

shown by nmr and ir spectra. Purification of this product other than by glpc proved difficult.

endo,exo-Tricyclo[3.2.2.0^{2,4}]nonan-6-ol (10). A solution of 7.2 g of olefin 9 in 100 ml of tetrahydrofuran at 0° was treated with a stream of diborane generated from a solution of 4.75 g of NaBH₄ in diglyme and 25 ml of BF₃·Et₂O in 30 ml of diglyme according to the procedure previously used.^{2a} This led to 7.31 g (87%) of a solid which upon crystallization from pentane had mp 165–168°. Glpc (B) of the original mixture indicated greater than 90% of a single alcohol, 10, nmr τ 6.4 (1) m, 6.95 (1) s, 8.15 (3) m, 8.5 (3) m, 8.88 (1) m, 8.18 (2) m, 9.8 (2) m.

Anal. Calcd for C₉H₁₄O: C, 78.26; H, 10.14. Found: C, 77.98; H, 10.05.

endo-Tricyclo[3.2.2.0^{2,4}]nonan-6-one (11). To a stirred suspension of 25 g of chromic acid in 250 ml of pyridine at 0° was slowly added a solution of 7.3 g of alcohol 10 in 80 ml of pyridine. The mixture was stirred for 39 hr at room temperature followed by addition of 100 ml of water and extraction ten times with 150-ml portions of pentane. The pentane extracts were washed with cold 10% hydrochloric acid, 10% sodium carbonate, and water. After drying and removal of the solvent through a Vigreux column, 5.86 g of crude ketone 11 was obtained. Glpc (B) indicated only 65% purity. Distillation at 100° (0.5 Torr) yielded the pure ketone: *n*²⁰_D 1.5094; nmr τ 7.55 (2) m, 8.15 (2) d, 8.31 (4) m, 8.91 (2) m, 9.72 (2) m.

Anal. Calcd for C₉H₁₂O: C, 79.41; H, 8.82. Found: C, 79.52; H, 8.99.

endo,endo-Tricyclo[3.2.2.0^{2,4}]nonan-6-ol (12). To a solution of lithium aluminum tri-*tert*-butoxyhydride at –65°, prepared according to the procedure of Brown,²⁰ was added 0.9 g (0.007 mol) of ketone 11 in 15 ml of tetrahydrofuran. After 24 hr at this temperature the reaction mixture was warmed to room temperature and worked up as in the other reductions. Glpc analysis indicated 79% of a single alcohol, mp 136–140°, nmr τ 6.3 (1) m, 7.08 (1) s, 8.0 (2) m, 8.5 (5) m, 8.9 (1) t, 9.2 (2) m, 9.7 (2) m.

Anal. Calcd for C₉H₁₄O: C, 78.26; H, 10.14. Found: C, 78.42; H, 10.31.

Europium Shift Reagent Studies. The Eu(fod)₃ used was taken directly from a fresh bottle supplied by Norell. The alcohols were subjected to glpc purification directly before use and then dissolved in CCl₄ for analysis. The shift reagent was weighed out and added in increments of about 10 mg, after which the nmr was observed and recorded. Since in many instances the peaks were broad, the centers of gravity of the peaks were used and shift values were deduced from these.

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Registry No.—2, 50744-35-9; 3, 50744-41-7; 4, 50898-31-2; 5, 51260-36-7; 6, 51260-35-6; 7, 51260-37-8; 8, 50744-36-0; 9, 27019-95-0; 10, 51260-33-4; 11, 51260-38-9; 12, 51260-34-5; cyclopropene, 2781-85-3; 1,3-cyclohexadiene, 592-57-4.

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Synthesis and Relative Stereochemical Assignment of the Four Isomeric Cyclopropane-Bridged Tricyclo[3.2.2.0^{2,4}]nonan-6-ols^{1,2d}

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The four isomeric tricyclo[3.2.2.0^{2,4}]nonan-6-ols, containing a cyclopropane ring fused in a homocyclopropylcarbinyl relationship to the alcohol functionality, have been synthesized from the corresponding alkenes. Stereochemical assignments are accomplished by chemical means and with the aid of nmr shift reagents.

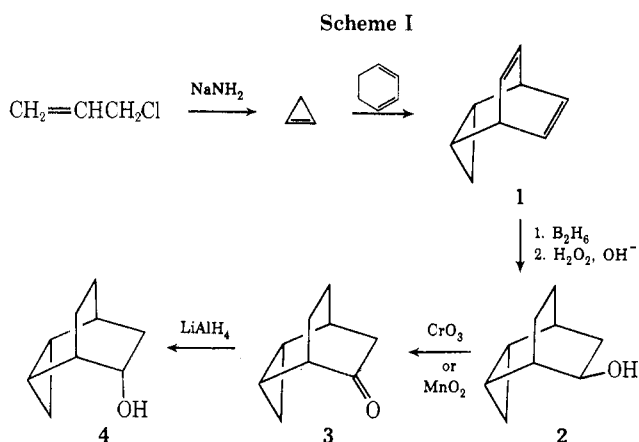
Reactivity studies³ of various polycyclic compounds containing bridged or fused cyclopropane rings have revealed the great diversity of reactivity of 2-cyclopropylethyl derivatives from the highly activated and reactive^{3a,b,e-h} to the highly deactivated and unreactive^{3c,d} systems. Despite the inherent problems of dissecting strain effects from electronic interaction effects and neighboring group effects, we have extended our earlier work⁴ with conformationally unrestrained 2-cyclopropylethyl systems to studies using compounds with structural frameworks that

have geometries and relative orientations of reactive groups that are well defined, namely, the four isomeric tricyclo[3.2.2.0^{2,4}]nonan-6-ols (*endo,endo*-, *endo,exo*-, *exo,endo*-, and *exo,exo*-)⁵ in which there are four correspondingly different homocyclopropylcarbinyl geometrical orientations. Solvolyses of the parent 2-bicyclo[2.2.2]octyl system are not strongly assisted by neighboring carbon participation and thus any resultant cyclopropane participation should appear in rate and product studies of the solvolyses and should not be swamped^{6a} by the dominant

reactivity patterns or by the structural symmetry of the corresponding hydrocarbon system, as is the case for the 2-norbornyl systems,^{6b} to which the present study is homologous.

In this paper the synthesis of the four isomeric tricyclo[3.2.2.0^{2,4}]nonan-6-ols (2, 4, 8, and 9) from the requisite olefins,⁷ characterization, and relative stereochemical assignment are reported. The acetolyses of the corresponding brosylate esters will be reported separately.

Synthesis of the Cyclopropyl Endo Epimers. The epimeric cyclopropyl endo alcohols, *endo,exo*- (2) and *endo,endo*-tricyclo[3.2.2.0^{2,4}]nonan-6-ol (4), were synthesized by a route similar to that employed by Wiberg and Wenzinger^{6b} in the synthesis of the corresponding tricyclo[3.2.1.0^{2,4}]octan-6-ols. This route is shown in Scheme I. Cyclopropene, generated by the procedure of Closs,^{8a} was added to 1,3-cyclohexadiene to form *endo*-tricyclo[3.2.2.0^{2,4}]non-6-ene (1). The overall yield of this reaction, which was quite low (1–5%, based on sodium amide^{8b}), was sensitive to a number of variables, notably the manufacturer, individual lot, and shelf age of the commercial sodium amide used.^{8c} In this case, despite the low overall yield, sufficient quantities of 1 were obtained, since the reaction proved amenable to large-scale operation. The 220-MHz nmr spectrum of 1⁷ confirms the expected *endo* configuration of the cyclopropane ring.

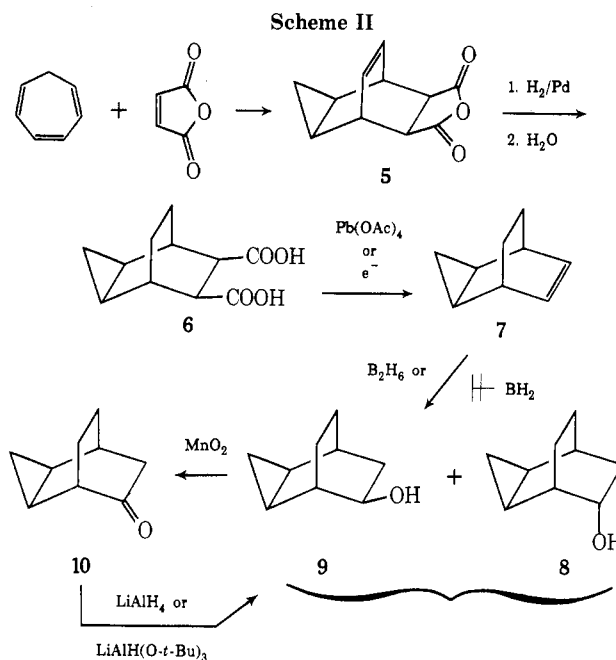


Hydroboration-oxidation⁹ yielded the *endo,exo* alcohol 2 as the only product. The stereospecificity of this reaction is a consequence of the *endo* cyclopropane ring, which shields the *endo* side of the double bond from attack by diborane. The *exo* orientation of the hydroxyl group, while not required by the spectrometric evidence, is established through the proof of orientation for the *endo,endo* epimer (4), described below.

endo-Tricyclo[3.2.2.0^{2,4}]nonan-6-one (3) was synthesized by the oxidation of 2, either by chromium trioxide in pyridine¹⁰ or activated manganese dioxide in pentane,¹¹ in 75–80% yield. Although the yields for both procedures were comparable, the manganese dioxide method is much the simpler and cleaner one. The physical and spectrometric properties of 3 are in excellent agreement with those reported independently.^{8c, 12}

Reduction of 3 with lithium aluminum hydride in ether yielded only the *endo,endo* alcohol (4). The nmr spectrum of this alcohol enables the assignment of the relative orientation of the cyclopropane ring and the hydroxyl group to be made unambiguously: the *endo* or interior secondary cyclopropyl proton of 4 is deshielded by 0.84 ppm (relative to the corresponding proton in the *endo,exo* epimer 2). This shift, indicative of the close proximity¹³ of the oxygen atom and the interior cyclopropyl methylene proton to each other in 4, confirms the *endo,endo* configuration of this compound.

Synthesis of the Cyclopropane Exo Epimers. The cyclopropane *exo* epimers, *exo,endo*- (8) and *exo,exo*-tricyclo[3.2.2.0^{2,4}]nonan-6-ol (9), were not isolated separately, but rather were obtained as mixtures of the two alcohols (which resisted all attempts at preparative separation), as was anticipated from inspection of molecular models. It is apparent from models that there may be only a slight steric advantage toward the *endo* side of 7. The identification and composition of these mixtures was determined through the use of an nmr shift reagent, Eu(fod)₃, described in detail below. Mixtures of 8 and 9 were synthesized according to procedures outlined in Scheme II.

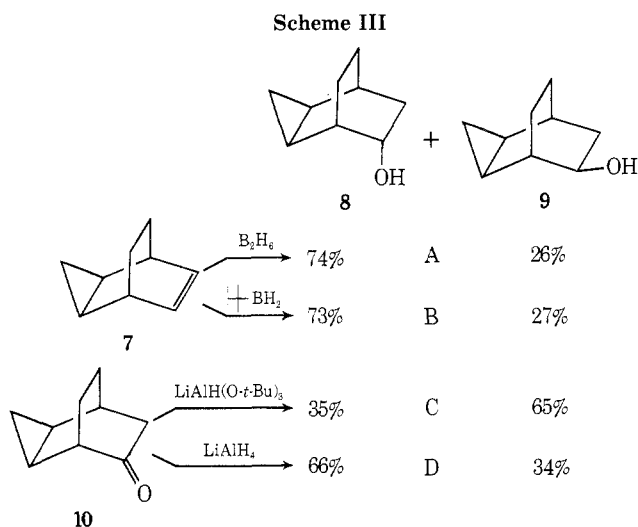


exo-Tricyclo[3.2.2.0^{2,4}]non-6-ene (7)⁷ was prepared via the decarboxylation of the diacid 6¹⁴ by two methods: anodic oxidation¹⁵ and lead tetraacetate decarboxylation.¹⁶ Although the yields for the two routes are comparable (30–40%) on a small scale, the lead tetraacetate procedure was found to be more convenient for larger scale preparations, owing to difficulties encountered in large-scale electrolyses. The anticipated *exo* configuration of the cyclopropane ring is confirmed by the 220-MHz nmr spectrum, the details of which have been reported.⁷

Hydroboration-oxidation⁹ of 7 yielded a product (in better than 80% yield) whose physical and spectrometric properties were consistent with a mixture of *exo,endo*- (8) and *exo,exo*-tricyclo[3.2.2.0^{2,4}]nonan-6-ol; this result is not surprising, since 7 lacks the obvious steric bias between *exo* and *endo* attack present in *endo* olefin 1 or in norbornene. This epimeric mixture (mixture A) was shown *via* nmr shift reagent analysis to consist of 74% 8 and 26% 9 (see below). In order to maximize the effect of any steric bias inherent in 7, the hydroboration was performed with the bulky 2,3-dimethyl-2-butylborane¹⁷ (thexyl borane), followed by oxidation. The product (mixture B) appeared to be identical with mixture A, described above; shift reagent analysis showed it to consist of 73% 8 and 27% 9. The apparent lack of effect of the bulkier thexyl borane on the composition of the mixture may indicate that the preference of *endo* attack by boron on 7 is electronic in origin, perhaps involving interaction with the cyclopropane ring, or that the stereochemistry of the reactions is determined by product control and is insensitive to the steric bulk of the reagents.

The mixture of *exo,endo* and *exo,exo* alcohol from conventional hydroboration-oxidation (mixture A) was clean-

ly oxidized by MnO₂ in pentane to a single ketone, *exotricyclo*[3.2.2.0^{2,4}]nonan-6-one (10), whose spectrometric properties were consistent with this structure.¹⁸ This ketone was reduced with lithium aluminum tri-*tert*-butoxyhydride in ether, again in an effort to take advantage of any steric bias present in 10. The product (mixture C), which in other respects appeared to be identical with mixture A, was shown by shift reagent analysis to have the composition 35% 8 and 65% 9. This result, which indicates a preference for *endo* attack of hydride on the carbonyl group of 10, may be anticipated from inspection of models of 10: the tertiary cyclopropyl protons are held somewhat further away and at a wider angle from the reactive site than are the protons of the saturated C-8-C-9 bridge. The stereoselectivities of these reactions are summarized in Scheme III. Thus it may be seen that the stereochemistry of reactions A, B, and D are determined by product development control, while in reaction C, showing the result of a steric bias, the stereochemical preference is determined by steric approach control. Similar hydride reduction selectivities are noted in the accompanying paper by Wenzinger and Ors.¹



Identification and Composition of Mixture of Cyclopropane Exo Epimers. The mixtures described above were characterized through analysis of their nmr spectra taken in the presence of a paramagnetic rare-earth chelate complex: tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-5-octa-4,6-dionato)europium(III), or Eu(fod)₃. A similar europium chelate [with 2,2,6,6-tetramethyl-3,5-heptanedione, Eu(thd)₃], first described by Eisentraut and Sievers,²⁰ produces downfield shifts in proton nmr spectra. The use of this and other europium chelates produces little line broadening [owing to the short relaxation time of Eu(III)] and little effect on coupling constants. Hinckley²¹ observed large shifts for compounds with heteroatoms bearing unshared electrons (especially alcohols and amines, with smaller shifts for carbonyls and ethers). A postulated mechanism²¹ involves reversible incorporation of the heteroatom in the europium coordination sphere. Shift magnitudes correlate linearly with the relative concentration of substrate to chelate. The magnitude of the shifts for individual protons correlates with the estimated distance of the proton from the metal atom.

DeMarco and coworkers²² have shown that the Eu(thd)₃-induced shifts ($\Delta\delta_{Eu}$, in parts per million, for equimolar solutions of alcohol and chelate) of the protons of a series of rigid secondary alcohols can be correlated with the distance *R*, in Å) of each proton from the oxygen atom in each alcohol. For rigid, monofunctional alcohols in deuteriochloroform, they observed a linear correlation between

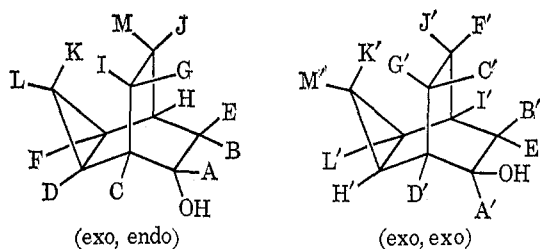
$\log \Delta\delta_{Eu}$ and $\log R$, over a wide range of shifts (0.7–20 ppm) and distances (2–10 Å). The hydroxyl and carbinol methine (OHOH) protons deviated significantly from the linear plot and are more strongly shifted than anticipated. Deviations probably result from failure to include an angle function ($3 \cos^2 - 1$) and from measurement of distances to the alcohol oxygen instead of to the europium atom. Rondeau and Sievers²³ have discovered that Eu(fod)₃ gives larger shifts with weak donors; this chelate is a stronger Lewis acid, owing to the electron-withdrawing fluorine substituents. It is also appreciably more soluble in carbon tetrachloride than Eu(thd)₃. The use of these reagents and common assumptions and limitations on their use have been reviewed recently.^{23b}

The nmr spectra of mixture A and mixture C in the presence of approximately 0.25 equiv of Eu(fod)₃ are described in detail in the Experimental Section. For simplicity we will assume that which is subsequently proven: that the major isomer in mixture A is 8, and the major isomer in mixture C is 9. Mixture A is thus 74% 8 and 26% 9, while mixture C is 35% 8 and 65% 9. These are the ratios of the areas of the peaks at 12.1 and 10.1 ppm in each spectrum, corresponding to the CHOH proton in 8 and 9, respectively.²⁴ By a careful analysis of the multiplicity and relative areas of peaks and through decoupling of the shifted spectra it is possible to make structural assignments of the remaining regions in each spectrum of the different mixtures (A and C) and determine the number of protons from either 8 or 9 absorbing in each region. Through double-irradiation experiments, it was possible to determine a number of the coupling constants accurately. For compound 8 the following coupling constants may be assigned: $J_{AE} = 9.1$, $J_{BE} = 13.5$, and $J_{AB} = 2.3$ Hz. For compound 9 the corresponding coupling constants are $J_{A'E'} = 10.0$, $J_{B'E'} = 13.0$, and $J_{A'B'} = 2.3$ Hz. Coupling constants for geminal protons in medium-size rings are typically 11–14 Hz; vicinal coupling constants in such systems vary with dihedral angle. Typical values are 8–10 Hz for $\phi = 0^\circ$, 2–3 Hz for $\phi = 60^\circ, 120^\circ$, and near zero for $\phi = 90^\circ$. These partial coupling patterns for both 8 and 9 are consistent with the structures shown.

The results of additional double-irradiation experiments provide more information about the relationships between the protons of 8 and 9. Irradiation at 6.0 ppm in the spectrum of mixture C ($H_{B'}$ and $H_{C'}$), in addition to decoupling $H_{A'}$ and $H_{E'}$ (from $H_{B'}$; see Table I), results in the collapse of a doublet ($J = 10$ Hz) at 4.1 ppm ($H_{F'}$) and the collapse of a doublet ($J = 12$ –13 Hz) at 3.1 ppm ($H_{G'}$). Thus $H_{C'}$ is geminal to $H_{C'}$, and $H_{F'}$ is vicinal to $H_{C'}$, at a dihedral angle of about 0° . The isolated position in the shifted spectrum and coupling pattern (triplet, $J = 7$ –8 Hz) of $H_{M'}$ suggest that it is the exterior secondary cyclopropyl proton of 9. Irradiation in the 5.8–6.4-ppm region of mixture A (H_D) resulted in changes in the splitting pattern in the 1.7–2.2-ppm region (H_K, H_L, H_M ; see Table I). However, it was not possible to obtain any coupling constants or definite assignments owing to the complexity of this region.

Thus far the shift reagent has been used solely as a tool to modify spectral appearance to simplify analyses and the corresponding assignments. In addition, if these chelate complexes are similar to those studied by DeMarco,²² there should be correlation of the distance of the proton from the chelate. It is inherent in these assumptions that there is only one (or one predominant) chelate complex formed for each alcohol and that the conformations involved are similar. (In the accompanying paper by Wenzinger and Ors¹ magnitudes of shifts were shown to be linear with concentration of shift reagent for similar compounds.) Utilizing the data and postulates summarized

Table I



$\Delta\delta$, ppm	Proton ^a	Region, ppm rel to Eu(fod) ₃	Proton ^a	$\Delta\delta$, ppm
8.2	H _A	11.8–12.4	H _{A'}	6.1
5.6	H _B	9.9–10.3		
4.8	H _C	7.6–7.9		
4.7–5.0	H _D	6.7–6.9	H _{B'} , H _{C'}	4.0
		5.8–6.4	H _{D'}	3.7
4.0	H _E	5.5–5.7		
		4.9–5.4	H _{E'}	3.1
		4.3–4.8	H _{F'}	2.3
2.8–2.9	H _F , H _G	3.7–4.1	H _{G'} , H _{H'} , H _{I'}	1.9, 1.5–1.6
1.2–1.6	H _H , H _I , H _J	2.4–3.6	H _{J'} , H _{K'} , H _{L'}	1.0–1.4
0.5–1.5	H _K , H _L , H _M	1.7–2.2	H _{M'}	0.5
		1.0–1.4		

^a Letter assignments are used for protons to indicate magnitudes of observed shifts; A protons are shifted the most in the spectra.

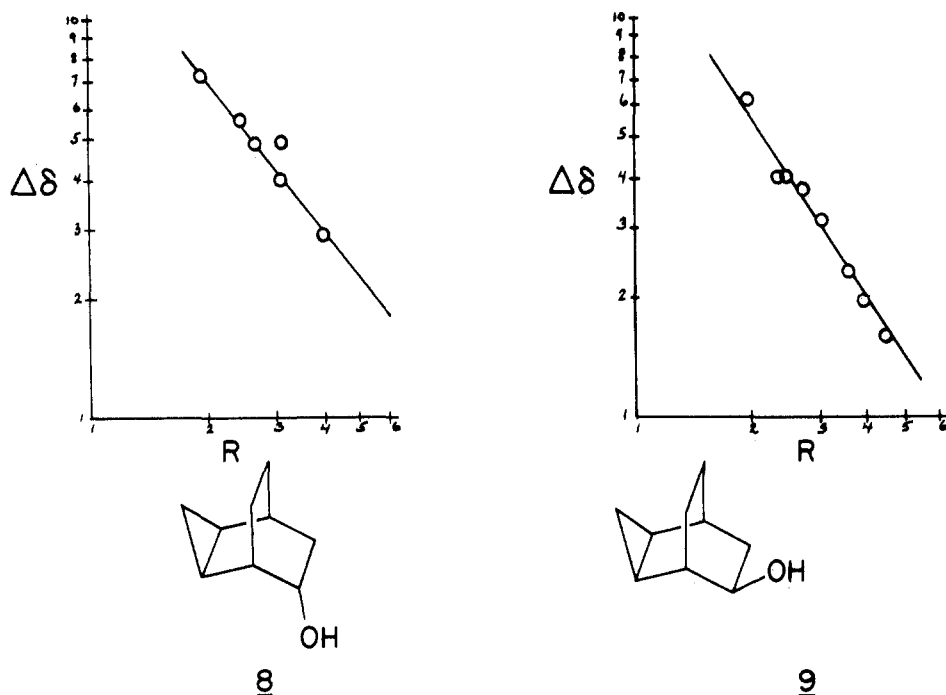


Figure 1.

above,^{23b} the proton assignments listed in Table I, and the estimated chemical shift differences due to the paramagnetic reagent ($\Delta\delta$) in Table I, may be correlated with the distances of each proton from the oxygen atom (estimated from models). Shift differences were evaluated as the chemical shift in the presence of chelate (relative to the chelate proton resonance) minus the chemical shift in the absence of chelate (relative to TMS) for each proton. The use of the chelate resonance as a reference position leads to some difficulties. The position of the chelate protons is 0.5 ppm upfield from TMS (in the absence of alcohol). DeMarco²² has demonstrated that the chelate position does vary with the relative concentrations of chelate and alcohol, but the variation is not large. Thus, although precise quantitative results ($\Delta\delta$ per mole) are not obtainable from the obtained data, the qualitative correlations

observed should be relatively insensitive to this choice of reference.

Using the values in Table I, plots of $\log \Delta\delta$ vs. $\log R$ (Figure 1) show good linearity, as observed by DeMarco and coworkers,²² especially for the exo,exo alcohol 9, for which the greater number of firm chemical shift assignments (eight) may be made. Measured $\Delta\delta$ values were used directly, rather than extrapolated to unit concentration of chelate, since extrapolation based on only one concentration of chelate is not justified (however, see ref 1). Although distances should obviously be measured from the protons to the europium atom, this is not possible with these systems, as spacial orientation and distances are not known for these complexes. The slopes of the plots are about -2 , which is typical.^{23b}

The assignments for both isomers, based on analyses of

peak multiplicities, chemical shifts, and peak areas for both mixtures A and C, are in good agreement with correlation of induced shifts *vs.* distance from the oxygen atoms for both alcohols 8 and 9, with the exception of H_D in 8, the nearer tertiary cyclopropyl proton, which is shifted downfield about 1 ppm more than anticipated. This suggests greater proximity of this cyclopropyl proton and the europium atom, further supporting the stereochemical assignments of 8 and 9. These stereochemical assignments are further supported by the products of solvolyses of the corresponding brosylates (to be reported later), providing also a mechanistic consistency for the assignments of these structures.

The fact that the CHOH proton in one isomer (8) is shifted about 2 ppm further downfield than the corresponding proton in the other isomer (9) cannot be a consequence of a difference in their respective distances from the oxygen. A plausible explanation for this difference is that the europium chelate complexes preferentially with isomer 8, *i.e.*, the equilibrium constant for incorporation of 8 into the coordination sphere of the europium is larger than the equilibrium constant for incorporation of 9, resulting in greater shifts for alcohol 8. This may be readily accounted for in terms of a steric effect. The oxygen of 8 is in a sterically less crowded environment, as may be seen from models. This is also consistent with the observed steric effects in the hydride reductions.

Experimental Section

Nmr spectra were recorded on a Varian Associates A-60 spectrometer or a Hitachi Perkin-Elmer R-20B spectrometer. All decoupling experiments were performed on the latter instrument. Chemical shifts are reported in units of δ (parts per million) downfield from TMS. Spectral data are presented as follows: chemical shift, splitting pattern (number of protons or relative area, coupling constant J in hertz, assignment where known). Infrared spectra were recorded on a Perkin-Elmer 337 grating infrared spectrophotometer or a Beckman IR-5 spectrophotometer. Mass spectra were recorded on a Varian Associates Model M-66 spectrometer and are reported as follows: peak, m/e (per cent of base peak). Melting points are uncorrected.

endo-Tricyclo[3.2.2.0^{2,4}]non-6-ene (1). Cyclopropene was generated by a modification of the method used by Closs and Krantz^{8a} as adapted by DiFate.^{8c} Sodium amide (400 g, 10 mol) was suspended in light paraffin oil in a flask fitted with dropping funnel, dry nitrogen source, mechanical stirrer, and Dry Ice-carbon tetrachloride condenser. 3-Chloropropene (800 g, 10.4 mol) was added dropwise over 12–15 hr to the stirred suspension, which was maintained at 90–100°. The resultant gas was passed through the Dry Ice condenser and through 2 l. of 25% sulfuric acid. The gas was then passed into 1,3-cyclohexadiene (125 g, 1.56 mol) and stirred at 0° in an ice-water bath with a magnetic stirrer. After generation was complete the mixture was dried with anhydrous potassium carbonate, kept at 0–5° for 12 hr, and filtered. Atmospheric distillation through a 6-in. Vigreux column gave 1,3-cyclohexadiene at 60–80° (80–100 g) and *endo*-tricyclo[3.2.2.0^{2,4}]non-6-ene at 160–170° as a waxy solid (collected with an air condenser heated intermittently with a hot-air pistol to prevent plugging), average yield of 17 g. The yield of product varied from 5 to 40 g depending chiefly on the commercial sodium amide used.^{8c} The average yield of 17 g (0.14 mol) represents a 1.4% yield based on sodium amide, or 14% based on Closs' estimate of 10% yield of cyclopropene generated. Spectral details are identical with those reported.^{7,8c}

endo,exo-Tricyclo[3.2.2.0^{2,4}]nonan-6-ol (2). Diborane, generated by the addition of sodium borohydride (2.5 g, 0.066 mol) dissolved in 50 ml of dry diglyme to boron trifluoride-ethyl ether (20 g, 0.141 mol) in 50 ml of dry diglyme, was passed into a solution of *endo*-tricyclo[3.2.2.0^{2,4}]non-6-ene (15.0 g, 0.125 mol) in 300 ml of dry tetrahydrofuran, stirred at 0°. (Excess diborane was passed into running water.) After generation was complete (about 1 hr), the tetrahydrofuran solution was stirred under a dry nitrogen atmosphere at room temperature for an additional 2 hr. The solution was cooled to 0°, and 15 ml of 10% aqueous sodium hydroxide was carefully added dropwise, followed by the careful dropwise addition of 15 ml of 30% aqueous hydrogen peroxide. This mix-

ture was then stirred at 0° for 3 hr and at room temperature for 1 hr. The mixture was then diluted with 1 l. of water and extracted with five 200-ml portions of ether. The combined ether extracts were washed with five 500-ml portions of water and once with 500 ml of saturated sodium chloride solution. The ether layer was dried over anhydrous potassium carbonate and the solvent was removed *in vacuo*. The residue (10 g, 59%) was crystallized from purified pentane, mp 155–160° (sealed tube).

Anal. Calcd for C₉H₁₄O: C, 78.21; H, 10.21. Found: C, 78.44; H, 10.57.

Nmr 0.33, m (2 H, secondary cyclopropyl protons), 0.95, m (2 H, tertiary cyclopropyl protons), 1.20–2.20, broad m (8 H, methylene and bridgehead protons), 3.00, sharp s (1 H, hydroxyl proton), 3.75 ppm, m (1 H, CHOH proton).

Ir spectrum 3610, 3070, 3010, 2940, 2865, 1460, 1405, 1345, 1100, 1020, 1000 cm⁻¹.

endo-Tricyclo[3.2.2.0^{2,4}]nonan-6-one (3). A. To a stirred suspension of chromic anhydride-pyridine complex,¹⁰ prepared by the careful addition of chromic anhydride (11.0 g, 0.11 mol) to 60 ml of dry pyridine, was added 2 (3.0 g, 0.022 mol) in 15 ml of dry pyridine. The mixture was stirred at room temperature under nitrogen for 24 hr. Water (100 ml) was added and the aqueous solution was extracted with ten 50-ml portions of purified pentane. The pentane extracts were washed with 200-ml portions of 10% HCl solution, water, and saturated sodium bicarbonate. The pentane solution was dried over anhydrous magnesium sulfate and the solvent was removed *in vacuo*. The product was crystallized from pentane and purified by sublimation at atmospheric pressure, yield (white solid) 2.3 g (75%), mp 122–124° (sealed tube).

Anal. Calcd for C₉H₁₂O: C, 79.37; H, 8.88. Found: C, 78.49, 78.28; H, 9.26, 9.56.

The nmr, ir, and mass spectra are identical with those reported.^{8,12}

B. 2 (5.0 g, 0.0362 mol) was dissolved in 300 ml of purified pentane. Activated manganese dioxide^{11,25} (50 g) was added, and the mixture was stirred at room temperature for 100 hr. The reaction mixture was filtered and solvent was removed *in vacuo*. The infrared spectrum of the crude product showed the presence of unreacted alcohol (*ca.* 10%). The residue was dissolved in 50 ml of pentane and stirred with 2 g of activated alumina for 10 min, then filtered. The alumina was washed with a few milliliters of pentane, the pentane layers were combined, and solvent was removed *in vacuo*. The product showed no OH stretching bands in the infrared, yield 4.0 g (81%). The product was identical in all respects with the ketone prepared by the preceding method.

endo,endo-Tricyclo[3.2.2.0^{2,4}]nonan-6-ol (4). A solution of 3 (2.0 g, 0.015 mol) in 30 ml of dry ether was added dropwise at room temperature to a stirred suspension of lithium aluminum hydride (0.30 g, 0.008 mol) in 30 ml of dry ether. After the addition was complete (about 15 min) the mixture was stirred for an additional 15 min, then cooled to 0° with an ice-water bath. Water and wet sodium sulfate (to a total of about 50 ml) were added carefully. The ether layer was separated, washed with 50-ml portions of water and saturated sodium chloride solution, and dried over anhydrous potassium carbonate. The ether was removed *in vacuo*, and the residue was crystallized from pentane, yield 1.5 g (75%), mp 173–175° (sealed tube).

Anal. Calcd for C₉H₁₄O: C, 78.21; H, 10.21. Found: C, 78.26; H, 10.40.

Nmr 0.30, complex m (1 H, exterior cyclopropyl proton), 0.83, m (2 H, tertiary cyclopropyl protons), 1.17, m (1 H, interior cyclopropyl proton), 1.3–1.8, m (6 H, methylene protons), 2.05, broad s (2 H, bridgehead protons), 2.67, sharp s (1 H, hydroxyl proton), 3.71 ppm, m (1 H, CHOH proton).

Ir spectrum 3620, 3360, 2015, 2925, 2880, 1464, 1440, 1120, 1080, 1037, 1009 cm⁻¹.

exo-Tricyclo[3.2.2.0^{2,4}]non-8-ene-exo-6,exo-7-dicarboxylic Anhydride¹⁴ (5). Maleic anhydride (255 g, 2.6 mol) and cycloheptatriene²⁶ (270 g, 2.9 mol) were dissolved in 1000 ml of xylene. The mixture was heated at reflux for 90 hr. The solution was cooled to 5° and the crystals were isolated by vacuum filtration, yield 300 g (62%), mp 101–103° (lit. mp 101°).¹⁴

exo-Tricyclo[3.2.2.0^{2,4}]nonane-exo-6,exo-7-dicarboxylic Anhydride¹⁴ 5 (10.0 g, 0.526 mol), dissolved in 75 ml of acetone, and palladium (10% on activated charcoal, 0.6 g, prerduced) in 100 ml of acetone were mixed and stirred under hydrogen at atmospheric pressure. Hydrogen was absorbed over a period of 3 hr (1.20 l., 0.053 mol, 101%). The mixture was filtered and the acetone was removed *in vacuo*, yield (white solid) 10.0 g (99%). A small sample was recrystallized from 50% ether-pentane to give long, flat needles, mp 137–139° (lit. mp 140).¹⁴

Nmr (CDCl₃) 0.67–1.05, complex m (2 H, secondary cyclopropyl protons), 1.1–1.5, m (2 H, tertiary cyclopropyl protons), 1.47, broad s (4 H, methylene protons), 2.72, broad s (2 H, bridgehead protons), 3.43 ppm, broad s (2 H, anyhydride methine protons).

exo-Tricyclo[3.2.2.0^{2,4}]nonane-*exo*-6,*exo*-7-dicarboxylic Acid (6). *exo*-Tricyclo[3.2.2.0^{2,4}]nonane-*exo*-6,*exo*-7-dicarboxylic anhydride (20 g, 0.104 mol) was added to 500 ml of distilled water containing sodium hydroxide (12 g, 0.30 mol). The mixture was heated to 75–85° and stirred until solution was complete. The hot solution was filtered and acidified to pH 1 (hydrion A paper) with 37% HCl (approximately 40 ml). The diacid immediately appeared as a fine white precipitate. After cooling to 5°, the product was isolated by vacuum filtration, washed thoroughly with distilled water, and dried to constant weight in a vacuum desiccator,²⁷ yield (white solid) 20.0 g (95%). A small portion was recrystallized from distilled water, mp 173° dec (lit. mp 173–174°).¹⁴

exo-Tricyclo[3.2.2.0^{2,4}]non-6-ene (7). A. A modification of the procedure of Grob¹⁶ was used. To a cooled suspension (ice-water bath) of **6** (21 g, 0.10 mol) in 500 ml of dry benzene containing dry pyridine (40 g, 0.51 mol) was added lead tetraacetate (containing acetic acid, 10% by weight, 75 g, 0.17 mol). The stirred mixture was slowly heated. Between 40 and 50° the mixture turned to a clear yellow-orange solution. Between 65 and 70° the reaction became exothermic, and gas was rapidly evolved. The mixture thickened, and a voluminous tan precipitate appeared. The mixture was stirred at 75–80° for 2 hr, cooled to room temperature, and filtered by suction. The solid was washed with 100 ml of benzene. The combined benzene solutions were washed with 500-ml portions of water, 5% NaOH (twice), water, 10% HCl (twice), water, saturated sodium bicarbonate, and saturated sodium chloride solution. The benzene layer was dried over anhydrous potassium carbonate and distilled at atmospheric pressure. The product, a waxy solid, was distilled using an air condenser heated with a hot air pistol, yield 4.3 g (36%), bp 162–168°.

Nmr spectrum 0.53 ppm, complex m (1 H, exterior secondary cyclopropyl proton), 0.82 ppm, m (1 H, interior secondary cyclopropyl proton), 0.95–1.55, m (6 H, tertiary cyclopropyl and methylene protons), 2.60, broad s (2 H, bridgehead protons), 6.32 ppm, AB d (2 H, vinyl protons).

Ir spectrum 3050, 3010, 2940, 2865, 1640, 1550, 1460, 1435, 1368, 1318, 1250, 1160, 1088, 1040, 1000, 953, 860 cm⁻¹.

Mass spectrum *m/e* (rel intensity) 120 (56), 105 (78), 93 (10), 92 (58), 91 (66), 80 (12), 79 (100), 78 (38), 77 (36), 66 (22), 65 (14), 51 (14), 41 (8), 39 (20).

B. **6** (3.0 g, 0.015 mol) was dissolved in 150 ml of 90% aqueous pyridine containing 2 ml of triethylamine. The solution was electrolyzed,¹⁵ with a platinum mesh anode and a platinum wire cathode, at initial values of 70 V DC and 1.8 A. After 4.5 hr, the values were 100 V and 0.25 A. The solution was diluted with 500 ml of cold water and extracted with two 250-ml portions of pentane. The combined pentane layers were washed with 250-ml portions of water, 10% HCl (twice), water, and saturated sodium bicarbonate solutions. The pentane layer was dried over anhydrous K₂CO₃, and solvent was removed *in vacuo*. The residual yellow oil was distilled at atmospheric pressure through an air condenser to give the product (0.64 g, 37%), which was identical in all respects with that obtained above.

exo,endo- and exo,exo-Tricyclo[3.2.2.0^{2,4}]nonan-6-ol (8, 9). A. **Via Diborane, Mixture A.** Diborane, generated by the addition of sodium borohydride (5.0 g, 0.13 mol) in 175 ml of dry diglyme to boron trifluoride-ethyl ether (30.0 g, 0.21 mol) in 50 ml of dry diglyme, was passed into a solution of **7** (28.0 g, 0.233 mol) in 250 ml of dry tetrahydrofuran. The solution was stirred at room temperature under nitrogen for 2 hr after addition was complete, then cooled in an ice-water bath. Aqueous sodium hydroxide (10%, 40 ml) was added dropwise, followed by 40 ml of 30% hydrogen peroxide. The mixture was stirred at 0° for 2 hr. The mixture was added to 1 l. of water and extracted with five 200-ml portions of ether. The combined ether extracts were washed with five 1-l. portions of water and one portion of saturated sodium chloride solution. The ether layer was dried over anhydrous potassium carbonate, and the solvent was removed *in vacuo*, yield (crude) 28.6 g (89%). The product was recrystallized from pentane (60–70% yield), mp 159–164°.

Anal. Calcd for C₉H₁₄O: C, 78.21; H, 10.21. Found: C, 77.83; H, 10.10.

Nmr 0.1–0.7, complex m (2 H, secondary cyclopropyl protons), 0.7–2.5 (major peaks at 1.25 and 1.97), m (10 H, tertiary cyclopropyl, methylene, and bridgehead protons), 2.55, s (1 H, hydroxyl proton), 3.90 ppm, m (1 H, CHOH proton).

Ir spectrum 3620, 3360, 3080, 3010, 2940, 2880, 1478, 1452, 1350, 1235, 1110, 1040, 1030, 975 cm⁻¹.

Mass spectrum *m/e* (rel intensity) 138 (29), 120 (29), 105 (26), 95 (23), 94 (68), 93 (28), 92 (47), 91 (45), 83 (13), 81 (15), 80 (21), 79 (100), 78 (32), 77 (29), 70 (13), 67 (19), 66 (29), 55 (13), 53 (13), 41 (19), 39 (17).

A solution of the above alcohol mixture (0.13 g, 0.000943 mol) and Eu(fod)₃ (0.21 g, 0.000201 mol, molar ratio of shift reagent to alcohol 0.215) in spectrophotometric grade carbon tetrachloride was prepared. The nmr spectrum of the mixture is reported below, with relative peak areas given. (Note: the chemical shifts are given relative to an external standard, TMS in CCl₄).

Nmr –1.3 [Eu(fod)₃ protons], –0.15, m (0.7 H), 0.6–1.1 (peaks at 0.75 and 0.95), m (3.8 H), 1.47, m (3.8 H), 1.6–2.4, m (2.0 H), 2.79, m (2.6 H), 4.02, AB d (1.3 H, *J* = 9, 13.5 Hz), 4.60 m (0.4 H), 4.8–5.3, m (1.6 H), 5.96, broad s (1.0 H), 6.75, d (1.0 H, *J* = 13.5 Hz), 9.25 ppm, m (0.3 H), 11.20, m (1.0 H, *J* = 9 Hz).

B. Via Thexyl Borane,¹⁷ Mixture B. Diborane, generated by the addition of sodium borohydride (1.50 g, 0.0395 mol) dissolved in 50 ml of dry diglyme to boron trifluoride-ethyl ether (5.69 g, 0.040 mol) in 50 ml of dry diglyme, was passed into a solution of 2,3-dimethyl-2-butene (3.68 g, 0.0438 mol) in 100 ml of dry tetrahydrofuran, with a stream of dry nitrogen. After the addition was complete, the solution was stirred at room temperature under nitrogen for 2.5 hr. **7** (2.51 g, 0.021 mol) dissolved in 15 ml of dry tetrahydrofuran was then added in one portion to the above solution. The mixture was stirred at room temperature for 20 hr. The mixture was then cooled to 0° (ice-water bath), and 10 ml of a 10% NaOH solution was added dropwise, followed by 10 ml of 30% hydrogen peroxide. The mixture was stirred for 3 hr at 0° and 1 hr at room temperature. It was then diluted with 300 ml of water and extracted with five 50-ml portions of purified pentane. The combined pentane layers were washed with five 200-ml portions of water and with saturated sodium chloride solution. The pentane extract was dried over anhydrous potassium carbonate and filtered, and the solvent was removed *in vacuo* (*tert*-hexyl alcohol was also removed in this process). The product, a pasty solid, was dissolved in CCl₄ along with approximately 0.2 equiv of Eu(fod)₃. The nmr spectrum of this mixture was very similar to that of the alcohol mixture produced by conventional hydroboration (see above), yielding a ratio of *exo,endo* to *exo,exo* alcohol of 2.7:1.0. It was not purified further, yield 1.7 g (59%).

exo-Tricyclo[3.2.2.0^{2,4}]nonan-6-one (10). A mixture of *exo,endo*- and *exo,exo*-tricyclo[3.2.2.0^{2,4}]nonan-6-ols (mixture A, 5.00 g, 0.0366 mol) was dissolved in 300 ml of pentane. Activated manganese dioxide (50 g) was added and the mixture was stirred at room temperature for 120 hr. The mixture was then filtered and the residue was washed with an additional 100 ml of pentane. Activated alumina (1 g) was added and the solution was swirled for 2 min to remove any unreacted alcohol. The mixture was filtered and the solvent was removed *in vacuo*, yield 4.18 g (84%). The product was further purified by sublimation at atmospheric pressure, mp 119–121°.

Anal. Calcd for C₉H₁₂O: C, 79.37, H, 8.88. Found: C, 78.23, 78.05; H, 9.01, 8.82.

Nmr 0.38–0.96, m (6 H, tertiary cyclopropyl, C-8 and C-9 methylene), 2.15, m (2 H, C-7 methylene protons, adjacent to carbonyl), 2.15, m (2 H, C-7 methylene protons, adjacent to carbonyl), 2.30 ppm, broad s (2 H, bridgehead protons).

Ir spectrum 3065, 3015, 2938, 2865, 1730, 1463, 1410, 1285, 1114, 860 cm⁻¹.

Mass spectrum *m/e* (rel intensity) 136 (92), 108 (40), 94 (55), 93 (54), 92 (23), 91 (20), 80 (24), 79 (63), 77 (20), 67 (22), 66 (25), 54 (22), 53 (12), 41 (18), 39 (21), 32 (28), 28 (100).

exo,endo- and exo,exo-Tricyclo[3.2.2.0^{2,4}]nonan-6-ol (9, 8). A. **Via Lithium Aluminum Tri-*tert*-Butoxyhydride, Mixture C.** 10 (2.86 g, 0.00212 mol) was dissolved in 60 ml of dry ether. Lithium aluminum tri-*tert*-butoxyhydride (6.00 g, 0.00236 mol) was added and the mixture was stirred at room temperature for 67 hr. A saturated aqueous solution of ammonium sulfate was added dropwise (to a total of 60 ml) and the layers were separated. The aqueous layer was washed with two 25-ml portions of ether. The combined ether layers were washed with water and saturated sodium chloride solution and dried over anhydrous potassium carbonate, and the solvent was removed *in vacuo*. The product was recrystallized from pentane, yield 2.18 g (75%), mp 159–164°.

Nmr 0.2–0.7 complex m (1.5 H, secondary cyclopropyl protons), 0.8–2.3 (peaks at 0.88, 1.29, 2.00), m (10.5 H, tertiary cyclopropyl, methylene, and bridgehead protons), 3.95, sharp s (1 H, hydroxyl proton), 3.8–4.3 m (1 H, CHOH proton).

A solution of this alcohol mixture (0.141 g, 0.00102 mol) and

Eu(fod)₃ (0.248 g, 0.00024 mol, molar ratio of shift reagent to alcohol 0.235) was prepared. The description of the nmr spectrum of that solution follows.

Nmr -2.70 [Eu(fod)₃ protons], -1.47, m (1.7 H), -0.74, m (5.1 H), 0.0-1.4, m (8.9 H, 1.88, AB d (1.3 H), 2.47, AB d (0.6 H), 2.8-3.7, m (4.0 H), 4.27, broad s (0.5 H), 5.00, d (0.5 H, *J* = 13-14 Hz), 7.40, m (1.0 H), 9.20 ppm, m (0.5 H). Irradiation at 9.20 ppm yields a doublet at 2.47 ppm (*J* = 13.5 Hz). Irradiation at 1.88 ppm yields a broad singlet at 7.40 ppm, and the coalescence of two peaks (*J* = 13 Hz) in the 2.8-3.7-ppm multiplet to a singlet. Irradiation at 3.30 ppm yields a broad singlet at 1.15 ppm (collapse of doublet, *J* = 12 Hz), and the collapse of a doublet (*J* = 12 Hz) at 0.40 ppm.

B. Via Lithium Aluminum Hydride, Mixture D. 10 (1.05 g, 0.00772 mol) in 10 ml of dry ether was added dropwise to a stirred suspension of lithium aluminum hydride (0.15 g, 0.00395 mol) in 10 ml of dry ether. After addition was complete, the mixture was stirred for an additional 15 min, then cooled in an ice-water bath. Water and wet sodium sulfate were added, and the layers were separated. The water layer was washed with an additional 20 ml of ether, and the combined ether layers were washed with water and saturated sodium chloride solution. The ether layer was dried over anhydrous potassium carbonate and solvent was removed *in vacuo*. The product was recrystallized from pentane, yield 0.80 g (75%), mp 158-163°. The nmr spectrum of this mixture in the presence of Eu(fod)₃ (0.35 equiv) was similar to that of the mixture produced *via* hydroboration-oxidation (see mixture A); the ratio of exo,endo to exo,exo alcohol was 2.0:1.

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Registry No.—1, 7092-05-9; 2, 51260-33-4; 3, 51260-38-9; 4, 51260-34-5; 5, 944-41-2; 6, 51175-60-1; 7, 27019-94-9; 8, 51260-36-7; 9, 51260-35-6; 10, 51260-37-8; 3-chloropropene, 107-05-1; 1,3-cyclohexadiene, 592-57-4; maleic anhydride, 108-31-6; cycloheptatriene, 544-25-2; *exo*-tricyclo[3.2.2.0^{2,4}]nonane-*exo*-6,*exo*-7-dicarboxylic anhydride, 944-40-1.

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- (27) Caution: desiccation under high vacuum for extended periods leads to substantial dehydration to the anhydride. Observation of R. Leight in this laboratory.

Conformational Analysis of Some Bicyclo[4.2.0]octanes by Hydrogen-1 Nuclear Magnetic Resonance

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7,7-Diphenyl-2,5-dioxabicyclo[4.2.0]octane (1), 7,7-diphenyl-2,5,8-trioxabicyclo[4.2.0]octane (2), and 7,7-dimethyl-2,5,8-trioxabicyclo[4.2.0]octane (3) were shown to exist as *cis*-fused chairs. The conformational analyses were accomplished by a combination of Eu(fod)₃ shift ratios and the Buys *R* method. The Eu(fod)₃ was shown to have no effect on the conformation. The bicyclooctanes were synthesized through the photocycloaddition of acetone, benzophenone, and 1,1-diphenylethylene to 1,4-dioxene.

Buys² and Lambert³ have developed methods for determining the conformation of rigid six-membered ring systems, containing heteroatoms in the 1 and 4 positions, by

nmr. These methods relate the ratio of the average *trans* and *cis* vicinal coupling constants to the conformation.

Slessor and Tracy⁴ have written a computer program,