ARTICLE

OBC
www.rsc.org/obc

# Reactions of lithiated (*E*)-3-halo-1-phenylsulfonylprop-1-enes and (*Z*)-1-halo-3-phenylsulfonylprop-1-enes with aldehydes

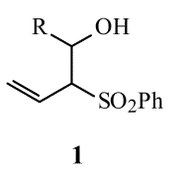
**Eva T. Gallagher and David H. Grayson***
*Centre for Synthesis and Chemical Biology, Department of Chemistry, Trinity College, Dublin 2, Ireland*

***Received 22nd January 2003, Accepted 27th February 2003***
***First published as an Advance Article on the web 25th March 2003***

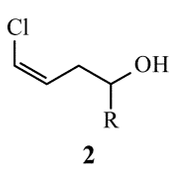
(*E*)-3-Chloro-1-phenylsulfonylprop-1-ene and its iodo- and bromo- analogues, (*Z*)-1-iodo-3-phenylsulfonylprop-1-ene and (*Z*)-1-bromo-3-phenylsulfonylprop-1-ene, have each been successfully converted into lithiated carbanions which react regioselectively with aromatic aldehydes to give γ-alkylated products whose nature depends upon the halogen substituent: the chloro-sulfones yield (2*Z*)-1-aryl-2-chloro-4-phenylsulfonylbut-2-en-1-ols but the bromo- and iodo-derivatives behave differently, yielding (1*E*)-*trans*-4-aryl-3,4-epoxy-1-phenylsulfonylbut-1-enes. In sharp contrast, the same lithiated sulfones react with aliphatic aldehydes to give *anti*-configured β-hydroxysulfones which are formed *via* diastereoselective α-alkylation reactions.

## Introduction

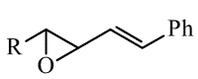
Synthetic applications of heteroatom-substituted carbanions have attracted considerable attention in recent years. Thus, the reactions of lithio derivatives of simple allylic sulfones with aldehydes are well established, and generally proceed in a regiospecific manner to give α-alkylated products **1**.[1,2] On the other hand, lithiation of allyl chloride[3,4] followed by reaction of the derived anion with a variety of aromatic aldehydes affords[4] predominantly (*Z*)-configured γ-substituted products **2**. Conversely, cinnamyl chloride can be deprotonated[5] to give a lithio derivative which reacts with aromatic ketones and aldehydes to yield epoxides **3**, which must arise *via* initial alkylation α to the halogen atom. α-Halosulfones react with base under phase-transfer[6] or other[7,8] conditions to give α-anions which undergo Darzens-like reactions with aldehydes and ketones, giving *trans*-α,β-epoxysulfones **4**.



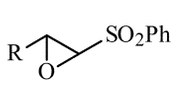

**1**




**2**




**3**

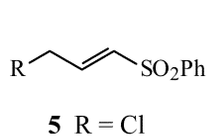



**4**

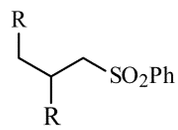
In this paper we describe the results that we have obtained when a number of (*E*)-3-halo-1-phenylsulfonylpropene and (*Z*)-1-halo-3-phenylsulfonylpropene derivatives are deprotonated to give delocalised 1-halo-3-sulfonylpropenyl carbanions which are then reacted with either aromatic or aliphatic aldehydes.

## Results and discussion

3-Chloro-1-phenylsulfonylprop-1-ene **5** was prepared from the readily available[9] alcohol **6** *via* reaction with phosphorus pentachloride. The chloride **5** was[9] easily converted into the iodide **7** by Finkelstein reaction with sodium iodide in acetone. This is, as noted by Bordwell *et al.*,[10] a facile process which contrasts sharply with the poor reactivity of chloromethylphenylsulfone towards nucleophiles.

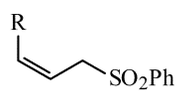



**5** R = Cl
**6** R = OH
**7** R = I
**8** R = Br




**10** R = Br
**14** R = Cl

The corresponding bromide **8** was most conveniently obtained[11] from 1-phenylsulfonylprop-2-ene **9** *via* bromination of its double bond to give the dibromide **10** followed by dehydrobromination using triethylamine. Careful control of reaction conditions was required for this step, since overexposure to triethylamine gave bromide **8** that was contaminated with some of the deconjugated sulfone (*Z*)-1-bromo-3-phenylsulfonylprop-1-ene **11** from which it could not be separated by chromatography.




**9** R = H
**11** R = Br
**12** R = Cl
**13** R = $Et_3N^+I^-$

Deliberate treatment of the bromo-compound **8** with triethylamine with the intention of completely converting it into the vinylic halide **11** led, at best, to mixtures containing 20% of **8** and 80% of **11**.

The chloride **5** could be cleanly deconjugated to give the (*Z*)-vinylic chloride **12** when it was treated with triethylamine in chloroform solution, but the iodide **7** yielded a mixture of products which apparently included the ammonium salt **13** under these conditions.

The base-mediated deconjugation of (*E*)-γ-substituted-α,β-unsaturated allylic sulfones to yield (*Z*)-γ-substituted-β,γ-unsaturated sulfones has been explored by Inomata *et al.*[12] who have invoked a "*syn*-effect" in order to rationalise their results. The (*Z*)-chlorosulfone **12** has been described by Mikhailova *et al.*,[13] who obtained it from the dichloride **14** by treatment with base. The same authors report[13] that treatment of the dibromide **10** with bases afforded the *conjugated* bromosulfone

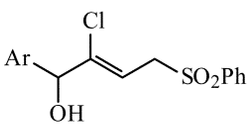
DOI: 10.1039/b300925b

**8**, but this differs from our experience in that we find that **8** easily isomerises to give mainly the β,γ-compound **11** under such conditions.

Initial attempts to lithiate the allylic halides **5**, **7** or **8** were not encouraging. Dark red solutions of anions were formed when they were treated with *n*BuLi–THF but, even at low temperatures, these rapidly became brown, and aqueous work-up after the addition of an electrophile such as benzaldehyde led to complex mixtures of what appeared to be homocoupling products derived from the starting sulfones.

Much more satisfactory results were obtained when lithiation was carried out in the presence of the electrophile. Thus, addition of a THF solution containing equimolar amounts of the chlorosulfone **5** and of benzaldehyde to 1.2 equivalents of *n*-BuLi in THF at −18 °C led, after aqueous quenching, to a reaction mixture which contained one major product **15a** together with a little of the isomerised vinylic chloride **12**. These were easily separated by chromatography.




**15a** Ar = $C_6H_5$
**15b** Ar = 4-Cl-$C_6H_4$
**15c** Ar = 2-MeO-$C_6H_4$
**15d** Ar = 3-F-$C_6H_4$

In its $^1$H NMR spectrum, the hydroxy-sulfone **15a** exhibits a 2H doublet, $J$ 7.7 Hz, at $\delta$ 4.07 ppm that is associated with a methylene carbon resonance at $\delta$ 55.9 ppm. These chemical shifts, and the vicinal coupling constant, are very similar to those observed in the NMR spectra of the vinylic chloride **12** whose methylene group appears as a 7.7 Hz doublet at $\delta$ 4.04 ppm, with the corresponding $^{13}$C signal at $\delta$ 54.6 ppm, but differ markedly from the data for the allylic chloride **5** where the methylene proton resonance occurs at $\delta$ 4.19 ppm with $J_{vic}$ 5.2 Hz and the relevant $^{13}$C signal appears at $\delta$ 41.2 ppm.

Using the same successful protocol, the chloride **5** was reacted with a number of other aromatic aldehydes to give the analogous (*Z*)-1-aryl-2-chloro-4-phenylsulfonylbut-2-en-1-ols **15b**–**15d**. These exhibited $^1$H and $^{13}$C NMR signals for their allylic methylene groups that were almost identical to those given by **15a** above.

The stereochemistry of the olefinic double bond of the representative sulfone **15b** was firmly established by NOE experiments in which irradiation of the –C*H*OH proton at $\delta$ 5.19 ppm enhanced by 8.5% the signal at $\delta$ 6.16 ppm which is due to the olefinic proton (Fig. 1).

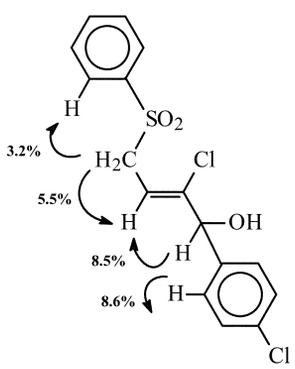
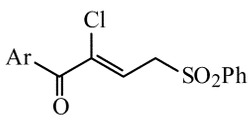
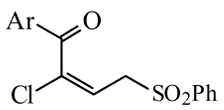



**Fig. 1**

Oxidation of **15b** using chromic acid led to the derived ketone **16b** (82%) together with some of its (*E*)-isomer **17b** (18%). The (*Z*)-compound **16b** showed $\delta_H$ 6.56 ppm for its olefinic proton, whereas the olefinic proton *trans* to the carbonyl group in **17b** resonated further upfield at $\delta$ 6.33 ppm. These ketones could not be separated by chromatography. Attempts to further equilibrate **16b** and **17b** under acidic conditions met with failure. The related alcohols **15c** and **15d** were likewise oxidised using chromic acid to give the derived ketones **16c** and **16d** which were similarly obtained as inseparable mixtures with minor amounts of their (*E*)-isomers **17c** and **17d**.



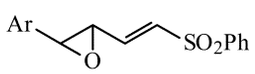




**16b** Ar = 4-Cl-$C_6H_4$
**16c** Ar = 2-MeO-$C_6H_4$
**16d** Ar = 3-F-$C_6H_4$

**17b** Ar = 4-Cl-$C_6H_4$
**17c** Ar = 2-MeO-$C_6H_4$
**17d** Ar = 3-F-$C_6H_4$

Reduction of the ketone **16d** using sodium borohydride gave back the starting alcohol **15d** in high yield, confirming their stereochemical relationship. The fact that only a single geometric isomer of the alcohol was obtained from this reaction is suggestive of the existence of a rapid equilibrium between the (*Z*)- and (*E*)-isomers of the ketone **16d**, with the (*Z*)-compound undergoing reduction faster than its (*E*)-isomer.

Using the same lithiation–alkylation protocol, the iodide **7** and the bromide **8** were also successfully deprotonated and reacted with the same series of aromatic aldehydes. Each of these allylic halo-derivatives yielded the products **18a**–**18d** which were entirely different to those that were obtained from the analogous chloro-compound **5** under the same conditions, but which are related to the epoxides **4** derivable from simple α-halosulfones and aldehydes in the presence of base.[6–8]

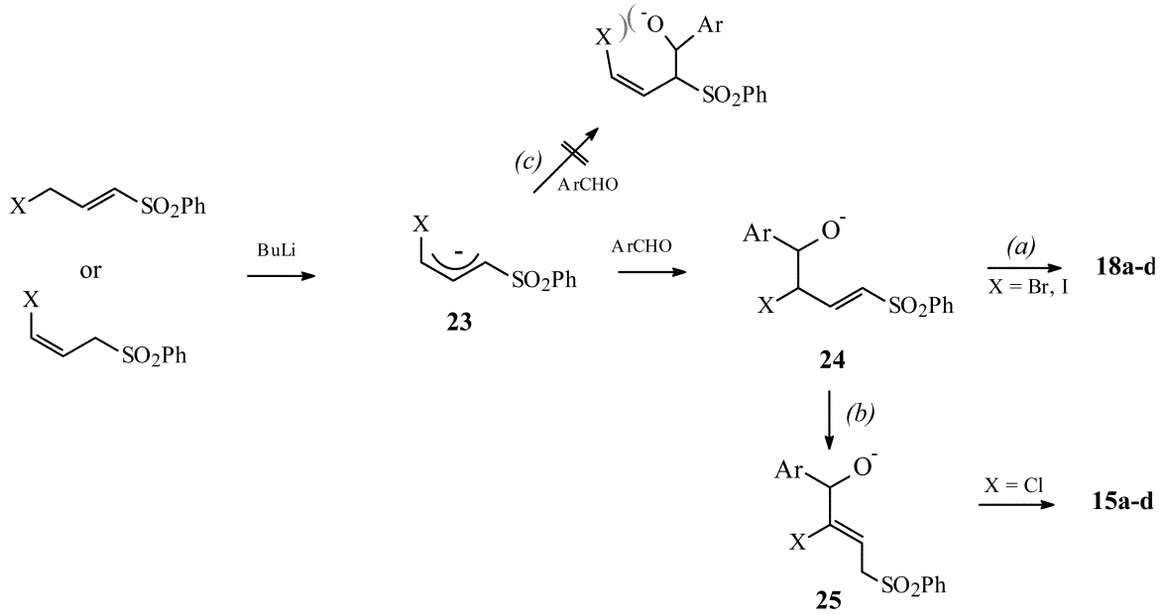



**18a** Ar = $C_6H_5$
**18b** Ar = 4-Cl-$C_6H_4$
**18c** Ar = 2-MeO-$C_6H_4$
**18d** Ar = 3-F-$C_6H_4$

The novel epoxides **18a**–**18d** were readily identified from their spectroscopic data. Thus, the (*E*)-configuration of the double bond, $J_{trans}$ ~ 15 Hz, and the *trans*-configuration at the oxirane ring, $J_{vic}$ ~ 1.8 Hz, could be assigned on the basis of these coupling constants, and the other features of their $^1$H and $^{13}$C NMR spectra (experimental section) were in full agreement with the structures shown.

Brief treatment of the epoxide **18b** with $BF_3{\cdot}Et_2O$ afforded a mixture consisting largely of the ketone **19** together with a little of the aldehyde **20** (*ca.* 4%). Longer reaction times led to multicomponent product mixtures. The predominant formation of the ketone **19** from the epoxide **18b** is in accord with mechanistic expectation in that the Lewis acid-mediated rearrangement proceeds preferentially *via* the derived stabilised benzylic carbonium ion **21** rather than the alternative and less stable sulfonyl-substituted allylic cation **22**.

Exactly the same sets of alkylation products **15a**–**15d** or **18a**–**18d** were obtained when either the vinylic chloride **12** or the vinylic bromide **11** were, respectively, lithiated and then reacted with aromatic aldehydes (Table 1), supporting the contention that delocalised anions are formed immediately upon deprotonation.

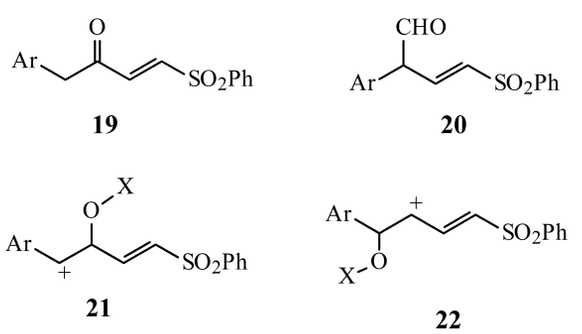


**Scheme 1**

**Table 1** Reactions of lithiated halosulfones with aryl aldehydes

| Halosulfone | Aldehyde | Product | Yield (%)[a] |
|---|---|---|---|
| **5**, **12** | $C_6H_5CHO$ | **15a** | 72, 68 |
| **5**, **12** | 4-Cl–$C_6H_4CHO$ | **15b** | 62, 63 |
| **5**, **12** | 2-MeO–$C_6H_4CHO$ | **15c** | 72, 71 |
| **5**, **12** | 3-F–$C_6H_4CHO$ | **15d** | 62, 63 |
| **7**, **8**, **11** | $C_6H_5CHO$ | **18a** | 73, 75, 72 |
| **7**, **8**, **11** | 4-Cl–$C_6H_4CHO$ | **18b** | n/a, 77, n/a |
| **7**, **8**, **11** | 2-MeO–$C_6H_4CHO$ | **18c** | 75, 81, 75 |
| **7**, **8**, **11** | 3-F–$C_6H_4CHO$ | **18d** | n/a, 80, n/a |

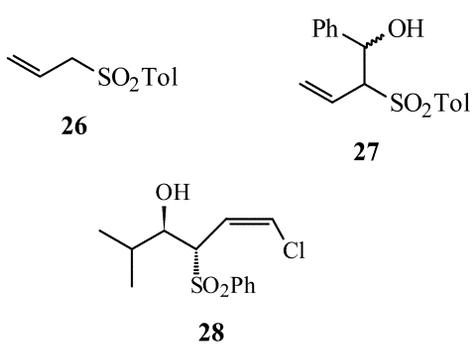
[a] Yields are of purified products.



**Ar** = 4-Cl-$C_6H_4$

We regard the formation of the hydroxy-sulfones **15a**–**15d** and of the epoxides **18a**–**18d** as proceeding *via* the mechanisms outlined in Scheme 1. Thus, each of the unsaturated halosulfones **5**, **7**, **8**, **11** and **12** is deprotonated to give an anion **23** which then reacts with an aromatic aldehyde to yield an intermediate lithium alkoxide **24**. When X = Br or I, the alkoxide **24** undergoes rapid Williamson cyclisation to give the epoxides **18** (path *a*), but when the poorer leaving group X = Cl is present allylic rearrangement of **24** to **25** takes precedence and protonation during work-up then leads to the vinylic chlorides **15** (path *b*).

The γ-regiospecificity involved in reactions of the anion **23** with aromatic aldehydes is in marked contrast to that normally seen when simple allylic sulfones are the substrates. Thus, 1-toluenesulfonylprop-2-ene **26** affords a lithio-derivative which reacts[14] with benzaldehyde to give a 2 : 1 mixture of both diastereoisomers of the regioisomeric α-alkylation product **27**.



We rationalise our observed γ-specificity on the basis that although alkylation α to the phenylsulfonyl group may be the kinetically favoured reaction pathway, the intermediate thus formed (path *c*, Scheme 1) is sterically crowded due to the presence of the large halogen atom at the terminus of the (*Z*)-configured double bond. Accordingly, this alkoxide collapses to return the carbanion **23** together with the conjugated aryl aldehyde, which then reacts at the γ-carbon of **23** to yield the observed products **15a**–**15d** or **18a**–**18d**.

Supporting this view, we have found that β,γ-unsaturated sulfones are obtained when *aliphatic* aldehydes (which do not possess the benefits of conjugation, making them poorer leaving groups) are reacted with the carbanions derived from either of the chlorosulfones **5** or **12**. These products arise as a result of alkylation α to the phenylsulfonyl group.

Thus, reaction with isobutyraldehyde of the lithiated anion derived from **5** afforded 3,4-*anti*-1-chloro-5-methyl-3-phenylsulfonylhex-1-en-4-ol **28** (75%), together with the deconjugated chloro-compound **12** (20%). No γ-alkylated compounds were observable, even in the crude reaction product.

The $^1$H NMR spectrum of **28** revealed that there was no apparent vicinal coupling $J_{3,4}$ between the two methine protons C*H*OH–C*H*$SO_2$Ph. Small vicinal coupling constants (~1.0–2.5 Hz) for analogous protons have previously been reported for a number of simple *anti*-configured β-hydroxysulfones.[15] Notably, the –C*H*OH proton H-4 of **28** resonates at rather low field ($\delta$ 4.23 ppm), and exhibits a large vicinal coupling constant of 9.0 Hz to neighbouring H-5, suggesting a strong conformational preference in solution.[16] The assignment to H-4 of the resonance at $\delta$ 4.23 ppm rather than a similar 10.5 Hz doublet at $\delta$ 4.33 ppm is based upon the clear coupling of the latter to its neighbouring olefinic proton. The structure of **28** was fully

confirmed by a single-crystal X-ray structure determination[17] which revealed (Fig. 2) a dihedral angle of almost 90° between H-3 and H-4.

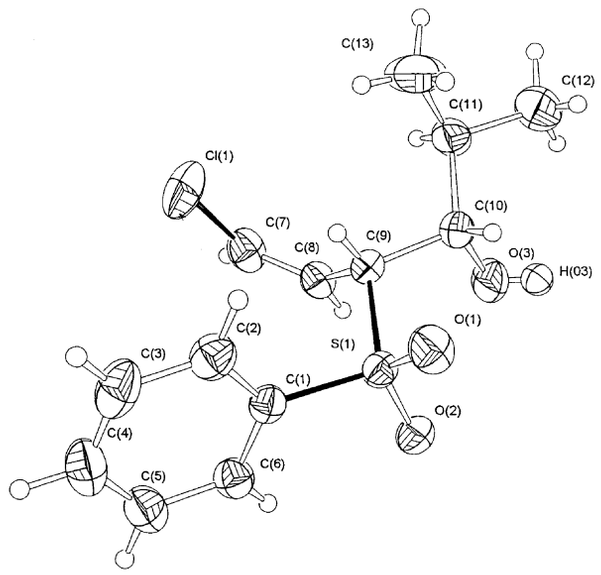
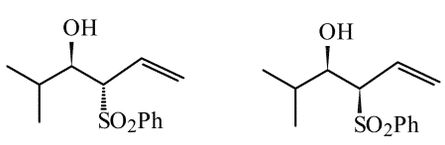



**Fig. 2**

The regioselectivity of the reaction between the lithiated chlorosulfone **5** and isobutyraldehyde to yield **28** contrasts sharply with that observed when an aromatic aldehyde is the electrophile, and is quite remarkably diastereoselective, but the possibility of base-catalysed retro-aldol reactions that lead to *syn–anti* interconversion under the conditions that were employed cannot be ruled out.

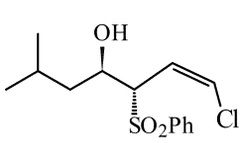
However, we have shown that reaction of the lithio derivative of 1-phenylsulfonylprop-2-ene **9** with isobutyraldehyde under similar conditions yields *both* of the possible diastereoisomeric products of α-alkylation, *viz.*, the *anti*-compound **29** (54%) and its *syn*-isomer **30** (9%). The $^1$H NMR spectrum of *anti*-**29** is very similar to that of the analogous chloro-derivative **28**. In particular, the methine protons which are α to the sulfonyl and hydroxyl groups are not mutually coupled. Contrastingly, the corresponding methine protons of the *syn*-diastereoisomer **30** resonate as apparent triplets, exhibiting vicinal coupling constants $J$ of *ca.* 9.7 Hz (*cf.*[15]).




**29**



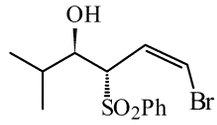

**30**




**31**

The carbanion derived from the chlorosulfone **5** reacted with isovaleraldehyde to give the *anti*-configured hydroxy-sulfone **31** (65%), the vinylic chloride **12** (30%) and two very minor products (5%). The $^1$H NMR spectrum of **31** again revealed that the methine protons adjacent to the hydroxyl and sulfonyl groups were not mutually coupled, confirming its *anti*-stereochemistry.

When the bromo-sulfone **8** was lithiated and reacted with isobutyraldehyde in the usual way the outcome of the reaction was not as clean as was the case when the chlorides **5** or **12** were employed. Nevertheless, the $^1$H NMR spectrum of the crude product mixture indicated that its major component was the *anti*-diastereoisomer of the β-hydroxysulfone **32**.




**32**

When the iodo-sulfone **7** was lithiated in the presence of isobutyraldehyde, a product mixture was obtained which contained (NMR) recovered starting material **7**, 1-phenylsulfonylprop-2-ene **9** and the *anti*-β-hydroxysulfone **29** in the ratio 8 : 6 : 3. We account for the formation of compounds **9** and **29** by assuming that the anion initially formed from the iodide **7** abstracts iodine from unreacted starting material to generate the anion of allyl phenyl sulfone together with an α,α-di-iodo compound which does not survive the work-up procedure.

## Experimental

Unless otherwise stated, $^1$H NMR spectra were recorded for solutions in $CDCl_3$ using JEOL PMX-60, Bruker WP-80, Bruker MSL 300 MHz or Bruker Avance DPX 400 MHz spectrometers. Coupling constants are given in Hz. Assignments were verified where appropriate by $^1$H–$^1$H COSY, $^1$H–$^{13}$C COSY and DEPT experiments. IR spectra were recorded for Nujol mulls (N) or liquid films (L) between sodium chloride plates using Perkin-Elmer 883 or Paragon 1000 spectrometers. Mass spectra were obtained at the University of Edinburgh using a Kratos instrument. Melting points (uncorrected) were measured in unsealed capillary tubes using a Stuart Scientific SMP2 digital apparatus or an Electrothermal IA9100 apparatus. Thin layer chromatography was carried out using Merck Kieselgel 60 $F_{254}$ 0.2 mm silica gel plates. Column chromatography was carried out using Merck Kieselgel 60 (70–230 mesh) silica gel. All solvents were dried and distilled before use. Ethereal extracts of reaction products were dried over anhydrous magnesium sulfate. Combustion analyses were obtained from the Microanalytical Laboratory, University College, Dublin.

### Crystal data for 28

$C_{13}H_{17}Cl_1O_3S$, $M$ = 288.78. Triclinic, $a$= 8.4685(9), $b$ = 8.7296(9), $c$ = 11.4820(13) Å, $V$ = 712.29(13) Å$^3$, space group $P1$, $Z$ = 2, $D$ (calculated) = 1.346 g cm$^{-3}$, crystal dimensions 0.45 × 0.3 × 0.6 mm.

**Data collection and processing.** Enraf-Nonius CAD-4 diffractometer, temperature 293(2) K, wavelength 0.71073 Å, absorption coefficient 0.412 mm$^{-1}$, theta range for data collection 1.85 to 24.98°, 2635 reflections collected, index ranges $0 \le h \le 9$; $-9 \le k \le 9$; $-12 \le l \le 12$, 2450 independent reflections [$R$(int) = 0.0124].

**Structure analysis and refinement.** The structure was solved by direct methods and refined by full matrix least squares analysis on $F^2$. Data were corrected for Lorentz and polarisation effects but not for absorption. Hydrogen atoms were included in calculated positions with thermal parameters 30% larger than the atom to which they were attached. The non-hydrogen atoms were refined anisotropically. Final $R$ indices [$I \ge 2\sigma(I)$] were $R_1$ = 0.0391 and w$R_2$ = 0.0972. The ORTEX program was used to obtain the drawings.[18]

### (*E*)-3-Chloro-1-phenylsulfonylprop-1-ene 5

This was prepared according to the literature procedure[9] and was obtained as needles, mp 58 °C (ethanol–hexane) (*lit.*[9] mp

58.5 °C); $\nu_{max}$(N) 1279 and 1144 cm$^{-1}$; $\delta_H$ (300 MHz) 4.19 (2H, dd, *J* 5.2 and 1.7, –C*H*$_2$Cl), 6.66 (1H, dt, *J* 14.7 and 1.8, –SO$_2$C*H*=CH–), 7.03 (1H, dt, *J* 14.8 and 5.2, –CH=C*H*CH$_2$Cl), 7.55 (2H, m, *m*-ArH), 7.63 (1H, m, *p*-ArH) and 7.63 (2H, d, *J* 8.0, *o*-ArH) ppm; $\delta_C$ (75 MHz) 41.25 (–*C*H$_2$Cl), 127.8 (*o*-Ar*C*), 129.4 (*m*-Ar*C*), 133.4 (–SO$_2$*C*H=C–), 133.7 (*p*-Ar*C*), 139.66 (quaternary Ar) and 139.8 (–*C*=*C*HCH$_2$Cl) ppm.

**(*E*)-3-Iodo-1-phenylsulfonylprop-1-ene 7**

This was obtained according to the literature[9] procedure and had mp 62 °C (*lit.*[9] mp 67–68 °C); $\nu_{max}$(N) 1305 and 1146 cm$^{-1}$; $\delta_H$ (400 MHz) 3.89 (2H, dd, *J* 8.0 and 1.0, –C*H*$_2$I), 6.43 (1H, dd, *J* 15.0 and 1.0, –SO$_2$C*H*=CH–), 7.07 (1H, dt, *J* 15.0 and 8.0, –CH=C*H*CH$_2$I), 7.57 (2H, m, *m*-Ar*H*), 7.65 (1H, m, *p*-Ar*H*) and 7.88 (2H, d, *J* 7.9, *o*-Ar*H*) ppm; $\delta_C$ (100 MHz) −2.02 (–*C*H$_2$I), 127.7 (*o*-Ar*C*), 129.3 (*m*-Ar*C*), 132.2 (–SO$_2$*C*H=C–), 133.6 (*p*-Ar*C*), 139.76 (quaternary-Ar*C*) and 141.3 (–CH=*C*HCH$_2$I) ppm.

**(*E*)-3-Bromo-1-phenylsulfonylprop-1-ene 8**

1,2-Dibromo-3-phenylsulfonylpropane **10** was prepared according to the method of Eisch and Galle[11] when it had mp 75 °C (*lit.*[11] mp 78–79 °C). The dibromide **10** (3.0 g) was dissolved in chloroform (30 cm$^3$) with triethylamine (0.89 g; 1 eq.). After 5 min, the mixture was washed sequentially with dilute hydrochloric acid and with water, dried and evaporated to give an oily solid which was recrystallised (ether–hexane) to give the bromide **8** (1.6 g; 70%), mp 50–51 °C (*lit.*[9] mp 34–35 °C); $\nu_{max}$(N) 1303 and 1145 cm$^{-1}$; $\delta_H$ (400 MHz) 4.10 (2H, d, *J* 6.9, –C*H*$_2$Br), 6.68 (1H, dt, *J* 16.0 and 1.4, –SO$_2$C*H*=CH–), 7.16 (1H, dt, *J* 14.9 and 6.9, –CH=C*H*CH$_2$Br), 7.56 (2H, m, *m*-Ar*H*), 7.65 (1H, dt, *J* 7.5 and 1.3, *p*-Ar*H*) and 7.89 (2H, d, *J* 8.0, *o*-Ar*H*) ppm; $\delta_C$ (100 MHz) 26.9 (–*C*H$_2$), 127.4 (*o*-Ar*C*), 129.0 (*m*-Ar*C*), 133.3 (–SO$_2$–*C*H=CH–), 133.6 (*p*-Ar*C*), 139.1 (–SO$_2$–CH=*C*H–) and 139.2 (quaternary Ar*C*) ppm.

**(*Z*)-1-Bromo-3-phenylsulfonylprop-1-ene 11**

(*E*)-3-Bromo-1-phenylsulfonylpropene **8** (1.0 g) was stirred with triethylamine (0.39 g) in chloroform (10 cm$^3$) for 2 h. The reaction mixture was then washed with dilute hydrochloric acid and with water, dried and evaporated to give the bromo-sulfone **11** as a thick brown oil that contained *ca.* 10% of unchanged starting material **8** from which it could not be separated; $\nu_{max}$(L) 1338 and 1138 cm$^{-1}$; $\delta_H$ (60 MHz) 4.0 (2H, d, *J* 7.0, –C*H*$_2$Br), 6.4 (2H, m, –C*H*=C*H*Br) and 7.66 (5H, m, Ar*H*) ppm.

**(*Z*)-1-Chloro-3-phenylsulfonylprop-1-ene 12**

The (*E*)-chloro-sulfone **5** (5.0 g) was stirred with triethylamine (2.34 g) in chloroform (50 cm$^3$) for 75 min. After this time, the reaction mixture was washed with dilute hydrochloric acid and with water, dried and evaporated to yield a solid which was recrystallised (hexane–benzene) to give the chloride **12** (3.5 g; 70%) as needles, mp 43 °C (*lit.*[13] mp 43–44 °C); $\nu_{max}$(N) 1338 and 1138 cm$^{-1}$; $\delta_H$ (300 MHz) 4.04 (2H, dd, *J* 7.7 and 1.2, –C*H*$_2$SO$_2$–), 5.88 (1H, q, *J* 7.7, –CH$_2$C*H*=CH–), 6.27 (1H, d, *J* 7.3, –C*H*Cl), 7.53 (2H, m, *m*-Ar*H*), 7.63 (1H, m, *p*-Ar*H*) and 7.87 (2H, d, *J* 8.0, *o*-Ar*H*) ppm; $\delta_C$ (75 MHz) 54.61 (–*C*H$_2$SO$_2$–), 118.5 (–C=*C*Cl), 126.1 (*o*-Ar*C*), 128.3 (*m*-Ar*C*), 129.1 (–CH$_2$–*C*H=C–), 133.9 (*p*-Ar*C*) and 138.1 (quaternary Ar*C*) ppm.

**General procedure for reaction of the carbanions derived from the sulfones 5, 7, 8, 11 or 12 with aldehydes**

*n*-Butyllithium (2.5 M in hexane; 3.6 mmol; 1.2 eq.) was added, under nitrogen, to dry THF cooled to −18 °C using an ice–salt bath. A solution of an aldehyde (3 mmol; 1 eq.) and a sulfone (3 mmol; 1 eq.) in THF (10 cm$^3$ g$^{-1}$ of sulfone) was added to the solution of butyllithium. After stirring for 2 h at *ca.* −15 °C the reaction was quenched by the addition of water. The products were extracted with ether in the usual way and the combined extract was dried and evaporated under reduced pressure. Products were generally purified by column chromatography using ether–hexane 2 : 3 as eluant and then, if solids, were recrystallised from the solvents indicated.

***(Z)*-2-Chloro-1-phenyl-4-phenylsulfonylbut-2-en-1-ol 15a.** **15a** was obtained from benzaldehyde and either of the lithiated sulfones **5** (72%) or **12** (68%) as a *solid*, mp 77 °C (ether–hexane); $\nu_{max}$ 3481, 1311 and 1145 cm$^{-1}$; $\delta_H$ (300 MHz) 2.90 (1H, br s, exch. D$_2$O, –O*H*), 4.05 (2H, d, *J* 7.7, –C*H*$_2$SO$_2$–), 5.19 (1H, s, –C*H*OH), 6.16 (1H, dt, *J* 7.8 and 1.1, –CH$_2$C*H*=C–), 7.27 (5H, m, Ar*H*), 7.45 (2H, m, *m*-Ar*H*–SO$_2$), 7.61 (1H, tt, *J* 7.6 and 1.3, *p*-Ar*H*–SO$_2$) and 7.83 (2H, d, *J* 8.0, *o*-Ar*H*–SO$_2$) ppm; $\delta_C$ (75 MHz) 55.86 (–*C*H$_2$SO$_2$), 76.8 (–*C*HOH), 113.4 (–CH$_2$–*C*=C–), 126.7 (*o*-Ar*C*), 128.3 (*o*-Ar*C*–SO$_2$–), 128.5 (*m*-Ar*C* and *p*-Ar*C*), 129.13 (*m*-Ar*C*–SO$_2$), 133.9 (*p*-Ar*C*–SO$_2$), 138.24 (quaternary, Ar*C*–SO$_2$), 139.2 (quaternary, Ar*C*) and 143.8 (quaternary, –CH$_2$CH=*C*Cl) ppm. [*Found:* C 59.70, H 4.80. C$_{16}$H$_{15}$ClO$_3$S *requires:* C 59.53, H 4.68%.]

***(Z)*-2-Chloro-1-(4′-chlorophenyl)-4-phenylsulfonylbut-2-en-1-ol 15b.** **15b** was obtained from 4-chlorobenzaldehyde and either of the lithiated sulfones **5** (62%) or **12** (63%) as a *solid*, mp 106 °C (ether–hexane); $\nu_{max}$ (N) 1338 and 1138 cm$^{-1}$; $\delta_H$ (300 MHz) 2.61 (1H, br s, exch. D$_2$O, –O*H*), 4.07 (2H, d, *J* 7.7, –C*H*$_2$SO$_2$–), 5.19 (1H, s, –C*H*OH), 6.16 (1H, dt, *J* 7.7 and 1.0, –CH$_2$C*H*=C–), 7.18 (2H, m, *o*-Ar*H*–Cl), 7.29 (2H, m, *m*-Ar*H*–Cl), 7.48 (2H, m, *m*-Ar*H*–SO$_2$), 7.65 (1H, tt, *J* 7.5 and 1.3, *p*-Ar*H*–SO$_2$) and 7.87 (2H, d, *J* 8.0, *o*-Ar*H*–SO$_2$) ppm; $\delta_C$ (75 MHz) 55.8 (–*C*H$_2$SO$_2$–), 76.8 (–*C*HOH), 113.5 (–CH$_2$*C*H=C–), 128.0 (*o*-Ar*C*–Cl), 128.3 (*o*-Ar*C*–SO$_2$), 128.7 (*m*-Ar*C*–Cl), 129.2 (*m*-Ar*C*–SO$_2$), 134.0 (*p*-Ar*C*–SO$_2$), 134.3 (quaternary, Ar*C*–Cl), 137.7 (quaternary, Ar*C*–SO$_2$), 138.3 (quaternary, Ar*C*–Cl) and 143.5 (quaternary, –CH=*C*Cl) ppm. Irradiation of the –C*H*OH proton at $\delta$ 5.19 enhanced the olefinic proton signal at $\delta$ 6.16 by 8.5% and the signal for the 2′-protons of the adjacent *p*-Cl–C$_6$H$_4$ ring by 8.6%. Irradiation of the olefinic proton signal at $\delta$ 6.16 enhanced the methylene proton resonance at $\delta$ 4.07 by 5.5%. Irradiation of the methylene signal enhanced the resonance due to the *o*-protons of the adjacent C$_6$H$_5$ ring by 3.2%. [*Found:* C 53.97, H 4.03. C$_{16}$H$_{14}$Cl$_2$O$_3$S *requires:* C 53.79, H 3.98%.]

***(Z)*-2-Chloro-1-(2′-methoxyphenyl)-4-phenylsulfonylbut-2-en-1-ol 15c.** **15c** was obtained from 2-methoxybenzaldehyde and either of the lithiated sulfones **5** (72%) or **12** (71% after purification by column chromatography) as an *oil*, $\nu_{max}$(L) 3489, 1309 and 1145 cm$^{-1}$; $\delta_H$ (300 MHz) 2.25 (1H, br s, exch. D$_2$O, –O*H*), 3.86 (3H, s, –OC*H*$_3$), 4.03 (2H, dd, *J* 7.7 and 3.2, –C*H*$_2$SO$_2$–), 5.49 (1H, s, –C*H*OH), 6.08 (1H, dt, *J* 7.7 and 1.1, –CH$_2$C*H*=C–), 6.92 (2H, m, Ar*H*-OMe), 7.15 (1H, dd, *J* 7.6 and 1.7, Ar*H*-OMe), 7.32 (1H, dt, *J* 7.9 and 1.8, Ar*H*-OMe), 7.47 (2H, m, *m*-ArH–SO$_2$), 7.56 (1H, t, *J* 7.5, *p*-Ar*H*SO$_2$) and 7.81 (2H, d, *J* 7.9, *o*-Ar*H*–SO$_2$) ppm; $\delta_C$ (75 MHz) 55.4 (–O*C*H$_3$), 55.9 (–*C*H$_2$SO$_2$–), 72.5 (–*C*HOH), 110.6 (*o*-Ar*C*-OMe), 113.2 (–CH$_2$–*C*=CCl), 120.7 (*m*-Ar*C*-OMe), 127.1 (quaternary, Ar*C*-OMe), 128.0 (*p*-Ar*C*-OMe), 133.7 (*p*-Ar*C*–SO$_2$), 138.2 (quaternary, Ar*C*–SO$_2$), 143.1 (quaternary, –CH$_2$C=*C*Cl) and 156.6 (quaternary, Ar*C*-OMe) ppm. [*Found:* C 58.15, H 4.86. C$_{17}$H$_{17}$ClO$_4$S *requires:* C 57.87, H 4.86%.]

***(Z)*-2-Chloro-1-(3′-fluorophenyl)-4-phenylsulfonylbut-2-en-1-ol 15d.** **15d** was obtained from 3-fluorobenzaldehyde and either of the lithiated sulfones **5** (62%) or **12** (63% after purification by column chromatography) as an *oil*; $\nu_{max}$ (N) 3477, 1308 and 1146 cm$^{-1}$; $\delta_H$ (300 MHz) 3.30 (1H, br s, exch. D$_2$O, –O*H*), 4.05 (2H, d, *J* 7.7, –C*H*$_2$SO$_2$–), 5.19 (1H, s, –C*H*OH),

6.16 (1H, dt, *J* 7.67 and 0.9, –$CH_2CH$=C–), 6.98 (3H, m, *o*- and *p*-Ar*H*–F), 7.25 (1H, m, *m*-Ar*H*–F), 7.47 (2H, m, *m*-Ar*H*–$SO_2$), 7.65 (1H, t, *J* 7.6, *p*-Ar*H*–$SO_2$) and 7.87 (2H, d, *J* 8.0, *o*-Ar*H*–$SO_2$) ppm; $\delta_C$ (75 MHz) 55.7 (–$CH_2SO_2$–), 76.02 (–*C*HOH), 113.5 (d, *J* 21.0, *o*-Ar*C*–F), 113.7 (–$CH_2CH$=C–), 115.2 (d, *J* 21.0, *p*-Ar*C*–F), 122.3 (d, *J* 21.0, *o*-Ar*C*–F), 128.2 (*o*-Ar*C*–$SO_2$), 129.2 (*m*-Ar*C*–$SO_2$), 129.9 (d, *J* 7.6, *m*-Ar*C*–F), 134.0 (*p*-Ar*C*–$SO_2$), 137.9 (quaternary, Ar*C*–$SO_2$), 141.7 (quaternary, d, *J* 6.41, Ar*C*–F), 143.4 (quaternary, –CH=*C*–Cl) and 162.6 (quaternary, d, *J* 244, Ar*C*–F) ppm. [*Found:* C 56.49, H 4.35. $C_{16}H_{14}ClFO_3S$ *requires:* C 56.34, H 4.35%.]

### Oxidation of (*Z*)-2-chloro-1-(4′-chlorophenyl)-4-phenylsulfonylbut-2-en-1-ol 15b

The alcohol **15b** (0.8 g) was dissolved in ether (8 $cm^3$) and stirred at 0 °C with a solution (3.5 $cm^3$) containing sodium dichromate dihydrate (245 mg), concentrated sulfuric acid (0.17 $cm^3$) and water until no further change occurred (TLC). The mixture was then diluted with ether, washed sequentially with water and with aqueous sodium hydrogen carbonate solution, dried and evaporated. The crude oil so obtained (0.66 g) was chromatographed using ether–hexane 3 : 7 as eluant to separate the product *(Z)-2-chloro-1-(4′-chlorophenyl)-4-phenylsulfonylbut-2-en-1-one* **16b** (0.56 g; 71%), contaminated with the isomeric ketone *(E)-2-chloro-1-(4′-chlorophenyl)-4-phenylsulfonylbut-2-en-1-one* **17b**, from unreacted starting material (60 mg). The ketones **16b** and **17b** were obtained in 82 : 18 ratio as an *oil*; $\nu_{max}$(L) 1674, 1325 and 1145 $cm^{-1}$; $\delta_H$ (300 MHz) 4.01 (0.33H, d, *J* 8.3, (*E*)–C$H_2SO_2$–), 4.27 (1.66H, d, *J* 7.7, (*Z*)–C$H_2SO_2$–), 6.33 (0.18H, t, *J* 8.3, (*E*)–$CH_2CH$=C–), 6.56 (0.82H, t, *J* 7.7, (*Z*)–$CH_2CH$=C–) and 7.25–7.95 (9H, overlapping ms, Ar*H*) ppm. [*Found:* C 53.75, H 3.69. $C_{16}H_{12}Cl_2O_3S$ *requires:* C 54.08, H 3.38%.]

### Attempted acid-catalysed isomerisation of the ketones 16b and 17b

The 82 : 18 mixture of the isomeric ketones **16b** and **17b** described above (0.12 g) was refluxed with methanesulfonic acid (0.1 g) in benzene (5 $cm^3$) for 2 h and then left at rt overnight. The mixture was diluted with ether, washed with water and with sodium hydrogen carbonate solution, dried and evaporated to return the ketones in unaltered ratio. In another experiment, the mixture of ketones **16b** and **17b** was stirred with acetic acid (80%) containing a small amount of concentrated sulfuric acid. After the usual work-up, the ratio of (*Z*) : (*E*) isomers was virtually unchanged.

### Oxidation of (*Z*)-2-chloro-1-(2′-methoxyphenyl)-4-phenylsulfonylbut-2-en-1-ol 15c

This alcohol (0.2 g) was oxidised in ether (2 $cm^3$) with a solution (2.0 $cm^3$) containing sodium dichromate dihydrate (140 mg), concentrated sulfuric acid (0.1 $cm^3$) and water until no further change occurred (TLC). Work-up as described above for the oxidation of **15b** afforded a thick *oil* (0.17 g; 85%) which contained (NMR) *(Z)-2-chloro-1-(2′-methoxyphenyl)-4-phenylsulfonylbut-2-en-1-one* **16c** and *(E)-2-chloro-1-(2′-methoxyphenyl)-4-phenylsulfonylbut-2-en-1-one* **17c** in 8 : 1 ratio; $\nu_{max}$(L) 1678, 1289 and 1145 $cm^{-1}$; $\delta_H$ (300 MHz) 3.78 (0.33H, s, (*E*)-OC$H_3$), 3.80 (2.66H, s, (*Z*)-OC$H_3$), 4.21 (2H, d, *J* 7.8, (*Z*)- and (*E*)-C$H_2SO_2$–), 6.25 (0.11H, t, *J* 8.1, (*E*)-$CH_2CH$=C–), 6.59 (0.88H, t, *J* 7.8, (*Z*)-$CH_2CH$=C–) and 6.66–6.80 (9H, overlapping ms, Ar*H*) ppm.

### Oxidation of (*Z*)-2-chloro-1-(3′-fluorophenyl)-4-phenylsulfonylbut-2-en-1-ol 15d

This alcohol (0.2 g) was oxidised in ether (2 $cm^3$) with a solution (2.0 $cm^3$) containing sodium dichromate dihydrate (140 mg), concentrated sulfuric acid (0.1 $cm^3$) and water until no further change occurred (TLC). Work-up as described above for the oxidation of **15b** afforded an *oil* (0.16 g; 87%) which contained (NMR) *(Z)-2-chloro-1-(3′-fluorophenyl)-4-phenylsulfonylbut-2-en-1-one* **16d** and *(E)-2-chloro-1-(3′-fluorophenyl)-4-phenylsulfonylbut-2-en-1-one* **17d** in 5 : 1 ratio; $\nu_{max}$(L) 1675, 1288 and 1143 $cm^{-1}$; $\delta_H$ (300 MHz) 4.01 (0.33H, d, *J* 8.2, (*E*)-C$H_2SO_2$–), 4.27 (1.66H, d, *J* 7.7, (*Z*)-C$H_2SO_2$–), 6.32 (0.17H, t, *J* 8.2, (*E*)-$CH_2CH$=C–), 6.56 (0.83H, t, *J* 7.7, (*Z*)-$CH_2CH$=C–) and 7.25–7.92 (9H, overlapping ms, Ar*H*) ppm.

### Reduction of (*Z*)-2-chloro-1-(3′-fluorophenyl)-4-phenylsulfonylbut-2-en-1-one 16d using sodium borohydride

The ketone **16d**, containing 20% of the (*E*)-isomer **17d**, (0.2 g), in methanol–water (90%; 2 $cm^3$), was reacted for 1 h with sodium borohydride (10 mg). The mixture was quenched with aqueous acetic acid, extracted with ether, washed with sodium hydrogen carbonate solution and with water, dried and evaporated to give only (NMR) the alcohol **15d** (0.185 g; 92%).

***(E)-trans-3,4-Epoxy-4-phenyl-1-phenylsulfonylbut-1-ene* 18a.** **18a** was obtained from benzaldehyde and either of the lithiated sulfones **7** (73%), **8** (75%) or **11** (72%) as a *solid*, mp 91 °C (ethyl acetate–hexane), which had $\nu_{max}$ (N) 1309 and 1149 $cm^{-1}$; $\delta_H$ (300 MHz) 3.49 (1H, dd, *J* 5.7 and 1.7, *H*-3), 3.82 (1H, br s, *H*-4), 6.68 (1H, d, *J* 14.9, *H*-1), 6.94 (1H, dd, *J* 15.0 and 5.7, *H*-2), 7.33–7.71 (8H, m, Ar*H*) and 7.90 (2H, d, *J* 7.9, *o*-Ar*H*–$SO_2$–) ppm; $\delta_C$ (100 MHz) 58.8 (*C*H), 61.2 (*C*H), 125.1 (Ar*C*), 127.4 (Ar*C*), 128.3 (Ar*C*), 128.5 (Ar*C*), 129.1 (Ar*C*), 132.4 (–$SO_2$–*C*H=C–), 133.3 (Ar*C*), 134.9 (quaternary, Ar*C*), 139.3 (quaternary, Ar*C*) and 141.0 (–$SO_2CH$=*C*–) ppm. [*Found:* C 67.07, H 4.92. $C_{16}H_{14}O_3S$ *requires:* C 67.13, H 4.89%.]

***(E)-trans-4-(4′-Chlorophenyl)-3,4-epoxy-1-phenylsulfonylbut-1-ene* 18b.** **18b** was obtained from 4-chlorobenzaldehyde and the lithiated sulfone **8** (75%) as a *solid*, mp 104–105 °C (ether–hexane), which had $\nu_{max}$ (N) 1343, 1146 and 1242 $cm^{-1}$; $\delta_H$ (300 MHz) 3.45 (1H, dd, *J* 5.7 and 1.8, *H*-3), 3.79 (1H, d, *J* 1.6, *H*-4), 6.68 (1H, d, *J* 15.0, *H*-1), 6.91 (1H, dd, *J* 15.0 and 5.7, *H*-2), 7.19 (2H, d, *J* 8.5, 2*H*-2′), 7.33 (2H, d, *J* 8.5, 2*H*-3′), 7.61 (3H, m, Ar*H*) and 7.90 (2H, d, *J* 8.0, *o*-Ar*H*–$SO_2$–) ppm; $\delta_C$ (100 MHz) 58.8 (*C*H), 60.5 (*C*H), 126.5 (Ar*C*), 127.4 (Ar*C*), 128.5 (Ar*C*), 129.3 (Ar*C*), 132.6 (–$SO_2$–*C*H=C–), 133.4 (Ar*C*), 133.5 (quaternary, Ar*C*), 134.2 (quaternary, Ar*C*), 139.2 (quaternary, Ar*C*) and 141.4 (–$SO_2CH$=*C*–) ppm. [*Found:* C 59.91, H 4.32. $C_{16}H_{13}ClO_3S$ *requires:* C 59.85, H 4.08%.]

***(E)-trans-3,4-Epoxy-4-(2′-methoxyphenyl)-1-phenylsulfonylbut-1-ene* 18c.** **18c** was obtained from 2-methoxybenzaldehyde and either of the lithiated sulfones **7** (75%), **8** (81%) or **11** (75%) as a *solid*, mp 120 °C (ethyl acetate–hexane), which had $\nu_{max}$ (N) 1343, 1147 and 1254 $cm^{-1}$; $\delta_H$ (400 MHz) 3.42 (1H, dd, *J* 5.5 and 1.5, *H*-3), 3.80 (3H, s, –OC$H_3$), 4.10 (1H, d, *J* 1.5, *H*-4), 6.70 (1H, d, *J* 15.0, *H*-1), 6.95 (3H, m, *H*-2 and Ar*H*), 7.13 (1H, dd, *J* 7.5 and 1.5, Ar*H*), 7.31 (1H, m, Ar*H*), 7.63 (3H, m, Ar*H*) and 7.94 (2H, d, *J* 8.5, *o*-Ar*H*–$SO_2$–) ppm; $\delta_C$ (100 MHz) 54.95 (–O*C*$H_3$), 57.2 (*C*H), 58.1 (*C*H), 109.8 (Ar*C*), 120.3 (Ar*C*), 123.5 (quaternary, Ar*C*), 124.5 (Ar*C*), 127.4 (Ar*C*), 128.9 (Ar*C*), 129.1 (Ar*C*), 132.0 (–$SO_2$–*C*H=C–), 133.2 (Ar*C*), 139.5 (quaternary, Ar*C*), 141.4 (–$SO_2CH$=*C*–) and 157.7 (quaternary, Ar*C*) ppm. [*Found:* C 65.54, H 5.13. $C_{17}H_{16}O_4S$ *requires:* C 64.54, H 5.10%.]

***(E)-trans-3,4-Epoxy-4-(3′-fluorophenyl)-1-phenylsulfonylbut-1-ene* 18d.** **18d** was obtained from 3-fluorobenzaldehyde and the lithiated sulfone **8** (80%) as a *solid*, mp 92.5 °C (ether–hexane), which had $\nu_{max}$ (N) 1316, 1146 and 1254 $cm^{-1}$; $\delta_H$ (300 MHz) 3.46 (1H, dd, *J* 5.7 and 1.8, *H*-3), 3.81 (1H, d, *J* 1.5, *H*-4), 6.68 (1H, d, *J* 15.0, *H*-1), 6.70–7.07 (4H, overlapping ms, *H*-2 and Ar*H*), 7.31 (1H, m, Ar*H*), 7.57 (2H, m, Ar*H*), 7.65 (1H,

m, Ar*H*) and 7.90 (2H, d, *J* 8.4, *o*-Ar*H*–$SO_2$–) ppm; $\delta_C$ (75 MHz) 59.2 (*C*H), 60.8 (*C*H), 112.2 (d, *J* 22.74, Ar*C*–F), 115.8 (d, *J* 20.6, Ar*C*–F), 121.4 (d, *J* 2.91, Ar*C*–F), 127.8 (Ar*C*), 129.4 (Ar*C*), 130.3 (quaternary, d, *J* 8, Ar*C*–F), 133.2 (Ar*C*), 133.7 (–$SO_2$–CH=*C*–), 137.0 (quaternary, d, *J* 8, Ar*C*–F), 139.6 (quaternary, Ar*C*), 140.7 (–$SO_2$*C*H=C–) and 163.0 (quaternary, d, *J* 244.9, Ar*C*–F) ppm. [*Found:* C 62.86, H 4.32. $C_{16}H_{13}FO_3S$ *requires:* C 63.14, H 4.31%.]

**(*E*)-4-(4′-Chlorophenyl)-1-phenylsulfonylbut-1-en-3-one 19**

The epoxide **18b** (0.32 g) in dichloromethane (20 $cm^3$) was treated with boron trifluoride etherate (1 eq.) for 1 h. The mixture was then diluted with ether and the extract was washed with water, dried and evaporated to give a crude solid product which (NMR) contained the title compound together with about 4% of the aldehyde **20** (NMR). The crude product was triturated with ether to give the *ketone* **19** as a *solid* (0.26 g) which could not be satisfactorily purified by recrystallisation; $\nu_{max}$(N) 1700, 1338 and 1157 $cm^{-1}$; $\delta_H$ (300 MHz) 3.89 (2H, s, –C$H_2$C=O), 7.11 (1H, d, *J* 15.1, –$SO_2$C*H*=CH–), 7.12 (2H, d, *J* 8.5, Ar*H*–Cl), 7.21 (1H, d, *J* 15.0, –$SO_2$CH=C*H*–), 7.32 (2H, d, *J* 8.5, Ar*H*–Cl), 7.60 (2H, apparent t, *J* 8.0 and 7.5, Ar*H*–$SO_2$), 7.71 (2H, t, *J* 7.5, Ar*H*–$SO_2$) and 7.88 (2H, d, *J* 8.0, Ar*H*–$SO_2$) ppm; $\delta_C$ (100 MHz) 48.7 (*C*$H_2$), 128.3 (Ar*C*), 129.3 (Ar*C*), 129.6 (Ar*C*), 130.9 (Ar*C*), 133.6 (quaternary, Ar*C*$SO_2$–), 134.4 (Ar*C*), 134.6 (–$SO_2$*C*H=CH–), 138.4 (quaternary, Ar*C*), 141.4 (–$SO_2$CH=*C*H–) and 194.21 (quaternary, *C*=O) ppm; HRMS: *m*/*z* 320.02740. *Calculated* for $C_{16}H_{13}ClO_3S$: 320.02739.

**(1*Z*)-3,4-*anti*-1-Chloro-5-methyl-3-phenylsulfonylhex-1-en-4-ol 28**

This was obtained from the lithiated sulfone **5** (0.65 g) and isobutyraldehyde (0.216 g) as a *solid* (0.62 g; 72%), mp 106 °C (ether–pentane), which had $\nu_{max}$(N) 3493, 1305 and 1146 $cm^{-1}$; $\delta_H$ (300 MHz) 0.83 (3H, d, *J* 6.6, –C$H_3$), 1.01 (3H, d, *J* 6.6, –C$H_3$), 1.60 (1H, m, *J* 6.6 and 2.2, –C*H*($CH_3$)$_2$), 3.2 (1H, d, *J* 1.8, exch. $D_2O$, –O*H*), 4.23 (1H, d, *J* 9.0, –C*H*OH), 4.33 (1H, d, *J* 10.5, –C*H*$SO_2$–), 6.14 (1H, dd, *J* 10.5 and 7.2, –C*H*=CHCl), 6.28 (1H, d, *J* 7.2, –CH=C*H*Cl), 7.54 (2H, m, Ar*H*), 7.65 (1H, t, *J* 7.6, Ar*H*) and 7.86 (2H, d, *J* 8.6, Ar*H*) ppm; $\delta_C$ (75 MHz) 18.5 (*C*$H_3$), 19.0 (*C*$H_3$), 32.2 (–*C*H($CH_3$)$_2$), 65.5 (–C*H*$SO_2$–), 73.3 (–C*H*OH–), 120.2 (–C=*C*HCl), 126.7 (–C*H*=CHCl), 128.9 (overlapping signals, Ar*C*atoms), 134.1 (Ar*C*) and 137.2 (quaternary, Ar*C*) ppm; HRMS: *m*/*z* 289.06558. *Calculated* for $C_{13}H_{18}ClO_3S$: 289.06651.

**3,4-*anti*-5-Methyl-3-phenylsulfonylhex-1-en-4-ol 29 and 3,4-*syn*-5-methyl-3-phenylsulfonylhex-1-en-4-ol 30**

To 1-phenylsulfonylprop-2-ene **9** (0.74 g) in dry THF (5 $cm^3$), cooled to −78 °C under nitrogen, was added *n*-butyllithium (2.5 M in hexane, 1.76 $cm^3$, 1.2 eq.). After 5 min, isobutyraldehyde (0.29 g) in THF (1 $cm^3$) was added and the mixture was stirred for 1 h. It was then brought to rt, quenched with water and extracted with ether. The ethereal extract was washed with water, dried and evaporated to give a crude oily product (0.98 g) which was chromatographed using ethyl acetate–hexane 1 : 9 as eluant to give recovered starting material **9** (37%) and the *hydroxysulfones* **29** and **30**.

***3,4-anti-5-Methyl-3-phenylsulfonylhex-1-en-4-ol* 29. 29** was obtained as a *solid* (54%), mp 88–89 °C (ether–pentane), which had $\nu_{max}$(N) 3518, 1307 and 1146 $cm^{-1}$; $\delta_H$ (400 MHz) 0.78 (3H, d, *J* 6.8, –C$H_3$), 1.02 (3H, d, *J* 6.6, –C$H_3$), 1.65 (1H, m, –C*H*($CH_3$)$_2$), 3.05 (1H, s, exch. $D_2O$, –O*H*), 3.64 (1H, d, *J* 10.1, –$SO_2$C*H*–), 4.07 (1H, d, *J* 9.1, –C*H*OH–), 5.01 (1H, dd, *J* 17.3 and 1.2, –CH=C$H_a$H), 5.36 (1H, d, *J* 10.3, –CH=C$H_b$H), 6.02 (1H, dt, *J* 17.3, 10.1 and 10.1, –C*H*=$CH_2$), 7.52 (2H, m, Ar*H*), 7.65 (1H, m, Ar*H*) and 7.85 (2H, d, *J* 8.6, *o*-ArH) ppm; $\delta_C$ (100 MHz) 18.3 (*C*$H_3$), 19.1 (*C*$H_3$), 31.9 (–*C*H($CH_3$)$_2$), 71.9 (–*C*H$SO_2$–), 73.3 (–*C*HOH–), 125.4 (–CH=*C*$H_2$), 125.8 (–*C*H=$CH_2$), 128.9 (Ar*C*), 129.0 (Ar*C*), 133.9 (Ar*C*) and 137.2 (quaternary, Ar*C*) ppm; HRMS: *m*/*z* 254.09761. *Calculated* for $C_{13}H_{18}O_3S$: 254.09766.

***3,4-syn-5-Methyl-3-phenylsulfonylhex-1-en-4-ol* 30. 30** was obtained as an *oil* (9%), which had $\nu_{max}$(L) 3518, 1306 and 1148 $cm^{-1}$; $\delta_H$ (400 MHz) 0.83 (3H, d, *J* 6.6, –C$H_3$), 1.08 (3H, d, *J* 6.8, –C$H_3$), 1.74 (1H, m, –C*H*($CH_3$)$_2$), 3.66 (1H, t, *J* 9.7, –$SO_2$C*H*–), 3.96 (1H, s, exch. $D_2O$, –O*H*), 4.20 (1H, d, *J* 9.8, –C*H*OH–), 4.97 (1H, d, *J* 17.0, –CH=C$H_a$H), 5.26 (1H, d, *J* 10.0, –CH=C$H_b$H), 5.53 (1H, dt, *J* 17.0, 10.2 and 10.2, –C*H*=$CH_2$), 7.57 (2H, m, Ar*H*), 7.67 (1H, m, Ar*H*) and 7.86 (2H, d, *J* 8.3, *o*-ArH) ppm; $\delta_C$ (100 MHz) 12.5 (*C*$H_3$), 19.6 (*C*$H_3$), 31.1 (–*C*H($CH_3$)$_2$), 71.4 (–*C*H$SO_2$–), 74.2 (–*C*HOH–), 123.4 (–CH=*C*$H_2$), 127.2 (–*C*H=$CH_2$), 128.4 (Ar*C*), 128.9 (Ar*C*), 133.5 (Ar*C*) and 137.2 (quaternary, Ar*C*) ppm; HRMS: *m*/*z* 254.09768. *Calculated* for $C_{13}H_{18}O_3S$: 254.09766.

**(1*Z*)-3,4-*anti*-1-Chloro-6-methyl-3-phenylsulfonylhept-1-en-4-ol 31**

This was obtained from the lithiated sulfone **5** (0.64 g) and isovaleraldehyde (0.26 g) as an *oil* which was purified by column chromatography using ether–hexane 2 : 3 as eluant to give pure material (0.63 g) that had $\nu_{max}$(N) 3521, 1305 and 1149 $cm^{-1}$; $\delta_H$ (400 MHz) 0.92 (3H, d, *J* 6.6, –C$H_3$), 0.95 (3H, d, *J* 6.6, –C$H_3$), 1.16 (1H, m, –C$H_a$–CH($CH_3$)$_2$), 1.50 (1H, m, –C*H*($CH_3$)$_2$), 1.79 (1H, m, –C$H_b$–CH($CH_3$)$_2$), 3.11 (1H, s, exch. $D_2O$, –O*H*), 4.19 (1H, d, *J* 10.5, –C*H*$SO_2$–), 4.78 (1H, dd, *J* 8.8 and 4.1, C*H*OH), 6.16 (1H, dd, *J* 10.5 and 7.4, –C*H*=CHCl), 6.36 (1H, d, *J* 7.4, –CH=C*H*Cl), 7.58 (2H, m, Ar*H*), 7.71 (1H, t, *J* 7.6, Ar*H*) and 7.91 (2H, d, *J* 8.6, *o*-ArH) ppm; $\delta_C$ (75 MHz) 21.9 (*C*$H_3$), 22.8 (*C*$H_3$), 24.3 (–*C*H($CH_3$)$_2$), 43.3 (*C*$H_2$), 66.4 (–C*H*$SO_2$–), 67.4 (–C*H*OH–), 119.8 (–C=*C*HCl), 127.0 (–C*H*=CHCl), 128.4 (Ar*C*), 129.0 (Ar*C*), 134.1 (Ar*C*) and 137.1 (quaternary, Ar*C*) ppm; HRMS: *m*/*z* 303.08146. *Calculated* for $C_{14}H_{20}ClO_3S$: 303.08217.

**Reaction of lithiated (*E*)-3-bromo-1-phenylsulfonylpropene 8 with isobutyraldehyde**

This was carried out as described above for the reaction of the lithiated chlorosulfone **5** with isobutyraldehyde and yielded a product mixture which contained principally (on the basis of its NMR spectrum) (1*Z*)-3,4-*anti*-1-bromo-5-methyl-3-phenylsulfonylhex-1-en-4-ol **32**.

**Reaction of lithiated (*E*)-3-iodo-1-phenylsulfonylpropene 7 with isobutyraldehyde**

This was carried out as described above for the reaction of the lithiated chlorosulfone **5** with isobutyraldehyde and yielded a product mixture which contained (NMR) unreacted iodide **7** (47%), 1-phenylsulfonylprop-2-ene **9** (35%) and 3,4-*anti*-4-hydroxy-5-methyl-3-phenylsulfonylhex-1-ene **29** (18%).

## Acknowledgements

We thank Forbairt, the V. K. Krieble Fund and the Trinity Trust for financial support to E. T. G., Dr Sylvia M. Draper for carrying out the X-ray crystallographic analysis, Dr John O'Brien for NMR spectra and Dr Neil Work for some preliminary experiments.

## References

1 N. S. Simpkins, *Sulfones in Organic Synthesis*, Pergamon Press, Oxford, 1993.
2 N. S. Simpkins, *Tetrahedron*, 1990, **46**, 6951.

3 P. Ongoka, B. Mauze and L. Miginiac, *J. Organomet. Chem.*, 1985, **284**, 139.
4 K. Mallaiah, J. Satyanarayana, H. Ila and H. Junjappa, *Tetrahedron Lett.*, 1993, **34**, 3145.
5 S. Florio and L. Troisi, *Tetrahedron Lett.*, 1996, **37**, 4777.
6 A. Jonczyk, K. Banko and M. Makosza, *J. Org. Chem.*, 1975, **40**, 266.
7 P. F. Vogt and D. F. Tavares, *Can. J. Chem.*, 1969, **47**, 2875.
8 F. Bohlmann and G. Haffer, *Chem. Ber.*, 1969, **102**, 4017.
9 C. C. J. Culvenor, W. Davies and W. E. Savige, *J. Chem. Soc.*, 1949, 2198.
10 F. G. Bordwell and G. D. Cooper, *J. Am. Chem. Soc.*, 1951, **73**, 5184; F. G. Bordwell and B. B. Jarvis, *J. Org. Chem.*, 1967, **33**, 1182.
11 J. J. Eisch and J. E. Galle, *J. Org. Chem.*, 1979, **44**, 3277.
12 K. Inomata, S. Sasaoka, T. Kobayashi, Y. Tanaka, S. Igarashi, T. Ohtani, H. Kinoshita and H. Kotake, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 1767; T. Kobayashi, Y. Tanaka, T. Ohtani, H. Kinoshita, K. Inomata and H. Kotake, *Chem. Lett.*, 1987, 1209; K. Inomata, T. Hirata, H. Suhara, H. Kinoshita, H. Kotake and H. Senda, *Chem. Lett.*, 1988, 2009; K. Inomata, T. Hirata, Y. Sasada, T. Asada, H. Senda and H. Kinoshita, *Chem. Lett.*, 1990, 2153.
13 V. N. Mikhailova, A. D. Bulat and V. P. Yurevich, *Zh. Org. Khim.*, 1970, **6**, 1256.
14 S. Igarashi, O Yoshihisa, Y. Nishida, H. Kinoshita and K. Inomata, *Chem. Lett.*, 1985, 931; S. Igarashi, Y. Haruta, M. Ozawa, Y. Nishide, H. Kinoshita and K. Inomata, *Chem. Lett.*, 1989, 737.
15 W. E. Truce and T. C. Klingler, *J. Org. Chem.*, 1970, **35**, 1834.
16 C. Alvarez-Ibarra, R. Cuervo-Rodriguez, M. C. Fernadez-Monreal and M. P. Ruiz, *Tetrahedron*, 1996, **52**, 11239. These authors concluded that the solution conformations of β-hydroxysulfones were determined by polar interactions rather than by steric effects or by intramolecular hydrogen-bonding.
17 Additional data available for structure **28** includes tables of atomic coordinates and of bond lengths and angles. CCDC reference number 200535. See http://www.rsc.org/suppdata/ob/b3/b300925b/ for crystallographic data in .cif or other electronic format.
18 P. McArdle, *J. Appl. Crystallogr.*, 1995, **28**, 65.