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Activation of Oxaziridines by Lewis Acids: Application in Enantioselective Sulfoxidation

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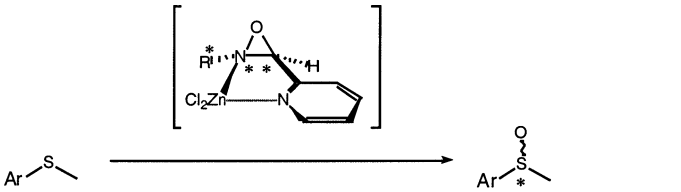
Received September 14, 2004

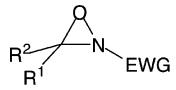


The preparation of new and easily accessible chiral *N*-alkyloxaziridines for asymmetric sulfides oxidation was investigated. Most significantly, we report here that inert *N*-alkyloxaziridines can be activated by Lewis acids to achieve a fast, selective, and efficient oxygen atom transfer to sulfides. Asymmetric sulfoxidation by three new chiral oxaziridines (two of them were structurally characterized by X-ray analysis) afforded enantioselectivities ranging from 22% to 63% ee with the simplest aryl alkyl sulfides.

Introduction

Oxaziridines, characterized by a reactive strained C, N, O three-membered ring, have shown interesting reactivities as nitrogen and oxygen atom transfer reagents since their first isolation in the mid-1950s by three independent groups.[1] It has been established that amino group transfer is the normal reaction of *N*-H, *N*-alkyl, *N*-aryl, *N*-acyl, *N*-carboxyamido, and *N*-alkoxycarbonyl oxaziridines with various nucleophiles such as sulfides, amines, phosphines, and carbanions.[2] However, when the oxaziridine is substituted by bulky[3] or electron-withdrawing[4] substituents on the nitrogen atom or both the nitrogen and the carbon atoms of the three-membered ring (Scheme 1), the electrophilic reactivity is shifted from the nitrogen to the oxygen atom and many oxidations are allowed. For example, amines can be efficiently converted to *N*-hydroxylamines, nitrones, or *N*-oxides and alkenes, selenides, sulfides, and phosphines can be converted to their corresponding oxides, whereas unactivated alkanes can be oxidized to alcohols when the highly reactive perfluorinated oxaziridines are used.[4]

SCHEME 1. Activation of Oxaziridines by Electron-Withdrawing Groups



EWG: Ph_2PO-, F_3C-, R^3SO_2- (R^3: alkyl, amine)

Probably the most commonly used oxaziridines are those developed by Davis and co-workers who reported the use of *N*-sulfonyloxaziridines as the only oxaziridines able to oxidize nucleophilic substrates at rates comparable to peracids.[5] Indeed, these reagents quantitatively oxidize most sulfides to sulfoxides within a few minutes and with high chemioselectivity, avoiding the formation of sulfones as overoxidation products. A valuable extension of oxidations by oxaziridines has been the use of

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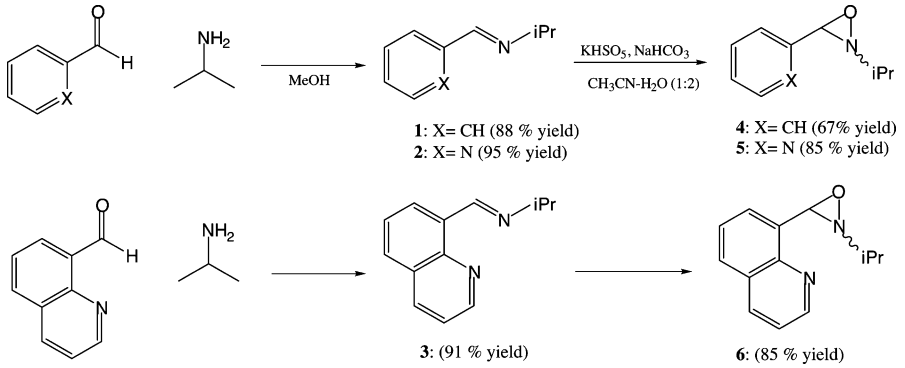
10.1021/jo048380k CCC: $30.25
Published on Web 12/09/2004

SCHEME 2. Synthesis of the Imines 1-3 and of the Corresponding Oxaziridines 4−6



optically active *N*-sulfonyl[5c,6] and sulfamyl[7] oxaziridines and related systems[8] as well as chiral phosphinoyloxaziridines.[9] Although yields for asymmetric sulfoxidations are excellent, enantioselectivities are highly substrate-dependent and usually range from low to moderate ee's and reach a high level only with bulky sulfides. To the exception of the system developed by Page and co-workers using chiral sulfonylimine as a catalyst (10 and 20% mol) and potassium percarbonate as an oxidant, which affords low enantiomeric excesses,[10] all the other reported catalytic asymmetric sulfoxidations are performed with 1 equiv of imine with regard to sulfide.[4] The imine could be recovered nearly quantitatively at the end of the reaction; thus, these reactions qualify as catalytic sulfoxidations even though no catalytic turnovers were reported using substoichiometric quantities of chiral imine.

Oxaziridinium salts, first reported by Lusinchi in 1976, have also been shown to be extremely reactive for oxygen transfer to nucleophilic substrates.[11] Several chiral iminium salts, oxidized in situ by Oxone to the corresponding oxaziridinium salt, have essentially been used as catalysts in asymmetric epoxidations.[12]

The first report of an enantioselective sulfoxidation by an oxaziridinium salt prepared from (+)-norephedrine showed moderate enantioselectivity over the course of the oxidation of methyl *p*-tolyl sulfide to sulfoxide.[12a] It was also demonstrated that oxygen atom transfer from *N*-alkyloxaziridine to sulfides could be promoted by acid.[13] Activation of the oxaziridine was proposed to result from protonation of the basic nitrogen leading to the corresponding oxaziridinium, which was thought to be the active oxidizing species. However, this reaction gives moderate yields and enantiomeric excesses and requires strong acids (trifluoroacetic acid or methanesulfonic acid) generally incompatible with a number of functional groups.

In this paper, we investigated new and easily accessible chiral *N*-alkyloxaziridines for asymmetric sulfoxidation. Most significantly, we show for the first time that inert *N*-alkyloxaziridines can be activated not only by protons but also by general Lewis acids, in particular $ZnCl_2$.

Results

Synthesis of the Oxaziridines 4−6. To investigate the potential of Lewis acids as activating agents of oxaziridines for sulfide oxidation, three oxaziridines, namely 2-isopropyl-3-phen-2-yloxaziridine (**4**),[14] 2-isopropyl-3-pyridin-2-yloxaziridine (**5**), and 2-isopropyl-3-quinolin-8-yloxaziridine (**6**) bearing one or two nitrogens as potential coordinating sites, were synthesized (Scheme 2). They were easily and efficiently prepared in two steps via the formation of the Schiff bases benzylideneisopropylamine (**1**),[15] isopropylpyridin-2-ylmethyleneamine (**2**),[16] and isopropylquinolin-8-ylmethyleneamine (**3**) by condensation of the corresponding aldehydes with isopropylamine in methanolic solution. The oxidation of the resulting imines was then performed using Oxone as oxidant according to the convenient monophasic procedure developed by Yang and co-workers.[17] In all cases, excellent stereoselectivity was achieved leading to only

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TABLE 1. Effect of the Nature of the Lewis Acid and of the Solvent on the Oxidation of Methyl Phenyl Sulfide by 5[a]

Lewis acid	**5**/Lewis acid/ sulfide ratio (mM)	solvent	yield (%) (reaction time[a])	entry
$ZnCl_2$	10:10:100	Et_2O	0[b] (60 min)	1
	10:10:100	acetone	95 (5 min)	2
	10:10:100	CH_3CN	95 (5 min)	3
	10:10:100	$CHCl_3$	98 (5 min)	4
	10: 1:100	$CHCl_3$	45 (1 h)	5
	10:10:100	CCl_4	0[b] (60 min)	6
	10:10:100	EtOH	75 (5 min)	7
BF_3	10:10:100	$CHCl_3$	43 (5 min) (100)[c]	8
	10:10:100	CH_3CN	57 (5 min) (100)[c]	9
	10:10:100	CH_3COCH_3	75 (30 h) (90)[c]	10
$AlCl_3$	10:10:100	$CHCl_3$	80 (3 h)	11
$Ag(O_2CCF_3)$	10:10:100	$CHCl_3$	45 (5 min) (94)[c]	12
	10:10:100	CH_3CN	50 (5 min) (94)[c]	13

[a] Time for maximal conversion. [b] Formation of a precipitate. [c] Recalculated yield (%) based on the consumed oxaziridine.

one diastereoisomer which was then purified by distillation for **4** and by column chromatography on deactivated (Et_3N) silica for **5** and **6**. Due to the high stereoselectivity of the oxidation leading to the formation of single diastereomers, we may assume that all the compounds **4**−**6** have a trans configuration.

Oxidation of Sulfides. Oxidation of methylphenylsulfide by oxaziridines **4**−**6** (10 mM) was then investigated as a probe reaction with 10 equiv of sulfide in chloroform and under air atmosphere. Preliminary studies were carried out with a stoichiometric amount of $ZnCl_2$ with regard to the oxidant, and the results were compared to those obtained from the reaction without $ZnCl_2$. The reaction products were identified and quantified by GC−MS during the course of the reaction. A fast and efficient oxidation was observed with **5** and **6** in the presence of $ZnCl_2$ and resulted in the formation of the sulfoxide (98% yield, 5 min) as the only oxidation product and the release of the precursor imines **2** and **3,** respectively (NMR determination). No sulfone could be detected. When the reaction was carried out with **4** or without $ZnCl_2$ no oxidation occurred, demonstrating the crucial importance of both the heterocyclic aromatic ring and the Lewis acid for the activation of the oxaziridine.

To optimize the oxidation of methylphenylsulfide by **5**, several solvents and Lewis acids were tested under the conditions described above (10:10:100 mM oxaziridine/Lewis acid/substrate ratio; Table 1; entries 1−4, 6−13).

The reactivities of BF_3, $AlCl_3$, $ZnCl_2$, and $Ag(O_2CCF_3)$ were then compared in several solvents (Table 1). Using $ZnCl_2$ as a Lewis acid, most of the solvents tested afforded excellent yields (up to 95%) after only a few minutes except Et_2O and CCl_4, for which a precipitate was observed as soon as $ZnCl_2$ was added to the mixture (entries 1 and 6, respectively). All the Lewis acids allowed the formation of the corresponding sulfoxide with moderate to high yields. $ZnCl_2$ in chloroform proved to be the most efficient reagent, and the reaction was much faster than with the hard $AlCl_3$ Lewis acid (98% yield after 5 min for $ZnCl_2$ (entry 4) as compared to 80% after 3 h for $AlCl_3$ (entry 11)). On the other hand, BF_3 and Ag^+ also afforded high yields (based on measurement of the consumed oxaziridine). However, in both cases, the oxaziridine was not fully consumed at the end of the reaction (entries 8−10, 12, 13).

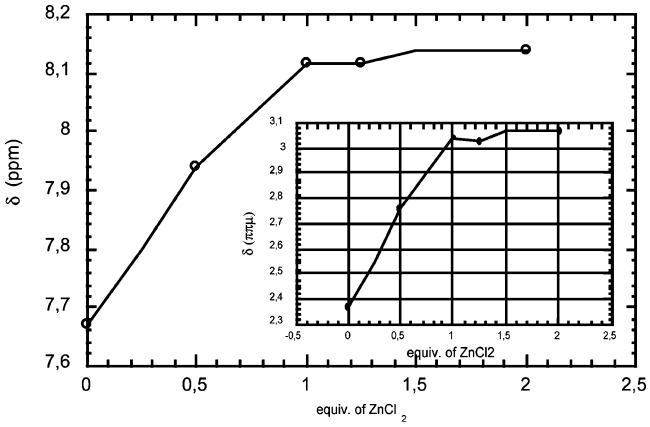

FIGURE 1. Evolution of the chemical shifts of the H_4 of the pyridinyl moiety and the H methine of the isopropyl substituent (inset) of **5** as a function of increasing addition of $ZnCl_2$ to compound **5**.

Determination of the Active Species Involved in the Oxidation. In the following section, we describe experiments aimed at identifying the active species formed during the reaction of $ZnCl_2$ and oxaziridine **5**. ^1H NMR spectroscopy was used to analyze the reaction of increasing amounts of $ZnCl_2$ added to a solution of **5** in $CDCl_3$. Significant shifts in the resonances of a majority of protons could be observed (i.e., from 4.7 to 5.2 ppm for the proton located on the oxaziridine ring and from 7.67 to 8.12 for the H_4 proton of the pyridine ring). It is worth noting that even under substoechiometric conditions a single species could be observed by NMR spectroscopy suggesting a fast equilibrium between **5** and a $ZnCl_2$/**5** adduct. Moreover, the spectrum modification reached its maximum after addition of 1 equiv of $ZnCl_2$ as shown in Figure 1 for the chemical shifts corresponding to H_4 of the pyridinyl substituent and the H methine of the isopropyl moiety. From this, one may conclude the formation of a $ZnCl_2$/**5** adduct of 1:1 stoechiometry.

This hypothesis is also supported by UV spectroscopy experiments. The light absorption spectrum of **5** in chloroform displays a broad band in the 235−280 nm region. Addition of $ZnCl_2$ from 0 to 1.5 equiv by 0.25 equiv portions with regard to **5** resulted in a significant red shift and an increased intensity. The optical changes occurred with an isobestic point (252 nm) indicating the presence of only two species in the solution during the conversion of **5** to the $ZnCl_2$/**5** adduct (Figure 2).

Catalytic Activity of $ZnCl_2$. The catalytic activity of $ZnCl_2$ was then explored during oxidation of the test substrate by **5** (10 mM) in chloroform. With a 1:0.1:10 **5**/$ZnCl_2$/substrate ratio, we observed that $ZnCl_2$ displayed catalytic activity (Table 1, entry 5). However, the reaction rate was greatly decreased (4.5 turnovers in 1 h), and the reaction stopped after formation of 45% of the sulfoxide with regard to the oxidant. We speculate that the reason for this behavior resides in the stronger affinity of the imine **2** (one of the reaction products) for $ZnCl_2$ as compared to **5**. Thus, accumulation of **2** would result in increased scavenging of $ZnCl_2$, within a $ZnCl_2$-(**2**) complex, and consequently, inactivation of the cata-

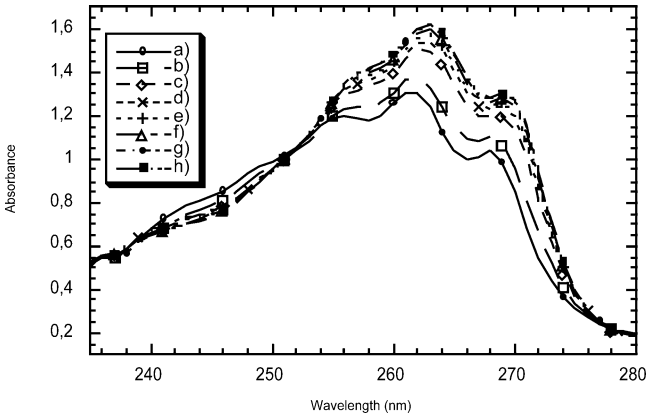

FIGURE 2. Electronic spectra of **5** (0.4 mM, $CHCl_3$) in the presence of (a) 0, (b) 0.25, (c) 0.50, (d) 0.75, (e) 1.00, (f) 1.25, (g) 1.50, (h) 1.75 equiv of $ZnCl_2$.

TABLE 2. Oxidation of a Variety of Sulfides by 5 in the Presence of $ZnCl_2$[a]

R^1-S-R^2		yield (%) (reaction time[b])
R^1	R^2	
4-CH_3O-C_6H_4−	$-CH_3$	97 (5 min)
C_6H_5−	$-CH_3$	98 (1 h)
4-Br−C_6H_4−	$-CH_3$	98 (2 h)
4-NO_2−C_6H_4−	$-CH_3$	81 (5 h)
C_6H_5−	$-CH_2CH_3$	98 (30 min)
C_6H_5−	$-CH_2C_6H_5$	95 (30 min)
naphthyl-	$-CH_3$	87 (30 min)
4-methyldibenzothiophene		14 (1 h)
2-phenyl-1,3-dithiane		98 (5 min)
thianthrene		60 (30 min)

[a] 12:12:10 mM **5**/$ZnCl_2$/substrate ratio in chloroform. [b] Time for maximal conversion.

lyst. The inhibition effect of **2** was confirmed in an experiment using a 1:1:1 **5**/$ZnCl_2$/substrate ratio in the presence of 1 equiv of **2**. Under such conditions, low yield was achieved (34% instead of 85% when the reaction was carried out without any additional imine) with consumption of almost half of **5** (data not shown).

Evidence for the formation of a 1:1 complex between **2** and $ZnCl_2$ was confirmed by X-ray crystallography. Slow evaporation of the solvent from a 1:1 mixture of the imine **2** and $ZnCl_2$ in chloroform resulted in the formation of crystals of a $ZnCl_2$(**2**) complex suitable for X-ray analysis. The structure of the complex, shown in the Supporting Information section, indicates that the zinc binds the two nitrogen atoms of **2** and keeps the two Cl^- ligands. The evidence for the presence of the same complex also in solution was confirmed by positive ESI-MS. Indeed, mass spectrometry analysis of a solution of these crystals in methanol afforded *m/z* fragmentations at 247.1 and 394.8 corresponding to $[ZnCl(\mathbf{2})]^+$and $[ZnCl(\mathbf{2})_2]^+$, respectively.

Oxidation of a Variety of Sulfides by 5. Finally, an optimized procedure for oxidation of sulfides was achieved with small excesses of both **5** and zinc chloride with regard to the substrate (**5**/$ZnCl_2$/sulfide = 12:12:10 mM) in chloroform. Under these conditions, the oxidation of a variety of sulfides was assayed and the results are reported in Table 2. With the exception of the bulky 4-methyldibenzothiophene, the corresponding sulfoxides were obtained in good to excellent yields and with excellent selectivities, since no overoxidation products could be detected. Expectedly, the oxidation of the more nucleophilic sulfides was faster and was nearly quantitative after a few minutes, whereas a few hours were needed for full oxidation of sulfides bearing electron-withdrawing substituents. As an example, 4-methoxyphenyl methyl sulfide was oxidized in 5 min in 97% yield whereas 5 h were needed for its nitro homologue, and in this case, the reaction yield was lower (81%). Moreover, oxidation of disulfides also proceeded with high selectivity with the formation of the mono-oxide as the only product even in the case of the highly reactive 2-phenyl-1,3-dithiane.

Enantioselective Sulfoxidation. The asymmetric version of the above system was investigated using the optically pure (*S*)-1-phenylethylamine as a cheap chiral auxiliary. Condensation of this amine with freshly distilled 2-pyridinecarbaldehyde in refluxing methanol afforded the imine **7** as a single isomer (assumed to be the trans isomer) in excellent yield.[18] Oxidation of **7** was then performed with Oxone as for **4**, **5,** and **6** and resulted in the formation of three diasteroisomers in a 7:28:65 ratio. Column chromatography on deactivated (Et_3N) silica gave the two major isomers **8a** and **8b** in reasonable yields (33% and 55%, respectively). Absolute configuration of the minor isomer **8a** $(C_S-N_S)_{oxa}-C_S$ was determined by X-ray analysis of single crystals obtained by slow evaporation of the solvent from a purified solution of **8a** (Scheme 3; Supporting Information). The absolute configuration of **8b** has not been determined.

Condensation of the chiral amine with 2,2′-dipyridinyl ketone to prepare the imine **9** required more vigorous conditions and was achieved in the presence of $BF_3{\cdot}OEt_2$, as a catalyst, in refluxing toluene using the Dean−Stark apparatus.[19] Oxidation by slow addition of Oxone yielded a unique isomer **10**. After chromatographic purification, the oxaziridine **10** was isolated in good yield (87%). X-ray structural analysis of suitable single-crystal established the absolute configuration of **10** to be $(N_R)_{oxa}-C_S$, (Scheme 3; Supporting Information).

The ability of the chiral oxaziridines **8a**, **8b**, and **10** to carry out enantioselective oxidations was then evaluated during the oxidation of various alkyl aryl sulfides under the conditions described in Table 3 (12:12:10 mM oxaziridine/$ZnCl_2$/substrate ratio in chloroform). After the reaction stopped, most of the solvent was evaporated and the resulting solution was added to a large volume of ether. The resulting precipitate was filtered, extracted with dichloromethane and washed with saturated $NaHCO_3$ aqueous solution to recover, after concentration, the corresponding imines **5** or **7** in good yields (higher than 70%). The sulfoxides present in the etheral solution were purified by column chromatography. The enantiomeric excesses were measured either by chiral HPLC (Pirkle Covalent (*R*,*R*) Whelk-O2) or by ^1H NMR spectroscopy in the presence of 2 equiv of (*R*)-(+)-2,2′-binaphthol as a chiral shift reagent with regard to the isolated sulfoxide.[20] The configurations of the sulfoxides were determined from analogy with the spectroscopic behavior of the (*R*)-

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SCHEME 3. Imines 7 and 9 and Related Oxaziridines 8a and 10

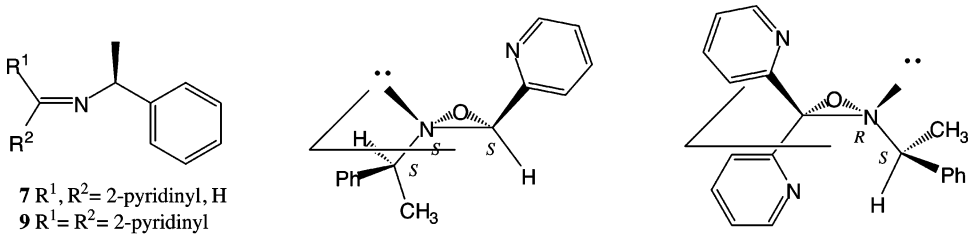


TABLE 3. Asymmetric Oxidation of Aryl Alkyl Sulfides[a]

R^1-S-R^2		8a		8b		10	
R^1	R^2	yield (%)	ee[b] (config)[c]	yield (%)	ee[b] (config)[c]	yield (%)	ee[b] (config)[c]
4-CH_3O-C_6H_4−	$-CH_3$	75	37 (*S*)	69	39 (*R*)	85	33 (*R*)
C_6H_5−	$-CH_3$	45	32 (*S*)	53	31 (*R*)	55	42 (*R*)
4-Br-C_6H_4−	$-CH_3$	40	42 (*S*)	38	43 (*R*)	41	48 (*R*)
2-Br-C_6H_4−	$-CH_3$	35	22 (*S*)[e]	31	46 (*R*)[e]	33	50 (*R*)[e]
4-NO_2-C_6H_4−	$-CH_3$	23	33 (*S*)	25	32 (*R*)	30	55 (*R*)
C_6H_5−	$-CH_2C_6H_5$	55	42[d]	50	56[b]	60	63[b]
naphthyl−	$-CH_3$	29	53 (*S*)	33	60 (*R*)	52	58 (*R*)

[a] Oxaziridine/$ZnCl_2$/substrate ratio = 12:12:10 mM in chloroform. [b] ee's were determined by NMR spectroscopy using (*R*)-(+)-2,2′-binaphthol as chiral shift reagent. [c] See ref 21. [d] Absolute configuration not determined. [e] ee determination by chiral HPLC.

methyl phenyl sulfoxide in the presence of the (*R*)-(+)-2,2′-binaphthol.[21] In most cases, absolute configuration was confirmed by chiral HPLC by comparison with optically pure commercially available samples.

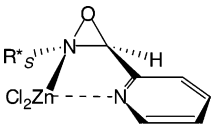
The results are reported in Table 3. They show that despite lower yields (ranging from 23 to 85%) and longer reaction times (more than 3 h for completion) than those observed for the less hindered oxaziridine **5**, low to good enantiomeric excesses were obtained. Interestingly, the enantioselectivity does not depend on the absolute configuration of the methylbenzyl moiety but on that of the oxaziridine ring as shown with **8a** and **8b** which afforded the *S* and *R* sulfoxide enantiomer as the major product, respectively. As observed for **5**, the rates of oxidation of sulfides having electron-attracting groups were also smaller in agreement with a S_N2 mechanism (data not shown).[22] One may also note the positive effect of the presence of an additional pyridinyl group (**10** compared to **8a**,**b**) affording better yields and enantiomeric excesses in most cases.

Under the conditions described, no sulfone were formed, which indicated that the enantioselectivities were a direct result of the asymmetric sulfide oxidation and not of a kinetic resolution by overoxidation of the resulting sulfoxide.

Discussion

It is now admitted that the oxygen atom transfer from an oxaziridine to sulfides involves an S_N2-type displacement of the imine by the nucleophile.[23] Consequently introduction of electron-withdrawing groups on the nitrogen atom increases the electrophilic nature of the oxygen atom and thus its reactivity. This is generally

SCHEME 4. Activation of Oxaziridines by $ZnCl_2$



achieved with sulfonyl, sulfamyl, phosphinoyl, or trifluoromethyl substituents.[4–9] Activation by formation of oxaziridinium salts has also proven its efficiency for such reactions.[10,12] In this paper, we now demonstrate that Lewis acids, different from H^+, also have the potential to activate the oxaziridine ring for sulfide oxidation. However,when using the most efficient Lewis acid $ZnCl_2$, a heteroaromatic (i.e., pyridin-2-yl or quinolin-8-yl) substituent must be present since no reaction take place when these groups are replaced by a phenyl one. This suggests that, in the presence of a pyridinyl moiety acting as an additional metal-complexing site, an active 1:1 oxaziridine/$ZnCl_2$ adduct is formed. Formation of a complex, such as that shown in Scheme 4, would explain the activation of the oxaziridine. Indeed, coordination of the Lewis acid by the nitrogen atom of the oxaziridine ring increases the electron deficiency of the oxygen atom and thus its electrophilic character. One may also note that no difference in reactivity (yield and rate) was observed when pyridin-2-yl or quinolin-8-yl, responsible for the formation of a five- or a six-membered chelate ring, respectively, in the activated state, was used as a substituent.

The involvement of such a complex is supported by (i) the changes of the UV−vis and NMR spectra of the oxaziridine during addition of $ZnCl_2$ (Figures 1 and 2) and (ii) the crystal structure of the imine **2**/$ZnCl_2$ adduct which demonstrates chelation by the two nitrogen atoms.

Except with low polarity solvents such as diethyl ether and CCl_4 in which the oxaziridine/$ZnCl_2$ adduct is not soluble, the sulfoxidation is weakly affected by the nature of the solvent. Indeed, whatever the solvent used, high yields were achieved within a few minutes. However, one may note the lower yield (75%) obtained in ethanol which

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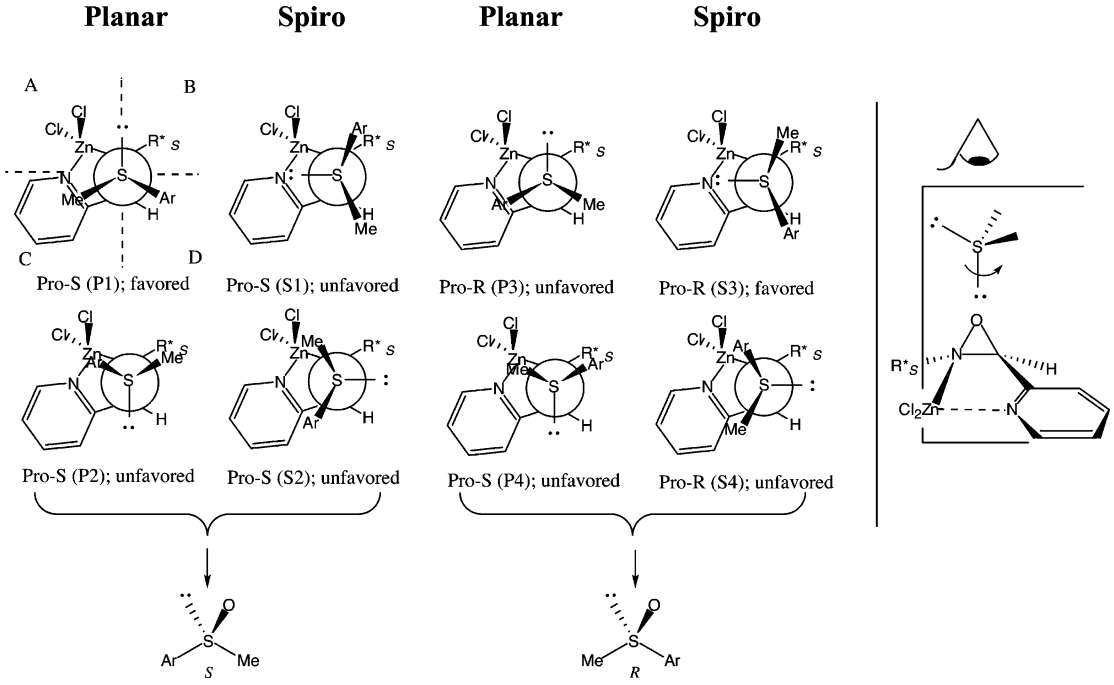
SCHEME 5. Hypothetical Transition States Involved in the Enantioselective Oxidation of Alkyl Aryl Sulfides by Oxaziridine 8a Activated by $ZnCl_2$[a]



[a] These are Newman-like representations in which the S and O atoms are superimposed.

could be attributed to a weaker oxaziridine−$ZnCl_2$ association in protic solvents.

In view of the efficiency of the $ZnCl_2$/oxaziridine system toward sulfide oxidation, the asymmetric induction of various chiral oxaziridines and the catalytic activity of $ZnCl_2$ were investigated.

As observed for asymmetric oxidations using enantiopure *N*-sulfonyloxaziridines, the product stereochemistry in the reaction reported here is controlled by the configuration of the oxaziridine three-membered ring with steric factors being responsible for the chiral recognition.[6b,23a] It was established that oxygen transfer from oxaziridine to sulfide can proceed through two possible transition states, planar and spiro.[24] In the planar state, both electron pairs on the sulfur atom are in the plane containing the oxaziridine ring. In contrast, in the spiro one, the plane containing the two electron pairs is perpendicular to this plane. With the constraint of its $(C_S-N_S)_{oxa}$ configuration of the oxaziridine ring, the eight possible transition states in the case of the oxaziridine **8a** are depicted in Scheme 5. The pro-*S* (P1) and the pro-*R* (S3) arrangements are clearly the most sterically favorable ones since the aryl group of the sulfide is on the less hindered quadrant D, away from the three large groups of the oxaziridine. However, P1 and S3 differ from each other regarding the relative position of the sulfide methyl group and the oxaziridine pyridinyl group, with less steric hindrance in the case of S3. From this analysis, the (*S*) sulfoxide should be formed predominantely which is in agreement with the experimental results.

Consequently, increasing the difference in size of the two substituents of the sulfide should result in a better asymmetric induction. This was indeed observed when the aryl group varied from phenyl to naphthyl (32% to 53% ee for **8a**, 31% to 60% ee for **8b**, 42% to 58% ee for **10**). This effect was defined by Davis and co-workers as the group size difference (GSD) effect.[7,12b,25] On the basis of this effect transposed to the oxaziridine, one should expect better stereoselectivities with **8a** as compared to **10** which enjoys a greater topological symmetry. This, in fact, was not the case except for 4-methoxyphenyl methyl sulfide. A closer look at the interactions between the substituents ($\pi-\pi$ stacking, steric interactions, approach of the sulfide controlled by the Lewis acid, ...) should allow a better understanding of the reaction mechanism implying such oxaziridines.

The sulfoxidation by the reported oxaziridines goes with the parallel formation of the corresponding imine which undoubtedly is a stronger Lewis base than the oxaziridine. Consequently, both bases compete for $ZnCl_2$, and the equilibria are shifted toward the formation of the more stable imine−$ZnCl_2$ adduct as the reaction progresses since the concentration of the imine formed increases and that of the unreacted oxaziridine decreases. The strong affinity of the imine **2** for $ZnCl_2$ has been demonstrated and the crystal structure of the complex obtained. Furthermore, inhibition of sulfoxidation by the imine has been shown when the reaction was carried out in the presence of the imine. On the other hand, it is noticeable that, under standard conditions, the reaction is nearly quantitative within a few minutes, suggesting that the oxygen atom transfer from the oxaziridine−$ZnCl_2$ adduct is a very efficient reaction and proceeds likely with a high rate constant. Finally, this inhibitory effect is probably at the origin of the limitation we encountered to make the system catalytic in $ZnCl_2$. Even though we clearly demonstrated the possibility of using

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$ZnCl_2$ as a catalyst with regard to the oxaziridine, the reaction stopped after a few turnovers. In designing a catalytic system, we will need to solve this competition problem.

Conclusion

It is well-known that oxaziridines can be activated by an electron-withdrawing group covalently bound to the nitrogen atom and used as reagents for sulfides oxidation. In this paper, we describe a novel, simple, and general mechanism for activation of oxaziridines. We demonstrate that oxaziridines, easily accessible in two steps from inexpensive starting material, are able to transfer their oxygen atom to sulfides efficiently, simply upon addition of a Lewis acid such as $ZnCl_2$. Asymmetric sulfoxidation by three new chiral oxaziridines (two of them were structurally characterized by X-ray analysis) afforded enantioselectivities ranging from 22% to 63% ee with the simplest alkyl aryl sulfides in moderate to good yields. We are fully aware that the enantioselectivities obtained by the described system are not yet optimized. However, we draw attention to the fact that (i) this is the first example of Lewis acid-promoted oxidation of sulfides by oxaziridines, (ii) the level of asymmetric induction is in the upper range of that reported with other oxaziridines, and (iii) it is likely that new oxaziridines, with stronger asymmetric induction groups, will provide larger ees, thus improving the system. This aspect is currently being investigated in our laboratory.

Experimental Section

Benzylideneisopropylamine (1).[15] Under a nitrogen atmosphere, a solution of isopropylamine (700 mg; 11.9 mmol) in methanol (50 mL) was added for 15 min to a solution of freshly distilled benzaldehyde (1.08 g; 10.2 mmol) in methanol (100 mL) cooled to 0 °C. The resulting clear solution was stirred for another 1 h at room temperature. Concentration in vacuo afforded the crude product as a yellow oil. Distillation under reduce pressure (bp = 75 °C; 25 mbar) afforded **1** as a colorless oil (1.32 g; 8.98 mmol; 88%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.29 (s, 1H); 7.73−7.68 (m, 2H); 7.40−7.34 (m, 3H); 3.52 (hept, 1H, J = 6.3 Hz); 1.25 (d, 6H, J = 6.3 Hz). ^{13}C NMR (76 MHz, $CDCl_3$) δ: 158,0.0 (CH); 136.3 (C); 130.2 (CH); 128.3 (CH); 127.9 (CH); 61.5 (CH); 24.0 (CH_3). IR: 3062, 3027, 2968, 2930, 2850, 1648, 1451, 1383, 1397, 1142, 968, 756, 694 cm^{-1}. ESI-MS: *m/z* 148.1 (100) $[1 + H]^+$.

Isopropylpyridin-2-ylmethyleneamine (2).[16] Under a nitrogen atmosphere, a solution of isopropylamine (650 mg; 10.5 mmol) in methanol (50 mL) was added over 1 h to a solution of freshly distilled 2-pyridincarboxaldehyde (1.07 g; 10.0 mmol) in methanol (100 mL) cooled to 0 °C. The resulting yellow solution was stirred for 1 h at room temperature. After concentration in vacuo, the crude yellow oil residue was distilled under reduce pressure (bp = 90 °C; 33 mbar) yielding the imine as a pale yellow oil (1.41 g; 9.52 mmol; 95%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.59 (ddd, 1H, J = 4.8, 1.5, 1.1 Hz); 8.36 (s, 1H); 7.94 (ddd, 1H, J = 7.8, 1.2, 1.1 Hz); 7.67 (ddd, 1H, J = 7.8, 7.8, 1.5 Hz); 7.24 (ddd, 1H, J = 7.8, 4.8, 1.2 Hz); 3.59 (q, 1H, J = 6.3 Hz); 1.23 (d, 6H, J = 6.3 Hz). ^{13}C NMR (76 MHz, $CDCl_3$) δ: 159.2 (CH); 154.8 (C); 149.3 (CH); 136.4 (CH); 124.4 (CH); 121.3 (CH); 61.3 (CH); 23.9 (CH_3). IR: 3055, 3009, 2969, 2926, 2863, 1647, 1588, 1567, 1467, 1140, 974, 775 cm^{-1}. ESI-MS, *m/z*: 149.1 (100) $[\mathbf{2} + H]^+$; 171.0 (45) $[\mathbf{2} + Na]^+$; 203.0 (15) $[\mathbf{2} + Na + MeOH]^+$.

Crystallographic data for the $ZnCl_2$(**2**) complex: orthorhombic, $P2(1)2(1)2(1)$, a = 7.1662(14) Å, b = 7.6325(15) Å, c = 23.207(5) Å, V = 1269.3(4) Å^3, Z = 4, R = 0.0956, R_w = 0.1703.

Isopropylquinolin-8-ylmethylenamine (3). Under a nitrogen atmosphere, a solution of isopropylamine (250 mg; 4.04 mmol) in methanol (50 mL) was added over 1 h to a solution of freshly distilled 8-quinolinecarboxaldehyde[26] (576 mg; 3,67 mmol) in methanol (100 mL) cooled to 0 °C. The resulting yellow solution was stirred for 1 h at room temperature. After concentration in vacuo, the crude yellow oil residue was purified by silica gel column chromatography (ethyl acetate/hexane = 3/7) and **3** was obtained as a colorless oil (574 mg; 3.34 mmol; 91%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.64 (s, 1H); 8.93 (dd, 1H, J = 3.9, 1.8 Hz); 8.40 (dd, 1H, J = 7.5, 1.5 Hz); 8.16 (dd, 1H, J = 8.4, 1.8 Hz); 7.86 (dd, 1H, J = 8.1, 1.5 Hz); 7.59 (dd, 1H, J = 8.1, 7.5 Hz); 7.42 (dd, 1H, J = 8.4, 3.9 Hz); 3.76 (hept, 1H, J = 6.3 Hz); 1.31 (d, 6H, J = 6.3 Hz). ^{13}C NMR (76 MHz, $CDCl_3$) δ: 156.3 (CH); 149.9 (CH); 146.6 (C); 136.4 (CH); 133.3 (C); 130.1 (CH); 128.2 (C); 127.7 (CH); 126.5 (CH); 121.2 (CH); 61.9 (CH); 24.2 (2 CH_3). IR: 1635 cm^{-1}. ESI-MS, *m/z*: 261.1 (100) $[\mathbf{3}+H]^+$; 284.1 $[\mathbf{3} + Na]^+$. Anal. Calcd for $C_{13}H_{14}N_2$: C, 78.75; H, 7.12; N, 14.13. Found: C, 79.08; H, 7.15; N, 14.21.

2-Isopropyl-3-phenyloxaziridine (4).[14] To a solution of **1** (850 mg; 5.8 mmol) in acetonitrile (50 mL), cooled at 0 °C, were successively added a solution of $NaHCO_3$ (1.94 g; 23.1 mmol) in water (50 mL) at 0 °C and for 15 min a solution of $KHSO_5$ (5.33 g; 8.7 mmol) in water (50 mL). The colorless solution was vigorously stirred. After 45 min, the product was extracted with $CHCl_3$ (4 × 20 mL). The organic layer was dried over Na_2SO_4, and the solvent was removed under vacuo to afford **4** as a colorless oil. The oxaziridine was distillated under reduced pressure (bp = 80 °C; 25 mbar) to yield a colorless oil (792 mg; 4.9 mmol; 84%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.44−7.34 (m, 5H); 4.48 (s, 1H); 2.34 (hept, 1H, J = 6.3 Hz); 1.31 (d, 3H, J = 6.3 Hz); 1.16 (d, 3H, J = 6.3 Hz). ^{13}C NMR (76 MHz, $CDCl_3$) δ: 135.1 (C); 129.9 (CH); 128.4 (CH); 127.4 (CH); 80.0 (CH); 62.6 (CH); 21.2 (CH_3); 18.9 (CH_3). IR: 3068, 3036, 2972, 2931, 2876, 1461, 1312, 1161, 879, 856, 756, cm^{-1}. ESI-MS, *m/z*: 185.9 (100) $[\mathbf{4} + Na]^+$.

2-Isopropyl-3-pyridin-2-yloxaziridine (5). A solution of **2** (850 mg; 5,74 mmol) in acetonitrile (50 mL) was cooled to 0 °C. To this vigorously stirred colorless solution were successively added a solution of $NaHCO_3$ (1.93 g; 23.00 mmol) in water (50 mL) cooled to 0 °C and, over 10 min, a solution of $KHSO_5$ (5.30 g; 8.61 mmol) in water (50 mL) at 0 °C. After extraction with $CHCl_3$, the solution was dried over Na_2SO_4 and concentrated under vacuo to give a colorless oil. Purification by silica gel column chromatography (ethyl acetate/hexane = 2/8) previously treated with Et_3N afforded **5** as a colorless oil (800 mg; 4.88 mmol; 85%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.49 (ddd, 1H, J = 4.8, 1.8, 1.2 Hz); 7.61 (ddd, 1H, J = 7.8, 7.8, 1.8 Hz); 7.27 (ddd, 1H, J = 7.8, 1.2, 1.2 Hz); 7.21 (ddd, 1H, J = 7.8, 4.8, 1.2 Hz); 4.62 (s, 1H); 2.32 (q, 1H, J = 6.3 Hz); 1.24 (d, 3H, J = 6.3 Hz); 1.11 (d, 3H, J = 6.3 Hz). ^{13}C NMR (76 MHz, $CDCl_3$) δ: 154.9 (C); 148.9 (CH); 136.7 (CH); 124.4 (CH); 121.2 (CH); 80.0 (CH); 62.5 (CH); 21.1 (CH_3); 18.7 (CH_3). IR: 3061, 3013, 2974, 2933, 2881, 1593, 1573, 1465, 1439, 1383, 1368, 1163, 862, 772 cm^{-1}. ESI-MS, *m/z*: 186.9 (100) $[\mathbf{5} + Na]^+$. Anal. Calcd for $C_9H_{12}N_2O$: C, 65.83; H, 7.37; N, 17.06. Found: C, 65.90; H, 7.41; N, 17.02.

2-Isopropyl-3-(quinolin-8-yl)oxaziridine (6). A solution of the imine **3** (396 mg, 1.0 mmol) in acetonitrile (25 mL) was to cooled to 0 °C, and then a solution of $NaHCO_3$ (336 mg, 4 mmol) in water (25 mL) was successively added at 0 °C followed by a solution of $KHSO_5$ (862 mg, 1.4 mmol) in water (25 mL) over 15 min. The colorless solution was vigorously stirred for 45 min. The product was extracted with $CHCl_3$ (4 × 20 mL), and the organic layer was dried over Na_2SO_4. The solvent was removed under vacuo to afford **6** as colorless oil. The crude residue was purified by silica gel column chromatography (ethyl acetate/hexane = 3/7), and **6** was obtained as a colorless oil (182 mg, 0.85 mmol, 85%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.92 (dd, 1H, J = 4.2, 1.5 Hz); 8.15 (dd, 1H, J = 8.4, 1.5 Hz); 7.81 (dd, 1H J = 8.1, 1.2 Hz); 7.73 (dd, 1H, J = 7.5, 1.2 Hz); 7.53 (dd, 1H, J = 8.1, 7.5 Hz); 7.42 (dd, 1H, J =

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8.4, 4.2 Hz); 2.57 (hept, 1H, J = 6.3 Hz); 1.35 (d, 3H, J = 6.3 Hz, 3H); 1.30 (d, 3H, J = 6.3 Hz). ^{13}C NMR (76 MHz, $CDCl_3$) δ: 150.0 (CH); 147.3 (C); 136.1 (CH); 133.1 (C); 128.9 (CH); 127.8 (C); 127.2 (CH); 126.4 (CH); 121.3 (CH); 76.9 (CH); 62.7 (CH); 21.4 (CH_3); 18.9 (CH_3). IR: 3037, 2972, 2932, 2877, 1596, 1583, 1503, 1468, 1361, 1261, 1232, 1159, 884, 822, 792, 765, 627. ESI-MS, *m/z*: 277.1 (45) [**6** + H]$^+$; 260.1 (100) [**6** − OH]$^+$. Anal. Calcd for $C_{13}H_{14}N_2$: C, 72.87; H, 6.59; N, 13.07; O, 7.47. Found: C, 72.95; H, 6.61; N, 12.98.

(1-Phenylethyl)[2]pyridinylmethyleneamine (7). Under a nitrogen atmosphere, a solution of 1(*S*)-phenylethylamine (1.14 g; 9.43 mmol) in methanol (20 mL) was added over 30 min to a cooled (0 °C) solution of freshly distilled 2-pyridinecarboxaldehyde (1.11 g; 10.4 mmol) in methanol (75 mL). The resulting yellow solution was stirred for an additional 1 h at room temperature. Concentration in vacuo afforded the crude product as a yellow oil. The oxaziridine was purified by silica gel column chromatography (ethyl acetate/hexane = 2/8) previously treated with Et_3N, and **7**was obtained as a yellow oil (1.72 g; 8.19 mmol; 87%). $[\alpha]^{25}_D$: +85 (c 0.6, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.29 (s, 1H); 8.60 (ddd, 1H, J = 4.8, 1.5, 0.9 Hz); 8.45 (s, 1H); 8.08 (dd, 1H, J = 7.8, 0.9 Hz); 7.74 (ddd, 1H, J = 7.8, 7.5, 1.5 Hz); 7.42 (d, 2H, J = 7.2 Hz); 7.33 (dd, 2H, J = 7.2, 7.2 Hz); 7.27 (ddd, 1H, J = 7.5, 1.2, 1.2 Hz); 7.25 (t, 1H, J = 7.2 Hz); 4.63 (q, 1H, J = 6.6 Hz); 1.60 (d, 3H, J = 6.6 Hz). ^{13}C NMR (76 MHz, $CDCl_3$) δ: 160.4 (CH); 154.7 (C); 149.2 (CH); 144.5 (C); 136.5 (CH); 128.4 (CH); 127.0 (CH); 126.6 (CH); 124.7 (CH); 121.4 (CH); 69.5 (CH); 24.4 (CH_3). IR: 3060, 3028, 2972, 2927, 2862, 1647, 1568, 1468, 1371, 968, 763, 700 cm^{-1}. ESI-MS, *m/z*: 233.1 (40) [**7** + Na]$^+$; 224.1 (100) [(**7**)$_2$ + Na]$^+$.

3-Pyridinyl-2-(1-méthylbenzyl)oxaziridine (8). To a vigorously stirred solution of **7** (336 mg; 1.6 mmol) in acetonitrile (20 mL) cooled to 0 °C were successively added a solution of $NaHCO_3$ (538 mg; 6.4 mmol) in water (20 mL) and, over 30 min, a solution of $KHSO_5$ (1.47 g; 2.39 mmol) in water (20 mL). After extraction with $CHCl_3$ the solution was dried over Na_2SO_4 and concentrated in vacuo. The crude product was obtained as a yellow oil containing three stereoisomers (1:4:9.3 ratio). Silica gel chromatographic purification using chromatotron apparatus (ethyl acetate/hexane = 15/85) previously treated with Et_3N afforded **8a** as a colorless solid (128 mg, 35%) and **8b** as a colorless oil (160 mg, 50%). **8a**. $[\alpha]^{25}_D$: +59 (*c* 0.5, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.59 (ddd, 1H, J = 4.8, 1.5, 0.9 Hz); 7,70 (ddd, 1H, J = 7.5, 7.5, 1.8 Hz); 7.60 (m, 2H); 7.37 (m, 3H); 7.28−7.34 (m, 2H); 4.85 (s, 1H); 3.42 (q, 1H, J = 6.9 Hz); 1.53 (d, 3H, J = 6.9 Hz). ^{13}C NMR (76 MHz, $CDCl_3$) δ: 154.8 (C); 149.0 (CH); 141.6 (C); 136.9 (CH); 128.5 (CH); 127.6 (CH); 127.0 (CH); 124.6 (CH); 121.5 (CH); 80.5 (CH); 70.3 (CH); 19.5 (CH_3). IR: 3062, 3029, 2979, 2932, 1593, 1572, 1439, 1390, 1083, 995, 776, 698 cm^{-1}. Crystallographic data: orthorombic, *P*2(1)2(1)2(1), a = 15.139(3) Å, b = 7.9773(16) Å, c = 10.163(2) Å, V = 1227.4(4) Å^3, Z = 4, R = 0.0492, R_w = 0.0887. **8b.** $[\alpha]^{25}_D$: −38 (*c* 0.5, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.48 (ddd, 1H, J = 4.8, 1.5, 0.9 Hz); 7.65 (ddd, 1H, J = 7.5, 1.8, 1.8 Hz); 7.5−7.2 (m, 7H); 4.81 (s, 1H); 3.34 (q, 1H, J = 6.3 Hz); 1.66 (d, 3H, J = 6.3 Hz). ^{13}C NMR (76 MHz, $CDCl_3$) δ: 154.6 (C); 149.0 (CH); 139.5 (C); 136.8 (CH); 128.7 (CH); 128.0 (CH); 127.3 (CH); 124.5 (CH); 121.5 (CH); 80.4 (CH); 71.2 (CH); 21.5 (CH_3). IR: 3062, 3029, 2979, 2932, 1593, 1572, 1439, 1390, 1083, 995, 776, 698 cm^{-1}. ESI-MS *m/z*: 209.2 (100) [**8b** − H]$^+$; 227.0 (15) [**8b** + H]$^+$; 248.9 (22) [**8b** + Na]$^+$; 444.1 (55) [(**8b**)$_2$ + Na]$^+$. Anal. Calcd for $C_{14}H_{14}N_2O$: C, 74.31; H, 6.24; N, 12.38. Found: C, 74.28; H, 6.30; N, 12.39.

(1-Phenylethyl)[2]bispyridinylmethyleneamine (9). Under a nitrogen atmosphere, a solution of 2,2-dipyridinyl ketone (368.4 mg; 2.0 mmol), 1(*S*)-phenylethylamine (262 mg; 2.0 mmol), and boron trifluoride diethyl etherate (30 μL; 0.24 mmol) in toluene (25 mL) was refluxed for 24 h using Dean−Stark apparatus. The resulting orange solution was concentrated in vacuo yielding the crude product as an orange oil. The residue was purified by silica gel column chromatography (ethyl acetate/hexane = 3/7) previously treated with Et_3N and **9** was obtained as pale yellow crystals (471 mg; 1.64 mmol; 82%). $[\alpha]^{25}_D$: −5 (*c* 0.19, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.74 (d, 1H, J = 4.8 Hz); 8.48 (d, 1H, J = 4.8 Hz); 8.29 (d, 1H, J = 8.1 Hz); 7.75 (ddd, 1H, J = 15.6, 7.5, 1.8 Hz); 7.40−7.10 (m, 9H); 4.58 (q, 1H, J = 6.3 Hz); 1.53 (d, 3H, J = 6.3 Hz). ^{13}C NMR (76 MHz, $CDCl_3$) δ: 164.9 (C); 157.2 (C); 155.6 (C); 149.7 (CH); 148.7 (CH); 145.2 (CH); 136.3 (CH); 135.9 (CH); 126.7 (CH); 126.6 (CH); 124.0 (CH); 124.0 (CH); 123.4 (CH); 123.0 (CH); 122.5 (CH); 61.4 (CH); 24.5 (CH_3). IR: 3061, 3029, 2979, 2932, 1590, 1571, 1437, 1387, 991, 772, 698 cm^{-1}. ESI-MS *m/z*: 288.0 (100) [**9** + H]$^+$; 310.1 (45) [**9** + Na]$^+$; 596.8 (45) [(**9**)$_2$ + Na]$^+$. Anal. Calcd for $C_{19}H_{17}N_3$: C, 79.41; H, 5.96; N, 14.62. Found: C, 79.36; H, 6.01; N, 14.63.

3,3-Bispyridinyl-2-(1-methylbenzyl)oxaziridine (10). To a solution of **9** (240 mg; 836 μmol) in acetonitrile (20 mL), cooled to 0 °C, were successively added a solution of $NaHCO_3$ (281 mg; 3.35 mmol) in water (10 mL) and, over a 1 h period, a solution of $KHSO_5$ (770 mg; 1.25 mmol) in water (20 mL). The resulting solution was vigorously stirred for completion for an additional 1 h at room temperature. After extraction with $CHCl_3$, the organic layer was dried over Na_2SO_4 and the solvent was evaporated to afford a pale yellow oil. The crude product was obtained as a yellow oil. Purification by silica gel (previously treated with Et_3N) chromatography using chromatotron apparatus (ethyl acetate/hexane = 3/7) yielded **10** as a colorless oil (200 mg, 660 μmol, 79%). $[\alpha]^{25}_D$: +10 (*c* 0.10, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.50−8.44 (m, 2H); 7.73 (ddd, 1H, J = 7.8, 7.8, 1.8 Hz); 7.70−7.68 (m, 1H); 7.67 (ddd, 1H, J = 7.8, 7.8, 1.8 Hz); 7.58 (ddd, 1H, J = 7.8, 1.2, 0.9 Hz); 7.28 (ddd, 1H, J = 7.5, 4.8, 1.2 Hz); 7.23−7.18 (m, 3H); 7.17 (ddd, 1H, J = 6.3, 4.8, 2.7 Hz); 6.97−6.91 (m, 2H); 3.27 (q, 1H, J = 6.3 Hz); 1.62 (d, 3H, J = 6.3 Hz). ^{13}C NMR (76 MHz, $CDCl_3$) δ: 157.4 (C); 153.8 (C); 149.0 (CH); 148.9 (CH); 139.9 (C); 136.7 (CH); 135.7 (CH); 128.3 (CH); 127.7 (CH); 127.2 (CH); 124.4 (CH); 123.7 (CH); 123.6 (CH); 122.6 (CH); 86.6 (C); 63.2 (CH); 22.9 (CH_3). IR: 3061, 3029, 2973, 2931, 1641, 1570, 1442, 1390, 975, 765, 697 cm^{-1}. ESI-MS *m/z*: 286.2 (100) [**10** − H]$^+$; 325.9 (10) [**10** + Na]$^+$. Anal. Calcd for $C_{19}H_{17}N_3O$: C, 75.23; H, 5.65; N, 13.85. Found: C, 75.27; H, 5.61; N, 13.90. Crystallographic data: orthorombic, *P*2(1)2(1)2(1) a = 8.0723(16) Å, b = 12.111(2) Å, c = 34.684(7) Å, V = 3391.0(12) Å^3, Z = 8, R = 0.0462, R_w = 0.0825.

Standard Conditions for Sulfoxidation Were As Follows: To a solution of the oxaziridine (100 μmol) in 8.3 mL of solvent were successively added sulfide (83 μmol) and Lewis acid (100 μmol) (1.2:1.2:1 oxaziridine/Lewis acid/sulfide ratio). An internal standard (30 μL of a 1 M solution of benzophenone or fluorenone in toluene) was added to the reaction mixture. The characterization of the sulfoxides was done by GC−MS. Unambiguous identification of the products was made by comparison with pure compounds, which were either prepared independently or commercially available. All the sulfoxides were isolated by column chromatography on silica gel (ethyl acetate/hexane = 20/80 then 80/20). The enantiomeric excesses were determined by ^{1}H NMR in $CDCl_3$ for the purified products as follows: 1−2 equiv of (*R*)-(+)-2,2′-binaphthol were added by small portions until a good splitting of the CH_3 singlet (between 2.7 and 3.0 ppm) was obtained.[21] The ee was calculated from the deconvolution of these two peaks.

Acknowledgment. We are grateful to the "Ministère Français de la Recherche et de la Technologie" for an "ACI Jeunes Chercheurs 2000" grant. We also thank C. Lebrun (DRFMC, CEA-Grenoble) for the ES-MS analysis.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra of all the compounds excepted **1** and **4** and X-ray crystallographic data for the $ZnCl_2$(**2**) complex, **8a**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO048380K