132 mg) was used. The title product (11) was recrystallized from methanol: 65% yield (165 mg); mp 216–218 °C; IR 3250 (br), 1700, 1365, 895, 750, 680 cm^{-1}; NMR (CF_3COOH) δ 7.8 (m). Anal. Calcd for $C_{32}H_{22}N_2O_4$: C, 77.09; H, 4.45; N, 5.62. Found: C, 76.79; H, 4.41; N, 5.82.

2-Phenacylidene-3-methyl-1*H*-quinoxaline 4-Oxide (13a). 2-Benzoyl-3-methylquinoxaline 4-oxide (14, 1.12 g) was dissolved in ethanol (40 mL). Acetophenone (0.6 g) was added, and the mixture was brought to boiling on a steam bath. Methanolic potassium hydroxide (10%, 5 mL) was added, and the mixture was allowed to cool to room temperature. After dilution with water and extraction with chloroform, the concentrated solution was subjected to thick-layer chromatography. Repeated chromatography (benzene) gave the title product (13a) as an orange-yellow solid which was recrystallized from benzene–methanol: 20% yield (0.22 g); mp 167–169 °C; IR (KBr) 1580, 1335, 745 cm^{-1}; NMR ($CDCl_3$) δ 15.9 (br s 1 H), 8.4 (m, 1 H), 7.9 (m, 2 H), 7.5 (m, 6 H), 6.3 (s, 1 H), 2.7 (s, 3 H). Anal. Calcd for $C_{17}H_{14}N_2O_2$: C, 73.36; H, 5.07; N, 10.07. Found: C, 73.04; H, 5.21; N, 9.96.

Product **13a** was obtained in 4% yield from the reaction of 2-methylquinoxaline 1,4-dioxide (1; 176 mg, 1 mmol) and acetophenone (145 mg, 1.2 mmol) in methanolic KOH solution (10 mL of 5% KOH solution). After the solution was heated on a steam bath for 5 min, the solution was cooled, acidified with HCl, and extracted with C_6H_6. The product was isolated by TLC (silica gel, C_6H_6–CH_3OH, 25:1). The product (10 mg) was recrystallized from CH_3OH–H_2O and found to be identical with **13a** (mixture melting point, IR, and NMR).

Cleavage of 7 to 13a. The application of 7 (210 mg) on an alumina (Merck, grade II) column and elution with C_6H_6–CH_3OH (98:2) gave product **13a** (40 mg, 60%). A similar result was obtained when a benzene–methanol (95:5) solution of 7 was stirred in a slurry of alumina in benzene. The reaction is accompanied by a color change from red to yellow-orange.

2-Phenacylidene-3-phenyl-1*H*-quinoxaline 4-Oxide (13b) and 2-Phenacylidene-3-phenyl-1*H*-quinoxaline (16). 2-Phenylquinoxaline 1,4-dioxide (4; 120 mg, 0.5 mmol) and acetophenone (100 mg, 0.8 mmol) were dissolved in methanol (10 mL). Methanol potassium hydroxide (10%, 3 mL) was added. The dark red mixture was heated at the reflux temperature of methanol for a few minutes. Water was added to the mixture until incipient crystallization. Product **13b** was collected and recrystallized from methanol: red needles; 75 mg (45%); mp 184–185 °C; IR 3400 (vw), 3050, 1580 (br), 1485, 1350 (s), 1300, 1100, 1070, 1020, 760, 690 cm^{-1}; NMR ($CDCl_3$) δ 15.9 (br s, 1 H), 8.5 (m, 1 H), 7.6 (m, 13 H), 5.9 (s, 1 H).

Product **13b** (75 mg, 0.2 mmol) was dissolved in hot methanol (20 mL). Sodium dithionite (200 mg in 3 mL of water) was added dropwise. The reaction mixture turned yellow and was heated for an additional 5 min. Thereafter it was diluted with water and extracted with $CHCl_3$. Evaporation of $CHCl_3$ and recrystallization of the residue from methanol gave orange crystals of **16**: 40 mg (70%); mp 161–163 °C. A mixture melting point determination with a sample prepared from *o*-phenylenediamine and dibenzoylacetylene showed no depression: IR 3040, 1570 (br), 1540, 1350, 1275, 740, 685 cm^{-1}.

1,3-Diphenylphenazine (18). 2-Benzoyl-3-methylquinoxaline (17; 0.5 g, 2 mmol) was dissolved in methanol (20 mL). Acetophenone (0.3 g, 2.5 mmol) was added. Potassium hydroxide (0.5 g) was added, and the mixture was heated at reflux temperature for 0.5 h. Upon concentration of the mixture and cooling, the yellowish orange product crystallized out (140 mg). Recrystallization from $CHCl_3$–CH_3OH gave purified product: 100 mg (15%); mp 167–168 °C; IR 3050, 1395, 1130, 750, 690 cm^{-1}; NMR ($CDCl_3$) δ 8.5 (d, 1 H), 8.3 (m, 3 H), 7.5–7.9 (m, 14 H). Anal. Calcd for $C_{24}H_{16}N_2$: C, 86.72; H, 4.85; N, 8.43. Found: C, 86.84; H, 4.89; N, 8.46.

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Registry No. 1, 6639-86-7; 2, 18080-49-4; 3, 65896-77-7; 4, 5023-53-0; 5, 6449-86-1; 6, 1087-09-8; 7, 80765-45-3; 8, 80780-61-6; 9, 80765-46-4; 10, 80765-47-5; 11, 80765-48-6; 13a, 80765-49-7; 13b, 80765-50-0; 14, 19803-53-3; 16, 57436-88-1; 17, 22239-97-0; 18, 80765-51-1.

Chemistry of Oxaziridines. 2.[1] Improved Synthesis of 2-Sulfonyloxaziridines

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2-Sulfonyloxaziridines **2** are a new class of stable, aprotic, and neutral oxidizing reagents of considerable synthetic and mechanistic versatility.[1] These reagents oxidize sulfides and disulfides to sulfoxides and thiosulfinates, respectively,[2] epoxidize olefins in a syn-stereospecific manner,[3] and hydroxylate carbanions.[4,5] Chiral 2-sulfonyloxaziridines afford optically active sulfoxides[6] and have been used in the chiral synthesis of (+)-kjellmanianone.[5] Recently the application of these reagents to the preparation and study of sulfenic acids (RSOH), a biologically important functional group, has been reported.[7-9] In this paper we describe an improved method for the preparation of these oxidizing reagents using phase-transfer catalysts.

The general preparation of 2-sulfonyloxaziridines **2** as developed in our laboratories is outlined in Scheme I.[1] An alkane- or arenesulfonamide (RSO_2NH_2) is heated with the diethyl acetal of an aromatic aldehyde to give sulfonimine **1**.[1] Oxidation of **1** to **2** utilizes biphasic conditions and involves the addition of a 2.2-fold excess of *m*-chloroperbenzoic acid (MCPBA) in chloroform to a rapidly stirring solution of **1** in chloroform–water–10% sodium bicarbonate at 0 °C.[1] After a reaction time of 4–5 h the yields of **2** were in the range of 43–70%, depending on substituents.

A Baeyer–Villiger-type mechanism has been proposed for the oxidation of **1** to **2** involving attack of the peroxy acid anion (RCO_3^-) on the electron-deficient C–N bond of the sulfonimine **1**.[1] The principal limitation of the oxidation procedure outlined in Scheme I appears to be in bringing the hydrophobic sulfonimine, dissolved in the organic phase, together efficiently with the hydrophilic peroxy acid anion, dissolved in the aqueous phase. Competing with this reaction is hydrolysis of **1** to the sulfonamide and aldehyde.

It was thought that a lipophilic phase-transfer catalyst (PTC) such as benzyltriethylammonium chloride (BTEAC) might increase the efficiency of the oxidation reaction while minimizing hydrolysis. Indeed, the yield of **2** dramatically increased when 0.1 molar equiv of BTEAC was used in the oxidation (Scheme I). The yields of **2** increased from 43–64% to 80–92%, and the reaction time was lowered from 4–5 h to a maximum of 1 h. Furthermore, only a slight excess, 1.1 equiv, of MCPBA was necessary for

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Scheme I

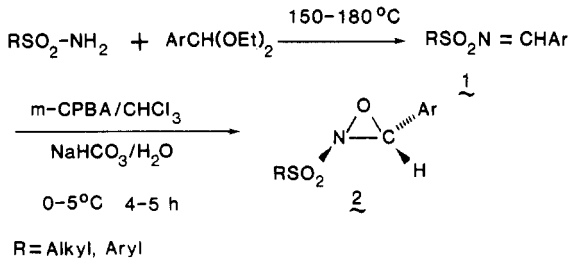


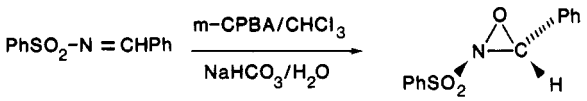
Table I. Preparation of 2-Sulfonyloxaziridines 2 by Using BTEAC

2			% yield[a]	
R	Ar	crystallization solvent	this procedure	old procedure[1]
Ph	Ph	EtOAc/ *n*-pentane	92	61
Ph	3-NO_2Ph	EtOH	83	
Ph	4-NO_2Ph	MeOH	80	43
Me	Ph	EtOAc/ *n*-pentane	85	64
$PhCH_2$	Ph	EtOAc/ *n*-pentane	90	50

[a] Isolated yields.

complete oxidation. Finally, the 2-sulfonyloxazridines prepared by using this modification were easier to purify. These results are summarized in Table I.

When the oxidation of *N*-benzylidine-2-benzenesulfonamide (3) was carried out by using a chiral phase-transfer catalyst, optically active 2-benzenesulfonyl-3-phenyloxazridine (4) was obtained. Thus oxidation of 3 with 0.1



molar equiv of (−)-benzylquinidinium chloride (QUIBEC) and (+)-benzylcinchoninium chloride (BCNC) gave (−)- and (+)-4, respectively. The asymmetric induction (% ee) of (−)- and (+)-4 was determined, using $Eu(hfc)_3$, to be 1.4–10.6% ee.

Attempts to effect the oxidation of 1 to 2 (R = Ph; Ar = *p*-NO_2Ph) by using PTC and more economical oxidizing agents such as alkaline H_2O_2, *t*-BuOOH, or NaOCl were unsuccessful. In each case only hydrolysis products were obtained.

Experimental Section

Melting points were determined on a Mel-Temp apparatus and are uncorrected. ^1H NMR spectra were measured on a Varian A-60A NMR spectrometer. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. MCPBA was purchased from Aldrich, and solvents were used without additonal purification. (−)-QUIBEC and (+)-BCNC were purchased from Fluka.

General Procedure for Oxidation of Sulfonimines 1 to 2-Sulfonyloxaziridines 2. In a 500-mL three-necked Morton flask, equipped with a mechanical stirrer and dropping funnel, were placed 100-mL of saturated aqueous $NaHCO_3$, 10 g of the sulfonimine 1, and 0.11 molar equiv of benzyltriethylammonium chloride (BTEAC) in 75 mL of chloroform. The reaction mixture was cooled to 0–5 °C in an ice bath and stirred vigorously. A solution of 1.1 equiv of MCPBA (85% Aldrich) in 100 mL of chloroform was added dropwise over 30 min. After the mixture was stirred for an additional 15 min, the chloroform layer was separated and washed successively with 50 mL of water, 50 mL of 10% aqueous Na_2SO_3, water (2 × 50 mL), and finally 20 mL of saturated aqueous NaCl. After being dried over the anhydrous K_2CO_3, the solution was filtered and the solvent evaporated in vacuo below 40 °C. The crude oxaziridine was crystallized from the appropriate solvent (see below and Table I).

2-Benzenesulfonyl-3-(*m*-nitrophenyl)oxaziridine. The crude oxaziridine as obtained above was triturated under 50 mL of methanol for 3–5 min, filtered, washed with another 10 mL of methanol, and air-dried to give 8.75 g (83%) of a white powder, mp 108–110 °C. An analytical sample was crystalized from ethanol: mp 113–114 °C; IR (Nujol) 1528 and 1350 cm^{-1} (NO_2); NMR ($CDCl_3$) δ 5.62 (s, 1 H, oxaziridine 3-H), 7.6–8.3 (m, 9 H, Ar). Anal. Calcd for $C_{13}H_{10}N_2O_5S$: C, 50.98; H, 3.29. Found: C, 50.64; H, 3.31.

2-Benzenesulfonyl-3-(*p*-nitrophenyl)oxaziridine. The crude oxaziridine as obtained above was triturated under 50 mL of methanol for 3–5 min, filtered, washed with another 10 mL of methanol, and air-dried to give 8.63 g (80%) of white fluffy crystals: mp 134–136 °C; IR (Nujol) 1525 and 1350 cm^{-1} (NO_2); NMR ($CDCl_3$) δ 5.78 (s, 1 H, oxaziridine 3-H), 7.55–8.33 (m, 9 H, Ar). Anal. Calcd for $C_{13}H_{10}N_2O_5S$: C, 50.98; H, 3.29. Found: C, 50.70; H, 3.00.

(+)- and (−)-2-Benzenesulfonyl-3-phenyloxaziridine (4). A solution of 2.45 g (0.01 moL) of *N*-benzylidinebenzenesulfonamide (3) and 0.0015 moL of (−)-QUIBEC or (+)-BCNC in 20 mL of chloroform and 30 mL of saturated aqueous Na_2CO_3 was treated as described above with 3.23 g (0.018 moL) of MCPBA in 15 mL of chloroform. After the workup, the residue was extracted with portions of ether (2 × 30 mL). The combined extracts were filtered, and the solvent was removed in vacuo to afford the crude optically active oxaziridine which was crystalized from ether/*n*-pentane.

(−)-4: first crop of crystals, 20%, mp 96–98 °C, $[\alpha]_D$ −0.56° (*c* 1.0, $CHCl_3$) (3.1% ee); second crop of crystals, 15%, mp 96–97 °C, $[\alpha]_D$ −2.63° (*c* 1.0, $CHCl_3$) (10.6% ee).

(+)-4: first crop of crystals, 23%, mp 96–98 °C, $[\alpha]_D$ +0.49° (*c* 1.0 $CHCl_3$) (1.4% ee); second crop of crystals, 15%, mp 96–98 °C, $[\alpha]_D$ +1.16° (*c* 1.0 $CHCl_3$) (10.2% ee).

Determination of Enantiomeric Compositions. The optical purity of (+)- and (−)-4 in $CDCl_3$ was determined by a series of 60-MHz ^1H NMR spectra obtained at increasing concentrations of the chiral shift reagent tris[3-[(heptafluoropropyl)hydroxymethlene]-*d*-camphorato]europium(III) derivative [$Eu(hfc)_3$]. When the shift difference of the oxaziridine 3-proton was approximately 9 Hz, the peak areas were determined by integration.

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Registry No. 2 (R = Ph; Ar = 3-NO_2Ph), 80997-73-5; **2** (R = Ph; Ar = 4-NO_2Ph), 78377-89-6; **2** (R = Me; Ar = Ph), 73844-99-2; **2** (R = $PhCH_2$; Ar = Ph), 73845-00-8; (−)-4, 80997-74-6; (+)-4, 80997-75-7.

Reductive Cyclization of 2-[(2-Propynyl)oxy]ethyl Bromides by a Cobalt Complex, Cobaloxime(I). A New Method for the Synthesis of α-Methylene-γ-butyrolactones

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The α-methylene-γ-butyrolactone structural unit is present in a wide variety of sesquiterpenes and other natural products[1] and has been suggested to be of central

