(+)-(3-Oxocamphorsulphonyl)oxaziridine as a Highly Stereoselective Reagent for the Oxidation of Sulphides to Chiral Sulphoxides

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The synthesis of the title oxaziridine and its application to the enantio- or diastereo-selective oxidation of sulphides to sulphoxides is described. Enantiomeric excesses up to 66% are observed, showing the reagent to be superior to most other oxidizing systems. The exceedingly mild reaction conditions (aprotic, neutral) allow the preparation of several chiral α-sulphinyl aldehydes. The properties of these compounds are discussed.

The continuing interest in the chemistry of natural products has led to the development of a variety of methods for introducing chirality in the target molecules. Among these methods, chirality transfer from sulphur to carbon by chiral sulphoxides is one of the most important, and extensive reviews on this subject are available.[1] Highly elegant syntheses of chiral natural products, *e.g.* α-cuparenone,[2] podorhizon,[3] hexadecano-1,5-lactone,[4] pentalenene,[5] methyl jasmonate,[6] santalene,[7] talaromycin,[8] and aphidicolin,[9] demonstrate recent applications of this principle.

The standard method for the preparation of enantiomerically pure (or at least enriched) sulphoxides involves the reaction of carbanions with sulphinates of chiral alcohols, *e.g.* menthol.[10] As these sulphinates have to be prepared in several steps from sulphinic acids or thiols, a more direct approach would be desirable. The asymmetric oxidation of unsymmetrical sulphides to chiral sulphoxides is an appealing alternative, provided that enantio- or diastereo-selective methods for this oxidation are available.

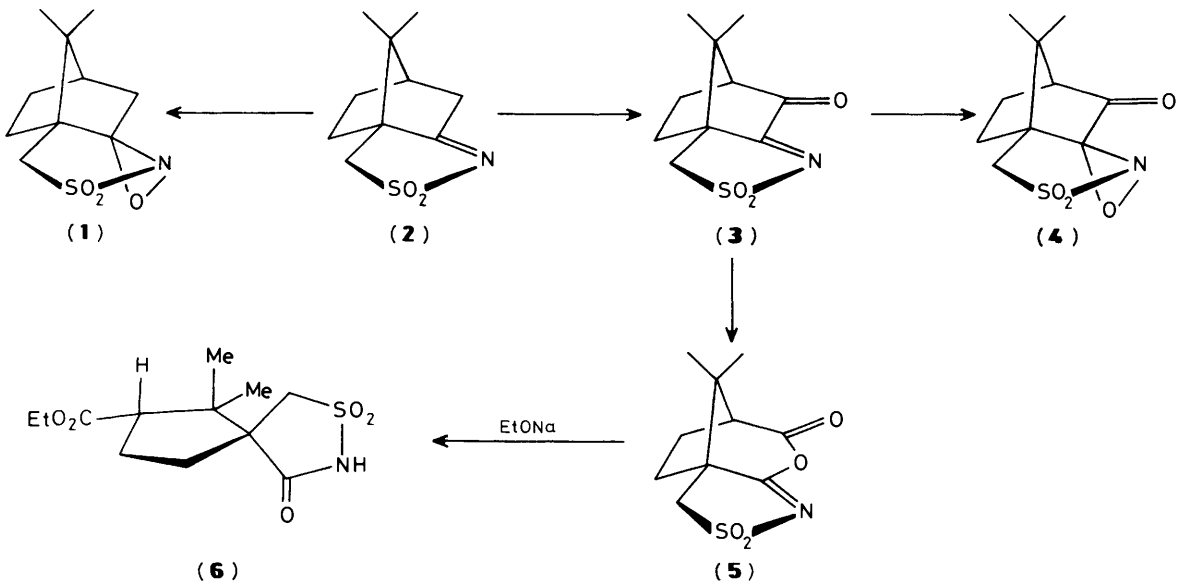
An excellent review on oxidation methods for the sulphide/sulphoxide conversion has been published.[11] The first approaches using chiral peracids[12] have been disappointing, leading only to low enantiomeric excesses (e.e.). More recent chiral oxidizing reagents include halogenated nitrogen compounds in combination with chiral alcohols,[13] adsorption of sulphides on chiral supports with sodium metaperiodate as oxidant,[14] and oxaziridines.[15,16] The most successful procedures employ transition metal catalysts (*e.g.* Kagan's modification[17] of the Sharpless reagent), albumin or enzymes,[18] or micro-organisms,[19] leading to e.e.s up to 98%.

However, reaction and/or work-up involve aqueous and sometimes alkaline conditions which may damage more sensitive sulphoxides containing other functional groups. On the other hand, the essentially mild conditions (inert solvent, room temperature or below) which can be used with chiral oxaziridines seem to be an attractive feature. For convenience, the oxidation reagent should be directly accessible in enantiomerically pure form from the natural chiral pool in only a few steps, and recycling of the chiral material should be possible.

Results and Discussion

The camphor-derived[20] oxaziridine (**1**) fulfils these conditions, but the observed enantioselectivities in the oxidation of sulphides to sulphoxides are not as high as might be expected from the rigid structure of (**1**). However, we suspected that a modification of the stereochemical and electronic environment of the oxaziridine moiety, *e.g.* the introduction of a carbonyl group, might improve the selectivity. We therefore prepared (4a*S*,8a*R*)-9,9-dimethyl-6,7-dihydro-4H-4a,7-methano-oxazirino[3,2-*i*][2,1]benzisothiazol-8(5*H*)-one 3,3-dioxide, more conveniently named as (+)-(3-oxocamphorsulphonyl)oxaziridine (**4**), as outlined in the Scheme.

The synthesis makes use of the selenium dioxide oxidation



Scheme.

Table 1. Oxidation of sulphides R^1SR^2 by the chiral oxaziridines (**1**) and (**4**)

Entry[a]	R^1	R^2	Solvent	Temp. (°C)	Time (h)	Yield (%)	$[\alpha]_D^{24}$[b] (°)	E.e (%)	Configuration of major sulphoxide product
1	Ph	Me	Toluene	20	20	45	+5	3.4[c]	*R*
2	Ph	Me	Toluene	20	1	78	−37	25	*S*
3	Ph	Me	Toluene	−78	48	65	−72	49	*S*
4	Ph	Me	CCl_4	20	1	80	−86	59	*S*
5	Ph	Me	CCl_4	0	48	85	−82	56	*S*
6	Ph	Me	CCl_4	−20	72	78	−88	60	*S*
7	Ph	Me	CH_2Cl_2	20	1	70	−31	21	*S*
8	Ph	Me	CH_2Cl_2	−78	24	72	−37	25	*S*
9	Ph	Me	Hexane	20	16	65	−46	31	*S*
10	Ph	Me	Dioxane	20	16	73	−56	38	*S*
11	Ph	Me	Et_2O	20	1	73	−77	53	*S*
12	Ph	Me	Pr^iOH	20	3	62	−53	36	*S*
13	Ph	Me	$MeCO_2Me$	20	15	65	−52	35	*S*
14	4-MeC_6H_4	Et	CCl_4	20	3	86	−117	61[d]	*S*
15	4-MeC_6H_4	Et	Toluene	20	2	80	−107	56	*S*
16	4-MeC_6H_4	Et	Toluene	−78	48	82	−119	62	*S*
17	4-MeC_6H_4	Me	CCl_4	20	20	79	−79	56[d]	*S*
18	4-MeC_6H_4	Me	CCl_4	0	72	86	−82	58	*S*
19	4-MeC_6H_4	Ph	CCl_4	20	24	88	−7.3	27[d]	*S*
20	4-MeC_6H_4	Ph	Toluene	−78	48	80	−1.7	6.3	*S*
21	$PhCH_2$	Et	CCl_4	20	20	79	+17	32[e]	*R*
22	$PhCH_2$	Et	Toluene	−78	24	75	+23	45	*R*
23	Bu	EtO_2CCH_2	CCl_4	20	20	71	−8.2	39[f]	?
24	Bu	EtO_2CCH_2	Toluene	−78	46	70	−2.8	13	?
25	Pr	Pr^i	CCl_4	20	20	73	−18	5[f,g]	?
26	Pr	Pr^i	Toluene	−78	70	70	−25	7	?
27	Mes[h]	Ph	CCl_4	20	48	65	−197	*h*	?
28	Me	Et	CCl_4	20	3	82	+11	14[i]	*S*
29	Pr	$HO[CH_2]_2$	CCl_4	20	21	70	+3.2	8.2[f]	?
30	Ph	c-C_6H_{11}	CCl_4	20	3	79	−97[j]	49[k]	?
31	Ph	$PhCH_2$	CCl_4	20	3	68	−91[l]	36[m]	*S*
32	Ph	CH_2=CH	CCl_4	20	4	75	−120[l]	39[n]	*S*
33	Ph	CH_2=$CHCH_2$	CCl_4	20	3	78	−107	61[m]	*S*

[a] Entry 1: Oxaziridine (**1**); other entries: oxaziridine (**4**). [b] Optical rotations measured in ethanol, *c* 1, unless otherwise stated. [c] U. Folli, D. Iarossi, F. Montanari, and G. Torre, *J. Chem. Soc. C*, 1968, 1317. [d] K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simmons, and A. L. Ternay, Jr., *J. Am. Chem. Soc.*, 1965, **87**, 1958; A. L. Cope and E. A. Caress, *ibid.*, 1966, **88**, 1711. [e] K. Mislow, M. M. Green, and M. Raban, *ibid.*, 1965, **87**, 2761. [f] E.e. determined with $Eu(tfc)_3$. [g] Baseline separation not complete; e.e. 5 ± 4%. [h] Mes = 2,4,6-trimethylphenyl; determination of e.e. was impossible with all shift reagents tested; $[\alpha]_D^{24}$ −203° (*c* 0.7 in acetone); the work by S. Colonna, S. Banfi, and R. Annunziata, *J. Org. Chem.*, 1986, **51**, 891 correlates $[\alpha]_D$ +35° (in acetone) with e.e. 40%, which is certainly erroneous. [i] E.e. determined with $Yb(tfc)_3$; e.e. 10% (M. Mikołajczik and M. Para, *Chem. Commun.*, 1969, 1192). [j] Solvent: acetonitrile. [k] T. Komori and T. Nonaka, *J. Am. Chem. Soc.*, 1984, **106**, 2656. [l] Solvent: acetone. [m] Ref. 19. [n] Ref. 17.

of imines[21] whose general applicability has been discovered only recently.[22] The electronically poor imine (**2**) requires comparatively drastic reaction conditions, but a high yield of the product ketone (**3**) is obtained. This compound can be converted into the oxaziridine (**4**) by standard peracid techniques.[16] *m*-Chloroperbenzoic acid (MCPBA) and peracetic acid gave highly reproducible yields, while potassium peroxomonosulphate proved to be less satisfactory. If the solution becomes too acidic during the reaction (pH <5), a by-product is formed, which we have identified as the Baeyer–Villiger oxidation product (**5**) by its spectral data and its ready ethanolysis to the spiro compound (**6**). Similar Baeyer–Villiger products have been observed in the case of other sulphonylimines, and have been considered as proof for a two-step mechanism for the formation of oxaziridines from imines by peracids.[23] If a solution of compound (**5**) in dimethyl sulphoxide is left for 5 days at room temperature, compound (**4**) can be detected as constituting *ca.* 30% of the mixture, showing that lactone (**5**) is a probable intermediate in the synthesis of the oxaziridine (**4**).

Table 1 illustrates solvent and temperature dependence of the oxidation of sulphides to sulphoxides by compounds (**1**) and (**4**).

The reaction is carried out by adding the sulphide and the oxaziridine (**4**) to the solvent under the conditions specified in Table 1. Vigorous stirring is necessary due to the low solubility of compound (**4**) in many solvents. The work-up consists simply of filtration to remove imine (**3**) and excess of (**4**), concentration of the filtrate, and purification of the sulphoxide by chromatography. The reduction product of compound (**4**), the imine (**3**), is isolated in 85—90% yield after recrystallization, and may be recycled to give (**4**), thus keeping the loss of the chiral auxiliary very low. The synthesis can therefore be considered to be among the most economic for chiral sulphoxides.

A comparison of the selectivity of oxaziridines (**1**) (Table 1, entry 1) and (**4**) (entry 2) shows not only the much higher ability of compound (**4**) to induce chirality at sulphur, but also the fact that the configuration of the sulphoxide formed is reversed. We explain this by the different stereochemical environment of the oxaziridine moiety [sp^3-carbon in (**1**), and sp^2-carbon in (**2**)] which leads to different approaches of the smaller and larger substituents of the sulphide to the oxygen atom of the oxaziridine ring, as shown in the Figure. Entries 2—13 show the solvent dependence of the oxidations of thioanisole at room temperature, indicating the general tendency to higher e.e.s in solvents of lower polarity, despite the limited solubility of

Table 2. ^{1}H N.m.r. data of sulphoxides R^1·SO·R^2 (360 MHz in $CDCl_3$)

R^1	R^2	δ_H
Pr	$[CH_2]_2OH$	1.10 (3 H, t, *J* 7.4 Hz, Me), 1.84 (2 H, m, CH_2Me), 2.69 (1 H, m), 2.87 (2 H, m), 2.95 (1 H, m), 4.10 (2 H, m, CH_2OH), and 4.21 (1 H, m, OH)
Bu	CH_2CO_2Et	0.96 (3 H, t, *J* 7.3 Hz, *Me*$[CH_2]_3$), 1.30 (3 H, t, *J* 7.1 Hz, *Me*CH_2O_2C), 1.49 (2 H, m), 1.78 (2 H, m), 2.85 (2 H, t, *J* 7.8 Hz, CH_2CH_2SO), 3.76 (2 H, s, $SOCH_2CO_2$), and 4.24 (2 H, q, *J* 7.1 Hz, CO_2CH_2)
4-MeC_6H_4	$Me_2C(CHO)$[a]	1.33 (3 H, s, MeC), 1.43 (3 H, s, MeC), 2.40 (3 H, s, 4-*Me*Ph), 7.38 (4 H, m, Ph), and 9.50 (1 H, s, CHO)
Me	Cyon[a,b]	1.76—2.18 (5 H, m), 2.48 (3 H, m), 2.57 and 2.67 (3 H, s[b]), and 3.45 (1 H, m)
4-MeC_6H_4	$Pr^iCH(CHO)$[a,c,d]	1.05 (3 H, d, *J* 6.5 Hz, Me), 1.36 (3 H, d, *J* 6.3 Hz, Me), 2.40 (3 H, s, *Me*Ph), 2.76 (2 H, m, CHCH), 7.34 (4 H, m, Ph), and 9.54 (1 H, d, *J* 4.4 Hz, CHO)
4-MeC_6H_4	$Pr^iCH(CHO)$[a,c,e]	1.17 (3 H, d, *J* 7.1 Hz, Me), 1.26 (3 H, d, *J* 7.1 Hz, Me), 2.38 (3 H, s, *Me*Ph), 2.48 (1 H, m, Me_2CH), 3.56 (1 H, dd, J_1 6.9, J_2 3.3 Hz, CHCHO), 7.34 (4 H, m, Ph), and 9.42 (1 H, d, *J* 3.3 Hz, CHO)

[a] New products. See Experimental section. [b] Cyon = 2-(1-oxocyclohexyl). [c] Mixture of diastereoisomers. [d] Main product. [e] Minor product.

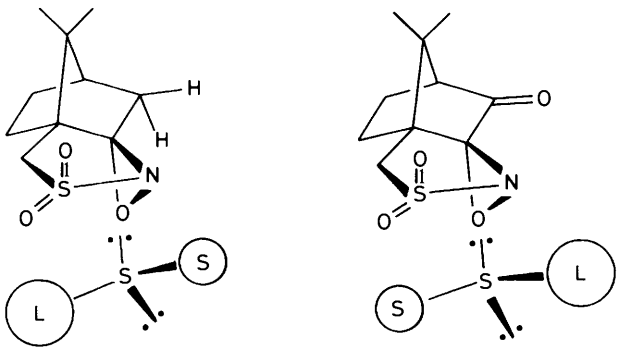
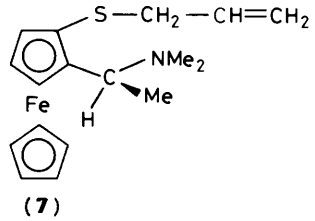


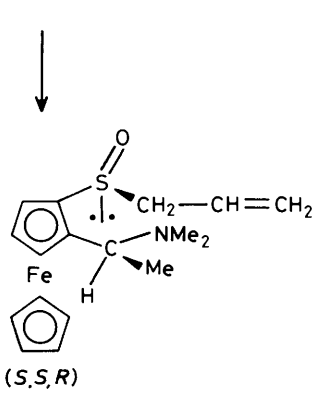
Figure.

compound (**4**) in these solvents. However, hexane gives only poor results, while tetrachloromethane seems to be the solvent of choice. The e.e.s are higher at lower temperatures, but the effect is not always very pronounced (compare entries 2—8, 15 and 16, and 17 and 18). In the cases where a correlation of the sign of the optical rotation with the configuration is known, the *S* enantiomer is formed in excess, in agreement with the steric arguments shown in the Figure, with the apparent exception of benzyl ethyl sulphoxide where the *R* enantiomer prevails. We do not have an explanation for this result. The oxaziridine (**4**) is capable of discriminating between very similar substituents of the sulphide, *e.g.* between methyl and ethyl (entry 28, e.e. 14%), and between phenyl and 4-methylphenyl (entry 19, e.e. 27%). This is difficult to achieve with any other chiral oxidizing reagent. A comparison with the titanium(IV)–diethyl tartrate catalyst [17] (see Experimental section) shows that the oxaziridine is only slightly inferior in its discriminating ability in the case of the simple 4-methylphenyl ethyl sulphide.

With sulphides containing more chiral elements, very high diastereoselectivities are observed as well, *e.g.* with the ferrocene derivative (**7**) where appreciably better results are obtained than with the previously applied oxidizing reagents [24] [equation (1)].



(1)



(**7**)

(*S,S,R*)

(**8**)

The great advantage of the reagent, however, is shown in cases of highly sensitive materials. This is particularly true for chiral α-sulphinyl aldehydes. Various attempts to prepare them by other methods, *e.g.* the sulphinylation of α-metallated hydrazones followed by hydrolysis, gave good results with ketones but failed with aldehydes.[25] A synthetic method for the preparation of the precursors of such α-sulphinyl aldehydes, the enantiomerically enriched α-sulphenyl aldehydes, *via* imines with chiral *N*-substituents, has already been developed.[26] Several compounds of this type have been oxidized with the oxaziridine (**4**) (see Experimental section), and the sulphoxides have been isolated in good yields. It is interesting to note that Kagan's reagent does not react with any of these α-sulphenyl compounds.

The spectral data of the new sulphoxides are collected in Table 2. The α-sulphinyl aldehydes containing an α-hydrogen exhibit a keto–enol tautomerism in ethanolic solution which does not influence the sulphoxide chirality, but the crystals which separate from a solution in dichloromethane–diethyl ether do not show further sulphoxide bands in the i.r. spectrum. After dissolving the crystals in ethanol the chirality is lost, but the i.r. and n.m.r. spectra of this material are identical with those of the starting α-sulphinyl aldehyde. An equilibrium of the following type might explain this observation:

$$R^1CH(CHO)SO\text{–}R^2 \underset{\text{solution}}{\rightleftharpoons} R^1C(SOR^2)\text{=}CHOH \rightleftharpoons \underset{\text{solid}}{R^1C(CHO)\text{=}S(R^2)OH}$$

The general stability of the α-sulphinyl aldehydes is not very high. After 1 day in chloroform solution at room temperature, even compounds not containing α-hydrogens decompose to products which we did not identify. Considering this instability, the oxidation of the α-sulphenyl aldehydes with the oxaziridine (**4**) is probably the only method available to prepare the α-sulphinyl aldehydes in enantiometrically enriched form. As both enantiomers of camphorsulphonic acid are commercially available, both enantiomers of the oxaziridine (**4**) may be prepared, and thus the two enantiomeric forms of the chiral α-sulphinyl aldehydes can be obtained, giving easy access to this new class of compounds with potential synthetic applications.

Experimental

N.m.r. spectra were recorded with a Bruker AM 360 instrument, with Me_4Si as internal standard. Optical rotations were measured on a Roussel Jouan Digital 71 polarimeter and i.r. spectra on a Perkin-Elmer 177 instrument. For chromatographic separations, preparative t.l.c. plates (silica gel, Merck) were used. Commercially available chemicals [(+)-camphorsulphonic acid, SeO_2, MCPBA] were used without further purification. Simple sulphides were prepared by standard methods. (−)-(Camphorsulphonyl)imine (**2**) [(3a*S*)-8,8-dimethyl-4,5,6,7-tetrahydro-3*H*-3a,6-methano-2,1-benzisothiazole 2,2-dioxide] was prepared as described;[27] yield 92%, m.p. 228 °C; $[\alpha]_D^{24}$ −33.5° (*c* 5.0 in $CHCl_3$). The synthesis and properties of the oxaziridine (**1**) were published recently.[16]

(3a*S*)-8,8-*Dimethyl*-5,6-*dihydro*-3H-3a,6-*methano*-2,1-*benzisothiazol*-7(4H)-*one* 2,2-*Dioxide* [(−)-3-(*Oxocamphorsulphonyl*)*imine*] (**3**).—A mixture of compound (**2**) (1.0 mol, 213.35 g) and SeO_2 (1.2 mol, 133.2 g) was refluxed in dry dioxane (1 l) for 14 days. The solution was filtered when still hot and the residue was washed with hot dioxane. The combined solutions were concentrated under reduced pressure and the residue was recrystallized from $CHCl_3$ to give the *title ketone* as a slightly yellow solid (168.3 g, 74%), m.p. 190—191 °C (Found: C, 52.9; H, 5.8; N, 6.1. $C_{10}H_{13}NO_3S$ requires C, 52.83; H, 5.76; N, 6.19%); $[\alpha]_D^{24}$ −178.5° (*c* 2.2 in acetone); $\nu_{max.}$(KBr) 1 750 (C=O), 1 640 (C=N), and 1 330 and 1 160 cm^{-1} (SO_2); δ_H (360 MHz; $CDCl_3$) 0.99 (3 H, s, Me), 1.17 (3 H, s, Me), 1.8—2.1 (2 H, m, CH_2), 2.2—2.4 (2 H, m, CH_2), 2.79 (1 H, d, *J* 4.8 Hz, CHCO), 3.24 (1 H, d, *J* 13.6 Hz, C*H*HSO_2), and 3.45 (1 H, d, *J* 13.6 Hz, CH*H*SO_2); δ_C(90.56 MHz; $CDCl_3$) 18.42 and 20.20 (Me), 22.68 and 28.05 (CH_2), 44.68 and 62.80 (C), 50.13 (CH), 59.11 (CH_2SO_2), 181.47 (C=N), and 197.72 (C=O).

(4a*S*,8a*R*)-9,9-*Dimethyl*-6,7-*dihydro*-4H-4a,7-*methano*-*oxazirino*[3,2-i][2,1]*benzisothiazol*-8(5H)-*one* 3,3-*Dioxide* [(+)-(3-*Oxocamphorsulphonyl*)*oxaziridine*] (**4**).—To a solution of compound (**3**) (22.7 g, 0.10 mol) in CH_2Cl_2 (100 ml) was added saturated aqueous $NaHCO_3$ (200 ml). To this stirred mixture at 0—5 °C was added dropwise a solution of MCPBA (85%) (20.2 g, 0.10 mol) or peracetic acid (70%) (10.8 g, 0.10 mol) in CH_2Cl_2 (100 ml) in such a way as to keep pH >7. The mixture was stirred for 20 h. The organic layer was extracted twice with brine and was then dried with $MgSO_4$. After concentration of the extract to *ca.* 50 ml, the *product* (**4**) was precipitated with Et_2O (19.5 g, 80%), m.p. 154 °C (decomp.) (Found: C, 49.4; H, 5.5; N, 5.7. $C_{10}H_{13}NO_4S$ requires C, 49.37; H, 5.38; N, 5.76%); $[\alpha]_D^{24}$ +71.3° (*c* 1.2 in CH_2Cl_2); $\nu_{max.}$(KBr) 1 775 (C=O) and 1 355 and 1 165 cm^{-1} (SO_2); δ_H(360 MHz; $CDCl_3$) 1.17 (3 H, s, Me), 1.24 (3 H, s, Me), 1.78—2.28 (4 H, m, CH_2CH_2), 2.70 (1 H, d, *J* 4.8 Hz, CHCO), 3.37 (1 H, d, *J* 14.4 Hz, C*H*HSO_2), and 3.60 (1 H, d, *J* 14.4 Hz, CH*H*SO_2); δ_C(90.56 MHz; $CDCl_3$) 17.74 and 21.31 (Me), 22.19 and 27.49 (CH_2), 44.00 and 59.67 (C), 48.92 (CH_2SO_2), 51.50 (CH), 89.68 (CNO), and 201.09 (C=O); *m/z* 243 (M^+) and 215 (M^+ − 28, 100%).

(3a*S*)-9,9-*Dimethyl*-5,6-*dihydro*-3H-3a,6-*methano*-*oxepino*-[2,3-c]*isothiazol*-7(4H)-*one* 2,2-*Dioxide* (**5**).—To a solution of compound (**3**) (2.27 g, 10 mmol) in CH_2Cl_2 (10 ml) at 0 °C were added MCPBA (85%) (2.02 g, 10 mmol) and $NaHCO_3$ (1.26 g, 15.0 mmol). After the mixture had been stirred for 3 h, it was extracted with saturated aqueous $NaHCO_3$ (40 ml). The organic layer was washed with brine, dried with $MgSO_4$, and concentrated. The *product* (**5**) was purified by recrystallization from $CHCl_3$ (1.58 g, 65%), m.p. 262—264 °C (Found: C, 49.6; H, 5.4; N, 6.0. $C_{10}H_{13}NO_4S$ requires C, 49.37; H, 5.39; N, 5.76%); $\nu_{max.}$(KBr) 1 825 (C=O), 1 620 (C=N), and 1 330 and 1 170 cm^{-1} (SO_2); $[\alpha]_D^{24}$ −94.5° (*c* 1.6 in Me_2SO); δ_H[360 MHz; $(CD_3)_2SO$] 0.98 (3 H, s, Me), 1.06 (3 H, s, Me), 1.7—2.4 (4 H, m, CH_2CH_2), 3.16 (1 H, d, *J* 6.4 Hz, CH), 3.89 (1 H, d, *J* 14.3 Hz, C*H*HSO_2), and 3.98 (1 H, d, *J* 14.3 Hz, CH*H*SO_2); δ_C[90.56 MHz; $(CD_3)_2SO$] 18.63 and 19.80 (Me), 23.5 and 31.81 (CH_2CH_2), 51.94 (CH), 53.05 and 61.36 (C), 59.02 (CH_2SO_2), 166.80 (C=N), and 178.69 (C=O).

(5S,7S)-*Ethyl*-6,6-*Dimethyl*-4-*oxo*-2-*thia*-3-*azaspiro*[4.4]-*nonane*-7-*carboxylate* 2,2-*Dioxide* (**6**).—A solution of compound (**5**) (0.24 g, 1.0 mmol) in 2M NaOH in ethanol (20 ml) was stirred for 20 h. The mixture was acidified with conc. aqueous HCl and filtered. The filtrate was concentrated to give the *ester* (**6**) as a solid (0.23 g, 80%), m.p. 93—95 °C (Found: C, 52.5; H, 6.95; N, 5.0. $C_{12}H_{19}NO_5S$ requires C, 52.72; H, 7.00; N, 5.15%); $[\alpha]_D^{24}$ +18° (*c* 0.9 in EtOH); $\nu_{max.}$ 3 700—3 000 (NH), 1 728br (C=O), and 1 315 and 1 150 cm^{-1} (SO_2); δ_H(360 MHz; $CDCl_3$) 1.11 (3 H, s, Me), 1.32 (3 H, s, Me), 1.28 (3 H, t, *J* 8.9 Hz, *Me*CH_2), 1.89 (2 H, m, CH_2C), 2.45 (1 H, m, CH), 2.59 (2 H, m, C*H*$_2$CH), 3.31 (1 H, d, *J* 13.6 Hz, C*H*HSO_2), 3.79 (1 H, d, *J* 13.6 Hz, CH*H*SO_2), 4.18 (2 H, m, C*H*$_2$Me), and 7.58 and 7.93 (1 H, m, NH); δ_C(90.56 MHz; $CDCl_3$) 14.27 and 57.18 (Et), 21.10 and 23.69 (Me), 24.97 and 35.02 (CH_2CH_2), 54.94 (CH), 48.56 and 60.74 (C), 61.50 (CH_2SO_2), and 171.44 and 172.12 (C=O).

Oxidation of the Sulphides R^1SR^2 *with the Oxaziridines* (**1**) *and* (**4**).—To a solution of the sulphide (5.0 mmol) in a solvent (25 ml) was added the oxaziridine (5.0 mmol) in 3 portions. The mixture was vigorously stirred under the conditions specified in Table 1. The mixture was evaporated to dryness at room temperature under reduced pressure, and the residue was extracted three times with diethyl ether (20 ml). The cloudy solution was filtered to remove the imine (**2**) or (**3**), respectively, and the filtrate was concentrated. The residue was purified by preparative t.l.c. (diethyl ether). The results are shown in Table 1, and spectral data of new sulphoxides are in Table 2.

(S,S,R)-1-*Allylsulphinyl*-2-(1-*dimethylaminoethyl*)*ferrocene* (**8**).—Following the general procedure (CCl_4; 20 °C; 20 h), the product was obtained from the corresponding (*S,R*)-sulphide[24] (**7**) after t.l.c. (CH_2Cl_2–MeOH 5:1), accompanied by traces of the (*R,S,R*)-sulphoxide, in 70% yield, $[\alpha]_D^{24}$ +203.4° (*c* 1 in EtOH) (lit.,[24] $[\alpha]_D^{20}$ −148°). This corresponds to a diastereoisomeric excess (d.e.) >90% (lit.,[24] d.e. 34% with $NaIO_4$–alumina).

2-*Methyl*-2-(4-*methylphenylsulphinyl*)*propanal*.—The corresponding sulphide[26] (0.97 g, 5.0 mmol) was dissolved in CCl_4 (10 ml) and the oxaziridine (**4**) (1.21 g, 5.0 mmol) was added at room temperature. After being stirred for 20 h, the mixture was filtered and the filtrate was concentrated. T.l.c. (Et_2O) afforded the *aldehyde* as an oil (0.80 g, 80%) (Found: C, 62.6; H, 6.8. $C_{11}H_{14}O_2S$ requires C, 62.83; H, 6.71%); $[\alpha]_D^{24}$ +66.5 (*c* 0.5 in EtOH); $\nu_{max.}$(film) 1 760 and 1 720 (C=O) and 1 050 cm^{-1} (S=O).

2-*Methylsulphinylcyclohexanone*.—The product was prepared as described above, starting with (−)-2-methylthiocyclohexanone {$[\alpha]_D^{20}$ −15.5° (*c* 1.5 in $CHCl_3$)},[26] and was an *oil* (65%) (Found: C, 52.4; H, 7.4. $C_7H_{12}O_2S$ requires C, 52.48; H, 7.55%); $[\alpha]_D^{24}$ −4.1° (*c* 1.3 in EtOH); $\nu_{max.}$ 1 700 (C=O) and 1 040 (S=O); d.e. 70%.

3-*Methyl*-2-(4-*methylphenylsulphinyl*)*butanal*.—The product was prepared as described above, starting with racemic 3-methyl-2-(4-methylphenylthio)butanal,[26] and was obtained as an *oil* (68%) (Found: C, 64.0; H, 7.5. $C_{12}H_{16}O_2S$ requires C, 64.25; H, 7.19%); $[\alpha]_D^{24}$ −14.6° (*c* 0.6 in EtOH); $\nu_{max.}$(film)

1 720 (C=O), 1 660 (C=C, enol), and 1 040 cm^{-1} (S=O); d.e. (from ^1H n.m.r.) 70%. After the product had been kept for 4 days in CH_2Cl_2–Et_2O, a crystalline product separated, m.p. 100—105 °C; $\nu_{max.}$(KBr) 2 800—2 500 (OH) and 1 680 cm^{-1} (C=O), no S=O; $\nu_{max.}$(CCl_4) 1 720 (C=O) and 1 040 cm^{-1} (S=O); $[\alpha]_D^{24}$ 0° (*c* 1 in EtOH); d.e. (from ^1H n.m.r.) 0%.

Oxidation of Ethyl (4-Methylphenyl) Sulphide with Bu^tO_2H–$Ti(OPr^i)_4$ *Diethyl Tartrate.*—Following Kagan's procedure,[17] ethyl (4-methylphenyl) sulphoxide was obtained in 60% yield, $[\alpha]_D^{24}$ +147° (*c* 1 in EtOH); e.e. 83%.

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