Supplementary Material Available: Crystal data and data collection, structure determination and refinement, numbering scheme, and tables of crystal data and structure determination, fractional atomic coordinates and isotropic thermal parameters, and interatomic distances and angles for $Cu[C(C_6H_4{\cdot}CN)_4]BF_4{\cdot}xC_6H_5NO_2$ (6 pages); listing of observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

(−)-α,α-Dichlorocamphorsulfonyloxaziridine: A Superior Reagent for the Asymmetric Oxidation of Sulfides to Sulfoxides†

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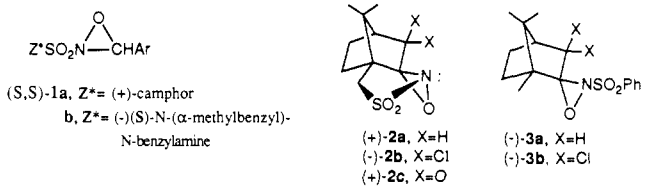
Received March 15, 1989

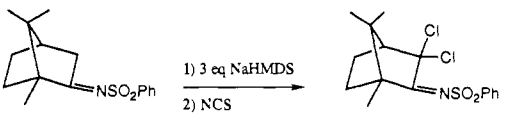
Optically active sulfoxides are important synthons for the asymmetric construction of C–C bonds[1,2] and have played pivotal roles in studies of the origins of asymmetric induction.[2,3] The Andersen procedure, the reaction of an organometallic reagent with a chiral sulfinate ester, is the method of choice for synthesis of most enantiomerically pure sulfoxides. However, an attractive alternative is the asymmetric oxidation of prochiral sulfides to sulfoxides with optically active oxidizing reagents.[2,4] Not only can the sulfoxide be formed in one step but also the synthesis of optically active sulfoxides, not possible by the Andersen procedure, can be realized. Unfortunately, the stereoselectivities for the asymmetric oxidizing reagents developed to date are variable, being both reagent and substrate dependent.[2-4]

The modified Sharpless reagent,[5,6] developed by Kagan et al., is the most effective of these reagents, affording moderate to excellent stereoselectivities for a variety of sulfides substrates (Table I).[6] The enantiomerically pure *N*-sulfonyloxaziridines **1** and **2a** are another class of asymmetric oxidizing reagents which are aprotic in nature.[4,7,8] The highest stereoselectivities (31–91% ee) are observed for the *N*-sulfamyloxaziridines **1b**,[4] which is unfortunate because (+)-(camphorylsulfonyl)oxaziridine (**2a**) is easily prepared and separation of the oxaziridine diastereoisomers, a problem with oxaziridines of type **1**, is not necessary for **2**.[7] While the α,α-dichloro and oxo derivatives, **2b** (56–74% ee)[9] and **2c** (5–62% ee),[10] afford improved stereoselectivities over **2a** (3–80% ee),[7] for sulfide oxidations these reagents are also substrate specific.



In this context we report that (−)-α,α-dichlorocamphorsulfonyloxaziridine (**3b**), a new class of *N*-sulfonyloxaziridines, is a highly efficient reagent for the asymmetric oxidation of sulfides to sulfoxides (68–>95% ee) and is also remarkably general (Table I).

(−)-Camphorsulfonimine **4** is readily prepared in 70% yield by refluxing equivalent amounts (100 mmol) of (+)-camphor and benzenesulfonamide with 0.5 equiv of titanium tetrachloride and 3 equiv of triethylamine in 1,1,2-trichloroethylene for 20 h.[11-13] Treatment of (−)-**4** with 3 equiv of bis(trimethylsilyl)amide (NHMDS) at −78 °C followed by addition of the azaenolate[14] to 3 equiv of *N*-chlorosuccinimide (NCS) gave (−)-**5** in 80% isolated yield.[13] Biphasic oxidation of sulfonimines (−)-**4** and (−)-**5**, with m-CPBA/saturated K_2CO_3 as previously described,[14] gives oxaziridines **3a–b** in 87 and 75% isolated yield, respectively, as single isomers following flash chromatography.[15] While oxidation of **4** to **3a** is complete within 4 h, **5** requires up to 4 days, reflecting the greater steric hindrance of the C–N double bond toward oxidation.



(−)-**4** (−)-**5**

Asymmetric oxidations were carried out by treating equivalent amounts of the sulfide with **3a–b** (typically 0.5–1.0 mmol) as outlined in Table I. The sulfoxides were isolated by preparative TLC, and the optical purities were determined by using Eu(hfc) and as described in Table I. The sulfonimine reduction products (−)-**4** and (−)-**5** were recovered in 80–90% yield and recycled.

(−)-α,α-Dichlorocamphorsulfonyloxaziridine (**3b**) in CCl_4 affords uniformly high stereoselectivities (66–>95% ee) for the asymmetric oxidation of alkyl aryl sulfides (entries 2, 4, 6, 7, and 9), functionalized sulfides (entries 10–13), and for a dialkyl sulfide (entry 14). Significantly, a number of the sulfoxides obtained in very high optical purity (entries 2, 9, 11, 13, and 14) are useful chiral synthons for the synthesis of enantiomerically pure compounds (EPC).[1,2] Oxidation using **3b** in most cases gave higher ee's than the modified Sharpless reagent. Lower ee's were observed for oxaziridine **3a** and for **3b** in CH_2Cl_2.

In 1983 we demonstrated that the configurational lability of the selenoxide moiety is the result of acid-catalyzed achiral hydrate formation.[16,17] For this reason enantiomerically pure *N*-

† The Chemical Abstracts Service name for the title compound (**3b**) is 3,3-dichloro-1,7,7-trimethyl-2′-(phenylsulfonyl)spiro[bicyclo[2.2.1]heptane-2,3′-oxaziridine]. The CAS name for **2a** is tetrahydro-9,9-dimethyl-4*H*-4a,7-methanooxazirino[3,2-*i*][2,1]benzisothiazole 3,3-dioxide.

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(8) For a review on the asymmetric oxidations of *N*-sulfonyloxaziridines, see: Davis, F. A.; Sheppard, A. C. *Tetrahedron*, in press.

(9) Weismiller, M. C., manuscript in preparation.

(10) Glahsl, G.; Herrmann, R. *J. Chem. Soc. Perkin Trans. 1* **1988**, 1753.

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(12) Independently, Jennings and Lovely described a similar method for the synthesis of camphorsulfonimines, see: Jennings, W. B.; Lovely, C. J. *Tetrahedron Lett.* **1988**, 3725.

(13) The sulfonimines isolated by flash chromatography had the following properties: (−)-**4**, mp 92–3 °C (EtOH); $[\alpha]_D^{20}$ −35.8° (*c* 3.0 $CHCl_3$); (−)-**5**, mp 141–2 °C (EtOH); $[\alpha]_D^{20}$ −28.7° (*c* 2.9 $CHCl_3$). All new compounds gave satisfactory elemental analysis.

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(15) Properties of the oxaziridines: **3a**, mp 133–5 °C (EtOH); $[\alpha]_D^{20}$ −198° (*c* 3.0 $CHCl_3$); **3b**, mp 121–2 °C (EtOH); $[\alpha]_D^{20}$ −150° (*c* 4.2 $CHCl_3$).

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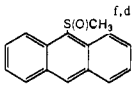
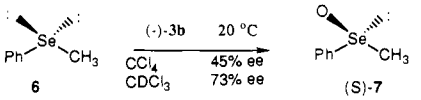
Table I. Asymmetric Oxidation of Prochiral Sulfides to Sulfoxides Using Camphorsulfonyloxaziridine **3** at 20 °C

3a-b + R-S-R′ → R-S(O)-R′ + (-)-**4** or (-)-**5**

entry	sulfoxide	solvent	% ee (configuration) [time (h)] % yield[a] **3a** (X = H)	**3b** (X = Cl)	$[\alpha]^{20}_D$ (in acetone)	modified Sharpless[b]
1	*p*-Tol-S(O)-CH_3[c,d]	CH_2Cl_2	28 (*S*) [1] 80	62 (*S*) [1] 60		96 (*R*)[e]
2		CCl_4	26 (*S*) [40] 22	95 (*S*) [4] 95	-139.0 (*c* 1.6)	
3	*p*-Tol-S(O)-*n*-Bu[f,d]	CH_2Cl_2	11 (*S*) [1] 70	61 (*S*) [1] 90		20 (*R*)[b]
4		CCl_4	8 (*S*) [18] 90	84 (*S*) [3] 90	-162.3 (*c* 3.2)	
5	*p*-Tol-S(O)-*i*-Pr[f,d]	CH_2Cl_2	11 (*S*) [1] 70	54 (*S*) [1] 95		63 (*R*)[b]
6		CCl_4	8 (*S*) [18] 90	66 (*S*) [6] 95	-119.0 (*c* 3.0)	
7		CCl_4	23 (*S*) [40] 23	92 (*S*) [18] 90	-131.6 (*c* 1.1)	95 (*R*)[g]
8		CH_2Cl_2	64 (*S*) [1] 70	95 (*S*) [1] 90	-138.8 (*c* 1.2)	86 (*R*)[g]
9		CCl_4	73 (*S*) [1] 80	95 (*S*) [48] 60		
10	Ph-S(O)-CH=CH_2[d]	CCl_4	21 (*S*) [40] 25	85 (*S*) [48] 60	-262.4 (*c* 1.7)	70 (*R*)[g]
11	Ph-S(O)$CH_2CO_2CH_3$[c,d]	CCl_4	23 (*S*) [40] 18	94 (*S*) [48] 65	-170.0 (*c* 1.5)[h]	64 (*R*)[g]
12	Ph-S(O)$CH_2C(O)CH_3$[c,d]	CCl_4	no reaction	84 (*S*) [48] 52	-183.2 (*c* 1.1)	60 (*R*)[g]
13	Ph-S(O)-CH_2CN[d]	CCl_4	no reaction	>95 (*S*) [48] 45	-170.1 (*c* 1.0)	34 (*R*)[g]
14	$(CH_3)_3C$-S(O)CH_3[c,d]	CCl_4	66 (*S*) [12] 85	94 (*S*) [18] 84	+7.1 (*c* 1.0)[i]	53 (*R*)[b]

[a] Isolated yields. [b] Oxidations at -20 °C for 4-22 h. See ref 6. [c] Ee's determined using Eu(hfc)$_3$. [d] Determined by comparison of the rotation to literature values. [e] Reference 6e. [f] The sulfoxide enantiomers were separated on a Regis Pirkle covalent phenylglycine HPLC column eluting with 95:5 hexane/isopropyl alcohol. The *S*-sulfoxides were the first to be eluted. See ref 4. [g] Reference 6b. [h] In ethanol. [i] In $CHCl_3$.

sulfonyloxaziridines are ideal reagents for the synthesis and study of optically active selenoxides because oxidations can be carried out under anhydrous conditions in the absence of acid.[18] Indeed oxidation of **6** by (-)-**3b** in $CDCl_3$ at 20 °C affords (-)-(*S*)-**7** in 73% ee (95% yield).[20] Oxidation at -60 °C improves the ee to 83%. Interestingly oxidation of **6** by **3b** is faster than methyl *p*-tolyl sulfide (<5 min vs 4 h), and higher ee's were observed in $CDCl_3$ compared to CCl_4.



The stereoselectivities for asymmetric oxidations using enantiomerically pure *N*-sulfonyloxaziridines can be predicted by using steric arguments.[7] However, the uniformly high ee's for a variety of sulfide substrates suggest that factors other than steric are important. The fact that solvent influences the stereoselectivities for asymmetric oxidations with **3b** having polar Cl groups but not for **3a** strongly suggests that electronic or polar elements influence the stereoselectivity. Consistent with this observation are the faster rates of oxidation for **3b** compared to **3a**, despite the fact that the active site in the former is more hindered.

Enantiomerically pure α,α-dichlorocamphorsulfonyloxaziridine (**3b**) is the most effective and generally asymmetric oxidizing reagent developed to date for the asymmetric oxidation of sulfides (selenides) to sulfoxides (selenoxides). Since the configuration of the oxaziridine three-membered ring controls the stereochemistry, both sulfoxide enantiomers are readily available simply by choice of the appropriate oxaziridine. Asymmetric oxidations using (-)-**3b** is now in many cases a viable alternative to the Andersen procedure for the synthesis of enantiomerically pure sulfoxides in both enantiomeric forms.

Acknowledgment. The financial support of the National Science Foundation and the National Institutes of Health (Institute of General Medical Sciences) through Grant GM 34014 are gratefully acknowledged.

Supplementary Material Available: Spectroscopic data and physical constants (yield, mp, IR, and ^{1}H NMR) for **3a**, **3b**, **4**, and **5** (1 page). Ordering information is given on any current masthead page.

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(18) The asymmetric oxidation **6** by **1a** gave **7** in 9% ee.[17] Low to moderate optical properties (18-49% ee) for the asymmetric oxidation of functionalized selenides to selenoxides by a modified Sharpless reagent has been reported.[19]

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(20) The isolation and manipulation of optically active methyl phenyl selenoxide (**7**) is described in ref 17. The specific rotation for (-)(*S*)-**7**, 27% ee, is $[\alpha]_D$ = -8.0° (*c* 0.7, $CDCl_3$) isolated in 50% yield.

The Mode of Triple Phosphoryl Group Transfer in Pyruvate Phosphate Dikinase Catalysis. Demonstration of the Intermediacy of Pyrophosphorylated and Phosphorylated Enzyme Species

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Received March 30, 1989

Pyruvate phosphate dikinase (PPDK)[1] catalyzes the reversible phosphorylation of pyruvate and orthophosphate utilizing the β- and γ-phosphates of a single molecule of ATP.[2] In C_4 plants where PEP serves as the primary acceptor in CO_2 fixation, PPDK

(1) Abbreviations used include the following: PPDK, pyruvate phosphate dikinase; ATP, adenosine 5′-triphosphate; ADP, adenosine 5′-diphosphate; AMP, adenosine 5′-monophosphate; PEP, phosphoenol pyruvate; P_i, orthophosphate; PP_i, pyrophosphate, K^+Hepes, potassium salt of *N*-(2-hydroxyethyl)piperazine-*N*′-2-ethanesulfonic acid; EPP, pyrophosphoryl PPDK; EP, phosphoryl PPDK.

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