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ASYMMETRIC SYNTHESIS AND STEREOCHEMICAL PROPERTIES OF OPTICALLY ACTIVE N-SULPHONYL-3-ARYLOXAZIRIDINES

MARIA BUCCIARELLI, ARRIGO FORNI, SERGIO MARCACCIOLI, IRENE MORETTI and GIOVANNI TORRE*
Istituto di Chimica Organica, via Campi 183, Università, 41100 Modena, Italy

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Abstract—Oxidation of prochiral sulphonimines ($RSO_2N=CHAr$) with (1S)-(+)-PCA, followed by fractional crystallization of the crude reaction products, provides highly optically-pure N-sulphonyl-3-aryloxaziridines ^1H NMR spectra recorded in the presence of chiral solvent or shift reagent, CD spectra, and the results observed by using them as new chiral oxidizing reagents, are also reported.

The synthesis and the structure of racemic N-sulphonyl-3-aryloxaziridines have been recently described by Davis *et al.*[1] In particular it was reported that these compounds can be obtained by oxidation of the corresponding sulphonimines with m-chloroperoxybenzoic acid, m-CPBA, under basic conditions.[1] This reaction is highly stereoselective and, starting from rapidly equilibrating *cis–trans* mixtures of sulphonimines, one obtains only the E diastereoisomer, stable at the pyramidal nitrogen of the oxazirane ring.[1] Optically-active examples of this new family of oxaziridines have been also obtained, as 66:33 mixtures of E 2(d-camphor-10-sulphonyl)-3-aryloxaziridine diastereoisomers, by oxidation of the corresponding chiral sulphonimines with the achiral m-CPBA.[2]

N-sulphonyloxaziridines contain a highly electrophilic oxygen atom,[3] and can be used as models to study the reaction of the oxazirane ring with nucleophilic reagents,[4] or to mimic complex oxygen-transfer processes.[5] Both these properties of the oxaziridines are receiving increasing attention from chemical[6] as well as biochemical[7] directions. It is therefore surprising that no attempt has been made until now in order to obtain optically active N-sulphonyloxaziridines by oxidation of the corresponding prochiral sulphonimines with chiral peroxyacids, i.e. by means of the reaction which is known to represent the most immediate and general way for asymmetric synthesis of N-alkyloxaziridines.[8,9] In this communication we report the stereochemical and chiroptical properties of highly optically pure enantiomers of type **2**, obtained by oxidation of the sulphonimines **1** with (1S)-(+)-peroxycamphoric acid, (+)-PCA **3**, under basic conditions (KOH; pH 9–10) and in CH_2Cl_2–CH_3OH solution (Scheme 1).

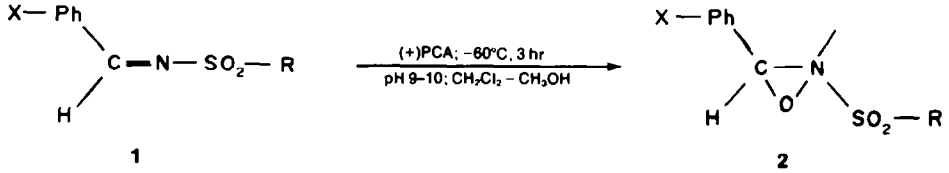
RESULTS AND DISCUSSION

The N-sulphonyl-3-aryloxaziridines **2** (90–95% yield) are crystalline solids and all show negative sign of optical activity. The ^1H NMR spectra of these compounds are characterized by a sharp singlet at δ 5.4–5.6 to be attributable to the resonance of the 3-H proton, and are consistent with the finding that oxidation of imines of type **1** is stereoselective and causes the formation of only the E-diastereoisomer **2**.[1] Highly optically pure E (−)-**2a**, (−)-**2b**, (−)-**2c** oxaziridines could be easily isolated by fractional crystallization to constant rotation of the crude reaction products. The rotatory powers and the NMR data of (−)-**2** enantiomers are reported in Table 1.

Relative ^1H NMR chemical shift difference and enantiomeric purity of (−)-2

^1H NMR spectra of enantiomerically enriched (−)-**2** were also recorded in the presence of (R)-(−)-2,2,2-trifluoro-1-(1-naphthyl)-ethanol **4** chiral solvating agent, and in the presence of chiral tris-[3-(heptafluoropropylhydroxymethylene)-d-camphorato]-europium (III), d-$Eu(fhc)_3$ **5** as shift reagent. The results reported in Table 2 show that both techniques can be used to distinguish the NMR signals of enantiotopic groups of oxaziridines of type **2**.

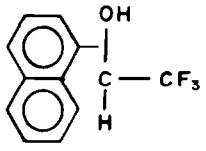
The NMR spectra of partially resolved (−)-**2** derivatives, when recorded in the presence of (R)-**4**, show chemical shift doubling in correspondence of the 3-H signals of **2a** and **2b**. The shift differences are not so high to allow accurate determination of enantiomeric purity, but are sufficient to clearly indicate that the 3-H proton of (−)-**2a** and (−)-**2b** resonates at *lower* (L) field than the enantiotopic proton of (+)-**2a** and (+)-**2b**. In



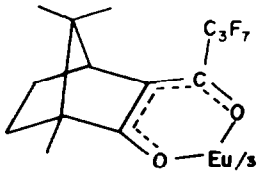
1 **2**

a: R = Me; X = H
b: R = Ph; X = H
c: R = Ph; X = p-Me

Scheme 1.



(R)-(-) 4



d-Eu(fhc)$_3$ 5

the presence of d-Eu(fhc)$_3$ **5**, the 3-H proton of both (−)-**2a** and (−)-**2b**, as well as (−)-**2c** oxaziridine, resonates at *higher* (H) field with respect to 3-H of (+)-**2**. Moreover, spectral non-equivalence with opposite *low* (L) "sense" of shift difference, is observed also in correspondence of the NMR signals of the SO_2CH_3 protons of **2a**. In all these cases, at the d-Eu(fhc)$_3$ concentration indicated, the peak separation corresponding to the signals of the enantiotopic groups, are sufficient to permit accurate integration of the resolved resonances. Taking into account the routine accuracy of the NMR technique (± 2%) comparison of the maximum optical values observed (Table 1) and calculated (Table 2) indicate that (−)-**2** oxaziridines are more than 95% optically pure.

Stereochemical properties of (−)-**2**

A check of the stereochemical properties of (−)-**2** was effected by using these compounds as chiral reagents for asymmetric oxidations of prochiral methyl-**6** and t-butyl phenyl sulphide **7**, carried out at −50° and in CH_2Cl_2. The optical activities of the corresponding sulphoxides **8** and **9**, recovered in 85–90% yield, are reported in Table 3.

Methyl phenyl sulphoxide **8** with (+)-(R) configuration has been obtained in oxidations carried out with (−)-**2b** and (−)-**2c** oxaziridines, whereas attempts to induce asymmetric synthesis of the same sulphoxide with (−)-**2a** have failed. On the contrary, oxidation of the t-butyl

Ph-S-R	Ph-SO-R
6: R = Me	**8**: R = Me
7: R = Bu^t	**9**: R = Bu^t

Table 1. Properties of optically active N-sulfonyl-3-aryloxaziridines **2**

Oxaziridine			$[\alpha]_D^{20}$ [a]	$[\alpha]_D^{20}$ [b]	NMR (δ) [f]		
	R	X					
2,a	Me	H	-32.0°	-191.0° [c]	3.2 (s,3H)	5.5 (s,1H)	7.4-7.5 (m,5H)
2,b	Ph	H	-25.4	-130.8 [d]		5.5 (s,1H)	7.4-8.1 (m,10H)
2,c	Ph	Me	-19.1	-117.2 [e]	2.4 (s,3H)	5.5 (s,1H	7.1-8.1 (m,9H)

[a] Optical activities of the reaction crude products (c 1-2, $CHCl_3$). [b] Optical activities of (-) **2** obtained by fractional crystallization to costant rotation of the reaction crude products. [c] M.p. 72-73 °C (racemate, m.p. 59-60 °C). [d] M.p. 60-61 °C (racemate m.p. 94-95 °C). [e] M.p. 98-99 °C (racemate m.p. 87-88 °C). [f] $CDCl_3$ solution, Me_4Si as internal standard.

Table 2. NMR nonequivalence and enantiomeric excess of optically active oxaziridines **2**, observed in the presence of (*R*)-(−) **4** solvent, or d-Eu(fhc)$_3$ **5** shift reagent

Oxaziridine			(R)-(-) **4**			d-Eu(fhc)$_3$ **5**					
			nonequivalence, [a] Hz [b]/sense [c]			$[\alpha]_D^{20}$ [d]	e.e. [e] %	$[\alpha]_D^{20}$ [f]	nonequivalence, [g] Hz [b]/sense [c]		
	R	X	H	R	X				H	R	X
2,a	Me	H	1.2/L	O	-	-129.9°	69	-188.3°	3.6/H	6.6/L	-
2,b	Ph	H	0.6/L	-	-	- 66.4	52	-127.7	9.5/H	-	-
2,c	Ph	Me	0	-	O	- 50.5	44	-114.8	5.6/H	-	O

[a] Nonequivalence was caused by adding *ca.* a 2-fold excess of (R)-(-) **4** to a dilute $CDCl_3$ solution of optically active **2**. [b] At 200 MHz and 20 °C. [c] H refers to highfield sense, and L to lowfield sense, relative to (-) **2** enantiomers. [d] Optical activities in $CHCl_3$ solution of enantiomerically enriched (-) **2**. [e] Enantiomeric excess determined from NMR spectra. [f] Maxima optical values calculated. [g] Nonequivalence observed in $CDCl_3$ solution *ca.* 0.04 M in shift reagent and 0.1 M in the **2** substrate.

Table 3. Asymmetric oxidation of methyl-6 and t-butyl-7 phenyl sulfides with (−) 2[a]

Oxaziridine		PhSOMe 8			PhSOBu[t] 9		
	% optical purity [b]	$[\alpha]_D^{20}$ [c]	% optical yield [d]	Absolute Configurat.	$[\alpha]_D^{20}$ [e]	% optical yield [f]	Absolute Configurat.
(−) 2,a	92	0 °	-	-	-4.9°	2.8	(S)
(−) 2,b	76	+4.6	3.1	(R)	-3.5	2.0	(S)
(−) 2,c	50	+3.1	2.1	(R)	-2.8	1.6	(S)

[a] In CH_2Cl_2 at -50 °C. [b] Based on the maxima optical values of Table 1. [c] c 5, ETOH. [d] Based on the value +146.2° (ETOH) reported in ref. 25. [e] c 4, $CHCl_3$. [f] Based on the value -174.6° ($CHCl_3$) reported in ref. 25.

derivative 7 provided in every case optically active sulphoxide 9 with the opposite (−)-(S) configuration to that of the methyl 8 derivative. The values of the optical yields of 8 and 9 (2–5%), indicate that the asymmetric bias for oxidations using 2 was not high. Nevertheless, both the qualitative and quantitative aspects of these asymmetric oxidations (Table 3) can be compared with the results obtained in similar reactions using chiral peroxyacids,[10] and this, if added to the fact that asymmetric oxidation of prochiral sulphonimines 1 with (+) or (−)-PCA represents a very simple and economical way to obtain highly optically pure E-N-sulphonyl-3-aryloxaziridines, suggests that these new chiral oxidizing reagents will be of utility for synthetic purposes, and for studies in biochemical as well as pharmacoligical field.

Moreover, optically active 8 and 9 sulphoxides of relatively low optical purity and with the opposite configuration at sulphur (+)-(R) and (−)-(S), respectively, have been obtained in other asymmetric oxidations of 6 and 7 performed with mixtures of (−)-N-sulphonyloxaziridine diastereoisomers carrying the asymmetric d-camphor-10-sulphonyl substituent at the ring nitrogen.[2] The correspondence of all these results suggests that the stereochemical and mechanistic aspects of the asymmetric oxidation of prochiral sulphides with optically active N-sulphonyloxaziridines should be independent on the nature of the R substituent at the SO_2 group. It is therefore likely that studies of this type, when carried out with chiral N-sulphonyloxaziridines of well established absolute configuration, will be valuable not only to indicate stereochemical correlations models of large applicability, but also to find clues toward understanding of the mechanistic details of the sulphide to sulphoxide oxidation by N-sulphonyloxaziridines.

Chiroptical properties of (−)-2

In Figs. 1–3 are depicted the UV and CD spectra of (−)-2 oxaziridines, recorded in isooctane solution. The corresponding numerical data, together with the UV and CD values in methanol, are summarized in Table 4. In the 200–300 nm spectral region, the UV spectra of 2 show only the typical ^1L_b and ^1L_a transitions of the benzene chromophore,[11] with vibrational structure at 250–280 nm (^1L_b transition) and maxima at 215 or 222–226 nm (^1L_a transition). This trend is consistent with the transparent character of the sulphonyl group in the region of the spectrum we are considering,[12] and with the report that the oxaziridine chromophore exhibits a first absorption maximum of low intensity (ϵ 100–200) at 200–210 nm.[13]

The CD spectra of Figs. 1–3 indicate that the electronic transitions of the benzene chromophore, or

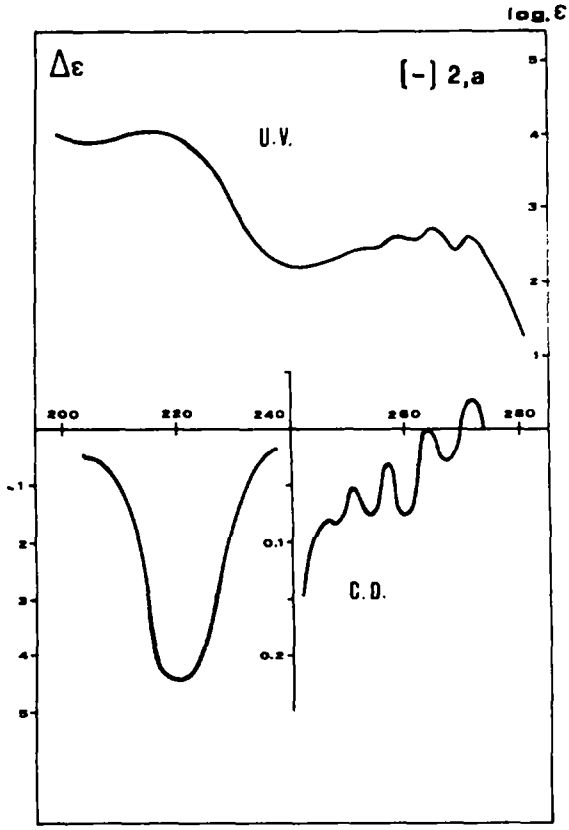


Fig. 1.

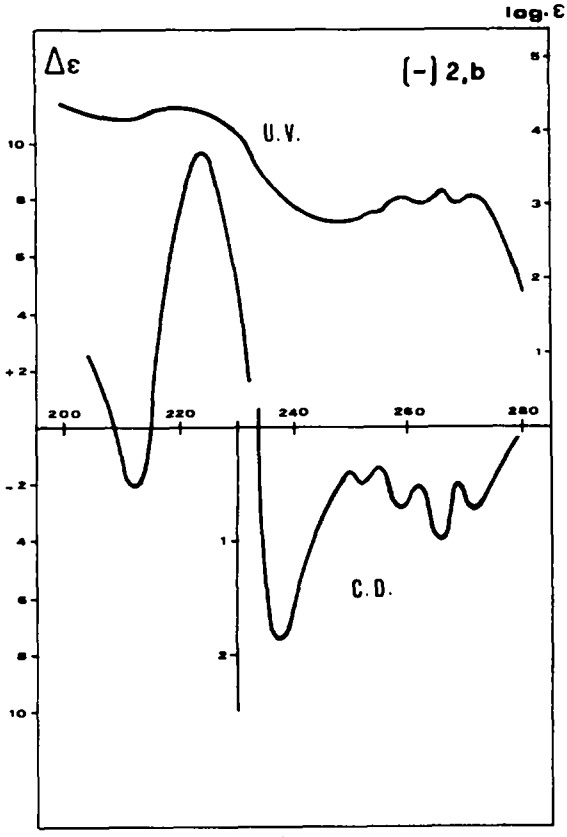


Fig. 2.

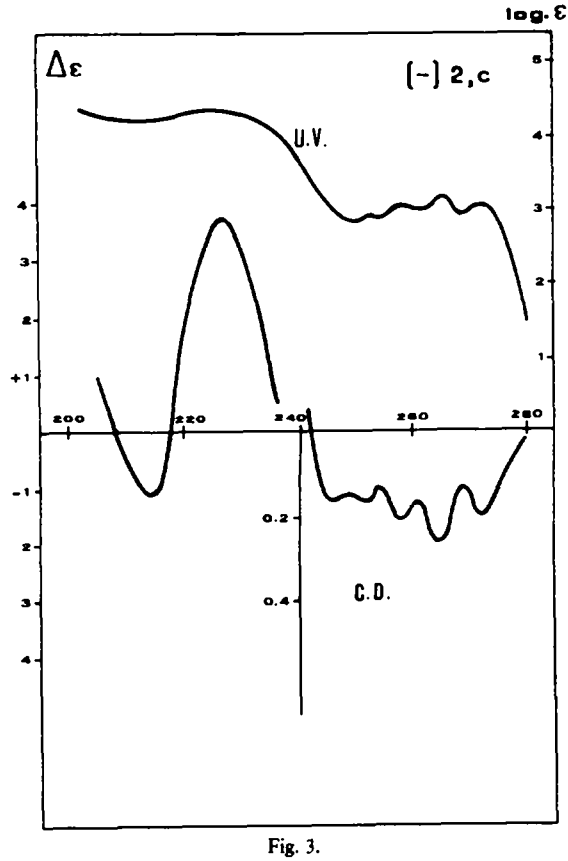


Fig. 3.

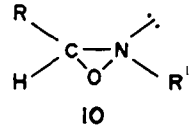
Figs. 1-3. UV and CD spectra of (−)-**2a**, (−)-**2b** and (−)-**2c** oxaziridines in isooctane.

chromophores of (−)-**2**, are optically active. The corresponding data of Table 4 show that the chiroptical properties of chiral N-sulphonyl-3-aryloxaziridines are not dependent on the nature of the solvent. On the contrary, these properties depend on the *alkyl* or *aryl* nature of the R substituent at the SO_2 group. In particular, the CD spectra of (−)-**2a**, which carries the SO_2CH_3 substituent at the ring nitrogen, are consistent with the chiroptical behaviour of a chiral benzenoid compound containing an asymmetrically perturbed isolated phenyl group,[14] and are characterized by a complex system of positive and negative bands of low intensity, and by a stronger negative Cotton effect, centered in correspondence of the ^1L_b and ^1L_a electronic transitions of the benzene chromophore, respectively (Fig. 1). The chiroptical properties of the *trans*-diphenyl **2b** and **2c** derivatives are relevant with the properties of chiral compounds which contain two benzene chromophores not-conjugated, but sufficiently close together to couple.[14] The CD spectra of these two compounds (Figs. 2 and 3), clearly reveal multiple negative Cotton effects in the 250–280 nm range, and a system of two strong bands of opposite, positive and negative, sign corresponding to a well definite maximum in the UV absorption (^1L_a band). This last trend represents the main feature of the CD behaviour of chiral N-phenylsulphonyl-3-aryloxaziridines, and suggests the existence of exciton optical activity.[15]

The CD spectra of (−)-**2** reveal another electronic transition in the 230–245 nm, i.e. in a spectral region which is noticeably distant from any absorption maximum. The position and the intensity of this optically active transition is rather indistinct in the CD spectra of (−)-**2a** and (−)-**2c**, probably owing to overlap and cancellation effects of the adjacent bands, whereas it is much more characterized in the corresponding spectra of (−)-**2b**. The origin of this optically active band is uncertain. However, it is worth to point out that the high value of the differential dichroic absorption of this transition, as it can be supposed from the $\Delta\epsilon$ of (−)-**2b** at 237 nm in isooctane ($\Delta\epsilon$ −1.86), and the lack of corresponding evidence in the isotropic absorption, are relevant to the nature of the first transition of the optically active oxaziridine chromophore of chiral 2,3,3-trialkyloxaziridines, as it has been described by recent experimental and theoretical work.[16]

Absolute stereochemistry of **2**

At present, configurational analysis of chiral N-sulphonyloxaziridines of type **2** represents a complex undertaking, owing to lack of investigations in this field. In particular, the limited knowledge on the relative importance of the electronic and steric effects of the sulphonyl substituent on the stereochemical behaviour of systems **1** and **2**, prevents any attempt to apply with confidence to our compounds the same configurational correlations observed for oxaziridines of type **10**, i.e. for N-alkyl derivatives of established absolute configuration, and structurally very similar to E-2.[19]



10

a: R = Ph; R' = Me, Bu^t
b: R = (*p*)Br-Ph; R' = CH(Me)Ph

Table 4. Chiroptical properties of (−)-2 oxaziridines in isooctane and methanol

Compd.	Solvent [a]		UV and CD maxima: λnm(ε or Δε)							
(−) 2,a	I	UV	271(430)		265(520)	259(430)	254(300)			216(10.500)
		CD	272(0.03)	267(−0.03)	264(0)	260(−0.07)	254(−0.07)	247(−0.08)		220(−4.44)
	M	UV	271(450)		265(550)	259(460)	254(360)			217(9.840)
		CD	272(0.07)	267(−0.03)	264(0.03)	260(−0.09)	254(−0.12)	248(−0.15)		220(−11.5)
(−) 2,b	I	UV	272(1.340)		266(1.660)	259(1.250)	254(820)			222(21.090)
		CD	272(−0.72)		266(−0.99)	259(−0.72)	252(−0.49)	237(−1.86)		223(9.70) 213(−2.19)
	M	UV	272(1.570)		266(1.940)	259(1.570)	253(1.200)			222(22.500)
		CD	272(−0.48)		266(−0.66)	259(−0.49)	252(−0.25)	240(−0.52)		226(6.93) 213(−5.74)
(−) 2,c	I	UV	273(1.200)		266(1.480)	258(1.150)	253(860)			226(22.800)
		CD	273(−0.20)		265(−0.26)	258(−0.21)	253(−0.16)	246(−0.16)		227(3.76) 215(−1.11)
	M	UV	274(1.320)		266(1.620)	260(1.390)	253(1.150)			227(24.100)
		CD	272(−0.65)		265(−0.80)	258(−0.67)	253(−0.36)			231(6.37) 218(−9.55)

[a] I (isooctane), M (methanol).

On the other hand, any configurational investigation of chiral **2**, which is based on theoretical approaches to the chiroptical properties of these compounds, need more knowledge than we presently have on the nature of the electronic transitions of the N-sulphonyl-3-ayloxaziridine chromophoric system, or on the factors which may control the mechanisms of the optical activity of the phenyl chromophore of **2a**, (one electron, dipole coupling, or electric-magnetic coupling, mechanisms),[14,22] and of the two phenyl rings of **2b**, and **2c** (exciton coupling mechanisms.[15,22] In this respect, more detailed experimental work and calculations are now in progress in order to put on a quantitative basis the contribution of the theoretical mechanisms to the optical acitivity of chiral 2 derivatives.

EXPERIMENTAL

Melting points are uncorrected. NMR spectra were recorded in $CDCl_3$ solution (Me_4Si as internal standard) on a JEOL JNM-C-60HL or Varian XL-200 instrument. UV spectra were measured with a Perkin–Elmer Coleman 515 spectrometer. CD spectra were obtained with a JASCO J-500A dichrograph.

Chiral (R) 2,2,2-trifluoro-1-(1-napthyl)ethanol **4**, b.p. 160° at 2 mmHg, $[\alpha]_D^{25}$ −21.1° (c 3.0, ethanol) {lit[23] m.p. 51.6–53.2°, $[\alpha]_D^{25}$ −25.7° (ethanol)} was obtained by reduction of the corresponding ketone by actively fermenting yeast.[24] Chiral tris-[3-(heptafluoropropylhydroxymethylene)-d-camphorato]-europium (III), d-Eu(fhc)$_3$ **5**, shift reagent, was purchased from Aldrich, and used without further purification.

Starting materials. Sulphonimines **1** were obtained in 80–90% yield as described in the literature.[1] They show the following properties. **1a** m.p. 91–92°, NMR ($CDCl_3$): δ 3.3 (s, 3H), 7.9 (m, 5H), 9.2 (s, 1H) {lit[1] m.p. 90–92°, NMR ($CDCl_3$): 3.0 (s, 3H), 7.4 (m, 3H), 7.7 (m, 2H), 8.85 (s, 1H)}; **1b** m.p. 75–76°, NMR ($CDCl_3$) σ 7.8 (m, 10H), 9.1 (s, 1H); **1c** m.p. 128–130°, NMR ($CDCl_3$) σ 2.7 (s, 3H), 7.8 (m, 9H), 9.2 (s, 1H). (1S)-(+)-peroxycamphoric acid **3** was prepared as recently described by Pirkle and Rinaldi.[25]

General synthesis of oxaziridines **2**. In a 250-ml three-necked flask equipped with mechanical stirrer and dropping funnel, were placed 10 mmol of **1** in 30 ml of CH_2Cl_2 and 30 ml of CH_3OH. This solution was cooled at −60° and added in few minutes of a solution of (+) **3** (11 mmol) in 10 ml of CH_2Cl_2 and 20 ml of CH_3OH, made alkaline (pH 9–10) with methanolic KOH. The reaction medium was maintained at −60° and pH 9–10 for additional 3 h, afterwards it was diluted with water and extracted with CH_2Cl_2. The CH_2Cl_2 extracts were washed with aqueous $NaHCO_3$, water and dried over Na_2SO_4. After the solution was dried, the solvent was removed on the rotatory evaporator keeping the bath temperature at 20–25°. The crude products of the reaction were recovered as optically active, negative solids (90–95% yield). Fractional crystallization to constant rotation (from ethyl ether) of the crude products of the reaction afforded in every case highly optically active (−)-**2** oxaziridines. The properties of (−)-E-N-sulphonyl-3-aryloxaziridines **2** prepared in this way are reported in Table 1.

Asymmetric oxidations of methyl phenyl and t-butyl phenyl sulphide with optically active **2**. A CH_2Cl_2 solution of (−)-**2** (1 mmol) was dropped into a cooled solution of methyl phenyl sulphide **6** (1 mmol) or of t-butyl phenyl sulphide **7** (1 mmol) in CH_2Cl_2, with the temperature maintained at −50° until the oxaziridine oxidant had disappeared (TLC on silica, CH_2Cl_2 elution solvent). At the end of the reaction, the solvent was evaporated off and the crude products were separated by preparative TLC (silica, CH_2Cl_2 elution solvent).

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[16]Experimentally, optically active N-alkyl and N-benzyl-oxaziridines of established (S) configuration at the nitrogen atom, and derived by oxidation of (−) camphorimines, show a clear positive Cotton effect ($\Delta\epsilon$ *ca* 1) in the 200–210 nm region, and in correspondence of weak inflection points at about 210 nm in the UV spectra.[17] SCF-CI calculations support the finding that the oxaziridine chromophore of 2,3,3-trialkyloxaziridines with (S)-absolute configuration at nitrogen, has positive CD for its first transition. The nature of this transition is best described as a mixed-valence Rydberg $\pi^*_{NO} \longrightarrow (\delta^*_{NO}, 3s_N)$ transition.[18]
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