X-Ray Structure and Stereochemical Properties of (*S,S*)-(−)-2-Methylsulphonyl-3-phenyloxaziridine and of (*S,S*)-(−)-2-Methylsulphonyl-3-(2-chloro-5-nitrophenyl)oxaziridine

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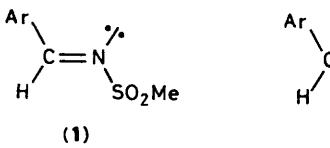
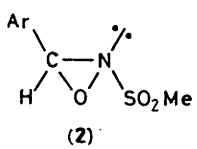
X-Ray analysis of crystalline, optically pure 2-methylsulphonyl-3-phenyloxaziridine (**2a**) and 2-methylsulphonyl-3-(2-chloro-5-nitrophenyl)oxaziridine (**2b**), obtained by asymmetric oxidation of the corresponding prochiral *N*-benzylidenemethylsulphonylimine (**1a**) and *N*-(2-chloro-5-nitrobenzylidene)methylsulphonylimine (**1b**) with (1*S*)-(+)-peroxycamphoric acid, (+)-PCA, followed by fractional crystallization of the crude products, shows that the absolute configuration at the chiral nitrogen and carbon atoms of the oxaziridine rings of both (−)-(**2a**) and (−)-(**2b**) derivatives is (*S,S*). C.d. spectra of (−)-(**2a**) and (−)-(**2b**) indicate that the chiroptical properties of these compounds can be correlated with the observed (*S,S*) configuration. On the other hand, asymmetric oxidations of prochiral sulphides and olefins, carried out with both (−)-(**2a**) and (−)-(**2b**) as chiral oxidizing reagents, indicate that the stereochemical properties of these oxaziridine derivatives are dependent on the substituted or unsubstituted structure of the phenyl group directly linked to the carbon atom of the three-membered ring.

The finding that optically active *N*-sulphonyloxaziridines show unusual chemical and stereochemical behaviour owing to the highly electrophilic oxaziridine oxygen atom[1] initiated extensive investigations on the synthesis and on the structural and stereochemical properties of these reagents. Most of this work has been done by Davis and his co-workers by using optically active *N*-sulphonyloxaziridine diastereoisomers (**3**).[2]

In a previous paper we reported the asymmetric synthesis of optically active 2-methyl- and 2-phenyl-sulphonyl-3-aryloxaziridines (**2**) and the stereochemical and chiroptical properties of the enantiomeric (−) species of these compounds.[3] In every case the absolute configuration of the reported oxaziridines was unknown. In this communication we describe the *X*-ray crystal structure of optically pure (**2a** and **b**) and we compare some stereochemical properties of these compounds with the corresponding ones reported[2] for 2-[(+)-camphorsulphonyl]-3-(2-chloro-5-nitrophenyl)oxaziridines (**3**).


(1)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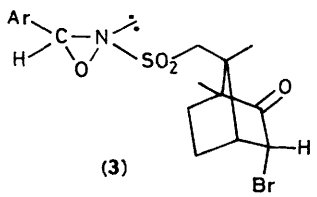
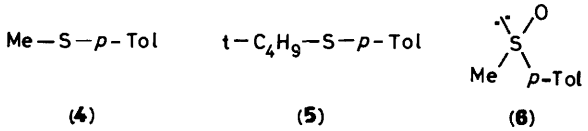

(3)

a; Ar = Ph
b; Ar = 2-Cl-5-$NO_2C_6H_3$

Results and Discussion

The synthesis of highly optically pure enantiomers (**2a** and **b**) has been performed by oxidation of the corresponding prochiral sulphonimines (**1a** and **b**) with (1*S*)-(+)-peroxycamphoric acid in basic medium, followed by fractional crystallization of the crude products. In both cases, *N*-sulphonyl-3-aryloxaziridines were recovered as crystalline solids and all show negative sign of optical rotation. ^{1}H N.m.r. spectra recorded in the presence of the chiral shift reagent tris-[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato]europium(III), (+)-Eu(fhc)$_3$, indicate that both oxaziridines (−)-(**2a**) and (−)-(**2b**) are > 95% optically pure. The rotatory powers and the ^{1}H n.m.r. data of (−)-(**2a**) and (−)-(**2b**), as well as their relative ^{1}H n.m.r. chemical-shift differences and enantiomeric purities, are reported in Table 1.

Molecular Geometries.—The crystal structures and absolute configurations of (**2a** and **b**) were determined by single-crystal *X*-ray diffraction analysis followed by a determining test based on selected Bijovet pairs.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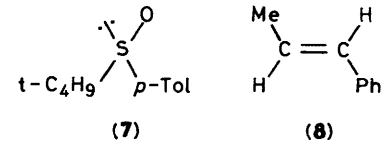
(7) (8)

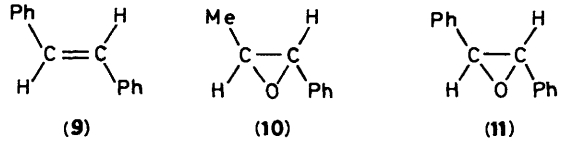
(9) (10) (11)

Table 1. Properties of optically active oxaziridines (**2a** and **b**)

Oxaziridine	$[\alpha]_D$[a](°)	$[\alpha]_D$[b](°)	Chemical shift δ($CDCl_3$)[c] CH_3	H	Ar	Noneq.[d] (Hz[e]/sense[f]) H	CH_3
(**2a**)[g]	−30.2	−191.0	3.2(s)	5.5(s)	7.4—7.6(m)	3.6/H	6.6/L
(**2b**)[h]	−17.7	−124.7	3.2(s)	5.9(s)	7.5—8.4(m)		7.6/L

[a] Optical activities of the reaction crude products (*c* 1—2 in $CHCl_3$). [b] Optical activities of (−)-(**2a** and **b**) obtained by fractional crystallization of the crude products to constant rotation. [c] ^1H N.m.r. at 200 MHz in $CDCl_3$ solutions, Me_4Si as internal standard. [d] Nonequivalence observed in $CDCl_3$ solution for the mixture 0.8M-oxaziridine–0.04M-Eu(fhc)$_3$. [e] At 200 MHz and 20 °C. [f] Field position of the anisochronous H and CH_3 groups of the (−)-oxaziridines (**2a** and **b**) with respect to the (+) ones; H refers to highfield and L to lowfield position. [g] M.p. 73—74 °C (m.p. racemate 60—61 °C). [h] M.p. 151—152 °C (m.p. racemate 127—128 °C).

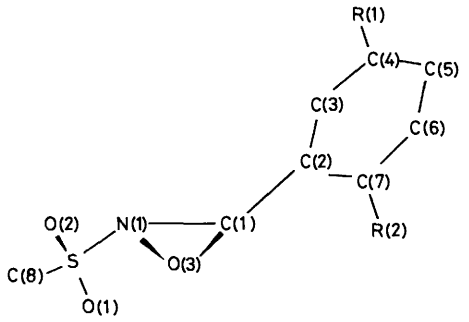

Figure 1. *X*-Ray structure and numbering scheme of oxaziridines (**2a** and **b**)

The molecular geometry of the racemic mixture of (**2a**), which was also obtained from a crystallographic study, is included for comparison and named (**2a-r**).

The general numbering scheme of the atoms is shown in Figure 1.

Crystal details of (**2a-r**), (**2a**), and (**2b**) are reported in Table 2; fractional co-ordinates of the same compounds are listed in Tables 3—5 respectively, while some selected bond distances and angles are reported in Table 6.

The orientation of the phenyl ring with respect to the oxaziridine plane can be defined by the acute angle θ between the normal to the phenyl ring and the distal bond N(1)–O(3),[4] a bisected (b) conformation being defined by θ 0° and a perpendicular (p) one being defined by θ 90°. As may be seen in Table 4 all but one molecules assume the b conformation. The geometry of the oxaziridine ring compares well with the values observed[5–8] and expected[9] in three-membered substituted heterocycles, showing a shortened C(1)–O(3) bond and a lengthened N(1)–O(3) one, while N(1)–C(1) is spread over a wider range.

The conformation around the N atom indicates that no significant lone-pair–*d*-orbital interaction involves the nitrogen and sulphur atoms. The S–N(1) bonds are in the range expected for a pure single bond and the N atom is strongly pyramidal, as is shown by the angle between the S–N(1) bond and the normal to the oxaziridine plane reported in Table 4 for all molecules studied. An almost equivalent definition is given by the height of the N atom over the plane containing its three substituents; for all four molecules we found the same value of 0.81 Å within experimental error. The N atom lone pair and the bisector of the two sulphonyl O atoms are rotated by *ca.* 120° around the N(1)–S bond. The nitro-group plane in (**2b**) is slightly twisted from the phenyl ring by 16.6(3)° in molecule A and 19.8(4)° in B. The presence of the nitro group and of the chlorine atom in the phenyl ring does not have a significant effect on the local geometry of the sulphonyl–oxaziridine moiety.

Chiroptical Properties of Oxaziridines (−)-(**2a**) *and* (−)-(**2b**).—Figure 2 depicts the u.v. and c.d. spectra of oxaziridines (−)-(**2a**) and (−)-(**2b**), recorded in iso-octane solution. Corresponding to the typical u.v. ^1L_b and ^1L_a transitions of the benzene chromophore the c.d. spectrum of (−)-(**2a**) is consistent with the chiroptical behaviour of a chiral benzenoid compound containing an asymmetrically perturbed isolated phenyl group,[10] and is characterized by a complex system of positive and negative bands of low intensity in the 272—250 nm spectral region, and by a stronger and clearly negative Cotton effect at 220 nm. A correlation between the negative sign of the ^1L_a transition of the benzene chromophore and the (*S*,*S*)

Table 2. Crystal details

Molecule	(**2a-r**) $C_8H_9NO_3S$	(**2a**) $C_8H_9NO_3S$	(**2b**) $C_8H_7ClN_2O_5S$
M_r	199.1	199.1	278.6
Space group	*Cc*	$P2_12_12_1$	$P2_1$
a (Å)	18.787(4)	5.650(1)	10.208(2)
b (Å)	5.055(1)	8.992(2)	5.521(3)
c (Å)	9.729(2)	18.859(4)	20.219(2)
β (°)	94.49(2)		100.70(2)
Z	4	4	4
V (Å^3)	921.1(3)	958.1(3)	1 119.7(7)
D_c (g cm^{-3})	1.436	1.380	1.65
λ (Å)	0.710 69	0.710 69	1.5418
μ (cm^{-1})	3.21	3.09	48.4
F(000)	416	416	568

Experimental conditions and refinement details

θ range	3° < θ < 28°	3° < θ < 28°	5° < θ < 60°
no of reflections	1 031	1 362	2 074
no of observed reflections*	1 000	554	1 560
R	0.053	0.058	0.075
wR	0.061	0.046	0.081

* With $I > 2.5\sigma(I)$.

Table 3. Fractional co-ordinates (× 10^4) of racemic 2-methylsulphonyl-3-phenyloxaziridine (**2a-r**)

Atom	*x*	*y*	*z*
S	1 557(0)	1 174(2)	355(0)
N	2 462(2)	693(10)	225(5)
O(1)	1 166(2)	−1 244(7)	351(5)
O(2)	1 565(3)	2 849(10)	1 541(4)
O(3)	2 554(3)	−1 617(12)	−685(5)
C(1)	2 705(3)	−1 866(11)	757(6)
C(2)	3 442(2)	−2 101(8)	1 337(4)
C(3)	3 601(2)	−3 945(8)	2 382(4)
C(4)	4 301(2)	−4 220(8)	2 956(4)
C(5)	4 843(2)	−2 652(8)	2 484(4)
C(6)	4 683(2)	−807(8)	1 439(4)
C(7)	3 983(2)	−532(8)	865(4)
C(8)	1 338(4)	2 968(13)	−1 132(6)

Table 4. Fractional co-ordinates ($\times 10^4$) of (*S,S*)-(−)-2-methylsulphonyl-3-phenyloxaziridine (**2a**)

Atom	*x*	*y*	*z*
S	9 903(6)	1 479(3)	6 673(1)
N(1)	10 558(14)	1 054(8)	5 807(4)
O(1)	7 554(13)	2 001(8)	6 755(4)
O(2)	10 620(17)	183(8)	7 042(4)
O(3)	9 439(13)	2 209(6)	5 346(3)
C(1)	8 488(25)	768(12)	5 386(5)
C(2)	8 656(10)	−212(8)	4 763(3)
C(3)	6 850(10)	−1 232(8)	4 631(3)
C(4)	6 966(10)	−2 154(8)	4 037(3)
C(5)	8 889(10)	−2 056(8)	3 576(3)
C(6)	10 696(10)	−1 036(8)	3 708(3)
C(7)	10 579(10)	−113(8)	4 302(3)
C(8)	11 898(24)	2 932(15)	6 820(7)

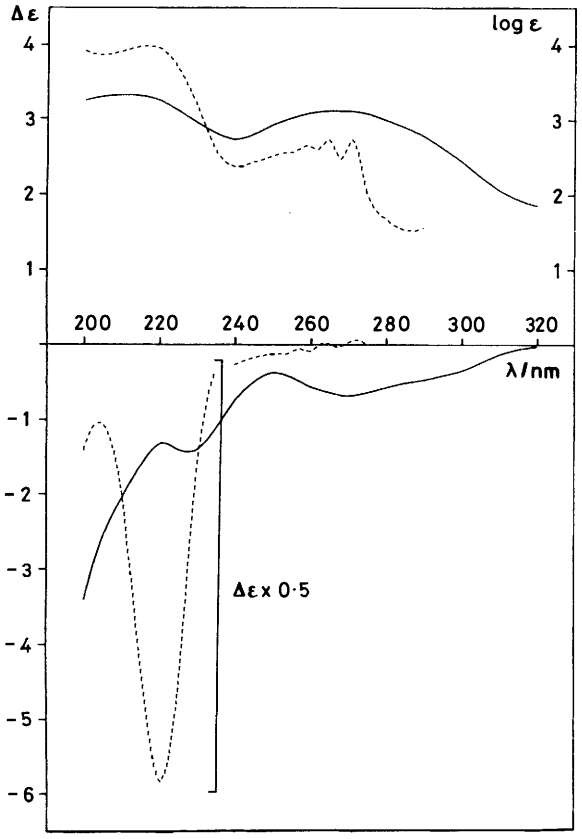

Figure 2. C.d. and u.v. spectra of oxaziridines (**2a**) (– – – –) and (**2b**) (——) in iso-octane solutions

configuration of the chiral oxaziridine is also observed at 230 nm in the c.d. spectrum of (−)-(**2b**) even if, in this case, the optically active band is not so intense as in the c.d. spectrum of (−)-(**2a**), probably owing to overlap of the adjacent stronger negative band.

Stereochemical Properties of (−)-(**2a**) *and* (−)-(**2b**).—Correlations between the absolute configurations of (−)-(**2a**) and (−)-(**2b**) and the stereochemical properties of these two compounds have been checked by using them as chiral reagents for asymmetric oxidations of prochiral methyl *p*-tolyl (**4**) and t-butyl *p*-tolyl (**5**) sulphides to the corresponding optically active sulphoxides (**6**) and (**7**), or for asymmetric epoxidation of *trans*-1-phenyl-2-methylethylene (**8**) and *trans*-stilbene (**9**) to the chiral epoxides (**10**) and (**11**).

Table 5. Fractional co-ordinates ($\times 10^4$) of the two independent molecules of (*S,S*)-(−)-2-methylsulphonyl-3-(2-chloro-5-nitrophenyl)-oxaziridine (**2b**)

	Molecule A		
Atom	*x*	*y*	*z*
Cl	1 974(3)	6 439(6)	2 542(2)
S	3 493(2)	402(5)	874(1)
O(1)	4 397(7)	−1 533(14)	868(4)
O(2)	2 094(6)	−21(20)	696(3)
O(3)	5 052(7)	1 416(18)	2 024(4)
O(4)	5 565(8)	5 020(19)	4 246(4)
O(5)	4 006(7)	4 798(16)	4 825(3)
N(1)	3 631(7)	1 654(15)	1 674(4)
N(2)	4 519(8)	4 202(19)	4 359(4)
C(1)	4 075(8)	−138(19)	2 197(4)
C(2)	3 670(7)	199(18)	2 854(4)
C(3)	4 250(8)	1 980(17)	3 298(4)
C(4)	3 868(8)	2 223(18)	3 898(4)
C(5)	2 922(9)	886(21)	4 113(5)
C(6)	2 372(9)	−925(22)	3 675(5)
C(7)	2 727(8)	−1 266(19)	3 053(4)
C(8)	4 009(10)	2 822(21)	432(5)
	Molecule B		
Atom	*x*	*y*	*z*
Cl	3 077(3)	−8 518(5)	−2 465(2)
S	1 374(2)	−2 021(5)	−948(1)
O(1)	1 343(7)	−4 318(14)	−636(3)
O(2)	2 566(6)	−705(19)	−875(4)
O(3)	−101(7)	−4 240(19)	−1 972(3)
O(4)	−533(8)	−66(22)	−4 211(4)
O(5)	964(7)	−435(16)	−4 816(3)
N(1)	911(7)	−2 235(17)	−1 820(3)
N(2)	473(8)	−914(18)	−4 329(4)
C(1)	1 189(9)	−4 658(21)	−2 073(5)
C(2)	1 461(8)	−4 625(19)	−2 782(4)
C(3)	813(9)	−2 847(21)	−3 241(5)
C(4)	1 098(8)	−2 875(18)	−3 860(4)
C(5)	2 009(9)	−4 406(21)	−4 076(5)
C(6)	2 614(9)	−6 125(21)	−3 635(5)
C(7)	2 324(8)	−6 249(18)	−2 992(4)
C(8)	94(9)	−222(22)	−777(4)

Oxidations of sulphides (**4**) and (**5**) have been carried out by dropwise addition of the chiral oxaziridines (−)-(**2a**) and (−)-(**2b**) to the prochiral substrates in CH_2Cl_2 or $CHCl_3$ solution at −50 °C; epoxidations of olefins (**8**) and (**9**) were accomplished in $CHCl_3$ solution at 61 °C. In both reactions optically active sulphoxides and epoxides were isolated by preparative t.l.c. in 80—90% yield. The optical yields of these reactions were determined from ^1H n.m.r. spectra recorded in the presence of a chiral solvating agent and by comparison of the optical rotations obtained with those reported in the literature.

Asymmetric oxidations of prochiral organosulphur compounds[5] and unfunctionalized olefins[11] have been recently performed by Davis and his co-workers by using diastereoisomeric oxaziridines (**3**) and of known absolute configuration as chiral oxidizing agents. These oxidizing agents afford sulphoxides and epoxides with better enantioselectivity than do chiral peracids or hydroperoxides. Moreover, the configuration at the chiral centres of the oxaziridine ring controls the stereochemistry of the products: oxaziridines (*S,S*)-(**3**) afford sulphoxides (**6**) and (**7**) with the (*S*) configuration at the asymmetric sulphur atom[5] and (−)-(*S,S*) epoxides (**10**) and (**11**),[11] whereas opposite stereochemistries are obtained with

Table 6. Some selected intramolecular distances and angles

Structure	(2a-r)	(2a)	(2b) Molecule A	(2b) Molecule B
Bond distance (Å)				
S(1)–N(1)	1.717(8)	1.733(5)	1.741(12)	1.742(7)
S(1)–O(1)	1.416(8)	1.426(4)	1.413(8)	1.419(8)
S(1)–O(2)	1.417(9)	1.430(4)	1.426(7)	1.402(8)
S(1)–C(8)	1.746(14)	1.729(6)	1.742(11)	1.723(11)
N(1)–O(3)	1.494(9)	1.484(7)	1.497(9)	1.506(12)
N(1)–C(1)	1.436(15)	1.454(7)	1.457(12)	1.478(14)
O(3)–C(1)	1.404(13)	1.416(7)	1.407(12)	1.389(12)
C(1)–C(2)	1.471(12)	1.456(6)	1.475(12)	1.512(13)
Bond angle (°)				
O(1)–S(1)–O(2)	119.1(5)	118.9(3)	120.0(5)	120.5(5)
O(1)–S(1)–C(8)	109.8(6)	111.0(3)	108.4(5)	110.1(5)
O(2)–S(1)–C(8)	110.6(6)	110.6(3)	112.4(5)	110.8(6)
N(1)–S(1)–O(1)	112.3(4)	112.8(2)	111.5(4)	111.4(4)
N(1)–S(1)–O(2)	102.8(4)	101.2(2)	101.7(4)	102.0(4)
N(1)–S(1)–C(8)	100.3(5)	100.6(3)	101.1(5)	99.7(4)
S(1)–N(1)–C(1)	113.0(7)	112.4(4)	111.4(6)	112.2(6)
S(1)–N(1)–O(3)	107.9(5)	108.3(3)	108.0(5)	107.6(5)
O(3)–N(1)–C(1)	57.2(6)	57.6(3)	56.9(5)	55.4(6)
N(1)–O(3)–C(1)	59.3(6)	60.1(4)	60.1(6)	61.3(6)
N(1)–C(1)–O(3)	63.5(6)	62.3(4)	63.0(6)	63.3(6)
O(3)–C(1)–C(2)	119.0(8)	120.0(5)	118.4(8)	119.0(8)
N(1)–C(1)–C(2)	119.7(10)	118.1(5)	117.8(8)	113.5(9)
Torsion angle (°)				
O(1)–S(1)–N(1)–O(3)	39.5(6)	35.3(4)	31.7(7)	32.5(7)
O(1)–S(1)–N(1)–C(1)	−21.7(8)	−26.5(5)	−29.0(7)	−26.6(8)
O(2)–S(1)–N(1)–O(3)	168.8(5)	163.3(4)	160.7(6)	162.4(6)
O(2)–S(1)–N(1)–C(1)	107.6(7)	101.6(4)	100.1(7)	103.3(7)
C(8)–S(1)–N(1)–O(3)	−77.1(7)	−83.0(4)	−83.4(6)	−83.7(6)
C(8)–S(1)–N(1)–C(1)	−138.3(8)	−144.7(4)	−144.0(6)	−142.8(7)
S(1)–N(1)–O(3)–C(1)	−106.3(7)	−105.4(4)	−104.3(7)	−105.2(7)
S(1)–N(1)–C(1)–O(3)	97.1(6)	98.2(4)	98.1(6)	96.7(7)
S(1)–N(1)–C(1)–C(2)	−153.1(7)	−150.8(4)	−152.3(7)	−151.5(7)
O(3)–N(1)–C(1)–C(2)	109.9(10)	111.1(5)	109.6(9)	111.9(9)
N(1)–O(3)–C(1)–C(2)	−110.9(10)	−108.2(5)	−108.6(9)	−103.4(9)
O(3)–C(1)–C(2)–C(3)	−147.0(8)	−137.2(5)	−179.7(8)	−140.8(10)
N(1)–C(1)–C(2)–C(3)	138.7(9)	150.3(4)	107.7(10)	147.8(9)
Plane–plane angle (°)				
N(1)–C(1)–O(3) C(2)–C(3)–C(4)–C(5)–C(6)–C(7)	95.3(10)	93.9(4)	71.0(4)	81.8(5)
Vector–plane angle (°)				
S(1)–N(1) N(1)–C(1)–O(3)	23.8(9)	24.0(5)	22.8(4)	23.1(5)
N(1)–O(3) C(2)–C(3)–C(4)–C(5)–C(6)–C(7)	8.2(5)	4.5(4)	35.1(5)	9.1(4)

oxaziridines (**3**) having the (*R,R*) configuration at the three-membered ring. Finally, no solvent effect is observed on the stereochemical behaviour of the reactions. These results have been rationalized in terms of chiral recognition models which are largely determined by steric factors and ignore electronic and solvent effects.[5,11]

The results obtained in the present work are summarized in Tables 7 and 8. Surprisingly, these results indicate that the stereochemical features of the asymmetric oxidations carried out with 2-sulphonyl-3-phenyloxaziridines (**2a** and **b**) strong depend on the structure of the phenyl ring directly linked to the carbon of the oxaziridine ring: the asymmetric oxidations performed with (−)-(*S,S*)-(**2a**), carrying an unsubstituted phenyl group, do not follow at all the stereochemical trends previously reported for oxaziridines (**3**);[5,11] on the other hand, the results obtained by using the 3-(2-chloro-5-nitrophenyl)-oxaziridine (−)-(*S,S*)-(**2b**), namely an oxaziridine derivative carrying NO_2 and Cl on the phenyl ring, are very similar to both the qualitative and quantitative stereochemical aspects to these observed by Davis and his co-workers in their oxidations. More particularly, from the results of Table 7 one realizes that: (i) oxidations of prochiral sulphides (**4**) and (**5**) carried out in $CHCl_3$ solution and with chiral oxaziridine (**2a**) afforded optically active methyl (**6**) and t-butyl (**7**) sulphoxides in 11.3 and 8.7% ee, respectively, *i.e.* with a degree of enantioselectivity which is quite similar to that observed in oxidations carried out with chiral peracids[12] [when the same reactions were performed with oxaziridine (**2b**) 17—38% optical yields were obtained]; (ii) oxidations with (−)-(*S,S*)-(**2a**) give (+)-(*R*) sulphoxides, whereas oxidations with (−)-(*S,S*)-(**2b**) furnishes (−)-(*S*) sulphoxides; (iii) in the reactions carried out in CH_2Cl_2 solution we observed no solvent effect when we used oxaziridine (**2b**) as chiral oxidant, whereas in the same medium oxaziridine (**2a**) gives sulphoxides (**6**) and (**7**) of low optical purity (2.7 and 0.4 ee%, respectively) and with the absolute configurations (+)-(*R*)-(**6**) and (−)-(*S*)-(**7**). Differences between oxaziridines (**2a** and **b**) have also been observed in the oxidations of olefins. All attempts to epoxidize olefins (**8**) and (**9**) with oxaziridine (−)-(*S,S*)-(**2a**) have failed; on the other hand we obtained 41—45% optical yields of epoxides (−)-(*S,S*)-(**10**) and (−)-(*S,S*)-(**11**) from the reactions carried out with oxaziridine (−)-(*S,S*)-(**2b**).

The stereochemical properties of oxaziridine (−)-(**2b**), together with the easy synthesis and the knowledge of the absolute configuration, indicate that 2-sulphonyloxaziridines (**2b**) are to be considered as powerful and efficient asymmetric oxidizing reagents for a variety of unfunctionalized substrates and for a large series of stereochemical studies involving asymmetric oxidations.

Experimental

Optical rotations were measured with a Perkin-Elmer 141 polarimeter. ^{1}H N.m.r. spectra were recorded in $CDCl_3$ solution (Me_4Si as internal standard) on a Bruker FT-80 or Varian XL-200 instrument. Elemental analyses were performed with a Carlo Erba Elemental Analyzer model 1106. M.p.s are uncorrected.

(*S*)-(+)-Peroxycamphoric acid has been used in crystalline form and prepared according to the literature.[13] Sulphides were prepared by standard methods. Alkenes were purchased from Janssen Chimica and used without further purification. Oxaziridine (**2a**) has been prepared as previously described.[3]

N-(2-*Chloro*-5-*nitrobenzylidene*)*methylsulphonylimine* (**1b**).—The imine (**1b**) (85%) was obtained from the corresponding 2-chloro-5-nitrobenzaldehyde diethyl acetal[14] as described in the literature.[5] The product was purified on washing with hot $CHCl_3$ and showed the following properties, m.p. 206—207 °C (Found: C, 36.4; H, 2.7; N, 10.9; S, 12.1. $C_8H_7ClN_2O_4S$ requires C, 36.6; H, 2.7; N, 10.7; S, 12.2%); $\nu_{max.}$ (KBr–Nujol) 1 610 (C=N), 1 310, and 1 150 cm^{-1} (SO_2); $\delta_H(CDCl_3)$ 1.7 (3 H, s, Me), 6.2—7.6 (3 H, m, Ar), and 8.02 (1 H, s, N=CH).

2-*Methylsulphonyl*-3-(2-*chloro*-5-*nitrophenyl*)*oxaziridine* (**2b**).—The oxaziridine (**2b**) (95%), $[\alpha]_D$ − 17.7° (*c* 2 in $CHCl_3$), was obtained from the corresponding imine as previously described.[3] Fractional crystallization of the crude product from diethyl ether–ethyl acetate (1:1) afforded the highly optically pure oxaziridine (−)-(**2b**), m.p. 151—152 °C; $[\alpha]_D$ − 124.7° (*c* 2 in $CHCl_3$) (Found: C, 34.4; H, 2.6; N, 10.1; S, 11.6. C_8H_7Cl-

Table 7. Asymmetric oxidations of sulphides (**4**) and (**5**) with (−)-(**2a** and **b**) at −50 °C

		p-TolylSOMe (**6**)			*p*-TolylSOBu^t (**7**)		
Oxaziridine[a]	solvent	$[\alpha]_D$[b] (°)	ee%[c]	Absolute configuration[c]	$[\alpha]_D$[b] (°)	ee%[c]	Absolute configuration[c]
(−)-(*S,S*)-(**2a**)	$CHCl_3$	+16.0	11.3	(*R*)	+16.5	8.7	(*R*)
	CH_2Cl_2	+3.9	2.7	(*R*)	−0.8	0.4	(*S*)
(−)-(*S,S*)-(**2b**)	$CHCl_3$	−53.2	37.7	(*S*)	−38.7	20.4	(*S*)
	CH_2Cl_2	−39.3	27.9	(*S*)	−32.5	16.8	(*S*)

[a] The oxaziridines were of 80—100% optical purity. [b] In EtOH 95% (*c* 2—3), values corrected to 100% of optical purities of the oxaziridines. [c] ee% and absolute configurations: K. Mislow, M. M. Green, P. Laur, J. T. Melillo, and A. L. Ternay, *J. Am. Chem. Soc.*, 1958, **80**, 1965.

Table 8. Asymmetric oxidations of alkenes (**8**) and (**9**) with (−)-(**2** and **b**) in $CHCl_3$ at 61 °C

	trans-1-Phenyl-2-methylethylene oxide (**10**)			*trans*-Stilbene oxide (**11**)		
Oxaziridine[a]	$[\alpha]_D$[b] (°)	ee%	Absolute configuration	$[\alpha]_D$[b] (°)	ee%	Absolute configuration
(−)-(*S,S*)-(**2a**)	*c*			*c*		
(−)-(*S,S*)-(**2b**)	−21.8	45.2[d]	(*S,S*)[d]	−101.5	40.7[e]	(*S,S*)[e]

[a] The oxaziridines were of 80—100% optical purity. [b] In $CHCl_3$ (*c* 1—2), values corrected to 100% of optical purities of the oxaziridines. [c] Formation of epoxides was undetected. [d] ee% and absolute configurations: H. E. Audier, J. F. Dupin, and J. Jullien, *Bull. Soc. Chim. Fr.*, 1966, 2811. [e] ee% and absolute configurations: J. Read and I. G. M. Campbell, *J. Chem. Soc.*, 1930, 2377.

requires C, 34.5; H, 2.5; N, 10.05; S, 11.5%); $\delta_H(CDCl_3)$ 3.28 (3 H, s, Me), 5.95 (1 H, s, CH), and 7.5—8.4 (3 H, m, Ar).

X-Ray Structural Analyses.—Experimental conditions and crystal data for (*S,S*)-(−)- and racemic 2-methylsulphonyl-3-phenyloxaziridine (**2a**) and of (*S,S*)-(−)-2-methylsulphonyl-3-(2-chloro-5-nitrophenyl)oxaziridine (**2b**) are summarized in Table 2.

Intensity measurements were collected on a Philips PW1100 diffractometer at room temperature with θ–2θ scan technique. Cell dimensions were obtained by least-squares 2θ to 20 reflections. Semiempirical absorption corrections were applied to (**2b**) on the basis of ψ-scan data with two different 2θ values. The structures were solved by direct methods with MULTAN80[15] and refined with the SHELX[16] program using the blocked full-matrix method. In order to minimize the number of refinable parameters, the geometry of the phenyl ring was kept fixed for (**2a**) and (**2a-r**), while in the case of (**2b**) the geometry appears to deviate significantly from standard values and therefore the phenyl carbon atoms were refined independently with isotropic thermal parameters. The hydrogen atoms were located both by Fourier maps and by theoretical calculus.

The absolute configuration of (**2a** and **b**) was determined with the aid of Bijovet pairs. For each structure the two antipodal sets of refined atomic co-ordinates were used in a structure factor calculation limited to the 50 (**2a**) and 85 (**2b**) more enantiomer-sensitive Friedel pairs. For (**2a**) the two weighted *R* factors are 0.052 [(*S,S*) model] and 0.087 [(*R,R*) model] while for (**2b**) the corresponding values are 0.080 [(*S,S*) model] and 0.118 [(*R,R*) model].

General Procedure for Asymmetric Oxidations.—Oxidations of sulphides. In a typical experiment sulphide (50 mg) was dissolved in the selected solvent (4 ml) and cooled to −50 °C. One equivalent of the chosen chiral *N*-sulphonyloxaziridine dissolved in the appropriate solvent (5—6 ml), after cooling to the same temperature, was added dropwise with stirring to the mixture. The mixture was allowed to stand at −50 °C for at least 3 h or until the oxaziridine oxidant had disappeared (t.l.c. on silica; CH_2Cl_2 elution solvent). The solvent was removed under vacuum and the crude products were separated by preparative t.l.c. on silica gel (CH_2Cl_2 elution solvent). In the case of the reactions carried out with the oxaziridine (**2b**) the crude products were washed with diethyl ether to solubilize the sulphoxides selectively with respect to the insoluble imine (**1b**). Imine (**1b**) was directly recovered as solid by filtration of the diethyl ether solution. Evaporation of this last solution gave the crude sulphoxide compounds which were further purified by preparative t.l.c.

Oxidations of Alkenes.—In a typical experiment alkene (50 mg) was dissolved in chloroform (4—5 ml) in a 25 ml round-bottom flask equipped with magnetic stirrer. One equivalent of chiral (−)-(**2b**) in $CHCl_3$ (4—5 ml) was added and the mixture, provided with a reflux condenser, was heated at 61 °C with stirring for 24—48 h until the oxaziridine has disappeared [t.l.c. on silica gel; diethyl ether–n-pentane (1:9) elution solvent]. The crude products were washed with diethyl ether to solubilize the epoxides with respect to the insoluble imine. The epoxides were then further purified by preparative t.l.c. on silica gel diethyl ether–n-pentane (1:9) as eluent.

The chemical purities of the recovered suphoxides and epoxides were checked by g.c. on capillary column SE 54, 80—200 °C, rate 10° min^{-1}, whereas their optical purities were ascertained by comparing the observed optical rotations with those reported in the literature for the optically pure derivatives. The optical yields determined in this manner were verified by ^1H n.m.r. spectra recorded in the presence of $Eu(hfc)_3$ as chiral shift reagent; the agreement between the two methods was approximately ±2.0 ee%.

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