constant as long as the ratio of the concentrations of A to B remains constant. Therefore, over a range of alcohol concentrations where the ratio of the two alcohols is constant, the apparent extinction coefficient of the complexes should remain constant and the method used to calculate the K's for the pure alcohols should be applicable for the calculation of the K_{app} for a mixture of alcohols.

Oxidation of Organic Compounds with Cerium(IV). VIII. Oxidation of Bicyclo[2.2.1]-2-heptanols and Bicyclo[2.2.2]-2-octanol[1]

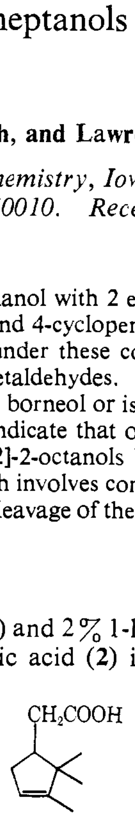
Walter S. Trahanovsky, Patrick J. Flash, and Lawrence M. Smith

Contribution from the Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa 50010. *Received March 4, 1969*

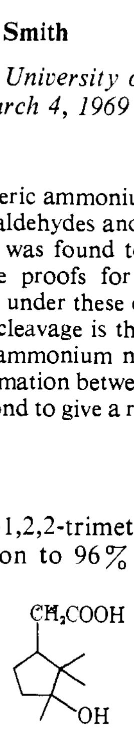
Abstract: It is reported that oxidation of either *exo*- or *endo*-2-norbornanol with 2 equiv of ceric ammonium nitrate in 50% aqueous acetonitrile at 50° gave three major products, 3- and 4-cyclopenteneacetaldehydes and 3-nitratocyclopentaneacetaldehyde. Oxidation of bicyclo[2.2.2]-2-octanol under these conditions was found to give 4-cyclohexeneacetaldehyde, and *cis*- and *trans*-4-nitratocyclohexaneacetaldehydes. Structure proofs for these products are described. The major product from the oxidation of either borneol or isoborneol under these conditions was found to be α-campholenic aldehyde. These results clearly indicate that oxidative cleavage is the preferred mode of oxidation of bicyclo[2.2.1]-2-heptanols and bicyclo[2.2.2]-2-octanols by ceric ammonium nitrate. From these and other experimental results a mechanism is proposed which involves complex formation between the cerium(IV) and alcohol followed by decomposition of this complex with cleavage of the C_1–C_2 bond to give a radical which is then oxidized by another ceric species.

Norcamphor has always been the oxidation product of all previously reported oxidations of either *exo*- or *endo*-2-norbornanol. These oxidations include an Oppenauer oxidation[2] and oxidations by chromium trioxide,[3,4] ammonium vanadate,[5] peroxides in carbon tetrachloride,[6] and nitric acid.[7] No product from oxidative cleavage was reported in these studies.

Most previously reported oxidations of borneol and isoborneol also produced the ketone. Camphor has been obtained from these alcohols by nitric acid oxidation,[7,8] Oppenauer oxidations,[7,9] and oxidation by hypobromite salts.[10] However, oxidation of isoborneol by chromium trioxide is reported to give 2% α-campholenic acid (**1**) and 2% 1-hydroxy-1,2,2-trimethyl-3-cyclopentaneacetic acid (**2**) in addition to 96% camphor.[11]

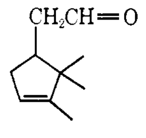


1

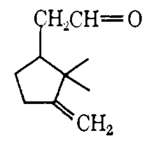


2

The lead tetracetate oxidation of isoborneol at 80° in benzene has been reported to give α-campholenic aldehyde (**3**), 2,2-dimethyl-3-methylenecyclopentaneacetaldehyde (**4**), and camphor in a ratio of 12:8:1, but absolute yields were not reported.[12,13] At 25°, only camphor and camphene were produced.



3



4

We have found that unlike previously reported oxidations of these bicyclo[2.2.1]-2-heptanols, the ceric ammonium nitrate (CAN) oxidation of these alcohols leads exclusively to products of oxidative cleavage. In this paper we report a study of the CAN oxidation of these alcohols and bicyclo[2.2.2]-2-octanol.

---

(1) (a) Part VII: L. B. Young and W. S. Trahanovsky, *J. Am. Chem. Soc.*, **91**, 5060 (1969). (b) This work was partially supported by Public Health Service Grant GM 13799 from the National Institute of General Medical Sciences. The mass spectrometer and Varian Model HA-100 nmr spectrometer were purchased with funds from the National Science Foundation and the Iowa State Alumni Research Foundation. We thank these organizations for their support. (c) Based on work by P. J. F. in partial fulfillment of the requirements for the degree of Master of Science at Iowa State University. (d) Preliminary communication: Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, p 166 S.

(2) N. J. Toivonen and J. Kaila, *Soumen Kemistilehti*, **28B**, 91 (1955); *Chem. Abstr.*, **49**, 7529 (1955).

(3) H. K. Hall, *J. Am. Chem. Soc.*, **82**, 1209 (1960).

(4) J. B. Miller, *J. Org. Chem.*, **26**, 4905 (1961).

(5) C. Cohen, U. S. Patent 2,991,308 (July 4, 1961); *Chem. Abstr.*, **49**, 7529 (1955).

(6) W. J. Jackson, *Ind. Eng. Chem. Prod. Res. Develop.*, **3**, 100 (1964).

(7) H. Toivonen, *Soumen Kemistilehti*, **30A**, 130 (1957); *Chem. Abstr.*, **51**, 17832 (1957).

(8) (a) S. Ando, *Nippon Senbai Kosha Chuo Kenkyusho Kenkyu Hokoku*, 41 (1956); *Chem. Abstr.*, **53**, 18975 (1959); (b) B. G. S. Acharya, R. C. Shah, and T. S. Wheeler, *J. Univ. Bombay*, **11A** [5], 113 (1943); *Chem. Abstr.*, 37, 5957 (1943).

(9) J. Stanek and J. Zemlicka, *Chem. Listy*, **51**, 493 (1957); *Chem. Abstr.*, **51**, 10448 (1957).

(10) M. Metayer and S. Roumens, *Compt. Rend.*, **225**, 1324 (1947).

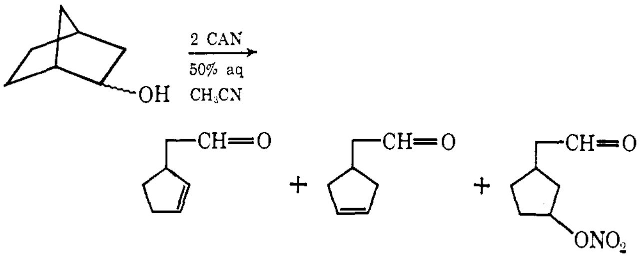
(11) W. A. Mosher and E. O. Langerak, *J. Am. Chem. Soc.*, 73, 1302 (1951).

(12) R. E. Partch, *J. Org. Chem.*, **28**, 276 (1963).

(13) Professor R. E. Partch has informed me that the absolute yield of products 3 and 4 was 65%.

Results

Oxidation of either *exo*- or *endo*-norbornanol with 2 equiv of CAN for 0.5 hr at 50° in 50% aqueous acetonitrile gave three major products, 3- and 4-cyclopenteneacetaldehydes and 3-nitratocyclopentaneacetaldehyde, in the yields shown.



exo	18%	20%	36%
endo	19%	20%	43%

The product mixtures from both alcohols contained <1% of the corresponding ketone, norcamphor.

The structures of the products were proved as follows. Distillation under vacuum of the product mixture from a large-scale oxidation of *exo*-norbornanol gave two main fractions. The lower boiling fraction was purified by glpc and was identified as either the 3- and/or 4-cyclopenteneacetaldehyde from its ir and mass spectra and comparison of the melting point of its 2,4-dinitrophenylhydrazone with literature values. This fraction was shown to be a mixture of the 3 and 4 isomers by comparison of its nmr spectrum with that of an authentic sample of 3-cyclopenteneacetaldehyde prepared by the solution phase photolysis of norcamphor.[14] The oxidation product spectrum showed the aldehydic proton as a pair of overlapping triplets while the authentic spectrum of the 3 isomer showed a clean triplet. Moreover, the olefin proton absorption of the oxidation product spectrum appeared as two overlapping peaks while that of the authentic 3 isomer was a single peak.

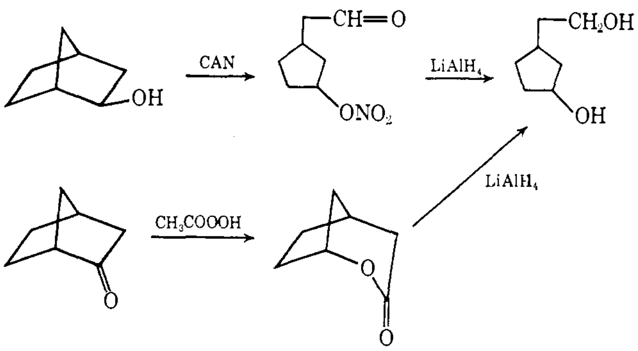
A sample of the cyclopenteneacetaldehyde mixture from oxidation of *exo*-norbornanol was reduced with lithium aluminum hydride. The resulting (cyclopentene)ethanols were converted to *p*-nitrobenzenesulfonates which were then solvolyzed in acetic acid at 100° for 13 hr. Glpc analysis of the acetolysis products using a Carbowax 20M column and an internal standard showed that 48% *exo*-norbornyl acetate and 45% 3-(cyclopentene)ethyl acetate were produced. From the work of Bartlett and coworkers,[15] Lawton,[16] and Closson and Kwiatkowski,[17] the acetolysis of 4-(cyclopentene)ethyl *p*-nitrobenzenesulfonate should lead to a quantitative yield of *exo*-norbornyl acetate while acetolysis of the 3 isomer should lead to >95% 3-(cyclopentene)ethyl acetate. Thus, these experiments further confirm the structure of the cyclopenteneacetaldehydes and show that the ratio of the 3 to 4 isomer is 48:52.

To check the possibility that the oxidation of the norbornanols was leading to only one cyclopenteneacetaldehyde which then isomerized to an equilibrium mixture of the 3 and 4 isomers, the stability of the 3 isomer under reaction conditions was tested by heating it in a cerium(III) solution that was comparable to the end solution of the reaction mixture. No evidence for isomerization of the 3 isomer was found by nmr analysis.

The nmr spectrum of the product mixture from the oxidation of the *endo* isomer showed signals in the olefin region identical with those of the *exo* isomer and it was thus assumed that approximately equal amounts of both cyclopenteneacetaldehydes were also obtained from the *endo* isomer.

The higher boiling fraction of the product mixture from a large-scale oxidation of *exo*-norbornanol was shown to be 3-nitratocyclopentaneacetaldehyde. Its ir spectrum showed the characteristic bands of aldehyde and nitrate functional groups,[18] and its nmr spectrum was consistent with this proposed structure. The aldehyde nitrate was reduced with lithium aluminum hydride to (3-hydroxycyclopentane)ethanol whose structure was confirmed by comparison of its ir and nmr spectra with those of an authentic sample of the *cis*-diol prepared from the lithium aluminum hydride reduction of the lactone, 2-oxabicyclo[3.2.1]-3-octanone. The lactone had been prepared by the Baeyer-Villiger oxidation of norcamphor.[19] This sequence is outlined in Chart I.

Chart I



Although the ir and nmr spectra and glpc behavior of the diol obtained from the aldehyde nitrate and those of authentic *cis*-diol were identical, we could not be sure that the diol from the aldehyde nitrate was the *cis* isomer unless we could show that the *trans* isomer had different characteristics from the *cis* isomer. Since the lithium aluminum hydride reduction of an alkyl nitrate to an alcohol goes with retention of configuration,[20] the diol and the aldehyde nitrate from which it was obtained should have the same stereochemistry. For mechanistic reasons discussed below, we wanted to know if the aldehyde nitrate was the pure *cis* isomer or a mixture of the *cis* and *trans* isomers. Attempts to prepare mixtures of the *cis* and *trans* diols by lithium aluminum hydride reduction of methyl 3-oxocyclopenteneacetate and hydration of (4-cyclopentene)ethanol gave material which was apparently only *cis*-diol by infrared and glpc analysis. Conformational analysis of 1,3-disubstituted cyclopentanes shows that the *cis* isomer should be more stable than the

---

[14] (a) Unpublished work by Professor O. L. Chapman and D. L. Garin; D. L. Garin, Ph.D. Thesis, Iowa State University of Science and Technology, Ames, Iowa, 1964; (b) footnote 10 of J. E. Baldwin and J. E. Gano, *J. Org. Chem.*, 32, 3506 (1967).

[15] (a) P. D. Bartlett and S. Bank, *J. Am. Chem. Soc.*, **83**, 2591 (1961); (b) P. D. Bartlett, S. Bank, G. Crawford, and H. Schmid, *ibid.*, **87**, 1288 (1965).

[16] R. D. Lawton, *ibid.*, **83**, 2399 (1961).

[17] W. D. Closson and G. T. Kwiatkowski, *ibid.*, **86**, 1887 (1964).

[18] K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day Inc., San Francisco, Calif., 1962.

[19] J. Meinwald and E. Frauenglass, *J. Am. Chem. Soc.*, **82**, 5235 (1960).

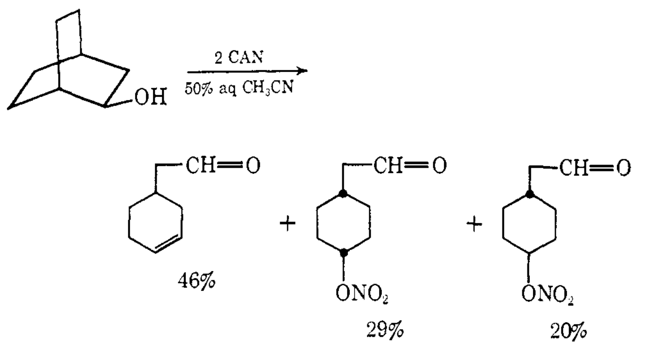
[20] E. W. Stoffer, E. W. Parotta, and J. D. Domenico, *ibid.*, 74, 5301 (1952).

trans, and in fact an equilibrium mixture of the two isomers of 1,3-dimethylcyclopentane contains 70% of the *cis* isomer.[21] Since one would expect the *trans* isomer to have significantly different spectral and chromatographic characteristics from the *cis* isomer, but a second isomer was never observed, we concluded that the *cis*-diol and aldehyde nitrate are so much more stable than the *trans* isomers that they always form preferentially. Thus we could attach no mechanistic significance to the stereochemistry of the aldehyde nitrate obtained from the norbornanols. However, the situation is different with respect to the stereochemistry of the aldehyde nitrate obtained from the oxidation of bicyclo[2.2.2]-2-octanol and this is discussed below.

The yields of the aldehyde olefins and aldehyde nitrate from the oxidation of the norbornanols were determined by nmr analysis and are averages of four runs with standard deviations of <5.8% for the total yields of aldehyde olefins and <10.2% for the yields of aldehyde nitrate.

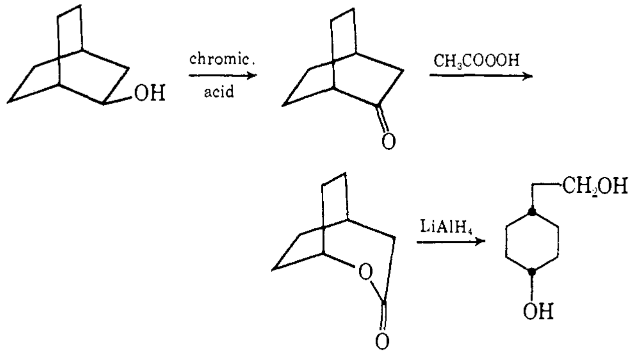
The similar product mixtures from both the *exo*- and *endo*-norbornanols could have resulted from isomerization of the *endo* isomer to the *exo* isomer before oxidation. This possibility was eliminated by showing that *endo*-norbornanol was stable for 30 min at 50° in a cerium(III) solution comparable to the solution at the end of an oxidation. Moreover, the *endo* alcohol is oxidized faster than the *exo* alcohol since (a) the *endo* alcohol decolorizes cerium(IV) faster than the *exo* alcohol and (b) oxidation of an equimolar mixture of the two alcohols by a limited amount of cerium(IV) leads to a reaction mixture that contains five times more *exo*-norbornanol than *endo*-norbornanol. In general, the more hindered isomer of a pair of stereoisomeric alcohols is oxidized faster by metal ions.[22]

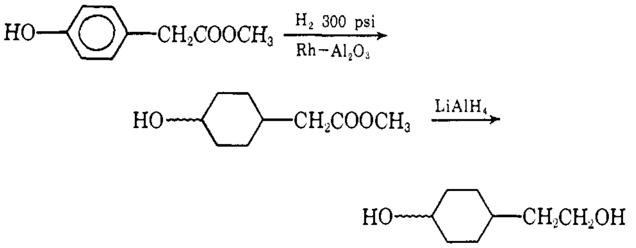
Oxidation of bicyclo[2.2.2]-2-octanol with 2 equiv of CAN in 50% aqueous acetonitrile at 50° for 0.5 hr gave three products, 4-cyclohexeneacetaldehyde and *cis*-, and *trans*-4-nitratocyclohexaneacetaldehydes.



The 4-cyclohexeneacetaldehyde was purified by glpc and its nmr and ir spectra were consistent with its structure. By analogy to the cyclopenteneacetaldehydes produced from the norbornanols, the position of the olefin was assigned to the 4 position. It is interesting to note that the definite assignment of the olefin to the 3 or 4 position of a cyclohexeneacetaldehyde is difficult by conventional spectral methods and the CAN oxidation of bicyclo[2.2.2]-2-octanol offers a means of preparing the pure 4 isomer.

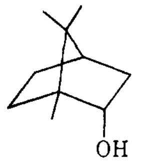
The aldehyde nitrates were reduced by lithium aluminum hydride to a mixture of diols. An authentic sample of the *cis* diol was prepared from the lithium aluminum hydride reduction of 2-oxabicyclo[3.2.2]-3-nonanone. This lactone was prepared by the Baeyer–Villiger oxidation of bicyclo[2.2.2]-2-octanone which was prepared by the chromic acid oxidation of bicyclo[2.2.2]-2-octanol. An authentic mixture of *cis*- and *trans*-diols was prepared by catalytic hydrogenation of methyl 4-hydroxyphenylacetate followed by a lithium aluminum hydride reduction. Glpc analysis of this diol mixture using an authentic sample of *cis*-diol showed it to be composed of 76% *cis*- and 24% *trans*-diol. Similar analysis of the diol mixture obtained from the reduction of the aldehyde nitrates showed it to be composed of 60% *cis*- and 40% *trans*-diol. Thus the aldehyde nitrates should also be composed of 60% *cis* and 40% *trans* isomers.[20] The ir and nmr spectra of the two mixtures of *cis*- and *trans*-diols and the pure *cis*-diol were very similar and no distinct differences that could be ascribed to stereochemical differences were apparent.



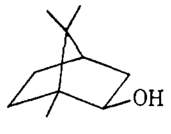


The yields of the aldehyde olefin and aldehyde nitrates from the oxidation of bicyclo[2.2.2]-2-octanol were determined by nmr analysis and are averages of two runs with standard deviations of 1% for the yield of aldehyde olefin and 5% for the total yield of aldehyde nitrates.

The products from the CAN oxidation of borneol (**5**) and isoborneol (**6**) were also determined. Both isomers gave the same product mixture which contained at least ten products based on glpc analysis. However, α-campholenic aldehyde (**3**) was the only major product: absolute yield by nmr analysis, 43% from borneol and 55% from isoborneol based on two runs for each



5



6

---

[21] E. L. Eliel, N. N. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, New York, N. Y., 1965, p 202.

[22] Reference 1a and references cited therein.

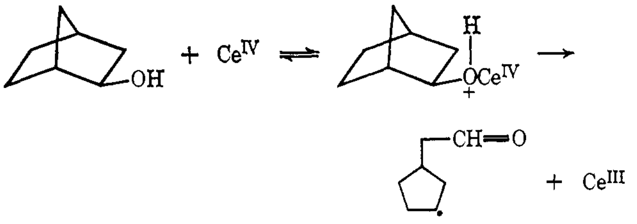
alcohol with standard deviations of <1% for both yields. Some of the minor products were aldehydes since the nmr yields of aldehydes were always 10–20% greater than the yields of α-campholenic aldehyde. No camphor was produced based on glpc analysis.

Since oxidative cleavages by CAN seem to be one-electron oxidations,[23] an attempt was made to trap the intermediate radical that would be formed during the CAN oxidation of *exo*-norbornanol. A sample of *exo*-norbornanol was oxidized in 50% aqueous acetonitrile that contained 10% acrylamide, a known radical trap under these conditions,[23] with the alcohol concentration being 0.04 *M* and the CAN concentration being 0.08 *M*. By the usual nmr analysis of the product mixture, no aldehydic products could be detected. The normal products were obtained when the trap was replaced with acetamide.

Discussion

The results clearly indicate that oxidative cleavage is the preferred mode of oxidation of bicyclo[2.2.1]-2-heptanols and bicyclo[2.2.2]-2-octanol by CAN. In no case was any detectable amount of ketone formed, yet total recovery of products was very high.

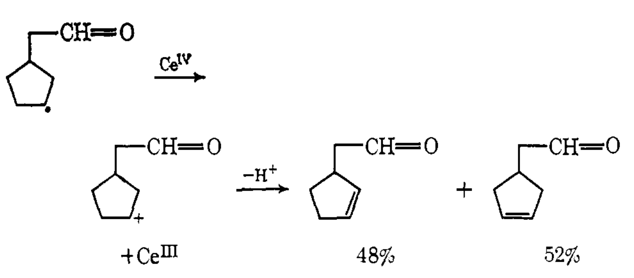
The first step of the oxidation is most likely complex formation since the CAN solution turns from orange to red as the alcohol is added.[22] That the cleavage step is a one-electron oxidative process like those previously observed with cerium(IV)[23] is supported by the radical-trapping experiments. The similar product mixtures from *exo*- and *endo*-2-norbornanols and borneol and isoborneol, and the production of both the *cis*- and *trans*-4-nitratocyclohexaneacetaldehydes from bicyclo-[2.2.2]-2-octanol, indicate that the radical is a free radical and is not associated with the carbaldehyde group at all. Thus the mechanism for the formation of the radical from *exo*-norbornanol may be represented as follows.



The radical, then, can be oxidized by a ligand-transfer or electron-transfer step. Kochi[24] and coworkers have suggested that substitution products from the oxidation of radicals result from ligand-transfer reactions and elimination products result from electron-transfer reactions. Our results support this contention. Since the cerium(IV) species under these conditions is highly nitrated,[1a] it seems likely that the nitrate is formed by a ligand-transfer reaction. The approximately equal

$$\mathrm{R}\cdot + \mathrm{ONO_2Ce^{IV}} \longrightarrow \mathrm{RONO_2} + \mathrm{Ce^{III}}$$

amounts of the 3- and 4-cyclopenteneacetaldehydes obtained from the oxidation of the norbornanols are readily explained by the oxidation of the radical to a cation which then loses β hydrogens randomly.



The high yield of cleavage products suggests that there may be some synthetic uses for the CAN oxidation of bicyclic alcohols. For example, the conversion of borneol to α-campolenic aldehyde is a very convenient way to prepare this aldehyde compared to previously reported methods.[12,25]

Experimental Section

Methods and Materials. Reagents and solvents were obtained from commercial sources and used without further purification. Most equipment has been previously described.[26] Nmr spectra were also taken with a Varian Model HA-100 spectrometer. Compounds except those described below were obtained from commercial sources and purified by column chromatography or recrystallization when necessary. Alcohols were converted to acetates by treating the alcohol with acetyl chloride in pyridine.

exo-**2-Norbornanol** was obtained from commercial sources and was prepared by the oxymercuration of norbornene.[27]

endo-**2-Norbornanol** was obtained by lithium trimethoxyaluminohydride reduction of norcamphor according to the procedure of Brown and Deck.[28]

Bicyclo[2.2.2]-2-octanol was prepared by the oxymercuration of bicyclo[2.2.2]octene[27] and purified by sublimation, yield 82%, mp 206–207° (lit.[29] mp 208–210°).

2-Oxabicyclo[3.2.1]-3-octanone was prepared by the peracetic acid oxidation of norcamphor following the procedure of Meinwald and Frauenglass;[19] nmr (CCl_4) δ 4.8–4.6 (m, 1) and 3.1–0.9 (m, 9).

Methyl 3-oxocyclopentaneacetate was prepared by the method of Meinwald and Frauenglass;[19] ir (CCl_4) 1733 (C=O) and 1450–1110 cm^{-1} (C—O); nmr (CCl_4) δ 3.6 (s, 3) and 2.9–1.2 (m, 9).

(4-Cyclopentene)ethanol was synthesized by the method of Bartlett and coworkers.[15]

(3-Cyclopentene)ethanol was obtained by reducing commercial 3-cyclopenteneacetic acid with lithium aluminum hydride using standard procedures.

cis-**(3-Hydroxycyclopentane)ethanol.** 2-Oxabicyclo[3.2.1]-3-octanone was reduced with lithium aluminum hydride in ether by the method of Rassat and Ourisson.[30] The aqueous layers were combined and continuously extracted with ether for 3 days. Evaporation of the ether gave the desired diol, ir ($CHCl_3$) 3330, 2860, and 995 cm^{-1}; nmr ($CDCl_3$) δ 4.4–4.1 (m, 1), 3.66 (t, 2, J = 7 Hz), and 2.4–0.9 (m, 11).

(3-Cyclopentene)ethanol was added to acetic acid that contained a trace of sulfuric acid. Glpc analysis of the products on a Carbowax 20M column using an authentic sample of the diacetate of *cis*-(3-hydroxycyclopentane)ethanol showed that the *cis* diacetate was produced but no evidence for the *trans* isomer was obtained.

cis- **and** *trans*-**(4-Hydroxycyclohexane)ethanols.** A mixture of these diols was prepared by a method patterned after that of Karim.[31] *p*-Hydroxyphenylacetic acid was converted to its ethyl ester which was then hydrogenated in absolute ethanol at 100° under H_2 at 500–1500 psi pressure using 5% rhodium on alumina

---

[23] (a) P. M. Nave and W. S. Trahanovsky, *J. Am. Chem. Soc.*, **90**, 4755 (1968); (b) W. S. Trahanovsky, L. H. Young, and M. H. Biermann, *J. Org. Chem.*, **34**, 869 (1969).

[24] R. A. Sheldon and J. K. Kochi, *J. Am. Chem. Soc.*, 90, 6688 (1968), and references cited therein.

[25] See W. C. Agosta and D. K. Herron, *J. Am. Chem. Soc.*, **90**, 7025 (1968), and references cited therein for other methods of preparing α-campholenic aldehyde.

[26] W. S. Trahanovsky and M. P. Doyle, *J. Org. Chem.*, **32**, 146 (1967).

[27] H. C. Brown, J. H. Kawakami, and S. Ikegami, *J. Am. Chem. Soc.*, **89**, 1525 (1967).

[28] H. C. Brown and H. R. Deck, *ibid.*, **87**, 5620 (1965).

[29] H. Walborsky, M. E. Baum, and A. A. Youssef, *ibid.*, **83**, 988 (1961).

[30] A. Rassat and G. Ourisson, *Bull. Soc. Chim. France*, 1133 (1959); *Chem. Abstr.*, **54**, 19523*a* (1960).

[31] M. A. Karim, *Indian J. Appl. Chem.*, **23**, 217 (1960); *Chem. Abstr.*, **55**, 24600*h* (1961).

as the catalyst. The cyclohexyl ester was reduced with lithium aluminum hydride in tetrahydrofuran. The hydrolysate was continuously extracted with ether for 2 days. Removal of the ether left a residue; ir ($CDCl_3$) 3330 cm^{-1}; nmr ($CDCl_3$) δ 4.2–3.4 (a broad peak and fuzzy t, 3, J = 7 Hz) 2.13 (s, 2), and 2.1–0.8 (m, 11). Glpc analysis using a FFAP column showed two peaks in the ratio of 76% to 24%. The larger peak was enhanced by simultaneous injection of a sample of the pure *cis* isomer.

***cis*-(4-Hydroxycyclohexane)ethanol.** Bicyclo[2.2.2]-2-octanone was obtained by the chromic acid oxidation of bicyclo[2.2.2]-2-octanol.[32] The ketone was converted to 2-oxabicyclo[3.2.2]-3-nonanone by the method of Meinwald and Frauenglass;[19] nmr (CCl_4) δ 4.4 (m, 1), 2.75 (d, 2, J = 4 Hz), and 2.4–1.0 (m, 9). The lactone was reduced with lithium aluminum hydride in ether. The hydrolysate was continuously extracted with ether and removal of the ether left a colorless oil which was purified by glpc using an SE-30 column. The ir spectrum was essentially indistinguishable from that of the *cis–trans* diol mixture and a 100-MHz nmr spectrum showed the same resonances as for the *cis–trans* diol mixture.

CAN Oxidation of *exo*-2-Norbornanol. A quantity of 2.5 mmol of the alcohol was dissolved in 4 ml of acetonitrile and 5 mmol of CAN was dissolved in 1 ml of acetonitrile and 5 ml of water. The solutions were warmed to 50–55° and the CAN solution was poured into the alcohol solution. The red color characteristic of cerium(IV)–alcohol complexes[22] appeared immediately. The solution was swirled for 60 sec during which time the red color disappeared. After 0.5 hr at 50°, the reaction mixture was cooled. For samples analyzed by nmr, a weighed amount of standard, *o*-dichlorobenzene, was added and the reaction mixture was poured into 10 ml of water in a separatory funnel and extracted with 10 ml of ether. The ether solution was washed with 10 ml of water,[33] dried ($MgSO_4$), filtered, and distilled to a small volume. The ether solution was analyzed by nmr. Integration of the signals for the aldehydic protons, aromatic protons, olefinic protons, and the protons α to the nitrate group enabled calculation of the total amount of aldehydes as well as the amounts of aldehyde olefins and aldehyde nitrate that were extracted relative to the standard. Relative extraction factors were calculated by adding the material from the first extraction to a cerium(III) solution similar to that obtained at the end of an oxidation, extracting with ether, and analyzing the extract by nmr as was done for the first extract. Use of the nmr analysis of the first extract and these extraction factors (which ranged from 1.053 to 1.322) enabled absolute yields of the products to be calculated. The yield of aldehyde nitrate reported was that obtained by subtracting the yield of olefin from the total aldehyde yield since accurate integration of the broad nmr signal from the proton α to the nitrate group was difficult. Glpc analysis using a Carbowax 20M column of the ether extract showed that <1% norcamphor was produced.

Products from the CAN Oxidation of *exo*-2-Norbornanol. Quantities of 2 to 5 g of *exo*-norbornanol were oxidized as described above except that no standard was added during work-up. The products were distilled under vacuum giving two main fractions: fraction 1, bp 28–30° (1.1 mm), and fraction 2, bp 111–115° (1.1 mm).

Fraction 1 was further purified by glpc using a Carbowax 20M column: ir (CCl_4) 2899 and 1724 cm^{-1}; nmr (CCl_4) δ 9.68 (t, 1, J = 2 Hz), 5.85–5.4 (m, 2), and 3.3–0.8 (m, 7); mass spectrum (70 eV) gave a parent peak at m/e 110 and a base peak at m/e 66 corresponding to a cyclopentadienyl fragment. A 2,4-dinitrophenylhydrazone derivative was prepared, mp 104–105° (lit. melting point for 3-cyclopenteneacetaldehyde,[34] 98–99°, lit. melting point for 4-cyclopenteneacetaldehyde,[35] 100–101°). This fraction was shown to be a mixture of 3- and 4-cyclopenteneacetaldehydes as described in the Results.

Fraction 2 had the following spectral characteristics: ir (CCl_4) 2940, 1724 (C=O), 1625 ($-ONO_2$), 1437, 1408, 1275 ($-ONO_2$), and 855 ($-ONO_2$) cm^{-1}; nmr (CCl_4) δ 9.68 (t, 1, J = 1.5 Hz), 5.5–4.9 (m, 1), and 2.7–0.8 (m, 9). This fraction was shown to be 4-nitratocyclopentaneacetaldehyde as outlined in the Results.

CAN Oxidation of *endo*-2-Norbornanol. The ir and nmr spectra and glpc trace using an SE-30 column of the product mixture from the *endo* isomer were very similar to those of the *exo* isomer. The absolute yields of the cyclopenteneacetaldehydes and 4-nitratocyclopentaneacetaldehyde were determined by nmr analysis as described for the products from the *exo* isomer. Since the nmr signal for the olefin protons was the same as that from the *exo* isomer, it was assumed that the ratio of 3 and 4 olefin was the same as that from the *exo* isomer, *i.e.*, 48:52.

CAN Oxidation of Bicyclo[2.2.2]-2-octanol. The oxidation was carried out as described for *exo*-norbornanol. The lower boiling product was purified by glpc using a Carbowax 20M column; ir (CCl_4) 2900, 1725 (C=O), and 1640 cm^{-1}; nmr (CCl_4) δ 9.7 (t, 1, J = 2 Hz), 5.5 (s, 2), and 2.5–0.7 (m, 9). These spectral data and analogy with the norbornanol system support 4-cyclohexeneacetaldehyde as the structure of the product.

Another product mixture was reduced with lithium aluminum hydride. After the hydrolysate was continuously extracted with ether, the lower and higher boiling components of the mixture were purified by glpc using an SE-30 column. The lower boiling product had spectra consistent with that of (4-cyclohexene)ethanol; ir (CCl_4) 3330 (OH), 2860, and 1050 cm^{-1} (CO); nmr (CCl_4), δ 5.6 (d, 2, J = 1 Hz), 3.6 (t, 2, J = 6.5 Hz), 3.4 (s, 1), and 2.5–0.8 (m, 9). The higher boiling product had ir and nmr spectra that were very similar to those of the mixture of *cis*- and *trans*-(4-hydroxycyclohexane)ethanols and the pure *cis* isomer. Analysis of the higher boiling product by glpc using an FFAP column showed two peaks which were enhanced when an authentic mixture of the *cis*- and *trans*-diols was coinjected into the glpc. The identity of the *cis*-diol was established by peak enhancement using an authentic sample of the pure *cis*-diol. Integration of the two glpc peaks obtained from the diol mixture from the CAN oxidation showed the mixture to be composed of 60% *cis*- and 40% *trans*-diols.

The absolute yields of the aldehyde olefin and aldehyde nitrates were determined by the method used for the norbornanol runs.

CAN Oxidation of Borneol and Isoborneol. The oxidations were carried out as described for *exo*-norbornanol. Glpc analysis using a Carbowax 20M column of the product mixture from each isomer showed identical product mixtures with at least ten components. However, there was one major product which was purified by glpc: ir (CCl_4) 2899, 1724 (C=O), 1447, 1370, and 1143 to 1080 cm^{-1}; nmr (CCl_4) δ 9.7 (t, 1, J = 2 Hz), 5.25–5.05 (s, 1), 2.6–1.4 (m, 8), 0.96 (s, 3), and 0.76 (s, 3). These spectral data and analogy with the norbornanol system support α-campholenic aldehyde (**3**) as the structure of the product. The absolute yield of α-campholenic aldehyde from each isomer was determined by the nmr method used for the norbornanol runs. No camphor was produced based on glpc analysis using a Carbowax 20M column.

Stability of *endo*-2-Norbornanol and 3-Cyclopenteneacetaldehyde under Oxidation Conditions. A normal CAN oxidation solution was prepared except that no alcohol was added. The cerium(IV) was reduced with ethanol. The appropriate compound was then added and the solution was heated for the desired time and extracted with ether in the usual fashion. The aldehyde olefin was analyzed by nmr and the *endo*-norbornanol run was analyzed by glpc using a Carbowax 20M column.

Oxidation of a Mixture of *exo*- and *endo*-2-Norbornanol. An equimolar mixture of the two alcohols was oxidized by enough CAN to oxidize half of the alcohols (mol of CAN = mol of alcohols) by the usual method. Glpc analysis using a Carbowax 20M column of the reaction mixture showed that the ratio of *exo* to *endo* alcohols recovered was 5:1.

Radical Trapping Experiments. *exo*-Norbornanol was oxidized under the usual conditions except that the alcohol concentration was 0.04 M and the CAN concentration was 0.08 M and the reaction mixture contained 10% acrylamide or acetamide. By the usual nmr analysis of the product mixture, no aldehydic products were detected when acrylamide was used, but normal products were observed when the trap was replaced with acetamide. Polymer formation was noted when acrylamide was used.

---

[32] L. T. Sandborn, "Organic Syntheses," Coll. Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1941, p 340.

[33] Recent experiments in these laboratories by Dr. Jürgen Cramer show that the product mixtures from CAN oxidations are usually cleaner and more stable if the ether extract is washed with a sodium bicarbonate solution, and we have found that this is the case for the product mixtures from these alcohols.

[34] C. W. Whitehead, J. J. Traverso, H. R. Sullivan, and F. J. Marshall, *J. Org. Chem.*, **26**, 2814 (1961).

[35] Z. H. Zalkow and A. C. Oehlschlager, *J. Am. Chem. Soc.*, **86**, 4208 (1964).