4-methylcyclohexanols. The hydrocarbons and the ketones were isolated by preparative vapor phase chromatography. Toluene and methylcyclohexane were identified by the nmr spectra. 2-Methylcyclohexanone (35%) had $[\alpha]^{25}\mathrm{D}$ $-14.6°$ (lit.[33] $[\alpha]^{25}\mathrm{D}$ $-15.22°$) and gave a semicarbazone, which melted at 193–195° (lit.[29] mp 197°). 3-Methylcyclohexanone (30%) had $[\alpha]^{25}\mathrm{D}$ $+0.572°$ (lit.[33] $[\alpha]^{25}\mathrm{D}$ $+13.06$) and gave a semicarbazone melting at 177–178° (lit.[29] mp 179°). 4-Methylcyclohexanone (35%) appeared as a shoulder on the peak corresponding to 3-methylcyclohexanone and was not separated.

Racemization of (−)-2-Methylcyclohexanone.—A small quantity of the (−)-2-methylcyclohexanone collected by vapor phase chromatography was refluxed in glacial acetic acid for 3 hr. The ketone that was recovered had no measurable optical activity.

Selenium Dioxide Oxidation of the Olefin Mixture in *n*-Butanol.—A stirred solution of 19.8 g (0.206 mol) of the 3:2 mixture of (+)-4-methylcyclohexene and (+)-3-methylcyclohexene in 70 ml of *n*-butanol was heated to reflux and 22.2 g (0.200 mol) of selenium dioxide in 100 ml of *n*-butanol was added dropwise. Reflux of the resultant mixture was continued for 30 hr. The reaction mixture was cooled and filtered to yield 6.2 g (39%) of black selenium. Fractional distillation of the filtrate gave 10 ml of a yellow liquid: bp 130–140° (30 mm). This material was treated with Raney nickel as described above to remove organoselenium impurities. Distillation through a spinning-band column gave 5.2 g of product: bp 90–95° (11 mm). Vapor phase chromatography on a Carbowax column showed five peaks. The material corresponding to the first and largest peak was collected and identified by its nmr spectrum as being a mixture of butoxycyclohexenes. The other peaks corresponded to methylcyclohexenones and methylcyclohexenols. The mixture of products was reduced catalytically in the presence of Adams catalyst in acetic acid. Vapor phase chromatography of the reduction product on a 12 ft × $^{3}/_{8}$ in. 23% polyamide on Chromosorb W column was carried out. The butyl ethers of commercially available methylcyclohexanols were prepared. By comparison with these and other commercially available authentic samples, the components of the reduction mixture were determined to be *cis*-2-butoxymethylcyclohexane, *trans*-3-butoxymethylcyclohexane, *cis*-4-butoxymethylcyclohexane, *trans*-2-butoxymethylcyclohexane, *cis*-3-butoxymethylcyclohexane, *trans*-4-butoxymethylcyclohexane, a mixture of methylcyclohexanones, and a mixture of methylcyclohexanols.

Registry No.—Selenium dioxide, 7446-08-4; 1,3-diphenylpropene-3-*d*, 16704-20-4; benzaldehyde-1-*d*, 3592-47-0.

Acknowledgment.—The authors would like to express their appreciation to the U. S. Army Research Office (Durham) for generous support of these studies.

Bicyclo[3.3.1]nonanes. IV. Dehydration of the Bicyclo[3.3.1]nonane-2,6-diols

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Bicyclo[3.3.1]nonane-2,6-dione (**2**), which was prepared from 1,3,5,7-tetracarbomethoxybicyclo[3.3.1]nonane-2,6-dione (**1**), was reduced with sodium borohydride in methanol to a mixture of epimeric bicyclo[3.3.1]nonane-2,6-diols (**3** and **4**). Dehydration of the diol mixture with sulfuric acid gave bicyclo[3.3.1]nona-2,6-diene (**9**), bicyclo[3.3.1]nona-2,7-diene (**8**), bicyclo[3.3.1]nonan-2-one (**5**), *endo*-bicyclo[3.3.1]non-6-en-2-ol (**10**), *endo*-bicyclo[3.3.1]non-7-en-2-ol (**11**), *endo*-bicyclo[3.3.1]non-3-en-2-ol (**12**), and a mixture of tricyclic oxides, which were tentatively identified as oxaadamantane (**6**) and 10-oxatricyclo$[3.3.1.1^{2,7}]$decane (**7**).

The first practical route to simply substituted bicyclo[3.3.1]nonanes was developed by Meerwein and Schürmann.[1] In their approach, dimethyl malonate was caused to react with formaldehyde or methylene iodide to produce 1,3,5,7-tetracarbomethoxybicyclo[3.3.1]nonane-2,6-dione (**1**) in good yield. Since **1** is so readily accessible, it appeared to be an attractive precursor to a number of derivatives that we were interested in preparing.

Upon reinvestigation of Meerwein's work,[1] we found that the preparation of **1** from formaldehyde could be simplified and expedited significantly by carrying out the initial phases of the condensation under anhydrous conditions and removing the water produced during the reaction by azeotropic distillation. Hydrolysis of the ester and decarboxylation of the resultant acid utilizing a procedure similar to that developed by Stetter and his group[2] afforded bicyclo[3.3.1]nonane-2,6-dione (**2**) in over-all yields as high as 38% based upon dimethyl malonate.

Reduction of **2** with sodium borohydride in methanol produced in high yield a mixture of two diols present in approximately equal percentages. In a previous paper,[3] we demonstrated that reduction of bicyclo[3.3.1]nonan-2-one (**5**) using similar conditions produces *endo*-bicyclo[3.3.1]nonan-2-ol (**14**) almost exclusively. We have also provided data that show that nucleophilic attack on the bicyclo[3.3.1]nonane system occurs almost exclusively from the *exo* face of the molecule. On these grounds, it is reasonable to presume that the first-formed product of reduction is a boron ester of 6-keto-*endo*-bicyclo[3.3.1]nonan-2-ol (**18**). Two routes for the reduction of the second carbonyl group would now be possible.

Bimolecular reduction of the second carbonyl group, initiated by an attack by borohydride ion on the keto alcohol or its boron ester, would be influenced by the same steric effects that were encountered during the reduction of the first carbonyl group. In this instance, the product would be *endo,endo*-bicyclo[3.3.1]nonane-2,6-diol (**4**). Alternatively, an intramolecular path for reduction is also available, but this route would lead to the formation of *endo,exo*-bicyclo[3.3.1]nonane-2,6-diol (**3**). The details of this process merit further discussion.

To allow the initially formed boron ester of **18** to approach sufficiently close to the second carbonyl group so that an interaction can occur, the rings must assume twist-boat conformations. The expenditure of energy required to bring about this conformational change will be compensated for by two factors, namely, the lower activation energy associated with the reduction of ketones by alkoxyborohydrides[4] and the

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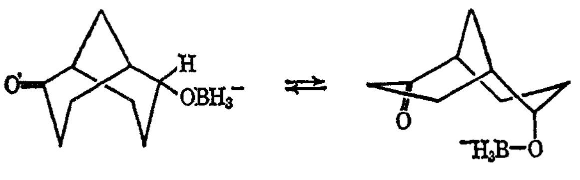
(1) H. Meerwein and W. Schürmann, *Ann.*, **398**, 196 (1913).

(2) H. Stetter, H. Held, and A. Schulte-Oestrich, *Ber.*, **95**, 1687 (1962).

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

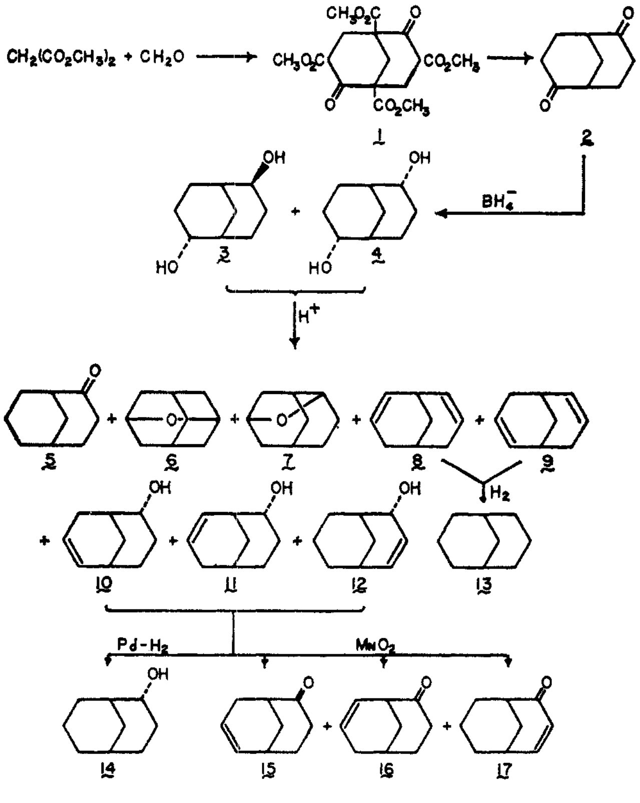
(4) H. C. Brown and J. Muzzio, *J. Amer. Chem. Soc.*, **88**, 2811 (1966).

more favorable entropy factors associated with an intramolecular and unimolecular rate process in contrast to a bimolecular reaction. Since almost equal amounts of **3** and **4** are produced by the reduction of **2**, it is apparent that the factors influencing the opposing reaction paths must nearly counterbalance each other.



By heating the mixture of **3** and **4** in 38% sulfuric acid using the conditions established by Meerwein,[5] eight different products were obtained. These are summarized in Scheme I. To facilitate the interpretation of our data, dione **2** was deuterated in the 3 and 7 positions by an acid-catalyzed exchange with deuterium oxide. It is interesting to note that, although base-catalyzed exchange of bridgehead hydrogens takes place readily for bicyclononanones[6,7] and bicyclo[3.3.1]non-1-ene can be prepared,[8,9] exchange under acidic conditions can be limited to the 3 and 7 positions of dione **2**. The deuterated dione subsequently was reduced to the corresponding 3,3,7,7-tetradeuteriodiol mixture, and the deuterated diol was dehydrated using the same conditions outlined for the nondeuterated mixture.[10–12]

SCHEME I



The lowest boiling fraction, which was a major product of dehydration, consisted of a diene mixture. Catalytic hydrogenation of this fraction produced bicyclo[3.3.1]nonane (**13**). In view of the structure of the diol precursors, it appeared to be reasonable to expect that the dehydration product was bicyclo[3.3.1]nona-2,6-diene (**9**). However, from an examination of the nmr spectrum and the mass spectral data of the diene fraction, it appeared that some bicyclo[3.3.1]nona-2,7-diene (**8**) was also present.

The mass spectrum (see Table I) of the diene fraction that resulted from dehydration of the deuterated diol showed that a small but significant percentage of the d_4-diene was present; the only reasonable route to this product would involve the sequence of reactions shown in Scheme II.

TABLE I

RESULTS OF MASS SPECTROMETRY[a]

Compd	Atoms of D/molecule[b]	D_0	D_1	D_2	D_3	D_4
Dienes	1.71 (1.76)	9.2	31.2	37.2	18.7	3.7
En-ols	2.42 (2.08)	12.8	16.5	31.5	28.8	10.4
Ketone	1.52 (1.60)	8.5	38.0	39.4	12.7	1.4
Oxides	1.86 (1.91)	6.4	27.1	40.6	21.2	4.7

[a] The data are given as relative abundances of the parent peaks and are uncorrected for the P + 1 peaks, P + 2 peaks, etc. For the nondeuterated compounds, it was found that the P − 1 peaks were negligible relative to the parent peaks. [b] Determined by Mr. J. Nemeth, Urbana, Ill. The values in parentheses were calculated from mass spectral data.

The detection of **9**-d_4, the isolation of *endo*-bicyclo[3.3.1]non-7-en-2-ol (**11**), and the detection of **11**-d_4 all clearly demonstrate that 1,2-hydride shifts occur readily in this system. Since **11**-d_4 must be a precursor to **9**-d_4, it therefore is reasonable to expect that it should also produce the 2,7 diene; the occurrence of a large percentage of diene containing three atoms of deuterium provides compelling evidence for the existence of substantial percentages of **8** in the diene fraction.[13]

The second most volatile component, which appeared to be homogeneous by vapor phase chromatography, had an extraordinarily high melting point (215–218°) and analyzed for $C_9H_{14}O$. A comparison of the nmr spectrum of this product with that of an authentic sample[14,15] of oxaadamantane (**6**) showed that our

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(5) H. Meerwein, F. Kiel, G. Klösgen, and E. Schoch, *J. Prakt. Chem.* **104**, 161 (1922).

(6) J. P. Schaefer and J. C. Lark, *J. Org. Chem.*, **30**, 1337 (1965).

(7) J. Dale, I. Laszlo, and W. Ruland, *Proc. Chem. Soc.* (London), 190 (1964).

(8) J. A. Marshall and H. Faubl, *J. Amer. Chem. Soc.*, **89**, 5965 (1967).

(9) J. R. Wiseman, *ibid.*, **89**, 5966 (1967).

(10) It should be noted that the composition of the diol mixture is probably significantly different from that used by Meerwein.[5] Meerwein reduced the dione with sodium amalgam in water and obtained a mixture of bicyclic and tricyclic alcohols. It has been shown recently that the reduction of **3** under equilibrating conditions gives a 2:1 mixture of *endo*-bicyclo[3.3.1]nonan-2-ol and *exo*-bicyclo[3.3.1]nonan-2-ol.[11] Since the steric course of sodium–alcohol reductions closely approximates the product composition that is obtained by equilibration,[12] it seems probable that Meerwein's[5] bicyclic diol mixture was rich in the *exo*,*exo* epimer.

(11) K. H. Baggaley, J. R. Dixon, J. M. Evans, and S. H. Graham, *Tetrahedron*, **23**, 299 (1967).

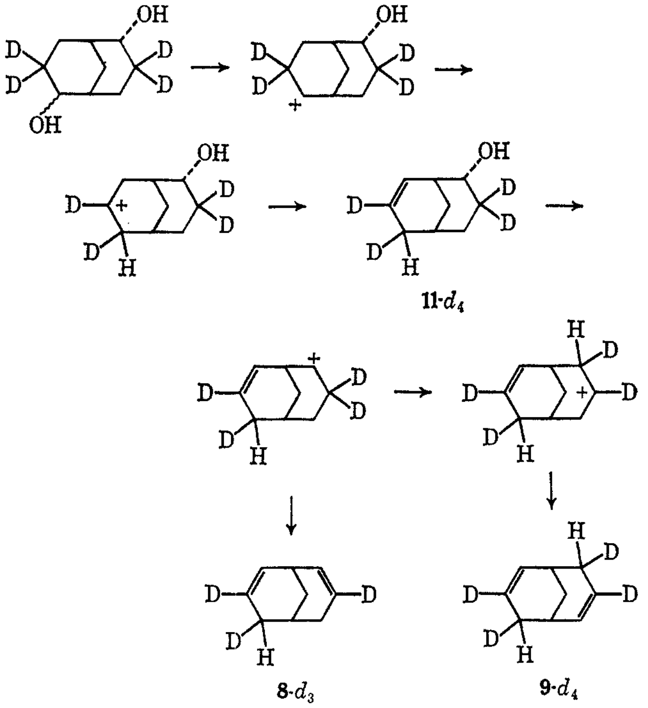
(12) C. P. Rader, G. E. Wicks, Jr., R. L. Young, Jr., and H. S. Aaron, *J. Org. Chem.*, **29**, 2252 (1964).

(13) A danger exists in too literal an interpretation of the percentages of d_4-diene, d_3-diene, etc, as ascertained from the mass spectrum. Since 31% of the diene fraction contained a single deuterium atom, it is apparent that loss of deuterium to solvent through a dynamic protonation–deprotonation equilibrium is occurring. Consequently, it is not possible to determine what percentage of the d_3-diene fraction is a primary reaction product and how much has arisen from loss of deuterium from **8**-d_4.

(14) Kindly provided by Professor H. Stetter.

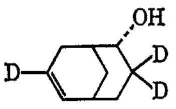
(15) H. Stetter and P. Tacke, *Angew. Chem.*, **74**, 354 (1962).

SCHEME II



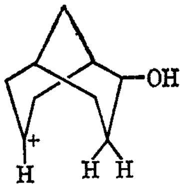
material was predominantly **6** contaminated with at least one other isomer; two reasonable possibilities for the structure of this second acid-stable oxide are 10-oxatricyclo[3.3.1.1^{2,7}]decane (**7**) and 10-oxatricyclo-[3.3.1.1^{2,6}]decane. The cationic precursors, **19** and **20**, of both oxides have been demonstrated to be reaction intermediates.

The large percentage of d_3-oxide requires that a major precursor of this product be **10**-d_3. Formation of

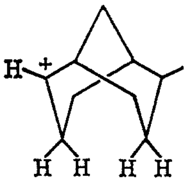


10-d_3

cation **19** by protonation of **10** should be favored over the formation of cation **20**, since the serious eclipsing



19

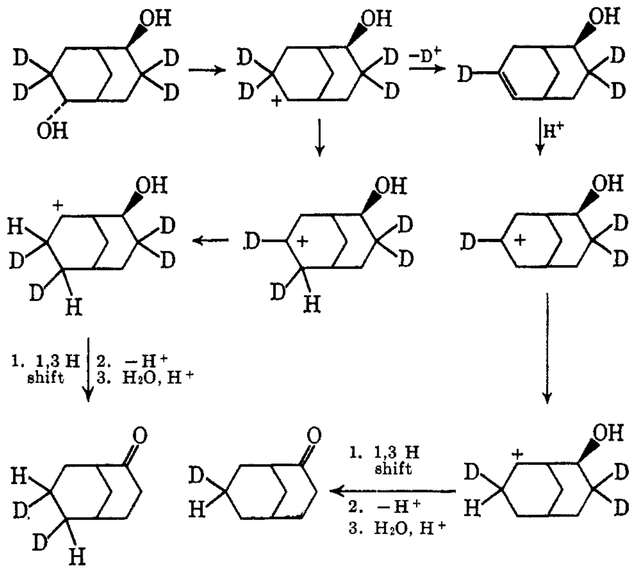


20

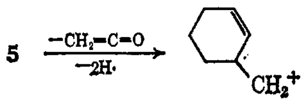
interactions that would exist in **20** would make it the less stable of the two.[16,17] Secondly, the formation of a bridged oxide from **20** would necessitate placing both rings of the cation in the energetically unfavored boat formation. On the other hand, **7** could be formed from **19** with only the ring bearing the hydroxyl group being in the boat formation. For these reasons, we consider the oxide impurity, which constituted about 25% of this fraction of the product mixture, to be **7**.

The third fraction, which constituted 10% of the product mixture, was readily identified as bicyclo[3.3.1]-nonan-2-one (**5**). It is evident that the formation of this compound must involve a transannular hydride shift. Since about 80% of the product was either mono- or dideuterated, the two paths illustrated in Scheme III seem to be the most probable.

SCHEME III

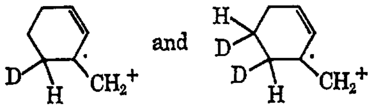


From a consideration of the mass spectra of **5** and of a sample of **5** that had been deuterated only at C_3, it is evident that the major course of degradation after electron impact is as shown in eq 1. The presence of



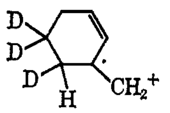
m/e 94 (1)

substantial fragments at both *m/e* 95 and 96 for the ketone that is produced from the deuterated diol is readily understood in terms of the species

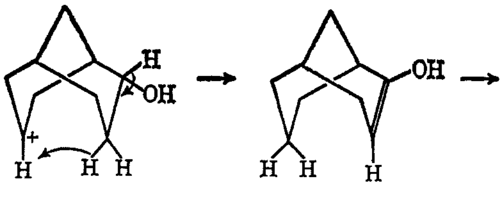


These would be expected to be present if the mechanism for ketone formation outlined above is valid.

A very significant feature of the mass spectrum of the ketone produced from the deuterated diol is the fragment at *m/e* 97 corresponding to



or something equivalent to this species. The presence of this fragment suggests that the sequence in eq 2 may be occurring. Hydride shifts of this type have been



(2)

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[16] M. Dobler and J. D. Dunitz, *Helv. Chim. Acta*, **47**, 695 (1964).

[17] W. A. C. Brown, J. Martin, and G. A. Sim, *J. Chem. Soc.*, 1844 (1965).

observed during the reactions of the 2,3-epoxide,[18] and the sequence outlined above would be stereoelectronically favored.

The last fraction that was produced consisted of a mixture of three en-ols. Oxidation of the mixture produced three unsaturated ketones that were easily identified by their characteristic uv spectra. Catalytic hydrogenation of the en-ol mixture produced a single alcohol, which was identified as *endo*-bicyclo[3.3.1]nonan-2-ol (**14**) by comparison with an authentic sample.[3] Detection of none of the *exo* isomer indicates that dehydration of the 2-*exo* alcohol is significantly faster than dehydration of the 2-*endo* alcohol. This is in accord with our recent observation[19] that the rate constant for solvolysis of the 2-*exo* brosylate is 80 times greater than that of its *endo* counterpart.

The mixture of diols **3** and **4** was dehydrated also under conditions other than those described by Meerwein.[5] When the mixture was heated at 100–105° in a sealed tube in the presence of 5% sulfuric acid, the only products were en-ols **10** and **11**. However, heating the sealed tube and its contents at 150–160° led to the same mixture of products that was obtained using Meerwein's conditions.

From this study it is evident that the dehydration of the diol mixture provides a practical route for the synthesis of bicyclo[3.3.1]nonane and *endo*-bicyclo[3.3.1]nonan-2-ol. In addition, from the results of deuterium-labeling experiments, it appears that 1,2-, 2,8-, and 3,7-hydride shifts occur with ease in the bicyclo[3.3.1]nonane system. Studies attempting to assess the importance of these effects in other reactions are in progress.

Experimental Section

1,3,5,7-Tetracarbomethoxybicyclo[3.3.1]nonane-2,6-dione.—Dimethyl malonate (264 g, 2.00 mol), 48 g (1.5 mol) of 95% paraformaldehyde, 400 ml of benzene, and 4 ml of piperidine were placed in a 2-l. flask fitted with a Dean–Stark trap and reflux condenser. The mixture was stirred with a magnetic bar and heated to reflux by means of a heating mantle. Reflux was continued until water ceased to accumulate in the trap; 26.5 ml (98% of the theoretical volume) was collected. Benzene was removed at reduced pressure, and the residue was dissolved in 150 ml of absolute methanol. The resulting solution was added rapidly to a stirred solution of sodium methoxide prepared from 32.6 g (1.42 g-atoms) of sodium and 400 ml of absolute methanol. More solvent was added as needed to facilitate stirring. This mixture was stirred and refluxed gently for 7 hr. After removal of the solvent at reduced pressure, the residue was dissolved in ice water and the mixture was extracted several times with diethyl ether. Precipitation of the product was achieved by bubbling carbon dioxide through the aqueous layer. The product was recovered by suction filtration, washed with water, dried in air, and combined with 300 ml of benzene. After removal of water by azeotropic distillation, the benzene solution was filtered while hot and then cooled. The product, which crystallized readily, was isolated by suction filtration and dried at room temperature under reduced pressure. The product weighed 108 g (56%) and had mp 145–154° (lit.[1] mp 163–164°).

Bicyclo[3.3.1]nonane-2,6-dione.—Modifications of the method of Stetter[2] were used.

Method A.—To a mixture of 35 g (0.10 mol) of 1,3,5,7-tetracarbomethoxybicyclo[3.3.1]nonane-2,6-dione and 106 ml of glacial acetic acid were added 36 ml of water and 36 ml of concentrated hydrochloric acid. Reflux and stirring were carried out for 11 hr. After removal of all readily volatile materials by distillation at reduced pressure, the residue was sublimed (3 mm, 120°) to afford 9.8 g (65%) of product, mp 119–135° after crystallization from benzene (lit.[1] mp 141°). Analysis by vapor phase chromatography (200° on a 10 ft × 0.25 in. column, 20% GE SE-30 on Chromosorb W) revealed the presence of only negligible amounts of impurity. The product was found to be suitable for use without further purification.

Method B.—The tetraester was refluxed in aqueous acid as described above. After removal of the acids and water, the residue was dissolved in methylene chloride. The methylene chloride solution was washed with several portions of 5% sodium hydroxide solution and with water, dried over anhydrous magnesium sulfate, filtered, and concentrated. The crude product was obtained in 19% yield. Acidification of the basic wash solutions afforded a sizable quantity of a substance that was identified as bicyclo[3.3.1]nonane-2,6-dione-1,5-dicarboxylic acid.

Method C.—The tetraester (10 g, 0.026 mol) was refluxed for 10 hr in aqueous acid as described above. After removal of the acids and water, 70 ml of bromobenzene was added to the residue. The flask was equipped for simple distillation, and 10 ml of material was distilled to ensure complete removal of the acids and water. The remaining solution was refluxed for 70 hr, after which time the evolution of carbon dioxide could no longer be detected. After removal of the bromobenzene by distillation under vacuum, the residue was sublimed (3 mm, 140°) to give 2.8 g (67%) of product.

Bicyclo[3.3.1]nonane-2,6-diol.—To a solution of 35.7 g (0.234 mol) of bicyclo[3.3.1]nonane-2,6-dione in 1 l. of absolute methanol was added 20 g (0.53 mol) of sodium borohydride in small portions. The contents of the flask were cooled by an ice–water bath and stirred with a magnetic bar during the addition. After 24 hr of stirring at room temperature, the solvent was removed at reduced pressure. Ice water was added to the residue, and continuous extraction with methylene chloride was carried out for 6 days. Filtration of the extract afforded 28.7 g of diol, mp 229.5–231.5° after crystallization from acetonitrile; evaporation of the solvent gave additional product. The total yield was 32.5 g (88.6%). An infrared spectrum (Nujol mull) showed absorption at ~3375 cm^{-1}. Vapor phase chromatography (160° on a 10 ft × 0.25 in. column, 5% QF-1 on 60/80 Chromosorb W) revealed the presence of two diols in nearly equal amounts.

Dehydration of Bicyclo[3.3.1]nonane-2,6-diol. Method A.—A modification of the procedure described by Meerwein[5] was employed. In a three-necked flask fitted with an addition funnel and equipped for steam distillation were placed 10 g (0.066 mol) of bicyclo[3.3.1]nonane-2,6-diol and 45 ml of 23% sulfuric acid. This mixture was stirred with a magnetic bar and heated with an oil bath maintained at 143–145°. After sufficient water had distilled from the mixture to bring the acid to a concentration of 38%, water was added from the funnel at a rate equal to the rate of distillation. Thus, the concentration of acid was kept at 38%. A white solid appeared in the distillate shortly after distillation was initiated. Distillation was terminated when organic material no longer appeared in the distillate. After saturation with sodium chloride, the distillate was extracted with several portions of diethyl ether. The ether extract was dried and concentrated to give 7.1 g of crude product.

Vapor phase chromatography (125° on a 5 ft × 0.25 in. column, 20% Carbowax on 80/100 neutral firebrick) of the dehydration product showed five distinct major peaks. The compounds or mixtures of compounds listed below in order of increasing retention time were isolated by preparative vapor phase chromatography (150° on a 6 ft × 0.25 in. column, 20% Carbowax on 50/60 firebrick) and identified.

1. **Bicyclo[3.3.1]nona-2,6-diene and bicyclo[3.3.1]nona-2,7-diene** (35%) were a colorless liquid; an infrared spectrum (film) revealed absorption at 710 and 1640 cm^{-1}; an nmr spectrum displayed a five-line pattern superimposed on a weak complex multiplet (4 H, total) centered at τ 4.4 and a multiplet (8 H) ranging from 7.4 to 8.4.

Anal. Calcd for C_9H_{12}: C, 89.93; H, 10.07. Found: C, 89.84; H, 10.30.

2. **2-Oxaadamantane and 10-oxatricyclo[3.3.1.1^{2,7}]decane** (10%) were a white solid with mp 215–218° (sealed capillary); an infrared spectrum (CCl_4) revealed absorption at 1193 cm^{-1}; an nmr spectrum showed a multiplet (2 H) centered at τ 5.8 and a multiplet (12 H) ranging from 7.5 to 8.4.

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.16; H, 10.50.

3. **Bicyclo[3.3.1]nonan-2-one** (9%) was identified by comparison with an authentic sample.[3] The mass spectrum of this

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(18) R. A. Appleton, J. R. Dixon, J. M. Evans, and S. H. Graham, *Tetrahedron*, **23**, 805 (1967).

(19) J. P. Schaefer and C. A. Flegal, *J. Amer. Chem. Soc.*, **89**, 5729 (1967).

ketone was characterized by the base peak, which occurred at *m/e* 94; the position of this peak was unchanged when the parent ketone was deuterated at the 3 position. An analysis of the mass spectrum of the ketone obtained by dehydration of the deuterated diol indicated the following relative abundances: *m/e* 94 (D_0), 15.7; *m/e* 95 (D_1), 39.7; *m/e* 96 (D_2), 33.3; *m/e* 97 (D_3), 11.3.

4. ***endo*-Bicyclo[3.3.1]non-6-en-2-ol and *endo*-bicyclo[3.3.1]non-7-en-2-ol** (46%) were a white solid; these compounds were collected together although partial separation was possible; an infrared spectrum displayed absorption at 704, 1650, and 3450 cm^{-1}; an nmr spectrum showed a multiplet (2 H) centered at τ 4.1, a singlet (1 H) centered at 6.2, and a multiplet (10 H) ranging from 7.3 to 8.6; further proof of the identity of these compounds was obtained by the procedures described below. No bicyclo[3.3.1]non-3-en-2-ol was detected in the material that was collected in this manner.

Method B.—A mixture of 2.0 g (0.013 mol) of bicyclo[3.3.1]nonane-2,6-diol and 20 ml of 5% sulfuric acid was heated in a sealed tube at 100–105° for 48 hr. The contents of the tube were extracted with pentane. The pentane solution was washed twice with water, dried, and concentrated to give a residue weighing 0.60 g (34%). The product was identified as a mixture of *endo*-bicyclo[3.3.1]non-6-en-2-ol and *endo*-bicyclo[3.3.1]non-7-en-2-ol by its infrared and nmr spectra and by vapor phase chromatographic analysis. After sublimation, the product had mp 132–134° (sealed capillary) (lit.[5] mp 133° for bicyclo[3.3.1]non-6-en-2-ol). Continuous extraction of the acid solution with methylene chloride led to the recovery of 1 g of starting material.

p-Nitrobenzoate derivatives were prepared by treating the unsaturated alcohols with *p*-nitrobenzoyl chloride in dry pyridine. After crystallization from ethanol–water and from pentane, the mixture of derivatives had mp 112–114°.

Anal. Calcd for $C_{16}H_{17}NO_4$: C, 66.89; H, 5.96. Found: C, 66.64; H, 5.75.

Method C.—A mixture of 1.0 g (0.006 mol) of bicyclo[3.3.1]nonane-2,6-diol and 20 ml of 5% sulfuric acid was heated in a sealed tube at 150–160° for 24 hr. The product was isolated as described for method B and sublimed to give 0.6 g of material, mp 171–178°. Analysis by vapor phase chromatography showed this material to be a mixture of the same compounds that were obtained by method A.

Manganese Dioxide Oxidation of the Dehydration Products.—A mixture of 0.2 g of the product obtained by dehydration of bicyclo[3.3.1]nonane-2,6-diol by method A, 1.0 of manganese dioxide,[20] and 15 ml of petroleum ether (bp 30–60°) was stirred for 7 days. After removal of the solid reagent by filtration, the solution was concentrated; the residue was sublimed (40 mm, 100°). An ultraviolet spectrum (95% ethanol) showed at 232 mμ, the strong absorption that is characteristic of an α,β-unsaturated ketone. However, oxidation by this method of the material obtained from subsequent dehydrations by method A gave a product that did not show this absorption band. Rather, the ultraviolet spectrum displayed an absorption maximum at 297 mμ. The amount of unsaturated ketone in the oxidation mixture was estimated by vapor phase chromatography, and log ϵ was found to be approximately 2.54. These data, being characteristic of a homoconjugated unsaturated ketone,[21] confirm the presence of bicyclo[3.3.1]non-7-en-2-ol in the starting material.

The unsaturated alcohols obtained by dehydration of the diol by method B were oxidized in the manner described above. An ultraviolet spectrum of the product confirmed the absence of any α,β-unsaturated ketone and revealed the presence of bicyclo-[3.3.1]non-7-en-2-one.

Catalytic Reduction of the Dehydration Products.—Catalytic hydrogenation of the unsaturated alcohols obtained by dehydration of bicyclo[3.3.1]nonane-2,6-diol according to method B was carried out on a microhydrogenation apparatus in the presence of 10% palladium on charcoal with 95% ethanol serving as solvent. After collection of the catalyst by filtration and removal of the solvent by distillation, sublimation of the residue afforded a product, identified as *endo*-bicyclo[3.3.1]nonan-2-ol, which had mp 172–176° (sealed capillary) (lit.[3] mp 177–178°). The melting point was depressed when the product was mixed with an authentic sample of *exo*-bicyclo[3.3.1]nonan-2-ol.[3] An infrared spectrum (CCl_4) showed the characteristic absorptions at 1025 and 1060 cm^{-1}.[22] The product gave an nmr spectrum that displayed a singlet (1 H) at τ 5.9, a multiplet (1 H) centered at 6.1, and a multiplet (12 H) ranging from 7.4 to 9.0.

A *p*-nitrobenzoate derivative was prepared by treating the product alcohol with *p*-nitrobenzoyl chloride in dry pyridine. After crystallization from ethanol–water, the derivative had melting point 102–103° (lit.[22] mp 102–103°).

The crude product mixture obtained by dehydration of the diol by method A was hydrogenated in the manner described above. The product mixture was analyzed by vapor phase chromatography. The peak corresponding to bicyclo[3.3.1]nona-2,6-diene had been replaced by a new peak corresponding to a compound that had the same retention time as bicyclo[3.3.1]nonane prepared from an authentic sample of bicyclo[3.3.1]non-2-ene.[3] The unsaturated alcohols had been converted into *endo*-bicyclo[3.3.1]nonan-2-ol, mp 171–174° (lit.[3] mp 177–178°), which was separated from the mixture by preparative vapor phase chromatography. The other two major components of the starting mixture remained unchanged.

Treatment of 2-Oxaadamantane and 10-Oxatricyclo[3.3.1.1^{2,7}]decane with Acid.—A mixture of the oxides (65 mg) and 2 ml of 5% sulfuric acid was heated in a sealed glass tube for 20 hr at 160°. The contents of the tube were poured into pentane, and the layers were separated. The pentane layer was washed with water, dried, and analyzed by vapor phase chromatography. The oxides were found to be intact, and no new products had been formed.

Deuteration of Bicyclo[3.3.1]nonane-2,6-dione.—To 20.0 ml of cold deuterium oxide was added with stirring 0.34 ml of phosphorous oxychloride. This solution was combined with 6.0 g (0.039 mol) of bicyclo[3.3.1]nonane-2,6-dione and 25 ml of ethanol-*d*, which had been prepared by treating triethyl orthoformate with deuterium oxide. Stirring was continued while the mixture was heated at 45–50° for 48 hr. The liquid components of the mixture were removed at reduced pressure (25 mm); care was taken to keep the oil-bath temperature below 50° during the distillation. The residue was treated again in the same manner with ethanol-*d* and deuterium oxide to which a small quantity of phosphorous oxychloride had been added. After 67 hr of stirring at 45–50° and concentration under the conditions described above, the residue was dissolved in 100 ml of methylene chloride. The methylene chloride solution was washed with small portions of cold, saturated sodium bicarbonate solution and with ice water. The organic solution was dried and evaporated to dryness; the amount of dione recovered was 5.6 g. The product had 31.10 atom % excess D or 3.73 atoms of D per molecule.

Bicyclo[3.3.1]nonane-2,6-diol-3,3,7,7-d_4.—Bicyclo[3.3.1]nonane-2,6-dione-3,3,7,7-d_4 was reduced to the corresponding diol in the manner described for the nondeuterated analogs.

Dehydration of Bicyclo[3.3.1]nonane-2,6-diol-3,3,7,7-d_4.—The deuterated diol was dehydrated according to method A described for the nondeuterated analog. The products were separated by preparative vapor phase chromatography under the conditions described above. The results of mass spectral analysis are given in Table I.

Registry No.—**1**, 6966-22-9; **2**, 16473-11-3; **3**, 16710-53-5; **4**, 16710-54-6; **5**, 2568-17-4; **6**, 281-24-3; **7**, 16710-57-9; **8**, 13534-06-0; **9**, 16710-59-1; **10**, 16710-60-4; **10** *p*-nitrobenzoate, 16710-61-5; **11**, 16710-62-6; **11** *p*-nitrobenzoate, 16710-63-7.

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