Preparation and Conformational Studies of Chiral Camphor-derived Oxaziridines

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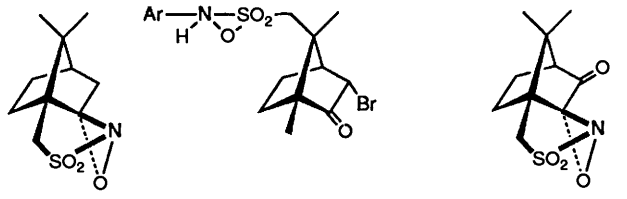
The syntheses and properties of new chiral *N*-sulphonyloxaziridines based on (−)-(camphorsulphonyl)-imine modified in position 3 of the camphor skeleton are reported. The preferred conformations of the 3-spiro-acetals and -thioacetals have been studied by NOE measurements.

Chiral *N*-sulphonyloxaziridines[1] have been introduced as enantioselective oxidizing agents for many compounds, *e.g.* sulphides[2,3] and carbanions.[4] The resulting chiral sulphoxides or α-hydroxy esters are useful starting materials for the synthesis of many naturally occurring compounds.[5] Of particular interest are such oxaziridines which can be derived from readily available materials from the chiral pool with a rigid structure, thus reducing the problem of separation of isomers during the synthesis. The camphor-derived oxaziridines (**1**)–(**6**) are of this type,[3,6,7] and often lead to quite enantioselective reactions, but other modifications of the principal structure are still of considerable interest for further improvement of these chiral oxidants.

In this paper, we report on the synthesis of such compounds with structural modifications in position 3 of camphor, and on their conformations in solution, which can be expected to give valuable hints on their ability for asymmetric oxidation.



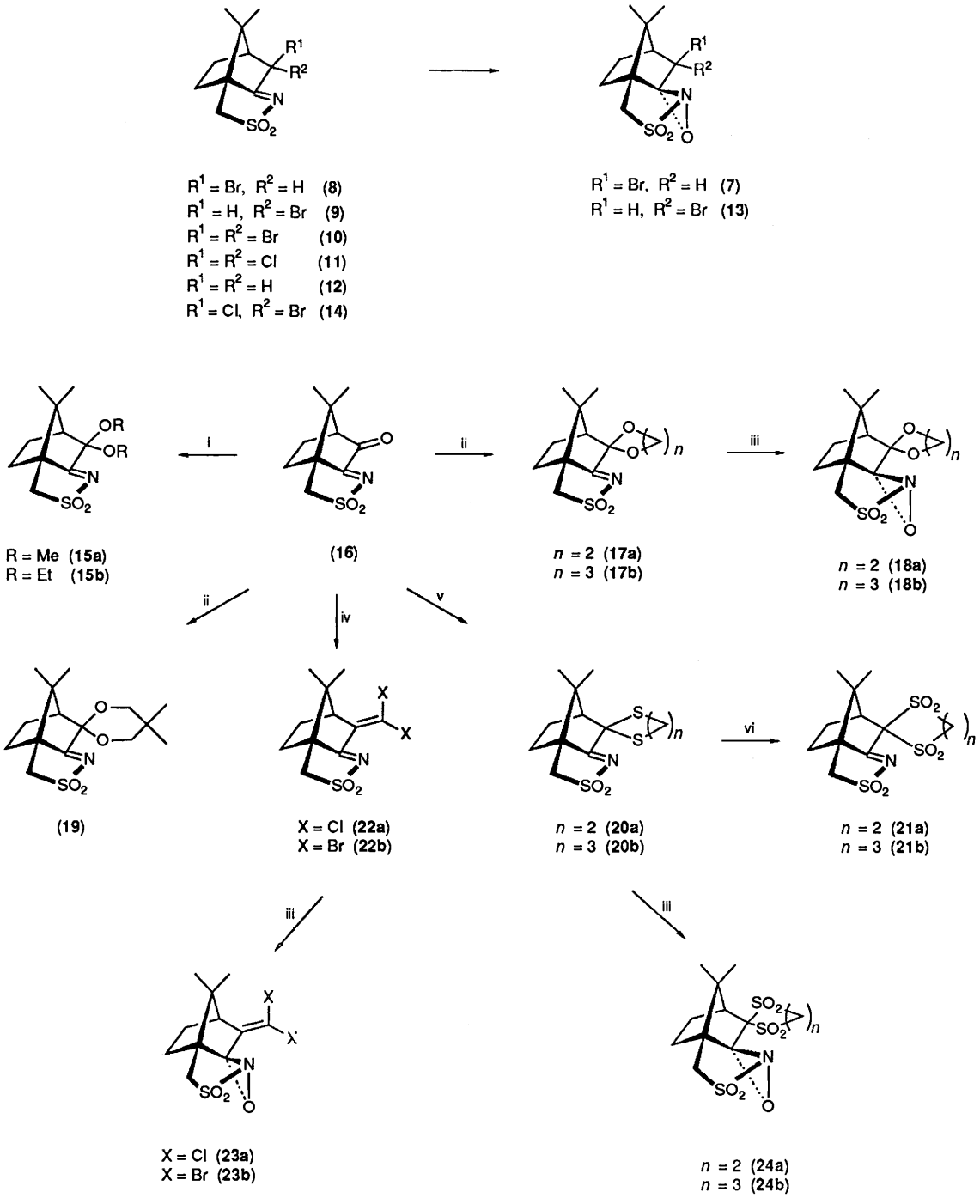
Results and Discussion

Synthesis.—The synthesis of the oxaziridines from the (−)-(camphorsulphonyl)imine (**12**), which is readily prepared from (1*S*)-(+)-camphor-8-sulphonic acid and is also commercially available, is straightforward and outlined in the Scheme.

The bromination of (−)-(camphorsulphonyl)imine (**12**) leads to an *exo*/*endo*-mixture of 3-bromo(camphorsulphonyl)imines (**8**) and (**9**) in the ratio *ca.* 3:7. Further bromination gives the 3,3-dibromo(camphorsulphonyl)imine (**10**) which, however, could not be oxidized to the oxaziridine, presumably because of steric reasons. Although it may be possible to separate the *exo*- and *endo*-isomers (**8**) and (**9**) by crystallization,[8] we found it more convenient to explore the different reactivity of the two isomers towards 3-chloroperbenzoic acid (MCPBA). Thus, at low concentrations of all reactants, a clean oxidation of the *exo*-isomer (**8**) occurs, leaving the *endo*-compound (**9**) almost unchanged. The *exo*-3-bromospiro-oxaziridine (**7**) is difficult to separate from the *endo*-imine (**8**), but can be identified by its NMR spectrum, and was used for oxidation without separation. It shows a much higher reactivity towards reducing agents like sulphite, and from oxidations with high concentrations of all reactands and a higher excess of MCPBA, where both imines are oxidized, the *endo*-3-bromospiro-oxaziridine (**13**) can be obtained in pure state by destruction of the *exo*-oxaziridine (**7**) by several rapid washes of a dichloromethane solution with sodium hydrogen sulphite.

Chlorination of the *endo*-3-bromo imine (**9**) leads to the (3*S*)-imine (**14**), and excess of chlorine forms the dichloro imine (**11**) from the imine (**12**).[8] The oxidation of these chlorinated imines to the corresponding oxaziridines by a large excess of MCPBA is possible, but occurs with very low yield, and we found it difficult to separate the oxaziridines from the starting materials. They are therefore not further considered here.

Oxidation of compound (**12**) with selenium dioxide leads to (3-oxocamphorsulphonyl)imine (**16**),[3] and the new carbonyl group allows for further modifications of the general structure. It readily forms acetals and thioacetals with alcohols and thiols, such as the simple acetals (**15**), or the spiro compounds (**17**), (**19**), and (**20**) with diols and dithiols. Surprisingly, we found it impossible to oxidize the simple acetals (**15**) with MCPBA; the difficulties in the oxidation of the sterically more hindered imine (**19**) are easier to explain. However, the spiro acetals (**17**) and the spiro thioacetals (**20**) readily react with MCPBA to form the oxaziridines (**18**) and (**24**); for the thioacetals, a large excess of MCPBA is necessary, as the sulphur atoms are oxidized first, forming mixed sulphoxide–sulphone compounds as intermediates. The introduction of the last oxygen at one of the sulphur atoms, however, is the most difficult step in this oxidation; for the five-membered ring ($n = 2$), only a mixture of three oxaziridines could be obtained, one of them being the fully oxidized compound (**24a**), according to mass spectral analysis, while the other oxaziridines are probably a mixture of the isomeric mixed sulphoxide–sulphones. The oxidation is cleaner with the six-membered thioacetal ($n = 3$). The pure disulphone-imines (**21**) can be obtained by oxidation of compounds (**20**) with hydrogen peroxide, and we found it



Scheme. *Reagents and conditions:* i, $HC(OR)_3$, Amberlyst 15, CH_2Cl_2; ii, diol, toluene, PTSA, 100 °C; iii, MCPBA, CH_2Cl_2–aq. Na_2CO_3; iv, PPh_3, CX_4, CH_2Cl_2; v, dithiol, BF_3·Et_2O, toluene, 100 °C; vi, H_2O_2, AcOH, 90 °C.

impossible to convert compounds (**20**) into the corresponding oxaziridines with MCPBA.

Finally, we found that the carbonyl function of compound (**16**) is readily converted into the dihalogenoalkene in the exocyclic olefins (**22**), a very clean reaction which has been described only for aldehydes,[9] and that the imines thus formed can be oxidized to the oxaziridines (**23**) with MCPBA, without attack at the C=C double bond.

It is interesting to note that all camphor-derived imines are oxidized to a single diastereoisomer of the corresponding oxaziridine; the bulky methyl groups efficiently shield the *exo* side and allow the approach of the peracid exclusively from the *endo* direction. The resulting oxaziridines thus have a definite configuration with an *endo* oxygen.[7,10]

Conformational Studies.—The efficiency of oxaziridines as chiral oxidants can be expected to depend strongly on both configuration and conformation, in particular in the region close to the oxaziridine ring. For example, it was found that compounds (**1**) and (**3**) form different enantiomers of methyl phenyl sulphoxide upon the oxidation of the corresponding sulphide,[3] a result which is probably due to steric factors. The

Table 1. ^{13}C NMR (90.56 MHz) data of imines and oxaziridines; δ-values in $CDCl_3$ if not otherwise specified.

Compound	Carbon(s) 1	2	3	4	5, 6	7	8	9, 10	11, 12	13
(7)	54.1	100.0	44.5	54.1	21.8, 27.9	44.2	49.6	20.4, 22.3		
(8)	64.3	191.2	53.2	42.3	26.8, 27.8	49.0	50.0	20.0, 20.6		
(9)	63.4	190.4	50.6	48.1	21.9, 28.3	44.8	50.5	18.6, 20.2		
(10)	63.8	190.3	53.0	61.6	27.3, 28.7	47.9	51.2	22.8, 22.9		
(11)	64.2	189.2	82.0	61.3	25.1, 27.4	47.9	50.8	21.6, 21.7		
(12)	54.5	195.6	35.6	44.3	26.3, 28.1	47.9	49.1	18.7, 19.1		
(13)	54.5	96.1	44.5	54.1	21.8, 28.0	47.1	49.6	20.2, 22.2		
(14)	63.9	189.5	66.7	61.7	25.2, 27.4	47.9	51.1	22.5, 21.9		
(15a)	64.3	198.1	103.1	52.3	20.8, 29.4	46.0	49.1	20.6, 20.7	50.4, 50.7	
(15b)	64.2	189.2	102.5	52.7	20.8, 29.5	45.9	49.2	20.7, 20.8	58.6, 58.7	15.0, 15.1
(17a)	63.8	192.2	107.9	52.8	20.6, 28.5	45.2	48.9	19.2, 19.9	63.9, 65.8	
(17b)	65.5	188.5	99.5	56.3	19.4, 29.6	45.6	48.1	20.4, 20.7	61.8, 62.9	25.3
(18a)	54.1	99.2	108.6	54.3	20.9, 28.0	45.2	48.4	19.6, 21.6	64.5, 66.3	
(18b)	55.0	98.4	99.5	55.0	19.5, 28.1	45.0	47.3	20.4, 21.8	62.2, 62.6	24.6
(19)	65.7	188.3	99.5	56.1	19.6, 29.5	45.8	48.3	20.3, 20.7, 21.6, 22.6[a]	72.2, 73.3	30.36
(20a)	65.0	198.8	66.7	57.2	27.5, 28.7	48.2	50.2	20.1, 21.2	41.4, 57.3	
(20b)	65.8	193.8	49.8	56.9	28.4	48.9	48.8	21.7, 22.7	22.2, 22.7, 24.4	
(21a)[b]	65.5	183.8	81.5	52.3	21.3, 27.9	48.7	52.5	18.9, 19.2	48.7, 49.6	
(21b)[b]	65.4	183.8	94.6	52.9	22.6, 28.2	49.4	46.2	19.5, 21.3	48.8, 49.3	14.2
(22a)	65.3	181.9	129.9	54.3	25.0, 28.7	48.3	49.1	18.7, 19.6	134.8	
(22b)	65.7	182.8	99.6	57.4	24.5, 28.4	48.6	49.3	19.3, 19.8	141.2	
(23a)	55.2	93.9	123.4	54.9	24.9, 28.2	46.8	47.8	17.8, 20.9	133.7	
(23b)	57.6	94.4	100.1	58.1	24.4, 28.4	46.3	47.9	19.3, 22.0	139.3	
(24b)	55.2	99.5	98.5	55.3	24.5, 28.1	45.0	47.2	20.3, 21.8	62.2, 62.6	19.4

[a] Methyl groups of camphor and acetal ring not separated. [b] Spectrum in $(CD_3)_2SO$.

principally rigid structure of the bicyclo[2.2.1]heptane skeleton does not allow for much conformational variation, and thus its simple derivatives can be judged on their configuration alone. The formation of spiro acetals and thioacetals, in particular those with six-membered rings, introduces new conformational flexibility, and we therefore thought it worthwhile to study their behaviour in solution. For comparison, we also include an analysis of the corresponding imines.

The general assignment of the ^{13}C signals is based on DEPT spectra[11] and, in some cases, C–H correlation,[12] and are given in Table 1.

For ^1H NMR spectra, the combination of COSY and ROESY[13] (measurement of nuclear Overhauser enhancement in the rotating frame) allowed both configurational and conformational assignment of the corresponding protons in many cases, and only for situations of severe overlap did some doubts remain. Interestingly, there is a strong dependence of chemical shifts and NOE effects on the solvent (*e.g.* $CDCl_3$ *vs.* [$^2H_6$]acetone), which means that its influence on the conformations and thus the efficiency in enantioselective oxidations may be considerable. The results for imines are summarized in Table 2, and for oxaziridines in Table 3. As no NMR data have been reported up to now for some of the halogenated imines, which have been known for almost 90 years, these are also included.

The chemical shifts follow the patterns observed for other bicyclohexanes.[14] The transition from an sp^2 carbon to an sp^3 carbon in the oxidation of the imine to the oxaziridine is associated with an upfield shift of this carbon of *ca.* 90 ppm; the normal range for the imines is δ_C 180–200, while the oxaziridines show the corresponding signals between δ_C 90–100. There is also an upfield shift of the ^1H NMR signals of hydrogens not too far away from the site of the oxidation; the effect is best seen in the bridgehead hydrogen 4-H ($\Delta\delta \leqslant 0.4$ ppm). The ^{13}C chemical shifts of the acetals, thioacetals, and disulphone rings are as expected.[15]

The assignment of the protons at the carbon atoms C-5 and C-6 as *exo* or *endo* is based on the absence of coupling between the bridgehead hydrogen 4-H and the *exo*-5-H, due to a similar dihedral angle between these atoms in all cases, which leads to a coupling constant of *ca.* zero; on the other hand, a very strong NOE effect between these hydrogens indicates their close proximity. The *endo*-5-H shows a coupling to 4-H of *ca.* 4 Hz in almost all cases, which confirms the general rigidity and similarity of the camphor moieties. In well resolved systems, the combination of coupling and NOE measurements allows us to identify *exo*- and *endo*-6-H as well. The geminal hydrogens at C-8 always appear as a pair of doublets with coupling constants of 12–14 Hz, as in almost all derivatives of camphorsulphonic acid; the rigidity of the heterocyclic ring fixes the hydrogens in upward (*exo*) and downward (*endo*) positions, and the *exo*-8-H can be assigned due to its stronger NOE effect with the methyl groups. These groups can also be distinguished by their NOE effects with 5-H and 6-H; the methyl group *anti* to the substituted C_2-bridge (10-H_3) has a medium NOE effect with 5-H and 6-H, while there is almost none with the *syn* methyl group (9-H_3).

In the cyclic acetals and thioacetals, no NOE effects are found between the camphor system and the heterocyclic ring, which means that there exists a general tendency in these spiro compounds to minimize steric strain by directing this ring away from the camphor moiety. In the five-membered ring systems, the NOE effects between all hydrogens of the heterocycle are of similar strength, which can be expected for such rigid systems. The six-membered rings allow for more flexibility, and several conformations of high relative stability are conceivable; there exist many examples for non-chair conformations (boat and twist forms) in heterocyclic rings.[16] In such rings not connected to other cycles, rapid equilibrations of the different conformations are observed, and only at quite low temperatures is this process slowed down sufficiently for direct observation by NMR techniques in the case of dioxanes and dithianes;

Table 2. ^{1}H NMR spectra (360 MHz) of (camphorsulphonyl)imines; δ-values (multiplicity, *J*-values in parentheses).

Compound	Solvent	Atom(s) 3	4	5	6	8	9, 10	11, 12	13
(8)	$CDCl_3$	4.68 (s)	2.50 (d, 4.6 Hz)	1.53 (1 H, m), 1.71 (1 H, m), 1.98 (2 H, m)		3.10, 3.25 (both d, 13.5 Hz)	1.10, 1.37		
(9)	$CDCl_3$	4.90 (d, 4.2 Hz)	2.38 (tr, 4.2 Hz)	1.70 (1 H, m), 2.00 (2 H, m), 2.20 (1 H, m)		3.00, 3.25 (both d, 13.3 Hz)	0.88, 1.57		
(10)	$CDCl_3$		2.90 (d, 4.2 Hz)	1.90, 2.02, 2.17, 2.43 (all 1 H, m)		3.21, 3.39 (both d, 13.6 Hz)	1.24, 1.28		
(11)	$CDCl_3$		2.80 (d, 3.7 Hz)	1.84 (1 H, m), 2.13 (2 H, m), 2.38 (1 H, m)		3.23, 3.41 (both d, 13.6 Hz)	1.18, 1.23		
(12)	$CDCl_3$	2.32 (d, 19.3 Hz, *endo*), 2.71 (ddd, 4.0, 6.5, 19.3 Hz, *exo*)	2.19 (t, 4.0 Hz)	1.42 (1 H, m), 1.67 (1 H, m), 2.02 (2 H, m)		2.92, 3.14 (both d, 14.3 Hz)	0.90, 1.03		
(14)	$CDCl_3$		2.92 (dd, 1.0, 4.1 Hz)	1.85 (1 H, m), 2.08 (2 H, m), 2.40 (1 H, m)		3.20, 3.38 (both d, 13.6 Hz)	1.20, 1.26		
(15a)	$CDCl_3$		2.28 (d, 3.1 Hz)	1.72 (3 H, m,), 2.00 (1 H, m)		2.95, 3.10 (both d, 13.5 Hz)	0.92, 1.02	3.25, 3.40 (both s)	
(15b)	$CDCl_3$		2.30 (s)	1.80 (3 H, m), 2.00 (1 H, m)		3.00, 3.20 (both d, 13.3 Hz)	1.00, 1.10	3.50 (1 H, m), 3.72 (2 H, m), 3.85 (1 H, m)	1.18, 1.12 (both t, 7.4 Hz)
(17a)	$CDCl_3$		2.09 (m)	1.87 (3 H, m), 2.09 (1 H, m)		2.99 (*exo*), 3.10 (*endo*) (both d, 13.4 Hz)	0.98 (*syn*), 1.02 (*anti*)	4.05 (2 H, m), 4.13 (1 H, m), 4.30 (1 H, m)	
(17b)	$CDCl_3$		2.07 (d, 4.1 Hz)	1.70 (m), 2.07 (m)	1.80 (m, *endo*), 1.91 (m, *exo*)	2.96, 3.13 (both d, 13.2 Hz)	1.01 (*syn*), 1.08 (*anti*)	3.86 (dd, 5.1, 11.8 Hz, eq), 4.58 (dt, 9.4, 11.8 Hz, ax), 3.99 (dd, 5.1, 11.8 Hz, eq), 4.46 (dt, 9.4, 11.8 Hz, ax)	1.47 (m, 1.5, 12.0 Hz, eq), 2.05 (m, 12.0 Hz, ax)
(17b)	$(CD_3)_2CO$		2.18 (d, 4.1 Hz)	1.61 (1 H, m), 1.69 (1 H, m), 1.82 (1 H, m), 2.07 (3 H, m)[a]		3.10, 3.29 (both d, 13.7 Hz)	0.95, 1.12	3.91 (m), 3.99 (m), 4.39 (dt), 4.50 (dt) (both 2.9, 11.8 Hz)	*a*

Table 2—*continued*

Compound	Solvent	Atom(s) 3	4	5	6	8	9, 10	11, 12	13
(19)	$CDCl_3$		2.21 (d, 3.9 ((Hz)	1.75 (m, *endo*) 1.98 (m, *exo*)	1.83 (m), 2.17 (m)	2.94, 3.10 (both d, 13.3 Hz)	1.04 (*syn*), 1.08 (*anti*)	3.42, 3.49 (both dd, 2.3, 11.3 Hz), 4.18, 4.31 (both d, 11.3 Hz)	0.81 (s), 1.18 (s)
(20a)	$CDCl_3$		2.42 (d, 4.0 Hz)	1.93 (2 H, m), 2.00 (1 H, m), 2.09 (1 H, m, 5-*endo*)		3.04 (*exo*), 3.19 (*endo*) (both d, 13.4 Hz)	1.05, 1.06	3.32, 3.41, 3.48, 3.61 (all 1 H, m)	
(20b)	$CDCl_3$		2.28 (d, 3.5 Hz)	1.96 (m), 2.28 (m)	2.05 (2 H, m)	3.03 (*exo*), 3.18 (*endo*) (both d, 13.4 Hz)	1.26 (*syn*), 1.14 (*anti*)	2.62 (m, 14.3 Hz), 2.78 (m, 14.4 Hz), 3.70 (ddd, 2.5, 12.9, 14.4 Hz), 3.81 (ddd, 2.6, 12.9, 14.3 Hz)	1.90 (m), 2.19 (m)
(20b)	$(CD_3)_2CO$		2.29 (d, 3.9 Hz)	1.89 (1 H, m), 2.20 (3 H, m)		3.19, 3.36 (both d, 13.8 Hz)	1.20, 1.25	2.71, 2.87 (both m, 14.3 Hz), 3.60, 3.69 (both ddd, 2.7, 12.6, 14.3 Hz)	1.79 (m), 2.17 (m)
(21a)	$CDCl_3$		3.00 (d, 6.0 Hz)	2.08 (m, *endo*), 2.31 (m, *exo*)	2.05 (2 H, m)	2.99 (*exo*), 3.22 (*endo*) (both d, 13.7 Hz)	1.00, 1.08	3.63, 3.71, 3.82, 3.90 (all 1 H, m)	
(21a)	$(CD_3)_2SO$		2.95 (s)	1.76 (1 H, m), 2.21 (3 H, m)		3.45, 3.78 (both d, 14.0 Hz)	1.00, 1.12	3.81 (2 H, m), 4.54 (1 H, m), 4.77 (1 H, m)	
(21b)	$CDCl_3$		3.31 (d, 4.6 Hz)	2.22 (m, *endo*), 2.49 (m, *exo*)	2.06 (m, *endo*), 2.38 (m, *exo*)	3.13 (*exo*), 3.22 (*endo*), (both d, 13.4 Hz)	1.09 (*syn*), 1.21 (*anti*)	3.38 (ddd, 2.8, 8.5, 16.1 Hz), 4.29 (ddd, 8.5, 10.2, 16.1 Hz), 3.50 (ddd, 2.8, 6.6, 15.0 Hz), 4.03 (ddd, 6.6, 10.2, 15.0 Hz)	2.49 (2 H, m)
(21b)	$(CD_3)_2SO$		3.18 (d, 3.1 Hz)	1.87 (1 H, m), 2.23 (1 H, m), 2.15 (1 H, m), 2.17 (1 H, m, 5-*endo*)		3.46, 3.74 (both d, 14.1 Hz)	0.95, 1.13	3.91 (4 H, m)	2.33 (2 H, m)
(22a)	$CDCl_3$		3.08 (d, 4.7 Hz)	1.64 (1 H, m), 1.84 (2 H, m), 2.14 (1 H, m)		3.04, 3.24 (both d, 13.3 Hz)	0.90, 1.08		
(22b)	$CDCl_3$		3.05 (d, 3.6 Hz)	1.58 (1 H, m), 1.72 (1 H, m), 2.02 (2 H, m)		3.00, 3.24 (both d, 13.4 Hz)	0.82, 1.00		

[a] Signals of atoms 5-, 6-, and 13-H_2 not separated.

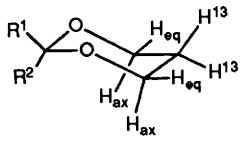
Table 3. ^{1}H NMR spectra (360 MHz) of (camphorsulphonyl)oxaziridines; δ-values (multiplicity, *J*-values in parentheses).

Compound	Solvent	Atom(s) 3	4	5	6	8	9, 10	11, 12	13
(7)	$CDCl_3$	4.02 (s)	2.28 (d, 4.1 Hz)	1.58 (1 H, m), 1.89 (2 H,), 2.05 (1 H, m)		3.18, 3.41 (both d, 13.5 Hz)	0.98, 1.41		
(13)	$CDCl_3$	4.95 (dd, 1.6, 4.2 Hz)	2.32 (t, 4.2 Hz)	1.95 (3 H, m), 2.20 (1 H, m)		3.15, 3.37 (both d, 14.1 Hz)	1.16, 1.23		
(18a)	$CDCl_3$		2.07 (d, 4.6 Hz)	1.92 (m, 5-*exo*), 2.17 (m, 5-*endo*)	1.86 (m), 1.92 (m)	3.09 (*endo*), 3.32 (*exo*) (both d, 13.9 Hz)	1.05 (*anti*), 1.35 (*syn*)	3.89 (2 H, m), 4.00 (2 H, m)	
(18b)	$CDCl_3$		2.29 (d, 4.9 Hz)	1.75 (m, 5-*endo*), 1.90 (m, 5-*exo*)	1.90 (m, 6-*endo*), 2.06 (m, *exo*)	3.05 (*endo*), 3.27 (*exo*) (both d, 13.9 Hz)	1.03 (*anti*), 1.29 (*syn*)	3.87 (2 H, m), 4.15 (2 H, m)	1.61 (m), 1.79 (m)
(18b)	$(CD_3)_2CO$		2.43 (d, 4.3 Hz)	1.81 (5-*endo*), 1.77, 1.96, 2.09 (all 1 H, m)		3.19, 3.65 (both d, 14.4 Hz)	1.10, 1.25	3.84, 4.00 (both 1 H, m), 3.96, 4.06 (both 1 H, m)	1.68 (2 H, m)
(23a)	$CDCl_3$		2.95 (d, 4.3 Hz)	1.68 (1 H, m), 1.98 (1 H, m), 2.10 (2 H, m)		3.19, 3.38 (both d, 14.1 Hz)	1.05, 1.17		
(23b)	$CDCl_3$		2.93 (d, 3.9 Hz)	1.62 (1 H, m), 2.00 (3 H, m)		3.15, 3.35 (both d, 14.1 Hz)	1.00, 1.12		
(24b)	$CDCl_3$		2.26 (d, 4.5 Hz)	1.75 (m, 5-*endo*), 1.91 (2 H, m) 1.98 (m, 5-*exo*)		3.06 (*endo*), 3.25 (*exo*) (both d, 13.9 Hz)	1.04 (*anti*), 1.30 (*syn*)	3.89 (2 H, m), 4.17 (2 H, m)	1.60 (1 H, m), 1.91 (1 H, m)
(24b)	$(CD_3)_2CO$		2.44 (d, 4.3 Hz)	1.79 (m, 5-*endo*), 1.94 (m, 5-*exo*)	1.79, 2.04 (both 1 H, m)	3.19 (*endo*), 3.65 (*exo*) (both d, 14.4 Hz)	1.10, 1.26	3.87, 4.04 (both m), 3.97, 4.07 (both m)	1.68 (2 H, m)

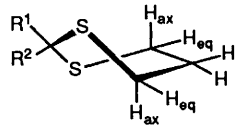
substitution of the rings with alkyl groups enhances the barrier towards equilibration.[17] This means that, in the case of our spiro compounds, which may be considered as strongly substituted heterocycles, such ring flipping should have quite a high activation energy, and we can expect to observe only the most stable conformations by the NOE measurements, and not an equilibrium mixture. The general absence of NOE effects between the camphor moiety and the heterocyclic rings excludes boat conformations, which would imply very low distances between the central CH_2 group of the ring and parts of the camphor system, *i.e.* the bridgehead hydrogen in one and the CH_2SO_2N group in the other boat conformation. The possibility of chair and some twist conformations remain. In the case of chloroform solutions of the oxaziridines (**18b**) and (**24b**), the CH_2 groups linked to the heteroatoms give rise to only two signals of the axial and equatorial protons (chair conformation assumed), and therefore no detailed analysis of the conformation is possible. An acetone solution of compound (**24b**), however, and chloroform solutions of the other spiro compounds, show more strongly split signals of these groups and allow for such analysis.

The imine (**17b**) shows the expected couplings (COSY) (over three bonds) of all hydrogens in the dioxane ring, and an additional long-range coupling between two hydrogens of the CH_2 groups linked to the oxygens (two dd at δ_H 3.86 and 3.99). This is best explained as a W-coupling between equatorial protons and implies that the dioxane ring must have a chair conformation. No NOE effect is observed between these atoms, but quite strong effects are found between all the other hydrogens linked over four bonds where no coupling is observed. This further confirms the chair conformation. The dithiane analogue (**20b**) shows formally a similar ^{1}H-pattern for the signals of the heterocyclic ring, but, contrary to the dioxane system, a coupling *and* a strong NOE effect between the signals at δ_H 2.62 and 2.78, combined with the absence of both coupling and NOE effects between the hydrogens at δ_H 3.70 and 3.81; the signals at δ_H 2.62 and 3.81 are caused by one CH_2 group, and those at δ_H 2.78 and 3.70 by the other. This cannot imply a chair conformation, but points to a twisted structure where it is possible to combine a distorted W-arrangement of two hydrogens with spatial proximity; the larger covalent radius of sulphur, compared with oxygen, assists the distortion from the chair conformation. The oxidation of the sulphur atoms in compound (**20b**) to form the disulphone-imine (**21b**) introduces different steric requirements at the sulphur centres, and the conformation of the oxidized dithiane ring switches back to the chair form, as indicated by the absence of coupling but strong NOE effects between the axial hydrogens of the CH_2 groups linked to oxygen (two ddd at δ_H 4.03 and 4.29). However, the ring does not form a perfect chair, as both equatorial hydrogens show W-coupling *and* an NOE effect (two ddd at δ_H 3.38 and 3.50). As for the dioxane ring, a perfect chair conformation would not allow for NOE effects between these equatorial hydrogens.

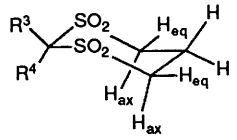
Surprisingly, the oxidation of the imine (**21b**) to the oxaziridine (**24b**) is combined with a rather strong change in the ^{1}H NMR pattern of the dithiane ring protons. Contrary to the case of the imines, the equatorial hydrogens of the CH_2 groups linked to oxygen appear at higher field (δ_H 4.04 and 4.07 *vs.* δ_H 3.87 and 3.97 for the axial hydrogens). On the other hand, the chair conformation seems to be maintained, as no coupling but strong NOE effects between the axial hydrogens are observed. If there is some distortion from the perfect chair conformation as in the imine, it cannot be deduced from the data available, as the difference in the chemical shifts of the equatorial hydrogens is too small to determine if an NOE effect is present; however, no W-coupling between these atoms could be detected.



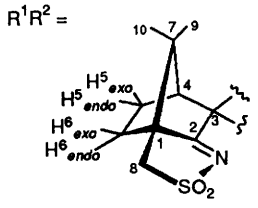
(17b)

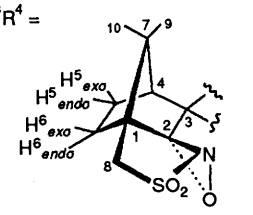


(20b)



(24b)





As for the conclusions from structural and conformational data with respect to the ability to facilitate enantioselective oxidations, *e.g.* of sulphides to chiral sulphoxides, it can be expected that the *exo*-bromo spiro-oxaziridine (**7**) will not be very different from the simple oxaziridine (**1**), in that the *endo* side, where the approach of the substrate to be oxidized occurs, is not much influenced by the *exo*-substituent. The same holds for the dihalogenomethylene oxaziridines (**23a**) and (**23b**), since the double bond fixes the substituents in an intermediate plane between the *exo* and *endo* parts of the molecule. On the other hand, the influence of the *endo*-bromine in compound (**13**) can be expected to be considerable, as its large covalent radius will allow the approach of a substrate only in a quite definite position, avoiding steric repulsion between the bromine and the larger parts of the substrate. The influence of the heterocyclic rings in the oxaziridines (**18a**), (**18b**), and (**24b**) should lead to similar effects, although the shielding of one side of the oxaziridine oxygen will probably be a bit less efficient than in the case of bromo compound (**13**), especially for the almost planar five-membered ring of compound (**18a**). We will report on such oxidations in due course.

Experimental

NMR spectra were recorded with a Bruker AM 360 instrument, with Me_4Si as internal standard. Nuclear Overhauser enhancements in the rotating frame were measured with the two-dimensional technique (ROESY) described in the literature[13] (spinlock time 0.3 s). Optical rotations were measured on a Roussel Jouan Digital 71 polarimeter, and IR spectra (KBr) on a Perkin-Elmer 177 spectrophotometer. Mass spectra have been obtained with a Varian CH5 instrument (70 eV). Commercially available chemicals were used without further purification. The preparation of (−)-(camphorsulphonyl)imine (**12**) [(3a*S*)-8,8-dimethyl-4,5,6,7-tetrahydro-3*H*-3a,6-methano-2,1-benzisothiazole 2,2-dioxide] and (−)-3-oxo(camphorsulphonyl)imine (**16**) [(3a*S*)-8,8-dimethyl-5,6-dihydro-3*H*-3a,6-methano-2,1-benzisothiazol-7(4*H*)-one 2,2-dioxide],[3,18] and the bromination of compound (**12**), leading to *exo*- and *endo*-

3-bromo-(camphorsulphonyl)imines (**8**) [(3a*S*,7*R*)-7-bromo-8,8-dimethyl-4,5,6,7-tetrahydro-3*H*-3a,6-methano-2,1-benziso-thiazole 2,2-dioxide] and (**9**) [(3a*S*,7*S*)-7-bromo-8,8-dimethyl-4,5,6,7-tetrahydro-3*H*-3a,6-methano-2,1-benzisothiazole 2,2-dioxide], and 3,3-dibromo(camphorsulphonyl)imine (**10**) [(3a*S*)-7,7-dibromo-8,8-dimethyl-4,5,6,7-tetrahydro-3*H*-3a,6-methano-2,1-benzisothiazole 2,2-dioxide], as well as the chlorination of compound (**12**) to form (3a*S*)-7,7-dichloro-8,8-dimethyl-3*H*-3a,6-methano-2,1-benzisothiazole 2,2-dioxide (**11**) and that of compound (**9**) to form (3a*S*,7*S*)-7-bromo-7-chloro-8,8-dimethyl-4,5,6,7-tetrahydro-3*H*-3a,6-methano-2,1-benzisothiazole 2,2-dioxide (**14**), has already been described.[8]

(3aS)-7,7-*Dimethoxy*-8,8-*dimethyl*-4,5,6,7-*tetrahydro*-3H-3a,6-*methano*-2,1-*benzisothiazole* 2,2-*Dioxide* (**15a**) *and* (3aS)-7,7-*Diethoxy*-8,8-*dimethyl*-4,5,6,7-*tetrahydro*-3H-3a,6-*methano*-2,1-*benzisothiazole* 2,2-*Dioxide* (**15b**).—To a solution of compound (**16**) (2.0 g, 8.7 mmol) in dichloromethane (50 ml) at −5 °C were added the trialkyl orthoformate (methyl or ethyl, respectively) (60 mmol) and Amberlyst 15 (2.0 g). The mixture was stirred for 12 h at the same temperature, then filtered, and the solvent was evaporated off. The residue was treated with diethyl ether, and the solid product was filtered off, and dried *in vacuo* (0.1 mmHg; 3 h) to give *compound* (**15a**) (70%), m.p. 176 °C; $[\alpha]_D^{23}$ +4.0° (*c* 1, acetone) (Found: C, 52.7; H, 7.0; N, 5.1. $C_{12}H_{19}NO_4S$ requires C, 52.7; H, 7.2; N, 5.1%); ν_{max} 1 650 (C=N), 1 335, and 1 165 cm^{-1} (SO_2); *m/z* 274 ($M^+ + 1$, 2%), 242 ($M^+ + 1 - 32$, 10), and 129 (100); and *compound* (**15b**) (45%), m.p. 128 °C; $[\alpha]_D^{23}$ −4.0° (*c* 1, acetone) (Found: C, 55.4; H, 7.7; N, 4.7. $C_{14}H_{23}NO_4S$ requires C, 55.9; H, 7.6; N, 4.6%); ν_{max} 1 660 (C=N), 1 350, and 1 060 cm^{-1} (SO_2); *m/z* 301 (M^+, 5%), 256 ($M^+ - 65$, 15), and 157 (100).

(3aS)-8,8-*Dimethyl*-5,6-*dihydro*-3H,4H,7H-3a,6-*methano*-2,1-*benzisothiazole*-7-*spiro*-2′-1′,3′-*dioxolane* 2,2-*Dioxide* (**17a**), (3aS)-8,8-*Dimethyl*-5,6-*dihydro*-3H,4H,7H-3a,6-*methano*-2,1-*benzisothiazole*-7-*spiro*-2′-1′,3′-*dioxane* 2,2-*Dioxide* (**17b**), *and* (3aS)-5′,5′,8,8-*Tetramethyl*-5,6-*dihydro*-3H,4H,7H-3a,6-*methano*-2,1-*benzisothiazole*-7-*spiro*-1′,3′-*dioxane* 2,2-*Dioxide* (**19**).—To a solution of compound (**16**) (2.0 g, 8.7 mmol) in toluene (100 ml) were added the corresponding glycol (43 mmol) and toluene-4-sulphonic acid (PTSA) (1.0 g). The mixture was heated to reflux with azeotropic removal of water for 7 days, and was then extracted successively with 1M-sodium hydroxide (100 ml) and water (100 ml), and dried with sodium sulphate. On concentration of the solution to 30 ml, the products crystallized out to afford *compound* (**17a**) (51%), m.p. 218 °C; $[\alpha]_D^{22}$ +11.5° (*c* 1, acetone) (Found: C, 52.6; H, 6.1; N, 5.0. $C_{12}H_{17}NO_4S$ requires C, 53.1; H, 6.1; N, 5.2%); ν_{max} 1 665 (C=N) and 1 340 cm^{-1} (SO_2); *m/z* 271 (M^+, 16%) and 127 (100); *compound* (**17b**) (52%), m.p. 205 °C; $[\alpha]_D^{22}$ +21.5° (*c* 1, acetone) (Found: C, 54.4; H, 6.1; N, 4.8. $C_{13}H_{19}NO_4S$ requires C, 54.7; H, 6.7; N, 4.9%); ν_{max} 1 655 (C=N) 1 350 cm^{-1} (SO_2); *m/z* 285 (M^+, 20%) and 141 (100); and *compound* (**19**) (46%), m.p. 174 °C; $[\alpha]_D^{22}$ +18.0° (*c* 1, $CHCl_3$) (Found: C, 57.0; H, 7.4; N, 4.4. $C_{15}H_{23}NO_4S$ requires C, 57.5; H, 7.3; N, 4.5%); ν_{max} 1 640 (C=N), 1 335, and 1 170 cm^{-1} (SO_2); *m/z* 313 (M^+, 16%), 249 ($M^+ - 64$, 32), and 169 (100).

(3aS)-8,8-*Dimethyl*-5,6-*dihydro*-3H,4H,7H-3a,6-*methano*-2,1-*benzisothiazole*-7-*spiro*-2′-1′,3′-*dithiolane* 2,2-*Dioxide* (**20a**) *and* (3aS)-8,8-*Dimethyl*-5,6-*dihydro*-3H,4H,7H-3a,6-*methano*-2,1-*benzisothiazole*-7-*spiro*-2′-1′,3′-*dithiane* 2,2-*Dioxide* (**20b**).—To a solution of the dithiol (32 mmol) in toluene (100 ml) was added a solution of (**16**) (7.2 g, 32 mmol) under nitrogen. A solution of BF_3-diethyl ether complex (4.5 g) in toluene (50 ml) was added dropwise, and the mixture was heated to reflux for 90 min. Methanol (200 ml) was added at room temperature, and after storage for 16 h, the precipitate was filtered off, washed successively with 1M-sodium hydroxide (100 ml) and water (100 ml), and dried *in vacuo* for 5 h. It was then dissolved in the minimum amount of chloroform and precipitated with methanol (100–150 ml) to give *compound* (**20a**) (90%), m.p. 200 °C; $[\alpha]_D^{22}$ +13.5° (*c* 1, acetone) (Found: C, 46.9; H, 5.6; N, 4.5. $C_{12}H_{17}NO_2S_3$ requires C, 47.4; H, 5.5; N, 4.5%); ν_{max} 1 660 (C=N), 1 345, and 1 120 cm^{-1} (SO_2); *m/z* 303 (M^+, 100%); and *compound* (**20b**) (60%), m.p. 207 °C; $[\alpha]_D^{22}$ −2.6° (*c* 1, acetone) (Found: C, 48.8; H, 5.7; N, 4.3. $C_{13}H_{19}NO_2S_3$ requires C, 49.2; H, 5.4; N, 4.4%); ν_{max} 1 640 (C=N), 1 345, and 1 140 cm^{-1} (SO_2); *m/z* 317 (M^+, 100%).

(3aS)-8,8-*Dimethyl*-5,6-*dihydro*-3H,4H,7H-3a,6-*methano*-2,1-*benzisothiazole*-7-*spiro*-2′-1′,3′-*dithiolane* 1′,1′,2,2-3′,3′-*Hexaoxide* (**21a**) *and* (3aS) 8,8-*Dimethyl*-5,6-*dihydro*-3H,4H,7H-3a,6-*methano*-2,1-*benzisothiazole*-7-*spiro*-2′-1′,3′-*dithiane* 1′,1′,2,2,3′,3′-*Hexaoxide* (**21b**).—To a solution of the spiro compound (**20a**) or (**20b**) (10 mmol) in acetic acid (100 ml) was added 30% hydrogen peroxide (60 ml, 300 mmol), and the mixture was kept at reflux for 6 h. After cooling to room temperature, the precipitate was filtered off, washed successively with water and diethyl ether, and dried *in vacuo* for 3 h to give *compound* (**21a**) (94%), m.p. 293 °C; $[\alpha]_D^{23}$ −27° (*c* 1, Me_2SO) (Found: C, 39.2; H, 4.7; N, 3.8. $C_{12}H_{17}NO_6S_3$ requires C, 39.2; H, 4.5; N, 3.8%); ν_{max} 1 650 (C=N), 1 350, and 1 130 cm^{-1} (SO_2); *m/z* 303 ($M^+ - 64$, 35%), 288 ($M^+ - 79$, 25), and 132 (100); and *compound* (**21b**) (90%), m.p. 293 °C; $[\alpha]_D^{22}$ +8.0° (*c* 1, Me_2SO) (Found: C, 40.9; H, 4.9; N, 3.8. $C_{13}H_{19}NO_6S_3$ requires C, 41.0; H, 4.9; N, 3.7%); ν_{max} 1 640 (C=N), 1 330, 1 345, and 1 130 cm^{-1} (SO_2); *m/z* 381 (M^+, 10%), 317 ($M^+ - 64$, 21), and 108 (100).

(3aS)-7-*Dichloromethylene*-8,8-*dimethyl*-4,5,6,7-*tetrahydro*-3H-3a,6-*methano*-2,1-*benzisothiazole* 2,2-*Dioxide* (**22a**) *and* (3aS)-7-*Dibromomethylene*-8,8-*dimethyl*-4,5,6,7-*tetrahydro*-3H-3a,6-*methano*-2,1-*benzisothiazole* 2,2-*Dioxide* (**22b**).—To a solution of imine (**16**) (4.4 g, 20 mmmol) and triphenylphosphine (10.5 g, 40 mmol) in dichloromethane (100 ml) was added dropwise a solution of CBr_4 (10.0 g, 30 mmol) or CCl_4 (4.6 g, 30 mmol) in dichloromethane (50 ml). The mixture was stirred for 16 h, concentrated to *ca.* 80 ml, and the product was purified by column chromatography (silica gel; dichloromethane–diethyl ether, 3:2). The products were eluted as the second band. *Compound* (**22a**) (45%), m.p. 186 °C; $[\alpha]_D^{23}$ +82.5° (*c* 1, acetone) (Found: C, 45.0; H, 4.5; N, 4.8. $C_{11}H_{13}Cl_2NO_2S$ requires C, 45.0; H, 4.4; N, 4.8%); ν_{max} 1 630 (C=N), 1 605 (C=C), 1 330 and 1 120 cm^{-1} (SO_2); *m/z* (rel. ^{37}Cl) 297 (M^+, 4%), 233 ($M^+ - 64$, 10), and 196 ($M^+ - 101$, 100). *Compound* (**22b**) (44%), m.p. 178 °C; $[\alpha]_D^{23}$ +94° (*c* 1, acetone) (Found: C, 34.2; H, 3.3; N, 3.6. $C_{11}H_{13}Br_2NO_2S$ requires C, 34.6; H, 3.4; N, 3.7%); ν_{max} 1 610 (C=N), 1 590 (C=C), 1 330 cm^{-1} (SO_2); *m/z* (rel. ^{81}Br) 385 (M^+, 5%), 317 ($M^+ - 64$, 16), and 69 (100).

(4aS,8R,8aR)-8-*Bromo*-9,9-*dimethyl*-5,6,7,8-*tetrahydro*-4H-4a,7-*methano*-*oxazirino*[3,2-i][2,1]*benzisothiazole* 3,3-*Dioxide* (**7**) *and* (4aS,8S,8aR)-8-*Bromo*-9,9-*dimethyl*-5,6,7,8-*tetrahydro*-4H-4a,7-*methano*-*oxazirino*[3,2-i][2,1]*benzisothiazole* 3,3-*Dioxide* (**13**).—*Compound* (**7**). To an efficiently stirred, 2-phase mixture (3:7) of the bromoimines (**8**) and (**9**) (2.9 g, 10 mmol) in dichloromethane (100 ml) and sodium carbonate (1.5 g, 15 mmol) in water (50 ml) was added dropwise a solution of 50% MCPBA (4.6 g, 15 mmol) in dichloromethane (100 ml). The mixture was stirred for 2 days, after which time the organic phase was extracted with brine (3 × 150 ml) and dried over sodium sulphate. After concentration to 20 ml and addition of diethyl

ether (100 ml), a mixture of imine (**9**) and the oxaziridine (**7**) (7:3) precipitated out (2.5 g), and could be used directly for oxidations.

Compound (**13**). To an efficiently stirred, 2-phase mixture (3:7) of the bromoimines (**8**) and (**9**) (2.9 g, 10 mmol) in dichloromethane (50 ml) and sodium carbonate (4.9 g, 50 mmol) in water (50 ml) was added dropwise a solution of 50% MCPBA (15.5 g, 50 mmol) in dichloromethane (80 ml). The mixture was stirred for 5 days, and the organic phase was then extracted successively with saturated aq. sodium hydrogen carbonate (3 × 150 ml) and brine (6 × 150 ml), rapidly with 10% aq. sodium sulphite (3 × 100 ml), and finally with brine (2 × 100 ml). After being dried over sodium sulphate, the mixture was concentrated to 20 ml and the product was precipitated by the addition of diethyl ether (80 ml) to afford *compound* (**13**) (0.88 g, 30%), m.p. 154 °C; $[\alpha]_D^{22}$ +130° (*c* 1 acetone) (Found: C, 38.8; H, 4.7; N, 4.5. $C_{10}H_{14}BrNO_3S$ requires C, 39.0; H, 4.5; N, 4.5%); ν_{max} 1 370 and 1 170 cm^{-1} (SO_2); *m/z* (rel. ^{81}Br) 309 (M^+, 9%), 228 (M^+ − 81, 16), and 148 (100).

(4aS,8aR)-9,9-*Dimethyl*-6,7-*dihydro*-4H,5H,8H-4a,7-*methano-oxazirino*[3,2-i][2,1]*benzisothiazole*-8-*spiro*-2′-1′,3′-*dioxolane* 3,3-*Dioxide* (**18a**) *and* (4aS,8aR)-9,9-*Dimethyl*-6,7-*dihydro*-4H,5H,8H-4a,7-*methano-oxazirino*[3,2-i][2,1]*benzisothiazole*-8-*spiro*-2′-1′,3′-*dioxane* 3,3-*Dioxide* (**18b**).—To a stirred, 2-phase mixture of an imine (**17a**) or (**17b**) (20 mmol) in dichloromethane (50 ml) and sodium carbonate [(5.7 g, 30 mmol) for (**17a**), (11.4 g, 60 mmol) for (**17b**)] in water (100 ml) was added dropwise a solution of 50% MCPBA [(9.3 g, 30 mmol) for (**17a**), (18.6 g, 60 mmol) for (**17b**)] in dichloromethane (100 ml). The mixture was stirred for 2 days after which time the organic layer was separated and washed with brine (3 × 100 ml). After being dried over sodium sulphate, the solution was concentrated to 30 ml, and the product was precipitated with diethyl ether (80 ml). *Compound* (**18a**) (75%), m.p. 180 °C (decomp.); $[\alpha]_D^{22}$ +75.5° (*c* 1, acetone) (Found: C, 50.2; H, 6.1; N, 4.8. $C_{12}H_{17}NO_5S$ requires C, 50.1; H, 5.9; N, 4.9%); ν_{max} 1 370 and 1 175 cm^{-1} (SO_2); *m/z* 287 (M^+, 35%) and 181 (100). Compound (**18b**) (80%), m.p. 186 °C (decomp.); $[\alpha]_D^{22}$ +65.0° (*c* 1, acetone) (Found: C, 43.6; H, 6.2; N, 4.8. $C_{13}H_{19}NO_5S$ requires C, 43.8; H, 6.3; N, 4.6%); ν_{max} 1 375 and 1 170 cm^{-1} (SO_2); *m/z* 301 (M^+, 28%) and 139 (100).

(4aS,8aR)-8-*Dichloromethylene*-9,9-*dimethyl*-5,6,7,8-*tetrahydro*-4H-4a,7-*methano-oxazirino*[3,2-i][2,1]*benzisothiazole* 3,3-*Dioxide* (**23a**) *and* (4aS,8aR)-8-*Dibromomethylene*-9,9-*dimethyl*-5,6,7,8-*tetrahydro*-4H-4a,7-*methano-oxazirino*[3,2-i][2,1]*benzisothiazole* 3,3-*Dioxide* (**23b**).—To an efficiently stirred, 2-phase mixture of an imine (**22a**) or (**22b**) (3.0 mmol) in dichloromethane (50 ml) and sodium carbonate (2.9 g, 30 mmol) in water (100 ml) was added dropwise a solution of 50% MCPBA (9.3 g, 30 mmol) in dichloromethane (100 ml). The mixture was stirred for 7 days, after which time the organic phase was extracted with brine (3 × 200 ml) and dried with sodium sulphate. The solution was then concentrated to 30 ml, and the products were precipitated with diethyl ether (100 ml) and purified by recrystallization from chloroform–diethyl ether (1:2). *Compound* (**23a**) (28%), m.p. 134 °C; $[\alpha]_D^{23}$ +103° (*c* 1, acetone) (Found: C, 42.6; H, 4.0; N, 4.2. $C_{11}H_{13}Cl_2NO_3S$ requires C, 42.7; H, 4.2; N, 4.5%); ν_{max} 1 605 (C=C), 1 360, and 1 230 cm^{-1} (SO_2); *m/z* (rel. ^{37}Cl) 313 (M^+, 4%), 249 (M^+ − 64, 13), and 158 (100). *Compound* (**23b**) (32%), m.p. 153 °C; $[\alpha]_D^{23}$ +112° (*c* 0.5, acetone) (Found: C, 32.9; H, 3.3; N, 3.7. $C_{11}H_{13}Br_2NO_3S$ requires C, 33.2; H, 3.3; N, 3.5%); ν_{max} 1 590 (C=C) and 1 360 cm^{-1} (SO_2); *m/z* (rel. ^{81}Br) 401 (M^+, 3%), 321 (M^+ − 80, 6), and 67 (100).

(4aS,8aR)-9,9-*Dimethyl*-6,7-*dihydro*-4H,5H,8H-4a,7-*methano-oxazirino*[3,2-i][2,1]*benzisothiazole*-8-*spiro*-2′-1′,3′-*dithiolane* 1′,1′,3,3,3′,3′-*Hexaoxide* (**24a**) *and* (4aS,8aR)-9,9-*Dimethyl*-6,7-*dihydro*-4H,5H,8H-4a,7-*methano-oxazirino*[3,2-i][2,1]*benzisothiazole*-8-*spiro*-2′-1′,3′-*dithiane* 1′,1′,3,3,3′,3′-*Hexaoxide* (**24b**).—To an efficiently stirred, 2-phase mixture of an imine (**20a**) or (**20b**) (10 mmol) in dichloromethane (20 ml) and sodium carbonate (56.0 g, 300 mmol) in water (200 ml) was added a solution of 50% MCPBA (93.0 g, 300 mmol) in dichloromethane (200 ml) dropwise. The mixture was stirred for 7 days, after which time the organic phase was extracted successively with brine (6 × 200 ml) and water (4 × 100 ml), and dried over sodium sulphate. After concentration to 30 ml, the products were precipitated with diethyl ether (100 ml) at −10 °C. Compound (**24a**) could not be obtained pure. *Compound* (**24b**) (10%), m.p. 245 °C; $[\alpha]_D^{23}$ +60° (*c* 0.3, acetone) (Found: C, 39.4; H, 5.0; N, 3.5. $C_{13}H_{19}NO_7S_3$ requires C, 39.3; H, 4.8; N, 3.5%); ν_{max} 1 370, 1 170, and 1 150 cm^{-1} (SO_2); *m/z* 301 (M^+ − 96, 5%) and 108 (100).

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