

an angle between HM and C_i-C_j. The frequency shifts were calculated according to the McConnell's equation¹⁴

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

where the magnetic susceptibility term, $X_L - X_T$, was taken to be -5.5×10^{-20} 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

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

	2n ¹ H	3x ¹ 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

with the calculated values on the basis of similar conformational considerations.

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

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

Synthesis of 2-Oxabicyclo[2.2.2]octane

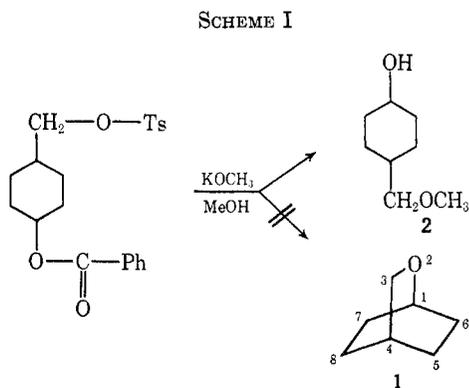
TULLIO A. GIUDICI¹ AND THOMAS C. BRUCE²

Department of Chemistry, University of California at Santa Barbara, Santa Barbara, California 93106

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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-Al₂O₃. The *cis* isomer was cyclized to the bicyclic lactone 6, which was then reduced to the *cis*-diol 7. Dehydration of 7 over Al₂O₃ 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.



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 coworkers⁴ 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

(1) Postdoctoral Fellow, Department of Chemistry, University of California at Santa Barbara.

(2) To whom inquiries should be addressed.

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(4) E. L. Wittbecker, H. K. Hall, Jr., and T. W. Campbell, *J. Amer. Chem. Soc.*, **82**, 1210 (1960).

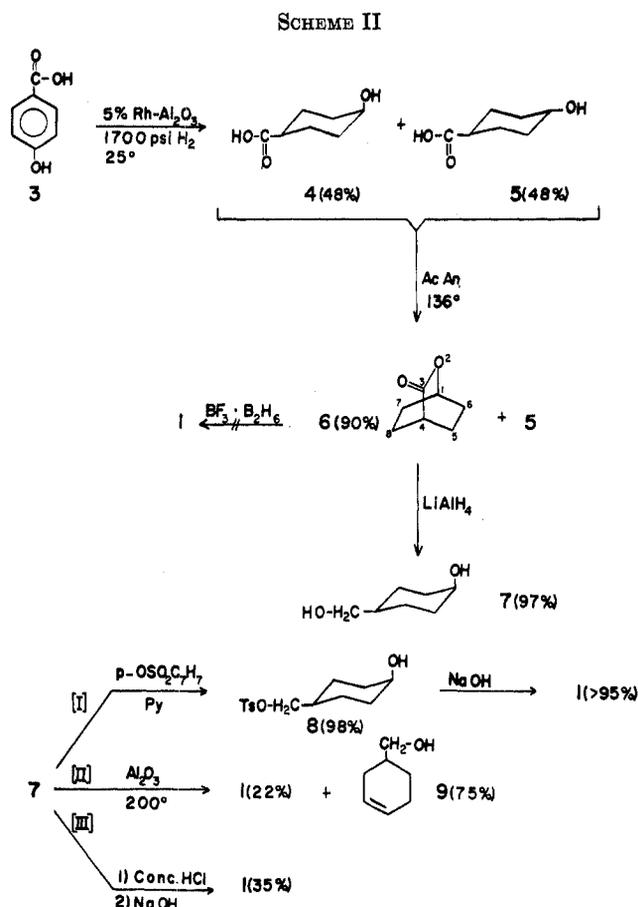
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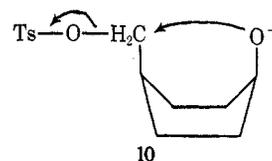
In our experience the procedure using PdO catalyst⁶ gave unacceptably low yields (<25%) of the reduced product. The alternate methods, although reported to give good yields of 4 and 5, involve the synthesis of additional intermediates. A more facile synthesis was desirable and we investigated the reduction with 5% Rh-Al₂O₃, a catalyst known to promote ring hydrogenation of aromatic phenols under relatively mild conditions.¹⁰ At 110 atm and at ambient temperature, the reduction of 3 in the presence of a small amount of 5% Rh-Al₂O₃ proceeded smoothly and nearly quantitatively.

Cyclization of the Isomeric Mixture of 4 and 5.—The *cis* conformational isomer 4 lactonized readily and the 2-oxabicyclo[2.2.2]octan-3-one (6) was isolated by sublimation of the reaction mixture. Crystalline 6 was obtained in excellent yield after extraction with petroleum ether. The melting characteristics of this compound depend on the heating rate, indicating the existence of polymorphic forms. A change in the crystal structure occurs between 82 and 85°. The new structure shows a higher temperature transition (127–128°) where liquefaction is finally observed. The *trans* isomer 5 (mp 148°)^{11,12} remained in the sublimator. The ir spectrum of 6 shows the absence of the OH band at 3400 cm⁻¹ and an intense carbonyl band at 1740 cm⁻¹. We assigned the nmr absorption at δ 4.46 to the bridgehead proton at the 1 position. The δ 2.38 absorption was assigned to the other bridgehead proton at the 4 position. At the concentration em-

ployed, both of these absorptions appeared as broad singlets and did not show any multiplicity. The integration of the peaks gave the correct relative number of hydrogens 1:1:8, consistent with structure 6.

The direct synthesis of 1 from 6 using BF₃·B₂H₆ according to the procedure of Pettit^{13,14} failed; however, we did not make an extensive investigation of this approach. The direct reduction of 6 to 1 was attempted by Wittbecker without success.⁴ An alternate scheme for the synthesis of 1 had to be employed. The reduction of 6 to 7 with LiAlH₄ was accomplished without problems. The *cis*-diol was obtained as a clear syrup and its physical properties were in agreement with those reported in the literature.⁸ The tosyl derivative of 7 was prepared by the usual methods. Under the conditions employed, the primary alcohol function of 7 was tosylated predominantly. The ir of the product 8 exhibited the expected hydroxyl, aromatic, and sulfonate absorptions of a tosyl intermediate.

1,4 Transannular Elimination (Methods I, II, and III).—Three different ring closure reactions were investigated. Two of these involve the formation of the alkoxide ion which then undergoes intramolecular displacement of the tosyl (or chlorine) leaving group as shown in 10 for intermediate 8, presumably in the boat conformation. Preliminary experiments indicated



that these methods would give acceptable results if the problems inherent in the isolation of the highly volatile bicyclic ether could be solved. A loss of 1 >70% was incurred if the usual procedures of extraction and solvent evaporation were applied during work-up. Samples of 1 could not be successfully separated by fractional distillation from any of the eluting solvents nor could 1 be recrystallized from a number of solvents without excessive loss of material.

To obviate these problems the elimination reaction was accomplished in the solid state without the use of solvents at any stage of the synthesis. (For apparatus, see Figure 1 in the Experimental Section.) Using this approach, a near-quantitative yield of 1 was achieved by method I. Method III involved the synthesis of the monochloromethyl derivative of the *cis*-diol and its cyclization to 1. Compound 8 was obtained as a yellow oil containing additional components, and because of the excellent outcome of method I, this product was not investigated in greater detail. The dehydration of 7 over alumina (method II) was accomplished in low yield (22% estimated, 6.7% actually isolated). The predominant component of the reaction mixture was a clear liquid identified as 1-hydroxymethyl-4,5-cyclohexene (9) by its ir spectrum (-OH at 3300 cm⁻¹ and C=C at 1650 cm⁻¹) and by its retention time when cochromatographed with an authentic sample.¹⁵ The minor component was characterized as the bicyclic ether 1 by its retention time and ir and nmr spectra.

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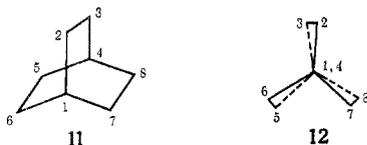
(15) We are deeply grateful to Professor Bruce Rickborn for providing a sample of 9 and for the use of his vpc instruments.

The melting characteristics of compound **1** closely parallel those of the lactone **6**. The volatile solid undergoes a crystal structure transition at approximately 42°; then the new crystal form rapidly vaporizes at the higher temperature range. The ir showed a strong absorption in the 1025–1035-cm⁻¹ range. These intense bands are indicative of a cyclic ether and are within the range assigned by Rosowsky to a series of bicyclic oxetanes and to those assigned to a series of cyclic ethers.^{16,17}

We assigned the nmr absorption at δ 3.65 to the tertiary bridgehead proton at position 1 and that at δ 3.46 to the methylene protons at position 3. Analogous to the lactone **6** case, the proton at position 1 in the bicyclic ether did not exhibit any multiplicity but gave only a broad unresolved singlet. The bridge methylene protons also appear as a broad singlet and not as a doublet. The nonequivalence of the methylene protons of the almost rigid cyclohexane boat conformation is further demonstrated by the unresolved doublet at δ 1.72–1.57. It is probable that the absorption at δ 1.92 is due to the tertiary bridgehead proton at the 4 position.

The protons at the 1 and 3 positions ($\delta_1 - \delta_3 = 11$ cps) did not integrate in a 1:2 ratio [found 1:3 = 1.4:1]; however, the integral sum of these two peaks showed a 3:9 hydrogen ratio in accord with structure **1**. It is conceivable that a contribution of the upfield methylene absorption coalesces into the absorption signal of the bridgehead proton. A similar absorption behavior, leading to incorrect integration, has been reported before, and it is encountered in analogous cases where the observed chemical shift is small.¹⁸

Recently the conformation of bicyclo[2.2.2]octane (**11**) was determined by single-crystal X-ray analysis.¹⁹ It was shown that the carbon bond angles do not deviate markedly from the tetrahedral value. In the crystal-

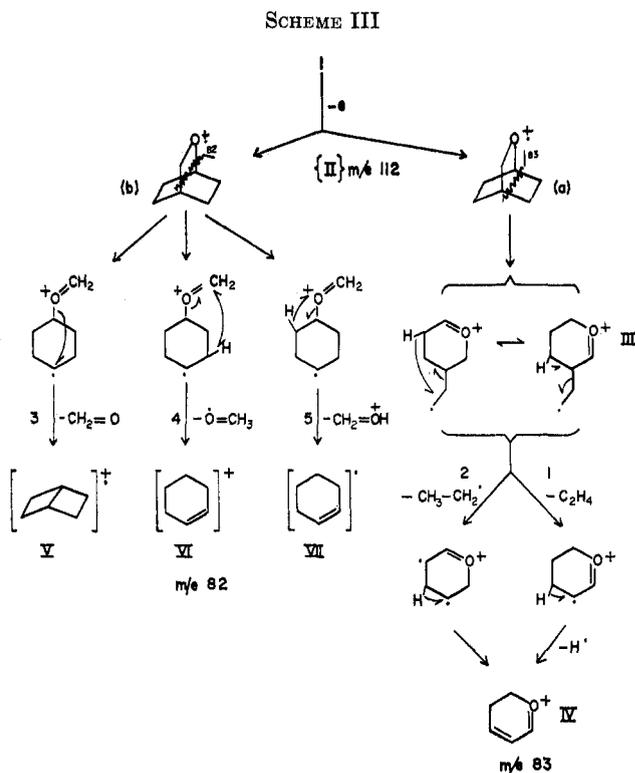


line state **11** is believed to exist in a slightly staggered conformation **12** rather than a fully eclipsed one, resulting in a torsional angle of the C(2)–C(3), C(5)–C(6), and C(7)–C(8) bonds of 5°. An analogy may be drawn between this system and the similar 2-oxabicyclo[2.2.2]octane structure. The heteroatom in **1** would not be expected to cause a great deviation from the tetrahedral value in the carbon–carbon bonds. In structure **11** the slightly staggered conformation is assumed to relieve or optimize the nonbonded hydrogen interactions. The relatively strain-free structure of **1** would be expected to show similar angular dependencies in the crystalline state.

Mass Spectrum of 1.—The structure assigned to the bicyclic ether was further supported by its mass spectrum. The intensity of the observed parent peak [M⁺ (10)] *m/e* 112 is small; however, such behavior

has been observed with many aliphatic ethers.²⁰ The existence of an oxygen atom in the fragmentation pattern is apparent from the intense mass peaks at *m/e* 31, 45, and 59; these could be considered to be homologous fragments of the H₂C=OH structure.

The favored decomposition mode of **1** would be expected to involve β cleavage. This could occur at two different positions [Scheme III, steps a and b] in the parent molecular ion (**II**).



The peak at *m/e* 83, could arise from a concerted β cleavage of the bicyclic ether *via* (a) and a concomitant α -ring cleavage of the ensuing cyclic alkyl oxonium ion (**III**). This ion could eliminate the molecule ethylene concurrent with the expulsion of a vicinal proton as H⁺, to give the (M – 29) cyclic oxonium ion fragment (**IV**) (Scheme III, path 1). Alternately, structure **III** could undergo intramolecular rearrangement of a hydrogen atom transferred *via* a six-membered cyclic intermediate concurrent with the migration of a vicinal proton (Scheme III, path 2). The expulsion of an ethyl radical could give the same cyclic oxonium ion (**IV**) postulated for path 1. Similar modes of H-atom transfer in molecules containing heteroatoms have been invoked to rationalize the observed fragmentation patterns of alkylated tetrahydrofuran and tetrahydropyran rings.^{21,22} The postulated six-membered hydrogen transfer scheme is not an absolute requirement, because similar transfers can occur through smaller, cyclic transition states.²³ In either case the proposed ion fragment would be resonance stabilized in the form of the cyclic oxonium ion (**IV**).

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β cleavage could also occur *via* (b) and at least three modes of fragmentation are possible. From the parent ion (II), paths 3 and 4 involve an α -ring cleavage by heterolysis of the carbon-oxygen bond. In path 3 the molecule of formaldehyde could be eliminated with formation of the bicyclo[2.2.0]hexane radical ion (V). In path 4 a methoxyl radical could be generated concomitant with the cyclohexenyl carbonium ion (VI). Similar modes have been demonstrated in the fragmentation of cyclic ethers.²⁴

Path 5 invokes a H-atom migration to the oxygen, concurrent with homolytic α cleavage of the carbon-oxygen bond giving the protonated form of formaldehyde and the cyclohexenyl radical (VII). Such a migration has been proposed for the fragmentation of vinyl ethers.²⁵

Only a low-intensity ($\ll 10\%$) ($M - 30$) peak is observed in the mass spectrum of the bicyclic ether, indicating that β cleavage as in (b) may not be a favored mode of fragmentation in this case. It is then assumed that cleavage, most likely occurs *via* (a) and probably by path 1. The peak at m/e 83 would then be due to the formation of the cyclic oxonium ion (IV). Without additional data a more valid selection of fragmentation modes is not possible and the conclusions reached here are only tentative.

Experimental Section

Materials and Equipment.—Reagent grade 4-hydroxybenzoic acid was recrystallized twice from ethanol-ether. High-pressure hydrogenation was carried out in a Parr Series 4000 hydrogenator using Engelhard 5% Rh- Al_2O_3 catalyst. All analytical vpc was done using a Varian Aerograph Series 200 with (a) an 18 ft \times 1/8 in. copper column packed with 10% 20M Carbowax on Chromsorb W, 60-80 mesh, (b) a 12 ft \times 0.25 in. copper column packed with 18% 6000 Carbowax on Chromsorb W, 60-80 mesh. The helium carrier gas flow rate was 46 cc/min for both columns. Preparative vpc was done on an Aerograph Model A-90-P with (c) a 25 ft \times 0.25 in. copper column packed with 20% 20M Carbowax on Chromsorb W 60-80 mesh and a helium flow rate of 55 cc/min. The ir spectra, unless otherwise stated, were obtained as films or KBr disks on a Perkin-Elmer Model 137 spectrophotometer calibrated with polystyrene film. The nmr spectra were obtained with a Varian Associates A-60 spectrometer using tetramethylsilane (TMS) as an internal standard. Chemical shifts are given on the δ scale in parts per million relative to TMS. The mass spectrum was obtained from an Associated Electrical Industries MS902 double-focusing instrument. A special apparatus was built to facilitate the sublimation and quantitative collection of highly volatile solids (Figure 1). Melting points are uncorrected. The elemental analysis were performed by Galbraith Laboratories Inc., Knoxville, Tenn.

***cis*- and *trans*-4-Hydroxycyclohexane-1-carboxylic Acid (4 + 5).**—Recrystallized *p*-hydroxybenzoic acid (3), 100 g (0.724 mol), was dissolved in 150 ml of warm glacial acetic acid and transferred to the steel cylinder of a Parr high-pressure hydrogenator. After the solution cooled to ambient temperature, 1.2 g of 5% Rh- Al_2O_3 catalyst was introduced, and 1500-psi H_2 pressure at 20°, was applied. After 24 hr the required volume of hydrogen was absorbed and the hydrogenation was discontinued. The catalyst was removed by filtration over Celite and the clear solution was distilled under vacuum until all the solvent was removed. A clear viscous liquid was obtained; it readily crystallized on addition of dry ethyl ether. The *cis-trans* mixture of 4-hydroxycyclohexanecarboxylic acid (4 + 5) was recrystallized from ethanol-ethyl ether to give a 96% yield of a white crystalline compound having a melting point range of 120-125° (lit.¹³ 120°). The ir spectrum (KBr) of 4 + 5 showed bands at 3400 (s), 2400,

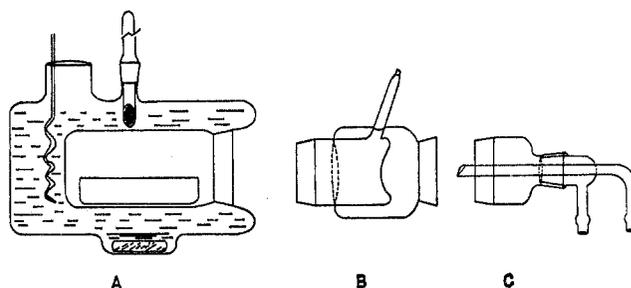


Figure 1.—Sublimation apparatus for a highly volatile component: (A) silicon oil vessel fitted with a magnetic stirring bar, glass boat, heating coil, and thermometer; (B) water-jacketed collection apparatus with a leur-tipped side arm and a 29/12 joint; (C) condenser attachment with a 29/12 joint.

2600 (broad), 1700 (s), 1055, 1020 (s), 955 (s), 740 (m) cm^{-1} ; no bands were present in the 1600- and 800-850- cm^{-1} range.

2-Oxabicyclo[2.2.2]octan-3-one (6).—The isomeric mixture of 4-hydroxycyclohexanecarboxylic acids (4 + 5), 29 g (0.2012 mol), was dissolved in 300 ml of acetic anhydride and refluxed for 6 hr under anhydrous conditions; then it was left for 24 hr at ambient temperature. The acetic anhydride was removed by vacuum distillation and a viscous liquid was obtained. The crude mixture of lactone 6 and *trans* isomer 5 was introduced into a 1-l. sublimator. At a pressure of 2.0 mm and at a silicon oil bath temperature range of 100-115° the lactone 6 was collected (over a 3-hr period) as a crystalline semisolid. The crystalline residue was predominantly the *trans*-4-hydroxycyclohexylcarboxylic acid (5) isomer. The crude compound isolated in a 55% yield was further purified by extraction with petroleum ether (bp 20-60°) in a Soxhlet apparatus during a 10-hr period. The bicyclic lactone 6 crystallized from petroleum ether in needle-shaped crystals with mp 126-127° (lit.¹² mp 127-128°) and gave a 90% yield (12.0 g) as calculated for the cyclization of the *cis* isomer 4. A sample of 6 dissolved in ethyl ether was analyzed by vpc (column A, temperature 178°, isothermal) and was found to be homogeneous (retention time 24.5 min). Infrared analysis (KBr) showed bands at 1740 (s), 1065 (s), 1000 (s), 955 (m), 878 (m), 770 (m) cm^{-1} ; no bands at 3550 cm^{-1} were obtained. The nmr spectrum of 6 in CCl_4 exhibited the following absorptions: δ 4.60 (broad s, 1 H), 2.50 (broad, 1 H), 1.87 (broad, 8 H); signals in the range of δ 12.0-10.4 were not present. The sample for elemental analysis was sublimed a second time and had mp 127-128°.

Anal. Calcd for $C_7H_{10}O_2$: C, 66.62; H, 8.00. Found: C, 66.53; H, 8.07.

***cis*-4-Hydroxymethylcyclohexanol (7).**—Under anhydrous conditions and a nitrogen atmosphere, a suspension of 6.0 g (0.1581 mol) of $LiAlH_4$ in dry ethyl ether was treated dropwise with a solution of 15 g (0.1189 mol) of 6 dissolved in 200 ml of dry ethyl ether. The addition was continued for 40 min; then after the exothermic reaction subsided, the mixture was refluxed for an additional 4 hr and left overnight at ambient temperature. Excess hydride was destroyed by the dropwise addition of 6 ml of a 10% KOH solution followed by 6 ml of water. The suspension was filtered over Celite and the residue was washed with ethyl ether. The ethereal phase was separated and dried over $MgSO_4$. The solvent was removed by vacuum distillation and a clear viscous liquid (10.22 g) was obtained. An additional amount (4.9 g) of 7 was obtained by continuous extraction of the residual salts in a Soxhlet apparatus using ethyl ether as the solvent. The combined yield was 15.10 g (97.6%): ir (film) 3300 (s), 1040, 1025 (s), 978 (s), 935 (m) cm^{-1} ; the band at 1750 cm^{-1} was not present. A solution of this material in *p*-dioxane was examined by vpc (column A, temperature 178°) and found to be homogeneous (retention time 46.7 min). A sample of 7 was distilled at 0.2 mm; the major fraction had a vapor temperature of 120-122° and μ^{20D} 1.4935. These values are in agreement with those reported for 7 when isolated from the reduction products of the *cis-trans* mixture of ethyl 4-hydroxycyclohexane-1-carboxylate.⁸

***cis*-4-Tosyloxymethylene-1-cyclohexanol (8).**—A solution of 11.95 g (0.0918 mol) of 7 in 50 ml of dry pyridine was cooled to -5°. A solution of *p*-toluenesulfonyl chloride (19.14 g, 0.1004 mol) in 35 ml of dry *p*-dioxane was then added dropwise over a

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2-hr period while the temperature was maintained at -5° . After the addition, the reaction mixture was allowed to remain at -5° for another 3-hr period; then it was left overnight at ambient temperature. The mixture was rapidly poured into a stirred slurry consisting of 100 ml of 6 *N* HCl and ice. A clear oily layer was formed. The aqueous phase was decanted and the residue was extracted with two 150-ml portions of chloroform. The organic layer was separated and dried with MgSO_4 . The solvent was removed by vacuum distillation and a light yellow, viscous oil 25.38 g (98% yield) was obtained. After 2 weeks at room temperature, **8** solidified to a semicrystalline compound: ir (film) 3550, 3400 (broad), 1600 (m), 1250 (s), 1175, 1190 (s), 815, 843 (s) cm^{-1} .

2-Oxabicyclo[2.2.2]octane (1). Method I.—The apparatus represented in Figure 1 was utilized for this step. Under anhydrous conditions and a nitrogen atmosphere, NaOH, 2.0 g (0.050 mol), was finely powdered and transferred to a glass boat containing 2.0 g (7.083 mmol) of **8**. The reactants were thoroughly mixed, and then the container was placed in the sublimator maintained at atmospheric pressure. The temperature of the surrounding silicon oil was gradually raised to a maximum of 150° and maintained for 1.5 hr. Clusters of white, needle-shaped crystals formed on the cooled surface of the collector. The apparatus was allowed to slowly cool to room temperature, then the collector was quickly removed and sealed. Compound **1** was obtained in a quantitative yield (0.795 g) and had a camphor-like odor: mp $76-77^{\circ}$ (sublimation); ir (CHCl_3) 2900 (s), 1190 (s), 1025-1035 (s), 955 (s), 865 (s), 810 (m) cm^{-1} ; nmr (CCl_4) δ 3.65 (fairly sharp singlet), 3.46 (fairly sharp singlet), 3 H, 1.93 (broad singlet, not fully resolved), 1.72, 1.57 (unresolved broad doublet) 9 H; mass spectrum (70 eV) (70°) *m/e* (relative intensities) 112 (M^+ , 10), 83 ($\text{M} - 29$, 11), 74 (63), 73 (13), 59 (97), 56 (13), 55 (16), 45 (80), 44 (12), 43 (29), 42 (10), 41 (29), 39 (13), 31 (100), 29 (97) (only those absorbances with a relative intensity of 10% or greater are listed). Crystallization of **1** from ethyl ether, methanol, and *p*-dioxane failed. A sample of the crystalline material dissolved in ethyl ether was analyzed by vpc and shown to be homogeneous: (column A, temperature 130° , isothermal) retention time 4.2 min, (178°) 2.17 min; (column B, temperature 130° , isothermal), 24.0 min. A sample for elemental analysis was further purified by a second sublimation at 50 mm and at a silicon oil bath temperature range of $48-58^{\circ}$. *Anal.* Calcd for $\text{C}_7\text{H}_{12}\text{O}$: C, 74.95; H, 10.77. Found: C, 74.74; H, 10.97.

Method II.—An apparatus was built to facilitate the short-path distillation and fraction collection of small volumes of distillate. Under anhydrous conditions, 2.01 g (0.0154 mol) of **7** and 2.0 g of activated alumina²⁶ were heated with a silicon oil bath to $220-230^{\circ}$ at atmospheric pressure. During the initial phase of the dehydration a biphasic liquid collected on the condenser and gradually formed a semicrystalline deposit. The condensed material was heterogeneous during the entire course

of the dehydration. Heating was discontinued when all of **7** had been dehydrated over the alumina bed. The semisolid product (1.36 g) was collected, and an aliquot dissolved in ethyl ether was examined by vpc (column A, temperature 130°) and found to contain the following compounds: (a) retention time 1.4 min, one or more unresolved highly volatile, low-molecular-weight compounds which were not investigated further; (b) 4.2 min, a highly volatile white crystalline compound identified as **1** by ir, nmr, and mass spectra; (c) 15.5 min, unidentified; (d) 24.1 min, isolated as a viscous clear liquid and characterized as **9** by ir 3300 (s), 1650 (w), 1025, 1035 (s), and 970 (m) and by comparison with the retention time of an authentic sample.²⁶ Compound **7** was not detected using this column at a temperature of 178° . The relative ratios of the peak areas of a:b:c:d were 0.64:1:0.14:1.14 (indicating approximately a 22% yield of the bicyclic ether). The combined fractions of **1** collected by preparative vpc, weighed 129.5 mg, an actual yield of 6.7%.

Method III.—The *cis*-diol **7** (0.50 g, 3.84 mmol) was dissolved in 1 ml of concentrated HCl and sealed in a vial under nitrogen. The vial was heated in a silicon oil bath at a temperature range of $115-120^{\circ}$ for 5.5 hr. During this period the solution became heterogeneous and a yellow-colored upper phase appeared. The reaction mixture was gradually cooled to room temperature; then the vial was opened, and a saturated NaHCO_3 solution (2 ml) was added. The mixture was extracted twice with 3 ml of chloroform; the organic layer was separated, washed with water, and dried over MgSO_4 . The solvent was removed by vacuum distillation at 30° and a yellow viscous liquid (0.40 g) was obtained in a 57% yield. It was stored in a vacuum desiccator over KOH. An aliquot, dissolved in ethyl ether was found to be heterogeneous when analyzed by vpc (column A, temperature 175°) with the following major components: (a) retention time 7.9 and 8.4 min, an unresolved doublet; (b) 25.5 and 26.4 min, an unresolved doublet. The *cis*-diol was not present. The relative ratio of the peak areas of a:b was 1:10.

The crude oil (0.183 g) was treated with 0.183 g of powdered NaOH, mixed into a slurry, and placed into a microsublimator. The temperature of the silicon oil bath was maintained at $130-140^{\circ}$ for 1 hr. Gradually the temperature was raised to 200° to expel all the volatile fractions from the solid residue. A biphasic liquid collected on the condenser; it was dissolved in ethyl ether, analyzed by vpc (column A, temperature 175° , isothermal), and found to contain the following components: (a) retention time 2.0 min, the most volatile component which was collected and identified as **1** by ir and nmr; (b) 7.8 and 8.3 min, unresolved doublet; (c) 25.5 and 26.3, min, unresolved doublet. The relative ratio of peak areas b:c (comparable with the previous a:b ratio) was ~ 5.6 . The estimated yield of a = 1 (assuming a:b:c = 100%) was 35%.

Registry No.—**1**, 280-39-7; **4**, 3685-22-1; **5**, 3685-26-5; **6**, 4350-84-9; **7**, 3685-24-3; **8**, 24472-55-7.

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(26) Alcoa activated alumina (F 6 $\frac{1}{4}$ 8).