Diastereoselective Synthesis of Cyclopropanes with Multiple Sulfur Substitution. X-Ray Molecular Structures of Phenylsulfonyl-substituted Cyclopropanes

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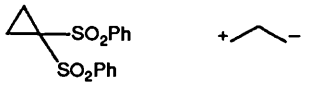
Reaction of 1-phenylsulfonyl-1-phenylthioalkenes **3** with lithiated phenyl phenylthiomethyl sulfone **4** gave 1-phenylsulfonyl-1,2-bis(phenylthio)cyclopropanes **5** as single diastereoisomers in good yield. The relative stereochemistry of the cyclopropane **5a** was established by an X-ray crystal-structure determination. Oxidation of the cyclopropane **5a** with *m*-chloroperbenzoic acid gave the tris-sulfone **6** which, either on heating or on treatment with base, was converted efficiently into the epimeric tris-sulfone **7**. The structures of both of these sulfones were established by X-ray crystal-structure determinations. Reaction of lithiated phenyl phenylthiomethyl sulfone with the 1-(phenylthio)vinylsulfoximide **9** gave the cyclopropanes **11a** and **11b** as a 3:1 mixture of diastereoisomers. The structure of the major product **11a** was established by an X-ray crystal-structure determination. Reaction of lithiated phenyl phenylthiomethyl sulfone with the simple vinylsulfoximide **10b** gave the 1-phenylsulfonyl-1-phenylthiocyclopropane **12** in moderate yield, and the structure was determined by X-ray crystallography. The structural parameters of the cyclopropanes are compared, and asymmetry parameters are reported.

The chemistry of cyclopropanes with sulfur substituents has been the focus of much recent interest.[1] Optically active 1-phenylsulfinylcyclopropane has been used in the asymmetric synthesis of α,α-disubstituted cyclobutanones,[2] and lithiated 1-phenylsulfonylcyclopropanes have been used as reagents for cyclopropyl anions,[3] since reductive removal of the phenylsulfonyl group is easy. Cyclopropanes with two sulfur substituents are also of significant synthetic value.[4] Several methods are available for the preparation of cyclopropanone dithioacetals,[5] and these compounds have been used as precursors to cyclopropyl anions.[6] The potential of 1,1-bis(phenylsulfonyl)cyclopropane **1** to behave as the synthetic equivalent of the 1,3-dipole **2** has also been demonstrated.[7]



1 **2**

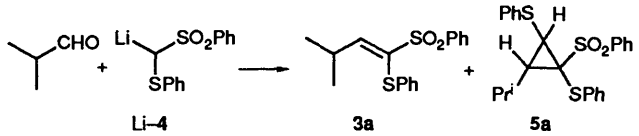
In the course of our work on the chemistry of 1-phenylsulfonyl-1-phenylthioalkenes,[8] we discovered a straightforward method for the stereoselective preparation of cyclopropanes with three sulfur substituents.[9] Related cyclopropanes have been prepared previously by the reaction of 1,1-dichloro-2-phenylsulfonylcyclopropanes with sodium phenylthiolate,[10] although their reactivity was not extensively investigated.

Results and Discussion

During our studies on the preparation of 1-phenylsulfonyl-1-phenylthioalkenes **3**,[8] we discovered that reaction of lithiated phenyl phenylthiomethyl sulfone **4** with 2-methylpropanal at −78 °C in tetrahydrofuran (THF), followed by warming to room temperature, led to the isolation not only of the desired alkene **3a** but also of a by-product identified as the cyclopropane **5a** (Scheme 1). By conducting the condensation of phenyl phenylthiomethyl sulfone with aldehydes at −78 °C, and then effecting formal elimination of lithium hydroxide from the intermediate addition product by treatment with acetic anhydride/triethylamine and a catalytic amount of 4-(dimethylamino)pyridine (DMAP), we were able to prepare the alkenes **3** in good yield.[8]

Table 1 Preparation of cyclopropanes **5a–d**

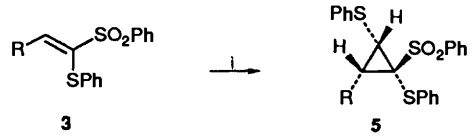
Alkene	R	Cyclopropane	Yield (%)
3a	Pr^i	**5a**	81
3b	Me	**5b**	73
3c	Ph	**5c**	42
3d	Bu^t	**5d**	62



Li-4 **3a** **5a**

Scheme 1

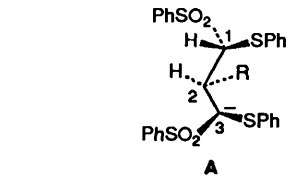
It appeared likely that the cyclopropane was being formed in our original procedure due to reaction of lithiated phenyl phenylthiomethyl sulfone with the alkene, followed by intramolecular displacement of benzenesulfinate, which is well precedented in other systems.[11] This was confirmed by treating the isolated 1-phenylsulfonyl-1-phenylthioalkenes **3** with lithiated phenyl phenylthiomethyl sulfone, which gave the cyclopropanes **5a–d** (Scheme 2). Our results are summarised in Table 1.



3 **5**

Scheme 2 *Reagents and conditions:* i, Li-4, THF, −78 to 0 °C or room temp.

All the cyclopropanes which we prepared appeared to be single diastereoisomers from inspection of ^{1}H NMR spectra, and the relative stereochemistry of the cyclopropane **5a** was firmly established by an X-ray molecular structure analysis (Fig. 1). The configuration of the double bond in the alkene **3a** is preserved in the cyclopropane **5a**. Comparison of proton–proton



A

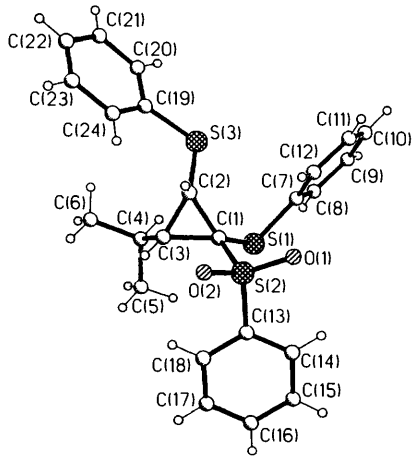


Fig. 1 The molecular structure of compound **5a**

coupling constants observed for each of the cyclopropanes **5b–d** suggested that the relative stereochemistry of these cyclopropanes was the same. The origin of the stereoselectivity in this process deserves some comment. The last intermediate in the formation of the cyclopropanes is likely to be species **A**, in which the phenylsulfonyl group at C-3 eclipses the hydrogen, and the two phenylthio groups eclipse each other. It is unclear, however, whether **A** is the stereoisomer which is initially formed, or whether it arises by subsequent fast proton transfer.

In view of the reactivity of 1,1-bis(phenylsulfonyl)cyclopropane **1** towards nucleophilic attack,[7] we prepared the tris(phenylsulfonyl)cyclopropane **6** by oxidation of the cyclopropane **5a** (98%) with *m*-chloroperbenzoic acid MCPBA (4 mol equiv.). Confirmation that no epimerisation had occurred in this process was provided by an X-ray molecular structure analysis (Fig. 2). The tris(phenylsulfonyl)cyclopropane **6** was insoluble in THF alone, and reactions were generally conducted in mixtures of *N*,*N*-dimethylformamide (DMF) and THF. For example, treatment of compound **6** with butyllithium in this solvent at −78 °C,* followed by quenching at this temperature, led to the isolation of a new tris(phenylsulfonyl)cyclopropane **7** (87%), which was also formed in quantitative yield on heating of a solution of compound **6** in DMF for 47 h at 100 °C. The structure of the tris(phenylsulfonyl)cyclopropane **7** was established by X-ray molecular structure analysis (Fig. 3), and demonstrated that epimerisation at the carbon bearing the isolated phenylsulfonyl group had occurred. Two reasonable mechanisms for the former process can be proposed, one of which involves formation of the lithiated tris(phenylsulfonyl)cyclopropane which then undergoes inversion, presumably to release steric congestion. An alternative mechanism would involve elimination of lithium benzenesulfinate from the lithiated cyclopropane to give the cyclopropene **8**. Subsequently, benzenesulfinate could then re-add from the opposite face, leading to

* The exact nature of the base in this solvent system is clearly open to debate, and could simply be lithium dimethylamide formed by reaction of butyllithium with DMF, or alternatively the initially formed tetrahedral intermediate prior to loss of dimethylamide anion.

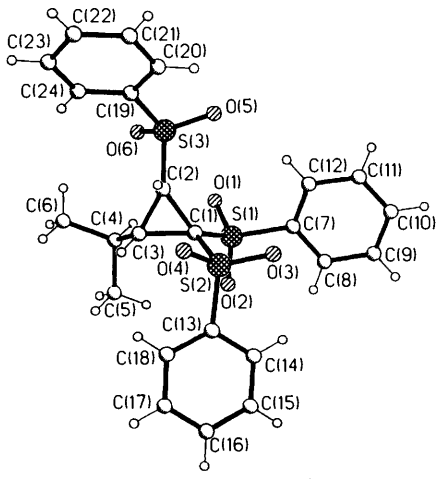


Fig. 2 The molecular structure of compound **6**

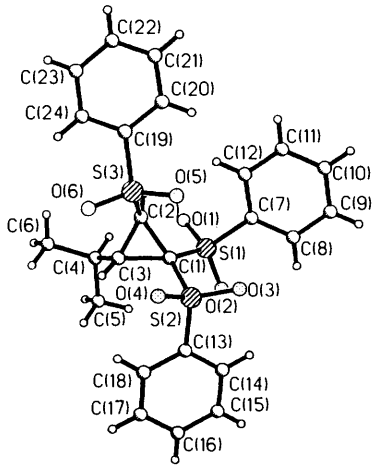
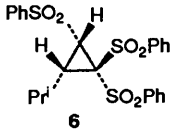


Fig. 3 The molecular structure of compound **7**

the epimeric cyclopropane after protonation. A related mechanism, in which elimination of benzenesulfinic acid occurs, could account for the thermal isomerisation of **6** to **7**. An attempted cross-over experiment involving treatment of compound **6** with one mole equivalent of sodium toluene-*p*-sulfinate in DMF at 100 °C for 32 h resulted in extensive decomposition. It is not possible at present to exclude homolytic cleavage of the C(1)–C(2) bond, followed by recombination as an alternative pathway.



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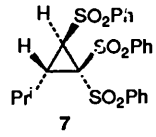

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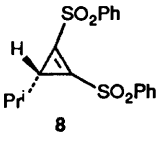


8

In order to extend the scope of the cyclopropanation (particularly to establish a route to enantiomerically pure sulfur-substituted cyclopropanes), we have investigated addition of lithiated phenyl phenylthiomethyl sulfone **4** to the α-phenylthio-substituted vinylsulfoximide **9** (which was prepared by reaction of the lithio anion of the unsubstituted vinyl sulfoximide[12] **10a** with diphenyl disulfide). The product of this reaction was, as anticipated, a mixture of two stereoisomeric cyclopropanes **11a** and **11b** in the ratio 3:1 (Scheme 3). The relative stereochemistry of the substituents about the ring in both stereoisomers was the same as that observed in the cyclopropane **5a**. Moreover, fractional crystallisation allowed the isolation of a pure sample of the isomer **11a**, whose structure was determined by X-ray molecular structure analysis (Fig. 4). This confirmed

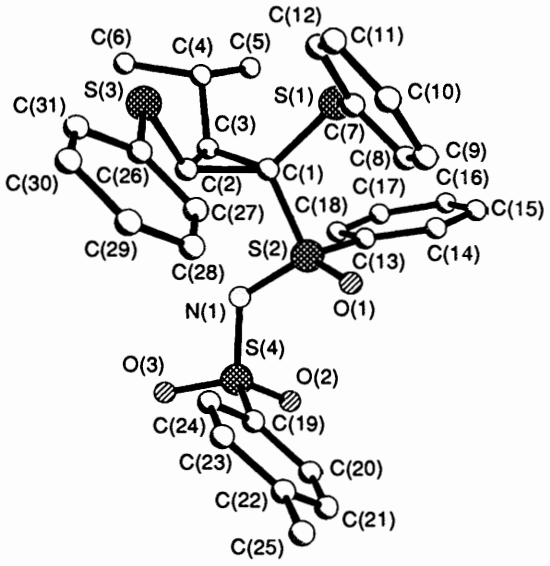
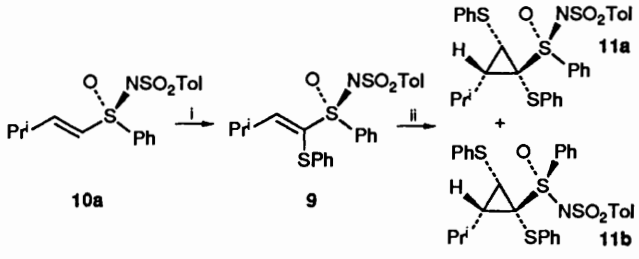


Fig. 4 The molecular structure of compound **11a**. For clarity, hydrogen atoms are omitted, and a different view direction is chosen. Molecule *b* is shown; molecule *a* is labelled analogously and shows no significant differences except in the orientation of the substituent groups.



Scheme 3 *Reagents and conditions:* i, BuLi, −78 °C, 5 min; then PhSSPh (1.5 mol equiv.); ii, Li-**4**, THF, −78 °C to room temp.

the assignment of relative stereochemistry about the cyclopropane ring, and also established that the diastereofacial selectivity induced by the sulfoximide group was the same as has been observed in nucleophilic epoxidations of the vinylsulfoximides using lithium *tert*-butyl peroxide. The formation of the two isomers **11a** and **11b**, with none of compound **5a** being detected, presumably reflects the greater anion-stabilising properties of the *N*-tolylsulfonylsulfoximide group compared with a phenyl sulfone.[13]

We have also investigated the reaction of lithiated phenyl phenylthiomethyl sulfone **4** with the simple vinylsulfoximide **10b**, which resulted in the formation of the cyclopropane **12** (49%) (Scheme 4). There was some evidence for the formation of a second cyclopropane (**13**) in this reaction, although it was not unambiguously identified due to the large number of stereoisomers possible. The cyclopropane **12** was a single stereoisomer, as determined by 200 MHz ^{1}H NMR analysis, and the relative configuration was established by X-ray molecular structure analysis (Fig. 5). The formation of two compounds can be easily understood on the basis of the relative anion-stabilising properties of a single *N*-tolylsulfonylsulfoximide group compared with the combined effect of a phenylthio and a phenylsulfonyl group, which appears to be marginally more effective. This is in sharp contrast to the situation observed in the formation of sulfoximides **11a** and **11b**. The relative leaving-group abilities of benzenesulfinate and the analogous sulfinamide derived anion **14** will also have an influence on product distribution. Precedent for the formation of the cyclopropane **12** is provided by analogous reactions of dibasic nucleophiles, such as dimethyl malonate, with simple *N*-

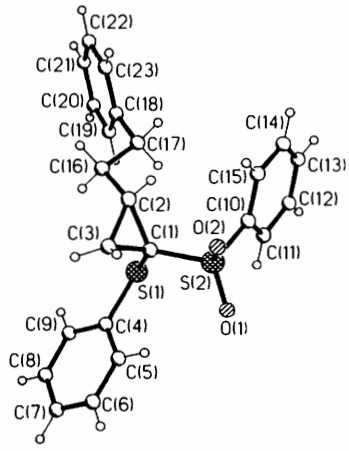


Fig. 5 The molecular structure of compound **12**

tolylsulfonylvinylsulfoximides which also give cyclopropane products with loss of the sulfoximide group.[14]

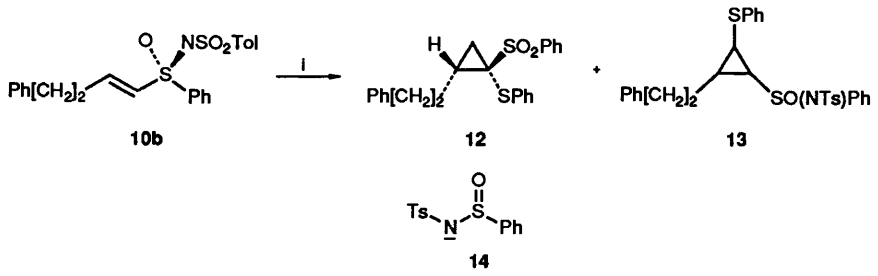
Discussion of Molecular Structures.—In general, the bond-lengths observed in the molecular structures of all the cyclopropanes reported in this paper follow the pattern observed by Allen[15] (Table 2). That is, for the cyclopropyl ring atom with the most strongly electron-accepting substituents, the distal ring bond is shortened, and the vicinal bonds are lengthened. Comparison of the two cyclopropanes **5a** and **6** shows that the length of the C(1)–C(2) bond is essentially the same in the donor–acceptor[16]-substituted cyclopropane **5a** as in the cyclopropane **6** in which all sulfur substituents are electron-withdrawing. The greater effectiveness of the *N*-tolylsulfonylsulfoximide group as an electron-withdrawing group when compared with a phenylsulfonyl group is illustrated by the significantly longer C(1)–C(2) bond (*D*3 in Table 2) in structure **11a** compared with the closely analogous structure **5a**. The structures of cyclopropanes **5a**, **11a** and **12** provide more information on the effect of captodative substitution on cyclopropane geometry.[17]

Experimental

For general procedures, see ref. 8. All NMR spectra were recorded in $CDCl_3$ as solvent. *J*-Values are given in Hz. Phenyl phenylthiomethyl sulfone **4**, the 1-phenylsulfonyl-1-phenylthioalkenes **3a**, **3b** and **3c**[8] and the vinylsulfoximides **10a** and **10b**[12] were prepared by previously reported procedures. Light petroleum refers to that fraction with boiling range 40–60 °C.

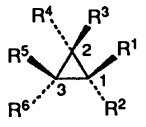
(E)-4-*Methyl*-1-*phenylsulfonyl*-1-*phenylthiopent*-1-*ene* **3d**.—This was prepared from 3-methylbutanal by using the general procedure described in the literature,[8] and was isolated as an *oil* which eventually solidified (0.410 g, 62%), m.p. 74–75 °C (from ethyl acetate–light petroleum) (Found: C, 64.6; H, 5.9. $C_{18}H_{20}O_2S_2$ requires C, 65.0; H, 6.1%); ν_{max}(film)/cm^{-1} 3062w, 3020w, 2958m, 2929w, 2897w, 2871w, 1583w, 1310s and 1155s; δ_H(300 MHz) 0.90 (6 H, d, *J* 6.7), 1.78–1.87 (1 H, m), 2.33 (2 H, dd, *J* 7.1 and 7.2), 7.01–7.04 (2 H, m), 7.09–7.16 (3 H, m), 7.39–7.45 (2 H, m), 7.49–7.55 (1 H, m), 7.81 (1 H, t, *J* 7.2) and 7.87–7.91 (2 H, m); *m*/*z* (EI) 332 (M^+), 191, 125, 109 and 81. Unchanged phenyl phenylthiomethyl sulfone (0.070 g, 13%) was also recovered.

General Procedure for the Preparation of Cyclopropanes **5a–d**.—A solution of phenyl phenylthiomethyl sulfone **4** (0.529 g, 2.0 mmol) in dry THF (8 cm^3) was cooled to −78 °C under nitrogen. Butyllithium (1.2 cm^3, 2.2 mmol; 1.85 mol dm^{-3}) was added dropwise and the reaction mixture was warmed to 0 °C



Scheme 4 *Reagents and conditions:* i, Li-**4**, THF, −78 °C to room temp.

Table 2 Ring bond lengths and asymmetry parameters for cyclopropanes



$D1$ = C(2)–C(3) Å
$D2$ = C(1)–C(3) Å
$D3$ = C(1)–C(2) Å

$\delta 1 = D1 - \Delta$ (Å × 10^3)
$\delta 2 = D2 - \Delta$ (Å × 10^3)
$\delta 3 = D3 - \Delta$ (Å × 10^3)
$\Delta = (D1 + D2 + D3)/3$

Cyclopropane	R^1	R^2	R^3	R^4	R^5	R^6	$D1$	$D2$	$D3$	Δ	$\delta 1$	$\delta 2$	$\delta 3$
5a	SO_2Ph	SPh	H	SPh	H	Pr^i	1.505(3)	1.532(3)	1.526(3)	1.521	−16	+11	+5
6	SO_2Ph	SO_2Ph	H	SO_2Ph	H	Pr^i	1.504(3)	1.539(3)	1.524(3)	1.522	−18	+17	+2
7	SO_2Ph	SO_2Ph	SO_2Ph	H	H	Pr^i	1.489(3)	1.537(3)	1.526(3)	1.517	−28	+20	+9
11a[a]	SO(NTs)Ph	SPh	H	SPh	H	Pr^i	1.499(3)	1.531(3)	1.546(3)	1.525	−26	+6	+21
11a[a]	SO(NTs)Ph	SPh	H	SPh	H	Pr^i	1.498(3)	1.530(3)	1.537(3)	1.522	−24	+8	+15
12	SO_2Ph	SPh	H	$Ph[CH_2]_2$	H	H	1.486(3)	1.516(2)	1.529(2)	1.510	−24	+6	+19

[a] Two independent molecules.

and stirred for 30 min before being recooled to −78 °C. A solution of an alkene **5** (2.0 mmol) in dry THF (3 cm^3) was added dropwise and then the reaction mixture was warmed to the temperature indicated and stirred for the time indicated (see below). Aq. NH_4Cl (5 cm^3; 10%) was added and the organic layer was separated. The aqueous phase was washed with dichloromethane (3 × 15 cm^3) and the organic phases were combined and dried. The solvent was removed under reduced pressure and the resulting residue was chromatographed using light petroleum–ethyl acetate (10:1).

(1RS,2RS,3SR)-3-*Isopropyl*-1-*phenylsulfonyl*-1,2-*bis*(*phenylthio*)*cyclopropane* **5a** was obtained, after the reaction mixture had been stirred for 3 h at room temperature, as an oil which eventually solidified (0.355 g, 81%), m.p. 133–135 °C (from ethyl acetate–light petroleum) (Found: C, 65.9; H, 5.5. $C_{24}H_{24}O_2S_3$ requires C, 65.4; H, 5.5%); ν_{max}(film)/cm^{-1} 3061w, 3022w, 2958m, 2927w, 2870w, 1582m, 1306s and 1151s; δ_H(200 MHz) 0.54 (3 H, d, *J* 6.2), 1.03 (3 H, d, *J* 6.4), 1.88–2.06 (1 H, m), 2.11 (1 H, dd, *J* 9.6 and 10.7),* 3.99 (1 H, d, *J* 9.6), 7.09–7.24 (8 H, m), 7.49–7.57 (2 H, m), 7.61–7.72 (3 H, m) and 7.94–7.98 (2 H, m); δ_C(50.3 MHz) 21.4, 21.9, 26.1, 36.6, 39.8, 55.4, 126.1, 127.4, 128.3, 128.7, 128.8, 129.7, 131.0, 131.4, 133.8, 135.6 and 137.6; *m*/*z* (EI) 440 (M^+, 49%), 397 (27), 331 (55), 299 (90), 255 (34), 221 (27), 189 (100), 147 (74), 110 (73) and 77 (52).

(1RS,2RS,3SR)-3-*Methyl*-1-*phenylsulfonyl*-1,2-*bis*(*phenylthio*)*cyclopropane* **5b** was obtained, after the reaction mixture had been stirred for 18 h at room temperature, as a *solid* (0.605 g, 73%), m.p. 114–116 °C (Found: C, 64.1; H, 4.7. $C_{22}H_{20}O_2S_3$ requires C, 64.05; H, 4.9%); ν_{max}(KBr)/cm^{-1} 3056w, 3003w, 2979w, 2930w, 1580m, 1304s and 1158s; δ_H(300 MHz) 1.24 (3 H, d, *J* 6.5), 2.96 (1 H, dq, *J* 6.5 and 9.8), 3.58 (1 H, d, *J* 9.8), 7.17–7.26 (8 H, m), 7.41–7.44 (2 H, m), 7.46–7.53 (2 H, m), 7.58–7.63 (1 H, m) and 7.82–7.85 (2 H, m); *m*/*z* (EI) 412 (M^+), 303, 271, 193, 162, 147, 125 and 109.

* Irradiation of the doublet at δ 3.99 causes the multiplet at δ 2.11 to collapse into a tented doublet with *J* 10.7.

(1RS,2RS,3SR)-3-*Phenyl*-1-*phenylsulfonyl*-1,2-*bis*(*phenylthio*)*cyclopropane* **5c** was obtained, after the reaction mixture had been warmed to 0 °C and stirred for 5.5 h, as a viscous, light brown oil which eventually solidified (0.200 g, 42%). Crystallisation from diethyl ether–light petroleum at −20 °C gave *crystals*, m.p. 80–82 °C (Found: C, 68.1; H, 4.65. $C_{27}H_{22}O_2S_3$ requires C, 68.3; H, 4.7%); ν_{max}(film)/cm^{-1} 3061w, 3025w, 1582m, 1498w, 1309s and 1150s; δ_H(300 MHz) AB system (δ_A 3.90, δ_B 4.15, J_{AB} 10.3), 6.96–7.03 (3 H, m), 7.18–7.30 (10 H, m), 7.33–7.36 (2 H, m), 7.45–7.50 (2 H, m), 7.60–7.66 (1 H, m) and 7.87–7.90 (2 H, m); *m*/*z* (EI) 474 (M^+), 365, 233, 255, 223, 147, 115, 110 and 77.

(1RS,2RS,3SR)-3-*Isobutyl*-1-*phenylsulfonyl*-1,2-*bis*(*phenylthio*)*cyclopropane* **5d** was obtained, after the reaction mixture was warmed to room temperature and stirred for 3 h, as a light brown oil which eventually solidified (0.220 g, 62%). Crystallisation from diethyl ether–light petroleum at −20 °C gave *cream crystals*, m.p. 105–106 °C (Found: C, 65.7; H, 5.8. $C_{25}H_{26}O_2S_3$ requires C, 66.0; H, 5.8%); ν_{max}(KBr)/cm^{-1} 3057w, 2951w, 2928w, 2892w, 2867w, 1581w, 1305s and 1149s; δ_H(300 MHz) 0.82 (3 H, d, *J* 6.5), 0.84 (3 H, d, *J* 6.4), 1.43–1.48 (3 H, m), 2.69–2.77 (1 H, m), 3.73 (1 H, d, *J* 9.9), 7.16–7.23 (8 H, m), 7.42–7.47 (2 H, m), 7.55–7.63 (3 H, m) and 7.84–7.87 (2 H, m); *m*/*z* (EI) 454 (M^+), 397, 345, 313, 235, 203, 147, 109 and 77.

(2RS,3SR)-3-*Isopropyl*-1,1,2-*tris*(*phenylsulfonyl*)*cyclopropane* **6**.—A solution of MCPBA (8.630 g, 40.0 mmol) in dry dichloromethane (120 cm^3) was cooled to 0 °C under nitrogen. A solution of (1*RS*,2*RS*,3*SR*)-3-isopropyl-1-phenylsulfonyl-1,2-bis(phenylthio)cyclopropane **5a** (4.032 g, 9.2 mmol) in dry dichloromethane (20 cm^3) was added dropwise, and the reaction mixture was warmed to room temperature and stirred for 2 days. The solution was washed thoroughly and successively with saturated aq. sodium sulfite (50 cm^3), aq. sodium hydrogen carbonate (3 × 30 cm^3) and saturated aq. sodium chloride (30 cm^3). After drying of the solution, the solvent was removed on a rotary evaporator and the resulting solid was

Table 3 Crystallographic data

Compound	**5a**	**6**	**7**	**11a**	**12**
Formula	$C_{24}H_{24}O_2S_3$	$C_{24}H_{24}O_6S_3$	$C_{24}H_{24}O_6S_3$	$C_{31}H_{31}NO_3S_4$	$C_{23}H_{22}O_2S_2$
M	440.6	504.6	504.6	593.8	394.5
Crystal system	triclinic	orthorhombic	triclinic	triclinic	orthorhombic
Space group	$P\bar{1}$	$P2_12_12_1$	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$
a/Å	10.637(1)	11.496(2)	10.163(3)	11.312(4)	8.0948(6)
b/Å	11.008(1)	11.839(2)	11.132(3)	13.842(5)	9.8570(6)
c/Å	11.171(1)	17.075(3)	11.585(3)	19.771(7)	25.735(2)
α/°	64.209(4)	90	89.60(2)	81.46(3)	90
β/°	73.438(4)	90	65.94(2)	86.47(3)	90
γ/°	79.665(5)	90	80.61(2)	73.36(3)	90
V/Å^3	1 126.6(2)	2 323.9(7)	1 178.2(6)	2 932.6(18)	2053.4(2)
Z	2	4	2	4	4
D_c/g cm^{-3}	1.299	1.442	1.422	1.345	1.276
Radiation, λ/Å	Mo-Kα, 0.710 73	Mo-Ka, 0.710 73	Mo-Kα, 0.710 73	Mo-Kα, 0.710 73	Cu-Kα, 1.541 84
μ/mm^{-1}	0.35	0.36	0.35	0.36	2.46
F(000)	464	1 056	528	1 248	832
Temperature/K	295	240	240	240	295
Crystal size/mm	0.70 × 0.45 × 0.12	0.48 × 0.40 × 0.36	0.56 × 0.20 × 0.12	0.56 × 0.48 × 0.24	0.72 × 0.68 × 0.48
No. reflections for cell, 2θ range/°	32, 20–25	32, 20–25	32, 20–25	32, 20–22	32, 40–50
$2\theta_{max}$/°	45	50	50	50	130
Maximum indices hkl	11, 11, 12	13, 14, 20	12, 13, 13	13, 16, 23	9, 11, 30
Reflections measured	4 199	6 593	4 149	12 859	13 707
Unique reflections	2 941	4 100	4 149	10 361	3 484
R_{int}	0.016	0.052		0.027	0.059
Weighting parameters a, b	0.0387, 0.4089	0.0400, 0.8566	0.0477, 0.7180	0.0284, 1.6755	0.0339, 0.1250
Extinction coefficient x	0.0087(13)	0	0	0.0006(2)	0.0059(3)
Absolute structure parameter		−0.04(7)			0.005(13)
No. of refined parameters	265	301	300	710	245
$wR2$ (all data)	0.085	0.087	0.117	0.099	0.077
$R1$ (all data)	0.036	0.037	0.055	0.047	0.027
Goodness of fit	1.05	1.06	1.10	1.07	1.07
Max. shift/e.s.d.	0.001	0.001	< 0.0005	0.001	0.002
Max., min. election density/e Å^{-3}	0.15, −0.21	0.24, −0.30	0.46, −0.34	0.38, −0.29	0.14, −0.13

crystallised from dichloromethane–light petroleum at −20 °C to yield (2RS,3SR)-3-*isopropyl*-1,1,2-*tris*(*phenylsulfonyl*)*cyclopropane* **6** as a solid (4.034 g, 87%). The mother liquor was concentrated under reduced pressure and chromatographed using dichloromethane–light petroleum (10:1) as eluent to give a further crop (0.522 g, 11%) of the product, m.p. 276–283 °C (from dichloromethane–light petroleum) (Found: C, 57.1; H, 4.6. $C_{24}H_{24}O_6S_3$ requires C, 57.1; H, 4.8%); ν_{max}(KBr)/cm^{-1} 3073w, 3009w, 2992w, 2930w, 2874w, 1580w, 1341s, 1327s and 1152s; δ_H(300 MHz) 0.98 (3 H, d, J 6.5), 1.22 (3 H, d, J 6.4), 2.33 (1 H, t, J 11.2), 3.29–3.39 (1 H, m), 3.90 (1 H, d, J 11.2), 7.50–7.61 (6 H, m), 7.67–7.77 (5 H, m), 7.96–8.00 (2 H, m) and 8.38–8.41 (2 H, m); m/z (FAB) 505 (MH^+, 94%), 363 (8), 141 (14), 125 (69) and 66 (100).

Reaction of(2RS,3SR)-3-*Isopropyl*-1,1,2-*tris*(*phenylsulfonyl*)-*cyclopropane* **6** *with Butyllithium*.—Dry THF (6 cm^3) was added to a solution of (2*RS*,3*SR*)-3-isopropyl-1,1,2-tris(phenylsulfonyl)cyclopropane **6** (0.252 g, 0.5 mmol) in dry DMF (4 cm^3) under nitrogen and the mixture was cooled to an internal temperature of −75 °C. Butyllithium (0.23 cm^3, 0.55 mmol; 2.4 mol dm^{-3}) was added dropwise while the temperature was kept below −73 °C, then the reaction mixture was stirred for 15 min at −75 °C before being quenched with phosphate buffer (5 cm^3; pH 7).* The mixture was allowed to warm to room temperature, the layers were separated, and the aqueous phase was extracted with dichloromethane (3 × 12 cm^3). The organic extracts were combined and dried, and the solvent was removed on a rotary evaporator. Chromatography using dichloromethane as eluent gave (2RS,3RS)-3-*isopropyl*-1,1,2-*tris*(*phenylsulfonyl*)*cyclopropane* **7** as a solid (0.220 g, 87%), m.p. 190–192 °C (from dichloromethane–light petroleum) (Found: C, 56.9; H, 4.65. $C_{24}H_{24}O_6S_3$ requires C, 57.1; H, 4.8%); ν_{max} (KBr)/cm^{-1} 2961w, 1586w, 1327s and 1145s; δ_H(300 MHz) 0.87 (3 H, d, J 6.6), 1.00 (3 H, d, J 6.7), 2.33–2.46 (1 H, m), 2.85 (1 H, t, J 10.2) 4.12 (1 H, d, J 10.2), 7.53–7.58 (6 H, m), 7.67–7.72 (3 H, m), 7.80–7.83 (2 H, m) and 7.97–8.10 (4 H, m); m/z (EI) 505 (MH^+, 1.5%), 363 (62), 221 (13), 141 (18), 125 (68) and 77 (100).

(2RS,3RS)-3-*Isopropyl*-1,1,2-*tris*(*phenylsulfonyl*)*cyclopropane* **7** (*Alternative Preparation*).—A solution of (2*RS*,3*SR*)-3-isopropyl-1,1,2-tris(phenylsulfonyl)cyclopropane **6** (0.100 g, 0.2 mmol) in dry DMF (4 cm^3) under nitrogen was stirred at 100 °C for 47 h. The solvent was removed under oil-pump vacuum at 75 °C to yield pure (2*RS*,3*RS*)-3-isopropyl-1,1,2-tris(phenylsulfonyl)cyclopropane **7** (0.100 g, 100%).

S-Phenyl-S-[(E)-3-*methyl*-1-*phenylthiobut*-1-*enyl*]-N-(p-*tolylsulfonyl*)*sulfoximide* **9**.—*S*-[(*E*)-3-*Methylbut*-1-*enyl*]-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfoximide **10a** (0.73 g, 2.01 mmol) was dissolved in dry THF (10 cm^3) and the solution was cooled to −78 °C. Butyllithium (0.87 cm^3, 2.01 mmol; 2.3 mol dm^{-3}) was added dropwise, at that temperature, to give a bright yellow solution, which was stirred for a further 5 min. Diphenyl disulfide (0.763 g, 3.5 mmol) was added as a solution in dry THF (2 cm^3) and the reaction mixture was stirred for 3 min before being quenched with phosphate buffer (10 cm^3; pH 7) and extracted with dichloromethane. The extract was dried and the solvent was removed to give a yellow oil. The crude product was purified by flash chromatography, using ethyl acetate–light petroleum (1:4) as eluent, to give the α-*phenylthio sulfoximide* **9** as an oil, which crystallised on storage to give a solid (0.51 g, 54%), m.p. 105–106 °C (Found: C, 61.3; H, 5.4; N, 3.0. $C_{24}H_{25}NO_3S_3$ requires C, 61.6; H, 5.3; N, 2.9%); ν_{max}(film)/cm^{-1}

* The buffer solution was prepared by dissolving potassium dihydrogen phosphate (85 g) and sodium hydroxide (14.5 g) in water (1 dm^3).

Table 4 Atomic co-ordinates (× 10^4) for compound **5a**

	x	y	z
C(1)	7 056(2)	6 702(2)	7 157(2)
C(2)	6 710(2)	5 820(2)	6 570(2)
C(3)	7 134(2)	5 157(2)	7 901(2)
C(4)	8 423(2)	4 347(2)	8 060(2)
C(5)	8 899(3)	4 403(3)	9 193(3)
C(6)	8 263(4)	2 884(3)	8 345(3)
C(7)	8 592(2)	8 662(2)	4 779(2)
C(8)	9 827(2)	9 105(2)	4 041(2)
C(9)	10 011(3)	9 997(3)	2 682(3)
C(10)	8 981(3)	10 428(3)	2 057(3)
C(11)	7 758(3)	9 992(2)	2 793(2)
C(12)	7 545(2)	9 118(2)	4 157(2)
C(13)	6 171(2)	7 748(2)	9 159(2)
C(14)	6 431(3)	9 015(3)	8 961(3)
C(15)	6 845(3)	9 140(3)	9 970(3)
C(16)	7 024(3)	8 025(4)	11 120(3)
C(17)	6 759(3)	6 783(3)	11 307(3)
C(18)	6 321(2)	6 629(3)	10 336(2)
C(19)	7 204(2)	4 334(2)	5 022(2)
C(20)	7 932(2)	3 917(3)	4 015(3)
C(21)	7 549(3)	2 848(3)	3 894(3)
C(22)	6 464(3)	2 181(3)	4 762(3)
C(23)	5 761(3)	2 576(3)	5 762(3)
C(24)	6 122(3)	3 650(3)	5 895(3)
S(1)	8 517.0(5)	7 565.4(6)	6 522.9(5)
S(2)	5 653.9(5)	7 546.3(5)	7 892.9(5)
S(3)	7 745.1(6)	5 767.3(6)	5 022.2(6)
O(1)	5 408.1(15)	8 861.1(15)	6 882(2)
O(2)	4 613.0(14)	6 633(2)	8 561(2)

Table 5 Atomic co-ordinates (× 10^4) for compound **6**

	x	y	z
C(1)	4125(2)	6034(2)	4779.3(14)
C(2)	4687(2)	6323(2)	5562.2(14)
C(3)	4500(2)	7250(2)	4972.8(15)
C(4)	3672(2)	8255(2)	5036(2)
C(5)	3416(3)	8707(2)	4213(2)
C(6)	4242(3)	9181(2)	5525(2)
C(7)	2364(2)	4278(2)	4586.5(15)
C(8)	1815(3)	3893(2)	3920(2)
C(9)	1558(3)	2745(3)	3861(2)
C(10)	1859(4)	2029(3)	4448(2)
C(11)	2421(4)	2417(2)	5105(2)
C(12)	2671(3)	3553(2)	5187(2)
C(13)	4967(2)	5849(2)	3187.2(14)
C(14)	4255(2)	5309(2)	2650(2)
C(15)	4245(3)	5672(3)	1882(2)
C(16)	4943(3)	6556(3)	1657(2)
C(17)	5652(3)	7092(3)	2199(2)
C(18)	5668(3)	6749(2)	2973(2)
C(19)	5381(2)	6265(2)	7079.1(14)
C(20)	5947(3)	5262(2)	7260(2)
C(21)	6996(3)	5312(3)	7659(2)
C(22)	7463(3)	6342(3)	7860(2)
C(23)	6889(3)	7329(3)	7679(2)
C(24)	5840(3)	7300(2)	7283(2)
S(1)	2589.9(4)	5753.3(5)	4667.5(4)
S(2)	5109.0(5)	5273.9(5)	4136.2(3)
S(3)	4073.9(6)	6201.6(6)	6530.9(4)
O(1)	2042.4(15)	6148(2)	5375.2(11)
O(2)	2264(2)	6241(2)	3931.9(11)
O(3)	4754(2)	4113.7(14)	4110.9(11)
O(4)	6258(2)	5543(2)	4415.4(11)
O(5)	3611(2)	5084(2)	6624.5(12)
O(6)	3378(2)	7163(2)	6724.3(11)

1597w, 1579w, 1478w, 1446w, 1319m, 816m and 741w; δ_H(200 MHz) 1.03 (3 H, d, *J* 6.6), 1.12 (3 H, d, *J* 6.7), 2.38 (3 H, s), 3.02 (1 H, m) and 6.84–7.93 (15 H, m); *m/z* (EI) 472 (MH^+, 1%) and 372 (23).

Table 6 Atomic co-ordinates (× 10^4) for compound **7**

	x	y	z
C(1)	4 930(2)	3 236(2)	7 697(2)
C(2)	4 380(2)	4 610(2)	7 837(2)
C(3)	5 814(3)	4 108(2)	6 786(2)
C(4)	7 245(3)	4 429(2)	6 696(2)
C(5)	8 500(3)	3 373(3)	6 042(4)
C(6)	7 482(4)	5 590(3)	5 983(3)
C(7)	3 584(3)	2 579(2)	10 231(2)
C(8)	3 243(3)	1 451(2)	10 635(3)
C(9)	1 913(3)	1 402(3)	11 637(3)
C(10)	936(3)	2 462(3)	12 189(3)
C(11)	1 283(3)	3 584(3)	11 777(3)
C(12)	2 618(3)	3 650(2)	10 800(2)
C(13)	5 808(3)	1 100(2)	6 024(2)
C(14)	6 049(4)	−35(2)	6 475(3)
C(15)	7 189(4)	−901(3)	5 688(3)
C(16)	8 071(4)	−650(3)	4 484(3)
C(17)	7 829(4)	482(3)	4 048(3)
C(18)	6 687(3)	1 363(3)	4 817(3)
C(19)	2 175(3)	6 647(2)	8 721(2)
C(20)	999(3)	6 648(3)	9 867(3)
C(21)	448(3)	7 702(3)	10 661(3)
C(22)	1 069(4)	8 712(3)	10 315(4)
C(23)	2 255(4)	8 711(3)	9 177(4)
C(24)	2 830(3)	7 671(2)	8 366(3)
S(1)	5 314.9(6)	2 662.0(5)	9 007.4(6)
S(2)	4 255.6(7)	2 196.9(5)	6 958.7(6)
S(3)	2 775.3(6)	5 342.1(5)	7 655.3(6)
O(1)	5 892(2)	3 589(2)	9 414(2)
O(2)	6 157(2)	1 456(2)	8 629(2)
O(3)	3 257(2)	1 590(2)	7 936(2)
O(4)	3 806(2)	2 897(2)	6 098(2)
O(5)	1 680(2)	4 585(2)	8 120(2)
O(6)	3 207(2)	5 748(2)	6 400(2)

(5RS,1SR,2SR,3RS)-3-*Isopropyl*-1,2-*bis*(*phenylthio*)-1-[*S*-*phenyl*-N-(p-*tolylsulfonyl*)*sulfoximido*]*cyclopropane* **11a**.—Butyllithium (1.9 cm^3, 2.64 mmol; 1.38 mol dm^{-3}) was added to a solution of phenyl phenylthiomethyl sulfone **4** (0.64 g, 2.4 mmol) in dry THF (10 cm^3) at −78 °C. The yellow solution thus formed was warmed to 0 °C and stirred at that temperature for 30 min, during which time a yellow precipitate appeared. After 30 min the mixture was cooled to −78 °C and a solution of *S*-phenyl-*S*-[(*E*)-3-methyl-1-phenylbut-1-enyl]-*N*-(*p*-tolylsulfonyl)sulfoximide **9** (1.13 g, 2.4 mmol) in dry THF (10 cm^3) was added. The reaction mixture was stirred at −78 °C for 10 min, warmed to room temperature, and then stirred for 18 h before being quenched with phosphate buffer (p H 7; 20 cm^3) and extracted with dichloromethane (3 × 20 cm^3). The extracts were combined and dried, and the solvent was removed under reduced pressure to give an oil. ^{1}H NMR analysis of the crude product indicated the presence of two diastereoisomers **11a** and **11b** in a 3:1 ratio. The crude product was purified by flash chromatography using ethyl acetate–light petroleum (1:4) as eluent, to give the cyclopropanes **11a** and **11b** as a pale orange oil which solidified on storage (1.07 g, 75%). Recrystallisation from ethyl acetate gave the *cyclopropane* **11a** as a crystalline solid as a 15:1 mixture of diastereoisomers, m.p. 156–158 °C (Found: C, 62.8; H, 5.2; N, 2.3. $C_{31}H_{31}NO_3S_4$ requires C, 62.7; H, 5.2; N, 24.%); ν_{max}(KBr)/cm^{-1} 3063s and 1480s; δ_H(200 MHz) 0.46 (d, *J* 6.3) and 0.58 (d, *J* 6.5) [3 H, ratio 15:1], 1.03 (d, *J* 6.5) and 1.06 (d, *J* 6.0) [3 H, ratio 15:1], 1.97 (1 H, m, *J* 6.3, 3.1), 2.17 (1 H, t, *J* 10.4), 2.38 (3 H, s), 3.84 (1 H, d, *J* 10.3) and 7.00–8.05 (19 H, m); *m/z* (FAB) 592 (MH^+, 3%), 549 (4) and 299 (56). Further recrystallisation from ethyl acetate gave a pure sample of the major diastereoisomer for X-ray analysis.

(1RS,2RS)-2-*Phenethyl*-1-*phenylsulfonyl*-1-*phenylthiocyclopropane* **12**.—Butyllithium (0.98 cm^3, 2.4 mmol; 2.45 mol dm^{-3})

Table 7 Atomic co-ordinates (× 10^4) for compound **11a**

	x	y	z
C(1A)	3 666(2)	4 499(2)	3 163.4(10)
C(2A)	3 071(2)	5 662(2)	3 089.6(10)
C(3A)	2 785(2)	4 999(2)	3 711.9(10)
C(4A)	1 531(2)	4 812(2)	3 851.5(11)
C(5A)	1 644(2)	3 796(2)	4 304.6(13)
C(6A)	688(2)	5 694(2)	4 186.7(13)
C(7A)	3 958(2)	3 600(2)	1 932.0(11)
C(8A)	4 796(2)	2 695(2)	1 803.1(13)
C(9A)	5 390(2)	2 628(2)	1 174.6(14)
C(10A)	5 171(2)	3 460(2)	678.8(14)
C(11A)	4 334(3)	4 358(2)	803.2(13)
C(12A)	3 711(2)	4 426(2)	1 424.6(12)
C(13A)	5 675(2)	2 862(2)	3 713.7(11)
C(14A)	6 457(2)	2 124(2)	3 367.5(12)
C(15A)	6 781(3)	1 126(2)	3 683.6(14)
C(16A)	6 308(3)	889(2)	4 321(2)
C(17A)	5 536(3)	1 634(2)	4 660.2(14)
C(18A)	5 214(2)	2 639(2)	4 362.2(12)
C(19A)	7 533(2)	5 250(2)	3 301.2(11)
C(20A)	8 643(2)	4 617(2)	3 110.4(14)
C(21A)	9 236(2)	4 903(2)	2 511.0(15)
C(22A)	8 736(3)	5 811(2)	2 100.9(14)
C(23A)	7 633(3)	6 439(2)	2 304.0(13)
C(24A)	7 027(2)	6 168(2)	2 897.1(13)
C(25A)	9 379(3)	6 101(3)	1 438(2)
C(26A)	2 774(2)	6 896(2)	1 843.9(11)
C(27A)	4 051(2)	6 666(2)	1 810.1(13)
C(28A)	4 614(3)	7 170(2)	1 281.7(14)
C(29A)	3 916(3)	7 881(2)	793.4(14)
C(30A)	2 653(3)	8 089(2)	820.1(13)
C(31A)	2 081(3)	7 598(2)	1 340.4(11)
S(1A)	3 178.0(5)	3 629.6(4)	2 742.9(3)
S(2A)	5 290.3(5)	4 134.4(4)	3 301.1(3)
S(3A)	1 925.1(5)	6 312.6(4)	2 481.9(3)
S(4A)	6 730.7(5)	4 898.5(5)	4 049.8(3)
O(1A)	5 941.4(14)	4 147.0(12)	2 651.3(7)
O(2A)	7 440(2)	3 909.9(15)	4 349.6(10)
O(3A)	6 448(2)	5 714(2)	4 456.8(9)
N(1A)	5 404(2)	4 878.4(14)	3 794.0(9)
C(1B)	9 001(2)	8 850(2)	8 243.4(10)
C(2B)	8 058(2)	9 902(2)	8 233.3(11)
C(3B)	8 122(2)	9 119(2)	8 850.5(11)
C(4B)	7 117(2)	8 600(2)	9 056.8(12)
C(5B)	7 650(3)	7 580(2)	9 493(2)
C(6B)	6 083(2)	9 310(2)	9 433(2)
C(7B)	8 898(2)	8 330(2)	6 897.6(11)
C(8B)	10 004(3)	8 268(2)	6 540.2(13)
C(9B)	9 995(3)	8 582(3)	5 839.7(15)
C(10B)	8 892(3)	8 950(3)	5 506.2(15)
C(11B)	7 800(3)	8 986(2)	5 855.7(14)
C(12B)	7 802(3)	8 670(2)	6 554.1(13)
C(13B)	11 208(2)	7 603(2)	8 832.3(11)
C(14B)	11 852(2)	6 813(2)	8 478.0(12)
C(15B)	12 267(2)	5 845(2)	8 832.1(15)
C(16B)	12 025(3)	5 678(2)	9 525(2)
C(17B)	11 397(3)	6 473(2)	9 873.8(14)
C(18B)	10 982(2)	7 454(2)	9 531.9(12)
C(19B)	11 920(2)	10 700(2)	8 110.2(11)
C(20B)	13 136(2)	10 430(2)	7 888.5(13)
C(21B)	13 436(2)	10 819(2)	7 233.3(13)
C(22B)	12 555(3)	11 472(2)	6 802.7(12)
C(23B)	11 343(2)	11 741(2)	7 040.7(13)
C(24B)	11 025(2)	11 356(2)	7 687.6(12)
C(25B)	12 882(3)	11 888(2)	6 087.9(14)
C(26B)	7 195(2)	11 068(2)	7 013.7(12)
C(27B)	8 401(2)	10 903(2)	6 769.1(13)
C(28B)	8 655(3)	11 493(2)	6 176.4(14)
C(29B)	7 712(4)	12 236(2)	5 831.0(15)
C(30B)	6 525(3)	12 407(2)	6 082(2)
C(31B)	6 261(3)	11 832(2)	6 668.7(14)
S(1B)	8 862.4(5)	7 864.8(4)	7 791.3(3)
S(2B)	10 576.8(5)	8 813.7(4)	8 357.6(3)
S(3B)	6 726.5(5)	10 321.1(5)	7 727.7(3)
S(4B)	11 485.4(5)	10 192.4(4)	8 931.9(3)
O(1B)	11 225.2(14)	8 859.3(12)	7 707.6(7)
O(2B)	12 551.8(15)	9 455.6(12)	9 230.5(8)
O(3B)	10 876(2)	11 027.0(12)	9 298.3(8)
N(1B)	10 412(2)	9 687.5(13)	8 797.4(9)

Table 8 Atomic co-ordinates (× 10^4) for compound **12**

	x	y	z
C(1)	3 407(2)	5 101(2)	6 485.4(6)
C(2)	3 931(2)	6 531(2)	6 647.3(6)
C(3)	2 170(2)	6 251(2)	6 525.2(7)
C(4)	2 030(2)	4 175(2)	5 559.2(7)
C(5)	676(3)	3 627(2)	5 806.8(8)
C(6)	−775(3)	3 386(2)	5 537.2(11)
C(7)	−844(4)	3 647(2)	5 011.8(11)
C(8)	486(4)	4 196(2)	4 766.1(9)
C(9)	1 926(3)	4 475(2)	5 035.2(7)
C(10)	5 554(2)	3 651(2)	7 127.9(6)
C(11)	6 412(3)	2 665(2)	6 866.6(8)
C(12)	8 106(3)	2 512(3)	6 979.1(11)
C(13)	8 840(3)	3 338(3)	7 331.9(12)
C(14)	7 977(3)	4 313(3)	7 584.5(11)
C(15)	6 322(3)	4 484(2)	7 486.6(8)
C(16)	5 090(2)	7 353(2)	6 317.0(7)
C(17)	6 876(2)	6 931(2)	6 413.6(8)
C(18)	8 163(2)	7 680(2)	6 103.0(6)
C(19)	8 723(3)	7 180(2)	5 631.6(6)
C(20)	9 970(3)	7 820(3)	5 363.0(7)
C(21)	10 674(3)	8 965(3)	5 556.8(9)
C(22)	10 135(3)	9 485(2)	6 019.2(9)
C(23)	8 876(3)	8 843(2)	6 289.7(7)
S(1)	3 966.7(5)	4 460.4(5)	5 865.6(2)
S(2)	3 432.6(5)	3 894.2(5)	7 001.73(15)
O(1)	2 749(2)	2 636(2)	6 830.9(6)
O(2)	2 722(2)	4 542(2)	7 450.4(5)

was added to a solution of phenyl phenylthiomethyl sulfone **4** (0.64 g, 2.4 mmol) in dry THF (5 cm^3) at −78 °C. The yellow coloured solution was warmed to 0 °C and stirred at that temperature for 30 min. This solution was then transferred to a solution of *S*-phenyl-*S*-(4-phenylbut-1-enyl)-*N*-(*p*-tolylsulfonyl)sulfoximide **10b** (0.85 g, 2.0 mmol) in dry THF (10 cm^3) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 3.5 h, quenched with phosphate buffer (20 cm^3; pH 7), and extracted with dichloromethane (3 × 20 cm^3). The extracts were combined and dried, and the solvent was removed under reduced pressure to give a thick orange oil. The crude product was purified by flash chromatography, using ethyl acetate–light petroleum (1 : 4) as eluent, to give the cyclopropane **12** as a cream-coloured solid. Recrystallisation from ethyl acetate yielded the pure *cyclopropane* **12** (0.386 g, 49%) as a crystalline solid, m.p. 84–85 °C; δ_H(200 MHz) 0.91 (1 H, dd, *J* 5.4, 7.3), 1.77–2.05 (2 H, m), 2.17 (1 H, dd, *J* 5.4, 9.7), 2.34 (1 H, m), 2.46–2.63 (2 H, m) and 7.10–7.97 (15 H, m); *m/z* (EI) 394 (M^+, 8%), 276 (18) and 218 (10) (Found: M^+, 394.1057. $C_{23}H_{22}O_2S_2$ requires *M*, 394.1061).

X-Ray Crystallography.—Crystal data for the cyclopropanes **5a**, **6**, **7**, **11a** and **12** are given in Table 3, together with information on data-collection and structure-determination procedures. Instrumentation and methods were as previously described,[8] except for structure refinement,[18] which was by full-matrix least-squares methods based on F^2 for all measured data. The weighting scheme was of the form $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where P is $(F_o^2 + 2F_c^2)/3$. Final residuals are defined as $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ (for comparison with conventional refinements based on F) and $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$. An isotropic extinction coefficient x was refined, such that F_c is multiplied by $[1 + 0.001xF_c^2\lambda^3/\sin 2\theta]^{-\frac{1}{4}}$. Semiempirical absorption corrections were applied only for compound **12**, with transmission factors 0.124–0.241. The absolute configuration for compounds **6** and **12** was established by refinement of the Flack parameter.[19] For consistency of presentation, the molecular structure shown in Fig. 2 is of the opposite configuration to that found for the crystal studied.

Refined co-ordinates for the five structures are given in Tables 4–8. Other parameters, together with full lists of bond lengths and angles, are available as supplementary material from the CCDC.*

* 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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