# Nuclear Magnetic Resonance Chemical Shifts of *exo*- and *endo-cis*-Bicyclo[3.3.0]oct-2-yl and -3-yl Derivatives

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*Received September 9, 1969*

*exo*- and *endo-cis*-bicyclo[3.3.0]oct-2- and -3-ols and their acetates were prepared in a stereoselective fashion and the nmr chemical shifts of the proton $\alpha$ to hydroxyl and acetoxyl were measured. The *endo*-2 proton was found to be more shielded than the *exo*-2 proton, as expected, but the *exo*-3 proton was found to be considerably more shielded than the *endo*-3 proton, quite contrary to previous predictions. This unusual shielding effect was interpreted by calculations (using McConnell's equation) based on probable conformations of bicyclooctane. The best fit to the observed chemical shifts was obtained when the "W" conformation was adopted except for the 2-*exo*-ol or -acetate, which were assumed to be in the "S" conformation because of the conformational energies of the hydroxyl or acetoxyl groups.

The stereochemistry of the *cis*-bicyclo[3.3.0]octane (hereafter abbreviated as the *3.3.0*) system, substituted in the 2 and 3 positions, has been defined by certain reactions of the system.[1,2] Hydroboration of the *3.3.0*-2-ene (I) gave mainly two alcohols, the *exo-3.3.0*-2-ol (IIx) and the *3.3.0*-3-ol (IIIx), assumed to be the *exo* isomer (IIIx).[3] Lithium aluminum hydride or sodium borohydride reduction of the *3.3.0*-2-one (V) yielded predominately the *endo-3.3.0*-2-ol (IIn), contaminated by a small amount of the *exo* isomer;[3,4] reduction of the *3.3.0*-3-one (VI) also gave two alcohols in a 4:1 ratio,[4] the major of which was assumed to be the *endo* alcohol and the minor to be the *exo* isomer (IIIx). This stereochemistry is reasonable on the basis of steric approach control where the *exo* side of the *3.3.0* system is less hindered than the *endo* side.

Using this defined stereochemistry, we unexpectedly found that the nmr chemical shift required that the 3-*exo* proton of the *3.3.0* is more shielded than the 3-*endo* proton, contrary to the previous prediction.[5] This suggests the possibility that the often assumed hypothesis of the greater shielding of *endo* protons might be incorrect, and that in some cases, the *endo* side is actually less hindered.

In the present paper, we present the observed chemical shifts of isomeric *3.3.0* alcohols and their acetate derivatives, the absolute configurations of which were ascertained independently. Calculation of the nmr shielding effects for each *3.3.0*-2- and 3-ol using various conformational models is presented and a comparison with the observed shifts is made.

## Results and Discussion

**Preparation and Stereochemical Identification of the *3.3.0* Alcohols and Their Acetates.**—The *exo* and *endo* isomers of the 2- and 3-hydroxybicyclo[3.3.0]octanes were prepared as shown in Scheme I. This series of reactions in conjunction with the previously determined stereochemistry of IIx and IIn[6] defined the stereochemistry of each of the four alcohols. See Table I for a summary of product composition.

TABLE I

PRODUCT COMPOSITION OF THE REACTIONS 1–6

| | Product, % | | | | | |
|---|---|---|---|---|---|---|
| Reaction | IIx | IIn | IIIx | IIIn | IVx | IVn |
| 1 | 44 | t[a] | 56 | t | | |
| 2a | | | | | 90 | 10 |
| 2b | 83 | t | 17 | t | | |
| 3 | 20 | 80 | | | | |
| 4 | | | 20 | 80 | | |
| 5 | | | | | 14 | 86 |
| 6 | | 77 | | 23 | | |

[a] t = trace.

Worthy of note is the relatively low stereoselectivity in the reduction reactions. Reduction of the epoxide IVx gave a 5:1 ratio of IIx:IIIx. This is consistent with Brown's report of reduction of an asymmetrically hindered epoxide giving both isomers.[7] We also found that hydride reduction of VI gave a 4:1 ratio of IIIn:IIIx, contrary to a previous report of exclusive formation of the *endo* isomer IIIn.[4]

**Nmr Chemical Shift and Conformation.**—Nmr measurements were carried out in carbon tetrachloride with $\delta$ values determined from a TMS–chloroform double reference standard. In addition to the measurement on each pure alcohol, nmr spectra were run on each possible combination of alcohols in order to avoid error from slight changes in the conditions of measurement. The observed $\delta$ (and $\Delta\delta$ values) are shown in Table II.

TABLE II

OBSERVED $\delta$ VALUES OF PROTONS $\alpha$ TO HYDROXYL AND ACETOXYL GROUPS

| | 2n H | 3x H | 2x H | 3n H |
|---|---|---|---|---|
| OH | 3.73 | 3.93 | 4.09 | 4.16 |
| AOc | 4.73 | 4.92 | 5.09 | 5.18 |

The most interesting finding was that the $\alpha$ *endo* proton of the *3.3.0* 3-alcohol or acetate is less shielded than the corresponding $\alpha$ *exo* proton. This is contrary to the previous prediction that the *endo* proton should be more shielded than the *exo* proton, a prediction which was based on shielding calculations in which the

(1) I. Tabushi, K. Fujita, and R. Oda, *Tetrahedron Lett.*, 3755, 3815 (1967).

(2) For example, A. C. Cope, M. Brown, and H. E. Petree, *J. Amer. Chem. Soc.*, **80**, 2852 (1958).

(3) H. C. Brown, W. J. Hammar, J. H. Kawakami, I. Rothberg, and D. L. V. Jagt, *ibid.*, **89**, 6381 (1967).

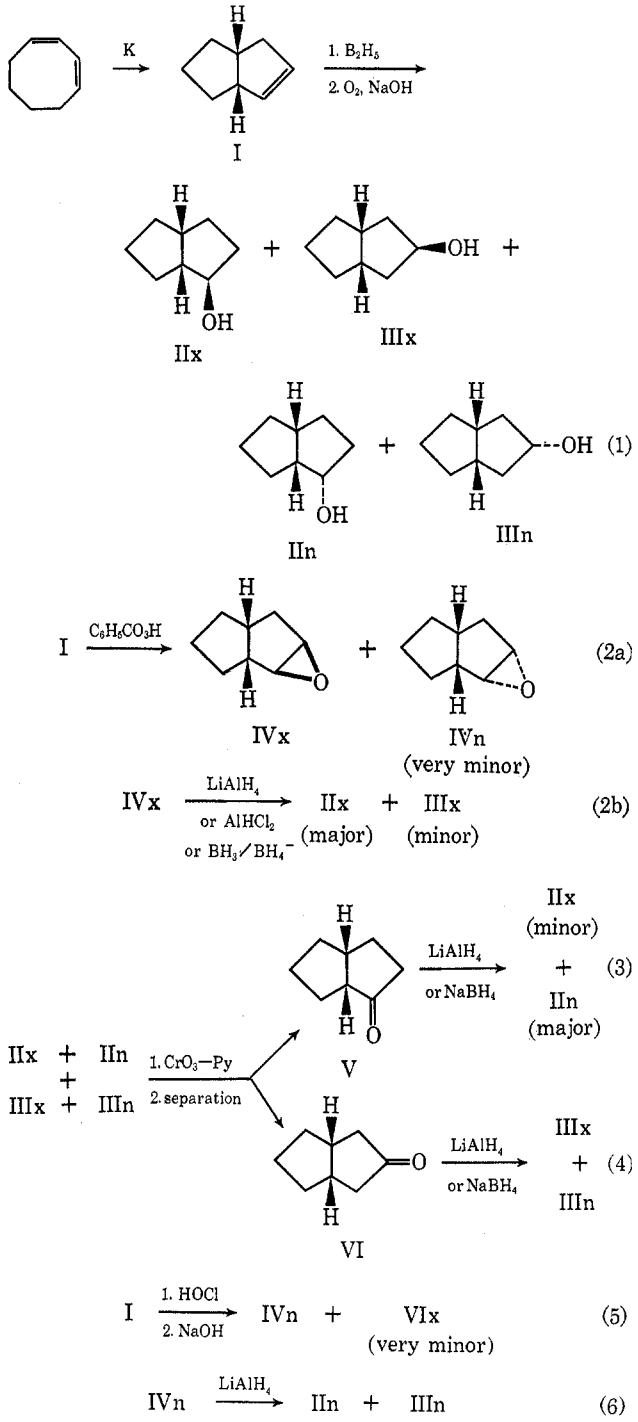
(4) Only the *endo* alcohol IIIn was reported as the product of the hydride reduction of the *3.3.0*-3-one (VI): R. Granger, P. Nau, and J. Nau, *C. R. Acad. Sci., Paris*, **247**, 2016 (1958).

(5) The previous calculation was made by assuming that the *3.3.0* was constructed of two planar cyclopentane rings: W. B. Moniz and J. A. Dixon, *J. Amer. Chem. Soc.*, **83**, 1671 (1961).

(6) IIx and IIn were obtained by the acid-catalyzed addition of formic acid to *cis,cis*-1,5-cyclooctadiene followed by hydrolysis: A. C. Cope and P. E. Peterson, *ibid.*, **81**, 1643 (1959).

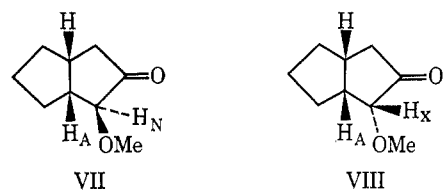
(7) H. C. Brown and N. M. Yoon, *ibid.*, **90**, 2686 (1968).

SCHEME I



"V" model containing two planar cyclopentane rings was assumed. This assumed "V" conformation seemed to offer a source of the disagreement, especially in conjunction with the fact that the *3.3.0*-3-one was reduced by hydride less stereospecifically than expected, suggesting a "W" rather than a "V" conformation. Therefore, we recalculated the expected shielding on the basis of other possible conformations. The best agreement between the observed and the calculated chemical shifts occurs by assuming a "W" conformation for both the *endo*- and *exo-3.3.0*-3-ol and for the *exo-3.3.0*-2-ol and an "S" conformation for the *endo-3.3.0*-2-ol. This shows that for the 3-alcohol, the skeletal stability ("W" shaped) determines the conformation, but for the 2-alcohol, the need for the 2-hydroxy to remain equatorial alters the conformation of the *3.3.0* skeletal system. This is consistent with the recent finding[8] that the $J$ value of the $\alpha$ proton of 2-*endo*-ethyl-*3.3.0*-2,3-*cis*-diol indicates it to be "S" shaped with the larger ethyl group adopting an equatorial configuration and thus determining the conformational stability.

Actually, both of the "W" and "S" conformers seem to twist somewhat in order to avoid torsional strain; the extent should not, however, be large since the "T-U," "T-W," and "$C_2$" conformers give unsatisfactory calculated shielding. Our present assumption of concurrent contribution of "W" and "S" conformers can also explain $\tau$ and $J$ values of some other *3.3.0* derivatives. For example, the following values were reported: $\delta$ 3.18, $J_{A-N}$ = 3.6 Hz for VII; and $\delta$ 3.72, $J_{A-X}$ = 5.0 Hz for VIII.[9] These $J$ values cannot be interpreted on the basis of the assumption that either the "W" or "S" conformer alone is present (from the Karplus equation, $J_{A-X}$ = 5.0 Hz corresponds to $\angle H_AH_X \sim 35°$; it then follows that $J_{A-N}$ is larger than 7 Hz).



VII VIII

## Experimental Section

**Preparation of I.**—I was prepared from 1,3-cyclooctadiene by isomerization with potassium.[10]

**Preparation of IVx.**—To 8.4 g (77.8 mmol) of I in 200 ml of chloroform was added dropwise 18 ml of a chloroform solution of perbenzoic acid (1.03 $N$). During the addition, the temperature was maintained below 25°; then the reaction mixture was stirred at room temperature for 2.5 hr. The mixture was washed with 10% aqueous NaOH solution three times, dried ($Na_2SO_4$), and concentrated. Distillation afforded 7.4 g of IVx, bp 83–87° (43 mm), $n^{30.0}D$ 1.4740. Vpc analysis (Apiezon Grease L, silicone DC-550 and PEG 6000) showed that IVx was accompanied by a small amount of IVn which was identified with the authentic sample (*vide infra*). Pure IVx, obtained by preparative vpc, had the following spectral values: nmr ($CCl_4$) $\tau$ 6.72 (t, $C_3$ **H**, $J$ = 2.2 Hz), 6.85 (d, $C_2$ **H**, $J$ = 2.2 Hz), and 7.0–9.2 (b, ring methylene and methine); ir (neat) 833 $cm^{-1}$ (characteristic absorption of oxirane). *Anal.* Calcd for $C_8H_{12}O$: C, 77.42; H, 9.67. Found: C, 77.58; H, 9.74.

**Preparation of IIx *via* Reaction 2b.**—A solution of 1.0 g of IVx in 15 ml of ether was added dropwise to a suspension of 0.092 g of lithium aluminum hydride in 10 ml of ether with stirring. The temperature was kept below 5° during the addition and then the mixture was stirred at room temperature for 17 hr. Dilute hydrochloric acid was added to the reaction mixture with ice cooling and the mixture was extracted with ether. The ether layer was dried ($Na_2SO_4$) and concentrated. Distillation, bp 73° (8 mm), gave 0.5 g of a mixture of alcohols IIx and IIIx (83.4 and 16.6%, respectively, on the basis of vpc analysis on Apiezon Grease L and PEG 6,000 of the corresponding acetates and ketones).

**Preparation of IIn *via* Reaction 3.**—IIn was prepared *via* the reduction of V with sodium borohydride.[11]

**Preparation of IIIx *via* Reaction 1.**—At room temperature under nitrogen a solution of 10.0 g of boron trifluoride–ether complex (47 wt %) in 12 ml tetrahydrofuran was added dropwise

(8) E. Ghera, *J. Org. Chem.*, **33**, 1042 (1968).
(9) R. Noyori and M. Katō, *Tetrahedron Lett.*, 5075 (1968).
(10) P. R. Stapp and R. F. Kleinschmidt, *J. Org. Chem.*, **30**, 3006 (1965).
(11) A. C. Cope, M. Brown, and H. E. Petree, *J. Amer. Chem. Soc.*, **80**, 2852 (1958).

TABLE III

INDIVIDUAL SHIELDING EFFECT OF EVERY C-C BOND ($\sigma_{av}$) ON THE *3.3.0*-2 AND -3 PROTONS

| | W | | | | S | | |
|---|---|---|---|---|---|---|---|
| $\sigma_{av}$ | $H_{2x}$ | $H_{2n}$ | $H_{3x}$ | $H_{3n}$ | $H_{2x}$ | $H_{3n}$ | $H_{3x}$ |
| $C_1$–$C_2$ | −0.330 | −0.330 | +0.094 | −0.076 | −0.330 | +0.094 | −0.084 |
| $C_2$–$C_3$ | −0.330 | −0.330 | −0.330 | −0.330 | −0.330 | −0.330 | +0.019 |
| $C_3$–$C_4$ | −0.072 | +0.090 | −0.330 | −0.330 | +0.090 | −0.330 | +0.019 |
| $C_4$–$C_5$ | +0.053 | +0.085 | +0.094 | −0.076 | +0.085 | +0.094 | −0.084 |
| $C_5$–$C_6$ | −0.017 | +0.032 | −0.083 | −0.019 | −0.046 | +0.097 | +0.094 |
| $C_6$–$H_7$ | +0.022 | +0.040 | +0.009 | +0.003 | +0.021 | +0.031 | −0.330 |
| $C_7$–$C_8$ | −0.042 | −0.053 | +0.009 | +0.003 | −0.015 | +0.031 | −0.330 |
| $C_8$–$C_1$ | −0.016 | +0.141 | −0.083 | −0.019 | −0.093 | +0.097 | +0.094 |
| $C_1$–$C_5$ | −0.075 | +0.023 | +0.109 | +0.053 | +0.023 | +0.109 | +0.109 |
| $\Sigma\sigma_{av}$ | −0.81 | −0.30 | −0.55 | −0.79 | −0.60 | −0.113 | −0.49 |

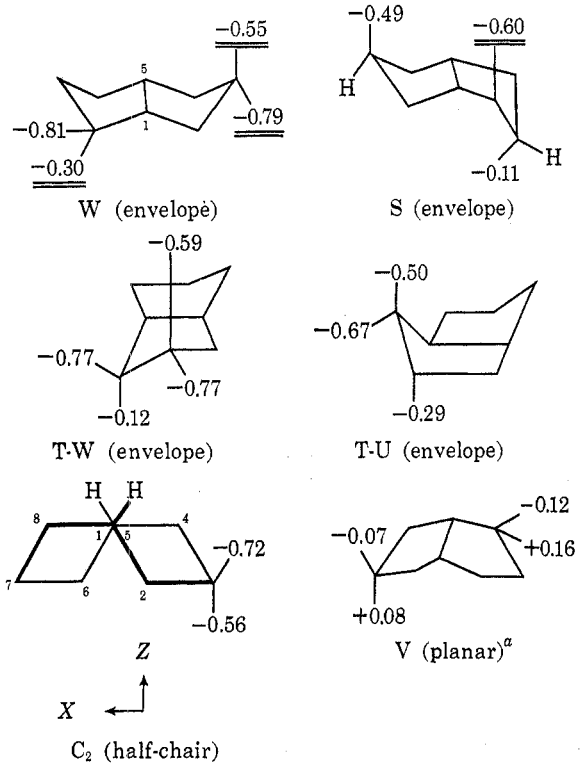



Figure 1.—Calculated overall shielding effect on the *3.3.0*-2 and −3 protons for every possible confomer. Calculated shielding in parts per million. [a] Previously predicted (ref 5).

with stirring to a mixture of 19.2 g of I, 2.0 g of sodium borohydride, and 300 ml of tetrahydrofuran. After 3 hr of stirring, the mixture was cooled in an ice bath and addition of 16 ml of 30% aqueous sodium hydroxide was followed by dropwise addition of 16 ml of 30% hydrogen peroxide over 2 hr. The mixture was extracted with ether; the ether extract was dried ($Na_2SO_4$) and concentrated. On distillation, 14.1 g of the mixture of IIx and IIIx was obtained at 90–95° (10 mm) together with a very small amount of IIn and IIIn. Pure IIIx was obtained by preparative vpc.

**Preparation of IVn *via* Reaction 5.**—A mixture of 2.1 g of I, 5 g of cracked ice, 1 ml of acetic acid, and 8 ml of an aqueous solution of monochlorourea[12] (containing 3.2 g of monochlorourea) was stirred with ice cooling for 2 days. After saturation with sodium chloride, the mixture was extracted three times with ether and the ether layers were combined and concentrated. The residue was added to a solution of 1.6 g of sodium hydroxide in 3 ml of water, and the mixture was stirred at room temperature overnight. The mixture was extracted with ether, and ether solution extracted was dried ($MgSO_4$) and concentrated. Distillation gave 0.6 g of IVn at 68–70° (27 mm). The nmr and ir spectra and the vpc showed that IVn was accompanied with a small amount of IVx. Pure IVn was obtained by preparative vpc. Spectral data follow: ir (neat) 843 $cm^{-1}$ (characteristic absorption of oxirane); nmr ($CCl_4$), $\tau$ 6.67 ($C_3$ **H**), 6.77 ($C_2$ **H**, the coupling constant was observed much smaller than that of IVx), and 7.25–9.20 (ring methylene and methine).

**Preparation of IIIn.**—With stirring and ice-cooling a solution of 0.6 g of IVn in 10 ml of ether was added to a suspension of 0.1 g of lithium aluminum hydride in 10 ml of ether; then the mixture was stirred at room temperature for 20 hr. Hydrolysis was effected at 0° with a small amount of water and then 3 *N* hydrochloric acid, and the mixture was extracted with ether. Following drying ($MgSO_4$) and concentration of the ether extracts distillation afforded 0.2 g of a mixture of IIn and IIIn, bp 52° (7 mm), ~49° (4 mm).

**General Procedure for Chromic Oxide–Pyridine Complex Oxidation of a Bicyclo[3.3.0]octyl Alcohol.**—Chromic oxide (30 g) was added in small portions to 380 ml of pyridine with stirring and with ice-cooling. This solution was stirred for 12 hr with a solution of 14 g of a *3.3.0*-octyl alcohol dissolved in 190 ml of pyridine at room temperature. The mixture was poured onto cracked ice and extracted with eight 200-ml portions of ether. The ether extracts were combined and washed with 6 *N* hydrochloric acid, saturated aqueous sodium bicarbonate solution, and water. Following drying ($Na_2SO_4$) and concentration of the ether, 8.8 g of the corresponding ketone was distilled.

**Calculations.**—In order to calculate the nmr frequency shifts on the basis of bond anisotropy, plausible models of the *3.3.0* system were investigated. The *3.3.0* structure was constructed from two fused cyclopentane rings which were assumed to be either envelopes or half-chairs.[13] Thus the "W," "S," "T," "T-U," and "$C_2$" conformers were taken as models for the calculation. In each conformer, the bond between carbon 1 and 5, $C_5C_1$, was defined as the *Y* axis, with the midpoint of the bond defined as the origin O. The plane bisecting the dihedral angle $H_1C_1(C_5)H_5$ was defined as *ZY* plane (except in conformers "S" and "W" where the dihedral angle was zero; here the plane $H_1C_1C_5H_5$ was taken *ZY* plane).

The "S" and "W" conformers were constructed from two envelopes. Carbons 1, 2, 4, and 5 were placed on one plane with carbons 1, 5, 6, and 8 on another plane. Bond lengths of C–C, 1.54 Å, and C–H, 1.09 Å, were adopted. The angles were assumed to be $\angle C_2C_1H = \angle C_5C_1H = \angle C_4C_5H = \angle C_6C_5H$; other ∠CCH, 109° 28′; and $\angle C_2C_1C_8 = \angle C_4C_5C_6$, 109° 28′. The "T-W" and "T-U" conformers were also constructed from two envelopes but in these cases, carbons 1, 5, 4, and 3 were placed on one plane with carbons 5, 1, 8, and 7 on another. The "$C_2$" conformer was constructed from two half-chairs. Thus $C_3$–O or $C_7$–O was the $C_2$ axis of the orginal cyclopentane and the *Z* axis was the molecular $C_2$ axis of the *3.3.0* system.

By means of vector analyses, the positions of all of the carbons and of the necessary protons in the above models were ascertained in order to obtain values for $\gamma$ and $\theta$; $\gamma$ is a distance between the proton in question and a midpoint (M) of a $C_i$–$C_j$ bond, and $\theta$ is

(12) H. B. Donakoe and C. A. Vanderwerf, "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p 157.

(13) Pitzer showed that the envelope conformer was the most stable; later Brutcher and Hoffmann agreed that the half-chair conformer was more stable than the envelope conformer: K. S. Pitzer and W. E. Donath, *J. Amer. Chem. Soc.*, **81**, 3213 (1959); F. V. Brutcher, Jr., and W. Bauer, Jr., *ibid.*, **84**, 2232 (1962); R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963). In the present calculations, the evelope model of Pitzer and the half-chair model of Brutcher were used. One of the referees pointed out that a torsional angle of about 45° at the ring junction is probably the safest and the equilibrium conformations of the half-chair and the envelope are now believed to be equivalent in energy for cyclopentane itself.

an angle between HM and $C_i$–$C_j$. The frequency shifts were calculated according to the McConnell's equation[14]

$$\sigma_{av} = \frac{(3\cos^2\theta - 1)(X_L - X_T)}{3\gamma^3}$$

where the magnetic susceptibility term, $X_L - X_T$, was taken to be $-5.5 \times 10^{-30}$ cm³/molecule.[15]

Examples of such calculations for the individual shielding effects of each C–C bond on the *3.3.0*-2 and -3 protons in the "W" and in the "S" conformation are given in Table III. These individual shielding effects are summed to give the frequency shift, $\Sigma\sigma_{av}$, of the proton. The frequency shifts of each significant proton in each model conformer are summarized in Figure 1.

Comparison of these calculated frequency shifts with the observed ones (Table IV) suggest that the *exo-3.3.0*-2-ol, the *exo-3.3.0*-3-ol, and the *endo-3.3.0*-3-ol are in the "W" conformation, while the *endo-3.3.0*-2-ol is in the "S" form. The observed frequency shifts of the *3.3.0* acetates are also in good agreement with the calculated values on the basis of similar conformational considerations.

(14) H. M. McConnell, *J. Chem. Phys.*, **27**, 226 (1957).

(15) A. A. Bothner-By and C. Naar-Colin, *Ann. N. Y. Acad. Sci.*, **70**, 833 (1958).

TABLE IV

NMR ABSORPTIONS OF THE 3.3.0-OLS AND -ACETATES. COMPARISON OF CALCULATED AND OBSERVED [$\delta_{rel}$ (2n H standard)]

| | 2n H | 3x H | 2x H | 3n H |
|---|---|---|---|---|
| Obsd OH | 0 | 0.20 | 0.36 | 0.43 |
| Obsd OAc | 0 | 0.19 | 0.36 | 0.45 |
| Present calcd | 0 | 0.22 | 0.30 | 0.49 |
| Previous calcd (V model) | 0 | 0.23 | 0.28 | 0.08 |

**Registry No.**—IIx, 23359-88-8; IIn, 24454-38-4; IIIx, 24454-39-5; IIIn, 24454-40-8; IVx, 24454-41-9; IVn, 24454-42-0.

**Ackowledgment.**—The authors are grateful to Dr. Elva Mae Nicholson for stimulating discussions.

# Synthesis of 2-Oxabicyclo[2.2.2]octane

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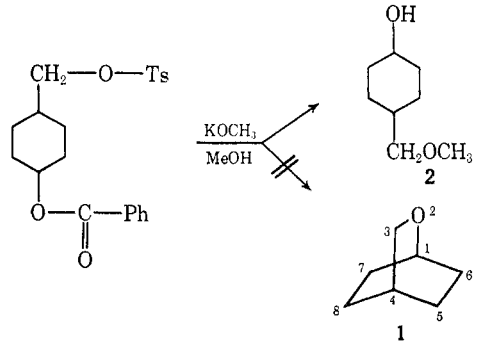
The synthesis of 2-oxabicyclo[2.2.2]octane (1) is described. Its structure was confirmed by mass spectrometry and nmr. Three different methods (I, II, III) for its preparation were investigated. Two of these involved a 1,4 transannular elimination; the other (II) was a dehydration procedure. Compound 1 was synthesized and isolated by all three methods; however, method I was shown to be superior. The *cis–trans* mixture of 4-hydroxycyclohexane-1-carboxylic acid (4 + 5) was obtained by hydrogenation of 3 over 5% Rh–$Al_2O_3$. The *cis* isomer was cyclized to the bicyclic lactone 6, which was then reduced to the *cis*-diol 7. Dehydration of 7 over $Al_2O_3$ gave 1 and the unsaturated alcohol 9 side product. Chlorination of 7, followed by a 1,4 elimination, also gave 1. The best procedure involved the formation of the *cis* tosylate 8 and its intramolecular alkoxide ion elimination to give 1.

At least two attempts to synthesize the 2-oxabicyclo[2.2.2]octane (1) system have appeared in the literature.[3,4] The first attempt was made by Owen using an isomeric mixture of *cis*- and *trans*-4-tosyloxymethylene-1-benzoyloxycyclohexane according to Scheme I.

SCHEME I




This synthetic route did not give 1; rather it seems to have involved intramolecular tosyl elimination by methoxide ion, concurrent with ester hydrolysis to give 4-methoxymethylene-1-cyclohexanol (2). Wittbecker and coworkers[4] reported that the dehydration of *cis*-4-hydroxycyclohexanemethanol (7) gave products other than the expected bicyclic ether; none of the reaction products was isolated or characterized.

In this paper we report some of the physical properties and the synthesis of 2-oxabicyclo[2.2.2]octane (1) which was prepared by three different methods (Scheme II), one of which (method II) is a reinvestigation of the alumina dehydration of the *cis*-diol 7, as attempted by Wittbecker. Method III is similar to the approach used by Clarke to synthesize the 2-oxabicyclo[3.2.1]-octane system.[5] The synthetic methods are summarized in Scheme II (the isomers are shown in their expected favored conformations).

## Results and Discussion

**Hydrogenation.**—The reduction of 4-hydroxybenzoic acid (3) to the isomeric mixture of *cis*- and *trans*-4-hydroxycyclohexane-1-carboxylic acid (4 and 5) has been accomplished previously.[6] Alternately the ethyl ester of 3 has been reduced at elevated pressure (270 atm) and temperature (220°).[7–9]

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(2) To whom inquiries should be addressed.

(3) L. N. Owen and P. A. Robins, *J. Chem. Soc.*, 326 (1949).

(4) E. L. Wittbecker, H. K. Hall, Jr., and T. W. Campbell, *J. Amer. Chem. Soc.*, **82**, 121 (1960).

(5) M. F. Clarke and L. N. Owen, *J. Chem. Soc.*, 2108 (1950).

(6) R. H. Levin and J. H. Pendergrass, *J. Amer. Chem. Soc.*, **69**, 2436 (1947).

(7) H. E. Unguade and F. V. Morriss, *ibid.*, **70**, 1898 (1948).

(8) W. Schneider and A. Huttermann, *Arch. Pharm. (Weinheim)*, **298**, 226 (1965).

(9) C. V. Banks, J. P. La Plante, and J. J. Richard, *J. Org. Chem.*, **23**, 1210 (1958).