

Preparation of Vinylic Sulphones by Peterson Olefination using Phenyl Trimethylsilylmethyl Sulphone

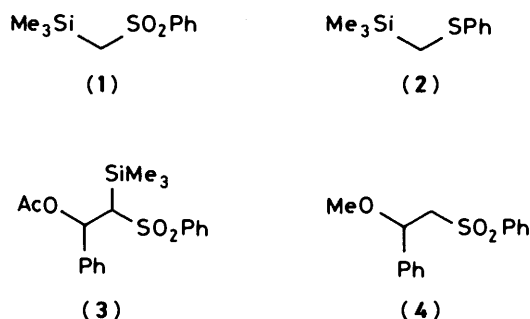
Donald Craig, Steven V. Ley,* and Nigel S. Simpkins
 Department of Chemistry, Imperial College, London SW7 2AY
 Gordon H. Whitham* and Michael J. Prior
 The Dyson Perrins Laboratory, South Parks Road, Oxford, OX1 3QY

The anion generated from phenyl trimethylsilylmethyl sulphone using butyl-lithium in dimethoxyethane, readily reacts at -78°C with various carbonyl compounds to afford vinylic sulphones on work-up at room temperature. The reaction conditions are tolerant of a number of otherwise reactive functional groups such as silyl ethers, cyclopropanes, esters, acetals, and epoxides. In ether solvent trapping of the intermediate alkoxide was possible by acylation.

The importance of vinylic sulphones in synthesis is now well established.¹ Their diverse reactivity, including conjugate addition,² cycloaddition,³ and deprotonation reactions⁴ makes methods of preparation of these useful synthetic intermediates important.⁵ We now report in full⁶ details of a modified Peterson olefination procedure⁷ allowing the conversion of both aldehydes and ketones to vinyl sulphones.

Results and Discussion

Phenyl trimethylsilylmethyl sulphone (**1**) may readily be obtained by reaction of sodium thiophenolate with chloromethyltrimethylsilane followed by oxidation of the resulting sulphide⁸ (**2**), by treatment of α -lithiothioanisole with

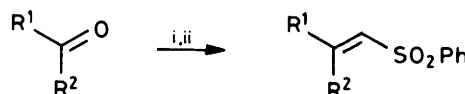


chlorotrimethylsilane followed by oxidation^{9,10} or by addition of a solution of the anion generated from methyl phenyl sulphone to trimethylsilane,¹¹ the first of these methods being more amenable to the preparation of multi-gram quantities. Treatment of a 1,2-dimethoxyethane (DME) solution of this reagent with 1 equiv. of butyl-lithium at -78°C followed by quenching of the resulting pale yellow anion solution with 1 equiv. of carbonyl compound directly affords a mixture of *Z*- and *E*-vinyl sulphones upon mild aqueous acidic work-up (Scheme 1), the results of which are summarised in Table 1. When tetrahydrofuran (THF) instead of DME was used as the solvent, some formation of the isomeric β,γ -unsaturated sulphones was observed; allylic sulphones are, in many cases, known to be more thermodynamically stable than their vinylic counterparts.¹² Use of ether, however, permitted trapping of the intermediate alkoxide by acylation, analogous to published work on non-silylated sulphones.¹³ Treatment of the lithio-anion derived from (**1**) in ether at -78°C with benzaldehyde followed immediately by addition of an excess of acetic anhydride or acetyl chloride gave a mixture of (*E*)-phenyl 2-

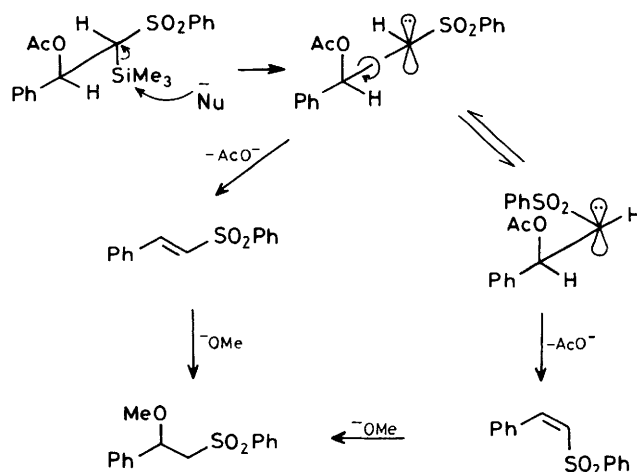
Table 1.

Carbonyl Compd.	Product	Yield ^a (%)	<i>Z</i> : <i>E</i> Ratio ^b
(5)	(6)	81	1:1
(7)	(8)	84	1:1
(9)	(10)	85	1:1
(11)	(12)	70	5:3
(13)	(14)	79	3:1
(15)	(16)	50	1:1
(17)	(18)	65	1:1
(19)	(20)	74	1:1
(21)	(22)	92	1:1
(23)	(24)	92	0:100
(25)	(26) and (27)	72	4:3
(28)	(29)	87	1:2

^a Isolated yield; ^b ¹H n.m.r.



Scheme 1. Reagents: i, $\text{Me}_3\text{SiCHLi SO}_2\text{Ph}$, DME, -78°C ; ii, NH_4Cl (aq.), 20°C

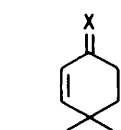


Scheme 2.

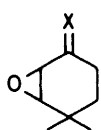
phenylvinyl sulphone and the β -acetoxy- α -silyl sulphone (**3**), indicated by ¹H n.m.r. to consist of a single diastereoisomer. Attempts to eliminate stereospecifically the elements of acetoxytrimethylsilane from (**3**) under a variety of conditions

Table 2. Products obtained from elimination of AcOSiMe₃ from (3)

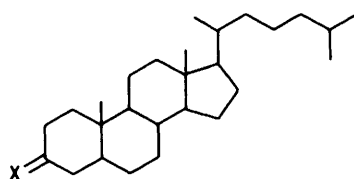
Reaction Conditions	Product Ratio ^a		
	(Z)-PhCH=CHSO ₂ Ph	(E)-PhCH=CHSO ₂ Ph	(4)
NH ₃ , MeOH, 18 °C, 17 h	17	83	0
KOH, MeOH, 0 °C, 1 h	17	33	50
KOH, MeOH, 18 °C, 17 h	0	20	80
KF, DMSO	35	65	0
Me ₃ NBnF	33	67	0

^a ¹H N.m.r.

(5) X = O

(6) X = CHSO₂Ph

(7) X = O

(8) X = CHSO₂Ph

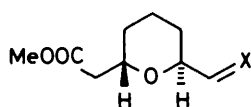
(9) X = O

(10) X = CHSO₂Ph

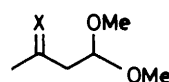
(11) X = O

(12) X = CHSO₂Ph

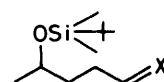
(13) X = O

(14) X = CHSO₂Ph

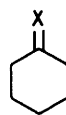
(15) X = O

(16) X = CHSO₂Ph

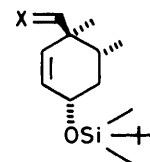
(17) X = O

(18) X = CHSO₂Ph

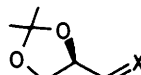
(19) X = O

(20) X = CHSO₂Ph

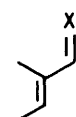
(21) X = O

(22) X = CHSO₂Ph

(23) X = O

(24) X = CHSO₂Ph (E)

(25) X = O

(26) X = CHSO₂Ph (Z)(27) X = CHSO₂Ph (E)

(28) X = O

(29) X = CHSO₂Ph

however always gave mixtures of *Z*- and *E*-vinyl sulphones, in addition to the elimination-addition product (4) when methoxide was used as the base (Table 2). This was disappointing in view of the well-precedented stereospecific *anti*-elimination from β -acetoxy- and β -tosyloxy sulphones to give geometrically pure vinyl sulphones,^{13,14} and may indicate a non-concerted *E*_{1cB}-type mechanism in which the α -sulphonyl carbanion generated under the reaction conditions has sufficient lifetime for rotation about the C(1)-C(2) bond to occur prior to displacement of acetate ion (Scheme 2).

Finally, it is worth noting that abstraction of an acidic α -proton from the carbonyl substrate may compete significantly with nucleophilic attack by the sulphone anion if the resulting enolate anion may undergo further reaction. This may explain the somewhat lower yield of vinyl sulphone realised when 4,4-dimethoxybutan-2-one was used as the substrate.

Experimental

¹H N.m.r. spectra were obtained on Bruker WH-400, Bruker WH-250, JEOL FX90Q and Varian EM-360A spectrometers

on deuteriochloroform solutions with tetramethylsilane as internal standard. I.r. spectra were recorded on a Perkin-Elmer 983 G spectrophotometer as liquid films or dichloromethane solutions. Mass spectra were obtained on a VG Micromass 7070B instrument. M.p.s were determined using a Kofler hot-stage apparatus and are uncorrected. Column chromatography was performed on MN-silica gel 60 230-400 mesh, under pressure. Light petroleum refers to the fraction boiling in the range 40-60 °C and ether to diethyl ether. Solutions were dried over anhydrous sodium sulphate, and solvents by standard methods.

Preparation of Phenyl Trimethyl Sulphide (2).—To a mixture of thioanisole (50 g, 0.4 mol) and *N,N,N',N'*-tetramethylethylenediamine (47.5 g, 0.41 mol) in dry THF (350 ml) at -40 °C under argon was added, dropwise with stirring, butyllithium (1.5M solution in hexane; 400 ml, 0.6 mol). The resulting pale yellow solution was maintained at -40 °C for 1 h and then cooled to -60 °C. Chlorotrimethylsilane (70 g, 0.64 mol) in dry THF was then added with stirring, and the mixture was maintained at -60 °C for a further 30 min; it was then allowed slowly to warm to room temperature during 12 h. Water (500 ml) was added with vigorous stirring, and the aqueous layer was extracted with light petroleum (2 × 400 ml). The combined organic layers were washed with 2M aqueous HCl (2 × 300 ml), saturated aqueous sodium hydrogen carbonate (2 × 300 ml), and brine, and dried. Evaporation of solvent followed by distillation afforded the pure product (78.6 g, 99%), b.p. 85-88 °C at 0.8 mmHg (lit.,⁸ b.p. 158.5 °C at 67 mmHg); v_{\max} (film) 1 580 (arom. C=C), 1 250 (CSi), and 845 cm⁻¹ (CSi); δ (60 MHz) 0.2 (9 H, s, SiMe), 2.2 (2 H, s, CH₂), 7.0-7.5 (5 H, m, SO₂Ph).

Preparation of Phenyl Trimethylsilyl Sulphone (1).—To a solution of (2) (84.0 g, 0.43 mol) in dichloromethane (800 ml) at 0 °C was added, dropwise with stirring, peracetic acid (4.6M solution; 280 ml, 1.29 mol) buffered with sodium acetate trihydrate (44 g, 0.33 mol). Upon completion of the addition the mixture was stirred at 0 °C for a further 90 min and then allowed to warm to room temperature during 1 h; it was then left for 15

h. Water (500 ml) was added and the aqueous layer extracted with dichloromethane (2 × 400 ml). The combined organic layers were washed with 2M-aqueous sodium hydroxide (2 × 200 ml) and brine and dried. Evaporation of solvent followed by distillation gave the product (95.4 g, 96%), b.p. 121 °C at 0.01 mmHg (lit.⁸ b.p. 160 °C at 6 mmHg); v_{\max} (film) 3 064 (sp² CH), 2 959, 2 903 (sp³ CH), 1 586 (arom. C=C), and 1 304 and 1 146 cm⁻¹ (SO₂); δ (90 MHz) 0.27 (9 H, s, SiMe), 2.79 (2 H, s, CH₂), 7.40—7.65 (3 H, m, *m*- and *p*-SO₂Ph), and 7.82—7.95 (2 H, m, *o*-SO₂Ph).

General Procedure for Olefination of Aldehydes and Ketones.—To a stirred solution of (1) in dry DME (5 ml mmol⁻¹ sulphone) under argon at -78 °C was added, dropwise *via* a syringe, a solution of butyl-lithium in hexane (1.0 equiv). The pale yellow solution was maintained at -78 °C for 20 min after which time the carbonyl compound (1.0 equiv.) was added *via* a syringe, either neat or as a solution in DME. The reaction mixture was immediately allowed to warm to room temperature, whereupon aqueous ammonium chloride was added. The layers were separated, and the aqueous layer extracted with dichloromethane. The combined organic layers were dried and evaporated under reduced pressure to yield the crude product, which was purified by chromatography. Analytical samples were further purified by passage through a short column of silica gel.

4,4-Dimethylcyclohex-2-en-1-ylidenemethyl phenyl sulphone (6).— v_{\max} (solution) 3 044 (sp² CH), 2 958, 2 867 (sp³CH), 1 619 (C=CHSO₂Ph), 1 574 (arom. C=C), 1 303 and 1 145 cm⁻¹ (SO₂); δ (250 MHz) 1.03 (3 H, s, Me), 1.05 (3 H, s, Me), 1.50—1.62 (2 H, m, 5-H), 2.39 and 2.90 (2 H, both m, 6-H), 5.85 (*E*-isomer; 0.5 H d, *J* 10 Hz, 2-H) and 7.21 (*Z*-isomer; 0.5 H dd, *J* 10.0, 1.0 Hz, 2-H), 5.95—6.10 (2 H, m, CHSO₂Ph and 3-H), 7.50—7.65 (3 H, m, *m*- and *p*-SO₂Ph), 7.90—7.95 (2 H, m, *o*-SO₂Ph); *m/z* (70 eV) 262 (*M*⁺), and 121 (*M*⁺ - SO₂Ph) (Found: C, 68.45; H, 6.95; S, 11.95. C₁₅H₁₈O₂S requires C, 68.67; H, 6.92; S, 12.22%).

2,3-Epoxy-4,4-dimethylcyclohex-1-ylidenemethyl phenyl sulphone (8). v_{\max} (film) 3 062 (sp² CH), 2 961, 2 871 (sp³ CH), 1 612 (C=CHSO₂Ph), 1 585 (arom. C=C), 1 307, 1 148 (SO₂), and 1 250 cm⁻¹ (epoxide); δ (400 MHz) 0.98, 1.04, 1.09, and 1.10 (all s, 6 H, Me), 1.12—1.27 (m) and 1.42—1.54 (m) (2 H, 5-H), 2.13 (dddd, *J* 16, 10.0 and 4.5, 2 Hz), 2.25 (dddd, *J* 16, 7, 4, and 1 Hz), 2.59 (dddd, *J* 18.5, 11.5, 6, and 2.5 Hz), and 2.82 (dtd, *J* 18.5, 5, and 1.5 Hz) (2 H, 6-H), 3.03 and 3.05 (1 H, both d, *J* 4.0 Hz, 3-H), 3.31 and 4.79 (1 H, both d, *J* 4 Hz, 2-H), 6.41 and 6.48 (1 H, both br s, CHSO₂Ph), 7.56 (2 H, m, *m*-SO₂Ph), 7.62 (1 H, m, *p*-SO₂Ph), and 7.93 (2 H, m, *o*-SO₂Ph); *m/z* (70 eV) 278 (*M*⁺), 263 (*M*⁺ - Me), 137 (*M*⁺ - SO₂Ph), and 121 (*M*⁺ - O-SO₂Ph) (Found: C, 64.45; H, 6.5; S, 11.75. C₁₅H₁₈O₃S requires C, 64.72; H, 6.52; S, 11.52%).

Cholestan-3-ylidenemethyl phenyl sulphone (10).¹⁵ v_{\max} (solution) 3 062 (sp² CH), 2 934, 2 867 (sp³ CH), 1 620 (C=CHSO₂Ph), 1 301, and 1 144 cm⁻¹ (SO₂); δ (250 MHz) 0.65—2.40 (44 H, m, aliph.), 3.22 and 3.52 (2 H, both m, γ to SO₂Ph), 6.10—6.15 (1 H, m, CHSO₂Ph), 7.49—7.65 (3 H, m, *m*- and *p*-SO₂Ph), and 7.88—7.93 (2 H, m, *o*-SO₂Ph); *m/z* (70 eV) 524 (*M*⁺), 509 (*M*⁺ - Me), 411 (*M*⁺ - C₈H₁₇), and 383 (*M*⁺ - SO₂Ph) (Found: C, 77.9; H, 10.15; S, 5.9. C₃₄H₅₂O₂S requires C, 77.81; H, 9.99; S, 6.11%).

3-Methylbut-1-enyl phenyl sulphone (12).¹⁶ v_{\max} (film) 3 059 (sp² CH), 2 966, 2 870 (sp³ CH), 1 620 (C=CHSO₂Ph), 1 585 (arom. C=C), 1 306 and 1 148 cm⁻¹ (SO₂); δ (250 MHz) *Z*-isomer: 0.99 (6 H, d, *J* 6.5 Hz, Me), 3.64 (1 H, double septet, *J* 11.0, 6.5 Hz, 3-H), 6.02 (1 H, t, *J* 11 Hz, 2-H), 6.19 (1 H, dd, *J* 11, 1 Hz, 1-H); *E*-isomer: 1.07 (6 H, d, *J* 6.5 Hz, Me), 2.52 (1 H, octet, *J* 6.5 Hz, 3-H), 6.25 (1 H, dd, *J* 15.5, 2 Hz, 1-H), 6.99 (1 H, dd, *J* 15.5, 6.5 Hz, 2-H); both isomers: 7.50—7.67 (3 H, m, *m*- and *p*-

SO₂Ph), 7.85—7.95 (2 H, m, *o*-SO₂Ph); *m/z* (70 eV) 210 (*M*⁺) and 69 (*M*⁺ - SO₂Ph) (Found: C, 62.9; H, 6.7; S, 15.25. C₁₁H₁₄O₂S requires C, 62.83; H, 6.71; S, 15.25%).

2-Cyclopropylprop-1-enyl phenyl sulphone (14). v_{\max} (film) 3 061 (sp² CH), 3 013 (cyclopropyl CH), 2 922 (sp³ CH), 1 600 (C=C), 1 337, and 1 144 cm⁻¹ (SO₂); δ (250 MHz) 0.65—0.92 (4 H, m, cyclopropyl ring CH₂); *Z*-isomer: 1.52 (3 H, d, *J* 1.0 Hz, Me), 2.90 (1 H, m, CHC=CHSO₂Ph); *E*-isomer: 1.50 (1 H, m, CHC=CHSO₂Ph), 1.94 (3 H, d, *J* 1 Hz, Me); both isomers: 6.19—6.22 (1 H, m, CHSO₂Ph), 7.49—7.65 (3 H, m, *m*- and *p*-SO₂Ph), and 7.89—7.95 (2 H, m, *o*-SO₂Ph); *m/z* (70 eV) 222 (*M*⁺), 194 (*M*⁺ - CH₂CH₂), and 81 (*M*⁺ - SO₂Ph) (Found: C, 64.9; H, 6.3. C₁₂H₁₄O₂S requires C, 64.84; H, 6.35%).

2-(6'- α -Methoxycarbonylmethyltetrahydropyran-2 β -yl)vinyl phenyl sulphone (16). v_{\max} (solution) 3 058 (sp² CH), 2 945 (sp³ CH), 1 735 (C=O), 1 629 (CH=CHSO₂Ph), 1 585 (arom. C=C) and 1 307 and 1 140 cm⁻¹ (SO₂); δ (250 MHz) 1.30—1.95 (6 H, m, tetrahydropyran H), 2.38 (dd, *J* 15.5, 4.0 Hz), 2.47 (dd, *J* 15.5, 6.0 Hz), 2.55 (dd, *J* 16.0, 8.5 Hz), 2.72 (dd, *J* 16.0, 8.0 Hz, 2 H, CH₂CO₂Me), 3.62 and 3.64 (3 H, both s, COMe), and 4.08—4.20 and 4.23—4.36 (1 H, both m, CHCH₂CO₂Me); *Z*-isomer: 5.39—5.50 (1 H, m, CHCH=CHSO₂Ph) 6.18 (1 H, dd, *J* 12, 1.5 Hz, CHSO₂Ph), and 6.47 (1 H, dd, *J* 12.0, 8.0 Hz, CH=CHSO₂Ph); *E*-isomer: 4.15—4.60 (1 H, m, CHCH=CHSO₂Ph), 6.73 (1 H, dd, *J* 16.0, 2.0 Hz, CHSO₂Ph), and 6.89 (1 H, dd, *J* 16.0, 2.0 Hz, CH=CHSO₂Ph); both isomers: 7.49—7.69 (3 H, m, *m*- and *p*-SO₂Ph), and 7.87—7.96 (2 H, m, *o*-SO₂Ph); *m/z* (70 eV) 324 (*M*⁺), 264 (*M*⁺ - HCOMe), 251 (*M*⁺ - CH₂COMe), and 183 (*M*⁺ - SO₂Ph) (Found: C, 58.95; H, 6.25. C₁₆H₂₀O₅S requires C, 59.24; H, 6.21%).

4,4-Dimethoxy-2-methylbut-1-enyl phenyl sulphone (18). v_{\max} (film) 3 062 (sp² CH), 2 939 (sp³ CH), 2 834 (Me CH), 1 625 (C=CHSO₂Ph), 1 585 (arom. C=C), and 1 304, 1 148 and 1 121 cm⁻¹ (SO₂); δ (90 MHz) *Z*-isomer: 1.93 (3 H, d, *J* 1.0 Hz, Me=CHSO₂Ph), 2.93 (2 H, d, *J* 6.0 Hz, CH₂), 3.36 (6 H, s, OMe), 4.56 [1 H, t, *J* 6.0 Hz, CH(OMe)₂], and 6.18 (1 H, br s, CHSO₂Ph); *E*-isomer: 2.13 (3 H, d, *J* 1.0 Hz, MeC=CHSO₂Ph), 2.38 (2 H, d, *J* 6.0 Hz, CH₂), 3.28 (6 H, s, OMe), 4.44 [1 H, t, *J* 6.0 Hz, CH(OMe)₂], and 6.26 (1 H, br s, CHSO₂Ph); both isomers: 7.45—7.70 (3 H, m, *m*- and *p*-SO₂Ph) and 7.80—7.99 (2 H, m, *o*-SO₂Ph); *m/z* (70 eV) 239 (*M*⁺ - OMe) and 141 (PhSO₂⁺) (Found: C, 57.9; H, 6.6. C₁₃H₁₈O₄S requires C, 57.76; H, 6.71%). This compound is unstable, even at 0 °C, and decomposes with double-bond migration to 4-phenylsulphonyl-3-methylbut-2-enal as a mixture of geometric isomers; v_{\max} (solution) 3 046 (sp² CH), 2 991, 2 862, (sp³ CH), 2 775 (OC-H), 1 677 (C=CCHO), 1 586 (arom. C=C), and 1 322 and 1 106 cm⁻¹ (SO₂); δ (250 MHz) 1.13 and 1.33 (3 H, both d, *J* 1.0 Hz, Me), 3.91 and 4.34 (2 H, both s, CH₂SO₂Ph), 5.59 and 6.08 (1 H, both br d, *J* 8 Hz, CHCHO), 7.55—7.73 (3 H, m, *m*- and *p*-SO₂Ph), 7.85—7.92 (2 H, m, *o*-SO₂Ph), and 9.36 and 9.94 (1 H, both d, *J* 8 Hz, CHO); *m/z* (70 eV) 224 (*M*⁺), 195 (*M*⁺ - SO₂Ph) (Found: C, 58.95; H, 5.3. C₁₁H₁₂O₃S requires C, 58.91; H, 5.39%).

5-*t*-Butyldimethylsilyloxyhex-1-enyl phenyl sulphone (20) v_{\max} (film) 3 063 (sp² CH), 2 955, 2 930, 2 857 (sp³ CH), 1 623 (C=CHSO₂Ph), 1 585 (arom. C=C), and 1 318 and 1 148 cm⁻¹ (SO₂); δ (250 MHz) 0.06 (6H, s, SiMe), 0.87 and 0.89 (9H, both s, SiBu^t), 1.12 and 1.14 (3H, both d, *J* 5 Hz, Me), 1.46—1.60 (2H, m, 4-H), 2.20—2.45 and 2.60—2.80 (2H, both m, CH₂CH=CHSO₂Ph), 4.70—4.90 (1H, m, CHOSiBu^tMe₂), 6.23—6.36 (m) and 7.05 (dt, *J* 16, 6.5 Hz) (2H, CH=CHSO₂Ph and CH=CHSO₂Ph), 7.50—7.68 (3H, m, *m*- and *p*-SO₂Ph), and 7.87—7.95 (2H, m, *o*-SO₂Ph); *m/z* (70 eV) 354 (*M*⁺), 339 (*M*⁺ - Me), 297 (*M*⁺ - C₄H₉), and 213 (*M*⁺ - SO₂Ph).

Cyclohexylidenemethyl phenyl sulphone (22). M.p. 32.5—34 °C, b.p. 135 °C at 0.001 mmHg; v_{\max} (film) 3 060 (sp² CH), 2 925, 2 857 (sp³ CH), 1 620 (C=CHSO₂Ph), 1 585 (arom. C=C),

and 1 310 and 1 140 cm^{-1} (SO_2); δ (90 MHz) 1.58 (6 H, br, $3 \times \text{CH}_2$), 2.17 (2 H, br, $\text{CH}_2\text{C}=\text{CHSO}_2\text{Ph}$), 2.70 (2 H, br, $\text{CH}_2\text{C}=\text{CHSO}_2\text{Ph}$), 6.16 (1 H, br s, CHSO_2Ph), 7.40–7.70 (3 H, m, *m*- and *p*- SO_2Ph), and 7.80–8.00 (2 H, m, *o*- SO_2Ph); *m/z* (70 eV) 236 (M^+) and 95 ($M^+ - \text{SO}_2\text{Ph}$) (Found: C, 66.1; H, 6.95; S, 13.45. $\text{C}_{13}\text{H}_{16}\text{O}_2\text{S}$ requires C, 66.10; H, 6.78; S, 13.56%).

(*E*)-2-(4' α -Dimethyl-*t*-butylsilyloxy-1' α ,6' α -dimethylcyclohex-2'-enyl)vinyl phenyl sulphone (24). ν_{max} (film) 3 070, 3 030 (sp^2 CH), 1 620 ($\text{CH}=\text{CHSO}_2\text{Ph}$), and 1 140 cm^{-1} (SO_2); δ (60 MHz) 0.09 (6 H, s, SiMe), 0.84 (3 H, d, *J* 7 Hz, 6'-Me), 0.90 (9 H, s, SiBu'), 1.03 (3 H, s, 1'-Me), 0.8–1.9 (3 H, m, 5'-H, 6'-H), 5.16 (1 H, dd, *J* 10, 2 Hz, 2'-H), 5.60 (1 H, br d, *J* 10 Hz, 3'-H), 6.13 (1 H, d, *J* 16 Hz, 1-H), 6.84 (1 H, d, *J* 16 Hz, 2-H), and 7.34–7.85 (5 H, m, SO_2Ph); *m/z* (70 eV) 406 (M^+), 391 ($M^+ - \text{Me}$), and 349 ($M^+ - \text{C}_4\text{H}_9$) (Found: C, 65.2; H, 8.65. $\text{C}_{22}\text{H}_{34}\text{O}_4\text{SSi}$ requires C, 64.98; H, 8.43%).

(*Z*)-(4'S)-2-(2',2'-Dimethyl-1',3'-dioxolan-4'-yl)vinyl phenyl sulphone (26). ν_{max} (film) 3 058 (sp^2 CH), 2 988, 2 937, 2 876 (sp^3 CH), 1 627 ($\text{CH}=\text{CHSO}_2\text{Ph}$), 1 585 (arom. C=C), and 1 307 and 1 150 cm^{-1} (SO_2); δ (250 MHz) 1.41 (3 H, s, Me), 1.45 (3 H, s, Me), 3.77 (1 H, dd, *J* 8.5, 6.0 Hz, 5-H) 4.42 (1 H, dd, *J* 8.5, 6.5 Hz, 5'-H), 5.66 (1 H, dt, *J* 6.0, 6.5 Hz, 4'-H), 6.29 (1 H, dd, *J* 11.0, 1.0 Hz, CHSO_2Ph), 6.38 (1 H, dd, *J* 11.0, 6.5 Hz, $\text{CH}=\text{CHSO}_2\text{Ph}$), 7.55–7.70 (3 H, m, *m*- and *p*- SO_2Ph), and 7.90–7.92 (2 H, m, *o*- SO_2Ph); *m/z* (70 eV) 268 (M^+), 253 ($M^+ - \text{Me}$), and 238 ($M^+ - \text{Me}$) (Found: C, 58.35; H, 6.05. $\text{C}_{13}\text{H}_{16}\text{O}_4\text{S}$ requires C, 58.19; H, 6.01%).

(*E*)-(4'S)-2-(2',2'-Dimethyl-1',3'-dioxolan-4'-yl)vinyl phenyl sulphone (27). ν_{max} (film) 3 062 (sp^2 CH), 2 988, 2 937, 2 881 (sp^3 CH), 1 630 ($\text{CH}=\text{CHSO}_2\text{Ph}$), 1 585 (arom. C=C), and 1 308 and 1 148 cm^{-1} (SO_2); δ (250 MHz) 1.37 (3 H, s, Me), 1.40 (3 H, s, Me), 3.70 (1 H, dd, *J* 8.5, 6.5 Hz, 5'-H), 4.21 (1 H, dd, *J* 8.5, 6.5 Hz, 5'-H), 4.71 (1 H, m, 4'-H), 6.65 (1 H, dd, *J* 14.5, 1.0 Hz, CHSO_2Ph), 6.95 (1 H, dd, *J* 14.5, 4.0 Hz, $\text{CH}=\text{CHSO}_2\text{Ph}$), 7.52–7.67 (3 H, m, *m*- and *p*- SO_2Ph), and 7.88–7.91 (2 H, m, *o*- SO_2Ph); *m/z* (70 eV) 268 (M^+), 253 ($M^+ - \text{Me}$), and 238 ($M^+ - 2\text{Me}$) (Found: C, 58.0; H, 6.3; S, 12.0. $\text{C}_{13}\text{H}_{16}\text{O}_4\text{S}$ requires C, 58.19; H, 6.01; S, 11.95%).

3-Methylpent-1,3-dienyl phenyl sulphone (29). ν_{max} (film) 3 056 (sp^2 CH), 2 919 (sp^3 CH), 1 629 (non-arom. C=C), 1 590 (arom. C=C), and 1 306 and 1 146 cm^{-1} (SO_2); δ (250 MHz) *Z,E*-isomer: 1.68 (3 H, br s, 3-Me), 1.69 (3 H, d, *J* 7.0 Hz, 5-H), 5.90 (1 H, br q, *J* 7.0 Hz, 4-H), 6.24 (1 H, d, *J* 12.0 Hz, CHSO_2Ph), 6.47 (1 H, d, *J* 12.0 Hz, $\text{CH}=\text{CHSO}_2\text{Ph}$); *E,E*-isomer: 1.71 (3 H, br s, 3-Me), 1.83 (3 H, d, *J* 7.0 Hz, 5-H), 6.10 (1 H, q, *J* 7.0 Hz, 4-H), 6.21 (1 H, d, *J* 15.0 Hz, CHSO_2Ph), 7.30 (1 H, d, *J* 15.0 Hz, $\text{CH}=\text{CHSO}_2\text{Ph}$); both isomers: 7.48–7.63 (3 H, m, *m*- and *p*- SO_2Ph), 7.87–7.92 (2 H, m, *o*- SO_2Ph); *m/z* (70 eV) 222 (M^+) and 80 [$M^+ - \text{HOS(O)Ph}$] (Found: C, 64.9; H, 6.25. $\text{C}_{12}\text{H}_{14}\text{O}_2\text{S}$ requires C, 64.84; H, 6.35%).

1-Acetoxy-1-phenyl-2-trimethylsilylethyl phenyl sulphone (3).—To a solution of silylsulphone (1) (5.0 g, 21.9 mmol) in dry ether (100 ml) was added butyl-lithium (1.6M. solution in hexane; 14.1 ml, 22.6 mmol) dropwise with stirring at -78°C under argon. Benzaldehyde (2.6 g, 24.5 mmol) was added, followed immediately by acetic anhydride (4.48 g, 43.9 mmol). The mixture was allowed to warm to -20°C during 1 h whereupon methanol (10 ml) followed by ether (30 ml) and water (100 ml) were added. The layers were separated and the aqueous phase extracted with dichloromethane (2×50 ml). The combined organic layers were then washed with aqueous saturated sodium hydrogen carbonate and brine, and then dried. Evaporation of solvent under reduced pressure gave a viscous oil (6.74 g). Trituration with a small amount of light petroleum and cooling gave a solid which upon recrystallisation from ether gave white crystals of the sulphone (3) (2.9 g, 35%) as a single diastereoisomer, m.p. 146–147 $^\circ\text{C}$; ν_{max} (solution) 1 647

(C=O), 1 372, 1 305, and 1 145 (SO_2), and 1 085 and 850 cm^{-1} (CSi); δ (60 MHz) 0.2 (9 H, s, SiMe), 1.65 (3 H, s, MeCO), 3.65 (1 H, d, *J* 7.6 Hz, 2-H), 6.1 (1 H, d, *J* 7.6 Hz, 1-H), 7.1 (5 H, br s, Ph), and 7.1–7.8 (5 H, m, SO_2Ph) (Found: C, 60.45; H, 6.55; S, 8.3. $\text{C}_{19}\text{H}_{24}\text{O}_4\text{SSi}$ requires C, 60.06; H, 6.4; S, 8.5%). Evaporation of the mother liquors from the recrystallisation gave an oil (3.7 g) which was short-path distilled to give (*E*)-2-phenylvinyl phenyl sulphone (3.2 g, 60%) which eventually crystallised to give a solid, m.p. 67–69 $^\circ\text{C}$ (lit.,¹⁷ m.p. 73.5 $^\circ\text{C}$); ν_{max} (film) 1 612 (C=C), 1 438, 1 368, 1 300, 1 150 (SO_2), 970, and 810 cm^{-1} ; δ (60 MHz) 6.9 (1 H, d, *J* 15.5 Hz, 1-H), 7.0–8.3 (11 H, m, arom. C-H and 2-H).

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