05 g, 16.7 mmol), and after purification by flash column chromatography (15% then 25% ethyl acetate in light petroleum), was obtained the alkenyl sulfone **15h** (266 mg, 68%) as a colourless oil, ν_{max}(KBr)/cm^{-1} 1741, 1316, 1171, 1128, 1098 and 1028; δ_H(250 MHz; $CDCl_3$) 1.08 and 1.17 (2 × 3 H, t, *J* 7.6, 1-H and 6-H), 1.26 (3 H, t, *J* 7.5, OCH_2CH_3), 2.25 (2 H, dq, *J* 7.5, 7.5, 5-H), 2.44 (2 H, q, *J* 7.5, 2-H), 3.93 (2 H, s, SO_2CH_2), 4.19 (2 H, q, *J* 7.5, OCH_2CH_3) and 6.71 (1 H, t, *J* 7.5, 4-H); δ_C(68 MHz; $CDCl_3$) 13.12, 13.30 and 14.22 (3 × CH_3, C-1, C-6 and CH_2CH_3), 20.40 and 22.10 (2 × CH_2 and C-5), 58.56 and 62.45 (2 × CH_2, SO_2CH_2 and CH_2CH_3), 140.45 (C, C-3), 146.88 (CH, C-4) and 162.84 (C=O); *m/z* (EI) 235 (MH^+, 5%), 153 (27), 83 (70), 67 (77) and 55 (100) (Found: M^+, 234.0937. $C_{10}H_{18}O_4S$ requires *M*, 234.0926).

Cyclopent-1-en-1-yl methyl sulfone 17. Following the above general procedure using episulfone **16** (250 mg, 1.89 mmol) and methyl iodide (3.95 g, 28 mmol) and after purification by flash column chromatography (30% ethyl acetate in light petroleum), was obtained the alkenyl sulfone **17** (78 mg, 28%) as a colourless oil, ν_{max}(KBr)/cm^{-1} 2923, 1620, 1292 and 1138; δ_H(250 MHz; $CDCl_3$) 2.06–2.20 (2 H, m, CH_2, H-4), 2.59 (2 H, m) and 2.72 (2 H, m, 2 × CH_2, H-3 and H-5), 2.93 (3 H, s, SO_2CH_3) and 6.75 (1 H, m, H-2); δ_C(68 MHz; $CDCl_3$) 23.71, 31.14 and 32.88 (3 × CH_2), 41.23 (CH_3), 143.81 (CH) and 143.89 (C); *m/z* (EI) 235 (M^+, 35%), 83 (53), 69 (100) and 55 (88) (Found: M^+, 146.0413. $C_6H_{10}O_2S$ requires *M*, 146.0402).

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