CdN_3 unit with a "ruffled" O_2N_3 arrangement (Figure 2c). Overall, the coordination number is 5, with two monodentate nitrates, at normal bond lengths, completing the coordination shell. As expected, these nitrate groups are displaced more to the side of the complex away from the N_3 donor set [O1-Cd-O4 = 132.5 (2)°] than in the corresponding complex of the 17-membered ring [O1-Cd-O4 = 141.2 (1)°], in which electron density from the coordinated ether oxygens is present on this side.[29]

Although applying to the solid state, the X-ray structural data for each complex nevertheless parallel in all essential detail the proposed coordination behavior of the respective macrocycles in solution. Namely, the coordination or otherwise of the ether functions in the solid Zn(II) and Cd(II) complexes occurs in a directly analogous manner to their proposed interaction with these ions in solution.

Concluding Remarks

Dislocation behavior of the type just discussed has been little studied in the past even though it provides a potentially powerful mechanism for achieving metal-ion discrimination within suitable systems. Apart from the implications for the design of new metal-ion specific reagents, an awareness of this mechanism will also likely contribute to a more general understanding of metal-ion recognition involving a range of other organic (including biological) substrates.

Acknowledgment. We thank the Australian Research Grants Scheme, the Australian Institute of Nuclear Science and Engineering, the Science and Engineering Research Council (U.K.), and I.C.I. Organics Division (U.K.) for support. We also thank B. Harrison for experimental assistance.

Registry No. 1, 77016-63-8; **2**, 77016-65-0; **3**, 85735-81-5; **4**, 77016-64-9; **5**, 85735-80-4; **6**, 85735-82-6; **7**, 85735-83-7; [Zn(OenNdienH$_4$)(ClO$_4$)$_2$], 117094-72-1; [Zn(OenNdienH$_4$)(NO$_3$)$_2$], 89014-48-2; [Cd(OenNdienH$_4$)(NO$_3$)$_2$], 89043-23-2; [Cd(OenNdienH$_4$)(H$_2$O)(NO$_3$)]ClO$_4$, 117094-77-6; [Cd(OenNentnH$_4$)(NO$_3$)$_2$], 117094-79-8; [Cd(OenNditnH$_4$)(NO$_3$)$_2$], 117094-73-2; [Cd(OenNenbnH$_4$)(NO$_3$)$_2$], 117094-74-3; [Cd(OenNdienH$_4$)(I$_2$)], 117094-78-7.

Supplementary Material Available: Crystal data, details of data collection and refinement, anisotropic thermal parameters, complete lists of bond lengths and angles, and hydrogen atom coordinates (27 pages); structure factors for all three structures (49 pages). Ordering information is given on any current masthead page.

(28) However, a molecular mechanics investigation failed to reveal any evidence of significant bonding interaction between the cadmium and the ether oxygens. The starting coordinates for the calculations were those obtained from the X-ray diffraction investigation. No bonds were defined between the above-mentioned atoms, and the structure was minimized with use of a version of the Allinger force field (Allinger, N. L. *Adv. Phys. Org. Chem.* **1976**, *13*, 1) modified to account for the presence of the central cadmium atom (see below). The minimized structure was found to be very similar to that of the starting structure. In particular, the conformation of the flexible C-O-C-H_2-CH_2-O-C backbone of the macrocycle remained quite close to that found in the X-ray diffraction study—with individual bond angles in this part of the molecule all falling within 2.5° of the corresponding X-ray values. In contrast, the presence of significant Cd-ether bonding interactions (which would not be modeled by the molecular mechanics procedure used for this complex) might be expected to lead to a marked (apparent) conformational difference in the backbone observed in the X-ray study compared to that obtained from the molecular mechanics study. It should be noted that a set of force field parameters for those portions of the complex involving the cadmium atom were initially obtained by a trial and error process involving the corresponding 17-membered-ring complex, [Cd(OenNdienH$_4$)(NO$_3$)$_2$]. The parameters thus defined were then used in the calculations for [Cd(OenNditnH$_4$)(NO$_3$)$_2$] without alteration. While there are limitations in defining force field parameters in this manner (ideally, the force field parameter set should be derived from a *range* of similar structures) the procedure is nevertheless adequate for the present purpose.

(29) The mean of the O_1-Cd-O_{1a}, O_1-Cd-O_{1b}, O_4-Cd-O_{1a}, and O_4-Cd-O_{1b} angles for [Cd(OenNdienH$_4$)(NO$_3$)$_2$] is 74.2° while for [Cd(OenNditnH$_4$)(NO$_3$)$_2$] it is 69.1°.

Chemistry of Oxaziridines. 11.[1] (Camphorylsulfonyl)oxaziridine, Synthesis and Properties

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Abstract: The synthesis, reactions, properties, and crystal structure of (+)- and (-)-(camphorylsulfonyl)oxaziridines **2** are described. These optically active oxaziridines are prepared from (+)- and (-)-camphorsulfonic acid in 77% overall yield. In contrast to other optically active sulfonimines, which give on oxidation mixtures of oxaziridine diastereoisomers, oxidation of camphorsulfonimine **5** with Oxone produces only a single isomer in >90% yield. For the asymmetric oxidation of prochiral sulfides by **2**, the enantioselectivities are lower than those reported for optically active *N*-sulfamyloxaziridine **1** (5-73 vs 35-60% ee) and are discussed in terms of different active site structures for the two oxaziridines. As observed with other optically active *N*-sulfonyloxaziridines, the configuration of the oxaziridine three-membered ring in **2** controls the stereochemistry of the product, with (+)-**2** and (-)-**2** giving the opposite senses of asymmetric induction, respectively. While other *N*-sulfonyloxaziridines readily oxidize amines and epoxidize alkenes, **2** does not, even on heating. An improved method for the synthesis of Oppolzers' sultam chiral auxiliary **6** is described.

The development of reagents for the *reagent-controlled* asymmetric oxidation of prochiral alkenes, sulfides, and enolates with high enantioselectivities (>95% ee) is an important synthetic goal. To date relatively few reagents, with general applicability, have been developed. Homochiral peracids are ineffectual, affording only low levels of asymmetric induction for the oxidation of sulfides and alkenes (0-9% ee).[2] Chiral organometallic peroxides are much more efficient asymmetric oxidizing reagents,[3] with the best

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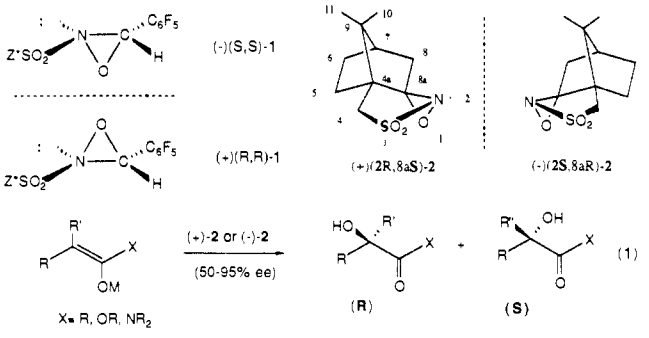
example being the Sharpless reagent. Very high levels of asymmetric induction for the catalytic asymmetric epoxidation of structurally diverse allylic alcohols (>90% ee) are observed with the Sharpless reagent.[4] However, epoxidation of nonfunctionalized or isolated alkenes does not work with this reagent, and other chiral metal peroxides give low stereoselectivities (up to 50% ee in one isolated example).[5-7] Modification of the Sharpless reagent with water[8] or with excess diethyl tartrate[9] affords a species that gives good to excellent stereoselectivities (33–98% ee) for the asymmetric oxidation of sulfides to sulfoxides. However, none of these oxidizing systems can be used for the asymmetric oxidation of enolates.

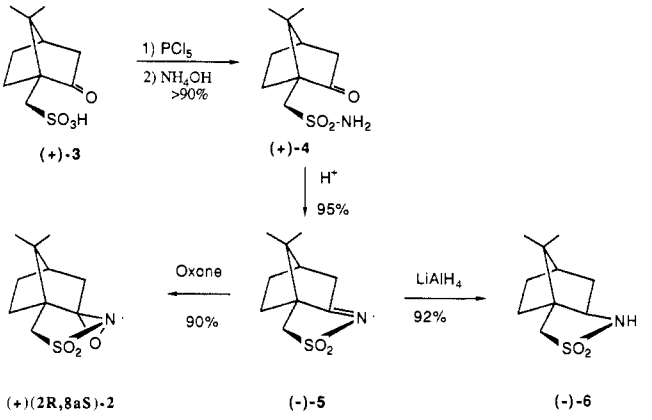
An important class of synthetically useful optically active oxidizing reagents developed in our laboratories is the diastereomerically pure *N*-sulfonyloxaziridines.[10] (Pentafluorophenyl)-*N*-sulfamyloxaziridines, (+)-(*R*,*R*)-**1** and (−)-(*S*,*S*)-**1**, for example, afford the highest enantioselectivities reported for the asymmetric oxidation of nonfunctionalized alkenes (45–62% ee).[11] The stereoselectivities for the asymmetric oxidation of prochiral sulfides to sulfoxides with these reagents are similar to, and in some cases better than, those reported for the modified Sharpless reagents (40–90% ee).[10]

N-Sulfonyloxaziridines are aprotic and neutral oxidizing reagents and are the only chiral oxidizing reagents yet devised for the asymmetric oxidation of prochiral enolates to optically active α-hydroxy carbonyl compounds (eq 1).[12] (Camphoryl-



sulfonyl)oxaziridines, (+)-(2*R*,8a*S*)-**2** and (−)-(2*S*,8a*R*)-**2**, are the reagents of choice for asymmetric enolate oxidations, because they afford useful levels of asymmetric induction (50–95% ee), give high chemical yields irrespective of the counterion, and each give the opposite sense of the asymmetric induction, respectively. Asymmetric oxidation of chiral enolates, double asymmetric synthesis, with (+)-**2** and (−)-**2** affords tertiary α-hydroxy amides in high optical purity (90% de).[13]

Scheme I



In this paper we report details of the synthesis of (camphorylsulfonyl)oxaziridines (+)-(2*R*,8a*S*)-**2** and (−)-(2*S*,8a*R*)-**2**, along with their structure and properties.

Results and Discussion

Synthesis of (Camphorylsulfonyl)oxaziridines. Our synthesis of oxaziridine (+)-(2*R*,8a*S*)-**2** is outlined in Scheme I and begins with (+)-(1*S*)-camphorsulfonic acid (**3**) which is converted to the sulfonyl chloride as reported by Bartlett and Knox.[14] After being dried, the crude sulfonyl chloride is dissolved in methylene chloride and treated with ammonium hydroxide solution to give the camphorsulfonamide **4** in greater than 90% isolated yield. Azeotropic removal of water using toluene and Amberlyst 15 ion-exchange resin as the acid catalyst affords the camphorsulfonimine **5** nearly quantitatively (>95%).

Camphorsulfonimine **5** has been the subject of several syntheses,[15] most recently in the synthesis of the sultam chiral auxiliary **6**.[16] The advantage of our procedure is that by using ammonium hydroxide the camphorsulfonyl chloride is converted to the sulfonamide **4** in greater than 95% yield. The sulfonamide **4** is of sufficient purity that it can be used directly in the cyclization step, which under acidic conditions is quantitative in less than 4 h. These modifications result in the production of **5** in 86% overall yield from 50 g (21.5 mmol) of camphorsulfonic acid **3**.

Because of the lack of solubility of **5** in THF, reduction with $LiAlH_4$ to give Oppolzer's chiral auxiliary **6** requires large amounts of solvent.[16] We found that the amount of solvent can be significantly reduced by using a Soxhlet extractor to slowly convey **5** into the reducing solution.

Oxidation of chiral sulfonimines ($R^*SO_2N{=}CHAr$) is normally effected by oxidation for several hours with biphasic basic solutions of *m*-chloroperbenzoic acid (*m*-CPBA)[10,15] and more recently with peroxymonosulfate (Oxone).[17] Mixtures of the diastereomeric oxaziridines (−)-(*S*,*S*)-**1** and (+)-(*R*,*R*)-**1** are usually formed in 1:1 ratios, necessitating separation. Initial attempts to oxidize camphorsulfonimine **5** with *m*-CPBA for 8 h proved unsuccessful. However, after 5 days and a total of 4 equiv of *m*-CPBA, (+)-**2** was obtained in 80% yield. Purification required flash chromatography because **2** was contaminated with (ca. 20%) bis(*m*-chlorobenzoyl) peroxide formed under the long oxidation times.

Subsequently, the work of Curci on the synthesis of dioxiranes using potassium peroxymonosulfate (Oxone) attracted our attention because of the similarities in the mechanisms for generation of dioxiranes and *N*-sulfonyloxaziridine.[18] Indeed, oxidation of **5** using Oxone, buffered to pH ca. 7.5 with $KHCO_3$ and 18-crown-6 ether in toluene gave after 5 days a 90% isolated yield

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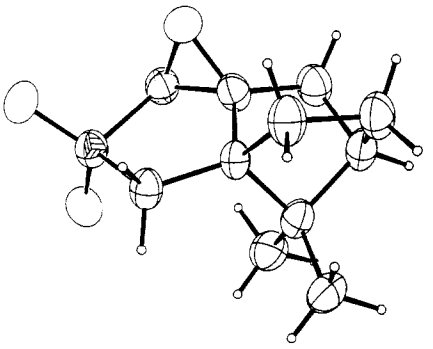


Figure 1. Computer-generated structure of (+)-(2*R*,8a*S*)-(camphorylsulfonyl)oxaziridine **2**.

of (+)-**2**. Significantly, when the oxidizing mixture was buffered with K_2CO_3 to pH 9.0, the oxidation of (−)-**5** to (+)-**2** was complete within 1.5 h and the phase-transfer catalyst was not necessary. Oxidation of the (+)-camphorsulfonimine **5**, prepared form (−)-(1*R*)-10-camphorsulfonic acid, gave the other isomer, (−)-(2*S*,8a*R*)-(camphorylsulfonyl)oxaziridine **2**.

(Camphorysulfonyl)oxaziridines **2** *are stable crystalline solids melting without decomposition. Samples of* **2** *kept for more than 1 year at room temperature exhibited no detectable signs of decomposition or loss of optical purity.*

Structure. Significantly, and in contrast to the oxidation of all other optically active sulfonimines studied to date,[10,15] **2** is obtained as a single oxaziridine isomer. Since oxidation is possible only from the sterically least hindered endo face of the C–N double bond in **5**, the configuration of the oxaziridine three-membered ring in (+)-**2** must be 2*R*,8a*S* and 2*S*,8a*R* in (−)-**2**. The oxaziridine carbon in the ^{13}C NMR spectra of **2** appears at δ 98.8 ppm and is 20 ppm higher than observed for other *N*-sulfonyloxaziridines (δ 75–77 ppm).[18] The higher chemical shift probably reflects both greater alkyl substitution and increased ring strain caused by the spiro nature of the system.[10]

Figure 1 shows a computer-generated X-ray structure of (+)-(camphorylsulfonyl)oxaziridine **2**. The structure confirms the assignment of the oxaziridine three-membered ring in (+)-**2** as 2*R*,8a*S*. The structure of the oxaziridine three-membered ring is not statistically different from other *N*-sulfonyloxaziridines previously reported.[10] As previously observed, the nitrogen atom is pyramidal (sp^3), indicating that there is little if any p–d π bonding between the sulfonyl group and the nitrogen long pair of electrons. In the region of the oxaziridine active site oxygen, the sterically most demanding region appears to be in the vicinity of C-5–C-6 bond (vide infra).

In considering the mechanism of oxygen transfer for the asymmetric oxidation of enolates by **2**, the question of an "open" vs a "closed" transition state is particularly relevant.[12] A closed transition state requires the presence of Lewis base sites in **2** that could chelate with the metal enolate defining the geometry of the transition state. One possible site of Lewis basicity is at the sulfonyl oxygens in **2**. Indeed, there are several reports of metal chelation to sulfonyl oxygens.[19,20] For example, in metal-promoted Diels–Alder reactions employing **6** as a chiral auxiliary, Oppolzer evokes metal chelation involving the sulfonyl oxygen to explain the stereoselection.[20] Other potential sites of Lewis basicity in **2** are the oxaziridine N and O atoms.

NMR shift reagents were used to identify the Lewis base sites in **2**, the rationale being that the shift reagent would complex with the site of greatest Lewis basicity. These results are summarized in Figure 2. The 4-CH_2 protons adjacent to the sulfonyl group and the 10-methyl group are the protons most effected by the shift reagent Resolve-A1 EuFOD [Eu(fod)$_3$]. The 8-exo and -endo

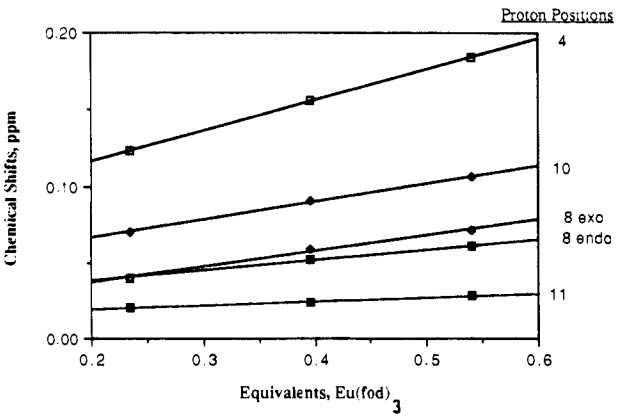
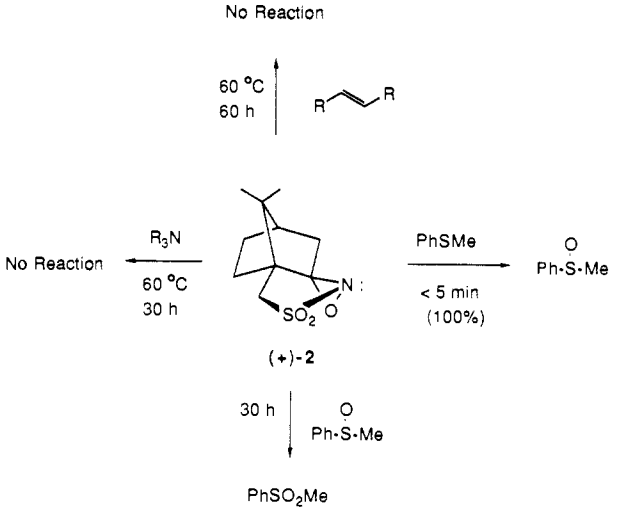


Figure 2. Induced chemical shifts for the different protons of (+)-(camphorylsulfonyl)oxaziridine **2** with increasing concentration of Eu(fod)$_3$.

Scheme II



protons near the oxaziridine O and N atoms are among the least effected by this shift reagent. This suggests that the primary site of complexation by the shift reagent is the sulfonyl oxygen away from the active site oxygen and nearest the 10-methyl group (Figure 1). It is worthwhile noting that even at 1.0 M equiv of Eu(fod)$_3$ the shift is only 0.19 ppm. With sulfoxides and carbonyl groups, Eu(fod)$_3$ generally results is induced shifts of 5–6 ppm.[21] Similar, although less conclusive, results were observed with Pr(fod)$_3$ and Yb(fod)$_3$. While it may be concluded from these studies that the site of greatest Lewis basicity is the sulfonyl oxygen nearest the 10-methyl group, it appears to be a rather weak Lewis base site.

It can be argued that the Lewis base sites in **2** are too sterically hindered for effective coordination with a shift reagent. However, there was little if any change in either the ^{13}C or ^1H NMR spectra of (+)-**2** on addition of 1.0 M $LiClO_4$ in THF-d_8. These studies support our earlier assumptions that molecular recognition for asymmetric enolate oxidations by **2** involves an open transition state controlled by nonbonded steric interactions.[12b]

Reactions. *N*-Sulfonyloxaziridines rapidly oxidize nucleophilic substrates such as sulfides[22] and amines[23] within a few minutes

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Table I. Asymmetric Oxidation of Sulfides to Sulfoxides by (Camphorysulfonyl)oxaziridines 2 at 25 °C

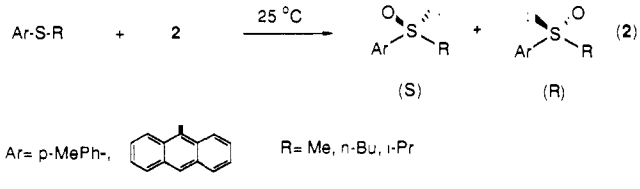
			sulfoxide,[a] % ee (configuration)				
			p-tolyl-S-R		9-anthryl-S-R		
entry	oxaziridine	solvent	R = *n*-Bu	R = *i*-Pr	R = Me	*R* = *n*-Bu	*R* = *i*-Pr
1	(+)-**2**	$CHCl_3$	2.9 (*S*)	4.7 (*S*)	72.7 (*S*)	74.3 (*S*)	66.2 (*S*)
2	(+)-**2**	EtOH		1.1 (*R*)			65.1 (*S*)
3	(+)-**2**	PhH		5.1 (*S*)			73.4 (*S*)
4	(+)-**2**	MeCN		15.6 (*R*)			69.3 (*S*)
5	(+)-**2**	H_2O		2.4 (*S*)			69.6 (*S*)
6	(−)-**2**	$CHCl_3$	3.5 (*R*)	5.3 (*R*)	77.5 (*R*)		68.0 (*R*)
7	(−)-(*S*,*S*)-**1**[b]	$CHCl_3$	30.7 (*S*)	36.6 (*S*)	50.0 (*S*)		59.9 (*S*)
8	(+)-(*R*,*R*)-**1**[b]	$CHCl_3$	34.6 (*R*)	34.6 (*R*)	50.3 (*R*)		56.6 (*R*)

[a] Sulfoxide enantiomers were separated on a Regis Pirkle covalent phenylglycine HPLC column. See ref 10. [b] Data taken from ref 10.

at 25 °C.[24] For complete reaction, epoxidation of alkenes generally requires heating at 60 °C for several hours.[25] (Camphorylsulfonyl)oxaziridine **2** also oxidizes sulfides to sulfoxides, but at a slower rate (Scheme II). A competitive rate experiment reveals that **2** oxidizes phenyl methyl sulfide (PhSMe) only half as fast as 2-(phenylsulfonyl)-3-phenyloxaziridine (**1**, Z* = C_6F_5 = Ph). On the other hand, **2** oxidizes phenyl methyl sulfoxide to the sulfone 10 times slower than 2-(phenylsulfonyl)-3-phenyloxaziridine.

Oxaziridine **2** does not oxidize amines to amine oxides or epoxidize alkenes, even on heating at 60 °C for 12–50 h (Scheme II). The much lower reactivity of **2** compared with other *N*-sulfonyloxaziridine is likely related to two factors. First, electron-donating groups attached to the oxaziridine carbon are known to reduce its oxidizing potential.[26] A second reason may be steric hindrance to approach of these nucleophiles to the active site oxygen in **2**. However, for the reasons discussed below the active site microenvironment in **2** appears to be less sterically hindered than in **1**.

Asymmetric Oxidation of Sulfides to Sulfoxides. The asymmetric oxidations of prochiral alkyl 9-anthryl and *p*-tolyl sulfides to sulfoxides by (+)-**2** and (−)-**2** are summarized in Table I. Inspection of these results shows that the steroselectivity for the asymmetric oxidation of the alkyl 9-anthryl sulfides is considerably higher than for the alkyl *p*-tolyl sulfides, i.e. 65–73% vs 1–16% ee. Solvent effects were noticeable only for the alkyl *p*-tolyl sulfides where the asymmetric induction was low. As observed for all other asymmetric oxidations employing optically active *N*-sulfonyloxaziridines, the product stereochemistry is controlled by the configuration of the oxaziridine three-membered ring.[10,24] (+)-(2*R*,8a*S*)-(Camphorylsulfonyl)oxaziridine **2** gave the (*S*)-sulfoxides while (−)-(2*S*,8a*R*)-**2** gave the (*R*)-sulfoxides (table).



The geometry of the transition state for the oxidation of sulfides to sulfoxides by *N*-sulfonyloxaziridines has recently been established as planar.[10] In the planar transition-state geometry, the sulfide attacks the oxaziridine active site oxygen with both electron pairs in the plane of the oxaziridine three-membered ring. Nonbonded steric interactions are primarily responsible for the chiral recognition. Thus, the preferred diastereomeric transition state for oxidations by (+)-**2** is predicted to be the one where the large (Ar) and small (R) groups of the sulfide have the fewer nonbonded steric interactions in the region of the oxaziridine three-membered ring (Figure 3).

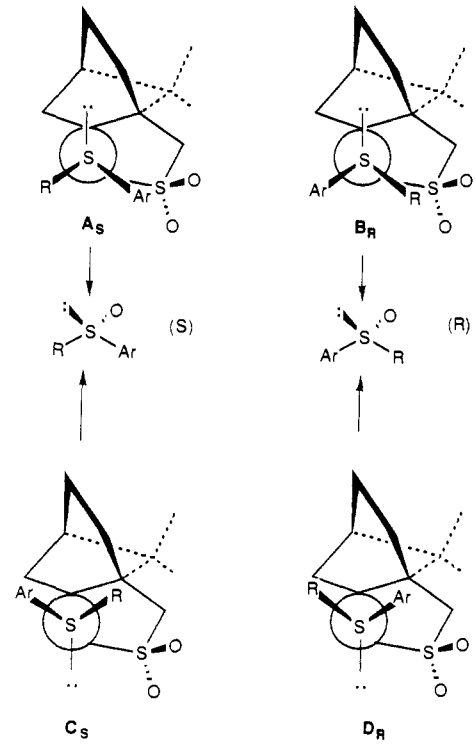


Figure 3. Transition states for the oxidation of sulfides to sulfoxides by (+)-**2**.

Since (+)-**2** gives predominantly (*S*)-sulfoxides, this must mean that transition states A_S and C_S are preferred over B_R and D_R (Figure 2). In the vicinity of the active site oxygen, the sterically most demanding region is the 5–6 carbon–carbon bridge (Figure 1). Thus, in transition states C_S and D_R, nonbonded interactions between the R and Ar groups of the sulfide and the 5–6 C–C bond in (+)-**2** are unfavorable with the latter being the most unfavorable. However, only when the aryl (Ar) in the sulfide is a very large anthryl group does this unfavorable nonbonded interaction in D_R have a significant influence on the chiral recognition.[27] It may further be concluded that the steric size of the sulfone oxygen nearest the active site oxygen is small. These results are in general accord with the sterochemistry for the asymmetric oxidation of ketone enolates by **2**.[12b]

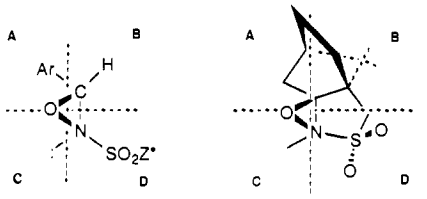
As previously described, the active sites of oxaziridines **1** and **2** can be divided into quadrants as shown in structures **8** and **9**, respectively.[10] The quadrants are given priorities according to group steric size and are based on the structure reactivity trends. For **8**, quadrants A and D are occupied by large groups while B

(24) For a review on the oxygen-transfer reactions of oxaziridines, see: Davis, F. A., and Haque, S. M. In *Advances in Oxygenated Process*; Baumstark, A. L., Ed.; JAL: Greenwich, CT, in press.

(25) (a) Davis, F. A.; Abdul-Malik, N. F.; Award, S. B.; Harakal, M. E. *Tetrahedron Lett.* **1981**, *23*, 917. (b) Davis, F. A.; Harakal, M. E.; Awad, S. B. *J. Am. Chem. Soc.* **1983**, *105*, 3123. (c) Davis, F. A.; Sheppard, A. C. *J. Org. Chem.* **1987**, *52*, 954.

(26) Davis, F. A.; Billmers, J. M.; Gosciniak, D. J.; Towson, J. C.; Bach, R. D. *J. Org. Chem.* **1986**, *51*, 4240.

(27) Molecular mechanics calculation using MODEL indicates that the minimum energy conformation for the anthryl sulfides is where the R group is approximately perpendicular to the plane of the anthryl ring.



8 9

and C are occupied by small groups. The studies reported here suggest that only the B quandrant in **9** is occupied by a large group. Thus, oxaziridines **1** and **2** have different active site structures as reflected in their asymmetric oxidations. For example, **1** gives higher stereoselectivities for the oxidation of alkyl *p*-tolyl sulfides than does **2** (30–37% vs 3–5% ee) but somewhat lower stereoselectivities for oxidation of the alkyl 9-anthryl sulfides (50–60% vs 66–73% ee, table). For the asymmetric oxidation of enolates, **2** gives consistently higher stereoselectivities than do oxaziridines of type **1**.[12,13]

Summary. (Camphorylsulfonyl)oxaziridines **2** are easily prepared in three steps in 77% overall yield from inexpensive camphorsulfonic acid. This oxaziridine is the first optically active *N*-sulfonyloxaziridine to be obtained as a single isomer on oxidation of the sulfonimine. While asymmetric oxidations of neutral substrates (sulfides, alkenes, amines) with **2** appear to be limited, their real value is in the oxidation of anionic species. For example, **2** gives high chemical yields and stereoselectivities (50–98% ee) in the asymmetric oxidation of prochiral enolates to optically active α-hydroxy carbonyl compounds.[12,13] Furthermore, since both (+)-**2** and (−)-**2** are readily available, both optical isomers of the α-hydroxy carbonyl compounds are easily accessible. A potentially exciting application of (+)-**2** and (−)-**2** is in the area of double asymmetric synthesis, as, for example, in the asymmetric oxidation of chiral amide enolates to optically active tertiary α-hydroxy amides (90% de).[12] Oxaziridine **2** is also useful for the hydroxylation of organometallic reagents, affording good to excellent yields of alcohols and phenols.[28]

Experimental Section

n-Butyl *p*-tolyl sulfide, isopropyl *p*-tolyl sulfide, methyl 9-anthryl sulfide, isopropyl 9-anthryl sulfide, and *n*-butyl 9-anthryl sulfide were prepared as previously described.[10] Methyl *p*-tolyl sulfide, methyl cyclohexene, *cis*- and *trans*-stilbene, styrene, *N*-methyl-*N*-ethyl-*N*-phenylamine. Amberlyst 15 ion-exchange resin, and Oxone were purchased from Aldrich Chemical Co.

Samples of Oxone that have been exposed to moisture for extended periods of time often gave reduced reactivity in the oxidation of the sulfonimine **5** to oxaziridine **2**. Generally, Oxone stored in the refrigerator under an inert atmosphere gave satisfactory results after opening.

General Procedure for the Oxidation of Sulfides to Sulfoxides. In a 5-mL round-bottomed flask equipped with magnetic stir bar and argon inlet was placed 5 mg (0.022 mmol) of (camphorylsulfonyl)oxaziridine (+)-**2** in 1 mL of the desired solvent. To this stirring solution was added 1.1 equiv of the appropriate sulfide dissolved in 1 mL of solvent. The reaction mixture was stirred for 1 h and then the sulfoxide was isolated by preparative TLC (silica gel G) by eluting with ether. The sulfoxide was always the lowest band on the TLC plate.

Preparation of (+)-(1*S*)-10-Camphorsulfonamide 4. In a 2-L three-necked Morton flask equipped with mechanical stirrer with a 65-mm Teflon stirring blade, 250-mL addition funnel, and glass plug was placed 450 mL of NH_4OH. The reaction mixture was cooled to 0 °C in an ice bath and stirred vigorously. A solution of 50.0 g (0.2 mol) of camphorsulfonyl chloride prepared by the method of Bartlett and Knox[14] in 450 mL of CH_2Cl_2 was then added dropwise in two protions over 30 min. The reaction mixture was stirred for an additional 2 h at 0 °C, then the lower CH_2Cl_2 layer was separated, and the NH_4OH layer was washed (2 × 100 mL) with CH_2Cl_2. The CH_2Cl_2 extracts were combined and dried over anhydrous $MgSO_4$, and the solvent was removed on the rotary evaporator to give 41.5 g (90%) of the crude camphorsulfonamide (+)-**4**; mp 127–130 °C (lit.[15] mp 131–132 °C); ^{1}HNMR ($CDCl_3$) δ 0.93 (s, 3 H, CH_3), 1.07 (s, 3 H, CH_3), 1.45–260 (m, 7 H), 3.14 and 3.53 (AB quartet, 2 H, CH_2SO_2, J = 15.1 Hz), 5.54 (br s, 2 H, NH_2).

Preparation of (−)-(1*R*)-10-camphorsulfonamide 4 was performed in a similar manner and with similar yield from (−)-(1*R*)-10-camphorsulfonic acid.

(−)-Camphorsulfonimine (5). In a 1-L round-bottomed flask equipped with a large egg-shaped magnetic stir bar, Dean–Stark trap, reflux condenser, and argon inlet were placed 5 g of Amberlyst 15 ion-exchange resin and 41.5 g of the crude camphorsulfonamide in 500 mL of toluene. The reaction mixture was heated to reflux for 4 h. The heat was removed, and while still warm, 200 mL of CH_2Cl_2 was added to solubilize the solid imine that forms. The warm solution was filtered, and the reaction flask and funnel were washed with an additional 75 mL of CH_2Cl_2. The CH_2Cl_2 was rotary evaporated from the solution until ~275 mL was collected. If desired, the toluene may be evaporated and the crude camphorsulfonimine recrystallized from absolute ethanol to give 36.4 g (95%) of (−)-**5** as a white crystalline solid: mp 225–228 °C (lit.[15] mp228.2 °C; $[\alpha]_D$ −32.73° (*c* 1.89, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.88 (s, 3 H, CH_3), 1.09 (s, 3 H, CH_3), 1.47–2.73 (m, 7 H), 2.98 and 3.19 (AB quartet, 2 H, CH_2SO_2, J = 13.3 Hz); ^{13}CNMR ($CDCl_3$) δ 19.01 (q, CH_3-C8), 19.45 (q, CH_3C8)8 26.64 (t, C5), 28.44 (t, C4), 35.92 (t, C3), 44.64 (d, C6), 48.00 (s, C8), 49.46 (t, C7), 64.52 (s, C3a), 195.52 (s, C7a); IR (KBr) 2975 (CH, 164 (C=N), 1320, 1170 (SO_2) cm^{-1}; EI-MS, m/z (rel abund) 213 (M^+, 1.30), 149 (9.56), 134 (25.21), 109 (28.86) 93 (43.60), 82 (21.32), 79 (13.18), 67 (31.46), 55 (12.94), 53 (12.91), 41 (31,28); R_f 0.28 (using CH_2Cl_2 as the eluent and 10% molybdophosphoric acid in ethanol as the developer).

(+)-Camphorsulfonimine 5 was prepared in a similar manner and yield from (−)-(1*R*)-10-camphorsulfonic acid; $[\alpha]_D$ +31.47° (*c* 2.11, $CHCl_3$).

(−)-Sultam 6. In a dry 2-L three necked round-bottomed flask equipped with an egg-shaped Teflon stirring bar, 500-mL addition funnel, 200-mL Soxlet extraction apparatus with argon inlet, and a glass plug were placed 500 mL of dry THF and 6.35 g (0.1664 mol) of $LiAlH_4$. Into the thimble of the Soxlet extraction apparatus was placed 35.5 g (0.1664 mol) of (−)-camphorsulfonimine **5**. The reaction mixture was stirred and heated to reflux. The camphorsulfonimine was dissolved by the siphoning action of the Soxlet extraction. After 4 h of siphoning, the heating was stopped and the reaction was allowed to cool to room temperature. The unreacted $LiAlH_4$ was hydrolyzed by the addition of 450 mL of a 1 N aqueous HCl solution. The addition must be very slow at first (1 drop/5 s) until the vigorous reaction has subsided. The contents of the flask were then transferred to a 1-L separatory funnel, the lower, silver-colored aqueous layer was separated, and the upper THF layer was placed in a 1000-mL Erlenmeyer flask. The aqueous layer was returned to the separatory funnel and washed (3 × 100 mL) with CH_2Cl_2. The flask was washed with 50 mL of CH_2Cl_2. The CH_2Cl_2 washings were combined with the THF, dried over anhydrous $MgSO_4$, and filtered through a 300-mL coarse sintered glass funnel into a 1000-mL round-bottomed flask, and the solvent was removed on a rotary evaporator to give 35.1 g (98.0%) of the crude (−)-sultam **6**. The crude solid was placed in a 500-mL Erlenmeyer flask and recrystallized from ~60 mL of absolute ethanol. The recrystallized product was collected on a 150-mL coarse sintered glass funnel and dried in vacuo to give 31.6 g (88.3%) of a crystalline white solid. A second crop of crystals can be gained by evaporating 50% of the filtrate and recrystallizing as above to give 1.4 g (4.0%) (combined yield 92.3%) of a crystalline white solid: mp 183–184 °C (lit.[15] mp 182–183 °C); $[\alpha]_D$ −30.5° (*c* 4.0, $CHCl_3$) [lit.[15] for (+)-**6**: $[\alpha]_{578}$ +32.5° (*c* 1.01, $CHCl_3$, at 21.6 °C)]; ^{1}HNMR ($CDCl_3$) δ 0.94 (s, 3 H, CH_3), 1.14 (s, 3 H, CH_3), 1.33 (m, 1 H), 1.47 (m, 1 H), 1.80–1.95 (5 H), 3.09 (d, 1 H, J = 14 Hz), 3.14 (d, 1 H, J = 14 Hz), 3.43 (m, 1 H), 4.12 (br s, 1 H, NH); ^{13}C NMR ($CDCl_3$) δ 20.17 (q, CH_3-8a), 20.17 (q, CH_3-8b), 26.51 (t, C5), 31.55 (t, C4), 35.72 (t, C7), 44.44 (d, C6), 47.15 (s, C8), 50.08 (t, C3), 54.46 (s, C3a), 62.48 (d, C7a); IR (KBr) 2960 (CH), 3300 (NH), 1335, 1140 (SO_2) cm^{-1}.

(+)-(2*R*,8a*S*)-(Camphorylsulfonyl)oxaziridine 2. In a 5-L two-necked Morton flask equipped with an efficient mechanical stirrer with a 125-mm Teflon stirring blade, a Safe Lab stirring bearing, and a 500-mL addition funnel were placed the toluene solution of (−)-**5** from above and a solution of 493 g (3.57 mol, 7 equiv based on Oxone) of K_2CO_3 in 750 mL of distilled H_2O. The reaction mixture was cooled to 0 °C in an ice bath and stirred vigorously, and a solution of 315 g [0.51 mol (6 equiv of $KHSO_5$)] of Oxone in 1250 mL of distilled H_2O was added dropwise in three poritons over 45 min. After addition of the oxone, the reaction mixture was warmed to room temperature. As noted, Oxone that has been exposed to moisture for several months prior to use gives reduced reactivity in this oxidation. If this occurs, Oxone is added until oxidation is complete as determined by TLC. Potassium carbonate is added as needed to maintain the pH at ~9.0. After the oxidation was complete, the reaction mixture was stirred vigorously for an additional hour, filtered to remove any solids, and transferred to a 3-L separatory funnel. The toluene layer was separated, and the aqueous layer was washed (3 × 100 mL) with CH_2Cl_2. The filtered solids and any solids

(28) Davis, F. A.; Wei, J.; Sheppard, A. C.; Gubernick, S. *Tetrahedron Lett.* **1987**, *2*, 5115.

remaining in the Morton flask were washed with 200 mL of CH_2Cl_2. The organic extracts were combined, washed with 1 × 100 mL of saturated Na_2SO_3, and dried over anhydrous $MgSO_4$, and the solvent was evaporated to give 38 g of a white solid. The crude solid was placed in a 1000-mL Erlenmeyer flask and recrystallized from ~500 mL of 2-propanol. The recrystallized product was collected on a 150-mL coarse sintered glass funnel and dried in vacuo to give 35.2 g (90%, 77% from camphorsulfonyl chloride) of (+)-**2** as crystalline white solid: mp 165–167 °C; $[\alpha]_D$ +44.59° (*c* 2.19, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.03 (s, 3 H, CH_3), 1.18 (s, 3 H, CH_3), 1.45–2.18 (m, 6 H), 2.65 (d, 1 H), 3.10 and 3.28 (AB quartet, 2 H, CH_2SO_2, J = 14.0 Hz); ^{13}CNMR ($CDCl_3$) δ 19.45 (q, CH_3-C9), 20.42 (q, CH_3-C9), 26.55 (t, C6), 28.39 (t, C5), 33.64 (t, C4), 45.78 (d C7), 48.16 (s C9), 48.32 (t, C8), 54.07 (s, C4a), 98.76 (s, C8a); IR (KBr) 2960 (CH), 1160, 1340 (SO_2) cm^{-1}; R_f 0.62 (using CH_2Cl_2 as the eluent and 10% molybdophosphoric acid in ethanol as the developer); EI-MS, m/z (rel abund) 229 (M^+, 4.34), 201 (12.50), 148 (19.82), 122 (70.32), 108 (49.85), 93 (52.37), 79 (41.72), 67 (56.90), 55 (48.42), 41 (100). Anal. Calcd for $C_{10}H_{15}NO_3S$: C, 52.38; H, 6.59. Found: C, 52.55; H, 6.76.

(−)-(**2*S*,8a*R***)-(**Camphorylsulfonyl**)**oxaziridine 2** was prepared in a similar manner and yield by oxidation of (+)-**5**; $[\alpha]_D$ −43.59° (*c* 2.16, $CHCl_3$).

X-ray Analysis of (+)-(Camphorylsulfonyl)oxaziridine 2. Data were collected on an Enraf-Nonius CAD4 diffractometer using a crystal of dimensions 0.35 × 0.30 × 0.20 mm. Crystal data: $C_{10}H_{15}NO_3S$; M_r 229.30; orthorombic, $P2_12_12_1$; a = 7.381 (1), b = 8.935 (1), c = 16.779 (1) Å; V = 1106.6 Å^3; Z = 4, D_{calcd} = 1.376 g cm^{-3}, λ (CuKα) = 1.54184 Å, ν = 24.7 cm^{-1}. Lattice parameters were determined from 25 reflections with $35 \le 2\theta \le 60°$. A total of 990 reflections were measured by using the ω–2θ scan technique with $6 \le 2\theta \le 120°$. Intensities of three standard reflections (133, 205, 223) recorded every 3000 s of X-ray exposure showed no significant decay. A total of 780 unique, observed reflections with $I > 3\sigma(I)$ were used during structure refinement. Data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by MULTAN 11/82.[29] H atoms were found from subsequent difference Fourier syntheses. Refinement by full-matrix least squares to minimize $\sum_w(|F_o| - |F_c|^2)$ led to R = 0.058 and R_w = 0.063 for 136 variables with $w = 1/[1 + [(F_o - 68.5)/413.8]^2]$. The maximum least-squares shift to esd ratio was 0.02 in the final refinement cycle. The largest residual electron densities in the final difference map were +0.19 and −0.38 eÅ^{-3}. All computers programs were from the Enraf-Nonius SDP package.[30]

Acknowledgment. This work was supported by grants from the National Science Foundation (CHE 8502076) and the National Institutes of Health (Institute of General Medical Sciences) through Grant GM 34014.

Registry No. (+)-**2**, 104322-63-6; (−)-**2**, 104372-31-8; (+)-**4**, 60933-63-3; (−)-**4**, 72597-34-3; (+)-**5**, 107869-45-4; (−)-**5**, 60886-80-8; (−)-**6**, 94594-90-8; *p*-tolylSBu, 21784-96-3; *p*-tolylSPr-*i*, 14905-81-8; 9-anthrylSMe, 89249-29-6; 9-anthrylSBu, 74851-72-2; 9-anthrylSPr-*i*, 86129-61-5; (*S*)-*p*-tolylS(O)Bu, 72174-23-3; (*R*)-*p*-tolylS(O)Bu, 20288-49-7; (*S*)-*p*-tolylS(O)Pr-*i*, 37067-60-0; (*R*)-*p*-tolylS(O)Pr-*i*, 1517-74-4; (*S*)-9-anthrylSMe, 89616-63-7; (*R*)-9-anthrylSMe, 89616-64-8; (*S*)-9-anthrylSBu, 108167-47-1; (*S*)-9-anthryls, 108167-45-9; (*R*)-9-anthrylSPr-*i*, 108167-46-0; (+)-camphorsulfonyl chloride, 21286-54-4; (−)-(1*R*)-10-camphorsulfonic acid, 35963-20-3.

Supplementary Material Available: Experimental section including general information on the instrumentation used, the general procedure for determinig the optical purity of the sulfoxides, the general procedure for monitoring the attempted oxidation of alkenes and amines by **2**, the competitive rate study of the oxidation of sulfides to sulfoxides by 2-(phenylsulfonyl)-3-phenyloxaziridine, and the shift reagent studies for (+)-(camphorylsulfonyl)oxaziridine **2** and tables of X-ray data including atomic positional parameters, thermal parameters, and bond distances and bond angles for (camphorylsulfonyl)oxaziridines (7 pages). Ordering information is given on any current masthead page.

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