(c 1.4, MeOH); ^{1}H NMR (100 MHz, $CDCl_3$) δ Me_4Si 1.24 (3 H, s), 3.13 (1 H, $^1/_2$ ABq, J = 14.6 Hz), 3.23 (1 H, $^1/_2$ ABq, J = 14.6 Hz), 3.53 (3 H, br s), 7.2–7.4 (5 H, m); IR (NaCl, neat) 3410, 3060, 1585, 1485, 1440, 1365, 1045, 735 cm^{-1}.

Utilizing exactly the same procedure above on the crude epoxide obtained from (-)-DET afforded (*R*)-(-)-**8**: $[\alpha]^{25}_D$ -2.631° (c 0.8, MeOH).

(*S*)-(+)-2,2,4-Trimethyl-4-[(phenylthio)methyl]-1,3-dioxolane (9). A solution of the crude diol **8** (1.4 g, ca. 2.2 mmol, 1.0 equiv) and D-camphorsulfonic acid (20 mg) was stirred in 2,2-dimethoxy propane (5 mL) at room temperature for 6 h. The mixture was diluted with CH_2Cl_2, poured into 0.1 N NaOH, and thoroughly extracted with CH_2Cl_2. The combined extracts were dried over anhydrous sodium sulfate, filtered, evaporated, and separated on silica gel (eluted with 5% Et_2O in hexanes and then 20% Et_2O in hexanes) to afford 181 mg (35% overall from **6**) of the acetonide **9** (oil): $[\alpha]^{25}_D$ +4.27° (c 1, $CHCl_3$); ^{1}H NMR (100 MHz, $CDCl_3$), δ Me_4Si 1.39 (9 H, s), 3.15 (2 H, s), 3.73 (1 H, $^1/_2$ ABq, J = 8.8 Hz), 4.00 (1 H, $^1/_2$ ABq, J = 8.8 Hz), 7.23–7.38 (5 H, m); IR (NaCl, neat) 3060, 1585, 1480, 1440, 1370, 1210, 1055, 980, 730, 685 cm^{-1}.

From (*R*)-(-)-**8**, (*R*)-(-)-**9** was obtained: $[\alpha]^{25}_D$ -4.545° (c 2.0, $CHCl_3$).

(*S*)-2,2,4-Trimethyl-4-[(phenylsulfinyl)methyl]-1,3-dioxolane (10). To a stirred solution of sulfide **9** (180 mg) in CH_2Cl_2 (5 mL) was added *m*-chloroperoxybenzoic acid (28 mg, 0.16 mmol) at room temperature. After 1.5 h, sequential addition of 10-mg portions of *m*-chloroperoxybenzoic acid was carried out every hour until the total amount added reached 93 mg. The mixture was diluted with CH_2Cl_2, poured into 0.1 N NaOH solution, and thoroughly extracted with CH_2Cl_2. The combined extracts were dried over anhydrous sodium sulfate, filtered, evaporated, and separated on PTLC silica gel (eluted with 25% hexanes in Et_2O) to afford a mixture of diastereomeric sulfoxides **10** (125 mg, 23% overall from **6**). A pure sample of each diastereomer could be obtained by repeated PTLC on silica gel (eluted with 25% hexanes in Et_2O).

One Isomer: ^{1}H NMR (100 MHz, $CDCl_3$) δ $CHCl_3$ 1.42 (6 H, s), 1.49 (3 H, s), 2.95 (2 H, d), 3.81 (1 H, $^1/_2$ ABq, J = 8.8 Hz), 4.40 (1 H, $^1/_2$ ABq, J = 8.8 Hz), 7.4–7.6 (5 H, m). **The Other isomer**: ^{1}H NMR (60 MHz, $CDCl_3$) δ $CHCl_3$ 1.36 (6 H, s), 1.62 (3 H, s), 2.96 (2 H, d), 3.80 (1 H, $^1/_2$ ABq, J = 9 Hz), 4.08 (1 H, $^1/_2$ ABq, J = 9 Hz), 7.3–7.7 (5 H, m). The mixture of diastereomers obtained from the initial reaction was used directly for the subsequent Pummerer reaction, without purification.

(*R*)-(+)-2,2,4-Trimethyl-4-(hydroxymethyl)-1,3-dioxolane (2). A stirred solution of the sulfoxide **10** (286 mg, 1.1 mmol, 1.0 equiv) and sodium acetate (550 mg, 6.6 mmol, 6.0 equiv) was heated to reflux in acetic anhydride (12 mL) for 11 h. The mixture was allowed to come to room temperature, diluted with CH_2Cl_2, poured into 1 N NaOH solution, and thoroughly extracted with CH_2Cl_2. The combined extracts were dried over anhydrous sodium sulfate, filtered, evaporated, and purified on PTLC silica gel (eluted with 25% Et_2O in hexanes) to afford 285 mg (88%) of the α-acetoxy sulfide, which was directly used for the subsequent reduction to **2** or hydrolysis to **1**.

Reduction to 2. To a stirred solution of the crude acetate obtained above (270 mg, 0.91 mmol, 1.0 equiv) in dry Et_2O (10 mL) at 0 °C was added lithium aluminum hydride (182 mg, 4.55 mmol, 5.0 equiv) in one portion. After 1 h, a saturated aqueous sodium sulfate solution was added dropwise to quench the excess hydride. The mixture was filtered and evaporated followed by a bulb-to-bulb distillation (ca. 1 mm) to afford the alcohol **2** (105 mg, 80%) as a colorless oil: $[\alpha]^{25}_D$ +4.42° (c 2.4, CH_2Cl_2) (85% ee based on resolved **2** $[\alpha]^{25}_D$ +5.2°).

From (*R*)-(-)-**9**, (*S*)-(-)-**2** was obtained: $[\alpha]^{25}_D$ -4.46° (c 1.3, CH_2Cl_2) (85% ee based on resolved **2** $[\alpha]^{25}_D$ -5.33°).

To verify the % ee calculated above, the (*S*)-acetonide alcohol **2** (16 mg, 0.11 mmol, 1.0 equiv) was treated with triethylamine (0.017 mL, 0.12 mmol, 1.11 equiv), and (-)-camphanyl chloride (**3**, 24 mg, 0.11 mmol, 1.0 equiv) in THF (0.8 mL) for 2 h at room temperature. The mixture was filtered and evaporated to afford 39 mg (100%) of the corresponding camphanyl esters; HPLC analysis (silica gel B10, eluted with 10% EtOAc in hexanes) indicated an 92.5:7.5 ratio of **5**:**4**, which corresponds to ca. 85% diastereomeric excess.

(*S*)-(-)-2,2,4-Trimethyl-1,3-dioxolane-4-carboxaldehyde (1). Procedure A: Swern Oxidation of 2. To a stirred solution of oxalyl chloride (0.24 mL, 2.75 mmol, 1.1 equiv) in CH_2Cl_2 (10 mL) at -78 °C was added Me_2SO (0.39 mL, 5.5 mmol, 2.2 equiv) over a 5-min period. After the suspension was stirred for 20 min, (*R*)-(+)-**2** (365 mg, 2.5 mmol, 1.0 equiv) in CH_2Cl_2 (3 mL) was added at -78 °C. After stirring for 55 min, Et_3N (1.75 mL, 12.5 mmol, 5.0 equiv) was added at -78 °C and the cooling bath was removed. The thick white suspension was stirred for 3.5 h at room temperature, diluted with Et_2O (70 mL), washed with water, dried over anhydrous sodium sulfate, filtered, evaporated, and carefully bulb-to-bulb distilled to afford 156 mg (43%) of the optically active (*S*)-aldehyde **1** as a clear, colorless oil: $[\alpha]^{25}_D$ -11.561° (c 5.0, CH_2Cl_2); ^{1}H NMR (100 MHz, $CDCl_3$) δ Me_4Si 1.37 (3 H, s), 1.40 (3 H, s), 1.43 (3 H, s), 3.72 (1 H, $^1/_2$ ABq, J = 9.0 Hz), 4.23 (1 H, $^1/_2$ ABq, J = 9.0 Hz), 9.63 (1 H, s).

Procedure B. To a stirred solution of the α-acetoxy sulfide (obtained above from the Pummerer reaction) (400 mg, 1.35 mmol, 1.0 equiv) in MeOH (5 mL) was added K_2CO_3 (100 mg), and the mixture was refluxed for 2 h. After being cooled to room temperature, Et_2O (25 mL) was added, and the mixture was filtered, carefully evaporated, and bulb-to-bulb distilled to afford 100 mg (51%) of the pure aldehyde as a clear, colorless oil.

The aldehyde **1** was obtained from the (-)-DET sequence: $[\alpha]^{25}_D$ +10.42° (c 0.2, CH_2Cl_2).

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Institutes of Health Grant No. 1R01AIGM18957-01 for support of this work. The Nicolet R3-m/E diffractometer and computer system used in the determination of the structure of compound **5** were purchased with funds provided by the National Science Foundation under Grant No. CHE8103011. ^{1}H NMR measurements at 360 MHz were obtained at the Colorado State University Regional NMR Center, funded by the National Science Foundation Grant No. CHE78-18581.

Registry No. (*S*)-**1**, 79243-92-8; (±)-**2**, 86884-87-9; (*R*)-**2**, 86940-97-8; (*S*)-**2**, 86940-98-9; (-)-**3**, 39637-74-6; (-)-**4**, 86884-88-0; (-)-**5**, 86940-99-0; **6**, 513-42-8; (*R*)-**7**, 86884-89-1; (*S*)-**7**, 86884-90-4; (*S*)**8**, 86884-91-5; (*S*)-**9**, 86884-92-6; (*S*)-**10** (isomer 1), 86884-93-7; (*S*)-**10** (isomer 2), 86884-94-8; PhSH, 108-98-5; 2,2,4-trimethyl-4-[acetoxy(phenylthio)methyl]-1,3-dioxolane, 86884-95-9.

Supplementary Material Available: Table I, atomic coordinates for **5**; Table II, bond lengths for **5**; Table III, bond angles for **5**; Table IV, anisotropic thermal parameters for **5**; and Table V, hydrogen atom positions for **5** (5 pages). Ordering information is given on any current masterhead page.

Synthesis and Conformational Aspects of *cis*- and *trans*-3-Carbomethoxy-6-oxabicyclo[3.1.0]hexane

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It is recognized that 3-aminocyclopentanecarboxylic acid is a valuable probe for the study of the biological action of the neurotransmitter γ-aminobutyric acid (GABA). Striking differences in activity are noted for the cis and trans isomers in both neurotransmitter uptake[1] and action at the receptor.[2]

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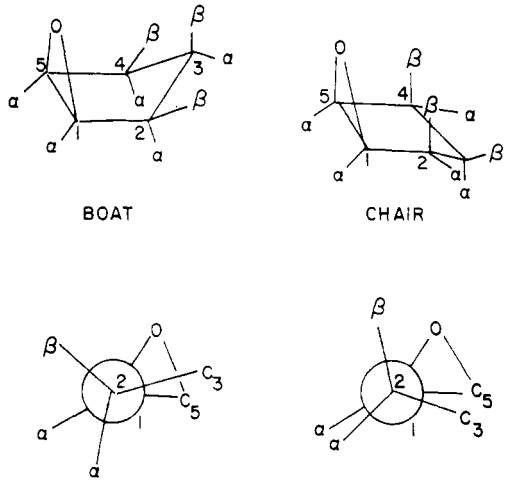
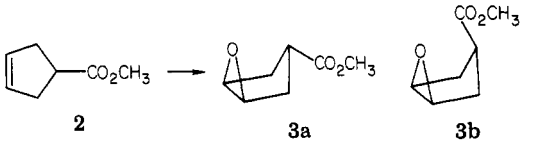


Figure 1. The two major conformations of 6-oxabicyclo[3.1.0]-hexane.

In our studies on the synthesis of affinity labeling agents for the GABA receptor it is essential to verify the stereochemistry of the isomers of 3-carbomethoxy-6-oxabicyclo[3.1.0]hexane (**3a**, **3b**) that will be used as precursors in the synthesis of a bicyclic aziridine analogue of GABA. Chromatographic separation was achieved for epoxides **3a** and **3b**, and isomer assignments were made on the basis of the ^{1}H NMR spectra and the known conformational preferences of the oxabicyclic ring system. Unlike six-membered rings that exist in several well-defined energetically distinct conformational forms, five-membered rings interconvert readily between many minimal energy forms by "pseudorotation" or ring puckering.[3,4] Substituents that change the torsional strain of the ring and increase the potential barrier to "pseudorotation", however, stabilize some conformations relative to others. The conformational analysis of these compounds can be carried out by various spectral techniques. In general, it has been observed that those conformations in which such substituents are situated in the most puckered part of the cyclopentane ring are preferred,[3c] regardless of their "axial" or "equatorial" orientation on the ring.[5] The epoxide ring in **3** would, a priori, be expected to have a dramatic influence on the conformational equilibrium of this molecule. Raman,[6] far infrared,[7,8] and microwave[9-11] spectral studies, as well as dipole moment measurements[9,11,12] and ab initio (SCF) molecular orbital calculations,[13] in fact, all indicate that oxabicyclohexane and bicyclo[3.1.0]hexane (BCH) both exist in only one stable conformation, the pseudo-boat form (Figure 1). When the total energies of the different possible conformers of BCH were plotted as a function of the angle ϕ between the plane of ring carbons 1, 2, 4, and 5 and the plane created by carbons 2–4, a single energy minimum was observed that corresponded to $\phi = +24.7°$.[13]

Scheme I



2 3a 3b

Table I. ^{13}C and ^{1}H Chemical Shifts for *cis*- and *trans*-3-Carbomethoxy-6-oxabicyclo[3.1.0]hexane (3b, 3a)[a]

	3a (trans)		3b (cis)	
	δ[c]	$\Delta\delta$[d]	δ[c]	$\Delta\delta$[d]
carbonyl carbon[b]	175.03	1.60	174.94	4.91
C_1, C_5	55.89	8.55	55.88	11.29
OC	51.55	1.35	51.68	3.10
C_3	37.47	3.50	38.12	7.05
C_2, C_4	31.50	2.93	30.52	5.01
OCH_3	3.63	0.88	3.63	0.72
1, 5-Hα	3.47	2.52	4.42	1.12
3-H	(β) 2.65	2.24	(α) 2.60	1.42
2,4-Hβ	2.35	1.90	2.70	1.54
2,4-Hα	1.85	1.62	1.85	0.82

[a] Chemical shifts are reported in parts per million (δ) downfield from the internal standard, tetramethylsilane; the solvent was deuteriochloroform ($CDCl_3$). [b] The assignments are noted in the structure illustrated in the reaction scheme. [c] All ^{13}C assignments were based on off-resonance decoupled spectra. [d] Chemical shift difference at a mole ratio of 0.2 tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorato]europium(III)($Eu(hfc)_3$ to **3**.

The normal shape of this curve represents mainly the 3-methylene group moving across the energy barrier between the energy minima of the two puckered conformations, i.e., the pseudo-boat and pseudo-chair forms. Typically, this potential function is asymmetric, and two minima are observed that differ in energy if one ring conformer is more stable than the other. The existence of a single energy minimum at a positive value of ϕ, therefore, indicates that normally there is no stable chairlike conformer for this compound. This preference was explained for the oxabicyclic system, by Steyn and Sable,[14] using models. In the pseudo-boat conformation the dihedral angle between $1H_\alpha$ and $2H_\alpha$ is 55°, whereas in the pseudo-chair form this angle is decreased to 25° or less.

McCullough and co-workers[12] studied the dipole moments of some 3-substituted oxabicyclo[3.1.0]hexanes. They verified that the boatlike form, favored by torsional energies about bonds C_1–C_2 and C_4–C_5, is generally preferred. The *cis*- and *trans*-3-cyano compounds were both found to exist in this conformation. Their study also revealed, however, that steric interactions or dipole–dipole interactions between the 3-substituent and the epoxide oxygen can be large enough, as in the case of the *cis*-3-bromo derivative, to make the chairlike conformation the more stable one.

The isomeric epoxides **3a** and **3b** were prepared by the route shown in Scheme I. From mechanistic considerations of the epoxidation reaction with peracids[15,16] it was expected that both epoxide isomers would be formed. It was predicted that the steric bulk of the ester group could restrict the formation of the cyclic intermediate and result

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Table II. Observed and Calculated Proton Coupling Constants for *cis*- and *trans*-3-Carbomethoxy-6-oxabicyclo[3.1.0]hexane (3b, 3a)[a]

	observed coupling constants (Hz)		calculated coupling constants[b] (Hz) (dihedral angles)			
J protons	3a (trans)	3b (cis)	*trans*-chair	*trans*-boat	*cis*-chair	*cis*-boat
$1\alpha, 5\alpha$	0	0				
$1\alpha, 2\alpha; 5\alpha, 4\alpha$	0	0				
$1\alpha, 2\beta; 5\alpha, 4\beta$	0	0				
$2\alpha, 3\alpha; 4\alpha, 3\alpha$	*c*	8			8.8 (15°)	8.3 (20°)
$2\alpha, 3\beta; 4\alpha, 3\beta$	9	*d*	1.2 (105°)	7.2 (145°)		
$2\alpha, 2\beta; 4\alpha, 4\beta$	14	14				
$2\beta, 3\alpha; 4\beta, 3\alpha$	*c*	0			5.5 (135°)	0.8 (100°)
$2\beta, 3\beta; 4\beta, 3\beta$	8	*d*	8.8 (15°)	7.8 (25°)		

[a] Coupling constants are reported in Hz; the solvent was deuteriochloroform ($CDCl_3$). [b] The dihedral angles were estimated from Drieding models. The out of plane angles for the 3-carbon were approximated using references 12 and 14 as model systems. An angle of +15° was assumed for the *cis* boat[14] and a slightly larger angle of +18° was used for the *trans*-boat.[12] The out-of-plane angles for the chair forms were assumed to be less than the −14.25° calculated for the *cis*-bromoepoxypentane[12] because the ester group does not exert the severe dipole-dipole repulsion of the bromine atom on the epoxide oxygen. It would not be expected to force the molecule into a conformation where $H_{1\alpha}$ and $H_{2\alpha}$ were totally eclipsed. An angle of 10° was considered to be more realistic; possibly it would be smaller but not larger. [c] The carbomethoxy group is in the 3α position in this isomer. [d] The carbomethoxy group is in the 3β position in this isomer.

in a predominance of the thermodynamically stable trans isomer **3a**. It could also be argued that the carbomethoxy group is in a favorable position to participate in the formation of the transition state, directing the epoxy oxygen cis, as described by Cerefice and Fields[17] for the epoxidation of dihydrophthalates. The interpretation of the stereochemical outcome of the Cerefice and Fields experiments is controversial, however, and others have proposed a reasonable steric explanation.[18,19] Since it is possible that both of these effects could be operating in our epoxidation, we attempted to determine their relative importance to the observed isomer ratio by running the reaction in methylene chloride and in ether. Ether was selected because it is a polar solvent capable of disrupting the hydrogen bonding that is important in the cyclic transition state leading to both products and essential to any cis directing effects of the carbomethoxy group. When the product of the epoxidation reaction in methylene chloride was chromatographed on silica, two compounds were obtained in a 3:1 ratio; the more abundant compound was eluted first. Both substances had satisfactory elemental analysis (±0.40%) for the desired product, identical mass and ^{13}C NMR spectra. When the reaction was carried out in ether, it proceeded at least 5 times slower than in methylene chloride, as expected. The same two compounds were isolated with the same isomer predominating. The isomer ratio, however, was 87:13. These results suggested that the major isomer is the trans isomer.

The ^1H NMR spectra of the two isomers were distinctly different. The spectrum of the minor isomer appeared to be a simple first-order spectrum. Chemical shifts and coupling constants for this isomer could be measured with a 60- and an 80-MHz instrument. The spectrum of the major isomer was complex and it was necessary to carry out decoupling experiments on a 90-MHz spectrometer in order to determine the chemical shifts and coupling constants. The chemical shift assignments for both isomers are listed in Table I.

The coupling constants measured for **3a** and **3b** are listed in Table II. The dihedral angles corresponding to these J values were calculated by the Karplus equation, modified by Altona and co-workers[20] and applied by Steyn and Sable[14] to the 3-hydroxy isomers of 6-oxabicyclo[3.1.0]hexane. Either the cis and trans isomers are both in pseudo-boat form or the trans is in the pseudo-boat form and the cis is in the pseudo-chair form because of steric or dipole repulsion.

As noted, McCullough and co-workers[12] suggested that the dipole repulsions in the *cis*-3-bromo derivative of 6-oxabicyclo[3.1.0]hexane contributed to the assumption of the pseudo-chair form. The question addressed in this work is the effect of the 3-ester on the conformation of the fused ring system. The predicted coupling constants 2 or $4H_\alpha$–$3H_\alpha$ and 2 or $4H_\beta$–$3H_\alpha$ in the pseudoboat structure can be calculated from the dihedral angles estimated from models (Table II). If the cis isomer **3b** is in the pseudo-chair form, the dihedral angle for the 2β–3α protons is estimated from models to have a coupling constant of about 5 Hz. Alternatively, in the pseudo-boat form the dihedral angle (100°) should give a coupling constant approaching 0 Hz. The latter was observed for the minor isomer. This is in agreement with the coupling constants observed for 3-hydroxy,[14,21] 3-acetoxy,[14] 3-cyano,[12] and more recent studies of the solvolysis of sulfonate esters of the 3-hydroxymethyl derivatives.[22] The assignment of the methylene signals in the minor isomer was made on the basis of this coupling. The downfield methylene protons, which were not coupled to the C-3 proton, were consistent with the β-pseudo-equational protons of the cis isomer in the pseudo-boat conformation. In the major isomer both methylene protons are coupled to each other and to the C-3 proton and their shift valves are very close so that unambiguous assignment of α and β hydrogens could not be made. When the upfield proton was irradiated in a 90-MHz NMR, the downfield signal collapsed to a doublet with J = 8 Hz. The upfield proton appeared more strongly coupled to the C-3 proton (J = 9 Hz) consistent with the diaxial orientation of these two protons in the pseudo-boat conformation of the trans isomer. Although our correlation of coupling constants for these two protons with isomer assignment agreed very well with those of Steyn and Sable,[14] there was no correlation between assignment of chemical shifts valves for the methylene protons. Pre-

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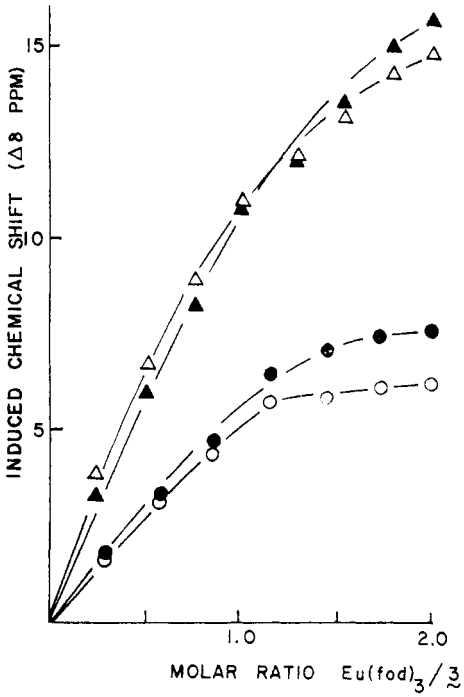

Figure 2. Plot of the lanthanide-induced chemical shift profiles ($\Delta\delta$) for the C-1 and C-5 protons (○, △) and C-3β (▲) and C-3α (●) protons of the major isomer **3a** (△, ▲) and the minor isomer **3b** (○, ●) of 3-carbomethoxy-6-oxabicyclo[3.1.0]hexene vs. the mole ratio of shift reagent Eu(fod)$_3$ (tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium) to **3**. Incremental amounts of the shift reagent dissolved in $CDCl_3$ were added to solutions of **3a** (0.32 M) or **3b** (0.42 M).

sumably, this is due to the differing inductive and field effects of the hydroxy and carbomethoxy substituents.

In order to further substantiate the isomer assignments, ^{13}C and ^1H NMR studies were carried out with Eu(hfc)$_3$ and Eu(fod)$_3$. This would be a credible way to differentiate the cis and trans isomers of **3** if our conformational analysis were correct.[23] There are two potential coordination sites for the europium ion in **3**, the epoxide oxygen and one of the two ester oxygens. In the pseudo-boat form (but not the pseudo-chair) conformation of the cis isomer the europium can bind simultaneously to these two sites to form a seven-membered ring chelate in which the metal is octacoordinate. This is not true for either conformation of the trans isomer. For this isomer a preference for the exo lone pair of electrons on the epoxide oxygen, with possible dimer formation in concentrated solution, was predicted. The results of the NMR experiments were consistent with this interpretation (Figure 2).

The observed chemical shift changes were linear from 0 to 0.4 mol ratio (mr) of Eu(hfc)$_3$ to compound, with correlation coefficients greater than 0.996. The values for mr = 0.2 are listed in Table I. The ^{13}C data clearly shows both epoxide and ester are involved in binding europium to the minor isomer, while only the carbons of the epoxide ring are significantly shifted in the major isomer. The ^1H NMR data indicates that the β and α protons of the minor isomer are in very different environments when europium is present, confirming that the europium is bound on one face of the molecule preferentially. In the major isomer the methylene protons are affected by the shift reagent almost to the same extent, while the β proton on C_3 is greatly deshielded. Figure 2 suggests that the minor isomer forms a 1:1 complex with the shift reagent, whereas the major isomer does not. This technique was recently used to establish the stereochemistry of isobenxofuran photodimers.[24]

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Experimental Section

All materials obtained from commercial suppliers, except sodium metal and *m*-chloroperbenzoic acid, were purified prior to use. All liquid starting materials were distilled. Ethanol and methanol were distilled over magnesium metal. Thionyl chloride was purified as described in Fieser and Fieser.[25] Triethylamine was distilled over calcium hydride and stored over sodium hydroxide pellets.[26] Solvents were passed through basic alumina (Merck reagent grade) and distilled. Silica gel 60 was used in column chromatography. Boiling points are reported uncorrected. IR spectra were recorded on a Beckman Model IR-33 spectrometer. ^1H NMR was determined on the following spectrometers: Varian T-60, Varian EM-360, Varian FT-80A, and Perkin Elmer R-32; ^{13}C spectra were obtained with a Varian FT-80 spectrometer. Both ^1H and ^{13}C spectra were taken in deuteriochloroform ($CDCl_3$) and chemical shifts are expressed in parts per million (δ) downfield from the internal standard, tetramethylsilane (Me_4Si). Mass spectra were obtained with positive chemical ionization (methane) on a Reibermag GC–MS instrument. Tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorato]europium(III) derivative (Eu(hfc)$_3$) and tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)europium (Resolve-Al EuFOD; 99% pure) were products of Aldrich Chemical Co.

***cis*- and *trans*-3-Carbomethoxy-6-oxabicyclo[3.1.0]hexane (3b, 3a).** 3-Cyclopentenecarboxylic acid (**1**), prepared by the method of Schmid and Wolkoff,[26] was converted to the acid chloride by treatment with thionyl chloride.[27] The addition of the acid chloride to a solution of methanol (excess) containing 1.3 equiv of triethylamine gave the ester **2** in 61% yield from the acid: bp 32 °C (1.2 mm); ^1H NMR δ 2.65 (d, 4 H), 3.08 (m, 1 H), 3.68 (s, 3 H), 5.63 (s, 2 H).

A solution of the ester **2** (17.0 g, 0.14 mol) in 60 mL of methylene chloride was cooled to 2 °C and *m*-chloroperbenzoic acid (Aldrich, 80%, 32.2 g, 0.19 mol) in 220 mL of methylene chloride was added dropwise over a 1-h period. The reaction mixture was stirred at room temperature for approximately 24 h. Freshly prepared sodium sulfite solution (10 mL) was added and stirring continued until a negative starch–iodide test was obtained. The methylene chloride layer was separated and washed successively four times with 20 mL of 10% sodium bicarbonate, two times with 20 mL of water, and two times with 20 mL of saturated sodium chloride solution, dried (Na_2SO_4), and concentrated at reduced pressure. The isomeric mixture of **3** was obtained (14.9 g, 0.11 mol) in a 78% yield as clear, colorless oil: bp 40 °C (0.4 mm).

The isomers **3a** and **3b** were separated on a medium-pressure silica gel column (1 m × 3 cm) using 20% ethyl acetate in hexane as eluant. The ratio of the first compound (**3a**) recovered off the column to the second (**3b**) was 3:1. The two compounds were verified as isomers by their mass spectra (*m/e* 142 (parent ion)) and elemental analysis (calcd for $C_7H_{10}O_3$, C, 59.14; H, 7.09; found for first isomer, C, 58.80; H, 7.18; found for second isomer, C, 58.78; H, 7.18]; ^1H NMR and ^{13}C NMR spectral data are presented in Tables I and II.

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