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## Absolute Configuration at Chiral Nitrogen in Oxaziridines. 2<sup>1</sup>

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Peracid oxidation of chiral imines leads to diastereomeric oxaziridines in high optical yields. The chiral substituent connected to nitrogen and the carbon skeleton of the imine have a similar inductive effect on the newly created asymmetric center in the oxaziridine ring. A correlation of the chirality of new oxaziridines with those of known absolute configuration is made on the basis of changes in molecular rotation.

Pyramidal nitrogen stability in oxaziridines has been established by the separation of invertomers (enantiomers and diastereomers) of these compounds formed in asymmetric synthesis.<sup>1-8</sup>

Previously, we have found<sup>1,2</sup> that m-chloroperbenzoic acid oxidation of imines containing a chiral substituent linked to the nitrogen yielded diastereomeric oxaziridines in high optical yield. Thus, we were able to synthesize optically pure oxaziridines suitable for x-ray analysis (i.e., a compound containing a heavy atom and a chiral center of known configuration).

As described in a preliminary communication,<sup>9</sup> oxidation of optically active (E)-imine, obtained from p-bromobenzaldehyde and (S)-(-)- $\alpha$ -phenylethylamine, gave four nonracemic oxaziridines (Scheme I). The composition of the mixture was determined by integration of the signal produced by the proton at C-3. The pertinent  $\delta$  values (CCl<sub>4</sub> s) are: 1, 4.32; 2, 4.38; 3, 5.0, and 4, 5.15 ppm. By analogy,<sup>1,6</sup> the trans configuration was assigned to 1 and 2, and cis to 3 and 4. The major product, diastereomer 1, was isolated from the mixture by crystallization; the other three products were separated by chromatography (SiO<sub>2</sub>; hexane-ether, 98:2).

Since the S chirality of the N substituent in the starting imine was known, and the x-ray study showed an opposite configuration at the carbon and nitrogen atoms in the oxaziridine ring, the absolute configuration of diastereomer 1 could be established as (2R,3R)-2-[(S)-1-phenylethyl]-3-pbromophenyloxaziridine.<sup>9</sup> Consequently, the configuration of diastereomer 2 was (2S,3S)-2-[(S)-1-phenylethyl]-3-pbromophenyloxaziridine.

In order to investigate the relative configuration of the cis isomers, compounds 3 and 4 were each thermally isomerized (120 °C, tetrachloroethylene). The isomerization occurred in the direction  $4 \rightarrow 1$  and  $3 \rightarrow 2$ .

The interconversion of the trans and cis oxaziridine isomers proceeded exclusively by a nitrogen inversion mechanism.<sup>10</sup> Thus, the structural assignments could be made for compounds **3** and **4** as shown in Scheme I.

In previously reported syntheses of oxaziridines,<sup>1,2,9</sup> derivatives of  $\alpha$ -phenylethylamine were used as substrates. Our present study concerns the effect of imine structure (i.e., the type of chiral substituent joined to the nitrogen or carbon in the imine) on the diastereoselectivity.

The use of (-)-menthylamine in the condensations with benzaldehyde and isobutyraldehyde provided optically active imines containing another kind of chiral substituent linked



to nitrogen. The resulting imines turned out to be pure E isomer.

Oxidation of the benzaldehyde derivative (Scheme II, R = Ph) gave three of four possible diastereomeric oxaziridines (5, 6 and 7; Table I) which were separated by silica gel column chromatography and elution with hexane or ether-hexane (2:98). The chemical shift of the C-3 proton in the <sup>1</sup>H NMR spectrum was used to determine the quantitative composition of the mixture and assign the relative geometry around the oxaziridine ring.

Oxidation of the isobutyraldehyde derivative (Scheme II, R = i-Pr) gave only two diastereomeric oxaziridines in a combined yield (8 and 9; Table II) of 67%. The C-3 proton signals were singlets at  $\delta$  3.48 and 3.25 ppm. The small difference in chemical shifts suggested that both compounds have the same configuration, most probably trans. The ratio of diastereomers in the mixture was determined by integration of the C-3 proton signals.

It was also of interest to investigate the effect of the chiral carbonyl component of the imine. Optically active imines of this type were derived from condensation of D-camphor with benzylamine and n-propylamine.

*N*-Benzylimine (Scheme III; 10a,  $R = PhCH_{2^{-}}$ ) contains about 95% of the *E* isomer (<sup>1</sup>H NMR), whereas the *n*-propylimine (Scheme III; 11a,  $R = CH_3CH_2CH_{2^{-}}$ ) is essentially the pure *E* isomer. When these compounds were oxidized, the yield of oxaziridine determined iodometrically was about 50%.



Scheme II

Table I								
Compd R = Ph	Configuration	δppm	% in mixture					
5 6 7	SSR trans RRR trans RSR cis	$\begin{array}{c} 4.34 \\ 4.25 \\ 5.05 \end{array}$	79 15 6					
Table II								
$\begin{array}{c} \text{Compd} \\ \mathbf{R} = i \cdot \mathbf{Pr} \end{array}$	Configuration	δppm	% in mixture					
8 9	SSR trans RRR trans	3. <b>48</b> 3.25	75 25					
Table III								
Compd	δ ppm 10-Me	δ ppm 9-Me	δ ppm 8-Me					
Imine, $R = PhCH_2$ Oxaziridine, $R = PhCH_2$	1.0 0.65	0.93 0.91	$\begin{array}{c} 0.75\\ 0.73\end{array}$					

This difference in yield in regard to other oxidations could have resulted (vide supra) from the difference in steric hindrance (Scheme III). In both cases (10a and 11a), only one compound with oxaziridine structure could be isolated. The <sup>1</sup>H NMR spectrum of oxaziridine, where  $R = PhCH_{2-}$ , permitted determination of the structure (Table III). Upon irradiation of the C-10 methyl signal at 0.65 ppm, no change in intensity of the benzylmethylene group signal was noted. Upon irradiation of the endo proton at C-3, a 5% increase in intensity of the signal due to the benzylmethylene group was observed, suggesting that this group is situated in the neighborhood of endo and exo protons at C-3 in the camphor moiety (Scheme III). Such a situation is possible only for an oxaziridine with the trans configuration represented by one of two structures, 10b and 10c (Scheme III). The decision between these two structures could be reached from comparison of chemical shifts of the methyl groups of imine 10a and the oxaziridine formed. An upfield shift was only observed for the signal due to the C-10 methyl group in the oxaziridine.

This observation indicated structure 10b for the isolated compound; in the case of alternative structure 10c an additional change of  $\delta$  ppm value for one of the groups, 9-Me or 8-Me, should also be observable.

The oxaziridine, where R = n-Pr, showed similar chemical



R = Ph(5, 6, 7)

(8, 9)



shifts of methyl groups; therefore, it probably has the same structure as 10b; i.e., the absolute configuration at the carbon and nitrogen atom in the oxaziridine ring is (S,S).

Generally, we have found that, regardless of the placement of the chiral substituent on nitrogen or on the double-bond carbon, the oxidation is highly stereoselective and results in a higher proportion of trans isomer.

Since all four oxaziridines (1-4) have a known absolute configuration, we would like to propose a general rule relating to optical rotation to derive the configurational relationships among oxaziridines obtained in our syntheses. This is in analogy to the Freudenberg's rule of shift.<sup>15</sup>

In formulating this rule, we considered enantiomers of compounds 1-4, since previously obtained oxaziridines, derivatives of  $\alpha$ -phenylethylamine, involved the *R* configuration at this asymmetric center.

In Table IV are given molecular rotations "[M]" and the difference between molecular rotations " $[\Delta M]$ " of oxaziridines and imines. The molecular rotations were all measured at 578 nm.

a No. 1-4 in CHCl<sub>3</sub>; no. 5-8 in EtOH.

Table V									
Imine	Registry no.	$\phi_{{}^{578}}$	Oxaziridine						
			$\phi_{\mathfrak{s} 78}$	Registry no.	$\Delta M_{578}$	Solvent			
NCH <sub>2</sub> Ph	63765-03-7	-56.6°	<b>10</b> b: 316.0°	63797-18-2	-259.4°	EtOH			
N-n-Pr	63765-04-8	-47.7°	11b: 222.4°	63765-05-9	$-174.7^{\circ}$	EtOH			

. .



## Figure 1.

Oxidation of ketimines which are derivatives of symmetrical ketones leads to two diastereomers, the predominant being A and the other B. When oxidation of an imine can give four possible isomers, as for imine derivatives of unsymmetrical ketones and aldimines, A and B pertain to trans isomers and C and D to cis isomers, respectively. The first line in Table I contains the data for model compounds 1-4. A large negative value,  $[\Delta M]_{578}$ , is observed for the predominant diastereomer. The large but positive value corresponds to isomer B. For diastereomers C and D, differences of molecular rotations  $[\Delta M]_{578}$  are found to be very large with respectively increasing positive values. It is readily apparent from the comparison of  $[\Delta M]_{578}$  values for isomer A in the first seven lines of Table IV that the generally observed value of  $[\Delta M]_{578}$  is either a large negative or a small positive value. The  $[\Delta M]_{578}$  for isomer B in each case is a large positive value. Thus, it is safe to conclude that compounds listed in a given column (A, B, C, or D) have the same absolute configuration at the C and N atoms of the oxaziridine ring.

In each case, the predominantly formed oxaziridine diastereomer, in which the chiral substituent linked to nitrogen has the R configuration, must have the absolute configuration S at the chiral nitrogen of the oxaziridine ring.

The assignment of absolute configuration can be extended from the above examples to the oxaziridine obtained by Italian authors<sup>11</sup> (line 8, Table IV) on the basis of a very large negative  $[\Delta M]_{578}$  value in column A. The absolute configuration S of the nitrogen in this compound was recently established unequivocally by x-ray crystallographic investigation.<sup>11</sup>

The absolute configurations shown on Scheme II were assigned to compounds 5 and 6 on the basis of changes in  $[\Delta M]_{578}$ , and to compound 7 on the basis of isomerization of this compound to isomer 6.

Application of this method of correlating configuration by  $[\Delta M]_{578}$  confirmed the assigned configurations for oxaziridines 10b and 11b (Table V).

A large negative value of  $[\Delta M]_{578}$  was observed in both cases, correlating with the values in Table IV. This confirmed the S,S configuration for the nitrogen and carbon atoms in the oxaziridine ring in 10b and 11b.

We have found in general that oxidation of chiral imines by m-chloroperbenzoic acid produces mainly that diastereomer having an absolute configuration on the nitrogen which is

opposite to the absolute configuration of the substituent linked to the nitrogen or carbon atom.

Knowledge of the stereochemistry of diastereomers 1-4 gave information concerning the direction of attack of peroxyacid on the imine double bond only. As shown in Figure 1, in reactions involving imines, in which the substituent linked to the C—N moiety has an R absolute configuration, attack of peroxyacid from the pro-S face is preferred. As a result, two diastereomers possessing the same S configuration at the carbon atom in the oxaziridine ring are predominantly formed (1 + 4, 63%). Attack from the pro-R face gives a 37% yield of diastereomers 2 and 3, both having the R configuration.

On the basis of our results it is not possible to distinguish between the stepwise and concerted mechanism of imine oxidation. The formation of four possible isomers can be explained by both mechanisms mentioned above. Regardless of the mechanism, the configuration of newly created asymmetric centers apparently depends only on the chirality of the substituent.

## **Experimental Section**

Melting points were measured on a micro hot plate and are not corrected. IR spectra were determined in CCl<sub>4</sub> solution with a Unicam SP.200. <sup>1</sup>H NMR spectra were measured with a JEOL 100-MHz spectrometer in CCl<sub>4</sub> solution (accuracy  $\pm 0.5$  Hz) and are given in  $\delta$  ppm. Optical rotations were measured with a Perkin-Elmer automatic photoelectric polarimeter (Model 141). Microanalyses were performed in our microanalytical laboratory (Z. Celler).

Aldimines were prepared by condensation of aldehydes with amines in methanol or ether solution.<sup>12,13</sup> Ketimines were prepared by condensation of ketones with amines in cyclohexane solution in the presence of molecular sieves.<sup>14</sup>

Active oxygen contents of oxaziridines were determined by iodometric titration with potassium iodide in a stirred mixture of dichloromethane, water, and glacial acetic acid.

Oxidation of imines to the corresponding oxaziridines was carried out as follows: A small excess of *m*-chloroperbenzoic acid (0.022 mol) in 40 mL methylene chloride was added with stirring and cooling (0–5 °C) to a solution of 0.02 mol of imine in 10 mL of methylene chloride. After the peroxyacid had been added, the reaction mixture was stirred for an additional 5 h at 0–5 °C. The *m*-chlorobenzoic acid was removed by filtration. The filtrate was washed twice with a dilute Na<sub>2</sub>SO<sub>3</sub> solution, twice with a solution of Na<sub>2</sub>CO<sub>3</sub>, and finally with water. After drying over MgSO<sub>4</sub> (anhydrous) the solvent was evaporated. The product was analyzed by <sup>1</sup>H NMR and then chromatographed over a column of SiO<sub>2</sub> using hexane–ether (98:2) as a solvent. Complete separation of diastereoisomers was achieved by repeated column chromatography using hexane. Solids were purified by crystallization until rotation was constant. Purity of isomers was checked by <sup>1</sup>H NMR, TLC, or high-pressure chromatography.

 $(S) \cdot (+) \cdot N \cdot p \cdot Bromobenzylidene \cdot \alpha \cdot phenylethylamine (R = p \cdot BrC_6H_4):^{12} [\alpha]^{20}_{578} + 93.7^{\circ}; \Phi^{20}_{578} + 269.8^{\circ}; [\alpha]^{20}_{436} + 231.6^{\circ} (c \ 1.03, EtOH); mp 86-87 °C (from 95% EtOH); IR 1650 cm<sup>-1</sup> (C=N); <sup>1</sup>H NMR 1.61 (d, 3, CH_3), 4.43 (m, 1, CH at N), 8.25 ppm (s, 1, CH=N).$ 

(R)-(-)-N-p-Bromobenzylidene- $\alpha$ -phenylethylamine:<sup>12</sup>  $[\alpha]^{20}_{578} - 88.8^{\circ}; [\alpha]^{20}_{436} - 222.9^{\circ} (c \ 1.01, EtOH); \Phi^{20}_{578} - 255.7^{\circ}.$ (IR,3R,4S)-(-)-N-Benzylidenementhylamine (R = Ph):<sup>12</sup>

(1*R*,3*R*,4*S*)-(-)-*N*-Benzylidenementhylamine (**R** = **P**h):<sup>12</sup> [ $\alpha$ ]<sup>25</sup><sub>578</sub> -156.8°;  $\Phi^{25}_{578}$  381°; [ $\alpha$ ]<sup>25</sup><sub>436</sub> -360.1° (*c* 1.01, EtOH); mp 70-72 °C (from hexane); IR 1645 cm<sup>-1</sup> (C=N); <sup>1</sup>H NMR 2.94 (m, 1, CH at N), 8.13 (s, 1, CH=N) ppm; UV  $\lambda_{max}$  (96% EtOH) 203.5 nm ( $\epsilon$  26 920), 246.5 (19 011). (1R,3R,4S)-(-)-*N*-2-Methylpropylidenementhylamine:<sup>13</sup> R = -CH(CH<sub>3</sub>)<sub>2</sub>;  $[\alpha]^{30}_{578}$ -99.7°;  $\Phi^{30}_{578}$ -208.3°;  $[\alpha]^{30}_{436}$ -206.6° (c 1.12, EtOH); bp 123-126 °C (17 mm); IR 1670 cm<sup>-1</sup> (C=N);  $n^{24}_{D}$  1.454; <sup>1</sup>H NMR 7.4 ppm (d, 1, CH=N).

(1R,4R)-(-)-N-(1,7,7,-Trimethylbicyclo[2.2.1]heptylidene)**benzylamine** (**R** =  $-CH_2Ph$ ):<sup>14</sup> [ $\alpha$ ]<sup>25</sup><sub>578</sub> -23.5°; [ $\alpha$ ]<sup>25</sup><sub>436</sub> -44.6° (*c* 1.02, EtOH); bp 119–120 °C (0.6 mm); IR 1680 cm<sup>-1</sup> (C=N);  $n^{24}$ <sub>D</sub> 1.5358; <sup>1</sup>H NMR 4.28 (s, 2, CH<sub>2</sub> from benzyl), 1 (s, 3, CH<sub>3</sub>-10), 0.93 (s, 3, CH<sub>3</sub>-9), 0.75 ppm (s, 3, CH<sub>3</sub>-8). (1,**R**,4**R**)-(-)-**N**-(1,7,7-Trimethylbicyclo[2.2.1]heptylidene)-

**propylamine** ( $\mathbf{R} = -\mathbf{CH}_2\mathbf{CH}_2\mathbf{CH}_3$ );<sup>14</sup>  $[\alpha]^{30}_{578} - 13.9^\circ$ ;  $[\alpha]^{30}_{436} - 48.2^\circ$ (c, 1.09, EtOH); bp 103–104 °C (18 mm); IR 1685 (C=N); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) 3.1 (t, 2, CH<sub>2</sub> at N), 1.08 (s, 3, CH<sub>3</sub>-10), 0.84 (s, 3, CH<sub>3</sub>-9), 0.73 ppm (s, 3, CH<sub>3</sub>-8).

2-[(S)- $\alpha$ -Phenylethyl]-3-p-bromophenyloxaziridine. Diastereomer 1. Isolated from the reaction mixture by crystallization from hexane:  $[\alpha]^{20}_{578}$  +146.3°;  $[\alpha]^{20}_{436}$  +303.3° (c, 1, EtOH); mp 128–129 °C (from hexane); UV  $\lambda_{max}$  (96% EtOH) 200 nm ( $\epsilon$  15 000), 210 (7095), 230 (6500), 252 (500), 260 (516.6), 265 (471.4), 272 (274), 277 (195); <sup>1</sup>H NMR 4.32 (s, 1, H-3), 3.13 (m, 1, CH at N), 1.59 ppm (d, 3, CH<sub>3</sub>); MS m/e 304.

Anal. Calcd for C<sub>15</sub>H<sub>14</sub>NOBr: C, 59.2; H, 4.6; N, 4.6. Found: C, 59.31; H, 4.59; N, 4.36.

Diastereomers 2, 3, and 4 were first separated by column chromatography (SiO<sub>2</sub>; hexane-ether, 98:2); further purification was achieved by repeated column chromatography using hexane as a solvent.

**Diastereomer 2:**  $[\alpha]^{20}_{578} - 59.4^{\circ}$ ;  $[\alpha]^{20}_{436} - 107.4^{\circ}$  (c, 1.01, EtOH); mp 58–59 °C (from hexane); UV  $\lambda_{max}$  (96% EtOH) 202 nm ( $\epsilon$  30 221), 217 (13 924), 230 (16 139), 252 (591.7), 259 (595), 266 (538), 272 (332), 277 (246);  $^1\!H$  NMR 4.38 (s, 1, H-3), 3.27 (m, 1, CH at N), 1.45 ppm (d, 3, CH<sub>3</sub>); MS m/e 304.

Anal. Calcd for C<sub>15</sub>H<sub>14</sub>NOBr: C, 59.2; H, 4.6; N, 4.6. Found: C, 58.8; H, 4.59; N, 4.36.

**Diastereomer 3:**  $[\alpha]^{20}_{578} - 238.5^{\circ}; [\alpha]^{20}_{436} - 512.5^{\circ} (c, 1.99, EtOH);$ mp 84–85 °C (from hexane); UV  $\lambda_{max}$  (96% EtOH) 202 nm ( $\epsilon$  21 070), 218 (11 210), 231 (11 210), 258 (636), 266 (510), 273 (300), 278 (188); <sup>1</sup>H NMR 4.97 (s, 1, H-3), 3.05 (m, 1, CH at N), 1.48 ppm (d, 3, CH<sub>3</sub>); MS m/e 304.

Anal. Calcd for C<sub>15</sub>H<sub>14</sub>NOBr: C, 59.2; H, 4.6; N, 4.6. Found: C, 59.39; H, 4.6; N, 4.47.

**Diastereomer 4:**  $[\alpha]^{20}_{578} - 297^{\circ}; [\alpha]^{20}_{436} - 618^{\circ} (c, 1.04, \text{EtOH});$ mp 109.5–110 °C (from hexane), UV  $\lambda_{max}$  (96% EtOH) 201.5 nm ( $\epsilon$ 38 700), 215 (15 900), 231 (18 100), 257 (910), 264 (720), 274 (368); <sup>1</sup>H NMR 5.15 (s, 1, H-3), 3.1 (m, 1, CH at N), 1.01 ppm (d, 3, CH<sub>3</sub>); MS m/e 304.

Anal. Calcd for C<sub>15</sub>H<sub>14</sub>NOBr: C, 59.2; H, 4.6; N, 4.6. Found: C, 58.91; H, 4.37; N, 4.21.

 $2-[(R)-\alpha-Phenylethyl]-3-p-bromophenyloxaziridine.$  All isomers were isolated as previously described for their enantiomers

**Diastereomer 1:**  $[\alpha]^{20}_{578} - 136.2^{\circ}; \Phi^{20}_{578} - 414^{\circ}; [\alpha]^{20}_{436} - 298.6^{\circ}$ (c 1.01, EtOH).

**Diastereomer 2:**  $[\alpha]^{20}_{578}$  +61.3°;  $\Phi^{20}_{578}$  +186.3°;  $[\alpha]^{20}_{436}$  +109.5° (c 0.9, EtOH).

**Diastereomer 3:**  $[\alpha]^{20}_{578} + 228.5^{\circ}; \Phi^{20}_{578} + 694.5^{\circ}; [\alpha]^{20}_{436} + 459.3^{\circ}$ (c 1.1, EtOH).

**Diastereomer 4:**  $[\alpha]^{20}_{578} + 315.6^{\circ}; \Phi^{20}_{578} + 959.6^{\circ}; [\alpha]^{20}_{436} + 631.6^{\circ}$ (c 0.91, EtOH).

2-[(1R,3R,4S)-Menthyl]-3-phenyloxaziridine. Compounds 5, 6, and 7 were separated by repeated column chromatography  $(SiO_2)$ with hexane-ether, 98:2, at first, and then hexane alone as a solvent.

**Diastereomer 5:**  $[\alpha]^{25}_{578} - 144^{\circ}; \Phi^{25}_{578} - 373.1^{\circ}; [\alpha]^{25}_{436} - 283.9^{\circ}$ (c 1.37, EtOH); UV  $\lambda_{max}$  (96% EtOH) 207 nm ( $\epsilon$  11 265.4), 214.5 nm (10 802.5); <sup>1</sup>H NMR 4.34 ppm (s, 1, H-3); MS m/e 259.

Anal. Calcd for C17H25NO: C, 78.76; H, 9.65; N, 5.4. Found: C, 78.55; H, 9.72; N, 5.19.

**Diastereomer 6:**  $[\alpha]^{25}_{578} + 17.9^{\circ}; \Phi^{25}_{578} + 46.4^{\circ}; [\alpha]^{25}_{436} + 40.2^{\circ} (c$ 

0.81, EtOH); mp 91–94.5 °C; UV  $\lambda_{max}$  (96% EtOH) 193 nm ( $\epsilon$  16 000), 208.5 (9325), 213.5 (9250); <sup>1</sup>H NMR 4.25 ppm (s, 1, H-3); MS m/e259.

Anal. Calcd for C<sub>17</sub>H<sub>25</sub>NO: C, 78.76; H, 9.65; N, 5.4. Found: C, 77.74; H, 9.85; N, 5.19.

**Diastereomer 7:**  $[\alpha]^{25}_{578} - 128.9^{\circ}; \Phi^{25}_{578} - 333.8^{\circ}; [\alpha]^{25}_{436} - 244.6^{\circ}$ (c 0.98, EtOH); mp 81–84 °C (from hexane) UV  $\lambda_{max}$  (96% EtOH) 193.5 nm (e 21 839), 218.5 (6606.3); <sup>1</sup>H NMR 5.05 ppm (s, 1, H-3); MS m/e 259.

Anal. Calcd for C<sub>17</sub>H<sub>25</sub>NO: C, 78.76; H, 9.65; N, 5.4. Found: C, 79.12; H, 10.25; N, 5.16.

2-[(1R,3R,4S)-Menthyl]-3-isopropyloxaziridine. ereomer 8:  $[\alpha]^{25}_{578} = 143.6^{\circ}; \Phi^{25}_{578} = 323.1^{\circ}; [\alpha]^{25}_{436} = 272.9^{\circ}$  (c 1.22, EtOH); oil; <sup>1</sup>H NMR 3.47 ppm (d, 1, H-3); MS *m/e* 225.

Anal. Calcd for C14H27NO: C, 74.66; H, 12.0; N, 6.2. Found: C, 74.89; H, 12.11; N, 6.01.

**Diastereomer 9:**  $[\alpha]^{20}_{578} - 26^{\circ}; \Phi^{25}_{578} - 58.5^{\circ}; [\alpha]^{20}_{436} - 55.0^{\circ} (c 1.02, EtOH); oil; <sup>1</sup>H NMR 3.25 ppm (d, 1, H-3); MS$ *m/e*225.

Anal. Calcd for C14H27NO: C, 74.66; H, 12.0; N, 6.2. Found: C, 74.86; H, 12.05; N, 5.98.

2-Benzyl-3-[(1R,4R)-1,7,7-trimethylbicyclo[2.2.1]heptyl]oxaziridine. Diastereomer 10: Isolated from the reaction mixture by silica gel chromatography with hexane as a solvent.  $[\alpha]^{25}_{578} - 123^{\circ};$  $[\alpha]^{25}_{436}$  –231.9° (c 1.03, EtOH); mp 52.5–55 °C (from methanol); UV λ<sub>max</sub> (96% EtOH) 202.5 nm (ε 9485.9); <sup>1</sup>H NMR 3.64, 3.44 (m, 2, CH<sub>2</sub> from benzyl); 0.91 (s, 3, CH<sub>3</sub>-9), 0.73 (s, 3, CH<sub>3</sub>-8), 9.65 ppm (s, 3, CH<sub>3</sub>-10) MS m/e 257.

Anal. Calcd for C17H23NO: C, 79.33; H, 9.01; N, 5.44. Found: C, 78.98; H, 9.38; N, 5.3.

2-Propyl-3-[(1R,4R)-1,7,7-trimethylbicyclo[2.2.1]heptyl]-

oxaziridine. Diastereomer 11:  $[\alpha]^{30}_{578} - 106.4^{\circ}; [\alpha]^{30}_{436} - 192.7^{\circ}$  (c 1.14, EtOH); n<sup>26</sup>D 1.472; <sup>1</sup>H NMR 0.9 (s, 3, CH<sub>3</sub>-9), 0.82 (s, 3, CH<sub>3</sub>-8), 0.55 ppm (s, 3, CH<sub>3</sub>-10); MS m/e 209.

Anal. Calcd for C13H23NO: C, 74.64; H, 11.0; N, 6.7. Found: C, 75.16; H, 11.0; N, 6.82.

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**Registry No.**— $2[(S) - \alpha$ -phenylethyl]-3-p-bromophenyloxyloxaziridine isomer 1, 60143-68-2; 2-[(S)-α-phenylethyl]-3-p-bromophenyloxaziridine isomer 2, 60183-42-8; 2-[(S)- $\alpha$ -phenylethyl]-3*p*-bromophenylorazixidine isomer 3, 60183-44-0;  $2 \cdot [(S) \cdot \alpha \cdot phenyl$ ethyl]-3-p-bromophenyloxaziridine isomer 4, 60183-43-9; (S)-(+)-N-p-bromobenzylidine- $\alpha$ -phenylethylamine, 60143-67-1.

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