THE JOURNAL OF Organic Chemistry®

Volume 27, Number 9 | September 12, 1962

The Mechanism of the Prins Reaction. I. The Structure and Stereochemistry of a New Alcohol from the Acid-Catalyzed Reaction of Cyclohexene and Formaldehyde[1]

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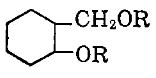
Received April 16, 1962

A new alcohol, *trans*-6-hydroxy-*cis*-3-oxabicyclo[4.3.0]nonane, was isolated from the sulfuric acid-catalyzed reaction of cyclohexene and formaldehyde in acetic acid solution. The structure and stereochemistry of the compound have been established by synthesis and a possible mechanism for its formation is discussed.

In connection with a study of the mechanism of the Prins reaction, it was necessary to prepare a large quantity of *trans*-2-hydroxymethylcyclohexanol. The most convenient synthesis of this compound appeared to be the sulfuric acid-catalyzed condensation of cyclohexene and formaldehyde in acetic acid solution, an example of the Prins reaction. This reaction has been studied by several groups of investigators[2-8] and, at the beginning of this study, four products had been identified with certainty[7]: the cyclic formal of *trans*-2-hydroxymethylcyclohexanol (*4*), the diacetate of *trans*-2-hydroxymethylcyclohexanol (*1a*), the acetate of *trans*-9-hydroxy-3-oxabicyclo[3.3.1]nonane (*2a*), and 3-acetoxymethylcyclohexene (*3a*).



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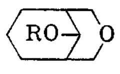
1b. R = H



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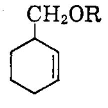

3a. R = Ac
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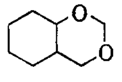

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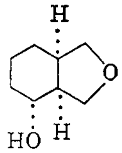
In our hands, fractional distillation of the reaction product gave roughly two fractions. The lower boiling fraction contained the cyclic formal *4* and the unsaturated acetate *3a*. The higher boiling fraction yielded upon saponification a mixture of *trans*-2-hydroxymethylcyclohexanol (*1b*), the 3-oxabicyclo[3.3.1]nonan-9-ol (*2b*), and a new alcohol which is shown to be *trans*-6-hydroxy-*cis*-3-oxabicyclo[4.3.0]nonane (*5*).



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Interestingly, the bicyclic alcohol 3-oxabicyclo-[3.3.1]nonan-9-ol was earlier assigned[6] structure *5*, but its correct structure (*2b*) has been demonstrated recently by Blomquist and Wolinsky.[7]

The new alcohol (*5*) was discovered by vapor phase chromatography of the mixture of alcohols obtained upon saponification of the higher boiling material from the Prins reaction of cyclohexene. The composition of the mixture is difficult to determine, but it contains approximately 60% *trans*-2-hydroxymethylcyclohexanol, 30% 3-oxabicyclo[3.3.1]nonan-9-ol, and 10% of the new alcohol. The new alcohol, separated by preparative vapor phase chromatography, was found to have a molecular formula, $C_8H_{14}O_2$, isomeric with *2b*.

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[1] Supported in part by the Petroleum Research Fund of the American Chemical Society, 195-A4, and a Faculty Research Grant from the Graduate School of the University of Oregon.

[2] J. Matti, *Bull. soc. chim. France*, [4] **51**, 974 (1932).

[3] S. Olsen and H. Padberg, *Z. Naturforsch.*, **1**, 448 (1946).

[4] S. Olsen, *ibid.*, **1**, 671 (1946).

[5] S. Olsen, *Angew. Chem.*, **59**, 32 (1947).

[6] S. Olsen, *Z. Naturforsch.*, **3b**, 314 (1948).

[7] A. T. Blomquist and J. Wolinsky, *J. Am. Chem. Soc.*, **79**, 6025 (1957).

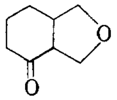
[8] E. Smissman and R. A. Mode, *ibid.*, **79**, 3447 (1957).

The infrared spectrum of the compound shows peaks at 910, 1050, 1070, 1190, 1350, and 1450 cm.$^{-1}$ in addition to a strong peak in the hydroxyl region. These peaks correspond closely to those found for a series of tetrahydrofuran derivatives (peaks at 910, 1070–1100, 1175–1190, 1350, and 1450 cm.$^{-1}$).[9]

The proton magnetic resonance (p.m.r.) spectrum[10] is consistent with the presence of a tetrahydrofuran ring. The spectrum shows two areas of absorption: peaks in the range of 5.71 to 6.56 τ values corresponding to six protons and peaks in the range 7.30 to 9.04 τ values corresponding to eight protons. The spectrum could not be analyzed in detail, but there appeared unresolved multiplets in the range 6.3–6.5 τ values suggesting a cyclic ether.[11]

Oxidation of the new alcohol with chromic acid in a heterogeneous system as described by Brown and Garg[12] yielded a ketone, $C_8H_{12}O_2$, whose infrared spectrum showed carbonyl absorption at 1705 cm.$^{-1}$ which can be ascribed to a cyclohexanone.

This evidence and mechanistic considerations suggested that the compound was a 3-oxabicyclo[4.3.0]nonan-6-ol. On this basis the ketone is formulated as a 3-oxabicyclo[4.3.0]nonan-6-one (*6*).



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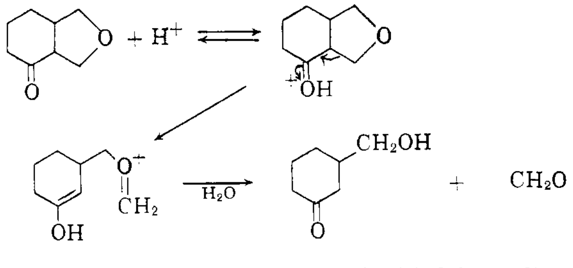
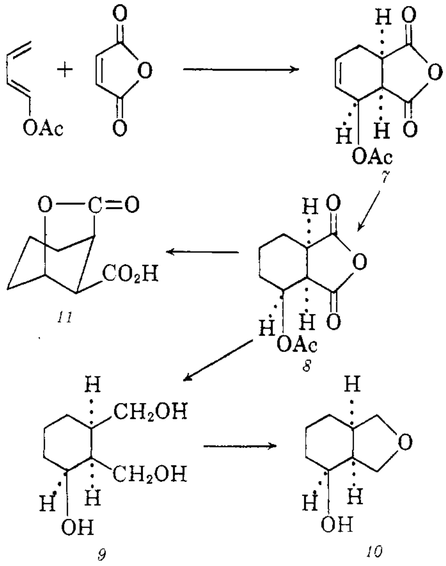
As a test of this hypothesis, it was hoped that acid-catalyzed enolization would result in fragmentation with the formation of formaldehyde by the following scheme.



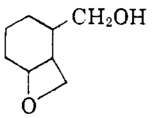
When the ketone was steam distilled from dilute sulfuric acid solution, formaldehyde was isolated as its dimedon derivative in small but significant yields.

With this evidence in hand, it seemed that the structural determination might be completed by an unambiguous synthesis which would also yield the stereochemistry of the compound. The synthesis which was chosen is shown below.



The Diels-Alder reaction between 1-acetoxybutadiene and maleic anhydride as described by Flaig[13] proceeded smoothly to furnish 3-acetoxy-1,2-cyclohex-4-enedicarboxylic acid anhydride (*7*). This was reduced without difficulty to the saturated acetoxyanhydride (*8*). Lithium aluminum hydride reduction then afforded the triol *9*, along with some low-boiling side products perhaps formed by base-catalyzed fragmentation similar to that observed in the fumagillin series.[14] The triol was cyclized in 10% yield by tosylation followed by treatment with base.

Chromic acid oxidation of the alcohol obtained by cyclization of the triol *9* provides a ketone which establishes that the cyclization does yield a 3-oxabicyclo[4.3.0]nonan-6-ol and not the oxetane *12* or the bridged compound *13*.



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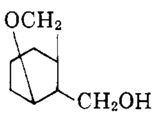

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The ketone obtained by this sequence was the same ketone that was prepared by chromic acid oxidation of the new alcohol from the Prins reaction of cyclohexene. The ketones were identical in their retention times on vapor phase chromatography and their infrared spectra. The corresponding 2,4-dinitrophenylhydrazones, obtained in two readily interconvertable forms, showed no melting point depression when the same forms were mixed and their infrared spectra were superimposable.

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(9) G. M. Barrows and S. Searles, *J. Am. Chem. Soc.*, **75**, 1175 (1953).

(10) The p.m.r. spectrum was determined in carbon disulfide solution with a Varian HR-60 operating at 60 Mc. We are indebted to Mr. B. J. Nist of the chemistry department of the University of Washington for this determination.

(11) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, 1958, p. 55.

(12) H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, **83**, 2952 (1961).

(13) W. Flaig, *Ann.*, **568**, 1 (1950).

(14) D. S. Tarbell, R. M. Carman, D. D. Chapman, S. E. Cremer, A. D. Cross, K. R. Huffman, M. Kunstmann, N. J. McCorkindale, J. G. McNally, Jr., A. Rosowsky, F. H. L. Varino, and R. L. West, *J. Am. Chem. Soc.*, **83**, 3100 (1961).

These results establish that the new alcohol from the Prins reaction of cyclohexene is a 3-oxabicyclo[4.3.0]nonan-6-ol.

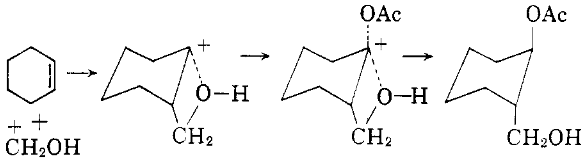
The alcohol (*10*) obtained by cyclization of the triol *9* differs in its infrared spectrum from its isomer isolated from the Prins reaction. While the *p*-nitrobenzenesulfonate esters of these two alcohols melt at the same temperature, they show a large melting point depression upon mixing.

The stereochemistry of the 3-oxabicyclo[4.3.0]-nonan-6-ol synthesized from the Diels-Alder adduct *6* follows from its method of synthesis and the eventual conversion of this adduct to a bicyclic γ-lactone. The Diels-Alder reaction using maleic anhydride fixes the ring juncture as *cis*, leaving only the configuration of the secondary hydroxyl group in doubt. As anticipated from other results,[15] the hydroxyl group must be *cis* to the carbonyl groups since the hydroxy acid obtained upon saponification of the acetoxy anhydride *8* undergoes a ready lactonization. This information allows the 3-oxabicyclo[4.3.0]nonan-6-ol obtained from this anhydride to be assigned the all *cis* configuration.

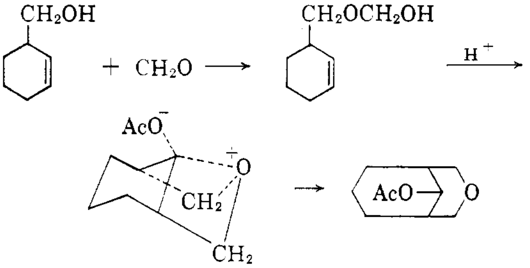
Although the alcohol obtained from the Prins reaction differs from the one prepared for comparison purposes, they are oxidized to the same ketone, which leads to the conclusion that they have the same stereochemistry at the ring juncture but differ in the configuration of the hydroxyl group. Thus, the new alcohol from the Prins reaction is *trans*-6-hydroxy-*cis*-oxabicyclo[4.3.0]nonane.

It is possible that epimerization of the ketone occurred during chromic acid oxidation, but it seems rather unlikely. First, the oxidation was carried out under the very mild conditions recently described by Brown and Garg.[12] Secondly, it was shown that acid-catalyzed enolization results in fragmentation of this particular ketone.

Any mechanism for the Prins reaction must account for the high degree of stereoselectivity exhibited. The stereoselectivity of the reaction is not consistent with a simple carbonium ion mechanism. Smissman and Witiak[16] suggest a solvated cyclic intermediate but give no clue to the structure of this species. Other investigators have suggested a solvated trimethylene oxide[17] as an intermediate and Blomquist and Wolinsky[7] have suggested an intramolecularly solvated carbonium ion as the species responsible for the stereoselectivity of the Prins reaction. The mechanism proposed by Blomquist and Wolinsky is shown below.



These authors account for the formation and stereochemistry of the 3-oxabicyclo[3.3.1]nonan-9-ol by an extension of this mechanism as shown below.



While the mechanism advanced by Blomquist and Wolinsky readily accounts for the formation and stereochemistry of *trans*-2-hydroxymethylcyclohexanol derivatives and 3-oxabicyclo[3.3.1]nonan-9-ol, it does not accommodate the formation of *trans*-6-hydroxy-*cis*-3-oxabicyclo[4.3.0]nonane found in the present investigation. Other lines of evidence offer little support for the intervention of intermediate carbonium ions in which important stabilization is offered by the oxygen of a hydroxyl or ether group in a four-membered ring. The solvolysis of trimethylene chlorohydrin yields no trimethylene oxide[18] and the rate can be interpreted[19] without postulating any type of four-membered, cyclic oxonium ion. The rate of solvolysis of trimethylene chlorohydrin is only about four times the rate of solvolysis of ethylene chlorohydrin which solvolyzes normally.[18] This small increase in rate can be ascribed to the greater distance of separation of the hydroxyl group from the reaction site.[19] In this series it has been shown that the hydroxyl group participates in the solvolysis of tetramethylene chlorohydrin.[18] A major product from this reaction is tetrahydrofuran and the rate of the reaction is enhanced by a factor of *ca.* 10^3 over the rate of solvolysis of trimethylene chlorohydrin.

In a study of the solvolysis of ω-methoxyalkyl *p*-bromobenzenesulfonates, Winstein and co-workers[20] found no evidence for oxygen participation in a four-membered ring. The rate of solvolysis of 3-methoxypropyl *p*-bromobenzenesulfonate is actually slower than the rate of solvolysis of *n*-butyl *p*-bromobenzenesulfonate. This evidence indicates that the methoxyl group does not stabilize the

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(15) R. L. Frank, R. D. Emmick, and R. S. Johnson, *J. Am. Chem. Soc.*, **69**, 2313 (1947); R. B. Woodward, F. E. Bader, H. Bickel, A. J. Frey, and R. W. Kiersted, *Tetrahedron*, **2**, 1 (1958).

(16) E. E. Smissman and D. T. Witiak, *J. Org. Chem.*, **25**, 471 (1960).

(17) H. E. Zimmerman and J. English, Jr., *J. Am. Chem. Soc.*, **75**, 2367 (1953).

(18) H. W. Heine, A. D. Miller, W. H. Barton, and R. W. Greiner, *ibid.*, **75**, 4778 (1953).

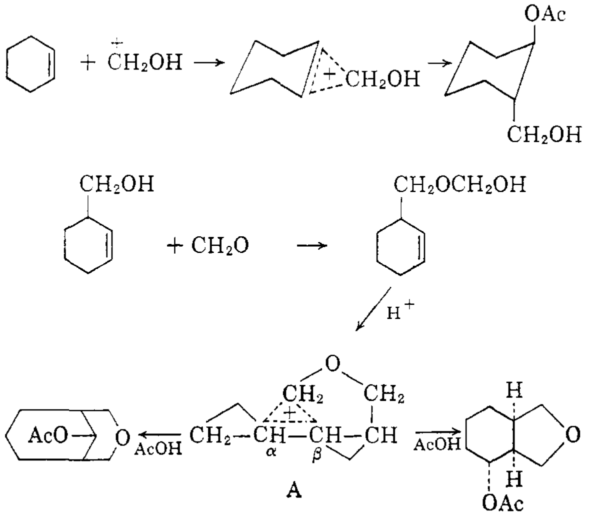
(19) A. Streitwieser, Jr., *Chem. Rev.*, **56**, 684 (1956).

(20) S. Winstein, E. Allred, R. Heck, and R. Glick, *Tetrahedron*, **3**, 1 (1958).

developing carbonium ion in the transition state by way of a four-membered ring. In fact, it appears that the interaction between the oxygen and the developing carbonium ion is destabilizing in this case. This is in contrast to the situation when oxygen can participate by way of a five- or six-membered ring.

Kinetic studies do not rigorously exclude the formation of four-membered oxonium ions in carbonium ion reactions. However, as it is often assumed that an intermediate will resemble the transition state leading to it, the kinetic studies argue against the intervention of four-membered oxonium ion intermediates. In this regard it is worthwhile to note that stabilization of carbonium ions by way of five- and six-membered cyclic oxonium ions is evidenced by kinetic studies as well as product studies.[18,20,21]

We would like to suggest a different mechanism for the Prins reaction. The intermediate is a three-membered cyclic ion similar to the intermediates suggested in other examples of electrophilic addition to double bonds.



As suggested previously, it seems likely that the 3-oxabicyclo[3.3.1]nonane-9-ol arises from 3-hydroxymethylcyclohexene by way of the hemiformal. The bridged ion, A, may suffer attack at C-α or C-β to give stereospecifically the acetates of *trans*-6-hydroxy-*cis*-3-bicyclo[4.3.0]nonane and *trans*-9-hydroxy-3-oxabicyclo[3.3.1]nonane.

Experimental[22]

Isolation of *trans*-6-Hydroxy-*cis*-3-oxabicyclo[4.3.0]nonane from the Sulfuric Acid-Catalyzed Reaction of Cyclohexene and Formaldehyde in Acetic Acid Solution.—Cyclohexene was allowed to react with paraformaldehyde in acetic acid solution in the presence of sulfuric acid following procedure A of Blomquist and Wolinsky.[23] From a typical preparation, fractional distillation yielded a mixture of acetates, b.p. 115–135° (6 mm.) n^{25}D 1.475 to 1.465, in a yield of about 30% by weight based upon cyclohexene. Saponification of this mixture afforded a mixture of alcohols, b.p. 100–120° (2 mm.) n^{25}D 1.491–1.486. This mixture showed three main peaks upon vapor phase chromatography with a 20% Carbowax 20 M on firebrick column at a temperature of 200°. The mixture was separated by preparative vapor phase chromatography using a Nester and Faust Prepko vapor phase chromatograph with a commercial Carbowax 6000 column at a temperature of 220°. The separating characteristics of this column were very similar to those of the analytical column. The most readily eluted component was identified as 3-oxabicyclo[3.3.1]nonan-9-ol, m.p. 185–191° (lit.[24] m.p. *ca.* 205°) by comparison with a sample isolated as previously described.[24] The highest boiling component was identified as *trans*-2-hydroxymethylcyclohexanol by comparison of its retention time and infrared spectrum with an authentic sample obtained by lithium aluminum hydride reduction of methyl *trans*-hydroxycyclohexanecarboxylate prepared from pure *trans*-2-hydroxycyclohexanecarboxylic acid, m.p. 110–112° (lit.[25] m.p. 111°). The central component, *trans*-6-hydroxy-*cis*-3-oxabicyclo[4.3.0]nonane,[26] boils at 118–120° (7 mm.), n^{25}D 1.4962.

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.27; H, 10.04.

The **3,5-dinitrobenzoate** of *5* melts at 110–112° after several crystallizations from aqueous ethanol.

Anal. Calcd. for $C_{15}H_{16}N_2O_7$: C, 53.57; H, 4.80; N, 8.33. Found: C, 53.68; H, 4.91; N, 8.51.

The ***p*-nitrobenzenesulfonate** of *5* melts at 97–98° after several crystallizations from benzene–petroleum ether.

Anal. Calcd. for $C_{14}H_{17}NO_6S$: C, 51.36; H, 5.23; N, 4.27. Found: C, 51.28; H, 5.14; N, 4.22.

***cis*-3-Oxabicyclo[4.3.0]nonan-6-one.**—Oxidation of 2.046 g. of *trans*-6-hydroxy-*cis*-3-oxabicyclo[4.3.0]nonane with chromic acid in a heterogeneous system as described by Brown and Garg[12] gave 1.610 g. (80%) of *cis*-3-oxabicyclo-[4.3.0]nonan-6-one, b.p. 98–100° (6 mm.), n^{25}D 1.4889. The infrared spectrum showed carbonyl absorption at 1705 cm.$^{-1}$.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.20, H, 8.53.

The 2,4-dinitrophenylhydrazone, prepared in the usual manner, was obtained as laths, m.p. 171–172°, or needles, m.p. 174–175°, from an ethanol–ethyl acetate solution. The material normally crystallized as laths, but either form could be obtained by seeding a hot solution with one of the forms. A mixture of about equal parts of the two forms melts from 171–175° and their infrared spectra in chloroform solution are superimposable.

Acid-Catalyzed Cleavage of *cis*-3-Oxabicyclo[4.3.0]nonan-6-one.—A 2.04-g. sample of the ketone was steam distilled from 80 ml. of water and 1 ml. of concentrated sulfuric acid. Additional water was added to maintain the level in the flask. About 120 ml. of distillate was collected and the last few drops still yielded a precipitate when treated with dimedon solution. A 30-ml. portion of the steam distillate was treated with dimedon. The precipitated derivative was collected, crystallized from ethanol, and sublimed to give 6 mg. of the dimedon derivative of formaldehyde, m.p. 190–191°, undepressed when mixed with authentic material. The infrared spectrum (KBr disk) was identical

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(21) D. S. Noyce and B. N. Bastian, *J. Am. Chem. Soc.*, **82**, 1246 (1960).

(22) All melting points and boiling points are uncorrected; distillations were carried out using a 65-cm. modified Podbielniak tantalum spiral column. Microanalyses are by Micro-Tech Laboratories, Skokie, Illinois, and Berkeley Analytical Laboratories, Berkeley, California. Unless otherwise noted, infrared spectra were determined in chloroform solution with a Beckman IR-7 infrared spectrophotometer.

(23) Ref. 7, p. 6028.

(24) Ref. 7, p. 6029.

(25) J. Pascual, J. Sistane, and A. Regas, *J. Chem. Soc.*, 1943 (1949).

(26) The author is indebted to Mr. Claire N. Lieske for assistance in the isolation of this compound.

to that of an authentic sample. The yield based upon total steam distillate was 10%.

***cis*-3-Acetoxy-*cis*-1,2-cyclohexanedicarboxylic Acid Anhydride.**—A solution of 50 g. of *cis*-3-acetoxy-*cis*-1,2-cyclohex-4-enedicarboxylic acid anhydride,[18] m.p. 54–55°, (lit.[18] m.p. 58°) and 100 ml. of ethyl acetate was hydrogenated at room temperature over 4.0 g. of a 5% rhodium on alumina catalyst at an initial pressure of three atmospheres. After 24 hr., 96% of the theoretical amount of hydrogen for one double bond had been absorbed. Distillation of the crude product yielded 45.0 g. (90%) of crystalline *cis*-3-acetoxy-*cis*-1,2-cyclohexanedicarboxylic acid anhydride. The analytical sample melted at 66–67° after several crystallizations from ether–petroleum ether.

Anal. Calcd. for $C_{10}H_{12}O_5$: C, 56.60; H, 5.70. Found: C, 56.14; H, 5.37.

***cis*-2,3-Di(hydroxymethyl)cyclohexanol (*9*).**—A solution of 27.68 g. of *cis*-3-acetoxy-*cis*-1,2-cyclohexanedicarboxylic acid anhydride in dry tetrahydrofuran was added slowly to a slurry of 21 g. of lithium aluminum hydride in 500 ml. of anhydrous tetrahydrofuran. The mixture was heated under reflux for 72 hr., cooled, and treated with water and then with 6 *N* hydrochloric acid. The mixture was extracted several times with ether and the aqueous portion was continuously extracted with ether for 72 hr. The ether extracts were combined and fractionated to yield 4.45 g. of forerun, b.p. 80–125° (0.5 mm.) and 7.366 g. (35%) of the triol, an extremely viscous unmanageable oil, b.p. 135–145° (0.2 mm.). The infrared spectrum of the forerun shows absorption at 1625 cm.$^{-1}$ suggesting the presence of olefinic compounds. None of the fractions showed carbonyl peaks in the infrared. Vapor phase chromatography using a Carbowax 20 M column at 200° showed the forerun to contain at least four compounds. Under similar conditions, the triol fractions gave no peaks whatsoever. All efforts to crystallize the triol failed and it was used in the next step without further purification.

***cis*-6-Hydroxy-*cis*-3-oxabicyclo[4.3.0]nonane.**—A solution of 7.30 g. of the triol *9* and 40 ml. of dry pyridine was treated with 8.81 g. of *p*-toluenesulfonyl chloride added over 30 min. at 0°. The mixture was allowed to stand overnight with stirring and worked up in the usual manner to provide 6.0 g. of the crude tosylate. The crude tosylate was dissolved in a solution of 50 ml. of 95% ethanol and 3.0 g. of sodium hydroxide and heated under reflux for 3 hr. The reaction mixture was poured into water and extracted with ether. Fractional distillation afforded 0.569 g. of material, b.p. 50–100° (4 mm.) and 0.842 g. of material b.p. 100–120° (4 mm.). Vapor phase chromatography showed the lower boiling fraction to contain several components. The infrared spectrum of the lower boiling fraction showed only weak hydroxyl absorption but strong absorption in the 1620-cm.$^{-1}$ region and the material was discarded. The higher boiling fraction contained *ca.* 80% of the desired compound, *cis*-6-hydroxy-*cis*-3-oxabicyclo[4.3.0]nonane, by vapor phase chromatography. The retention time of this material was identical to that of the new compound (*5*) from the Prins reaction. The higher boiling fraction was chromatographed on 15 g. of Woelm neutral alumina, activity one. Fractions of 20 ml. were collected and the progress of the separation was followed by vapor phase chromatography. Successive elution with 100 ml. each of 10% benzene–petroleum ether, 20% benzene–petroleum ether, pure benzene, and pure ether yielded 0.113 g. of olefinic material which was discarded. Elution with chloroform afforded 0.505 g. (10% based on starting triol *9*) of *cis*-6-hydroxy-*cis*-3-oxabicyclo[4.3.0]nonane, which showed only one peak in its vapor phase chromatogram. Distillation through a short path still, pot temperature 115° (6 mm.) gave an oil, n^{25}_{D} 1.4912.

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.57; H, 9.93. Found: C, 67.91; H, 9.70.

The *p*-nitrobenzenesulfonate ester melted at 96–97° after several crystallizations from benzene–petroleum ether. When mixed with the *p*-nitrobenzenesulfonate ester, m.p. 97–98°, of the new alcohol from the Prins reaction, the melting point was lowered to 80–83°.

Anal. Calcd. for $C_{14}H_{19}NO_6S$: C, 51.36; H, 5.23; N, 4.27. Found: C, 51.27; H, 5.23; N, 4.10.

***cis*-3-Oxabicyclo[4.3.0]nonan-6-one.**—A sample of *cis*-6-hydroxy-*cis*-3-oxabicyclo[4.3.0]nonane was oxidized by the procedure of Brown and Garg.[12] The crude ketone was isolated in the usual manner and subjected to vapor phase chromatography at 160° using a Carbowax 20 M column. The retention time was identical to that of the ketone obtained by oxidizing the new compound from the Prins reaction. Samples were collected from repeated injections and the infrared spectrum of the *cis*-3-oxabicyclo[4.3.0]-nonan-6-one obtained in this manner was identical to that of the ketone prepared from the Prins reaction product.

The 2,4-dinitrophenylhydrazone was prepared in the usual manner and showed the dimorphic behavior noted previously, m.p. of the laths 171–172° and needles, m.p. 174–175°. When the same forms of the two preparations were mixed, no depression in melting point was observed. Their infrared spectra were also identical.

Anal. Calcd. for $C_{14}H_{16}N_4O_5$: C, 52.49, H, 5.04, N, 17.45. Found: C, 52.48; H, 4.91; N, 17.56.

***cis*-3-Hydroxy-*cis*-1,2-cyclohexanedicarboxylic Acid Lactone.**—A solution of 7.52 g. of *cis*-3-acetoxy-*cis*-1,2-cyclohexanedicarboxylic acid anhydride, 8.0 g. of sodium hydroxide, and 100 ml. of water was allowed to stand overnight at room temperature and then warmed on the steam bath for 30 min. The solution was acidified with 50% sulfuric acid and continuously extracted with ether for 48 hr. Evaporation of the ether left 5.40 g. (85%) of a gum which showed strong absorption in the infrared at 1780 cm.$^{-1}$ suggesting the material had partly lactonized during isolation. A 4.50-g. sample of the crude lactone was adsorbed on 80 g. of silicic acid and eluted with chloroform. Chloroform removed 3.194 g. of the desired lactone which crystallized immediately. The analytical sample melted as 110–111° after several crystallizations from chloroform–petroleum ether. The infrared spectrum showed strong carbonyl absorption at 1780 and 1720 cm.$^{-1}$.

Anal. Calcd. for $C_8H_{10}O_4$: C, 56.46; H, 5.92; neut. equiv. 170. Found: C, 56.70, H, 5.89, neut. equiv. 172.