# Synthesis and Highly Diastereoselective Nucleophilic Epoxidation of *N*-(*p*-Tolylsulfonyl)vinylsulfoximines

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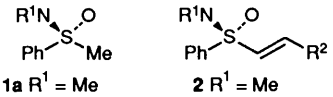
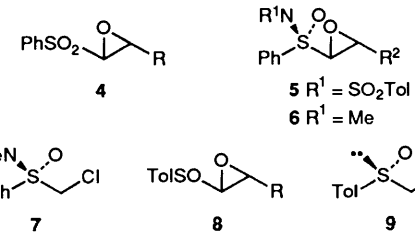
*N*-(*p*-Tolylsulfonyl)vinylsulfoximines **3** may be prepared in good yield in a one-pot process by reaction of lithiated *S*-methyl-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfoximine with aldehydes, followed by elimination using methanesulfonyl chloride–triethylamine. The vinylsulfoximines are formed as *E*-isomers with high selectivity. In one case, the stereochemistry of the double bond was confirmed by an X-ray crystal structure determination. Nucleophilic epoxidation of vinylsulfoximines using lithium *tert*-butylperoxide in THF (tetrahydrofuran) occurs rapidly at low temperatures to give good yields of the corresponding sulfoximinooxiranes **5**, with high diastereoselectivity. The sense of diastereoselectivity was established by an X-ray crystal structure determination. Vinylsulfoximines **3** may be deprotonated at the α-position and alkylated in fair yields. Epoxidation of these alkylated alkenes was much slower but nonetheless highly diastereoselective. The sense of diastereoselectivity was established to be the same as that in the case of α-unsubstituted examples by an X-ray crystal structure determination.

Since the pioneering work of Johnson on the synthetic applications of sulfoximines **1**,[1]† potentially chiral analogues of sulfones, the chemistry of these easily accessible and very useful intermediates has not been extensively studied. In particular the chemistry of vinyl sulfoximines, which in general mirrors that of vinyl sulfones, has remained largely unexplored. One additional advantage of sulfoximines is the possibility to fine-tune the reactivity of the double bond, merely by altering the substituent on nitrogen. The significant p*K*a difference between *N*,*S*-dimethyl-*S*-phenylsulfoximine **1a** (32) and *S*-methyl-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfoximine **1b** (24.5)[2] (which reflects the electron-withdrawing properties of the two groups) suggests that *N*-(*p*-tolylsulfonyl)vinylsulfoximines **3** should be significantly more reactive towards nucleophilic attack than the corresponding *N*-(methyl)vinylsulfoximines **2**. It is worth pointing out that *N*-(*p*-tolylsulfonyl)vinylsulfoximines **3** are also expected to be more reactive towards nucleophilic attack than analogous vinyl sulfones on the basis of the acidity of methyl phenyl sulfone (p*K*a 29.0). It is therefore surprising that *N*-(*p*-tolylsulfonyl)vinylsulfoximines **3** have been so little exploited in synthesis.




**1a** $R^1$ = Me **2** $R^1$ = Me
**1b** $R^1$ = $SO_2Tol$ **3** $R^1$ = $SO_2Tol$

In view of the synthetic utility of sulfonyloxiranes **4**,[3] we decided to investigate the preparation of analogous sulfoximinooxiranes **5**, which we planned to prepare by nucleophilic epoxidation of *N*-(*p*-tolylsulfonyl)vinylsulfoximines **3**. Control of diastereofacial selectivity in the epoxidation process was of prime importance, since use of enantiomerically pure *N*-(*p*-tolylsulfonyl)vinylsulfoximines **3** would then give access to enantiomerically pure oxiranes. *N*-Methylsulfoximinooxiranes **6** have previously been prepared as mixtures of diastereoisomers by non-stereoselective Darzens reaction between *S*-chloromethyl-*N*-methyl-*S*-phenylsulfoximine **7** and ketones.[4] Related enantiomerically pure *p*-tolysulfinyloxiranes **8** have been prepared by reaction of enantiomerically pure chloromethyl *p*-tolyl sulfoxides **9** with aldehydes and ketones.[5] This process results in the formation of two diastereoisomeric oxiranes when the substrates are aldehydes or unsymmetrical ketones (although 1,2-induction in this process is excellent), and these diastereoisomers require separation before being employed for the synthesis of enantiomerically pure products.




Johnson has briefly explored the reactivity of *N*-(*p*-tolylsulfonyl)vinylsulfoximines as ethylene transfer reagents to dibasic nucleophiles,[6] and Glass has investigated their reactivity in intermolecular Diels–Alder reactions.[7] This latter investigation has recently been extended to intramolecular reactions.[8] We have previously reported on the reactivity of vinylsulfoximines **3** with lithium cyanide and lithiophosphonates,[9] and we now report in full our investigations into the preparation and nucleophilic epoxidation of vinylsulfoximines **3**.[10,11]

When our work in this area began, there were a limited number of methods available for the preparation of *N*-(*p*-tolylsulfonyl)vinylsulfoximines **3**. These included the electrophilic addition of *N*-(*p*-tolylsulfonyl)arenesulfonimidoyl chlorides to alkenes, followed by elimination from the β-chlorosulfoximine intermediate,[12] elimination of water from a β-hydroxysulfoximine, in turn prepared by reduction of a β-ketosulfoximine,[4] and oxidation of a β-chlorosulfilimine, followed by dehydrochlorination.[7] More recently an *in situ* Peterson reaction was reported.[13] This method allowed the preparation of a variety of vinylsulfoximines **3** in good yield. After we had published our preliminary communication, an alternative method involving the use of an *in situ* Wadsworth–

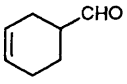
† The IUPAC systematic name for compounds of type **1** is sulfoximides, however for consistency with earlier work the term sulfoximines is used throughout this paper.

**Table 1** Preparation of β-hydroxysulfoximines

| Aldehyde | Product | $R^1$ | Yield (%) | Ratio of diastereoisomers |
|---|---|---|---|---|
| $Pr^iCHO$ | **10a** | $Pr^i$ | 70 | 7:1[a] |
| $C_3H_7CHO$ | **10b** | $C_3H_7$ | 63 | 2:1[b] |
| MeCHO | **10c** | Me | 60 | 3:1[b] |
| $C_5H_{11}CHO$ | **10d** | $C_5H_{11}$ | 70 | 3:1[b] |

[a] Ratio determined by isolation of each diastereoisomer. [b] Ratios determined from $^1H$ NMR spectroscopy.

**Table 2** Preparation of vinylsulfoximines

| Aldehyde | Product | $R^1$ | Yield (%) |
|---|---|---|---|
| $Pr^iCHO$ | **3a** | $Pr^i$ | 99 |
| $C_3H_7CHO$ | **3b** | $C_3H_7$ | 85 |
| MeCHO | **3c** | Me | 76 |
| $C_5H_{11}CHO$ | **3d** | $C_5H_{11}$ | 86 |
| $Ph(CH_2)_2CHO$ | **3e** | $Ph(CH_2)_2$ | 96 |
| $C_7H_{13}CHO$ | **3f** | $C_7H_{13}$ | 92 |
|  | **3g** |  | 99 |
| PhCHO | **3h** | Ph | 70 |
| PhCH=C(Me)CHO | **3i** | PhCH=C(Me) | 59 |

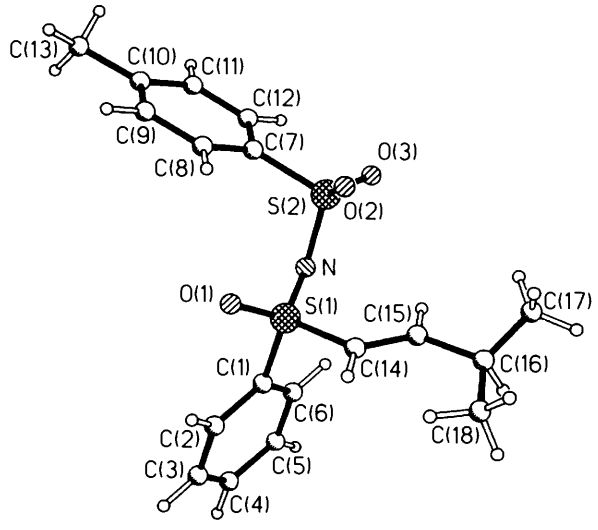
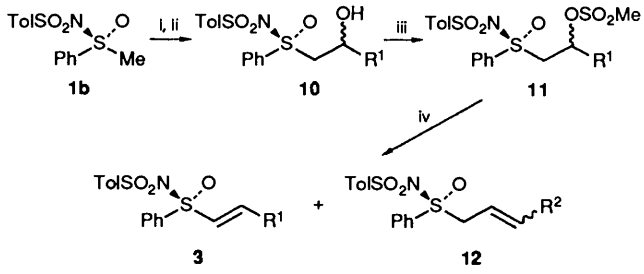



**Fig. 1**

Emmons reaction was reported.[14] The yields and stereoselectivities observed in both these latter two approaches are broadly similar.[15]

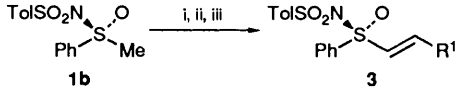
The main barrier to direct preparation of vinylsulfoximines **3** from *S*-methyl-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfoximine **1b** was the observation that treatment of the sodium salt of **1b** with either aldehydes or ketones yields oxiranes directly.[16] We decided to investigate the use of the corresponding lithium salt of **1b**[16] on the basis that the intermediate alkoxide would be less prone to cyclisation, which would then allow for the possibility of formal elimination of lithium hydroxide to give the required vinylsulfoximines.

Our first results suggested that addition of aldehydes to lithiated *S*-methyl-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfoximine **1b** in THF at −78 °C, followed by slow warming to room temperature, gave good yields of the corresponding β-hydroxysulfoximines **10a–d** with moderate diastereoselectivity (Table 1).[17] Treatment of the β-hydroxysulfoximines **10** with triethylamine–methanesulfonyl chloride gave the corresponding mesylates **11**. Treatment of these mesylates **11** with DBU in $CH_2Cl_2$ at room temperature without isolation[18] gave the required vinylsulfoximines **3**, but in most cases they were accompanied by variable amounts of the corresponding allylic sulfoximines **12**, formed by isomerisation of the initially formed vinylsulfoximines **3** (Scheme 1).[19] This process is not observed in the case of *N*-alkylvinylsulfoximines,[18] which presumably reflects the significantly greater anion stabilising properties of the *N*-(*p*-tolylsulfonyl)sulfoximine group. In order to suppress this side-reaction, we examined use of less basic amines, and were pleased to discover that triethylamine allows efficient conversion into the desired vinylsulfoximines **3** without double bond isomerisation under the conditions of the reaction.




**Scheme 1** *Reagents and conditions:* i, BuLi, −78 °C to room temp.; ii, $R^1CHO$, −78 °C to room temp.; iii $MeSO_2Cl$ (1.1 equiv.), $Et_3N$ (1.1 equiv.), $CH_2Cl_2$, 10 min; iv, DBU (1.1 equiv.), $CH_2Cl_2$

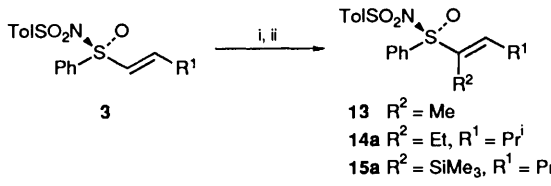
Finally, we examined a one-pot procedure for the preparation of vinylsulfoximines **3**, which involved mesylation of the intermediate lithio alkoxide, followed by treatment with triethylamine. This procedure allows the easy preparation of a variety of vinylsulfoximines **3a–i** in good overall yield (Scheme 2) (Table 2). Examination of the crude proton NMR spectra of all examples suggested that the reaction was highly selective for formation of *E*-vinylsulfoximines. This is an advantage when compared to the *in situ* Peterson and Wadsworth–Emmons procedures, which in some cases gives products containing up to 7% of the corresponding *Z* isomers. The stereochemistry of the vinylsulfoximine derived from 2-methylpropanal was established unambiguously by an X-ray crystal structure determination on the vinylsulfoximine **3a** (Fig. 1).




**Scheme 2** *Reagents and conditions:* i, BuLi, −78 °C to room temp.; ii, $R^1CHO$ (1.5 equiv.), −78 °C to 0°C; iii $MeSO_2Cl$ (1.1 equiv.), $Et_3N$ (1.1 equiv.), 0 °C, 20 min, then $Et_3N$ (1.1 equiv.), 0 °C to room temp.

In view of the ready α-deprotonation of vinylsulfones and quenching of the resulting lithio derivatives with electrophiles,[20] we have investigated the possibility of carrying out analogous substitution reactions on the *N*-(*p*-tolylsulfonyl)-vinylsulfoximines **3** as a route to α-substituted derivatives **13**. Preliminary reports on electrophilic substitution of *N*-methyl-vinylsulfoximines have appeared,[21] which suggested that this process would be feasible. Treatment of the *N*-(*p*-tolylsulfonyl)-vinylsulfoximines **3a**, **3c** and **3e** with butylithium at −78 °C, followed by addition of methyl iodide, gave the corresponding α-methylated products **13a**, **13c** and **13e** in good yield. Reaction with iodoethane was very inefficient under these conditions, although addition of DMPU did permit a modest increase in yield to give the α-ethylated product **14a**. Reaction of lithiated **3a** with chlorotrimethylsilane gave the α-silylated derivative **15a**. Our results are summarised in Table 3 (Scheme 3).

Treatment of vinyl sulfoximines **3** with lithium *tert*-butyl-peroxide in THF at −20 °C, conditions under which vinyl




**Scheme 3** *Reagents and conditions*: i, BuLi (1 equiv.), −78 °C, 10 min; ii, electrophile, −78 °C, 10 min

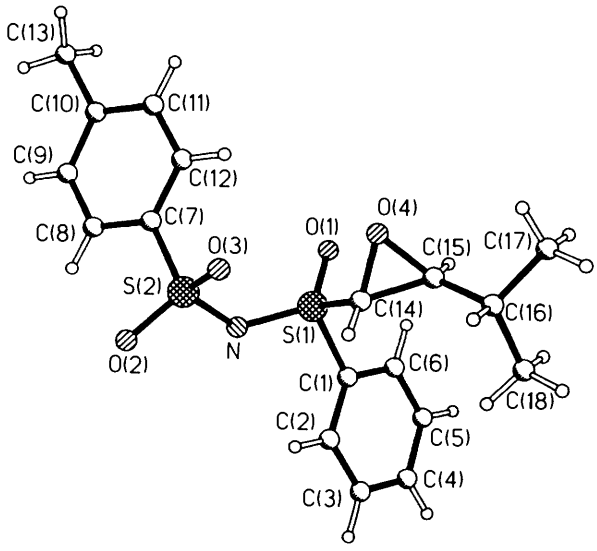
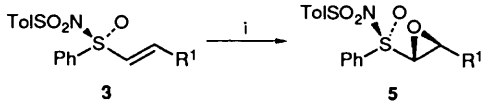



**Fig. 2**

sulfones are converted smoothly to the corresponding epoxides,[3,11] led to complete decomposition of starting material. In view of our expectation that vinyl sulfoximines **3** would be significantly more reactive towards nucleophilic epoxidation, we then conducted reactions by rapid addition of a solution of the vinyl sulfoximine **3** to lithium *tert*-butylperoxide in THF at −78 °C. The internal reaction temperature rose to −50 °C, and complete consumption of starting material was observed within 5 minutes. Under these conditions good to excellent yields of the desired sulfoximinooxiranes **5a–g** were isolated (Scheme 4). Our results are described in Table 4. All oxiranes prepared *via* this procedure were crystalline compounds, which after crystallisation appeared to be single diastereoisomers as judged by 300 MHz $^1$H NMR spectra. Inspection of the crude $^1$H NMR spectra of the product obtained from epoxidation of the alkene **3a**, indicated the presence of about 4% of a stereoisomeric *trans*-oxirane, which differed only in the relative configuration at sulfur (*vide infra*). The fact that epoxidation occurred with clean formation of *trans* geometry of the oxirane is reasonable, based on the stereospecific epoxidation observed with vinyl sulfones. However, the very high diastereofacial selectivity was somewhat unexpected.




**Scheme 4** *Reagents and conditions:* i, BuLi (1.1 equiv.), Bu$^t$O$_2$H (1.5 equiv.), −50 °C, 5 min

In order to establish that the other diastereoisomer was not in fact formed, we carried out an epoxidation of the vinyl sulfoximine **3a** using hydrogen peroxide–sodium hydroxide. This gave a 1.7:1 mixture of the oxiranes **5a** and **16a**, which exhibited clearly resolved signals for the oxirane methine protons in the $^1$H NMR spectra, allowing us to be confident of our assignment of diastereoselectivity in epoxidation by lithium *tert*-butylperoxide.

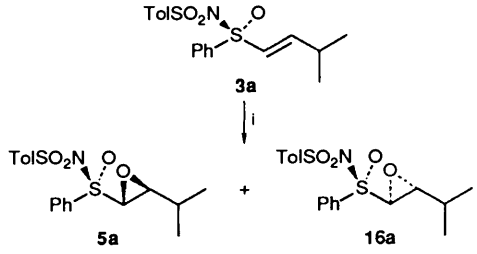
**Table 3** α-Substitution of vinylsulfoximines **3**

| Vinylsulfoximine | $R^1$ | Product | $R^2$ | Yield (%) |
|---|---|---|---|---|
| **3a** | Pr$^i$ | **13a** | Me | 74 |
| **3c** | Me | **13c** | Me | 79 |
| **3e** | $Ph(CH_2)_2$ | **13e** | Me | 71 |
| **3a** | Pr$^i$ | **14a** | Et | 48[a] |
| **3a** | Pr$^i$ | **15a** | $SiMe_3$ | 94 |

[a] DMPU (1.35 equiv.) was added prior to addition of the electrophile.

**Table 4** Epoxidation of vinylsulfoximines with lithium *tert*-butylperoxide

| Vinylsulfoximine | Sulfoximinooxirane | $R^1$ | Yield (%) |
|---|---|---|---|
| **3a** | **5a** | Pr$^i$ | 85 |
| **3b** | **5b** | $C_3H_7$ | 83 |
| **3c** | **5c** | Me | 72 |
| **3d** | **5d** | $C_5H_{11}$ | 86 |
| **3e** | **5e** | $Ph(CH_2)_2$ | 98 |
| **3f** | **5f** | $C_7H_{13}$ | 86 |
| **3g** | **5g** |  | 97 |




**Scheme 5** *Reagents and conditions:* i, NaOH, $H_2O_2$, 15 °C, 2 h

The sense of diastereofacial selectivity was determined by an X-ray crystal structure determination on the oxirane **5a** (Fig. 2). The extreme distortion of the oxirane ring [C(14)–O(4), 1.394(4) and C(15)–O(4), 1.452(5) Å] is noteworthy; the C(14)–O(4) bond length is one of the shortest which we have observed in our studies on heterosubstituted oxiranes.[22] This may again reflect the powerful electron-withdrawing properties of the *N*-(*p*-tolylsulfonyl)sulfoximine group. The oxirane **5d** was also subjected to X-ray crystal structure analysis, and we were able to establish that the relative configuration of the three asymmetric centres was the same as that observed in **5a**. Unfortunately, the pentyl side-chain gave rise to significant disorder, so the structure was not fully refined.

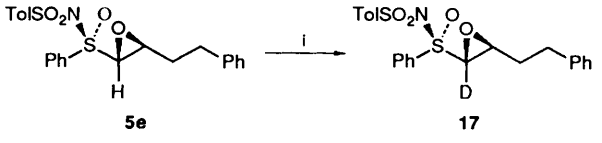
We had originally planned to lithiate the sulfoximinooxiranes **5**, with a view to subsequent reactions with electrophiles. Our efforts to generate and quench lithiated sulfoximinooxiranes under the same conditions that had proved satisfactory for sulfonyloxiranes[3] were unsuccessful. In all cases (including the use of reaction temperatures as low as −108 °C, and *in situ* quenching with trimethylsilyl chloride), we were unable to isolate any recognisable products. We ascribe these results to the greater instability of lithiated sulfoximinooxiranes compared with the corresponding lithiated sulfonyloxiranes. We were, however, able to generate the α-deuterio derivative **17** by treatment with MeOD–MeOLi at room temperature (Scheme 6). Under these conditions, no significant decomposition was observed.

In view of these disappointing results, we briefly investigated the possibility of carrying out nucleophilic epoxidation of the

**Table 5** Epoxidation of α-substituted vinylsulfoximines with lithium *tert*-butylperoxide

| Vinylsulfoximine | $R^1$ | $R^2$ | Product | Yield (%) |
|---|---|---|---|---|
| **13a** | $Pr^i$ | Me | **18a** | 91 |
| **13e** | $Ph(CH_2)_2$ | Me | **18e** | 51 |
| **14a** | $Pr^i$ | Et | | 0 |
| **15a** | $Pr^i$ | $SiMe_3$ | **5a** | 30[a] |

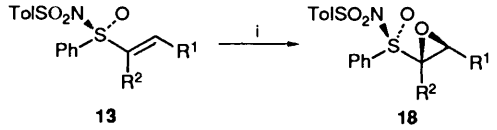
[a] Only desilylated material **5a** was isolated.




**5e** **17**

**Scheme 6** *Reagents and conditions:* i, MeOD, MeOLi, room temp., 36 h

α-substituted vinylsulfoximines **13**, **14a** and **15a** to give the α-substituted sulfoximinooxiranes **18**. Introduction of an α-substituent resulted in a dramatic reduction in the rate of epoxidation. Reaction conditions now typically involved treatment at ambient temperature for 12 h (Scheme 7). The only exception was the α-trimethylsilyl derivative **15a**, which was converted at −55 °C into the desilylated epoxide **5a** in poor yield. Fast initial desilylation under the reaction conditions is the most likely explanation. The combination of a bulky substituent at the β-position and any group larger than methyl at the α-position in **14a** completely prevented any reaction taking place. Our results are described in Table 5.




**13** **18**

**Scheme 7** *Reagents and conditions:* i, BuLi (1.1 equiv.), $Bu^tO_2H$ (1.5 equiv.), −78 °C to room temp, 12 h

The stereochemical course of epoxidation of the vinylsulfoximine **13a** was established by an X-ray crystal structure determination of the product **18a** (Fig. 3). This revealed that the sense of diastereofacial selectivity was the same as that previously observed on epoxidation of the α-unsubstituted vinylsulfoximines **3**. A possible rationalisation for the observed diastereoselectivity involves a reactive conformation of the vinylsulfoximine in which the *N*-tolysulfonyl group is *anti* to the vinyl group. In this conformation, delivery of lithium *tert*-butylperoxide is likely to be controlled by prior coordination to the sulfoximine oxygen (which should be a better donor site than the *p*-tolylsulfonyl nitrogen), which leads to the observed diastereoisomer.

Results of our investigations into the use of enantiomerically pure sulfoximinooxiranes for the synthesis of potentially useful synthetic intermediates will be reported in due course.

## Experimental

For general experimental procedures, see ref. 3. All NMR spectra were recorded in $CDCl_3$ as solvent at either 200 or 300 MHz. *J* values are given in Hz. Light petroleum refers to that fraction with boiling point 40–60 °C. *N*-Tosyl-*S*-methyl-*S*-phenylsulfoximine **1b** was prepared by the literature method.[16]

*General Procedure for the Preparation of* S-(2-*Hydroxyalkyl*)-S-*phenyl*-N-(p-*tolylsulfonyl*)*sulfoximines* **10**.—*S*-Methyl-*S*-phenyl-*N*-tosylsulfoximine **1b** was dissolved in dry THF (1 mmol per 5 $cm^3$) and cooled to −78 °C. BuLi (in hexane, 1 equiv.) was added, dropwise, to the reaction mixture.

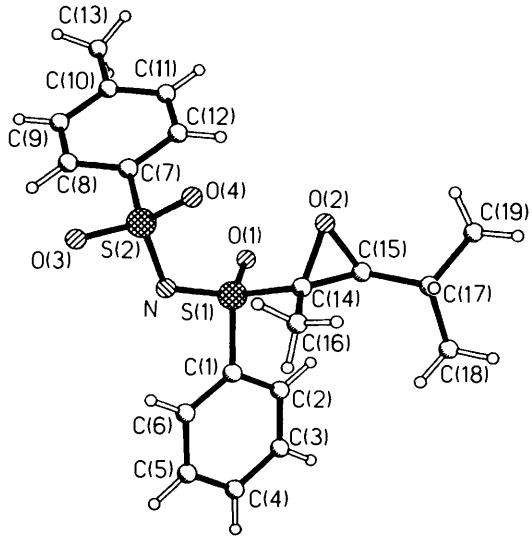



**Fig. 3**

The pale yellow solution was warmed to room temp. and stirred for 10 min during which time the yellow colour intensified. The reaction mixture was then cooled to −78 °C and the aldehyde (1.5 equiv.) was added. The reaction mixture was warmed, slowly, to 0 °C and stirred at that temperature for 45 min before being quenched with aqueous ammonium chloride (10%) and extracted with ethyl acetate. The ethyl acetate extract was dried and the solvent removed under reduced pressure giving a thick yellow (sometimes orange) oil. The crude product was purified by flash chromatography, using 1:1 ethyl acetate–light petroleum as eluent, to give the β-hydroxysulfoximine **10** as a mixture of diastereoisomers.

S-(2-*Hydroxy*-3-*methylbutyl*)-S-*phenyl*-N-(p-*tolylsulfonyl*)-*sulfoximine* **10a**. The two diastereoisomers were separated by flash chromatography, using 30% ethyl acetate in light petroleum as eluent. The major diastereoisomer was obtained as a white crystalline solid (450 mg, 1.18 mmol, 59%) m.p. 131–133 °C (Found: C, 56.2; H, 6.4; N, 3.4. $C_{18}H_{23}NO_4S_2$ requires C, 56.6; H, 6.5; N, 3.7%); $\nu_{max}$(film)/$cm^{-1}$ 3520br, 1599w and 1065s; $\delta_H$ 0.82 (3 H, d, *J* 6.7), 0.85 (3 H, d, 6.7), 1.68 (1 H, dq, *J* 5.0, 6.9), 2.38 (3 H, s), 2.63–3.09 (1 H, br), 3.44 (1 H, dd, *J* 9.1, 14.3), 3.59 (1 H, dd, *J* 1.9, 14.3), 3.99 (1 H, ddd, *J* 1.9, 5.0, 9.1) and 7.21–8.01 (9 H, m); *m/z* (E.I.) 382 ($MH^+$, 12%), 364 (4), 310 (15), 296 (80) and 278 (37). The minor diastereoisomer was isolated as a colourless oil (42 mg, 0.11 mmol, 8%); $\nu_{max}$(film)/$cm^{-1}$ 3501s br and 1599m; $\delta_H$ 0.84 (3 H, d, *J* 6.5), 0.87 (3 H, d, *J* 6.3), 1.72 (1 H, m), 2.40 (3 H, s), 2.75–2.79 (1 H, br, OH), 3.37 (1 H, d, *J* 14.2), 3.67 (1 H, dd, *J* 9.5, 14.2), 3.94 (1 H, dd, *J* 4.8, 9.3) and 7.23–8.02 (9 H, m); *m/z* (E.I.) 382 ($MH^+$, 30%), 338 (40), 296 (77) and 278 (30) (Found: $MH^+$, 382.1064. $C_{18}H_{24}NO_4S_2$ requires 382.1147).

S-(2-*Hydroxypentyl*)-S-*phenyl*-N-(p-*tolylsulfonyl*)*sulfoximine* **10b**. M.p. 84–85 °C (Found: C, 56.7; H, 6.2; N, 3.6. $C_{18}H_{23}NO_4S_2$ requires C, 56.6; H, 6.5; N, 3.7%); $\nu_{max}$(KBr)/$cm^{-1}$ 3483s br, 1600w, 1061m and 752s; $\delta_H$ 0.80–0.99 (3 H, m), 1.22–1.52 (4 H, m), 1.67 (1 H, br, OH), 2.40 (3 H, s), [3.32 (dm, *J* 14.3), 3.72 (dd, *J* 14.3, 9.4) and 3.44 (dd, *J* 14.3, 5.6), 3.57 (dd, *J* 14.3, 2.3) (2 H, ratio 1:2)], 4.16 (1 H, br m) and 7.23–8.03 (9 H, m); *m/z* (E.I.) 382 ($MH^+$, 10%), 338 (14), 310 (12), 296 (74) and 278 (30).

S-(2-*Hydroxypropyl*)-S-*phenyl*-N-(p-*tolylsulfonyl*)*sulfoximine* **10c**. M.p. 115–116 °C (Found: C, 54.3; H, 5.5; N, 3.8. $C_{16}H_{19}NO_4S_2$ requires C, 54.4; H, 5.4; N, 4.0%; $\nu_{max}$(KBr)/$cm^{-1}$ 3434s br, 1600w, 1059s, 760m and 734m; $\delta_H$ 1.22 (3 H, d, *J* 6.8), 2.40 (3 H, s), 2.65 (1 H, br, OH), [3.32 (dd, *J* 1.7, 14.3), 3.75 (dd, *J*

9.2, 14.3) and 3.45 (dd, *J* 8.1, 14.3), 3.56 (dd, *J* 3.0, 14.3) (2 H, 1:3 ratio)], 4.37 (1 H, m) and 7.23–8.00 (9 H, m); *m/z* (E.I.) 354 ($MH^+$, 74%) and 296 (82).

S-(2-*Hydroxyheptyl*)-S-*phenyl*-N-(p-*tolylsulfonyl*)*sulfoximine* **10d**. A colourless oil; $\nu_{max}$(film/$cm^{-1}$ 3574m, 3547m, 1596w and 1058s; $\delta_H$ 0.81–1.50 (11 H, m), 2.40 (3 H, s), 2.99 (1 H, d *J* 3.6, OH), [3.32 (dd, *J* 1.5, 14.3), 3.72 (dd, *J* 9.7, 14.3) and 3.44 (dd, *J* 8.6, 14.3), 3.57 (dd, *J* 2.3, 14.3) (2 H), ratio 1:3)] 4.20 (1 H, br m) and 7.23–8.04 (9 H, m); *m/z* (F.A.B.) 410 ($MH^+$, 100%), 310 (5), 296 (12) and 278 (8)

*General Procedure for the One-pot Preparation of* [(E)-*Alk*-1-*enyl*]-S-*phenyl*-N-(p-*tolylsulfonyl*)*sulfoximines* **3**.—*S*-Methyl-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfoximine **1b** was dissolved in dry THF (0.25 mmol per $cm^3$) and cooled to −78 °C. Butylithium (solution in hexane, 1 equiv.) was added at that temperature. The resultant pale yellow solution was warmed to room temp. and stirred for 10 min, during which time the yellow colour intensified. After 10 min the reaction mixture was cooled to −78 °C and the aldehyde (1.5 equiv.) was added to the lithiated sulfoximine. The reaction mixture was then warmed to 0 °C and stirred at that temperature for 45 min. During this time the intensity of the bright yellow colour diminished substantially resulting in a pale yellow (or even colourless) solution. Dry triethylamine (1.1 equiv.) was added to the reaction mixture, followed by dropwise addition of methanesulfonyl chloride (1.1 equiv.) at 0 °C. The resultant cream coloured precipitate was then stirred at 0 °C for 20 min after which a second equivalent of triethylamine was added. The reaction mixture was warmed to room temp. and stirred for a further 20 min. The reaction was quenched with aqueous $NH_4Cl$ (10%, 1 $cm^3$ per 1.5 mmol), transferred to a separating funnel and extracted with three portions of dichloromethane (10 $cm^3$ per mmol). The dichloromethane extract was dried and the solvent removed to give a yellow oil which on standing at room temp. crystallized to give a pale yellow solid. Recrystallisation from ethyl acetate gave the pure vinylsulfoximine **3** as a white crystalline solid.

[(E)-3-*Methylbut*-1-*enyl*]-S-*phenyl*-N-(p-*tolylsulfonyl*)*sulfoximine* **3a**. M.p. 108–110 °C; $\nu_{max}$(KBr)/$cm^{-1}$ 1622w, 1600w, 1496w and 740s; $\delta_H$ 1.05 (3 H, d, *J* 6.8), 1.06 (3 H, d, *J* 6.8), 2.39 (3 H, s), 2.53 (1 H, m), 6.34 (1 H, dd, *J* 15.0, 1.5), 7.0 (1 H, dd, *J* 15.0, 6.3) and 7.21–7.97 (9 H, aromatic, m); *m/z* (E.I.) 364 ($MH^+$, 25%), 363 (6) and 278 (100) (Found: $M^+$, 363.0929. $C_{18}H_{21}NO_3S_2$ requires 363.0963).

S-[(E)-*Pent*-1-*enyl*]-S-*phenyl*-N-(p-*tolylsulfonyl*)*sulfoximine* **3b**. M.p. 70–72 °C (Found: C 59.1; H; 5.8; N, 3.7. $C_{18}H_{21}NO_3S_2$ requires C, 59.5; H, 5.8; N, 3.7%); $\nu_{max}$(KBr)/$cm^{-1}$ 1634w, 1597w and 1056s; $\delta_H$ 0.91 (3 H, t, *J* 7.3), 1.49 (2 H, sext, *J* 7.3), 2.23 (2 H, dq, *J* 1.4, 7.0), 2.39 (3 H, s), 6.41 (1 H, dt, *J* 14.9, 1.4), 7.0 (1 H, dt, *J* 14.9, 6.8) and 7.22–8.00 (9 H, aromatic, m); *m/z* (E.I.) 364 ($MH^+$, 7%), 334 (13) and 155 (21).

S-[(E)-*Prop*-1-*enyl*]-S-*phenyl*-N-(p-*tolylsulfonyl*)*sulfoximine* **3c**. M.p. 120–123 °C (Found: C, 57.3; H, 5.2; N; 4.4. $C_{16}H_{17}NO_3S_2$ requires C, 57.2; H, 5.2; N, 4.4%); $\nu_{max}$(KBr)/$cm^{-1}$ 1640w, 1596w, 1058s and 744s; $\delta_H$ 1.94 (3 H, dd, *J* 1.6, 7.0), 2.38 (3 H, s), 6.44 (1 H, dq, *J* 14.8, 1.6), 7.0 (1 H, dq, *J* 14.8, 6.9) and 7.21–8.02 (9 H, aromatic, m); *m/z* (F.A.B.) 336 ($MH^+$, 100%), 310 (7) and 182 (8).

S-[(E)-*Hept*-1-*enyl*]-S-*phenyl*-N-(p-*tolylsulfonyl*)*sulfoximine* **3d**. M.p. 72–73 °C (Found: C, 61.0; H, 6.5; N, 3.5. $C_{20}H_{25}NO_3S_2$ requires C, 61.2; H, 6.4; N 3.5%); $\nu_{max}$(KBr)/$cm^{-1}$ 1631w, 1596w and 1058s; $\delta_H$(200 MHz) 0.86 (3 H, t, *J* 6.8), 1.20–1.48 (6 H, m), 2.24 (2 H, dq, *J* 1.5, 6.9), 2.39 (3 H, s), 6.40 (1 H, dt, *J* 14.9, 1.5), 7.0 (1 H, dt, *J* 14.9, 6.8) and 7.21–7.97 (9 H, m) *m/z* (F.A.B.) 392 ($MH^+$ 100%), 238 (10), 223 (5), 155 (18) and 139 (13).

S-*Phenyl*-S-[(E)-4-*phenylbut*-1-*enyl*]-N-(p-*tolylsulfonyl*)*sulfoximine* **3e**. M.p. 131–133 °C (Found: C, 65.0; H, 5.4; N, 3.2. $C_{23}H_{23}NO_3S_2$ requires C, 64.9; H, 5.4; N, 3.3%); $\nu_{max}$(KBr)/$cm^{-1}$ 1624w and 1601m; $\delta_H$ 2.37 (3 H, s), 2.57 (2 H, m), 2.76 (2 H, m), 6.36 (1 H, dt, *J* 1.3, 14.9), 6.98 (1 H, dt, *J* 6.7, 14.9) and 7.04–8.02 (14 H, m); *m/z* (E.I.) 425 ($M^+$, 85%) and 278 (30).

S-[(E)-*Non*-1-*enyl*]-S-*phenyl*-N-(p-*tolylsulfonyl*)*sulfoximine* **3f**. M.p. 70–71 °C; $\nu_{max}$(KBr)/$cm^{-1}$ 1597m and 656m; $\delta_H$ 0.83–0.89 (3 H, m), 1.24–1.67 (10 H, m), 2.04–2.31 (2 H, m), 2.39 (3 H, s), 6.40 (1 H, dt, *J* 1.5, 14.8), 6.97 (1 H, dt, *J* 6.8, 14.8) and 7.03–8.03 (9 H, m); *m/z* (E.I.) 420 ($MH^+$, 45%), 419 (11), 390 (7), 296 (35) and 278 (86) (Found: $M^+$, 419.1553. $C_{22}H_{29}NO_3S_2$ requires 419.1589).

S-[(E)2-(*Cyclohex*-3′-*enyl*)*vinyl*]-S-*phenyl*-N-(p-*tolylsulfonyl*)*sulfoximine* **3g**. M.p. 104–105 °C (Found: C, 62.5; H, 5.7; N, 3.4. $C_{21}H_{23}NO_3S_2$ requires C, 62.8; H, 5.8; N, 3.5%); $\nu_{max}$(KBr)/$cm^{-1}$ 1624w, 1599m and 1064s; $\delta_H$ 1.34–2.20 (6 H, m), 2.39 (3 H, s), 2.52 (1 H, m), 5.65 (2 H, m), 6.41 (1 H, dd, *J* 1.3, 15.0), 7.00 (1 H, dd, *J* 6.7, 15.0) and 7.03–7.98 (9 H, m); *m/z* (E.I.) 401 ($M^+$, 88%) and 278 (60).

S-*Phenyl*-2-*phenylvinyl*-N-(p-*tolylsulfonyl*)*sulfoximine* **3h**. M.p. 135–136 °C (Found: C, 63.0; H, 4.6; N, 3.5. $C_{21}H_{19}NO_3S_2$ requires C 63.3; H 4.8; N 3.5); $\delta_H$ 2.37 (3 H, s), 6.90 (1 H, d, *J* 15.2), 7.25 (1 H, d, 15.2) and 7.22–8.06 (14 H, m); *m/z* (E.I.) 398 ($MH^+$, 100%), 294 (10) and 278 (20). This data agrees closely with that reported for enantiomerically pure material.[13]

S-[(E)-3-*Methyl*-4-*phenylbuta*-1,3-*dienyl*]-S-*phenyl*-N-(p-*tolylsulfonyl*)*sulfoximine* **3i**. M.p. 119–121 °C (Found: 65.6; H 5.1; N 3.1. $C_{24}H_{23}NO_3S_2$ requires C, 65.9; H, 5.3; N, 3.2%); $\nu_{max}$(KBr)/$cm^{-1}$ 1590m, 1491m, 1057s and 970s; $\delta_H$ 1.97 (3 H, d, *J* 1.0), 2.37 (3 H, s), 6.44 (1 H, d, 14.8), 6.94 (1 H, s) and 7.26–8.03 (1 H vinyl, m and 14 H, m); *m/z* (E.I.) 438 ($MH^+$, 19%) and 296 (100).

*General Procedure for the Preparation of α-Methylated Vinylsulfoximines*.—The vinylsulfoximine (2.0 mmol) was dissolved in dry THF (10 $cm^3$) and the solution was cooled to −78 °C. BuLi (2.3 mol $dm^{-3}$ solution in hexane, 0.87 $cm^3$, 2.01 mmol) was added, dropwise, to give a bright yellow coloured solution which was stirred for 5 min at −78 °C. Methyl iodide (0.43 g, 0.19 $cm^3$, 3.02 mmol) was added dropwise at −78 °C and the reaction mixture stirred at that temperature for 7 min, during which time a pale yellow precipitate was observed. The reaction was quenched with phosphate buffer (pH 7, 10 $cm^3$) and extracted with dichloromethane. The dichloromethane extract was dried and the solvent removed under reduced pressure giving a yellow oil. The crude product was purified by flash chromatography, using a 30% ethyl acetate–light petroleum as eluent to give the α-methylated product.

S-[(E)-1,3-*Dimethylbut*-1-*enyl*]-S-*phenyl*-N-(p-*tolylsulfonyl*)-*sulfoximine* **13a**. M.p. 108–110 °C; $\nu_{max}$(KBr)/$cm^{-1}$ 2959m, 1645m, 1597m, 1447s, 1304s, 1151s and 1103s; $\delta_H$ 1.03 (3 H, d, *J* 6.6), 1.09 (3 H, d, *J* 6.6), 1.88 (3 H, d, *J* 1.3), 2.38 (3 H, s), 2.55 (1 H, m), 6.79 (1 H, dd, *J* 1.3, 9.9) and 7.21–7.95 (9 H, m); *m/z* (E.I.) 377 ($M^+$, 8%), 334 (17) and 278 (30) (Found: $M^+$, 377.1065. $C_{19}H_{23}NO_3S_2$ requires 377.1119).

S-[(E)-1-*Methylprop*-1-*enyl*]-S-*phenyl*-N-(p-*tolylsulfonyl*)-*sulfoximine* **13c**. Colourless oil; $\nu_{max}$(film)/$cm^{-1}$ 1599w and 1497w; $\delta_H$ 1.86 (3 H, d, *J* 6.2), 1.87 (3 H, s), 2.37 (3 H, s), 7.05 (1 H, q, *J* 6.2) and 7.22–7.93 (9 H, m); *m/z* (E.I.) 350 ($MH^+$, 7%) and 278 (22) (Found: $M^+$, 349.0890. $C_{17}H_{19}NO_3S_2$ requires 349.0882).

S-[(E)-1-*Methyl*-4-*phenylbut*-1-*enyl*]-S-*phenyl*-N-(p-*tolylsulfonyl*)*sulfoximine* **13e**. M.p. 100–101 °C; $\delta_H$ 1.71 (3 H, d, *J* 1.3), 2.36 (3 H, s), 2.56 (2 H, m), 2.80 (2 H, m), 6.97 (1 H, tq, *J* 1.3, 7.3) and 7.05–7.84 (14 H, m); *m/z* (E.I.) 440 ($MH^+$, 10%), 348 (18) and 278 (13) (Found: $MH^+$, 440.1319. $C_{24}H_{26}NO_3S_2$ requires 440.1322).

S-[(E)-1-*Ethyl*-3-*methylbut*-1-*enyl*]-S-*phenyl*-N-(p-*tolylsulfonyl*)*sulfoximine* **14a**. The procedure was as for α-methylation, except that dimethylpropylene urea (DMPU) (1.3 equiv.) was

added before addition of iodoethane; m.p. 75–76 °C (Found: C, 61.2; H, 6.4; N, 3.6. $C_{20}H_{25}NO_3S_2$ requires C, 61.4; H, 6.4; N, 3.4%); $\nu_{max}$(KBr)/cm$^{-1}$ 1634w, 1599w, 1497w, 835w, 816m, 802w and 768s; $\delta_H$ 0.79 (3 H, t, *J* 7.5), 1.06 (3 H, d, 6.6), 1.09 (3 H, d, *J* 6.6), 2.33 (2 H, dq, *J* 3.5, 7.5), 2.37 (3 H, s), 2.62 (1 H, dq, *J* 10.7, 6.6), 6.80 (1 H, d, *J* 10.7) and 7.20–7.95 (9 H, m); *m/z* (E.I.) 392 ($MH^+$, 14%), 334 (8) and 296 (50).

S-[(E)-S-*Phenyl*-N-(p-*tolylsulfonyl*)-l-*trimethylsilyl*-3-*methylbut*-l-*enyl*]*sulfoximine* **15a**. The procedure was as for α-methylation except chlorotrimethylsilane was used as the electrophile. The product was purified by recrystallisation from ethyl acetate–light petroleum; m.p. 104–106 °C (Found: C, 57.6; H, 6.7; N, 3.2. $C_{21}H_{29}NO_3S_2Si$ requires C, 57.9; H, 6.7; N, 3.2); $\nu_{max}$(KBr)/cm$^{-1}$ 1605m, 1590m, 1500w and 840s; $\delta_H$ 0.14 (9 H, s), 1.09 (6 H, d, *J* 6.5), 2.36 (3 H, s), 2.83 (1 H, m) and 6.99–7.80 (10 H); *m/z* (E.I.) 436 ($MH^+$, 10%) and 420 (27).

*General Procedure for Epoxidation of Vinylsulfoximines* **3**. BuLi (1.1 equiv.) was added to a solution of *tert*-butyl hydroperoxide in dry THF (1 cm$^3$ per 1.5 mmol) at −78 °C. The vinylsulfoximine **3**, in dry THF, was then added very quickly such that the temperature of the reaction mixture rose to −55 °C. The internal temperature dropped to between −65 and −70 °C after the solution had been stirred for 2–4 min. The reaction mixture was then quenched with solid sodium sulfite and stirred for a further 15 min before being diluted with dichloromethane and filtered through Celite. Evaporation of the solvent and filtration of the crude product, in dichloromethane, through a small pad of silica gave the sulfoximinooxirane **5**.

S-(trans-3-*Isopropyloxiran*-2-*yl*)-S-*phenyl*-N-(p-*tolylsulfonyl*)*sulfoximine* **5a**. M.p. 98–100 °C (Found: C, 56.7; H, 5.7; N, 3.5. $C_{18}H_{21}NO_4S_2$ requires C, 57.0; H, 5.5; N, 3.7%); $\nu_{max}$(KBr)/cm$^{-1}$ 1242m, 910w, 815w and 802w; $\delta_H$ 0.91 (3 H, d, *J* 7.0), 0.95 (3 H, d, *J* 7.0), 1.71 (1 H, m), 2.40 (3 H, s), 3.21 (1 H, dd, *J* 1.6, 6.4), 4.42 (1 H, d, *J* 1.6) and 7.26–8.00 (9 H, m); *m/z* (E.I.) 380 ($MH^+$, 25%), 296 (50), 278 (80), 155 (94) and 139 (100).

S-(trans-3-*Propyloxiran*-2-*yl*)-S-*phenyl*-N-(p-*tolylsulfonyl*)-*sulfoximine* **5b**. M.p. 125–127 °C (Found: C, 56.6; H, 5.4; N, 3.5. $C_{18}H_{21}NO_4S_2$ requires C, 57.0; H, 5.5; N, 3.7%); $\nu_{max}$(KBr)/cm$^{-1}$ 1250s, 1061s, 924m and 812s; $\delta_H$ 0.86 (3 H, t, *J* 7.3), 1.18–1.67 (4 H, m), 2.37 (3 H, s), 3.37 (1 H, dt, *J* 1.5, 6.3), 4.37 (1 H, d, *J* 1.5) and 7.21–7.97 (9 H, m); $\delta_C$(50.3 MHz) 13.47, 18.59, 21.42, 31.83, 58.67, 71.99, 126.65, 128.86, 129.17, 129.28, 129.54, 133.93, 134.98, 140.63 and 142.98; *m/z* (F.A.B.) 380 ($MH^+$, 30%), 364 (12), 296 (88) and 278 (100).

S-(trans-3-*Methyloxiran*-2-*yl*)-S-*phenyl*-N-(p-*tolylsulfonyl*)-*sulfoximine* **5c**. M.p. 110–112 °C (Found: C, 55.0; H, 5.1; N, 3.8. $C_{16}H_{17}NO_4S_2$ requires, C, 54.7; H, 4.8; N, 4.0%); $\nu_{max}$(KBr)/cm$^{-1}$ 1600m, 1578m, 1497m, 1246m, 1061s, 911w and 815w; $\delta_H$ 1.39 (3 H, d, *J* 5.3), 2.40 (3 H, s), 3.43 (1 H, dq, *J* 1.5, 5.3), 4.35 (1 H, d, 1.5) and 7.24–7.99 (9 H, m); *m/z* (F.A.B.) 352 ($MH^+$, 33%) and 210 (44).

S-(trans-3-*Pentyloxiran*-2-*yl*)-S-*phenyl*-N-(p-*tolylsulfonyl*)-*sulfoximine* **5d**. M.p. 70–72 °C; $\nu_{max}$(KBr)/cm$^{-1}$ 1599m, 1496w, 1249s and 917w; $\delta_H$ 0.84 (3 H, m), 1.21–1.40 (6 H, m), 1.49–1.68 (2 H, m), 2.39 (3 H, s), 3.37 (1 H, dt, *J* 1.6, 6.1), 4.36 (1 H, d, *J* 1.6) and 7.23–7.99 (9 H, m); *m/z* (F.A.B.) 392 ($MH^+$, 20%), 296 (80) and 278 (73).

S-*Phenyl*-S-[trans-3-(2′-*phenylethyl*)*oxiran*-2-*yl*]-N-(p-*tolylsulfonyl*)*sulfoximine* **5e**. M.p. 117–119 °C (Found: C, 62.4; H, 4.9; N, 2.8. $C_{23}H_{23}NO_4S_2$requires, C, 62.6; H, 5.2; N, 3.2%); $\nu_{max}$(KBr)/cm$^{-1}$ 1601s, 1246m, 920s and 814m; $\delta_H$ 1.90 (2 H, m), 2.40 (3 H, s), 2.71 (2 H, m), 3.38 (1 H, dt, *J* 1.4, 5.7), 4.43 (1 H, d, *J* 1.4) and 7.09–7.97 (14 H, m); *m/z* (E.I.) 444 ($MH^+$, 2%), 424 (3), 338 (2) and 308 (5).

S-(trans-3-*Heptyloxiran*-2-*yl*)-S-*phenyl*-N-(p-*tolylsulfonyl*)-*sulfoximine* **5f**. M.p. 55–56 °C (Found: 60.6; H, 6.6; N, 3.1. $C_{22}H_{29}NO_4S_2$ requires, C, 60.65; H, 6.7; N, 3.2%); $\nu_{max}$(film)/cm$^{-1}$ 1599s, 1497s, 1248w, 920s and 814m; $\delta_H$ 0.83–0.89 (3 H, m), 1.05–1.34 (10 H, m), 1.46–1.67 (2 H, m), 2.39 (3 H, s), 3.37 (1 H, dt, *J* 1.6, 5.1), 4.39 (1 H, d, 1.6) and 7.14–8.02 (9 H, m); *m/z* (E.I.) 438 (6%), 436 ($MH^+$, 1), 420 (4) and 403 (1).

S-(trans-3-*Cyclohex*-3′-*enyloxiran*-2-*yl*)-S-*phenyl*-N-(p-*tolylsulfonyl*)*sulfoximine* **5g**. A colourless oil, obtained as a mixture of 2 diastereoisomers due to the additional stereogenic centre; $\nu_{max}$(KBr)/cm$^{-1}$ 1599s, 1582s, 1497s, 1248m, 911s and 814m; $\delta_H$ 1.33–2.04 (9 H, m), 2.40 (3 H, s), 3.31 (1 H, m), 4.47 (d, *J* 1.6) and 4.48 (d, *J* 1.6) (1 H overall, ratio 1:1), 5.57–5.68 (2 H, m, vinyl) and 7.24–8.01 (9 H, m); *m/z* (E.I.) 418 ($MH^+$, 2%) and 402 (2) (Found: $MH^+$, 418.1094. $C_{21}H_{24}NO_4S_2$ requires 418.1147).

*Epoxidation of* S-[(E)-3-*Methylbut*-l-*enyl*]-S-*phenyl*)-N-(p-*tolylsulfonyl*)*sulfoximine* **3a** *Using Basic Hydrogen Peroxide*.—*S*-(*E*)-Methylbut-l-enyl]-*S*-phenyl)-*N*-(*p*-tolylsulfonyl)sulfoximine **3a** (364 mg, 1.00 mmol) was dissolved in a mixture of methanol (3 cm$^3$) and dichloromethane (1 cm$^3$) and then cooled in a water bath to *ca.* 15 °C. Aqueous hydrogen peroxide (27.5 mol dm$^{-3}$, 0.25 cm$^3$, 3.0 mmol) was added to the mixture followed by the dropwise addition of aqueous sodium hydroxide (3 mol dm$^{-3}$, 0.5 cm$^3$). The reaction mixture was stirred at 15 °C for 2 h, during which time a thick white precipitate was formed, then quenched with water (20 cm$^3$) and extracted with dichloromethane (20 cm$^3$). The dichloromethane extract was dried and the solvent removed under reduced pressure giving a colourless oil (350 mg, 0.92 mmol, 92%). TLC analysis and high field NMR spectroscopy indicated the presence of 2 diastereoisomers in an approximate ratio of 1.7:1 which were separated by flash chromatography, using a 20% mixture of ethyl acetate–light petroleum as eluent, giving both isomers as white crystalline solids.

Minor diastereoisomer **16a** (76 mg, 20%): m.p. 126–127 °C (Found: C, 56.8; H, 5.7; N, 3.4. $C_{18}H_{21}NO_4S_2$ requires, C, 57.0; H, 5.5; N, 3.7%); $\nu_{max}$(KBr)/cm$^{-1}$ 1599w, 1235m and 806w; $\delta_H$ 1.02 (3 H, d, *J* 6.8), 1.09 (3 H, d, *J* 6.9), 1.89 (1 H, m), 2.39 (3 H, s), 3.60 (1 H, dd, *J* 1.6, 6.1), 4.42 (1 H, d, *J* 1.6) and 7.22–8.06 (9 H, m); *m/z* (E.I.) 380 ($MH^+$, 2%), 364 (2), 296 (12), 278 (70) and 264 (100).

Major diastereoisomer **5a** (178 mg, 47%): for spectroscopic and physical data, see above.

S-[trans-2-*Deutero*-3-(2-*phenylethyl*)*oxiran*-2-*yl*]-S-*phenyl*-N-(p-*tolylsulfonyl*)*sulfoximine* **17**. *S*-[*trans*-3-(2- Phenylethyl)-oxiran-2-yl]-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfoximine **5e** (220 mg, 0.5 mmol) was dissolved in a mixture of [$^2$H]-methanol (3 cm$^3$), dry benzene (3 cm$^3$) and dry THF (1.5 cm$^3$). Lithium methoxide (19 mg, 0.5 mmol) was added and the reaction mixture was stirred at room temp. for 36 h. The mixture was quenched with water and extracted with ethyl acetate. The organic layer was separated and washed with water before being dried. The solvent was removed under reduced pressure to give **17** as an oily solid (205 mg, 0.46 mmol, 93%). The product was analysed without any further purification; $\nu_{max}$(film)/cm$^{-1}$ 1240m, 814m and 737m; $\delta_H$ 1.90 (2 H, m), 2.40 (3 H, s), 2.71 (2 H, m), 3.38 (1 H, t, *J* 5.7) and 7.07–7.98 (14 H, m); *m/z* (E.I.) 443 (< 1%, $MH^+$) and 427 (2).

*General Procedure for the Epoxidation of α-Methylated Vinylsulfoximines*.—Butyllithium (1.1 equiv.) was added to a solution of *tert*-butyl hydroperoxide in dry THF (1 cm$^3$ per 1.5 mmol alkene) at −78 °C. The α-substituted vinylsulfoximine **13** in dry THF was added at −78 °C. The reaction mixture was warmed to room temp. and stirred for 12 h before being quenched with solid sodium sulfite. The reaction mixture was stirred for a further 15 minutes before being diluted with dichloromethane and filtering through Celite. The solvent was removed under reduced pressure giving a thick opaque oil. The

**Table 6** Crystallographic data

| Compound | **3a** | **5a** | **18a** |
|---|---|---|---|
| Formula | $C_{18}H_{21}NO_3S_2$ | $C_{18}H_{21}NO_4S_2$ | $C_{19}H_{23}NO_4S_2$ |
| $M$ | 363.5 | 379.5 | 393.5 |
| Crystal system | monclinic | monoclinic | triclinic |
| Space group | $P2_1n$ | $P2_1/n$ | $P\bar{1}$ |
| $a$/Å | 12.143(1) | 10.469(1) | 10.027(1) |
| $b$/Å | 10.251(1) | 10.520(1) | 10.475(1) |
| $c$/Å | 15.449(1) | 18.188(2) | 10.526(1) |
| $\alpha$/° | | | 109.560(5) |
| $\beta$/° | 97.325(7) | 94.36(1) | 91.027(6) |
| $\gamma$/° | | | 106.538(5) |
| $U$/Å$^3$ | 1907.4 | 1997.3 | 990.8 |
| $Z$ | 4 | 4 | 2 |
| $D_c$/g cm$^{-3}$ | 1.266 | 1.262 | 1.319 |
| Radiation, $\lambda$/Å | Mo$K\alpha$, 0.710 73 | Mo$K\alpha$, 0.710 73 | Cu$K\alpha$, 1.541 84 |
| $\mu$/mm$^{-1}$ | 0.28 | 0.27 | 2.59 |
| $F$(000) | 768 | 800 | 416 |
| Crystal size/mm | 0.40 × 0.48 × 0.60 | 0.28 × 0.40 × 0.52 | 0.32 × 0.36 × 0.44 |
| No. refns. for cell, 2$\theta$ range/° | 32, 20–25 | 32, 20–25 | 32, 30–40 |
| $2\theta_{max}$/° | 50 | 50 | 130 |
| Maximum indices $hkl$ | 14, 12, 18 | 12, 12, 21 | 11, 12, 12 |
| Transmission factors | | | 0.45–0.52 |
| Reflections measured | 3437 | 4455 | 3298 |
| Unique reflections | 3351 | 3511 | 3298 |
| Observed reflections | 2700 | 2234 | 2870 |
| $R_{int}$ | 0.050 | 0.044 | |
| Weighting parameters $A_n$ | 9, −23, 148 −22, 13, 26 | 11, −1, 4 −30, 20, 8 | 6, −51, 134 −13, 7, 46 |
| Extinction parameter $x$ | 1.3(3) × 10$^{-6}$ | 0 | 2.8(5) × 10$^{-5}$ |
| No. of refined parameters | 221 | 236 | 251 |
| $R$ | 0.060 | 0.049 | 0.056 |
| $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$ | 0.072 | 0.055 | 0.066 |
| Goodness of fit | 0.92 | 1.15 | 1.13 |
| Mean, max. shift/e.s.d. | 0.005, 0.034 | 0.003, 0.072 | 0.009, 0.096 |
| Max., min. el. density/eÅ$^{-3}$ | 0.69, −0.41 | 0.46, −0.23 | 0.67, −0.38 |

**Table 7** Atomic coordinates ( × 10$^4$) for **3a**

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| S(1) | 7 168.9(6) | 2 022.2(7) | 6 909.8(4) |
| S(2) | 5 635.8(6) | 2 987.0(7) | 7 921.9(4) |
| N | 6 428(2) | 3 166(2) | 7 158(2) |
| O(1) | 6 676(2) | 771(2) | 6 675(2) |
| O(2) | 5 968(2) | 1 904(3) | 8 479(1) |
| O(3) | 5 562(2) | 4 241(2) | 8 318(2) |
| C(1) | 7 750(2) | 2 670(3) | 6 006(2) |
| C(2) | 8 008(3) | 1 795(3) | 5 388(2) |
| C(3) | 8 488(3) | 2 271(4) | 4 678(2) |
| C(4) | 8 704(3) | 3 572(4) | 4 612(2) |
| C(5) | 8 468(3) | 4 433(4) | 5 247(2) |
| C(6) | 7 981(3) | 3 976(3) | 5 957(2) |
| C(7) | 4 310(2) | 2 624(3) | 7 350(2) |
| C(8) | 4 066(3) | 1 365(3) | 7 077(3) |
| C(9) | 3 028(3) | 1 090(4) | 6 630(3) |
| C(10) | 2 221(3) | 2 043(4) | 6 460(3) |
| C(11) | 2 484(3) | 3 284(5) | 6 773(3) |
| C(12) | 3 518(3) | 3 594(4) | 7 210(2) |
| C(13) | 1 103(4) | 1 740(7) | 5 945(5) |
| C(14) | 8 311(3) | 1 740(4) | 7 695(2) |
| C(15) | 8 603(3) | 2 546(4) | 8 326(3) |
| C(16) | 9 579(5) | 2 361(8) | 9 025(4) |
| C(17) | 9 327(11) | 2 626(21) | 9 813(6) |
| C(18) | 10 313(9) | 1 373(12) | 8 920(7) |

**Table 8** Atomic coordinates ( × 10$^4$) for **5a**

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| S(1) | 1 836.3(7) | 4 379.0(6) | 7 798.0(4) |
| S(2) | 2 289.5(9) | 3 063.1(8) | 9 125.2(4) |
| O(1) | 1 971(2) | 5 728(2) | 7 907(1) |
| O(2) | 1 655(4) | 1 996(3) | 9 414(2) |
| O(3) | 3 577(3) | 2 877(3) | 8 927(1) |
| O(4) | 4 404(2) | 4 489(3) | 7 660(2) |
| N | 1 369(3) | 3 535(3) | 8 421(1) |
| C(1) | 715(3) | 4 043(3) | 7 050(2) |
| C(2) | 283(4) | 2 809(3) | 6 934(2) |
| C(3) | −541(4) | 2 573(5) | 6 318(3) |
| C(4) | −905(5) | 3 555(5) | 5 837(3) |
| C(5) | −454(5) | 4 762(5) | 5 968(2) |
| C(6) | 369(4) | 5 013(4) | 6 571(2) |
| C(7) | 2 325(3) | 4 277(3) | 9 794(2) |
| C(8) | 1 465(4) | 4 254(5) | 10 322(2) |
| C(9) | 1 554(5) | 5 159(6) | 10 874(3) |
| C(10) | 2 496(4) | 6 063(4) | 10 912(2) |
| C(11) | 3 340(5) | 6 074(4) | 10 372(3) |
| C(12) | 3 266(4) | 5 190(4) | 9 812(2) |
| C(13) | 2 615(8) | 7 025(8) | 11 537(4) |
| C(14) | 3 303(3) | 3 787(3) | 7 456(2) |
| C(15) | 3 872(3) | 4 530(3) | 6 899(2) |
| C(16) | 4 606(4) | 3 874(5) | 6 320(3) |
| C(17) | 5 726(6) | 4 626(8) | 6 148(5) |
| C(18) | 3 693(6) | 3 576(6) | 5 668(3) |

crude product was purified by flash chromatography, using 30% ethyl acetate–light petroleum as eluent, to give the α-methylated sulfoximinooxirane **18**.

S-[trans-3-*Isopropyl*-2-*methyloxiran*-2-*yl*]-S-*phenyl*-N-(p-*tolylsulfonyl*)*sulfoximine* **18a**. M.p. 102–103 °C (Found: C, 57.9; H, 5.8; N, 3.5; $C_{19}H_{23}NO_4S_2$ requires C, 58.0; H, 5.9; N, 3.6%); $\nu_{max}$(KBr)/cm$^{-1}$ 1289s, 1227s, 930s and 804s; $\delta_H$ 0.92 (3 H, d, $J$ 6.8), 1.08 (3 H, d, $J$ 6.5), 1.45 (1 H, m), 1.61 (3 H, s), 2.38 (3 H, s), 3.45 (1 H, d, $J$ 9.4) and 7.22–8.00 (9 H); $m/z$ 394 (MH$^+$, 45%).

S-[(E)-2-*Methyl*-3-(2′-*phenylethyl*)*oxiran*-2-*yl*]-S-*phenyl*-N-(p-*tolylsulfonyl*)*sulfoximine* **18e**. A colourless oil; $\nu_{max}$(film)/cm$^{-1}$ 1599w, 1584w, 1497w, 1238m, 1057s and 816m; $\delta_H$ 1.45 (3 H, s), 1.83 (2 H, m), 2.37 (3 H, s), 2.69 (2 H, m), 3.68 (1 H, t, $J$ 6.3) and

**Table 9** Atomic coordinates ( $\times 10^4$) for **18a**

| | *x* | *y* | *z* |
|---|---|---|---|
| S(1) | 2 856.1(7) | 2 637.3(6) | 3 405.9(7) |
| S(2) | 2 163.6(8) | −335.3(7) | 2 343.4(8) |
| O(1) | 4 358(2) | 3 152(2) | 3 726(2) |
| O(2) | 2 916(3) | 2 394(3) | 5 837(3) |
| O(3) | 1 280(2) | −1 375(2) | 1 150(3) |
| O(4) | 1 835(2) | −413(2) | 3 626(3) |
| N | 2 158(3) | 1 180(2) | 2 261(3) |
| C(1) | 2 283(3) | 3 809(3) | 2 819(3) |
| C(2) | 2 904(4) | 5 257(3) | 3 529(4) |
| C(3) | 2 515(4) | 6 207(3) | 3 077(4) |
| C(4) | 1 558(4) | 5 730(4) | 1 948(4) |
| C(5) | 950(4) | 4 295(3) | 1 256(4) |
| C(6) | 1 316(3) | 3 317(3) | 1 695(3) |
| C(7) | 3 885(3) | −425(3) | 2 178(3) |
| C(8) | 4 230(4) | −1 076(3) | 921(4) |
| C(9) | 5 568(4) | −1 161(4) | 797(4) |
| C(10) | 6 580(4) | −598(4) | 1 912(4) |
| C(11) | 6 210(4) | 52(4) | 3 167(4) |
| C(12) | 4 882(3) | 157(3) | 3 312(3) |
| C(13) | 8 042(4) | −689(6) | 1 757(5) |
| C(14) | 2 128(3) | 2 790(3) | 4 988(3) |
| C(15) | 3 040(4) | 3 891(4) | 6 185(4) |
| C(16) | 552(4) | 2 250(4) | 4 857(4) |
| C(17) | 2 547(5) | 4 609(5) | 7 482(4) |
| C(18) | 2 327(6) | 5 977(6) | 7 418(6) |
| C(19) | 3 636(7) | 4 909(7) | 8 661(5) |

7.05–8.01 (14 H, m); *m/z* (E.I.) 456 ($MH^+$, 23%), 440 (30) and 428 (65) (Found: $MH^+$, 456.1243. $C_{24}H_{26}NO_4S_2$ requires 456.1303).

*X-Ray Crystallography.*—Crystal data for **3a**, **5a** and **18a** are given in Table 6, together with information on data collection and structure determination procedures. Instrumentation and methods were as described previously.[22]

Refined coordinates are given in Tables 7–9. Lists of bond lengths and angles and of atomic displacement parameters are available as supplementary material from the CCDC.*

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* For details of the crystallographic deposition scheme, see 'Instructions for Authors (1993),' *J. Chem. Soc., Perkin Trans. 1*, 1993, Issue 1.

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