next: ir 5.83 μ; nmr δ 0.70–1.15 (complex set of sharp peaks, 15), *ca.* 1.80 (m, 1, $J = 7$ Hz), and *ca.* 2.40 (m, 2, $J = 7$ Hz). The nmr spectrum is clearly consistent with the postulated structure. The alternative structure, 4,4,5-trimethyl-3-hexanone, which would result from methylation of **6c** at the more highly substituted α position, is inconsistent in that it requires a quartet centered at *ca.* δ 2.40; the spectrum has a clear multiplet of at least sixth order in this region. The crude product composition follows: **3c**, 24%; **4c**, 5%; **5c**, 53%; **6c**, 11%; **7c**, 4%; and unidentified high-boiling material, 4%. A similar run on a smaller scale gave the following composition: **3c**, 17%; **4c**, 11%; **5c**, 51%; **6c**, 9%; **7c**, 7%; and unidentified high-boiling material, 3%.

Reduction–Methylations of 4,4-Dimethylcyclohex-2-enone (1d).—From 2.00 g (0.016 mol) of **1d**, 1.197 g (0.016 mol) of *t*-BuOH, 0.255 g (0.037 g-atom) of lithium in 750 ml of ether–ammonia, and 9.0 g (0.06 mol) of MeI was obtained 0.89 g (45% assuming the product to be only **5d**) of material, bp 75–85° (40 mm). Analysis by vpc[25] gave a composition of 30% **3d** and 70% **5d**, identified by comparison of retention times with those of authentic compounds from reduction runs.

In another run, the enolate was generated as usual from 1.243 g (0.01 mol) of **1d**, 0.741 g (0.01 mol) of *t*-BuOH, and 0.152 g (0.022 g-atom) of lithium in 800 ml of ether–ammonia. 4-Phenyl-2-butanone (**3a**), 1.485 g (0.01 mol), was added to the stirred mixture followed immediately by 8.52 g (0.06 mol) of MeI. For the material derived from **1d**, vpc analysis gave the following composition: **3d**, 10%; **5d**, 90%. For the material derived from **3a**, vpc analysis gave the following composition: **3a**, 59%; and two later eluting components, 38 and 3%. These two components gave vpc retention times similar, but not identical, with those of **5a** and **6a** and were probably isomeric mono- and dimethylation products.

Methylation of Saturated Ketones.—The saturated keton in three volumes of ether was added dropwise with stirring over 10 min to a solution of *t*-BuOLi in 1:1 ether–ammonia under N$_2$. The mixture was stirred for 10 min and MeI in three volumes of ether was added dropwise over 5 min. After 15 min, excess NH$_4$Cl was added and the mixture was worked up and analyzed as usual. The methylation of **3a** gave a monomethylation product with a vpc retention time similar but not identical with that of **5a**, probably the isomeric compound 1-phenyl-3-pentanone. The major dimethylation product had a vpc retention time identical with that of **6a**. Compounds **3d** and **3e** gave 2,4,4-trimethylcyclohexanone and 2,4,4,6-tetramethylcyclohexanone, respectively, with vpc retention times identical with those of authentic materials. Compound **3b** (**5a**) gave a mixture of three components which were collected by vpc and shown to be **5a**, **6a**, and **7a** by comparison of ir and nmr spectra with those of material from reduction–methylation runs. Compound **3c** gave a mixture of four or more methylation products. The two major components were collected by vpc and assigned structures as follows: 5-methyl-3-hexanone, nmr δ 0.90 (d, 6, $J = 6$ Hz, CHMe$_2$), 0.99 (t, 3, $J = 7.5$ Hz, CH$_2$CH$_3$), 2.22 (d, 2, $J = 2$ Hz, CHCH$_2$), *ca.* 2 (br, CH), and 2.33 (q, 2, $J = 7.5$ Hz, CH$_2$CH$_3$); and 2,5-dimethyl-3-hexanone, nmr 0.90 (d, 6, $J = 6$ Hz, CMe$_2$), 1.03 (d, 6, $J = 6.5$ Hz, CMe$_2$), 2.23 (d, 2, $J = 2$ Hz, CH$_2$), and *ca.* 2–2.5 (br, 2, CH).

Registry No.—**1a**, 1896-62-4; **1b**, 1901-26-4; **1c**, 141-79-7; **4c**, 108-11-2; **5b**, 13705-37-8; **5c**, 565-78-6; **6a**, 23936-95-0; **6c**, 6137-14-0; **7a**, 23936-97-2; **7c**, 23936-98-3; 5-methyl-3-hexanone, 623-56-3; 2,5-dimethyl-3-hexanone, 1888-57-9.

Acknowledgment.—We are grateful to Professor Drury Caine of Georgia Institute of Technology for helpful discussions and for obtaining some of the nmr spectra.

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[25] An Apiezon L column was used for the analysis. A second analysis on Carbowax 20M indicated the absence of starting material (**1d**).

On the Conformation of *endo*-Bicyclo[3.3.1]nonan-3-ol. A New Synthesis of Oxaadamantane

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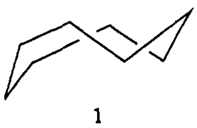
The results of spin-decoupling and variable-temperature nmr studies show a conformational equilibrium to be occurring in *endo*-bicyclo[3.3.1]nonan-3-ol. From the magnitude of the coupling constants, it is concluded that the major conformer is the chair–boat form. On the basis of a facile radical oxidation of the alcohol to the bridged ether, oxaadamantane, it is suggested that the minor conformer is the chair–chair form.

Transannular reactions commonly observed in medium-ring compounds have been widely studied, and generally interpreted on the basis of proximity effects.[2] As part of a continuing investigation on transannular radical and carbenoid reactions,[3] we have examined the bicyclo[3.3.1]nonane system, a potentially interesting homolog of cyclooctane.

In cyclooctane itself, the theoretically most stable conformation is the boat–chair, **1**.[4] Calculations also show that the crown form, **2**, and slightly modified forms thereof are somewhat disfavored relative to **1**, the differences in energy content being small and on the order of 2–3 kcal/mol.[4] Another conformer, **3**, is easily excluded in all calculations owing to the nonbonded interactions between the *endo* hydrogens. These theoretical conclusions have been supported by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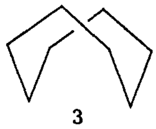
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[1] (a) To whom inquiries should be addressed. (b) Chargé de Recherches au CNRS; Boursier de l'OTAN, 1968–1969.

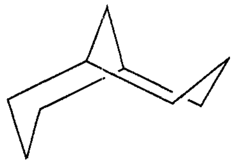
[2] For a recent review, see A. C. Cope, M. M. Martin, and M. A. McKervey, *Quart. Rev.* (London), **20**, 119 (1966).

[3] M. H. Fisch and H. D. Pierce, Jr., *J. Chem. Soc., D*, in press.

[4] (a) J. B. Hendrickson, *J. Amer. Chem. Soc.*, **86**, 4854 (1964); (b) K. B. Wiberg, *ibid.*, **87**, 1070 (1965); (c) N. L. Allinger, J. A. Hirsch, M. A. Miller, I. J. Tyminski, and F. A. Van-Catledge, *ibid.*, **90**, 1199 (1968); (d) M. Bixon, and S. Lifson, *Tetrahedron*, **23**, 769 (1967).

X-ray data on cyclooctane-1,2-*trans*-dicarboxylic acid, which is shown to exist in the boat–chair form.[5a] Elegant nmr studies extend this conclusion to cyclooctane and alkylcyclooctanes in solution.[5b]

If one attaches a methylene bridge from C-1 to C-5, the bicyclononane system is generated, and the derived conformers **4**–**6** may now be considered. Both **4** and **5** are destabilized relative to their cyclooctane analogs, **1** and **2**, by the interactions associated with cyclohexane boats. As a result, **6** is calculated to be the most stable conformer despite the interactions between the *endo* hydrogens at C-3 and C-7. The energy content of **6** is estimated to be 2.7 kcal/mol less than that of the second most stable conformer, **4**. Crystallographic data support the assignment of the parent molecule as chair–chair,[6] and have stimulated a variety of investigations on the ease of ionic transannular reaction involving C-3 and C-7.[7]



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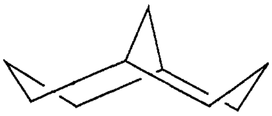

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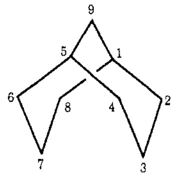
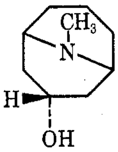


6

There is thus a delicate balance in the parent hydrocarbon between forms **4** and **6** in which the latter predominates. The main destabilizing factors in **6** are nonbonded repulsions (*ca.* 2 kcal/mol), torsional strain, and angle strain (at least 2 kcal/mol).[8] These destabilizing factors are aggravated without greatly affecting alternate conformer **4** by *endo* substituents at C-3. Hence, appropriate substitution could conceivably shift the conformational preference to favor the chair–boat form, **4**, in analogy with cyclooctane. Certainly, one might anticipate such a shift if the substituent were large, *e.g.*, methyl. On the other hand, substitution of hydroxyl, a group of intermediate size and one of immediate interest to us, does not lead to a clear-cut situation.

Chen and Le Fevre[9] and Parker, *et al.*,[10] have concluded from a first-order analysis of the nmr pattern corresponding to the carbinyl proton, CHOH, that the major conformer is analogous to the chair–boat form, **4**, in 3α-granatanol[9] (**7**) and in *endo*-1,5-dimethylbicyclo[3.3.1]nonan-3-ol[10] (**8a**), respectively. In the same way, Flegal reached an analogous conclusion for the parent alcohol, **8b**.[11]



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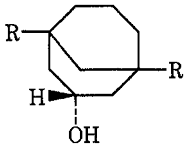

8a, R = CH_3
b, R = H

These interpretations, based on first-order analyses, are neither completely satisfying nor entirely unambiguous. If a rapid conformational equilibrium is present, the coupling constants observed between the carbinyl and vicinal protons will be weighted averages, and, without appropriate models for the chair–boat form, one cannot calculate how important the chair–chair conformer might be, or even whether the chair–chair form is present. Thus, whereas Chen and Le Fevre estimated that 14% of **7** exists in the chair–chair form at room temperature,[9] Parker suggested that it would be more prudent to reserve judgment.[10] Indeed, he showed that direct application of the method used by Chen and Le Fevre to the case of **8a** would result in an estimate of considerably more than 100% chair–boat conformer.

One may question also the validity of a direct first-order analysis in extracting the coupling constants for the present $AA'BB'X$ systems, although it turns out that the true values are not greatly different (see below).

The only other data relevant to the conformational preferences of these systems comes from the application of a semiempirical infrared method to the case of 3α-granatanol (**7**).[12] The conclusion, based on shapes and frequencies of the OH bands in the two epimeric alcohols, was that the chair–chair form analogous to **6** is preferred in the *endo* isomer. Noting that this result was counter to the previous nmr studies, Aaron, *et al.*, commented that their results did not constitute absolute proof in the absence of an appropriate model for the chair–boat form, but did show that the chair–chair form was certainly not to be excluded, and that further studies were clearly needed.

Results and Discussion

Faced with this situation, we sought to answer three questions: (A) is there a conformational equilibrium between chair–boat and chair–chair forms; (B) if so, what is the major conformer; (C) is it possible to direct transannular chemistry through a chair–chair form such as **9a**, and, in particular, to obtain oxaadamantane (**10**) by treatment of **8b** with radical oxidants?

Synthesis of the parent alcohol, *endo*-bicyclo[3.3.1]nonan-3-ol (**8b**), is described in the Experimental Section. The nmr pattern of the carbinyl proton,

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(5) (a) J. D. Dunitz and A. Mugnoli, *Chem. Commun.*, 166 (1966); (b) F. A. L. Anet and M. St. Jacques, *J. Amer. Chem. Soc.*, **88**, 2585, 2586 (1966).

(6) (a) M. Dobler and J. D. Dunitz, *Helv. Chim. Acta*, **47**, 695 (1964); (b) W. A. C. Brown, C. Eglinton, J. Martin, W. Parker, and G. A. Sim, *Proc. Chem. Soc.*, 57 (1964); (c) W. A. C. Martin, J. Martin, and G. A. Sim, *J. Chem. Soc.*, 1844 (1965); (d) I. Laszlo, *Rec. Trav. Chim. Pays-Bas*, **84**, 251 (1965).

(7) (a) R. A. Appleton and S. H. Graham, *Chem. Commun.*, 297 (1965); (b) R. A. Appleton, J. R. Dixon, J. M. Evans, and S. H. Graham, *Tetrahedron*, **23**, 805 (1967); (c) H. Stetter, J. Gartner, and P. Tacke, *Angew. Chem. Int. Ed. Engl.*, **4**, 153 (1965); (d) M. Eakin, J. Martin, and W. Parker, *Chem. Commun.*, 206 (1965), 955 (1967), and 298 (1968); (e) H. Dugas, R. A. Ellison, Z. Valenta, K. Wiesner, and C. M. Wong, *Tetrahedron Lett.*, 1279 (1965); (f) W. A. Ayer and K. Piers, *Chem. Commun.*, 541 (1965); (g) J. P. Schaefer and C. A. Flegal, *J. Amer. Chem. Soc.*, **89**, 5729 (1967); (h) M. A. Eakin, J. Martin, W. Parker, C. Egan, and S. H. Graham, *Chem. Commun.*, 337 (1968).

(8) G. J. Gleicher and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 582 (1967).

(9) C. Y. Chen and R. J. W. Le Fevre, *Tetrahedron Lett.*, 737 (1965); *J. Chem. Soc., B*, 539 (1966).

(10) W. D. K. Macrossan, J. Martin, and W. Parker, *Tetrahedron Lett.*, 2589 (1965).

(11) C. A. Flegal, Ph.D. Thesis, University of Arizona, 1968, p 7 ff.

(12) H. S. Aaron, C. P. Ferguson, and C. P. Rader, *J. Amer. Chem. Soc.*, **89**, 1431 (1967); see also L. Joris, P. von R. Schleyer, and E. Osawa, *Tetrahedron*, **24**, 4759 (1968).

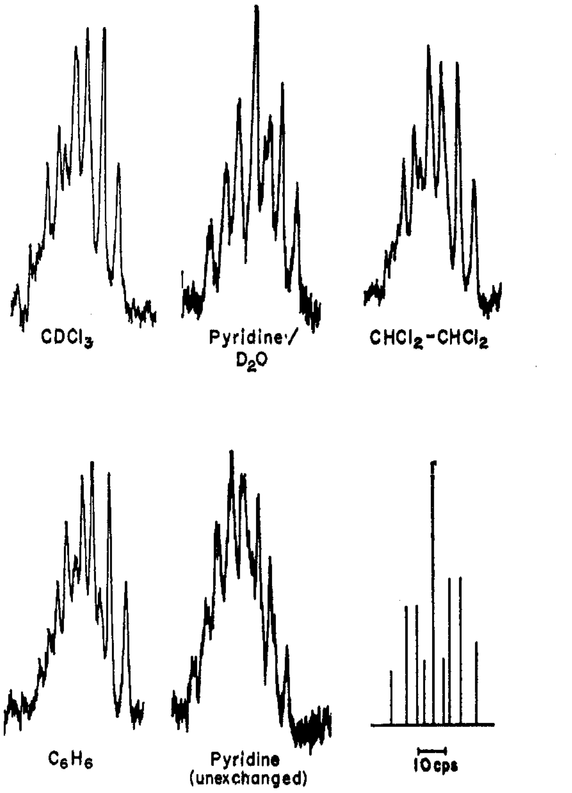
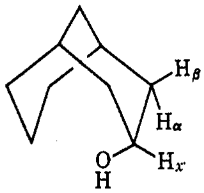


Figure 1.—Experimental and calculated spectra of the carbinyl proton of *endo*-bicyclo[3.3.1]nonan-3-ol (60 MHz).

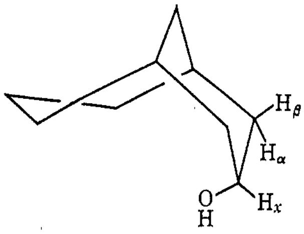
CHOD, following exchange of the hydroxyl hydrogen, is shown in various solvents in Figure 1. For comparison, a calculated spectrum (LAOCOON 3) for H_x is also shown, based on the coupling constants $J_{H_\alpha H_x}$ = 10.0 cps and $J_{H_\beta H_x}$ = 6.2 cps, with chemical shifts δ_{H_α} = 70 cps, δ_{H_β} = 123 cps, and δ_{H_x} = 246 cps relative to TMS. The computer spectrum consists of 16 significant transitions. In Figure 1, all lines separated by less than one cycle have simply been added. The result is seen to be a nine-line pattern which is slightly asymmetric owing to slanting. Changing the solvent results in changes in the chemical shifts of H_α, H_β, and H_x, and consequently affects the appearance of the pattern owing to variations in the overlap of the neighboring transitions.

The sample used had more than 90% of the hydroxyl proton exchanged for deuterium by five crystallizations from methanol-O-*d*/D_2O. The necessity for this precaution is apparent from the spectrum of an unexchanged sample in anhydrous pyridine (also shown in Figure 1), where exchange of the hydroxyl proton with solvent is slow (OH appears as a doublet, J = 4.5 cps). In the variable-temperature work (see below), the CHOH pattern of unexchanged samples lost structure in the vicinity of $-40°$. In the exchanged samples, this complication was avoided.

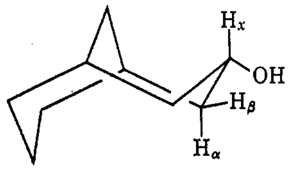
Consideration of models of **8b** yields an interesting conclusion. The three likely conformers, **9a–9c**, all resist efforts to deform them into twist–boat forms. Thus, one may consider as a first approximation only the classical chair forms for the substituted ring (**9a** and **9b**) and the classical boat form (**9c**). Noting that in **9c** the five-spin portion of interest has exactly the same geometrical relations as in a classical chair form where the hydroxyl group is equatorial, we used as models for **9a–9c** steroid systems of axial and equatorial alcohols where the A ring is known to be in a pure chair form. The expected coupling constants are then $J_{H_\alpha H_x} \cong 10$ cps and $J_{H_\beta H_x} = 5.5 \pm 1.0$ cps for the carbinyl proton axial, *i.e.*, **9c**;[13,14] and $J_{H_\alpha H_x} \cong J_{H_\beta H_x}$ = 2.0–3.2 cps for the carbinyl proton equatorial, *i.e.*, **9a** or **9b**.[13]



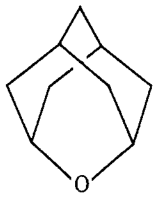
9a



9b



9c



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The most likely deformation from classical forms is a flattening as is found in the parent hydrocarbon. In the boat form, such a deformation would make both dihedral angles between H_x and the vicinal protons smaller than their initial values of 60 and 180°, which would lead to a somewhat smaller value for $J_{H_\alpha H_x}$ and a slightly larger value for $J_{H_\beta H_x}$.[15] For the chair form, flattening would increase one dihedral angle and decrease the other from their initial values of 60°, again with the same qualitative effects on $J_{H_\alpha H_x}$ and $J_{H_\beta H_x}$.[15] The anticipated coupling constants for the boat form, **9c**, are in fair agreement with the values obtained by first-order analysis for the related cases reported in the literature (Table I).

TABLE I

COUPLING CONSTANTS OF CHOH IN BICYCLO[3.3.1]NONANE SYSTEMS BY FIRST-ORDER ANALYSIS

Compd	$J_{H_\alpha H_x}$	$J_{H_\beta H_x}$	Ref
7	11	4	9
8a	10.5	6.0	10
8b	10.5	6.0	11

By double resonance (Table II), the true coupling constants were directly measured.[16] The unusally large separation (*ca.* 1 ppm) between the chemical shifts of H_α and H_β, as indicated by the frequencies of irradiation, is entirely consistent with an additional shielding of the axial protons, H_α, in the chair–boat form by the trimethylene bridge. If the predominant form were the chair–chair, one would expect a normal

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(13) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, pp 80 ff.

(14) F. A. L. Anet, *J. Amer. Chem. Soc.*, **84**, 1054 (1962).

(15) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); *J. Amer. Chem. Soc.*, **85**, 2870 (1963).

(16) For experimental reasons, only one of the coupling constants could be determined for the sample in pyridine solution at room temperature and was found to be 9.8 cps. Thus the unusually clear pattern obtained in pyridine is not the result of any profound change in the conformational mix, *e.g.*, owing to hydrogen bonding.

TABLE II

COUPLING CONSTANTS IN *endo*-BICYCLO[3.3.1]NONAN-3-OL ($CHCl_2CHCl_2$, 60 MHz, TMS = 0)

			Irradiation frequencies	
$J_{H_\alpha H_x}$, cps	$J_{H_\beta H_x}$, cps	Temp, °C	H_α	H_β
10.25 ± 0.25	6.5 ± 0.25	27°	62	127
8.0 ± 0.25	6.0 ± 0.25	117°	72	134

(*ca.* 0.6 ppm) or smaller than normal separation of H_α and H_β.[17] The fact that the unusually shielded proton is the one which is associated with the large constant, as well as the magnitude of the coupling constants, is explicable only on the basis of the chair–boat form, **9c**, which is therefore the predominant conformer. The magnitude of the smaller coupling constant suggests that some flattening of the ring may have occurred.

Raising the temperature affects the larger coupling constant more than the smaller one, as would be expected. Two changes appear in the pattern: (A) the total width decreases from 32.5 cps to 30.0 cps; (B) the deviation of the pattern from a simple septuplet becomes more apparent. These changes in the pattern are consistent with the variation in coupling constants measured by the double-resonance experiments.

It is clear from the data of Table II that the mean coupling constants decrease as the temperature is raised. We interpret this to mean that a *conformational equilibrium is occurring* and that, at higher temperatures, an increasingly important proportion of the mixture has the hydroxyl group axial, either **9a** or **9b**.

As a further proof of the existence of a conformational equilibrium, a variable-temperature study was undertaken and is summarized in Figure 2. The quality of the resolution was verified by measuring the width at half-height of added $CHCl_3$, and this value is listed beneath each pattern. Observation of the expected coalescence at low temperature strongly suggests that there is indeed a conformational equilibrium and that it is rapid at room temperature.

We cannot on the basis of these results identify the minor component. It might be the second boat–chair form, **9b**, the chair–chair form, **9a**, or some mixture of the two. Nor do we have the necessary data to determine the thermodynamic parameters.[18] In particular, we cannot estimate the proportion of the chair–boat form, **9c**, in the equilibrium mixtures other than to say it is clearly by far the major conformer.

The chemical reactivity of **8b** is pertinent here. We have found that treatment of the *endo* alcohol (97.2% isomeric purity) with lead tetraacetate in boiling benzene[19] yields oxaadamantane (89%), the parent ketone (6%), the acetate of the starting alcohol (4%), and an unidentified compound (<1%). Oxidation of the *endo* alcohol by irradiation in the presence of mercuric oxide and iodine leads to essentially pure oxaadamantane in 60% yield.

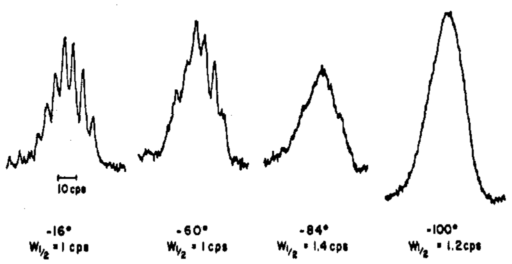

Figure 2.—Spectrum of the carbinyl proton of *endo*-bicyclo-[3.3.1]nonan-3-ol at various temperatures; $W_{1/2}$ refers to the width at half-height of added $CHCl_3$.

The *exo* isomer (92% isomeric purity) was found to be rather unreactive to lead tetraacetate, and, when subjected to mercuric oxide oxidation, led to the parent ketone as the major product. A small amount of oxaadamantane was formed from oxidation of the *exo* alcohol, which is easily explained as arising from the *endo* impurity.

From this control reaction, it is clear that there is no epimerization during the oxidation. With respect to the question of conformation, we see that the rate of transannular reaction in the *endo* alcohol, including ring inversion, must be fast with respect to the rate of oxidation to ketone. The rate of a second inversion to the alternate boat–chair form, **9b** (from which it is geometrically impossible to form oxaadamantane), may then be slower or faster than ether formation. In the latter case, one would have a small steady-state concentration of **9a** from which **10** is nonetheless formed in high yield. In either case, the presence of the chair–chair form, **9a**, is required, whereas we presently have no evidence for the alternate boat–chair form, **9b**. Consequently, our personal preference at this time is for the most economical interpretation of the chemical data, *i.e.*, that the chair–chair form, **9a**, is the second contributor to the conformational equilibrium.[20,20a]

Experimental Section[21]

Bicyclo[3.3.1]nonan-3-one was prepared by pyrolysis (350°) of the manganous salt of *cis*-cyclohexane-1,3-diacetic acid. The

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[17] The chemical-shift difference of 0.6 ppm or less is the most conservative estimate (*i.e.*, the largest value) taken from the discussion in J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution NMR Spectroscopy," Pergamon Press, Oxford, 1966, p 696 ff. Jackman (L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, pp 115–119) gives 0.1–0.7 ppm. From examination of the model, one sees that it is difficult to decide whether shielding by the trimethylene bridge will occur in the chair–chair form. If it does, only the equational proton vicinal to the hydroxyl will be affected and δ_{ae} will be less than normal.

[18] For an excellent recent review, see G. Binsch in "Topics in Stereochemistry," Vol. 3, E. L. Eliel and N. L. Allinger, Ed., Interscience Publishers, New York, N. Y., 1968, p 97.

[19] (a) K. Heusler and J. Kalvoda, *Angew. Chem. Int. Ed. Engl.*, **3**, 525 (1964). (b) Treatment of an *endo*-bicyclo[3.3.1]nonan-3-ol constrained to the chair–chair form is known to yield the bridged ether in high yield: W. A. Ayer, D. A. Law, and K. Piers, *Tetrahedron Lett.*, 2959 (1964).

[20] While this work was in progress, a report appeared [R. A. Appleton, C. Egan, J. M. Evans, S. H. Graham, and J. R. Dixon, *J. Chem. Soc., C*, 1110 (1968)] in which the conformational problem was approached by equilibration of *exo*- and *endo*-3-carbomethoxybicyclo[3.3.1]nonane. The measured value for the greater stability of the *exo* isomer (2.7 kcal/mol) was interpreted on the basis of plausible enthalpy calculations. Without attempting to assess the validity of the assumptions inherent in the work of Graham, *et al.*, it is interesting that the British group conclude that the major conformer is the chair–boat form, analogous to **9c**, the minor conformer is the chair–chair form, and the alternate boat–chair form analogous to **9b** "can certainly be ignored."

[20a] NOTE ADDED IN PROOF.—The isopropoxide-catalyzed equilibration of the epimeric bicyclo[3.3.1]non-3-ols has now been described. A free-energy difference of 2.51 kcal/mol in favor of the *exo* isomer was found [E. N. Marvell and R. S. Knutson, *J. Org. Chem.*, **35**, 388 (1970)], and $\Delta G°$ is thus independent of whether the 3 substituent is hydroxyl or carbomethoxy. If, as suggested, $\Delta G°$ therefore reflects only the skeletal change in the equilibrium, the second conformer of **8b** *must* be chair–chair form.

[21] Glpc analyses were performed with an F & M Model 700 instrument using a thermal (W-X filament) detector. Columns used were 10% QF-1 (0.125 in. × 10 ft at 120°) and 10% W-98 (0.125 in. × 6 ft at 120°). By calibration with known mixtures, the relative detector response was found to be as follows (by weight): oxaadamantane, 1.00; bicyclo[3.3.1]nonan-3-one, 1.08; the *exo* alcohol, 1.00; the *endo* alcohol, 1.00; the acetates, 1.22. Combustion analyses were by Spang Microanalytical Laboratories, Ann Arbor, Mich.

yield of bicyclo[3.3.1]nonan-3-one from this procedure was 56–61%.[22]

***endo*-Bicyclo[3.3.1]nonan-3-ol (8b).**—To a suspension of lithium aluminum hydride (500 mg) in dry tetrahydrofuran (5 ml), a solution of bicyclo[3.3.1]nonan-3-one (5 g) in tetrahydrofuran (10 ml) was added dropwise and the mixture was then heated at reflux with stirring for 7 hr. After cooling, the excess reagent was decomposed by the addition of water (2 ml) and 5% sodium hydroxide solution (3 ml). The mixture was filtered and the filtrate was concentrated at reduced pressure to give a residue which crystallized on standing. Recrystallization from hexane gave 3.5 g (70%) of **8b**, mp 124–126° (lit.[23] mp 121.5–124°). A second crop (200 mg, 4%), mp 110°, was obtained from the filtrate. Glpc analysis of the derived acetate showed the product to be 97.2% *endo*. The ir and nmr spectra agreed with those reported.[23]

***exo*-Bicyclo[3.3.1]nonan-3-ol.**—To a mixture of sodium (4 g, small pieces) in dry benzene (40 ml) was added dropwise a solution of bicyclo[3.3.1]nonan-3-one (1 g) in absolute ethanol (20 ml). The benzene solution was stirred and heated at reflux during the addition (1 hr), after which refluxing was continued for a further 1.5 hr. The solution was cooled and water (25 ml) was added dropwise with stirring. The aqueous phase was separated and extracted twice with 50-ml portions of benzene. The combined benzene extracts were concentrated and the residue was chromatographed on silica gel (3 g). Elution with hexane gave a total of 0.846 g of crude alcohol, uncontaminated with ketone. Recrystallization from hexane followed by sublimation gave 0.469 g (47%), mp 99–100° (lit.[23] mp 100–101°). Glpc analysis of the derived acetate showed the product to be 92.2% *exo*. The infrared and nmr spectra agreed with those reported.[23]

The acetates of the alcohols were prepared from the alcohol by treatment with pyridine–acetic anhydride. The solution was allowed to stand at room temperature for 2 hr and then was heated for 15 min on the steam bath. After cooling, water was added and the product was extracted with chloroform. The chloroform solution was washed successively with 1 *N* hydrochloric acid and water and then dried ($MgSO_4$).

Data for the *exo* acetate follow: ir (CCl_4) 1729, 1239, and 1027 cm^{-1}; nmr (CCl_4 *vs.* TMS) 114.5 (s, 3 H) and 309–339 cps (m, 1 H).

Data for the *endo* acetate follow: ir (CCl_4) 1727, 1741, 1229, 1250, 1022, and 1044 cm^{-1}; nmr (CCl_4 *vs.* TMS) 117 (s, 3 H) and 287–310 cps (br, 1 H).

A mixture of the acetates was purified by preparative glpc and analyzed.

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.48; H, 9.95. Found: C, 72.69; H, 9.84.

Lead Tetraacetate Reactions.[24]—A mixture of dry benzene (10 ml), commercial lead tetraacetate (2.0 g), and calcium carbonate (1.0 g) was heated for 15 min at reflux in a flask fitted with condenser and drying tube. The alcohol (300 mg in 10 ml of benzene) was then added in one batch through the condenser and refluxing was continued for 3 hr. The mixture was cooled and water (5 ml) was added with stirring during 30 min. After filtration, the solution was concentrated by distillation through a short Vigreux column and the residue was sublimed at 140° (1 atm).

From *endo*-bicyclo[3.3.1]nonan-3-ol there was obtained 255 mg (86%) of oxaadamantane (purity 89%) contaminated with ketone (6%), *endo* acetate (4%), and an unidentified compound (<1%). From *exo*-bicyclo[3.3.1]nonan-3-ol there was obtained 221 mg (74%) of unreacted alcohol together with trace amounts of the ketone and acetate.

Mercuric Oxide–Iodine Reactions.[24]—Iodine (4.0 g) and mercuric oxide (4.0 g) were placed in a 100-ml pear-shaped flask fitted with a side arm. The alcohol (300 mg) in carbon tetrachloride (75 ml) was added, and a condenser was attached. Agitation of the mercuric oxide suspension was maintained by bubbling in nitrogen through the side arm during irradiation with a GE 275-W sun lamp for 3.5 hr. Inorganic material was removed by filtration and the filtrate was concentratd by distillation through a short Vigreux column.

From *endo*-bicyclo[3.3.1]nonan-3-ol there was obtained 178 mg (60%) of essentially pure oxaadamantane.

From *exo*-bicyclo[3.3.1]nona-3-ol there was obtained 141 mg (47%) of a mixture containing the ketone and two unidentified compounds.

Oxaadamantane.—A sample was purified by chromatography on silica gel: mp 225–230° (sealed tube) (lit.[25] mp 232°); ir (CCl_4) 1020 and 1090 cm^{-1}; nmr (CCl_4 *vs.* TMS) 3.73–4.03 (2 H) and 1.4–2.25 ppm (12 H).

Nmr spectra were recorded either on a Varian Associates A-56-60A spectrometer or on an HA-60 (variable-temperature and decoupling measurements) at *ca.* 60-MHz operating frequency. High temperatures were calibrated by chemical shifts of ethylene glycol; low temperatures were calibrated with an iron–constantan thermocouple.

Registry No.—**8b**, 10036-10-9; **10**, 281-24-3; *exo*-bicyclo[3.3.1]nonan-3-ol, 10036-08-5; *exo*-bicyclo[3.3.1]-nonan-3-ol acetate, 23825-38-9; *endo*-bicyclo[3.3.1]-nonan-3-ol acetate 19490-34-7.

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[22] We thank Dr. John Schaefer for the details of this improved procedure.

[23] J. P. Schaefer, J. C. Lark, C. A. Flegal, and L. M. Honig, *J. Org. Chem.*, **32**, 1372 (1967).

[24] Yields are corrected for epimeric impurities in each starting material.

[25] H. Stetter and P. Tacke, *Chem. Ber.*, **96**, 694 (1963).