10 min. A complete minimization for molecules as large as decalin should not therefore take a prohibitive amount of computer time.[15]

(15) It should be added that these times could be greatly reduced in the case of larger molecules by using a matrix diagonalization subroutine of the Givens type. We have tried all these as they appeared, but we have always encountered special cases where they failed. For the sake of reliability we have therefore so far retained the Jacobi method. We are at present trying the latest version of Givens which is now claimed to be completely reliable; we hope that this will prove to be true.

Acknowledgment. The calculations reported here were carried out on the CDC 6600 computer at the University of Texas Computation Center.

Stereospecific Cationic Rearrangements of *syn*- and *anti*-Bicyclo[6.1.0]nonane Derivatives[1]

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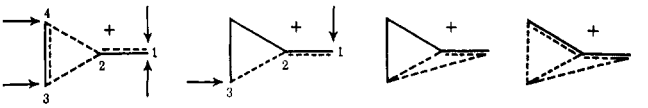
Abstract: Preparations of *syn*- and *anti*-bicyclo[6.1.0]nonan-2-ol (*syn*-**5d**-OH and *anti*-**5d**-OH) are described. Solvolysis of *syn*-**5d**-OPNB in 80% acetone–water gave *syn*-**5d**-OH (61%), *cis*-cyclononen-4-ol (*cis*-**11**-OH) (23%), and *cis*-**11**-OPNB (16%). Under similar conditions, *anti*-**5d**-OPNB gave *anti*-**5d**-OH (96%), *trans*-bicyclo-[5.2.0]nonan-*trans*-8-ol (*trans,trans*-**12**-OH) (4%), and *trans,cis*-**12**-OH (trace). Homoallylic brosylate *cis*-**11**-OBs in 80% acetone–water gave *syn*-**5d**-OH (82%) and *cis*-**11**-OH (18%). Hydrolysis of *trans,trans*-**12**-OBs was more complicated. Products in 80% acetone–water were *trans,trans*-**12**-OH, *trans,cis*-**12**-OH, and *trans,cis*-**12**-OBs. At a slightly slower rate, *trans,cis*-**12**-OBs hydrolyzed to a mixture of *trans,trans*- and *trans,cis*-**12**-OH. The stereospecific interconversions of *syn*-**5d**-OH and *cis*-**11**-OH are explained in terms of a nonclassical homoallylic cation (*cis*-**14**). Ionization of *anti*-**5d**-OPNB produces an isomeric homoallylic cation (*trans*-**14**) which can react with solvent to give *anti*-**5d**-OH or isomerize to a nonclassical cyclobutyl cation. The cyclobutyl ion is the precursor of *trans,trans*- and *trans,cis*-**12**-OH.

The cationic interconversions of cyclopropylcarbinyl, homoallylic, and cyclobutyl derivatives are of considerable theoretical and synthetic interest.[3] Early work suggested extensive charge delocalization upon solvolyses of these systems,[4] and subsequent studies, both experimental[5] and theoretical,[6] led to a proliferation of proposed cationic intermediates believed to be important in cyclopropylcarbinyl, homoallylic, and cyclobutyl solvolyses. Both rates and product distributions can be drastically altered by seemingly small changes in substitution or conformation of the parent system. The sensitivity of the parent system to change is partially responsible for the large number of cationic representations. Structures which have enjoyed recent support include the symmetrical homoallylic or bisected ion (**1**),[5d,e,6b–e,7] the homoallylic ion (**2**),[8] the bicyclobutonium ion (**3**),[9] and the symmetrical bicyclobutonium or delocalized cyclobutyl ion (**4**).[6f,10]



1 **2** **3** **4**

The solvolytic behavior of many cyclopropylcarbinyl derivatives can best be explained by a symmetrical homoallylic cation (**1**).[5e,7b,7c] Structure **1** is also consistent with the nmr spectra of some cyclopropylcarbinyl cations which were generated in superacid media.[5d,7a,11] However, the results from different systems cannot readily be interpreted in terms of **1**. We

(1) (a) This research was supported in part by the National Science Foundation. (b) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(2) (a) This investigation was supported in part by National Institutes of Health Postdoctoral Fellowships 1-F2-GM-29,317-01 and 2-F2-GM-29,317-02 from the Institute of General Medical Sciences. (b) Author to whom inquiries should be addressed at: Department of Chemistry, University of Utah, Salt Lake City, Utah 84112; (c) deceased, November 23, 1969.

(3) Recent reviews include: (a) H. G. Richey, Jr., in "Carbonium Ions," Vol. 3, G. A. Olah and P. von R. Schleyer, Ed., John Wiley & Sons, Inc., New York, N. Y., 1969; (b) M. Hanack and H. J. Schneider, *Angew. Chem. Intern. Ed. Engl.*, **6**, 666 (1967).

(4) (a) S. Winstein and R. Adams, *J. Amer. Chem. Soc.*, **70**, 838 (1948); (b) C. W. Shoppee, *J. Chem. Soc.*, 1147 (1946); (c) J. D. Roberts and R. H. Mazur, *J. Amer. Chem. Soc.*, **73**, 2509, 3502 (1951).

(5) (a) S. Winstein and E. M. Kosower, *ibid.*, **81**, 4399 (1959); (b) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver, and J. D. Roberts, *ibid.*, **81**, 4390 (1959); (c) E. F. Cox, M. C. Caserio, M. S. Silver, and J. D. Roberts, *ibid.*, **83**, 2719 (1961); (d) C. U. Pittman, Jr., and G. A. Olah, *ibid.*, **87**, 2998, 5123 (1965); (e) P. von R. Schleyer and G. W. van Dine, *ibid.*, **88**, 2321 (1966); (f) J. E. Baldwin and W. D. Foglesong, *ibid.*, **89**, 6372 (1967); (g) K. B. Wiberg and J. G. Pfeiffer, *ibid.*, **90**, 5324 (1968).

(6) (a) M. Simonetta and S. Winstein, *ibid.*, **76**, 18 (1954); (b) R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964); (c) R. Hoffmann, *Tetrahedron Lett.*, 3819 (1965); (d) T. Yonezawa, H. Nakatsuji, and H. Kato, *Bull. Chem. Soc. Jap.*, **39**, 2788 (1966); (e) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968); (f) J. E. Baldwin and W. D. Foglesong, *J. Amer. Chem. Soc.*, **90**, 4311 (1968); (g) C. Trindle and O. Sinanoğlu, *ibid.*, **91**, 4054 (1969).

(7) (a) C. D. Poulter and S. Winstein, *ibid.*, **91**, 3649 (1969); (b) P. von R. Schleyer and V. Buss, *ibid.*, **91**, 5880 (1969); (c) J. C. Martin and B. R. Ree, *ibid.*, **91**, 5882 (1969); (d) L. Birladeanu, T. Hanafusa, B. Johnson, and S. Winstein, *ibid.*, **88**, 2317 (1966).

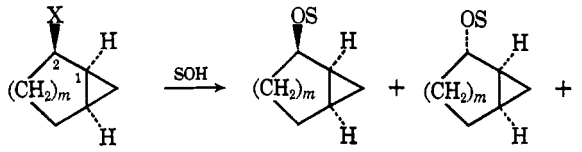
(8) (a) M. Gašić, D. Whalen, B. Johnson, and S. Winstein, *ibid.*, **89**, 6382 (1967); (b) D. Whalen, M. Gašić, B. Johnson, H. Jones, and S. Winstein, *ibid.*, **89**, 6384 (1967).

(9) W. B. Kover and J. D. Roberts, *ibid.*, **91**, 3687 (1969).

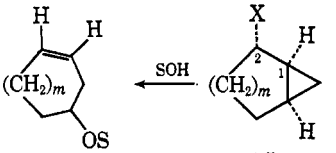
(10) K. B. Wiberg and J. E. Hiatt, *ibid.*, **90**, 6495 (1968).

(11) (a) G. A. Olah at the 21st National Organic Chemistry Symposium of the American Chemical Society, Salt Lake City, Utah, June 15–19, 1969; (b) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969).

have previously discussed[5a,7d] the possible multiplicity of nonclassical structures related to different cyclopropylcarbinyl, cyclobutyl, and homoallylic derivatives. We also outlined expected changes in stereochemical behavior among several different nonclassical cations. For example, solvolysis of cyclopropylcarbinyl derivatives through cation **1** should result in loss of stereochemistry at C_1 in the cyclopropylcarbinyl products. The same overall reaction through cation **2** would give retention of configuration at C_1. Both 2-substituted *syn*-bicyclo[*n*.1.0]alkanes (*syn*-**5a–c**) and *anti*-bicyclo[*n*.1.0]alkanes (*anti*-**5a–c**) solvolyze with substantial loss of stereochemistry at C_2.[12] However, certain 2-substituted bicyclo[*n*.1.0]alkanes (*n* = 7 and



syn-**5a**, *m* = 1
b, *m* = 2
c, *m* = 3



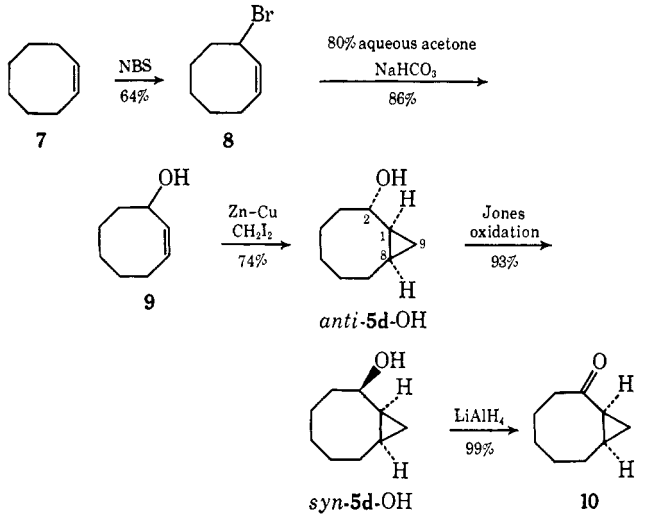
cis-**6a**-OS *anti*-**5a–c**

8) exhibited high stereoselectivity during solvolysis.[8] Solvolyses of both *syn*- and *anti*-cyclopropylcarbinyl derivatives gave cyclopropylcarbinyl product with retention of configuration at C_2. Also, the cyclopropylcarbinyl to homoallylic isomerizations were highly selective, giving either a *cis*- or a *trans*-disubstituted double bond. We have suggested that systems related to *syn*- and *anti*-**5b** give symmetrical homoallylic ions (**1**) upon solvolysis,[7d] whereas the cyclopropylcarbinyl derivatives constrained by a larger carbon bridge give homoallylic ions (**2**).[8] In order to understand better the relationship between ring size and stereoselectivity in 2-substituted bicyclo[*n*.1.0]alkanes, a study of *syn*- and *anti*-2-bicyclo[6.1.0]nonane derivatives (*syn*-**5d** and *anti*-**5d**) was undertaken. Also, these derivatives are not complicated by the complex substitution patterns found in the previously reported [7.1.0] and [8.1.0] systems.

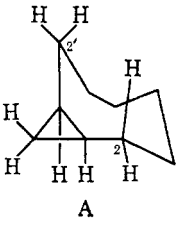
Results

Preparation of *syn*- and *anti*-Bicyclo[6.1.0]nonan-2-ol. *syn*-Bicyclo[6.1.0]nonan-2-ol (*syn*-**5d**-OH, *m* = 4) and *anti*-bicyclo[6.1.0]nonan-2-ol (*anti*-**5d**-OH) were prepared by the sequence outlined in Scheme I. Treatment of **9** with Simmons–Smith reagent gave *anti*-**5d**-OH, which was contaminated with only 0.5% of the *syn* epimer.[13] Oxidation of *anti*-**5d**-OH to **10** followed by reduction with lithium aluminum hydride gave *syn*-**5d**-OH contaminated with 1.7% of *anti*-**5d**-OH.

Scheme I



The assignments of stereochemistry at C_2 are based on comparisons of ir and nmr spectra and the expected direction of methylenation and hydride reduction. Either the hydroxyl group or the cyclopropane ring of *syn*-**5d**-OH must assume a hindered *endo* position with respect to the eight-membered ring. Both groups can occupy *exo* positions in the *anti* epimer. On the average, the hydroxyl group of *syn*-**5d**-OH should be less available for intermolecular hydrogen bonding.[14] Our assignments are in agreement with the fact that the ir bands for the free hydroxyl stretch in *syn*-**5d**-OH (3600 cm^{-1}) are significantly more intense than the corresponding bands for *anti*-**5d**-OH (3620 cm^{-1}). Nmr spectra show that the proton at C_2 in *syn*-**5d**-OH is deshielded by 1.28 ppm relative to *anti*-**5d**-OH. A neighboring cyclopropane ring is known to shield protons which are above the plane of the three-membered ring and deshield those which are in the plane of the three-membered ring.[15] The predominant conformations of *syn* and *anti*-**5d**-OH are not known with a high degree of certainty, but some assumptions can be made. Cyclooctene[16] and 9,9-dimethyl-9-azoniabicyclo[6.1.0]nonane iodide[17] both prefer a "chair–boat" conformation for the eight-carbon ring (see structure A). From models, a similar preferred con-



A

formation seems likely for *syn*- and *anti*-**5d**-OH. The proton at C_2 (or C_2') in *syn*-**5d**-OH is in the deshielding region of the cyclopropane ring, while the corresponding proton in *anti*-**5d**-OH is shielded. Chemical-shift differences between the *endo* and *exo* protons at C_2

(12) (a) E. C. Friedrich and S. Winstein, unpublished work; (b) K. E. Rubenstein, Ph.D. Dissertation, University of Wisconsin, 1967; (c) A. C. Cope, S. Moon, and C. H. Park, *J. Amer. Chem. Soc.*, **84**, 4850 (1962).

(13) We recently discussed reasons for the stereoselectivity observed during methylenation of cyclic allylic alcohols: C. D. Poulter, E. C. Friedrich, and S. Winstein, *ibid.*, **91**, 6892 (1969).

(14) Similar arguments have been used in assigning stereochemistries to *syn*- and *anti*-bicyclo[5.1.0]octan-2-ol: A. C. Cope, S. Moon, and P. E. Peterson, *ibid.*, **84**, 1935 (1962).

(15) K. B. Wiberg and B. J. Nist, *ibid.*, **83**, 1226 (1961).

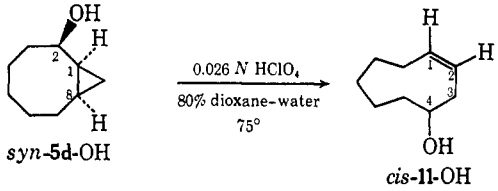
(16) M. St. Jacques, Ph.D. Dissertation, University of California, Los Angeles, Calif., 1967.

(17) L. M. Trefonas and R. Majeste, *Tetrahedron*, **19**, 929 (1963).

and C_2' were calculated[18] using the conformation shown in A, and ranged from 0.95 to 1.20 ppm in the proper direction. Reduction of ketone 10 from the least-hindered side (see structure A) gives *syn*-**5d**-OH, the predominant product. Finally, the ability of a hydroxyl group to direct methylene addition during the Simmons–Smith reaction to the nearest face of the double bond is consistent with the formation of *anti*-**5d**-OH from **9**.[13]

Acid-Catalyzed Isomerization of *syn*- and *anti*-Bicyclo-[6.1.0]nonan-2-ol. Treatment of *syn*-**5d**-OH with dilute perchloric acid in 80% dioxane–water cleanly gave *cis*-cyclononen-4-ol (*cis*-**11**-OH). The nmr spectrum of *cis*-**11**-OH (see Scheme II) is in agreement with the

Scheme II



syn-**5d**-OH — *cis*-**11**-OH

assigned structure.[20] The stereochemistry of the double bond was assigned by comparing the ir spectrum of *cis*-**11**-OH with those of *cis*- and *trans*-cyclononene.[21] The *cis*-olefins show strong absorptions at 730 and 780 cm^{-1} and only weak bands between 900 and 990 cm^{-1}, where *trans*-cyclononene has a strong absorption.

A sample of *syn*-**5d**-OH, which had been carefully purified by glpc, was submitted to the same acid treatment. The progress of the reaction was followed by removing samples which were immediately quenched by vigorous shaking with anhydrous sodium carbonate (see Table I). The starting material contained

Table I. Isomerization Rate Constants[a]

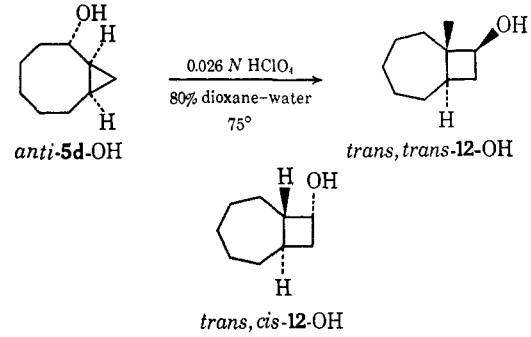
Alcohol	10^4k, sec^{-1}
syn-**5d**-OH	5.88 ± 0.13
anti-**5d**-OH	0.0256 ± 0.0003

[a] In 80% aqueous dioxane, 0.026 *M* $HClO_4$, 75°.

less than 0.1% of *anti*-**5d**-OH. At no time during the isomerization could we detect *anti*-**5d**-OH or products derived from the *anti* epimer (*vide infra*). Control experiments established that we could have easily detected 0.3% of *anti*-**5d**-OH and its isomerization products.

Acid-catalyzed isomerization of *anti*-bicyclo[6.1.0]-nonan-2-ol (*anti*-**5d**-OH) with dilute perchloric acid in 80% dioxane–water gave two alcohols which were only partially resolved by analytical glpc (see Scheme III). Jones oxidation[22] of the mixture gave *trans*-bicyclo-[5.2.0]nonan-8-one (*trans*-**13**), ir (CCl_4) 1775 cm^{-1}, which

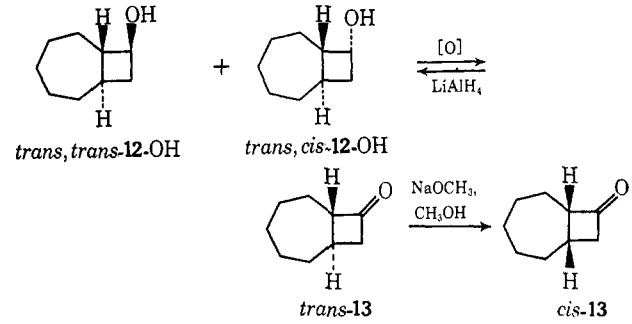
Scheme III



anti-**5d**-OH — *trans,trans*-**12**-OH — *trans,cis*-**12**-OH

reverted to its precursor alcohols when allowed to react with lithium aluminum hydride. Treatment of the ketone with sodium methoxide in methanol produced a second cyclobutyl ketone (*cis*-**13**), ir (CCl_4) 1775 cm^{-1}. The ir spectra of both ketones require that the carbonyl group be placed in a four-membered ring, and the nmr spectra of both ketones are similar. *cis*- and *trans*-bicyclo[5.2.0]nonan-8-one are the only $C_9H_{14}O$ cyclobutyl ketones which could epimerize during base treatment.[23] Models indicate that *trans*-**13** is considerably more strained than *cis*-**13** and that the isomerization should proceed as indicated in Scheme IV. Thus,

Scheme IV



trans,trans-**12**-OH — *trans,cis*-**12**-OH — *trans*-**13** — *cis*-**13**

both cyclobutyl alcohols have a *trans*-bicyclo[5.2.0]-nonane skeleton and differ in the relative orientation of the hydroxyl group at C_8. The final structural assignments are based on similarities among the nmr spectra of *trans*-bicyclo[4.2.0]octan-*trans*-7-ol,[25,26] *trans*-bicyclo[4.2.0]octan-*cis*-7-ol,[25] and a mixture of *trans,trans*-**12**-OH and *trans,cis*-**12**-OH. In the lower homologs, the proton at C_7 appears at higher field in the *trans,trans*-alcohol (3.43–3.93 ppm) than for its epimer (3.95–4.35 ppm).[27] The nmr spectrum of the

(18) A method similar to that used by Johnson and Bovey[19] for benzene was applied to cyclopropane. An initial adjustment of parameters (*R*, radius of ring current and *e*, number of electrons in ring current) was made to fit a molecule of known geometry. The method was then used to calculate chemical-shift differences of protons in other molecules of known geometry. Excellent agreement with the experimental data was obtained; unpublished results, R. S. Boikess, J. I. Brauman, and S. Winstein. A similar method has been developed by Professor J. D. Roberts, private communication.

(19) C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

(20) Unfortunately, the coupling constant between the *cis*-olefinic protons could not be readily extracted from the complex multiplet centered at 5.6 ppm.

(21) A. T. Bloomquist, L. H. Liu, and J. C. Bohrer, *J. Amer. Chem. Soc.*, **74**, 3643 (1952).

(22) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).

(23) The other possible bicyclic carbon skeleton which permits a cyclobutyl ketone, bicyclo[5.1.1]nonane, obviously would not epimerize. Also, ir and nmr spectra of an authentic sample[24] did not match either *cis*- or *trans*-**13**.

(24) W. F. Erman and H. C. Kretschmar, *J. Amer. Chem. Soc.*, **89**, 3842 (1967). We wish to thank Dr. Erman for copies of his spectra.

(25) (a) K. B. Wiberg and J. G. Pfeiffer, *ibid.*, **90**, 5324 (1968); (b) K. B. Wiberg and J. G. Pfeiffer, *ibid.*, **92**, 553 (1970). We thank Professor Wiberg for a preprint of his full paper.

(26) The first *trans* refers to the ring juncture and the latter refers to the relative orientation of the hydroxyl group and the nearest alkyl substituent on the cyclobutane ring.

(27) These assignments agree with observed chemical-shift differences for other epimeric cyclobutanols: I. Lillian and R. A. Doughty, *ibid.*, **89**, 155 (1967).

Table II. Solvolysis Rate Constants, 80% Acetone–Water

System	Temp, °C	10^5k, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
syn-**5d**-OPNB	100.0	1.86 ± 0.06	25.1 ± 0.8	−13.2 ± 2.3
	125.0	16.7 ± 0.6		
cis-**11**-OBs	25.0	36.5 ± 1.2		
anti-**5d**-OPNB	100.0	0.0841 ± 0.0024	28.9 ± 1.6	−19.3 ± 4.6
	125.0	1.04 ± 0.07		
trans,trans-**12**-OBs	25.0	25[a]		
trans,cis-**12**-OBs	25.0	3.30 ± 0.07[b]		
k_a		6.2[c]		
k_b		3.1[d]		
k_r		19[d]		

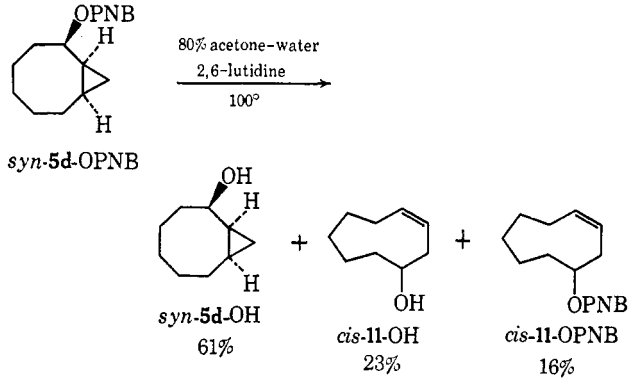
[a] ($k_a + k_r$). [b] Determined from the *trans,cis* isomer produced by internal return after the downward drift in the rate of *trans,trans*-**12**-OBs had stopped, *ca.* one half-life. [c] Determined by extrapolation of the instantaneous rate constants to $t = 0$. [d] Determined graphically, see Results.

mixture of cyclobutanols (*trans,trans*- and *trans,cis*-**12**-OH) has a poorly resolved four-line pattern centered at 3.53 ppm and a less intense pattern centered at 3.88 ppm, which can only be seen at high-spectrum amplitudes. Thus, the major product is *trans*-bicyclo[5.2.0]nonan-*trans*-8-ol (*trans,trans*-**12**-OH) and the minor product is its *trans,cis* epimer.

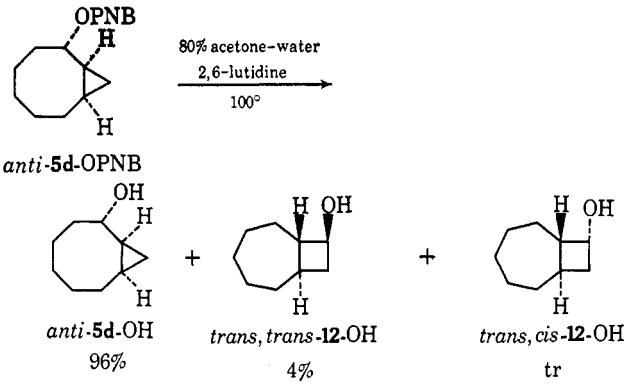
A sample of *anti*-**5d**-OH, which had been isolated by glpc (<0.1% *syn*-**5d**-OH), was submitted to the same acid treatment used for *syn*-**5d**-OH. The progress of the reaction was followed as previously described. Neither *syn*-**5d**-OH nor *cis*-**11**-OH was detected during the course of the isomerization. As little as 0.3% could easily have been seen.

Solvolysis Studies. Solvolysis studies of *syn*- and *anti*-2-bicyclo[6.1.0]nonyl *p*-nitrobenzoate (*syn*- and *anti*-**5d**-OPNB) were carried out using the sealed ampoule technique. The first-order rate constants and activation parameters are listed in Table II. For product studies, 2,6-lutidine was used to neutralize the *p*-nitrobenzoic acid generated by solvolysis. Control experiments established that the products (Scheme V)

Scheme V



were stable to the reaction conditions. The identities of the products were established by comparing their ir spectra with authentic samples and (or) by coinjection with authentic samples on two different glpc columns. After the components of the product mixtures had been identified and their glpc elution order determined, analytical runs on dilute solutions (0.005–0.01 *M*) were carried out without prior work-up of the samples. The rate of *anti*-**5d**-OPNB was sufficiently slow ($k_{100°} = 8.41 \times 10^{-7}$ sec^{-1}) to suspect acyloxygen cleavage; however, solvolysis of the *p*-nitrobenzoate in anhydrous methanol with 2,6-lutidine gave only



ether products.[28] Thus, the products in 60% acetone–water should be derived from alkyl oxygen cleavage.

Careful examination of the product mixture indicated that the solvolysis of both epimers was greater than 99.7% stereoselective. By control experiments, we found that 0.3% of "crossover" products could easily be seen. However, none were detected. Also, both *syn*- and *anti*-**5d**-OPNB were hydrolyzed with potassium hydroxide, and the resulting alcohols were >99.9% epimerically pure.

Hydrolysis of *cis*-**11**-OBs in the same solvent system used for *syn*-**5d**-OPNB gave *syn*-**5d**-OH and *cis*-**11**-OH, while hydrolysis of *trans,trans*-**12**-OBs produced a mixture of *trans,trans*-**12**-OH and *trans,cis*-**12**-OH. Both reactions were greater than 99.7% stereoselective. The titrimetric rate constant for *trans,trans*-**12**-OBs slowly drifted downward from 6.2×10^{-5} sec^{-1} to 3.3×10^{-5} sec^{-1} through approximately one half-life.[29] The data were treated according to Scheme VII, where solvolysis of *trans,trans*-**12**-OBs gives alcohols (liberated acid) and internal return to *trans,cis*-**12**-OBs, which then hydrolyzes at a slower rate. The instantaneous rate constant (k_i) or $(dx/dt)/(a - x)$ can be expressed as a composite of k_a and k_b, where a is the initial brosylate concentration, x is the concentration of reacted

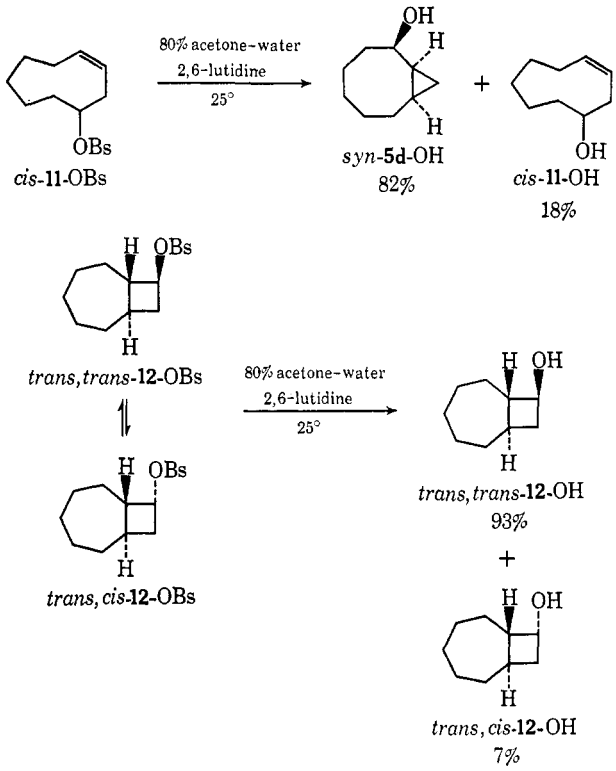
$$k_i = \frac{dx/dt}{(a - x)} = N_a k_a + N_b k_b = N_a k_a + (1 - N_a) k_b \quad (1)$$

material at time t, and N_a and N_b are the respective mole fractions of *trans,trans*-**12**-OBs and *trans,cis*-**12**-

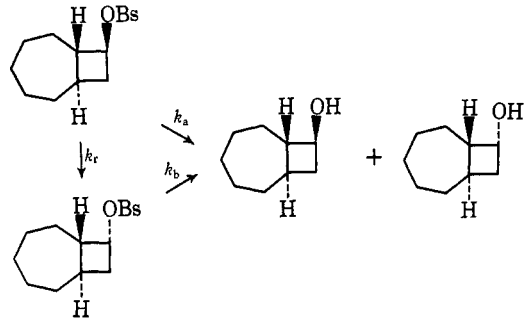
(28) Use of sodium acetate instead of 2,6-lutidine gave some (*ca.* 30%) acyl–oxygen cleavage.

(29) In a product study, the reaction was interrupted several times between 10 and 90% completion. The ratio of *trans,trans*- and *trans,cis*-**12**-OH remained constant.

Scheme VI



Scheme VII



OBs. From plots of $(a - x)$ *vs.* t, values of k_i or $(dx/dt)/(a - x)$ were obtained with a tangent meter.[30] Extrapolation of k_i to $t = 0$ gave k_a. After about 50% of the theoretical amount of acid had been liberated, the downward drift in k_i stopped and k_b could be measured directly. Values of k_b determined titrimetrically (3.30×10^{-5} sec^{-1}) and graphically (3.1×10^{-5} sec^{-1}) were in good agreement.

On the above basis, $(a - x)N_a$ represents the concentration of *trans,trans*-**12**-OBs and should show a first-order decay with time with an apparent rate constant of $(k_a + k_r)$, according eq 2. A plot of

$$\ln\left[\frac{a}{(a - x)N_a}\right] = (k_a + k_r)t \qquad (2)$$

$\ln[(a - x)N_a]$ *vs.* t was linear and $(k_a + k_r)$ was obtained from the slope. The rate constant for rearrangement was estimated to be 1.9×10^{-4} sec^{-1} at 25°.

Discussion

The solvolysis reactions of *syn*- and *anti*-bicyclo[6.1.0]non-2-yl *p*-nitrobenzoate are, within the capability of our analytical methods, completely stereospecific. As little as 0.3% of crossover between *syn* and *anti* reaction pathways would have been detected. The acid-catalyzed alcohol isomerizations were also stereospecific. If one makes the reasonable assumption that collapse of the cationic intermediate with solvent gives similar proportions of cyclopropylcarbinyl and homoallylic alcohols for both *p*-nitrobenzoate solvolysis and acid-catalyzed isomerization, then multiple ionization of the cyclopropylcarbinols preceded complete isomerization. Schemes V and VI point out that internal return is also important during solvolyses of *syn*-**5d**-OPNB and *trans,trans*-**12**-OBs. The maximum values for crossover can be adjusted downward from 0.3 to 0.08% for *syn*-**5d**- and to 0.01% of *anti*-**5d** systems.

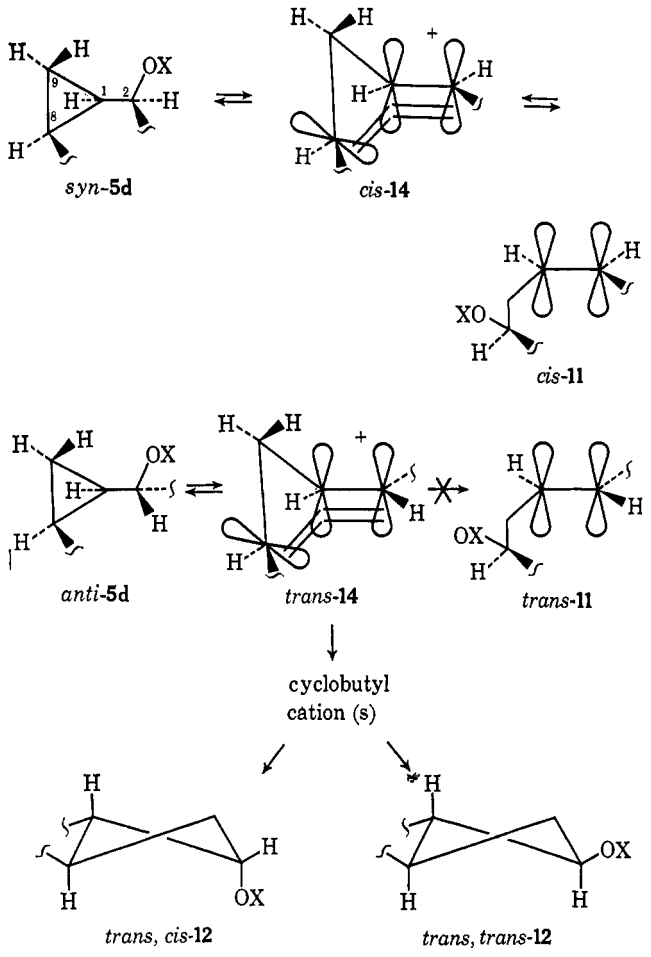
The behavior of *syn*-**5d**-OH parallels earlier work by Winstein and coworkers,[8] in which *syn*-cyclopropylcarbinols stereospecifically rearranged to *cis*-homoallylic alcohols. In addition we found that the homoallylic ring contraction of *cis*-**11**-OBs to *syn*-**5d**-OH is stereospecific. The product distributions of solvolysis of *syn*-**5d**-OPNB and *cis*-**11**-OBs are very similar. In fact, the ratio of cyclopropylcarbinyl to homoallylic product is slightly higher from *cis*-**11**-OBs (82:18) than from *syn*-**5d**-OPNB (73:27). Careful control experiments with *syn*-**5d**-OH, *p*-nitrobenzoic acid, and 2,6-lutidine in 80% acetone–water established that the differences did not result from isomerization of the cyclopropylcarbinyl product at 100°. The change in product distribution could arise from differences in the ion pairs derived from *syn*-**5d**-OPNB and *cis*-**11**-OBs or from a temperature effect on the relative rate of solvent collapse to both isomers. Product studies of *syn*-**5d**-OPNB were carried out at 100°, while *cis*-**11**-OBs was studied at 25°. The product distributions strongly support ionization of both isomers to a common nonclassical cation. *The ratio of cyclopropylcarbinyl to homoallylic alcohol was higher from the homoallylic precursor in spite of its being solvolyzed at a much lower temperature.* Any decrease in temperature would be expected to retard equilibration[25b] if more than one cation was involved.

An intermediate homoallylic cation accounts for the stereospecificity found for *syn*-**5d**-OPNB and *cis*-**11**-OBs. Ionization of *syn*-**5d** derivatives with utilization of the secondary–secondary C_1–C_8 bonding cyclopropane electrons would produce cation *cis*-**14**[31] stereospecifically by backside participation (see Scheme VIII). This is consistent with the ability of the alkyl substituent at C_8 to stabilize positive charge. The stereospecificity displayed during solvolysis and acid-catalyzed isomerization demands that no rotation occur about the C_1–C_2 bond prior to reaction of *cis*-**14** with solvent. This is certainly reasonable since rotation about the analogous bond in cyclopropyldimethylcarbonium ion is not observed on the nmr time scale at temperatures as high as −35°.[5d,7a] Collapse of *cis*-**14** with solvent at C_2 would be expected to follow the reverse path for ionization giving *syn*-**5d** products. Ionization of *cis*-**11**-OBs with anchimeric assistance by the homoallylic double bond also gives *cis*-**14** stereospecifically.

(30) S. Winstein and K. C. Schreiber, *J. Amer. Chem. Soc.*, 74, 2171 (1952).

(31) Structures *cis*- and *trans*-**14** are intended to represent preferential delocalization of positive charge to the more substituted rear carbon of the cyclopropane ring (C_8) at the transition state. Some delocalization to C_9 may occur in the homoallylic cation, but preferential delocalization to C_8 would be expected, based on current concepts about the ability of an alkyl group to stabilize positve charge.

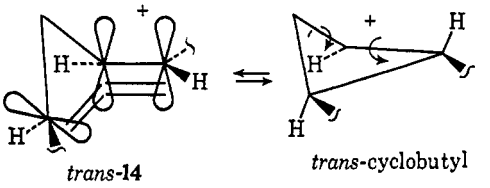
Scheme VIII



Ionization of *anti*-**5d**-OPNB with backside participation of the C_1–C_8 bonding electrons produces homoallylic cation *trans*-**14**. Solvent collapse at C_2 regenerates the *anti*-cyclopropylcarbinyl system. The six carbon bridge undoubtedly introduces considerable strain in *trans*-**14**. With regard to ring strain, the *trans* orientation of C_1 and C_2 coupled with bridging between C_1 and C_8 is approaches placing a *trans* double bond in an eight-membered ring. Glpc traces of the product mixtures from solvolysis of *anti*-**5d**-OPNB and isomerization of *anti*-**5d**-OH showed no minor products (>0.5%) which could possibly be assigned to *trans*-cyclononen-4-ol. It is not unreasonable that the transition state for solvent collapse leading to product which retains the strained *trans* orientation between C_1 and C_9 is significantly higher than that for formation of *anti*-**5d**-OH. Instead of isomerizing to *cis*-**14**, the *trans* cation rearranges irreversibly to a cyclobutyl cation.[32] Solvolysis of either the *trans,trans*- or *trans,cis*-cyclobutyl brosylate gave a mixture of both cyclobutyl products, but no cyclopropylcarbinyl alcohols were detected. In this instance the cyclobutyl cation(s) must be more stable than *trans*-**14**.

Wiberg and Szeimies[33] recently reported σ molecular orbital calculations (CNDO/2) dealing with homoallylic and cyclobutyl interconversions. Their results suggest that a disrotatory opening or closing (Scheme IX) is favored and are in agreement with our experimental findings. At least two cations, *trans*-**14** and *trans*-cyclobutyl, must intervene between *anti*-**5d**-OPNB and *trans,trans*-**12**-OH. In addition, the rearrangement is stereospecific and gives the *more strained trans*-fused carbon skeleton.

Scheme IX



In summary, the solvolyses of 2-substituted *syn*- and *anti*-bicyclo[6.1.0]nonanes are stereospecific. The *syn*- epimer gave *syn*-cyclopropylcarbinol and *cis*-homoallylic alcohol, while *anti*-**5d**-OPNB gave mostly *anti*-**5d**-OH. Homoallylic ring contraction of *cis*-**11**-OBs was also stereospecific producing the same compounds obtained during solvolysis of *syn*-**5d**-OPNB. In contrast to the lower homologs, a six carbon bridge in *syn*- and *anti*-2-bicyclo[6.1.0]nonane derivatives is large enough to permit formation of both *cis*-**14** and *trans*-**14** stereospecifically.

Experimental Section

General. Melting points were determined in open capillaries and are uncorrected. Elemental analyses were performed by Miss Heather King, University of California, Los Angeles, Calif. Ir spectra were obtained with 1 mg/10 μl solutions on a Perkin-Elmer Model 421 grating spectrometer. Nmr spectra were obtained on a Varian A-60, A-60D, or HA-100D spectrometer with chemical shifts measured downfield from tetramethylsilane (δ, ppm) internal standard. Unless otherwise specified, all preparative glpc separations were carried out with a 5 ft × 1/4 in. 5% Carbowax 20M column (60–80 Chromosorb W) on an Aerograph A-90 gas chromatograph. Analytical analyses were performed with a 10 ft × 1/8 in. 5% Carbowax 20 M column (80–100 Chromosorb W) or a 10 ft × 1/8 in. 5% DEGS column (80–100 Chromosorb W) on an Aerograph Hy-Fi Model 600 D. Care was taken to keep the columns free of acidic sites with periodic injections of dilute ammonium hydroxide solution.

Cycloocten-3-ol (9). Cycloocten-3-ol (**9**) was prepared by the method of Heap and Whitham,[34] bp 64–65° (1 mm), lit.[34] 94–105° (14 mm).

***anti*-Bicyclo[6.1.0]nonan-2-ol (*anti*-5d-OH).** A suspension of 25.7 g (0.394 mol) of zinc–copper couple,[35] a small crystal of iodine, 96.5 g (0.361 mol) of methylene iodide, and 100 ml of anhydrous diethyl ether was allowed to stir at reflux for 30 min. After the ether solution cooled to room temperature, 18.6 g (0.148 mol) of cycloocten-3-ol (**9**) in 100 ml of ether was added over a 20-min period. The progress of the reaction was followed by glpc. Periodically, samples were removed and quenched, and the ether layer was analyzed. After 1 hr less than 5% of **9** remained. Saturated ammonium chloride solution was added dropwise until the inorganic material precipitated. The ether layer was decanted, and the precipitate was washed with petroleum ether. The combined organic layers were dried and solvent was removed at reduced pressure. The light yellow residue was mixed with 100 ml of methanol and 30 g of sodium methoxide. After 2 days, the methanolic mixture was poured into water, and the resulting mixture was extracted with petroleum ether. The combined organic layers were washed with water and dried. Solvent was removed at reduced pressure, and the residue was distilled to give 15.3 g (74%) of a viscous colorless liquid: bp 67–69° (0.8 mm); ir (CCl_4) 3600, 3400, 3060, 2980, 2910, 2840, 1445, 1435, 1035, 990, and 955 cm^{-1}; nmr (CCl_4) −0.10 (1, m, *endo* H at C_9), 0.5 and 1.3 (13, m, H at

(32) Possibly more than one nonclassical cyclobutyl cation is involved.[25]

(33) K. B. Wiberg and G. Szeimies, *J. Amer. Chem. Soc.*, **92**, 571 (1970). We wish to thank Professor Wiberg for communicating his results to us prior to publication.

(34) N. Heap and G. H. Whitham, *J. Chem. Soc. B*, 164 (1966).

(35) R. S. Shank and H. Schechter, *J. Org. Chem.*, **24**, 1825 (1959).

C_1 and C_3–C_8, *exo* H at C_9), 2.96 (1, s, hydroxyl H), and 3.02 ppm (1, m, H at C_2). Glpc analysis before and after distillation showed *anti*-**5d**-OH to be contaminated by 0.5% of the *syn* epimer.

***anti*-Bicyclo[6.1.0]non-2-yl *p*-Nitrobenzoate (*anti*-5d-OPNB).** The *p*-nitrobenzoate ester was prepared at 5° by allowing 1.90 g (0.014 mol) of *anti*-**5d**-OH to react with 2.61 g (0.015 mol) of *p*-nitrobenzoyl chloride in 20 ml of pyridine. Work-up gave a light yellow solid which was recrystallized twice from petroleum ether to give 2.60 g (80%) of a pale yellow solid: mp 111–112°; ir (CS_2) 3100, 3060, 3000, 2920, 2850, 1720, 1340, 1320, 1270, 1112, 1097, 1013, 940, 870, and 720 cm^{-1}; nmr ($CDCl_3$) 0.33 (1, m, *endo* H at C_9), 0.6–2.3 (13, m, H at C_1 and C_3–C_8, *exo* H at C_9), 4.9 (1, m, H at C_2), and 8.24 ppm (4, s, aromatic H).

Anal. Calcd for $C_{16}H_{19}NO_4$: C, 66.44; H, 6.57; N, 4.84. Found: C, 66.61; H, 6.66; N, 4.64.

Bicyclo[6.1.0]nonan-2-one (10).[36] A solution of 5.02 g (0.036 mol) of *anti*-**5d**-OH in 75 ml of dry acetone was cooled in an ice–methanol bath. To the cold solution was added 10.0 ml of Jones reagent.[22] After 5 min, excess reagent was quenched with 6 ml of isopropyl alcohol. The resulting green suspension was poured into 100 ml of water, and the solid residue was dissolved in an additional 100-ml portion of water. The combined aqueous layers were extracted with pentane. The pentane extracts were washed with saturated sodium bicarbonate solution and dried. Solvent was removed at reduced pressure to give 4.61 g (93%) of a colorless oil which gave a single peak in glpc analysis. Samples for spectra and combustion analysis were collected by glpc: ir (CCl_4) 3076, 3000, 2920, 2855, 1685, 1444, 1383, 1367, and 862 cm^{-1}; nmr (CCl_4) 1.3–2.6 ppm (m).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.10; H, 10.08.

***syn*-Bicyclo[6.1.0]nonan-2-ol (*syn*-5d-OH).** To a stirred suspension of 0.400 g (0.042 equiv) of lithium aluminum hydride in 50 ml of dry diethyl ether was added 5.13 g (0.037 mol) of **10**. The mixture was allowed to stir for 10 hr before excess hydride was carefully decomposed with saturated ammonium chloride solution. The addition was continued until the inorganic material precipitated. The clear ether layer was decanted and the precipitate was washed several times with ether. The combined ether layers were dried. Solvent was removed at reduced pressure to yield 5.21 g (99%) of a colorless oil. Glpc analysis showed 1.7% of *anti*-bicyclo[6.1.0]nonan-2-ol in the product. Analytical samples were collected by glpc: ir (CCl_4) 3620, 3470, 3060, 2980, 2910, 2850, 1452, 1138, 1010, 912, and 846 cm^{-1}; nmr (CCl_4) 0.0–0.94 (4, m, H at C_1, C_8, and C_9), 1.5 (10 m, H at C_3–C_7), 2.00 (1, s, hydroxyl H), and 4.30 ppm (1, m, H at C_2). After several months at −10°, a small portion of the sample crystallized. Recrystallization from petroleum ether gave a white, low-melting solid, mp 30–31°.

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.04; H, 11.54.

***syn*-Bicyclo[6.1.0]non-2-yl *p*-Nitrobenzoate (*syn*-5d-OPNB).** Following the procedure described for *anti*-**5d**-OPNB, 1.98 g (0.014 mol) of *syn*-**5d**-OH, and 2.66 g (0.014 mol) of *p*-nitrobenzoyl chloride were allowed to react. Work-up and recrystallization from petroleum ether gave 2.77 g (80%) of a pale yellow solid: mp 95.5–96.5°; ir (CS_2) 3100, 3060, 3000, 2980, 2860, 1725, 1340, 1270, 1105, 1095, 1010, 865, and 842 cm^{-1}; nmr ($CDCl_3$) 0.0–2.2 (14, m, H at C_1 and C_3–C_9), 5.82 (1, m, H at C_2), and 8.23 ppm (4, m, aromatic H).

Anal. Calcd for $C_{16}H_{19}NO_4$: C, 66.44; H, 6.57; N, 4.85. Found: C, 66.43; H, 6.52; N, 4.86.

***cis*-Cyclononen-4-ol (*cis*-11-OH).** A solution of 1.22 g (0.087 mol) of *syn*-**5d**-OH in 40 ml of dioxane and 10 ml of 0.129 *N* perchloric acid was heated (bath temperature, 100°) for 315 min. The solution was poured into 100 ml of water, and the resulting suspension was extracted with pentane. The combined pentane layers were washed with saturated sodium bicarbonate solution and dried. Solvent was removed at reduced pressure to give 1.16 g (95%) of a colorless oil. Analytical samples were collected by glpc: ir (CS_2) 3600, 3340, 3000, 2920, 2850, 1680, 1440, 1028, 780, and 730 cm^{-1}; nmr (CCl_4) 1.54 (8, m, H at C_5–C_8), 2.3 (4, m, H at C_3 and C_9), 3.38 (1, s, hydroxyl H), 3.75 (1, m, H at C_4), and 5.6 ppm (2, m, H at C_1 and C_2).

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.07; H, 11.66.

***cis*-Cyclononen-4-yl *p*-Bromobenzenesulfonate (*cis*-11-OBs).** A solution of 169 mg (1.2 mmol) of *cis*-**11**-OH and 298 mg (1.2 mmol) of *p*-bromobenzenesulfonyl chloride in 2.0 ml of dry pyridine was allowed to stand at −5° for 48 hr. The cold solution and the crystals of pyridinium hydrochloride were swirled with 25 ml of cold, dry ether and about 0.5 g of anhydrous magnesium sulfate. Solids were removed by filtration, and the clear solution was concentrated at reduced pressure. During all solvent removals, no attempt was made to warm the flask. After initial concentration at aspirator vacuum (*ca.* 20 mm), the remaining pyridine was removed at about 0.02 mm. The last traces of pyridine were removed by adding 1.0-ml portions of petroleum ether and evacuating. After three portions had been added the residue solidified, giving light yellow crystals. Two recrystallizations from petroleum ether gave 164 mg (37%) of a white solid: mp 49–50°; nmr (CCl_4) 1.4 (8, m, H at C_5–C_8), 2.0–2.6 (4, m, H at C_3 and C_9), 4.43 (1, m, H at C_4), 5.2–5.8 (2, m, H at C_1 and C_2), and 7.58 ppm (4, m, aromatic H). The sample required refrigeration; it decomposed within 2 days at room temperature.

Anal. Calcd for $C_{15}H_{19}SO_3Br$: C, 50.28; H, 5.06. Found: C, 50.13; H, 5.17.

***trans*-Bicyclo[5.2.0]nonan-*trans*-8-ol (*trans,trans*-12-OH).** Following the general procedure outlined for *cis*-**11**-OH, a solution of 0.561 g (4.0 mmol) of *anti*-**5d**-OH in acidic dioxane was heated at 100° for 116 hr. Work-up of the sample gave 0.552 g (93%) of a colorless oil. Glpc analysis showed two components which were partially resolved. The major component (83% of the mixture) was eluted first, and samples for analysis were collected from glpc by trapping the first third of the peak: ir (CCl_4), 3610, 3320, 2960, 2910, 2840, 1441, and 1112 cm^{-1}; nmr (CCl_4) 1.2–2.3 (14, m), 3.53 (1, m, H at C_8), and 4.1 ppm (1, s, hydroxyl H).

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.19; H, 11.51.

The minor isomer (7%) could not be isolated pure. An nmr spectrum of the mixture had a weak centered pattern at 3.88, which was assigned to *trans,cis*-**12**-OH.

***trans*-Bicyclo[5.2.0]non-*trans*-2-yl *p*-Bromobenzenesulfonate (*trans,trans*-12-OBs).** Following the general procedure described for the preparation of *cis*-**11**-OBs, 0.533 g (3.8 mmol) of *trans,trans*-**12**-OH and 0.972 g (3.8 mmol) of *p*-bromobenzenesulfonyl chloride were allowed to react at −5° for 48 hr. Work-up of the sample followed by three recrystallizations from petroleum ether gave 0.673 g (49%) of a white solid: mp 42–43°; ir (CCl_4) 2980, 2920, 2845, 1575, 1470, 1450, 1390, 1370, 1180, 1170, 1090, 1065, 1010, 960, 900, and 870 cm^{-1}; nmr (CCl_4) 1.5 and 2.2 (14, m, H at C_1–C_7 and C_9), 4.2 (1, m, H at C_8), and 7.70 ppm (4, s, aromatic H).

Anal. Calcd for $C_{15}H_{19}SO_3Br$: C, 50.28; H, 5.06, Found: C, 50.13; H, 5.17.

***trans*-Bicyclo[5.2.0]nonan-8-one (*trans*-13).** Following the general procedure used to prepare **10**, 0.900 g (7.1 mmol) of *trans,trans*-**12**-OH was oxidized with 1.8 ml of Jones reagent. Work-up gave 0.720 g (71%) of a colorless oil which gave only a single symmetrical peak on a 150 ft Ucon capillary column: ir (CCl_4) 2920, 2850, 1775, 1442, and 1125 cm^{-1}; nmr (CCl_4) 1.0–2.8 ppm (broad m).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.28; H, 10.28.

Lithium Aluminum Hydride Reduction of *trans*-13. Using the same procedure described for the reduction of **10**, 51 mg (0.38 mmol) of *trans*-**13** was reduced with 5.0 mg (0.53 mequiv) of lithium aluminum hydride. Work-up of the reaction mixture gave 49 mg (92%) of a colorless oil. Glpc analysis revealed two components which, by coinjection, were assigned as *trans,trans*-**12**-OH (86%) and *trans,cis*-**12**-OH (14%).

***cis*-Bicyclo[5.2.0]nonan-8-one (*cis*-13).** A solution of 30 mg (0.22 mmol) of *trans*-**13** and 0.30 g of sodium methoxide in 4 ml of dry methanol was heated at reflux. The progress of the reaction was followed on a 150 ft Ucon capillary column.[37] After 60 hr, *trans*-**13** had cleanly isomerized to a single product (symmetrical peak on capillary glpc column). The reaction mixture was poured into 25 ml of water and the aqueous layer was extracted with pentane. The combined pentane extracts were washed with water and dried. Solvent removal at reduced pressure yielded 27 mg (90%) of a light yellow oil. Glpc purification gave a colorless oil: ir (CCl_4) 2920, 2840, 1775, 1456, 1447, 1440, 1390, and 1082 cm^{-1}; nmr (CCl_4) 1.0–3.5 (broad m).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.43; H, 10.24.

(36) C. H. DePuy and J. L. Marshall, *J. Org. Chem.*, 33, 3326 (1968).

(37) The isomeric ketones were not separated on 10 ft × 1/8 in. 5% Carbowax 20M or 5% DEGS columns.

Acid-Catalyzed Isomerization of *syn*-5d-OH and *anti*-5d-OH. (a) General Kinetic Procedures. *p*-Dioxane was treated by the procedure of Feiser,[38] distilled from sodium, and stored under nitrogen. A stock solution of 0.129 *N* perchloric acid was used for all kinetic and preparative isomerizations. Kinetic measurements of *syn*- and *anti*-5d-OH were carried out in freshly prepared 80% dioxane–water, 0.0258 *N* in perchloric acid, by mixing 100 ml of dioxane with 25 ml of the standard acid solution. Rates were measured with 0.01 *M* solutions using the sealed ampoule technique. Ampoules were removed from the constant temperature bath and shaken vigorously in an ice–water bath. The contents were transferred to a vial which contained approximately one-half of a pellet of potassium hydroxide that had been powdered. The vial was shaken vigorously for 1 min, and the dioxane layer was analyzed by glpc. Rates were calculated by comparing the relative areas of starting alcohol with isomeric products. Control experiments with an internal standard established that starting materials and products were stable to work-up and glpc conditions and that the isomerizations were quantitative.

(b) Glpc Analysis of Kinetic Samples. Standard solutions containing 4 mg of alcohol in 2.00 ml of carbon disulfide were prepared for *syn*-5d-OH, *anti*-5d-OH, *cis*-11-OH, and *trans,trans*- and *trans,cis*-12-OH. Solutions containing between 0.0 and 1.0%, in 0.1% steps, of the appropriate "crossover" contaminants were prepared and analyzed. In all cases a total contamination of 0.3% could easily have been detected. The same glpc conditions were used to analyze the isomerized products. No products of the *anti* series were found in the *syn* product and *vice versa*.

General Kinetic Procedures. Acetone was distilled from molecular sieves through a 40-plate bubble-cap column. The center fraction, boiling at 56°, was collected and stored under nitrogen. 80% acetone–water mixtures were prepared by mixing 800 ml of dry acetone with 200 ml of distilled water. The sealed ampoule technique was used for solvolyses at 100 and 125°. Rates at 25° were measured by quenching 5.00-ml aliquots in 20 ml of dry acetone and immediately titrating with a standard sodium methoxide–methanol solution to a blue end point, using 2 drops of a 1% methanol solution of bromothymol blue as an indicator. The reported values are the average of two runs (Table II). *syn*-Bicyclo[6.1.0]-non-2-yl *p*-nitrobenzoate did not liberate the theoretical amount of acid. However, the percentage of internal return calculated from the difference between the experimental and theoretical infinity titers agreed with the amount of *cis*-11-OPNB found during product studies (*vide infra*).

Preparative Solvolysis of *syn*-Bicyclo[6.1.0]non-2-yl *p*-Nitrobenzoate (*syn*-5d-OPNB). A solution of 1.510 g (5.23 mmol) of *syn*-5d-OPNB and 1.070 g (10.0 mmol) of 2,6-lutidine in 150 ml of 80% acetone–water was heated at 100° for 96 hr (*ca.* 10 half-lives). The solution was poured into 150 ml of saturated sodium chloride solution, and the resulting mixture was extracted with pentane. The combined pentane extracts were washed with water and dried. Glpc analysis (at 80 and 150°) showed no volatile products other than *syn*-5d-OH and *cis*-11-OH. Solvent was removed at reduced pressure, and 1.243 g of a light yellow oil remained. Column chromatography on Woelm alumina, activity II, gave two fractions. The minor component (eluted with hexane) was a pale yellow solid (272 mg). Recrystallization from petroleum ether gave 0.228 g of *cis*-cyclononen-4-yl *p*-nitrobenzoate (*cis*-11-OPNB): mp 47–48.5°; ir (CS_2) 3015, 2925, 2860, 1723, 1520, 1340, 1265, 1110, 1010, and 720 cm^{-1}; nmr ($CDCl_3$) 1.6 (8 m, H at C_5–C_8), 2.2 and 2.5 (4, m, H at C_3 and C_9), 5.08 (1, m, H at C_4), 5.65 (2, m, H at C_1 and C_2), and 8.17 ppm (4, s, aromatic H).

Anal. Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.85. Found: C, 66.29; H, 6.63; N, 4.81.

The other fraction (537 mg) was eluted with diethyl ether and consisted of two components. Glpc analysis showed the fraction to be composed of *syn*-5d-OH (73%) and *cis*-11-OH (27%). The alcohols were separated by glpc and identified by comparison of ir spectra with authentic samples.

Preparative Solvolysis of *anti*-Bicyclo[6.1.0]non-2-yl *p*-Nitrobenzoate (*anti*-5d-OPNB). A solution of 2.500 g (9.0 mmol) of *anti*-5d-OPNB and 1.610 g (15.0 mmol) of 2,6-lutidine in 150 ml of 60% acetone–water was heated at 100° for 213 hr (*ca.* 10 half-lives). The sample was worked up as described for *syn*-5d-OH to give 1.450 g of a light yellow liquid. Chromatography on Woelm alumina, activity II, gave a 0.991-g fraction which was eluted with ether. The fraction consisted of three components, *anti*-5d-OH (96%), *trans,trans*-12-OH (4%), and *trans,cis*-12-OH (trace). Each alcohol had identical glpc retention times as authentic samples, and an ir spectrum of *anti*-5d-OH was identical with that of an authentic sample. The remainder of the sample was 2,6-lutidine.

Analytical Product Solvolyses. Solutions 0.01 *M* in *p*-nitrobenzoate or *p*-bromobenzenesulfonate and 0.02 *M* in 2,6-lutidine were heated at the appropriate temperature. 80% acetone–water was used except for *anti*-5d-OPNB, for which 60% acetone–water was the solvent. Each sample was heated for approximately 10 half-lives. Glpc analyses (at both 80 and 150°) were carried out without prior work-up. The products from *syn*-5d-OPNB, *anti*-5d-OPNB, *cis*-11-OBs, and *trans,trans*- and *trans,cis*-12-OBs are shown in Schemes V and VI. In each case, identifications were made by coinjection with authentic samples on Carbowax 20M and DEGS glpc columns.

A mixture containing 2 μl of *syn*-5d-OH, 5 μl of 2,6-lutidine, 2 mg of *p*-nitrobenzoic acid, and 1 μl of *n*-dodecane in 2 ml of 80% acetone–water was heated at 100° for 96 hr. A comparison of glpc traces before and after heating showed *syn*-5d-OH was stable to the reaction conditions. Similar treatment of *anti*-5d-OH for 216 hr gave the same results.

Table III. Relative Retention Times[a]

Compd	Rel time
10	1.00
syn-5d-OH	1.38
anti-5d-OH	1.45
trans,trans-12-OH	1.59
trans,cis-12-OH	1.63
cis-11-OH	1.93

[a] On 5% Carbowax 20M, at 150°

(38) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, 1957, p 284.