Stereoselective Reactions of Lithio-vinylsulfoxides with Aldehydes

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A series of homochiral vinyl sulfoxides—synthesised by treating vinyl Grignard reagents with homochiral menthyl toluene-*p*-sulfinate or sulfinyl oxazolidinones **8a** and **9a**–were deprotonated with LDA and allowed to react with acetaldehyde, isobutyraldehyde, and trimethylacetaldehyde to give β-hydroxy sulfoxides with moderate diastereoselectivity. The sulfoxide **1** gave the best selectivity with the larger aldehyde. The same diastereoselectivity, within experimental error, is observed in the reactions with trimethylacetaldehyde of both *E*-**1** and *Z*-**1** giving 85:15 and 84:16 mixtures of **2c** and **3c** respectively; evidently, the geometry of the vinyl group does not affect the selectivity.

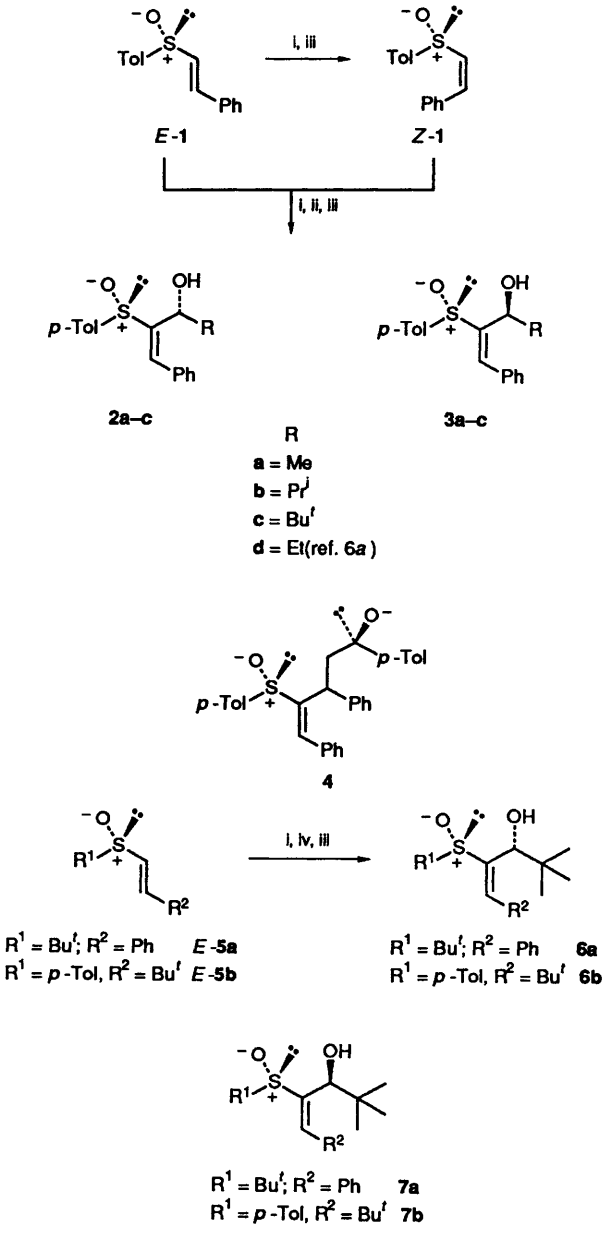
Homochiral sulfoxides are an important class of compounds that have seen widespread use in organic synthesis.[1] In particular, much attention has been focused on the use of metallated sulfoxides; high diastereoselectivity can be obtained upon alkylation[2] whereas moderate selectivity can be obtained upon reaction with carbonyl compounds.[3]

We have, for some time, been undertaking a study of α-heteroatom-stabilised vinyl anions,[4] so we were hopeful that metallated vinyl sulfoxides would show selectivity similar to their saturated counterparts. Vinyl sulfoxides themselves have been shown to be highly selective in a variety of reactions: namely, in electrophilic addition to the carbon–carbon double bond;[5] in the addition of nucleophiles in a Michael sense;[6] in Diels–Alder reactions;[7] and in 1,3-dipolar cycloadditions.[8]

Although the reaction of lithiated vinyl sulfoxides and aldehydes is not unprecedented[9]—in most cases the diastereoselectivity is poor—there appears to have been no methodical study. We therefore undertook such a study[10] and now report the results in full.

Results and Discussion

We studied the reaction of the lithio anions of *E*-**1** and *Z*-**1**, obtained by deprotonation† with lithium diisopropylamide (LDA) (conditions for which were optimised in the reaction with methyl iodide) with three aldehydes (Scheme 1). In each case a mixture of two diastereoisomeric alcohols **2a–c** and **3a–c** (Table 1) was obtained, the ratio being determined by HPLC. In all cases a very small amount (< 7%) of the dimer **4** was isolated, presumably formed by conjugate addition of the lithiosulfinyl anion to the starting material. Evidently as the aldehyde



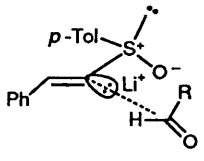
Scheme 1 *Reagents and conditions:* i, lithium diisopropylamide (LDA), THF, −78 °C; ii, RCHO; iii, NH_4Cl, H_2O; iv, Bu^{t}CHO

† We have no explicit evidence that the reaction is taking place *via* direct deprotonation, although this is the generally accepted mechanism for this type of reaction. An alternative explanation involves conjugate additon of diisopropylamine to the vinyl sulfoxide followed by aldol reaction and subsequent elimination of the amine, *i.e.* a Baylis–Hillman type reaction. This type of condensation has been observed in the reaction of vinyl sulfones with aldehydes catalysed by 1,4-diazabicyclooctane (DABCO) (25 °C, 1–10 weeks).[31] It is interesting to see that the Baylis–Hillman mechanism has not been ruled out in the fluoride-promoted condensation of α-silylvinyl sulfoxides with aldehydes.[9e] Since our reaction conditions involve low temperatures, short reaction times and a secondary amine—in marked contrast to the conditions of the Baylis–Hillman reaction—we favour the mechanism of direct depronation. Although this has no bearing on the results presented in this paper it does have important implications for the explanation of the diastereoselectivity.

Table 1 Diastereoisomers **3a–c** and **2a–c** obtained from *E*-**1** and *Z*-**1**

		Ratio by HPLC **2a–c**:**3a–c**	% Yield[a] **2a–c**	% Yield[a] **3a–c**
E-**1**	a	45:55	18	34
	b	34:66	16	44
	c	15:85	—	59
	d	45:55 (ref. 6*a*)	—	—
Z-**1**	a	47:53	18	25
	b	41:59	25	35
	c	14:86	—	71[b]

[a] Yield of pure material. [b] Total yield of both diastereoisomers.



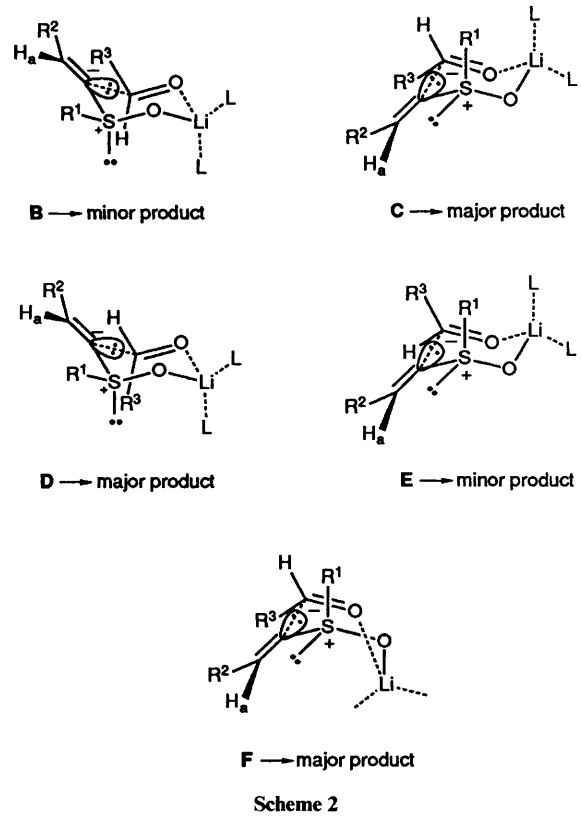
A

Fig. 1

becomes larger the selectivity increases from poor in the case of acetaldehyde (Marino[6a] has since reported similarly poor selectivity with propionaldehyde) to moderately high in the reaction with trimethylacetaldehyde. That the selectivities with *E*-**1** and *Z*-**1** are the same, within experimental error, is not surprising since Houk,[11] among others,[12] has shown that vinyl anions bearing an adjacent electron-withdrawing group are configurationally unstable. To prove this was so here, the anion of *Z*-**1** was reprotonated, and *E*-**1** was indeed obtained; it was of the same optical purity as the original sample thereby dismissing fears of racemisation. Similar behaviour of lithiovinyl sulfoxides has been reported.[13]

We have previously explained the diastereoselectivity by invoking reaction *via* the transition state **A** (Fig. 1). We reasoned that the anion would exist in a conformation where the lone pair of the sulfur atom can overlap with the π system of the carbon–carbon double bond, leaving the sulfoxide oxygen free to interact with the lithium atom. Such co-ordination has been proposed for other α-lithio sulfoxides.[14] In this model, the two planes of the alkene and carbonyl groups approach each other at the Bürgi–Dunitz angle; the approach of the aldehyde occurs so that the R group is on the less hindered side from the phenyl group. This picture is obviously very crude but begins to explain the increased selectivity in the reaction with trimethylacetaldehyde. We then set about testing the validity of the model by further experiments.

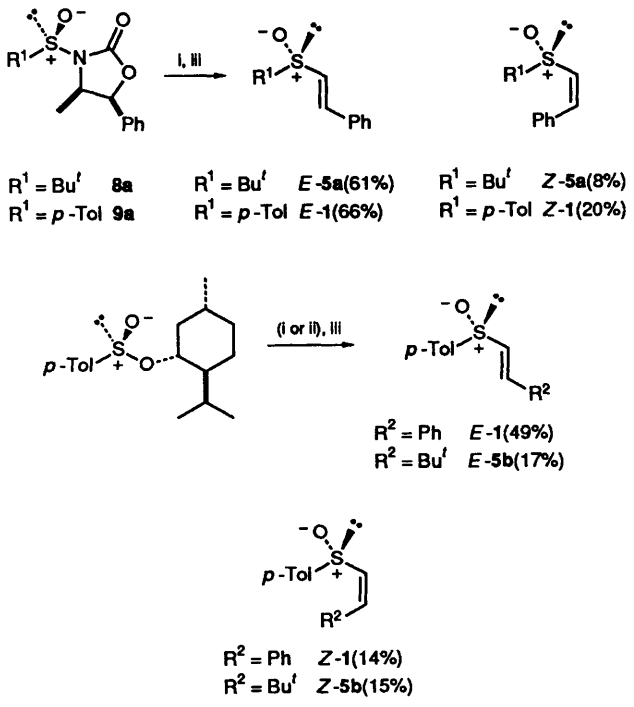
Replacing the *p*-tolyl group with a *tert*-butyl group did not lead to an appreciable difference in the diastereoselectivity of *E*-**5a** with trimethylacetaldehyde; a 4.6:1 mixture of **6a**:**7a** was obtained. Since the *p*-tolyl group in **A** is distant to the R group of the aldehyde this result is perhaps not too surprising. On the other hand replacing the phenyl group of **1** with a *tert*-butyl group, as in *E*-**5b**, did not lead to the expected selectivity in the reaction with trimethylacetaldehyde. Indeed, quite the opposite result was observed since a near equal amount of **6b** and **7b** was isolated from both isomers *E*-**5b** and *Z*-**5b**. Evidently the anion is again configurationally unstable; quenching the anion from *Z*-**5b** with aqueous ammonium chloride gave the *trans* isomer *E*-**5b**. The poor selectivity shown by **5b** illustrates that our model is very crude and, not surprisingly, it does not fully explain our results. We were obviously interested in developing a more sophisticated model. To this end we looked to the elegant studies of Boche[15] and Gais[16] who have both shown by X-ray crystallographic studies that in crystals of α-sulfonyl carbanions the lithium counter-ion is bound to oxygen and not carbon. The only crystal structure of an α-sulfinyl carbanion (as a tetramethylethylenediamine complex), again the work of Boche,[17] also shows that the lithium is bound to the sulfinyl oxygen. If this is also the case in our own work, we propose the models **B**–**E** shown in Scheme 2, where the anion reacts through



Scheme 2

a chair-like transition state (as will be seen, boat-like transition states such as **F** cannot, and should not, be ruled out). Considering the orientation of the sulfinyl group first. In all cases there is a play-off between the unfavourable $A^{1,3}$ interaction between R^1 and H_a and the positioning of the same R^1 group axial or equatorial; the geometry of the double-bond precludes minimisation of both of these interactions. Now concentrating on the positioning of the aldehyde, the R^3 group can either be axial or equatorial. When it is axial there are obviously unfavourable $A^{1,3}$ diaxial interactions with the R^1 and L groups. On the other hand if R_3 is equatorial there is now the *pseudo*-$A^{1,3}$ interaction between R^2 and R^3. Obviously the play-off between these and other interactions is well balanced, which may well explain why even in our best case the selectivity is only modest. Nevertheless, we favour reaction *via* model **C** which explains the increased selectivity with larger R^3 groups and also the reduced selectivity when R^2 is a *tert*-butyl group (associated with the increased $A^{1,3}$ interaction). It would be very presumptuous to deny that our new model is anything but a very crude approximation of the real picture. It would seem that the model lends itself to an interesting computational study.

The vinyl sulfoxides *E*-**1** and *Z*-**1** were made according to the Andersen procedure[18] (Scheme 3) by coupling of a mixture of *E* and *Z* β-bromostyrene and (1*R*,2*S*,5*R*)-menthyl (*S*)-toluene-*p*-sulfinate and were easily separated by chromatography and recrystallisation and had properties (m.p., NMR, $[\alpha]^D$) in agreement with those reported.[19] Similarly, the sulfoxides *E*-**5a** and *Z*-**5a** were derived from 1-bromo-4,4-dimethylbutene and (1*R*,2*S*,5*R*)-menthyl (*S*)-toluene-*p*-sulfinate. The synthesis of



Scheme 3 *Reagents and conditions:* i, PhCH=CHMgBr, room temp., 2 h; ii, Bu'CH=CHMgBr; iii, NH_4Cl, H_2O

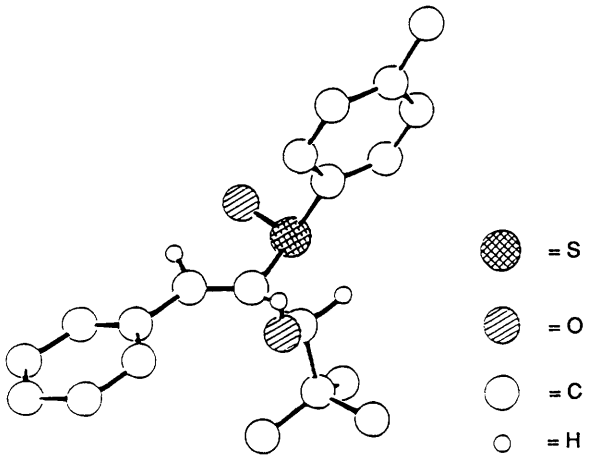
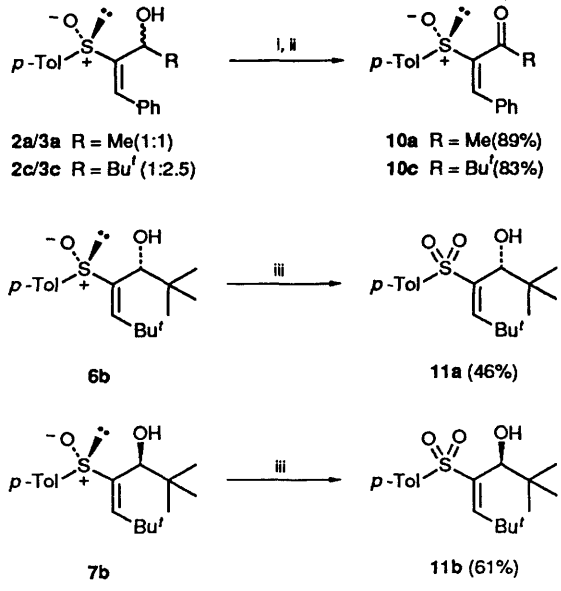


Fig. 2 X-Ray crystal structure of (S); (E)-4,4-dimethyl-2[(*S*)-*p*-tolylsulfinyl]pent-1-en-3-ol **3c**

the vinyl sulfoxides *E*-**5b** and *Z*-**5b** bearing a *tert*-butyl group attached to sulfur proved problematic since we had difficulty in obtaining (1*R*,2*S*,5*R*)-menthyl (*S*)-1,1-methylethanesulfinate. Unlike (1*R*,2*S*,5*R*)-menthyl (*S*)-toluene-*p*-sulfinate this sulfinate is not crystalline, making separation from its diastereosiomer that much more difficult—indeed we found that as prepared by the literature method,[20] although chromatographically homogeneous, it was actually a 1.6:1 diastereoisomeric mixture. We therefore decided to use a chiral auxiliary other than (1*R*,2*S*,5*R*)-menthol, namely Evans' norephedrine-derived (4*R*,5*S*)-4-methyl-5-phenyloxazolidin-2-one.[21] This oxazolidinone was treated with 1,1-dimethylethanesulfinyl chloride to give a mixture of the two diastereoisomers **8a** and **8b**, in a 2:1 ratio, which were fortunately easily separated by flash chromatography. The major isomer **8a**, which we arbitrarily assigned as being of *R* stereochemistry at sulfur, reacts with the Grignard reagent from β-bromostyrene to give a mixture of *E*-**5b** (61%) and *Z*-**5b** (8%). Casey has since shown that this assignment is correct as part of a general synthesis of homochiral sulfoxides.[22] Evans' auxiliary could also be used to make the *p*-tolyl sulfoxides *E*-**1** and *Z*-**1** by coupling toluene-*p*-sulfinyl chloride with 4-methyl-5-phenyloxazolidin-2-one in the same way, to give a 4:1 mixture of diastereoisomers **9a** and **9b** from which the major isomer was obtained by simple recrystallisation. This oxazolidinone reacts cleanly with *E*/*Z*-β-styrylmagnesium bromide to give *E*-**1** (66%){$[\alpha]_D$ +120} and *Z*-**1** (20%). Since the vinyl sulfoxide *E*-**1** has the same configuration as that derived from (1*R*,2*S*,5*R*)-menthyl (*S*)-toluene-*p*-sulfinate we can conclude that the configuration at sulfur in **9a** is *R*, assuming the substitution proceeds with inversion of configuration—a precedent well established by other sulfinic acid derivatives.[23] Again, since this work was carried out Prof. Evans *et al.* have reported, in full, the use of a variety of *N*-sulfinyloxazolidinones in the preparation of chiral organosulfur compounds.[24] The reported properties of **9a** are similar to those of our own showing our assignment to be correct.

The stereochemical assignment is based on a crystal structure determination on the major isomer **3c** (Fig. 2) from which it is clear that the configuration of the carbon bearing the hydroxy group is *S*.[25] Marino has also reported the crystal structure of **2d**.[6a] We have assumed that the major isomer of the mixtures **2a**/**3a** and **2b**/**3b** were of the same configuration as **3c**. We considered it more important to prove that the isomers **2** and **3** differed only in their configuration at C-2 in the case of **2a**/**3a** and at C-3 in the cases of **2b**/**3b** and **2c**/**3c** and not in the geometry of the double bond. The stereochemical relationship of the isomers was shown to be diastereoisomeric and not geometric (*E*/*Z*) since oxidation of **2a**/**3a** (1:1) and **2c**/**3c** (1:2.5) by Swern conditions—not a procedure that normally isomerises enones[26]—gave a single enone **10a** (89%) and **10c** (83%) in each case respectively (Scheme 4). Furthermore, oxidation of **6b** and **7b** with *m*-chloroperbenzoic acid gave the enantiomeric sulfones **11a** ($[\alpha]^D$ −20.8) and **11b** ($[\alpha]^D$ +21.3) respectively.



Scheme 4 *Reagents and conditions:* i, DMSO, ClCOCOCl, −78 °C, 1 h; ii, NEt_3, ⟶ room temp. 1 h; iii, MCPBA, CH_2Cl_2, −78 °C, 2 h then ⟶ room temp., 12 h

Experimental

90 MHz ^1H NMR spectra were recorded on a Varian EM-390 spectrometer. Highfield ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Brucker AM-400

spectrometer in the highfield NMR service at the University of Warwick. Mass spectra were recorded on a V.G. micromass 16B spectrometer. Elemental analysis was carried out by CHN Analysis, Wigston, Leicester. IR spectra were recorded on a Perkin-Elmer 298 spectrometer. M.p.s were determined on a Kofler hot-stage and were uncorrected.

Flash chromatography was carried out according to the method of Still *et al.*[27] using silica gel manufactured by Merck and Co., Kiesel 60, 230–400 mesh (ASTM). TLC was conducted on pre-coated aluminium sheets (60–254) with a 0.2 mm layer thickness, manufactured by Merck and Co.

The concentration of butyllithium was determined by back titration with 0.1 mol dm^{-3} hydrochloric acid from solutions in dibromoethane and water using phenolphthalein as an indicator.

Petroleum refers to the fraction of light petroleum with b.p. 40–60 °C; both light petroleum and ethyl acetate were distilled prior to use. Tetrahydrofuran (THF) and toluene were distilled from sodium metal in the presence of benzophenone. Ether refers to diethyl ether which was distilled from $LiAlH_4$.

LDA was prepared by the addition of butyllithium (1 mmol in hexanes) to diisopropylamine in ether (3 cm^3), at 0 °C under nitrogen. The solution was stirred for 0.5 h. Unless specified as otherwise, standard aqueous work-up involved addition of aqueous ammonium chloride and extraction with ether (× 3). The extracts were dried (Na_2SO_4), and evaporated under reduced pressure.

(E)- *and* (Z)-2-*Phenyl*-1-[(R)-p-*tolylsulfinyl*]*ethylene* **E-1** *and* **Z-1**.—To a solution of (1*R*,2*S*,5*R*)-menthyl (S)-toluene-*p*-sulfinate[18] (4.2 g, 14 mmol) in benzene (25 cm^3) was added dropwise a solution of β-styrylmagnesium bromide [from magnesium (0.46 g, 19 mmol) and β-bromostyrene (2.3 cm^3, 18 mmol)] at room temperature. The solution was stirred at room temperature for a further 2 h. Standard aqueous work-up, chromatography [SiO_2, ether–petroleum (4:1 v/v)], and recrystallisation (petroleum) gave the *trans*-sulfoxide[19] ***E*-1** (1.66 g, 49%) as needles; m.p. 78–79 °C (lit.,[19] 82 °C); $[\alpha]_D$ +162 (*c* 2.1 in $CHCl_3$) (lit.,[19] $[\alpha]_D$ +166); R_f 0.36 [ether–petroleum (4:1 v/v)]; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 330w, 2970w, 2860w, 1610w, 1595w, 1575w, 1490m, 1445m, 1255m, 1175m, 1085s, 1045brs, 1015m, 965s, 895w, 870m, 810s, 790m, 690br s and 620w; δ_H(300 MHz; $CDCl_3$) 2.40 (3 H, s, Me), 6.81 (1 H, d, *J* 15.5, PhCH=C*H*), and 7.25–7.59 (10 H, m, 9 × aromatic and PhCH); δ_C(75 MHz, $CDCl_3$) 21.39 (q), 124.84 (d), 127.67 (d), 128.81 (d), 129.67 (d), 130.08 (d), 133.04 (d), 133.75 (s), 135.89 (d), 140.66 (s) and 141.67 (s); *m/z* 242 (M^+), 226 (100), 211 (45), 194 (31), 179 (21), 178 (34), 166 (12), 135 (22), 121 (22) and 103 (16); and the *cis*-sulfoxide[19] ***Z*-1** (0.49 g, 14%) as needles, m.p. 48–51 °C (lit.,[19] 52–52.5 °C); $[\alpha]_D$ −700 (*c* 2.1 in $CHCl_3$) (lit.,[19] $[\alpha]_D$ −736); R_f 0.26 [ether–petroleum (4:1 v/v)]; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3020m, 2970m, 2860w, 1605s, 1595s, 1575m, 1490s, 1445m, 1395m, 1300w, 1205m, 1175m, 1085s, 1045brs, 1015s, 920m, 810s and 720br s; δ_H(300 MHz; $CDCl_3$) 2.39 (3 H, s, Me), 6.43 (1 H, d, *J* 10.6, PhCH=C*H*), 7.08 (1 H, d, *J* 10.6, PhC*H*=CH) and 7.26–7.58 (9 H, aromatic); δ_C(75 MHz; $CDCl_3$) 21.34 (q), 124.32 (d), 128.60 (d), 129.41 (d), 129.73 (d), 130.04 (d), 133.83 (s) 137.09 (d), 138.34 (d), 141.34 (s) and 141.48 (s); *m/z* 242 (M^+), 226 (100), 211 (46), 194 (35), 179 (23), 178 (35), 166 (13), 135 (25), 121 (24) and 103 (20).

(E)-1-*Phenyl*-2-[(R)-p-*tolylsulfinyl*]*propene*.—To a solution of LDA (1.0 mmol) was added dropwise a solution of the vinyl sulfoxide ***E*-1** (200 mg, 0.83 mmol) in THF (5 cm^3) at −78 °C. After 2 min methyl iodide (260 mm^3, 4.2 mmol) in THF (1 cm^3) was added to the resulting brown solution and the mixture stirred for a further 2 h at −78 °C. Standard aqueous work-up, chromatography (SiO_2, ether) and recrystallisation (petroleum) gave the vinyl sulfoxide[20] (118 mg, 56%) as a white solid, m.p. 74–76 °C (Found: C, 75.0; H, 6.3. $C_{16}H_{16}OS$ requires C, 75.00; H, 6.02%); R_f 0.39 [ether–petroleum (4:1 v/v)]; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3050s, 2980s, 1595m, 1490s, 1445s, 1420s, 1265brs, 1210m, 1180m, 1100m, 1080s, 1055s, 1015s, 960m, 925m, 895s, 810s and 735br s; δ_H(300 MHz; $CDCl_3$) 1.89 (3 H, d, *J* 1.4, CH=C*Me*), 2.39 (3 H, s, Me) and 7.26–7.56 (10 H, 9 × aromatic and CH=C); δ_C(300 MHz; $CDCl_3$) 10.47 (q), 21.24 (q), 125.10 (d), 128.24 (d), 128.40 (d), 129.14 (d), 129.70 (d), 131.64 (d), 134.62 (s), 139.52 (s), 141.27 (s) and 142.11 (s); *m/z* 256 (M^+) 240 (72), 225 (25), 208 (27), 181 (29), 140 (20), 124 (15), 117 (45) and 115 (100).

(2S)-(E)-4-*Phenyl*-3-[(S)-p-*tolylsulfinyl*]*but*-3-*en*-2-*ol* **3a** *and* (2R)-(E)-4-*Phenyl*-3-[(S)-p-*tolylsulfinyl*]*but*-3-*en*-2-*ol* **2a**.—To a solution of LDA (1 mmol) was added the vinyl sulfoxide ***E*-1** (200 mg, 0.83 mmol) at −78 °C. After 2 min acetaldehyde (280 mm^3, 5 mmol) in THF (5 cm^3) was added and the mixture stirred for 1 h at −78 °C. Standard aqueous work-up gave a crude 1.2:1 mixture of **3a**:**2a** which were separated by use of a chromatotron to give the (2*S*)-sulfoxide **3a** (80 mg, 34%) as an oil; $[\alpha]_D$ +11.5 (*c* 1.6 in $CHCl_3$); R_f 0.31 (ether); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3320br m, 3020w, 2970m, 2920m, 1595m, 1490m, 1445m, 1370m, 1100m, 1080s, 1030brs, 1010s, 925 m, 880m, 810s and 620m; δ_H(300 MHz; $CDCl_3$) 0.91 (3 H, d, *J* 6.7, CH*Me*), 2.39 (3 H, s, Me), 3.42 (1 H, br s, OH), 5.05 (1 H, br m, C*H*OH) and 7.25–7.72 (10 H, m, aromatic and C=CH); δ_C(300 MHz; $CDCl_3$) 21.46 (q), 22.16 (q), 65.46 (d), 126.15 (d), 128.58 (d), 129.69 (d), 131.25 (d), 134.06 (s), 140.54 (s), 141.89 (s) and 148.90 (s) (Found: M^+ + H, 286.1029. $C_{17}H_{18}O_2S$ requires M^+ + H, 286.1027); and the (2*R*)-sulfoxide **2a** (43 mg, 18%) as an oil; $[\alpha]_D$ +101 (*c* 1.9 in $CHCl_3$); R_f 0.33 (ether); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3360br w, 2970w, 2920w, 1595w, 1490m, 1450w, 1375w, 1250m, 1100m, 1075s, 1035br s, 1010s, 880w, 810s and 690br s; δ_H(300 MHz; $CDCl_3$) 1.36 (3 H, d, *J* 6.7, CH*Me*), 2.37 (3 H, s, Me), 2.60 (1 H, br s, OH), 5.02 (1 H, br m, C*H*OH) and 7.20–7.64 (10 H, m, aromatic and C=CH); δ_C(300 MHz; $CDCl_3$) 21.42 (q), 22.42 (q), 65.86 (d), 125.61 (d), 128.61 (d), 128.78 (d), 129.55 (d), 130.00 (d), 132.57 (d), 133.91 (s), 141.09 (s), 141.72 (s) and 147.58 (s) (Found: M^+ + H, 286.1014. $C_{17}H_{18}O_2S$ requires M^+ + H, 286.1027); and (E)-2,4-*diphenyl*-1,3-*bis*[(S)-p-*tolylsulfinyl*]*but*-3-*ene* **4** (8 mg, 2%) as an oil; R_f 0.33 (ether); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3030w, 2950m, 2870w, 1720m, 1595w, 1490m, 1445w, 1395w, 1380w, 1270br m, 1120br w, 1085s, 1045s, 1015m and 810s; δ_H(300 MHz; $CDCl_3$) 2.33 (3 H, s, Me), 2.38 (3 H, s, Me), 3.16 (1 H, dd, *J* 13.1 and 4.7, SCH_aH_b), 3.43 (1 H, dd, *J* 13.1 and 10.8, SCH_aH_b), 4.82 (1 H, dd, *J* 10.7 and 4.7, SCH_aH_bCH) and 7.05–7.54 (18 H, m, aromatic); δ_C(75 MHz; $CDCl_3$) 21.34 (q), 21.40 (q), 39.03 (d), 60.99 (t), 124.30, 125.64, 127.41, 128.50, 128.62, 128.65, 128.71, 129.04, 129.72, 129.85, 132.99, 134.15, 136.83, 140.08, 141.57, 141.63 and 147.22.

(3S)-(E)-4-*Methyl*-1-*phenyl*-2-[(S)-p-*tolylsulfinyl*][*pent*-1-*en*-3-*ol* **3b** *and* (3R)-(E)-4-*Methyl*-1-*phenyl*-2-[(S)-p-*tolylsulfinyl*]*pent*-1-*en*-3-*ol* **2b**.—In a similar fashion, the vinyl sulfoxide ***E*-1** (200 mg, 0.83 mmol), LDA (1 mmol) and isobutyraldehyde (113 mm^3, 1.2 mmol) gave the (3S)-*alcohol* **3b** (114 mg, 44%) as a white solid; m.p. 106–108 °C; $[\alpha]_D$ +24 (*c* 2.1 in $CHCl_3$) (Found: C, 72.7; H, 7.1. $C_{19}H_{22}O_2S$ requires C, 72.58; H, 7.05%); R_f 0.32 (ether); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3360br m, 3020m, 2960s, 2920m, 2870m, 1595m, 1490m, 1465m, 1445m, 1380m, 1300m, 1205m, 1175m, 1115m, 1080s, 1030br s, 930m, 910m, 810s and 620m; δ_H(400 MHz; $CDCl_3$) 0.56 (3 H, d, *J* 6.7, Me), 0.91 (3 H, d, *J* 6.5, Me), 2.02 (1 H, m, C*H*Me_2), 2.39 (3 H, s, Me), 2.95 (1 H, d, *J* 5.8, OH), 4.12 (1 H, dd, *J* 9.3 and 5.8, C*H*OH), 7.20 (1 H, s, PhC*H*) and 7.25–7.65 (9 H, m, aromatic); δ_C(100 MHz; $CDCl_3$) 18.98 (q), 19.06 (q), 21.32 (q), 31.52 (d), 75.46 (d), 126.10 (d), 128.32 (d), 128.43 (d), 129.46 (d), 129.96 (d), 133.12 (d), 134.22 (s), 139.94 (s), 142.06 (s) and 147.13 (s); *m/z* 314 (M^+),

298 (16), 271 (100), 255 (19), 213 (40), 175 (16), 157 (73), 140 (54), 139 (66), 131 (37), 129 (44) and 115 (43); and the (3R)-*alcohol* **2b** (42 mg, 16%) as a white solid; m.p. 133–135 °C; $[\alpha]_D$ +35 (*c* 2.0 in $CHCl_3$) (Found: C, 72.4; H, 7.2. $C_{19}H_{22}O_2S$ requires C, 72.58; H, 7.05%); R_f 0.37 (ether); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3380br w, 3020w, 2960m, 2920m, 2870m, 1595w, 1490m, 1465m, 1375w, 1365w, 1080s, 1040br s, 1015s and 810s; δ_H(400 MHz; $CDCl_3$) 0.72 (3 H, d, *J* 6.7, Me), 0.96 (3 H, d, *J* 6.5, Me), 1.70 (1 H, d, *J* 6.1, OH), 2.07 (1 H, m, C*H*Me_2), 2.39 (3 H, s, Me), 4.41 (1 H, dd, *J* 9.2 and 6.1, C*H*OH), 7.25 (1 H, s, PhCH) and 7.28–7.66 (9 H, m, aromatic); δ_C(100 MHz, $CDCl_3$) 18.71 (q), 19.10 (q), 21.31 (q), 32.17 (d), 74.53 (d), 125.63 (d), 128.50 (d), 128.55 (d), 129.30 (d), 129.99 (d), 133.29 (d), 134.25 (s), 141.56 (s), 141.78 (s) and 147.20 (s); *m/z* 314 (M^+), 298 (15), 296 (21), 271 (100), 255 (19), 225 (36), 213 (43), 157 (75), 140 (55), 139 (67), 131 (36), 129 (44) and 115 (38).

(3S)-(E)-4,4-*Dimethyl*-1-*phenyl*-2-[(S)-p-*tolylsulfinyl*]*pent*-1-*en*-3-*ol* **3c** *and* (3R)-(E)-4,4-*Dimethyl*-1-*phenyl*-2-[(S)-p-*tolylsulfinyl*]*pent*-1-*en*-3-*ol* **2c**.—In a similar fashion, the vinyl sulfoxide *E*-**1** (200 mg, 0.83 mmol), LDA (1 mmol) and trimethylacetaldehyde (220 mm^3, 2.0 mmol) gave the (3S)-*alcohol* **3c** (130 mg, 48%) as a white solid; m.p. 145–147 °C (from isopropyl ether); $[\alpha]_D$ +142 (*c* 2.0 in $CHCl_3$) (Found: C, 73.1; H, 7.5. $C_{20}H_{24}O_2S$ requires C, 73.13; H, 7.36%); R_f 0.39 (ether); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3360br m, 3020m, 2950s, 2870m, 1595m, 1490m, 1475s, 1445m, 1395m, 1365m, 1210m, 1180m, 1080s, 1050br s, 1015s, 810s and 620m; δ_H(300 MHz; $CDCl_3$) 0.91 (9 H, s, Me_3), 2.39 (3 H, s, Me), 3.51 (1 H, br s, OH), 4.32 (1 H, br s, C*H*OH), 7.15 (1 H, s, PhCH) and 7.23–7.63 (9 H, m, aromatic); δ_C(75 MHz; $CDCl_3$) 21.43 (q), 26.99 (q), 38.21 (s), 79.06 (d), 126.43 (d), 128.25 (d), 128.32 (d), 129.70 (d), 130.05 (d), 132.92 (d), 134.96 (s), 140.40 (s), 142.07 (s) and 146.39 (s); *m/z* 328 (M^+) 272 (20), 271 (100), 255 (31), 225 (17), 140 (36), 139 (36), 135 (24), 131 (27) and 115 (20); and the (3R) alcohol **2c** (31 mg, 11%) as a white solid; m.p. 189–192 °C (from isopropyl ether); $[\alpha]_D$ −52 (*c* 2.2 in $CHCl_3$) (Found: C, 73.0; H, 7.4. $C_{20}H_{24}O_2S$ requires C, 73.13; H, 7.36%); R_f 0.44 (ether); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3360br w, 2950m, 2860m, 1595w, 1490m, 1475m, 1365w, 1175w, 1075s, 1040br s, 1010s, 810s and 620w; δ_H(300 MHz; $CDCl_3$) 0.92 (9 H, s, Me_3), 1.57 (1 H, br s, OH), 2.39 (3 H, s, Me), 4.91 (1 H, br s, C*H*OH) and 7.20–7.79 (10 H, m, aromatic ad PhCH); *m/z* 328 (M^+), 272 (20), 271 (100), 255 (50), 238 (30), 225 (42) 210 (20), 140 (47), 139 (41), 135 (39), 131 (47) and 115 (47).

(E)-1-*Bromo*-3,3-*dimethylbutene*.—To a solution of 3,3-dimethylbut-1-yne (5 g, 61 mmol) in heptane at 0 °C was added diisobutylaluminium hydride (1 mol dm^{-3} solution in heptane; 61 cm^3, 61 mmol). After the addition the mixture was stirred for 2 h at 50 °C. The solvent was removed under reduced pressure and the white residue dissolved in THF (30 cm^3); bromine (3.2 cm^3, 61 mmol) in dichloromethane (25 cm^3) was then added to the solution at −50 °C. The mixture was allowed to warm to room temperature and sulfuric acid (20% aqueous solution; 20 cm^3) with cooling in an ice-bath. Once gas evolution had ceased the mixture was poured into an ice–sulfuric acid (20% aqueous solution) and the mixture extracted with dichloromethane (2 × 50 cm^3). The combined extracts were washed successively with aqueous sodium thiosulfate (100 cm^3) and aqueous sodium hydrogen carbonate (100 cm^3) and dried ($MgSO_4$). The solvent was removed under reduced pressure and Kugelrohr distillation gave the vinyl bromide[28] (4.4 g, 44%) as an oil, b.p. 134–136 °C (lit.,[28] 48 °C/50 mmHg) (Found: C, 44.6; H, 6.9. $C_6H_{11}Br$ requires C, 44.20; H, 6.80%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 2940s, 2890s, 2860s, 1610m, 1460s, 1360s, 1225m, 1195w, 1165m, 1100m, 1020m, 945s and 905m; δ_H(90 MHz; $CDCl_3$) 1.05 (9 H, s, Me_3), 5.90 (1 H, d, *J* 15, C*H*=CH) and 6.20 (1 H, d, *J* 15, CH=C*H*); *m/z* 164, 162 (M^+), 149 (14), 147 (16), 121 (10) and 119 (11).

(E)- *and* (Z)-3,3-*Dimethyl*-1-[(R)-p-*tolylsulfinyl*]*but*-1-*ene* E-**5b** *and* Z-**5b**.—In a similar fashion to the synthesis of *E*/*Z*-**1**, 2-*tert*-butylvinylmagnesium bromide [from magnesium (0.33 g, 13.5 mmol) and (*E*)-1-bromo-3,3-dimethylbutene (2 g, 12.03 mmol)] and (1*R*,2*S*,5*R*)-menthyl (*S*)-toluene-*p*-sulfinate (3.26 g, 12.3 mmol) gave a mixture of the *trans*-vinyl sulfoxide[29] *E*-**5b** (457 mg, 17%) as a white solid; R_f 0.46 (ether); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 2950s, 2860m, 1590w, 1490m, 1460m, 1390ww, 1360m, 1080s, 1040s, 1010s, 965s, 910m and 805s; δ_H(300 MHz; $CDCl_3$) 1.08 (9 H, s, Me_3), 2.40 (3 H, s, Me), 6.11 (1 H, d, *J* 15.4, Me_3CCH=C*H*), 6.59 (1 H, d, *J* 15.4, Me_3CC*H*=CH), 7.30 (2 H, m, aromatic) and 7.49 (2 H, m, aromatic); δ_C(75 MHz; $CDCl_3$) 21.36 (q), 28.74 (q), 34.14 (s), 124.58 (d), 129.93 (d), 131.09 (d), 141.15 (s), 141.21 (s) and 150.53 (d) (Found: M^+, 222.1059. $C_{13}H_{18}OS$ requires M^+, 222.1078); and the *cis*-vinyl sulfoxide[29] *Z*-**5b** (408 mg, 15%) as an oil, R_f 0.31 (ether); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 2960s, 2860m, 1595w, 1490m, 1470m, 1360m, 1205m, 1080s, 1030s, 1010s, 810m and 790m; δ_H(300 MHz; $CDCl_3$) 1.31 (9 H, s, Me_3), 2.39 (3 H, s, Me), 6.02 (1 H, d, *J* 10.9, Me_3CCH=C*H*), 6.11 (1 H, d, *J* 10.9, Me_3CC*H*=CH), 7.30 (2 H, m, aromatic) and 7.53 (2 H, m, aromatic); δ_C(75 MHz; $CDCl_3$) 21.31 (q), 31.33 (q), 35.35 (s), 124.26 (d), 129.92 (d), 134.51 (d), 141.01 (s), 141.73 (s) and 150.07 (d) (Found: M^+, 222.1074. $C_{13}H_{18}OS$ requires M^+, 222.1078).

(S)-(E)- *and* (R)-(E)-2,2,6,6-*Tetramethyl*-4-[(S)-p-*tolylsulfinyl*]*hept*-4-*en*-3-*ol* **6b** *and* **7b**.—To a solution of LDA (0.54 mmol) was added the vinyl sulfoxide *E*-**5b** (100 mg, 0.45 mmol) at −78 °C. After 2 min trimethylacetaldehyde (60 mm^3, 0.54 mmol) was added and the mixture stirred for 1 h at −78 °C. Standard aqueous work-up gave a crude 1.2:1 mixture of diastereoisomers **6b**, R_f 0.24 (ether); R_t (Partisil PXS 10/25, ether, 5 cm^3 min^{-1})/min 4.11; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3340br m, (OH), 2950s, 2860s, 1590w, 1470m, 1390m, 1360m, 1195m, 1175m, 1075s, 1045s, 1010s and 805s; δ_H(300 MHz; $CDCl_3$) 1.10 (9 H, s, Me_3), 1.12 (9 H, s, Me_3), 2.41 (3 H, s, Me), 4.88 (1 H, s, C*H*OH), 5.64 (1 H, d, *J* 0.6, C=CH), 7.31 (2 H, m, *meta*-Ph) and 7.55 (2 H, m, *ortho*-Ph); δ_C(75 MHz; $CDCl_3$) 21.43 (q), 27.72 (q), 30.66 (q), 34.88 (s), 36.29 (s), 77.84 (d), 126.41 (d), 129.77 (d), 141.02 (s), 141.61 (s), 145.32 (s) and 146.93 (d) (Found: M^+, 308.1797. $C_{18}H_{28}O_2S$ requires M^+, 308.1810); and **7b**, R_f 0.49 (ether); R_t (Partisil PXS 10/25, ether, 5 cm^3 min^{-1})/min 1.26; $[\alpha]_D$ +179 (*c* 1.4 in $CHCl_3$) (Found: C, 69.8; H, 8.95. $C_{18}H_{28}O_2S$ requires C, 70.1; H, 9.15%); δ_H(300 MHz; $CDCl_3$) 1.09 (9 H, s, Me_3), 1.12 (9 H, s, Me_3), 2.36 (3 H, s, Me), 4.88 (1 H, s, C*H*OH), 6.82 (1 H, s, C=CH), 7.23 (2 H, m, *meta*-Ph) and 7.56 (2 H, m, *ortho*-Ph); δ_C(75 MHz; $CDCl_3$) 21.41 (q), 27.49 (q), 30.83 (q), 34.68 (s), 36.21 (s), 75.28 (d), 125.77 (d), 129.72 (d), 141.37 (s), 141.91 (d), 143.02 (s) and 144.36 (s); *m/z* 308 (M^+), 251 (37%), 235 (21), 169 (32), 151 (51), 140 (100), 139 (47), 124 (49), 111 (71) and 109 (40).

(4R,5S)-3-[(R)-tert-*Butylsulfinyl*]-4-*methyl*-5-*phenyloxazolidin*-2-*one* **8a** *and* (4R,5S)-3-[(S)-tert-*Butylsulfinyl*]-4-*methyl*-5-*phenyloxazolidin*-2-*one* **8b**.—To a solution of the 4-methyl-5-phenyloxazolidon-2-one[21] (2.6 g, 14.7 mmol) in THF (50 cm^3) at −78 °C was added dropwise butyllithium (1.6 mol dm^{-3} solution in hexanes; 9.7 cm^3, 15.5 mmol). The solution was stirred at −78 °C for 15 min, after which 1,1-dimethylethanesulfinyl chloride (2.3 g, 16.4 mmol) in THF (50 cm^3) was added dropwise. The mixture was stirred for a further 2 h at − 78 °C. Standard aqueous work-up, chromatography {SiO_2, [petroleum–ethyl acetate (3:2 v/v)]}, and recrystallisation [petroleum–ethyl acetate (4:1 v/v)] gave the (*R*)-*tert*-butyl sulfoxide[22] **8a** (1.70 g, 41%) as a white solid, m.p. 82–84 °C (Found: C, 59.8; H, 6.8; H, 6.8; N, 5.0. $C_{14}H_{19}NO_3S$ requires C, 59.76; H, 6.81; N, 4.98%); R_f 0.48 [ethyl acetate–petroleum (1:1 v/v)]; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 2960w, 1755s, 1450m, 1365m, 1330s,

1190s, 1125s, 1115s, 1095s, 1060m, 1045m and 1010m; δ_H(300 MHz; $CDCl_3$) 0.95 (3 H, d, *J* 6.7, Me), 1.32 (9 H, s, Me_3), 4.50 (1 H, dq, *J* 7.8 and 6.7, NCH), 5.68 (1 H, d, *J* 7.8, PhCH) and 7.25–7.44 (5 H, m, Ph); δ_C(75 MHz; $CDCl_3$) 17.73 (q), 22.67 (q), 51.63 (d), 59.10 (s), 82.07 (d), 126.06 (d), 128.63 (d), 128.83 (d), 134.31 (s) and 157.80 (s); *m*/*z* 177 (13), 107 (100) and 105 (26); and the (*S*)-*tert*-butyl sulfoxide[22] **8b** (0.98 g, 24%) as a white solid, m.p. 98–99 °C (Found: C, 59.7; H, 6.8; N, 5.0. $C_{14}H_{19}NO_3S$ requires C, 59.76; H, 6.81; N, 4.98%); R_f 0.40 [ethyl acetate–petroleum (1:1 v/v)]; $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 2960w, 1760s, 1450w, 1365m, 1330m, 1210w, 1185m, 1135m, 1095s, 1065w, 1010w and 965w; δ_H(300 MHz; $CDCl_3$) 1.01 (3 H, d, *J* 6.5, Me), 1.37 (9 H, s, Me_3), 4.54 (1 H, quint, *J* 6.6, NCH), 5.70 (1 H, d, *J* 6.7, PhCH) and 7.29–7.43 (5 H, m, Ph); δ_C(75 MHz; $CDCl_3$) 16.12 (q), 22.55 (q), 57.06 (d), 66.30 (s), 80.41 (d), 125.63 (d), 128.43 (d), 128.56 (d), 132.86 (s) and 155.27 (s); *m*/*z* 225 (58), 177 (57), 118 (100), 177 (15), 107 (26) and 105 (11).

(E)-1-[(R)-tert-*Butylsulfinyl*]-2-*phenylethylene* E-**5a** *and* (Z) 1-[(R)-tert-*Butylsulfinyl*]-2-*phenylethylene* Z-**5a**.—To a solution of the oxazolidinone **8a** (700 mg, 2.5 mmol) was added at −78 °C dropwise a solution of β-styrylmagnesium bromide (4 mmol) [from magnesium (0.10 g, 4.22 mmol) and β-bromostyrene (0.51 cm^3, 4 mmol)] and the mixture stirred for 2 h. Standard aqueous work-up and chromatography {chromatotron [SiO_2, petroleum–ethyl acetate (3:2 v/v)]} gave the trans-*sulfoxide*[30] E-**5a** (316 mg, 61%) as a white solid, m.p. 89–91 °C; R_f 0.35 (ether) (Found: C, 69.5; H, 7.7. $C_{12}H_{16}OS$ requires C, 69.19; H, 7.74%); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 2960m, 1605w, 1490m, 1470m, 1455m, 1440m, 1360m, 1170m, 1045br s, 965s and 855m; δ_H(300 MHz; $CDCl_3$) 1.28 (9 H, s, Me_3), 6.80 (1 H, d, *J* 15.5, C*H*=CHPh), 7.22 (1 H, d, *J* 15.5, CH=C*H*Ph) and 7.31–7.48 (5 H, m, Ph); δ_C(75 MHz; $CDCl_3$) 22.98 (q), 55.53 (s), 126.64 (d), 127.44 (d), 128.70 (d), 128.80 (d), 129.39 (d), 134.03 (s) and 138.03 (d); *m*/*z* 208 (M^+), 153 (11), 152 (100), 136 (28), 135 (36), 134 (14) and 104 (28); and the cis-*sulfoxide*[30] Z-**5a** (39 mg, 8%) as an oil, R_f 0.18 (ether); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 2960m, 1600w, 1490m, 1455m, 1440m, 1360m, 1170m, 1025br s and 905m; δ_H(90 MHz; $CDCl_3$) 1.3 (9 H, s, Me_3), 6.2 (1 H, d, *J* 12, PhCH=C*H*) and 7.0–7.55 (6 H, m, aromatic and PhCH=C*H*).

(4R,5S)-4-*Methyl*-5-*phenyl*-3-[(R)-p-*tolylsulfinyl*]*oxazolidin*-2-*one* **9a**.—To a solution of (4*R*,5*S*)-4-methyl-5-phenyloxazolidin-2-one[21] (3 g, 17 mmol) in THF (75 cm^3) at −78 °C was added butyllithium (1.6 mol dm^{-3} solution in hexanes; 11 cm^3). Toluene-*p*-sulfinyl chloride (3.26 g, 18.7 mmol) in THF (75 cm^3) was added and the mixture stirred for a further 2 h at −78 °C. Standard aqueous work-up, chromatography [SiO_2, (petroleum–ethyl acetate, 7:3 v/v) and recrystallisation (ethyl acetate–petroleum, 2:1 v/v) gave the *oxazolidinone*[24] **9a** (1.22 g, 23%) as a white solid, m.p. 105–106 °C; $[\alpha]_D$ −220 (*c* 1.7 in $CHCl_3$); R_f 0.31 (petroleum–ethyl acetate 2:1 v/v) (Found: C, 64.5; H, 5.4; N, 4.42. $C_{17}H_{17}NO_3S$ requires C, 64.74; H, 5.43; N, 4.44); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 1760s (C=O), 1325m, 1190s, 1140m, 1115s, 1105m, 1070m, 1010m and 810m; δ_H(300 MHz; $CDCl_3$) 0.90 (3 H, d, *J* 6.7, Me), 2.47 (3 H, s, Me), 3.83 (1 H, quint, *J* 6.8, C*H*Me), 5.49 (1 H, d, *J* 7.4, C*H*Ph) and 7.17–7.68 (9 H, m, aromatic); δ_C(75 MHz; $CDCl_3$) 17.28 (q), 21.51 (q), 56.01 (d), 80.25 (d), 125.03 (d), 125.82 (d), 128.82 (d), 128.56 (d), 128.82 (d), 130.40 (d), 133.02 (s), 137.53 (s), 143.00 (s) and 155.74 (s); *m*/*z* 315 (M^+), 177 (12), 140 (12), 139 (50), 118 (15), 108 (12) and 107 (100).

(E)-1-*Phenyl*-2-[(R)-p-*tolylsulfinyl*]*but*-1-*en*-3-*one* **10a**.—To a solution of oxalyl chloride (0.322 cm^3, 3.69 mmol) in dichloromethane (5 cm^3) was added dimethyl sulfoxide (DMSO) (0.39 cm^3, 5.49 mmol) in dichloromethane (5 cm^3) at −78 °C. The mixture was stirred at −78 °C for 5 min after which a 1:1 mixture of alcohols **2a** and **3a** (0.56 g, 2.06 mmol) in dichloromethane (5 cm^3) was added. The solution was stirred for 1 h at −78 °C. Triethylamine (2 cm^3, 14.3 mmol) was added and the mixture was allowed to warm to room temperature. Standard aqueous work-up and chromatography [SiO_2, ether–petroleum (3:1 v/v)] gave the ketone **10a** (0.5 g, 89%) as needles, m.p. 123–125 °C (isopropyl ether); $[\alpha]_D$ +375 (*c* 0.59 in CH_2Cl_2); R_f 0.70 (ether); $\nu_{max}(CHCl_3)/cm^{-1}$ 3000s, 2920w, 1670s, 1610m, 1595m, 1490m, 1445m, 1355s, 1170s, 1080s, 1050s, 1010m, 930w, 910s, 805s, 690s and 635s; δ_H(300 MHz; $CDCl_3$) 1.79 (3 H, s, Me), 2.38 (3 H, s, ArMe), 7.28 (2 H, d, *J* 8.3, aromatic), 7.35–7.40 (5 H, m, Ph), 7.57 (2 H, d, *J* 8.3 aromatic) and 7.62 (1 H, s, PhCH); δ_C(75 MHz; $CDCl_3$) 21.50 (q), 30.87 (q), 125.73 (d), 128.85 (d), 129.15 (d), 129.93 (d), 130.01 (d), 133.37 (s), 135.11 (d), 139.12 (s), 142.40 (s), 147.03 (s) and 199.78 (s) (Found: M^+ + H, 285.0949. $C_{17}H_{17}O_2S$ requires M^+ + H, 285.0949); *m*/*z* 285 (16%, M^+ + H), 242 (15), 236 (30), 145 (20), 91 (35) and 43 (100).

(E)-2,2-*Dimethyl*-5-*phenyl*-4-[(R)-p-*tolylsulfinyl*]*pent*-4-*en*-3-*one* **10c**.—In a similar fashion, oxalyl chloride (0.63 cm^3, 7.2 mmol), DMSO (0.75 cm^3, 10.6 mmol), the alcohols **2c** and **3c** (1:2.5) (1.45 g, 5.4 mmol) and triethylamine (4 cm^3, 28.6 mmol) gave the *ketone* **10c** (1.2 g, 83%) as an oil, $[\alpha]_D$ +185 (*c* 4.0 in $CHCl_3$); ν_{max}(film)/cm^{-1} 3060w, 3020w, 2960s, 2930s, 2870s, 1725s, 1680s, 1600m, 1580w, 1495m, 1480m, 1460m, 1450m, 1395m, 1365m, 1280m, 1080s, 1020m, 935m, 810s, 740s and 700s; δ_H(300 MHz; $CDCl_3$) 0.98 (9 H, s, Me_3), 2.41 (3 H, s, Me), 7.34–7.28 (7 H, m, aromatic), 7.43 (1 H, s, PhCH) and 7.51 (2 H, d, *J* 8.4, aromatic); δ_C(75 MHz; $CDCl_3$) 21.38 (q), 26.48 (q), 44.84 (s), 125.91 (d), 128.58 (d), 128.93 (d), 129.51 (d), 129.71 (d), 131.76 (d), 133.76 (s), 138.80 (s), 142.32 (s), 145.62 (s) and 210.15 (s) (Found: M^+ + H, 327.1419. $C_{20}H_{23}O_2S$ requires M^+ + H, 327.1419); *m*/*z* 327 (M^+ + H, 100%), 310 (15), 187 (15), 131 (45), 91 (15) and 57 (35).

(S)-(E)-2,2,6,6-*Tetramethyl*-4-[p-*tolylsulfonyl*]*hept*-4-*en*-3-*ol* **11a**.—To a solution of the alcohol **6b** (65 mg, 0.21 mmol) in dichloromethane (5 cm^3) was added MCPBA (46 mg, 0.27 mol) at −78 °C and the mixture stirred for 2 h. It was then allowed to warm to room temperature and stand overnight; standard aqueous work-up then gave the sulfone **11a** (31 mg, 46%) as a white solid, m.p. 126–128 °C; $[\alpha]_D$ −20.8 (*c* 2.0 in $CHCl_3$) (Found: C, 66.2; H, 8.5. $C_{18}H_{28}O_3S$ requires C, 66.63; H, 8.70%); R_f 0.63 (ether); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3510m, 2950s, 1590w, 1360m, 1280m, 1250m, 1125s, 1080s, 1040m, 1015m and 810m; δ_H(300 MHz; $CDCl_3$) 1.096 (9 H, s, Me_3), 1.101 (9 H, s, Me_3), 2.44 (3 H, s, Me), 4.14 (1 H, br s, OH), 4.87 (1 H, s, C*H*OH), 6.17 (1 H, s, C=CH), 7.32 (2 H, m, aromatic) and 7.78 (2 H, m, aromatic); δ_C(75 MHz; $CDCl_3$) 21.58 (q), 27.63 (q), 30.39 (q), 35.24 (s), 36.14 (s), 76.57 (d), 127.65 (d), 129.51 (d), 139.30 (s), 141.98 (s), 143.95 (s) and 154.77 (d); *m*/*z* 268 (33), 267 (57), 157 (100), 140 (69), 139 (61) and 111 (69).

(R)-(E)-2,2,6,6-*Tetramethyl*-4-[p-*tolylsulfonyl*]*hept*-4-*en*-3-*ol* **11b**.—In a similar fashion, the alcohol **7b** (165 mg, 0.54 mmol) and MCPBA (115 mg, 0.67 mol) gave the *sulfone* **11b** (106 mg, 61%) as a white solid, m.p. 125–127 °C; $[\alpha]_D$ +21.3 (*c* 2.1 in $CHCl_3$) (Found: C, 66.50; H, 8.69. $C_{18}H_{28}O_3S$ requires C, 66.63; H, 8.70%); R_f 0.73 (ether); $\nu_{max}(CH_2Cl_2)/cm^{-1}$ 3510m, 2950s, 1590w, 1390m, 1360m, 1280m, 1250s, 1185m, 1125s, 1080s, 1040s, 1015s and 810m; δ_H(300 MHz; $CDCl_3$) 1.10 (18 H, s, 2 × Me_3), 2.43 (3 H, s, Me), 4.12 (1 H, d, *J* 11.4, OH), 4.86 (1 H, d, *J* 11.4, C*H*OH), 6.18 (1 H, s, C=CH), 7.31 (2 H, m, aromatic) and 7.77 (2 H, m, aromatic); δ_C(75 MHz; $CDCl_3$) 21.56 (q), 27.61 (q), 30.38 (q), 35.21 (s), 36.11 (s), 76.52 (d), 127.61 (d), 129.49 (d), 139.28 (s), 141.98 (s), 143.93 (s) and 154.72 (d); *m*/*z* 268 (48), 194 (26), 157 (100), 141 (22), 140 (95), 139 (89) 135 (36), 127 (29), 124 (29), 124 (32), 123 (34) and 111 (96).

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