methyl-2-nitrobenzene with potassium permanganate according to the method of Noelting and Gachot.[18]

2-Aminoisophthalic Acid. A mixture of 1 g (4.7 mmol) of 2-nitroisophthalic acid and 0.1 g of 10% palladium on carbon in 100 ml of glyme was shaken 4 hr with hydrogen at 40 psi. The catalyst was removed by filtration and the solvent by rotary vacuum evaporation. A portion of the product was recrystallized from dilute hydrochloric acid yielding off-white crystals. The hydrochloride was dissolved in water and precipitated by addition of ammonium hydroxide. The product was collected by fitration and dried 5 hr at 0.01 mm and 80°; infrared (KBr) 3450, 3340, 1690, and 1245 cm^{-1}.

Anal. Calcd for $C_8H_7NO_4$: C, 53.04; H, 3.90. Found: C, 53.34; H, 4.04.

Solvents. Dimethyl sulfoxide (reagent) was stirred over potassium hydroxide overnight, distilled under reduced pressure, then redistilled from potassium *tert*-butoxide or potassium superoxide at *ca.* 40° and 0.01 mm; the middle cut was retained and stored under nitrogen. Identical results were obtained using either DMSO prepared in this manner or Fischer spectranalyzed DMSO without purification; solvent fluorescence was negligible. Distilled water was passed through a deionizing column before use. 2-Methyl-2-propanol was distilled from potassium under dry nitrogen, then stored in a tightly stoppered bottle in a dry glove box. Acetonitrile, Eastman Spectrograde, was used without further purification.

Absorption spectra were recorded with a Cary 14 spectrophotometer. Fluorescence and chemiluminescence spectra were recorded with a Hitachi MPF-2A spectrophotofluorometer equipped with a thermostated sample cell holder. The spectra were corrected for variation in spectral sensitivity of the instrument using a computer program which has been previously described.[5b] Fluorescence spectra were also corrected for solvent fluorescence by subtracting the emission from suitable blanks identical with the sample solution except for the absence of the fluorescer. Chemiluminescence spectra were adjusted for luminol absorption below 450 nm in the following manner. The absorbance of the luminol solutions was estimated by preparing samples similar to those used for chemiluminescence measurements but with solvent which had been purged for 15 min with oxygen free nitrogen to remove dissolved oxygen. The adjustment to the initial chemiluminescence spectra was calculated assuming an effective path length of 0.5 cm.

Samples for fluorescence and chemiluminescence spectral measurements were prepared in 1-cm quartz cuvettes by mixing appropriate quantities of an aqueous base solution, water, DMSO, and a DMSO solution of the fluorescer or reactant (3-aminophthalic acid, luminol, etc.) (*e.g.*, a 5×10^{-5} *M* solution of 3-aminophthalate in 30 mol % water–70 mol % DMSO 0.015 *M* in sodium hydroxide was prepared by pipeting 0.15 ml of 0.3 *M* aqueous sodium hydroxide,[19] 0.15 ml of water, 2.1 ml of DMSO, and 0.6 ml of a DMSO solution 2.5×10^{-4} *M* in 3-aminophthalic acid hydrochloride[20] into the cuvette and mixing).

The effect of added salts (sodium chloride, potassium chloride, or tetraethylammonium chloride) on the fluorescence or absorption spectra was measured by adding microliter amounts of 2 *M* or 4 *M* aqueous salt solution to the cuvette with a micropipet, mixing thoroughly, and rerecording the fluorescence or absorption after each addition.

Solutions containing 2-methyl-2-propanol were mixed in a dry glove box immediately before recording the spectra, allowing only sufficient time after mixing for the solution to reach thermal equilibrium with the surroundings.

Stock aqueous solutions of the alkali metal hydroxides were prepared by dissolving reagent grade base in deionized water and filtering; precise base concentration was determined by titration with standard hydrochloric acid solution. A stock TBH solution was prepared by stirring an aqueous solution of tetrabutylammonium bromide over silver oxide for *ca.* 2 hr at room temperature, then filtering. The filtrate was stirred with neutral activated charcoal to remove fluorescent impurities which were found in the solution; the mixture was filtered again and the base concentration determined by titration with standard hydrochloric acid. Potassium *tert*-butoxide solution was prepared by dissolving potassium metal in distilled 2-methyl-2-propanol; base concentration was determined by titration (with standard acid) of a 1-ml aliquot diluted to 10 ml with water.

Acknowledgment. We thank the Public Health Service for its financial support (Research Grant No. 5 RO1 NS-07868 from the National Institute of Neurological Diseases and Stroke). We also thank Professor L. Brand and Mr. M. Loken for helpful discussions, and Dr. H. Kägi for some of the early fluorescence measurements on aminophthalic acid.

(18) E. Noelting and C. Gachot, *Ber.*, **39**, 73 (1906).

(19) The base was introduced first and then diluted with DMSO since reverse addition often results in incomplete solution of the alkali hydroxides.[3a]

(20) Neutral solutions of 3-aminophthalic acid hydrochloride in DMSO are not stable for long periods of time;[6] stock solutions were prepared within a few hours of use.

Solvolytic Studies in the 2-Bicyclo[3.1.0]hexyl System[1]

Edwin C. Friedrich* and Mahmoud A. Saleh

Contribution from the Department of Chemistry, University of California, Davis, California 95616. *Received September 21, 1972*

Abstract: A study of the kinetics and products of hydrolysis of the *endo*- and *exo*-2-bicyclo[3.1.0]hexyl 3,5-dinitrobenzoates (**1**-ODNB and **2**-ODNB) in 80% aqueous acetone at 100° has been carried out. Both isomeric 3,5-dinitrobenzoates reacted at similar rates and gave, within experimental error, identical product mixtures consisting of about 35% **1**-OH, 37% **2**-OH, 25% cyclohexen-4-ol, and 3% cyclohexen-3-ol. Studies of the products obtained from hydrolysis of 2-deuterio-substituted **1**-ODNB and **2**-ODNB it is felt showed the absence of any deuterium scrambling occurring *via* degenerate cyclopropylcarbinyl cation rearrangement for either isomer. Finally, it was found that introduction of a 5-methyl substituent produced a similar large acceleration of about 20 in the rates of hydrolysis of both **1**-ODNB and **2**-ODNB. These results are interpreted in terms of **1**-ODNB and **2**-ODNB both ionizing to bisected bishomoallyl type activated complexes and forming products *via* a single bisected bishomoallylic cyclopropylcarbinyl cation intermediate.

In studies of the acetolysis of the *endo*- and *exo*-2-bicyclo[3.1.0]hexyl *p*-toluenesulfonates (**1**-OTs and **2**-OTs), it was observed[2] that the rates and products of

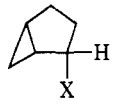
(1) This investigation was supported by the Petroleum Research Fund, administered by the American Chemical Society, and by the Academic Senate Committee on Research of the University of California, Davis. A preliminary report of part of this work has appeared in *Tetrahedron Lett.*, 1373 (1971).

(2) E. C. Friedrich, M. A. Saleh, and S. Winstein, *J. Org. Chem.*, **38**, 860 (1973).

Table I. Rates of Hydrolysis in 80% Aqueous Acetone[a]

3,5-Dinitrobenzoate	Temp, °C	$10^6 k_1$, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
endo-(1-ODNB)	100.0	12.4 ± 0.67	24.2 ± 0.3	−16.5 ± 0.8
	80.0	1.84 ± 0.11		
exo-(2-ODNB)	100.0	11.5 ± 0.64	26.1 ± 0.4	−11.7 ± 1.0
	80.0	1.52 ± 0.19		

[a] All errors shown are standard deviations, calculated from the duplicate runs.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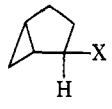
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reaction for both isomers were almost identical. This behavior was somewhat unexpected since from inspection of simple molecular models it was anticipated for stereoelectronic reasons that 1-OTs would react *via* a delocalized cationic species such as **3**, related to the cyclohexen-4-yl cation, but that 2-OTs would react *via* a species such as **4**, related to the cyclopentene-3-methyl


3


4

cation. Thus, we became interested in carrying out a detailed examination of the nature and behavior of the activated complexes and intermediates involved in solvolyses of *endo*- and *exo*-2-bicyclo[3.1.0]hexyl derivatives. Moreover, such a study would also provide information of considerable interest in connection with the effects of geometry on the type of delocalization involved in cyclopropylcarbinyl cation stabilization.[3]

For this study, we utilized 3,5-dinitrobenzoate ester derivatives rather than the *p*-toluenesulfonates 1-OTs and 2-OTs. This is because of the difficulties of preparation and instabilities of the *p*-toluenesulfonates, and because their rates of reaction are too rapid for highly accurate measurements.[2] Also, in this work with the 3,5-dinitrobenzoates 1-ODNB and 2-ODNB, we chose to study their hydrolyses in 80% aqueous acetone rather than their acetolyses. Preliminary control experiments indicated that the expected endo- and exo-bicyclic acetate products 1-OAc and 2-OAc were not stable in acetic acid buffered with sodium acetate under the vigorous conditions necessary for carrying out acetolysis product studies on 1-ODNB and 2-ODNB.

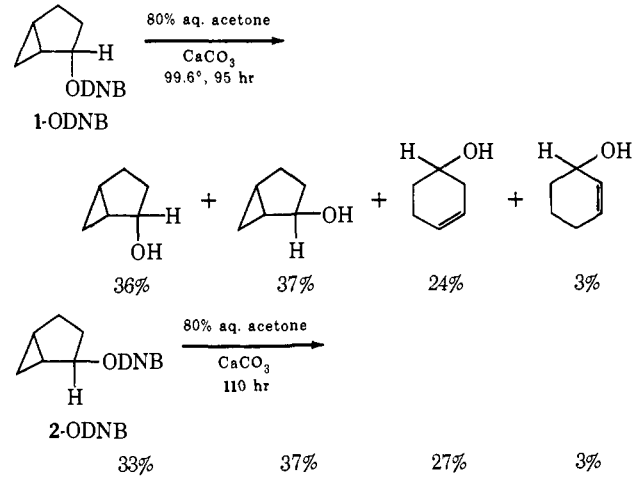
Results and Discussion

Simple Kinetics and Products of Hydrolysis. The 3,5-dinitrobenzoates 1-ODNB and 2-ODNB were prepared by the usual methods from the corresponding bicyclic alcohols.[4] The endo alcohol 1-OH was prepared isomerically pure and in good yield by the Le Goff[5] modification of the Simmons–Smith cyclopropane synthesis starting with cyclopenten-3-ol and methylene bromide. The exo alcohol 2-OH was prepared *via* aluminum isopropoxide in isopropyl alcohol equilibration of 1-OH, followed by preparative glpc separation of the resulting equilibrium mixture of 35% 1-OH and 65% 2-OH.

The rates of hydrolysis of 1-ODNB and 2-ODNB were measured in 80% aqueous acetone at 80 and 100°, and the results are summarized in Table I. Both esters followed good first-order kinetics and gave nearly theoretical production of acid at 10 half-lives. Although 1-ODNB is only slightly more reactive than 2-ODNB, the rates of both isomers are strongly accelerated, as evidenced by the fact that they can be estimated to be 10^5 times more reactive than cyclopentyl 3,5-dinitrobenzoate.[6] This behavior is similar to that observed earlier[2] in acetolysis of the corresponding *p*-toluenesulfonates at 25°.

The products obtained from hydrolysis of 1-ODNB and 2-ODNB in 80% aqueous acetone at 99.6° in the presence of a $CaCO_3$ buffer after about 5 half-lives for reaction were measured using glpc techniques and are summarized in Scheme I. The results given are the

Scheme I



averages of at least two runs, and are reproducible to about ±2%. No olefinic hydrocarbon products or rearranged dinitrobenzoates were detected. Controls, described in the Experimental Section, showed that a pure sample of the most reactive of the product alcohols, 1-OH, was rearranged only to the extent of about 5% under the reaction conditions, and it is reasonable to assume that the other product alcohols are even more stable. Also, controls were run which demonstrated that neither 1-ODNB or 2-ODNB undergoes interconversion or isomerization *via* ion-pair return during the course of their hydrolyses. Thus, within experimental error, both 1-ODNB and 2-ODNB gave identical mixtures of products. This is again similar to the behavior observed earlier[2] in acetolysis of 1-OTs and 2-OTs at 24°, although as might have been expected because of the differences in leaving groups, solvent, and temperature, the product ratios are different.

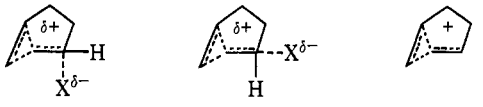
It should be noted at this point that after this section of our work was essentially complete, several reports

(3) (a) C. D. Poulter, E. C. Friedrich, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 4274 (1970), and references contained therein; (b) Y. E. Rhodes and V. C. DiFate, *ibid.*, **94**, 7582 (1972).
(4) M. Hanack and H. Allmendinger, *Chem. Ber.*, **97**, 1669 (1964).
(5) E. Le Goff, *J. Org. Chem.*, **29**, 2048 (1964).
(6) E. C. Friedrich and S. Winstein, unpublished work.

appeared in the literature also describing solvolytic studies of *endo*- and *exo*-2-bicyclo[3.1.0]hexyl derivatives but with different leaving groups and under different reaction conditions.[7] Brook and coworkers[7a] reported a study of the kinetics and products of hydrolysis of the *endo*- and *exo*-2-bicyclo[3.1.0]hexyl chlorides in 70% aqueous acetone at 25° and deaminations of the corresponding amines. Also, Schmid and Brown[7b] studied the solvolyses of the *endo*- and *exo*-2-bicyclo[3.1.0]hexyl-*N*-methyl-4-oxopyridinium iodides in 80% aqueous ethanol at 86°. Their kinetic results both agree closely with ours in that considerable rate acceleration was observed for the 2-bicyclo[3.1.0]hexyl derivatives, but the endo isomers reacted only slightly faster than the exo isomers. Also, their product results agree with ours in that they obtained, within experimental error, identical product mixtures when starting with either endo or exo derivatives. However, the actual ratios of the products again differ depending on the nature of the leaving group and solvent employed.

Another very recent report of work related to ours is that of McDonald and Davis[8] who studied the solvolysis of *endo*-2-bicyclo[2.2.0]hexyl 3,5-dinitrobenzoate in 60% aqueous acetone at 50° as a possible route to the homoallylic cyclohexen-4-yl cation. In comparison runs with **1**-ODNB and **2**-ODNB in the same solvent system at 90°, they observed within experimental error identical mixtures of **1**-OH, **2**-OH, and cyclohexen-4-ol starting with either epimeric dinitrobenzoate. That the relative amounts of their products differ from those observed by us in 80% aqueous acetone at 100° most likely results from the greater nucleophilicity of the solvent system employed in their work.

The simplest explanation for the similarities in reactivity of the *endo*- and *exo*-2-bicyclo[3.1.0]hexyl derivatives, and the fact that they give identical mixtures of products, is that both isomers react *via* similar activated complexes **5** and **6** and an identical intermediate **7** in which delocalization of the charge on C_2 simul-



5 **6** **7**

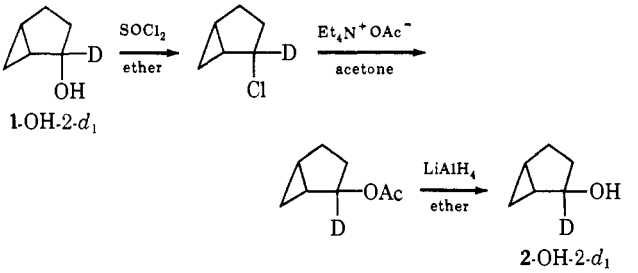
taneously involves both the 1,5 and 1,6 bonds of the cyclopropane ring. A similar explanation was also suggested by Brook and coworkers[7a] to account for their results. With such a bisected bishomoallyl cation intermediate, loss of stereochemistry at C_2 in formation of the cyclopropylcarbinyl products should be observed.[3] However, another explanation which cannot be discounted by the present data is that the isomeric 2-bicyclo[3.1.0]hexyl derivatives ionize initially to different delocalized cyclopropylcarbinyl cation intermediates such as **3** and **4** *via* corresponding types of activated complexes which by coincidence have similar energies, but then before attack by solvent occurs to give products these equilibrate rapidly to an identical mixture of species or rehybridize to a single different species such as **7**.

To employ more sensitive tests than those used above for proving the similarity or dissimilarity of the activated complexes and intermediates involved in reactions of *endo*- and *exo*-2-bicyclo[3.1.0]hexyl derivatives, the further studies described in the following sections were thus carried out.

Deuterium Scrambling Studies. Recently, Friedrich and Wight[9] observed in hydrolysis of the 2-deuterio-*endo*- and -*exo*-2-bicyclo[5.1.0]octyl 3,5-dinitrobenzoates that completely different deuterium scrambling behaviors due to the possibility of degenerate cyclopropylcarbinyl cation rearrangement are obtained for each isomer even though both give similar (but not completely identical) hydrolysis products in 80% aqueous acetone. After 81% reaction, the alcoholic products from the endo isomer retained unscrambled deuterium atoms. However, after 93% reaction, the deuteriums in the alcoholic products from the exo isomer were found to be greater than 90% scrambled. Similar differences were observed in racemization studies carried out on optically active undeuterated compounds. Thus, it is apparent that deuterium scrambling or racemization studies provide a much more sensitive test for the nature of the initial intermediates obtained in solvolysis of isomeric bicyclic cyclopropylcarbinyl systems than do simple product studies. It should be noted, however, that Friedrich and Wight[9] did not feel that their results enabled them to distinguish between conformationally isomeric bisected bishomoallyl cations, bicyclobutonium ions, or other sets of intermediate cations as a possible explanation for their results.

Because of the above results, we thus decided to carry out deuterium scrambling studies in product formation for the 2-deuterio-*endo*- and -*exo*-2-bicyclo[3.1.0]hexyl 3,5-dinitrobenzoates (**1**-ODNB-*2-d*$_1$ and **2**-ODNB-*2-d*$_1$). Preparation of the 2-deuterio endo alcohol precursor **1**-OH-*2-d*$_1$ of **1**-ODNB-*2-d*$_1$ was accomplished without difficulty *via* reduction of 2-bicyclo[3.1.0]hexanone with $LiAlD_4$ in ether. Conversion of **1**-OH-*2-d*$_1$ into the 2-deuterio exo alcohol **2**-OH-*2-d*$_1$ was accomplished as shown in Scheme II. The pure

Scheme II



1-OH-2-d_1 **2**-OH-2-d_1

2-deuterio exo alcohol was separated from the final mixture of alcoholic products by glpc techniques and converted into the 3,5-dinitrobenzoate by the usual procedures.

Deuterium scrambling studies on the 2-deuterio-*endo*- and -*exo*-2-bicyclo[3.1.0]hexyl 3,5-dinitrobenzoates were carried out in 80% aqueous acetone buffered with $CaCO_3$ at 100°. After reaction for about 10 half-lives, the product mixtures were worked up and separated into fractions by glpc. Nmr spectra of each fraction were then taken to determine the position of the deuterium in each of the products. If no scrambling *via*

(7) (a) P. R. Brook, R. M. Ellam, and A. S. Bloss, *Chem. Commun.*, 425 (1968); (b) G. H. Schmid and A. Brown, *Tetrahedron Lett.*, 4695 (1968).

(8) R. N. McDonald and G. E. Davis, *J. Amer. Chem. Soc.*, **94**, 5078 (1972).

(9) L. E. Friedrich and F. R. Wight, *ibid.*, **92**, 1807 (1970).

degenerate cyclopropylcarbinyl cation rearrangement had occurred, the initial deuterium on C_2 in the dinitrobenzoates should end up still entirely on C_2 in the bicyclic alcohol products and on C_1 in the cyclohexen-4-ol product. If scrambling had occurred, some of the deuterium initially on C_2 should also end up on C_5 of the bicyclic alcohol products and on C_4 of the cyclohexen-4-ol.

Unfortunately, because of the small quantities of materials available, combined with the limitations of the nmr analysis method, the results obtained cannot be given with high accuracy. Also, since the *exo*-2-bicyclo[3.1.0]hexanol and cyclohexen-4-ol products could not be cleanly separated by glpc, the nmr measurements had to be done on mixtures of these materials, which further limited their accuracy. However, in spite of these limitations, it is felt that it still can be very conservatively stated that starting with either **1**-ODNB-*2-d*$_1$ or *2*-ODNB-*2-d*$_1$ the *endo*-2-bicyclo[3.1.0]hexanol products retained greater than 95% D at C_2, the exo-2-bicyclo[3.1.0]hexanol products greater than 90% D at C_2, and the cyclohexen-4-ol products greater than 90% D on a vinylic carbon (C_1 or C_2). Although these results allow for the possibility that a small amount of deuterium scrambling may have occurred with one or both of the isomeric 2-deuterio dinitrobenzoates, it is felt that actually no deuterium scrambling occurred with either isomer. The reasons for this are based on the results which follow.

As another test for deuterium scrambling in the 2-bicyclo[3.1.0]hexyl system, samples of 2-deuterio-*endo*-2-bicyclo[3.1.0]hexanol (**1**-OH-*2-d*$_1$) and 2-deuterio-*exo*-2-bicyclo[3.1.0]hexyl acetate (**2**-OAc-*2-d*$_1$) were treated with perchloric acid in acetic acid as described in the Experimental Section. This procedure is known to convert these 2-bicyclo[3.1.0]hexyl derivatives completely to the product of thermodynamic control, an 85:15 mixture of cyclohexen-4-yl acetate and cyclohexen-3-yl acetate,[10] *via* formation of the 2-bicyclo[3.1.0]cation followed by repeated reformation of this ion from the initially produced endo and exo bicyclic acetates. Since acetic acid is less nucleophilic than 80% aqueous acetone, the 2-bicyclo[3.1.0]hexyl cations here should have more time to undergo possible degenerate cyclopropylcarbinyl cation rearrangement before attack by solvent occurs to give products. Also, the results in this study can be reported with much higher accuracy than in the 2-deuterio dinitrobenzoate study because of the simplicity of the product mixtures and their ease of separation by glpc. Thus, the complete absence of any deuterium scrambling in the cyclohexen-4-yl acetate products in these cases would show that it is clearly an unfavorable process in the 2-bicyclo[3.1.0]hexyl system.

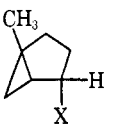
When the perchloric acid catalyzed rearrangements in acetic acid were carried out starting with the samples of **1**-OH-*2-d*$_1$ and **2**-OAc-*2-d*$_1$, each containing greater than 94% of one deuterium in their 2 positions, it was found that the cyclohexen-4-yl acetate products in both cases contained by nmr greater than 98% of one deuterium in a vinylic position. If scrambling had occurred, some of the deuterium would also have ended up in the 4 position on the carbon bearing the acetate group.

Thus, even using the above sensitive deuterium scrambling tests, both the *endo*- and *exo*-2-bicyclo[3.1.0]hexyl derivatives exhibited identical behavior, and no evidence for ionization initially to two different intermediates was obtained. However, the definite possibility still exists that ionization could be occurring to two different intermediates, neither of which undergoes deuterium scrambling.

One possible way to obtain information of help in resolving the above problem is to study the nature of the charge delocalization in the activated complexes involved in ionization for the isomeric dinitrobenzoates. This can be done readily by means of kinetic studies of the effects of substituents on the rates of reaction for the *endo*- and *exo*-dinitrobenzoates. The resulting information can be of use in saying something about the natures of the initial intermediates formed on ionization of the isomeric dinitrobenzoates since the type of delocalization involved in the activated complexes and in the intermediates which directly follow them should reasonably be expected to be similar. Thus, the methyl substituent effect studies described in the following section were carried out.

5-Methyl Substituent Effects. If the activated complexes involved in ionization of the *endo*- and *exo*-2-bicyclo[3.1.0]hexyl 3,5-dinitrobenzoates are of the homoallyl or bicyclobutonium type (related to the intermediates **3** and **4**, respectively), one would expect that introduction of an electron releasing 5-methyl substituent should result in acceleration of the rate of reaction of the endo isomer, but have little or no effect on the reaction of the exo isomer. This is because in activated complexes of these types only that derived from the *endo*-dinitrobenzoate has any delocalization of positive charge at C_5. On the other hand, if both the *endo*- and *exo*-dinitrobenzoates react *via* bisected bishomoallyl type activated complexes (**5** and **6**), one would anticipate that introduction of a 5-methyl substituent should result in acceleration of both of their rates of reaction since in both cases charge is delocalized at C_5.[11]

Preparation of the 5-methyl-*endo*- and -*exo*-2-bicyclo[3.1.0]hexanols (**8**-OH and **9**-OH) was accomplished



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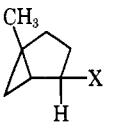

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without difficulty. Methylenation of 1-methylcyclopenten-3-ol using the Le Goff[5] modification of the Simmons–Smith procedure gave pure **8**-OH in satisfactory yield. Aluminum isopropoxide in isopropyl alcohol treatment of this material for a short period of time (not sufficient to establish equilibrium) produced a mixture containing approximately 53% of the exo alcohol **9**-OH which was purified by glpc. These were then converted into the 3,5-dinitrobenzoates **8**-ODNB and **9**-ODNB by the usual procedures.

The kinetics of hydrolysis of **8**-ODNB and **9**-ODNB were measured in 80% aqueous acetone at 60.0 and 80.0°, and the results obtained are shown in Table II. A brief product study with **8**-ODNB showed that 4-methylcyclohexen-4-ol was the major hydrolysis product, accompanied by less than 10% of other

(10) E. C. Friedrich and S. Winstein, unpublished work. With the higher [4.1.0] and [5.1.0] systems, the pure homoallylic acetates are obtained by this procedure.

(11) P. v. R. Schleyer and G. W. Van Dine, *J. Amer. Chem. Soc.*, **88**, 2321 (1966).

Table II. Rates of Hydrolysis in 80% Aqueous Acetone[a]

3,5-Dinitrobenzoate	Temp, °C	10^6k_1, sec^{-1}	$\Delta H^{\pm}$, kcal/mol	$\Delta S^{\pm}$, eu
endo-8-ODNB	80.0	40.4 ± 1.1	28.9 ± 1.4	+3.0 ± 4.0
	60.0	3.22 ± 0.28		
exo-9-ODNB	80.0	26.9 ± 0.8	27.5 ± 0.9	−2.0 ± 2.5
	60.0	2.40 ± 0.09		

[a] The errors shown for the rate constants are standard deviations, calculated from duplicate runs. The errors shown for the activation parameters are maximum deviations, calculated using the standard deviation values for the rate constants.

alcoholic products. It is seen that at 80° the *endo*-dinitrobenzoate **8**-ODNB reacted at a rate 1.5 times faster than that of the exo isomer **9**-ODNB. This is similar to the behavior exhibited by the unsubstituted dinitrobenzoates where the endo–exo rate ratio is 1.2 at 80°. Also, at 80° the *endo*- and *exo*-5-methyl derivatives react at factors of 22 and 18 times faster, respectively, than the corresponding unsubstituted derivatives **1**-ODNB and **2**-ODNB. However, there is one perplexing, unexpected feature of the kinetic results obtained in hydrolysis of **8**-ODNB and **9**-ODNB. This is the observation that, if taken at face value, the activation parameters for hydrolysis of **8**-ODNB and **9**-ODNB appear to indicate that the rate accelerations produced by 5-methyl substitution are due to entropy rather than to enthalpy factors. It is felt, however, that any discussion of the reality of, or an explanation for, this apparent observation is unwarranted in the absence of further kinetic data at other temperatures for both the unsubstituted and 5-methyl substituted derivatives. Rates of hydrolysis of **1**-ODNB, **2**-ODNB, **8**-ODNB, and **9**-ODNB were all measured at 80° and therefore comparisons can be made directly without using the activation parameters. Thus, it is felt that the similar large rate accelerations for both **8**-ODNB and **9**-ODNB do tend to support the intervention of the bisected bishomoallyl type activated complexes **5** and **6** in hydrolyses of the *endo*- and *exo*-2-bicyclo[3.1.0]hexyl derivatives. Also, as mentioned earlier, by extension they tend to support the proposal that ionization of both the endo and exo derivatives proceeds directly to a single bisected bishomoallylic intermediate **7** from which the identical products are obtained.

Comparisons with Other 2-Bicyclo[*n*.1.0]alkyl Systems. Since the present work on the 2-bicyclo[3.1.0]-hexyl system was initiated in 1966, a number of reports have appeared concerning solvolytic studies on other simple cis-ring-fused 2-bicyclo[*n*.1.0]alkyl nitrobenzoate ester systems.[12] Also, Wiberg and Nakahira[12f] have reported an interesting study of the kinetics and products of solvolysis of the trans-ring-fused *endo*- and *exo*-2-bicyclo[6.1.0]nonyl 3,5-dinitrobenzoates.

It is of interest to note that in the cis-ring-fused 2-bicyclo[*n*.1.0]alkyl systems (n = 2–7) studied, all except the 2-bicyclo[3.1.0]hexyl and [4.1.0]heptyl[12b] exhibit significant differences in rate for the endo and exo isomers. Also, only in the bicyclohexyl and bicycloheptyl[12b] systems do the *endo*- and *exo*-nitrobenzoate ester derivatives give, within experimental error, identical product mixtures on hydrolysis. Furthermore, recent studies by Friedrich and Schuster[12c] of deuterium scrambling in hydrolysis of the 2-deuterio-*endo*- and -*exo*-2-bicyclo[4.1.0]heptyl *p*-nitrobenzoates have shown a similar lack of significant deuterium scrambling for either isomer, as was observed by us in the 2-bicyclo-[3.1.0]hexyl system. Thus, by analogy to our results in the 2-bicyclo[3.1.0]hexyl system, it seems reasonable to explain the similar behavior in the [4.1.0]heptyl system as resulting from both endo and exo derivatives ionizing to and giving products *via* a single bisected bishomoallyl cation intermediate homologous with **7**.

With the 2-bicyclo[5.1.0]octyl 3,5-dinitrobenzoate system,[12d] the endo and exo derivatives on hydrolysis give similar but not identical product mixtures, although they give completely different deuterium scrambling results. This has already been discussed earlier in detail in connection with the introduction to our deuterium scrambling studies in the bicyclo[3.1.0]hexyl system.

On going to the large ring, flexible 2-bicyclo[6.1.0]-nonyl[12e] and [7.1.0]decyl[12g] *p*-nitrobenzoate ester systems, hydrolysis in 80% aqueous acetone at 100° gives completely different product mixtures from the endo and exo isomers. This has been explained[12e,g] in terms of the endo and exo isomers in these systems reacting entirely *via* different, noninterconverting homoallyl cation intermediates in which, however, for both intermediates only the 1,8- or 1,9-cyclopropyl bond, respectively, is involved in delocalization of charge. Recent work by Wiberg and Nikahira[12f] showed that in the cis-ring-fused 2-bicyclo[6.1.0]nonyl system neither the *endo*- nor the *exo*-3,5-dinitrobenzoate gives any deuterium scrambling in the products obtained on hydrolysis.

Thus, it is apparent that in the 2-bicyclo[*n*.1.0]alkyl systems studied, an entire spectrum of different types of behavior resulting from cyclopropyl participation is observed. However, the exact nature of the mode of cyclopropyl participation in all cases, especially in the 2-bicyclo[5.1.0]octyl system, is not yet clear. Also, it is unclear why deuterium scrambling has only been observed with the *exo*-[5.1.0]octyl system and not with any of the other cis-ring-fused systems. This may be related to the nature of the charge delocalization involved in ionization of the *exo*-[5.1.0]octyl system being unique among the series of compounds (*e.g.*, possibly exocyclic bicyclo butonium ion type with delocalization involving only the 1,8-cyclopropyl bond). Therefore, it is felt that information of value to solving this problem can be readily obtained by means of further studies of methyl substituent effects on reaction rate, such as those we carried out on the [3.1.0]hexyl system. Also, information regarding the nature of the process by which degenerate cyclopropylcarbinyl cation rearrangement takes place may be obtained by means of methyl sub-

(12) (a) K. B. Wiberg, V. Z. Williams, and L. E. Friedrich, *ibid.*, **92**, 564 (1970); (b) K. E. Rubenstein, Ph.D. Thesis, University of Wisconsin, 1967; H. L. Goering and K. E. Rubinstein, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., 1966, p K-11; (c) L. E. Friedrich and G. B. Schuster, *Tetrahedron Lett.*, 3171 (1971); (d) L. E. Friedrich and F. R. Wight, *J. Amer. Chem. Soc.*, **92**, 1807 (1970); (e) C. D. Poulter, E. C. Friedrich, and S. Winstein, *ibid.*, **92**, 4274 (1970); (f) K. B. Wiberg and T. Nakahira, *ibid.*, **93**, 5193 (1971); (g) C. D. Poulter and S. Winstein, *ibid.*, **92**, 4282 (1970).

stituent effects (*e.g.*, by determining if the rearrangement can be made an important process in the *exo*-2-bicyclo[4.1.0]heptyl system by means of placing methyl substituents in the 1 or 7 positions). Studies in these areas are currently being carried out in our laboratory.

Experimental Section

General. Melting points and boiling points are uncorrected. Infrared spectra were recorded with a Perkin-Elmer Model 237B grating spectrophotometer. Nmr spectra were obtained on a Varian A-60A instrument with chemical shifts measured in parts per million downfield from TMS external standard. Glpc analyses and separations were carried out at 100–120° using an Aerograph A90-P3 instrument equipped with a Pyrex injector insert. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

***endo*-2-Bicyclo[3.1.0]hexanol.** Using the Le Goff[5] modification of the Simmons–Smith cyclopropane synthesis, 100 g (1.2 mol) of cyclopenten-3-ol,[13] 600 g (3.44 mol) of methylene bromide, and 360 g (5.56 mol) of 30 mesh granular zinc–copper couple in 1 l. of anhydrous ether were stirred under reflux for 14 hr. After work-up by the addition of saturated ammonium chloride solution, followed by washing the ether layer with saturated sodium carbonate and saturated sodium chloride solutions and drying, distillation through a 60-cm tantalum spiral column gave 75 g (64% yield) of pure *endo*-2-bicyclo[3.1.0]hexanol: bp 79–81° (20 mm); n^{25}D 1.4782 [lit.[4] bp 76° (17 mm), n^{20}D 1.4788]; nmr (CCl_4) δ 0.5 (m, 2, cyclopropyl), 1.5 (m, 6), 3.9 (s, 1, OH), and 4.4 (m, 1, C*H*OH).

***endo*-2-Bicyclo[3.1.0]hexyl 3,5-Dinitrobenzoate.** This was prepared in 80% yield by the usual manner from *endo*-2-bicyclo[3.1.0]-hexanol and 3,5-dinitrobenzoyl chloride in pyridine at 0°, and recrystallized from warm methylcyclohexane: mp 122–124° [lit.[4] mp 124–124.8°]; nmr ($CDCl_3$) δ 0.7 (m, 2, cyclopropyl), 1.6 (m, 6), 5.5 (m, 1, C*H*ODNB), and 9.1 (s, 3, arom).

***exo*-2-Bicyclo[3.1.0]hexanol.** A sample of 50 g of *endo*-2-bicyclo[3.1.0]hexanol was heated under reflux for 120 hr with an equivalent amount of freshly distilled aluminum isoproproxide in 100 ml of anhydrous isopropyl alcohol containing 5 ml of anhydrous acetone. Glpc analysis on a 3.5 m × 0.25 in. 20% 3-nitro-3-methylpimelonitrile (NMPN) on 80–100 mesh Chromosorb W column showed that the resulting equilibrium mixture contained 65% of the *exo*- and 35% of the *endo*-2-bicyclo[3.1.0]hexanols. After work-up and distillation of the mixture, a pure sample of the exo alcohol was separated by glpc on the column described above and flash distilled through a microdistillation apparatus: n^{25}D 1.4750 [lit.[4] bp 73.5° (17 mm), n^{20}D 1.4801]; nmr (CCl_4) δ 0.00 (q, 1, cyclopropyl), 0.4 (m, 1, cyclopropyl), 1.5 (m, 6), 3.1 (s, 1, OH), and 4.1 (d, 1, J = 4 Hz, C*H*OH).

***exo*-2-Bicyclo[3.1.0]hexyl 3,5-Dinitrobenzoate.** This was prepared in the usual manner in 69% yield from the exo alcohol and recrystallized from a 1:1 mixture of methanol and methylcyclohexane: mp 96–98° [lit.[4] 98–98.6°]; nmr ($CDCl_3$) δ 0.0 (q, 1, cyclopropyl); 0.5 (m, 1, cyclopropyl), 1.6 (m, 6), 5.3 (d, 1, J = 4 Hz, C*H*ODNB), and 9.1 (s, 3, arom).

2-Deuterio-*endo*-2-bicyclo[3.1.0]hexanol. A solution of 2-bicyclo[3.1.0]hexanone[14] (8.0 g, 0.083 mol) in 200 ml of anhydrous ether was reduced with lithium aluminum deuteride (1.5 g, 0.035 mol, 100%) at 25° for 4 hr. After work-up in the usual manner, distillation gave 7.4 g (90%) of a mixture of 93% *endo* and 7% *exo*-2-deuterio-2-bicyclo[3.1.0]hexanols: bp 67–69° (15 mm), n^{24}D 1.4782 [lit.[4] bp 76° (17 mm), n^{20}D 1.4788 (for nondeuterated compound)]; ir (neat) 2100 cm^{-1} (C–D); nmr (CCl_4) δ 0.5 (m, 2, cyclopropyl); 1.5 (m, 6), and 5.0 (s, 1, OH). Careful nmr examination of this material showed that the endo alcohol contained greater than 94% D on C_2.

2-Deuterio-*endo*-2-bicyclo[3.1.0]hexyl 3,5-Dinitrobenzoate. This was prepared in 85% yield by the same procedure used for making the nondeuterated material: mp 125–126° [lit.[4] mp 124–124.8° (for nondeuterated material)]; nmr ($CDCl_3$) δ 0.7 (m, 2, cyclopropyl), 1.6 (m, 6), and 9.1 (s, 3, aromatic). Nmr examination showed the presence of greater than 96% D on C_2.

2-Deuterio-*exo*-2-bicyclo[3.1.0]hexanol. A 5.0 g (0.051 mol) sample of 2-deuterio-*endo*-2-bicyclo[3.1.0]hexanol, prepared as described above and contaminated with about 7% of the 2-deuterio exo alcohol, was converted into the corresponding chloride following the procedure of Freeman and coworkers.[15] Nmr analysis showed that it consisted of about 80% of the endo chloride. The crude, undistilled chloride was then reacted with 23.0 g (0.12 mol) of tetraethylammonium acetate[16] in 60 ml of anhydrous acetone at 50° for 30 hr. The reaction mixture was worked up by pouring it into ice–water, and the acetate product was extracted into *n*-pentane, washed with saturated sodium chloride, dried over $MgSO_4$, and roughly distilled through a simple microapparatus to give 2.8 g of an acetate mixture consisting of approximately 70% of the 2-deuterio-*exo*-2-bicyclo[3.1.0]hexyl acetate.

The crude acetate mixture prepared above was finally reduced with an excess of $LiAlH_4$ in ether to give 1.8 g of an alcohol mixture consisting of approximately 70% of 2-deuterio-*exo*-2-bicyclo[3.1.0]-hexanol. A small sample of the pure 2-deuterio exo alcohol was separated by glpc techniques on the 3.5-m nitromethylpimelonitrile column described earlier: ir (neat) 2100 cm^{-1} (C–D); nmr (CCl_4) δ 0.00 (m, 1, cyclopropyl), 0.4 (m, 1, cyclopropyl), 1.5 (m, 6), and 4.0 (s, 1, OH). Nmr analyses showed that the alcohol contained greater than 94% D in the 2 position.

2-Deuterio-*exo*-2-bicyclo[3.1.0]hexyl Acetate. A small sample of partially glpc purified 2-deuterio-*exo*-2-bicyclo[3.1.0]hexanol was converted into the corresponding acetate by the usual procedure with acetic anhydride in pyridine. The 2-deuterio-*exo*-2-bicyclo-[3.1.0]hexyl acetate was then purified by glpc techniques on a 4 m × 0.25 in. 20% diethylene glycol succinate (DEGS) on 60–80 mesh Chromosorb P column: nmr (neat) δ 0.0 (m, 1, cyclopropyl), 0.5 (m, 1, cyclopropyl), 1.6 (m, 6), 1.9 (s, 3, CH_3). Nmr examination showed that this material contained greater than 94% D on C_2.

2-Deuterio-*exo*-2-bicyclo[3.1.0]hexyl 3,5-Dinitrobenzoate. This was prepared in a 75% yield, from a partially glpc purified sample of the 2-deuterio exo alcohol, by the same procedure used for making the nondeuterated material: mp 96–98° [lit.[4] mp 98–98.6° (for the nondeuterated compound)]; nmr ($CDCl_3$) δ 0.0 (m, 1, cyclopropyl), 0.5 (m, 1, cyclopropyl), 1.6 (m, 6), and 9.1 (s, 3, arom). Nmr examination showed that this material contained greater than 98% D on C_2.

5-Methyl-*endo*-2-bicyclo[3.1.0]hexanol. Using the Le Goff[5] modification of the Simmons–Smith cyclopropane synthesis, 30 g (0.31 mol) of 1-methylcyclopenten-3-ol,[17] 150 g (0.86 mol) of methylene bromide, and 60 g (0.92 mol) of 30 mesh granular zinc–copper couple in 250 ml of dry ether were stirred under reflux for 2 hr. After work-up by the addition of saturated ammonium chloride solution, followed by washing the ether layer with saturated sodium carbonate and sodium chloride solutions and drying, distillation through a 60-cm tantalum spiral column gave 10 g (29%) of pure 5-methyl-*endo*-2-bicyclo[3.1.0]hexanol: bp 74° (15 mm), n^{25}D 1.6552 [lit.[17] bp 76° (18 mm)]; nmr (CCl_4) δ 0.3 (q, 1, cyclopropyl), 0.7 (t, 1, cyclopropyl), 1.2 (s, 3, CH_3), 1.6 (m, 5), 3.1 (s, 1, OH), and 4.3 (m, 1, C*H*OH).

5-Methyl-*endo*-2-bicyclo[3.1.0]hexyl 3,5-Dinitrobenzoate. This was prepared in 83% yield by the usual manner from the alcohol and 3,5-dinitrobenzoyl chloride in pyridine at 0° and recrystallized from warm methylcyclohexane: mp 101–101.5°; nmr ($CDCl_3$) δ 0.4 (q, 1, cyclopropyl), 0.8 (t, 1, cyclopropyl), 1,2 (s, 3, CH_3), 1.6 (m, 5), 5.5 (m, 1, C*H*ODNB), and 9.1 (s, 3, arom).

Anal. Calcd for $C_{14}H_{14}N_2O_6$: C, 54.90; H, 4.60; N, 9.14. Found: C, 54.79; H, 4.49; N, 8.92.

5-Methyl-*exo*-2-bicyclo[3.1.0]hexyl 3,5-Dinitrobenzoate. A solution of 4 g of 5-methyl-*endo*-2-bicyclo[3.1.0]hexanol and 4 g of freshly distilled aluminum isopropoxide in 30 ml of anhydrous isopropyl alcohol containing a few drops of dry acetone was refluxed for 2.5 hr (longer reflux time sufficient to establish true equilibrium was found to lead to an intractable product). The isopropyl alcohol was then removed by distillation under reduced pressure. About 100 ml of ether was added to the residue, and the ether solution was washed with 10% NaOH and saturated NaCl solutions and dried. Distillation (40–50°, 2 mm) gave 3.5 g of a mixture containing approximately 53% of the desired 5-methyl-*exo*-2-bicyclo[3.1.0]hexanol. Glpc separation on a 2 m × 3/8 in. 20% 3-nitro-3-methylpimelonitrile on 60–80 mesh firebrick column enabled partial purification of the exo alcohol: nmr (CCl_4) δ 0.30 (m, 2, cyclopropyl), 1.3 (s, 3, CH_3), 1.7 (m, 5), 3.7 (s, 1, OH), and 4.1 (d, 1, J = 4 Hz,

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(14) W. G. Dauben and G. H. Berezin, *J. Amer. Chem. Soc.*, **89**, 3449 (1967).
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(17) W. G. Dauben, L. Schutte, R. E. Wolf, and E. J. Deviny, *J. Org. Chem.*, **34**, 2512 (1969).

CHOH). It was not possible, however, to obtain this material in a pure enough condition for elemental analysis, so it was used directly for preparation of the 3,5-dinitrobenzoate derivative.

Preparation of the 3,5-dinitrobenzoate in 82% yield was accomplished in the usual manner from reaction of the partially purified exo alcohol and 3,5-dinitrobenzyl chloride in pyridine at 0° followed by recrystallization from warm methylcyclohexane: mp 96–97°; nmr ($CDCl_3$) δ 0.4 (m, 2, cyclopropyl), 1.3 (s, 3, CH_3), 1.7 (m, 5), 5.3 (d, 1, J = 4 Hz, CHODNB), and 9.1 (s, 3, aromatic).

Anal. Calcd for $C_{14}H_{14}N_2O_6$: C, 54.90; H, 4.60; N, 9.14. Found: C, 54.68; H, 4.59; N, 9.14.

General Kinetic Procedures. The 80 volume % aqueous acetone was prepared in the following manner. Reagent grade acetone was dried by allowing it to slowly percolate through a 2 ft × 1 in. column packed with $^1/_{16}$-in. pellets of type 4A Linde Molecular Sieve and distilling it from powdered Type 4A Molecular Sieve through a 40-cm Widmer column. Then 800 ml of the dry acetone was mixed with 200 ml of redistilled water using an automatic pipet.

As an example of the usual kinetic procedure, 50 ml of a *ca.* 0.01 *M* solution of the 3,5-dinitrobenzoate in 80% aqueous acetone was prepared, and *ca.* 6-ml portions were sealed in Pyrex ampoules. A set of ampoules was immersed in an oil bath at the appropriate temperature and, after allowing about 10 min for temperature equilibration, a zero point was taken. The ampoules were cooled quickly in ice and allowed to come to room temperature, and 5-ml aliquots were taken from the tubes using a calibrated automatic pipet and quenched in 20 ml of dry acetone for titration. Titration for acid formed was done with *ca.* 0.01 *N* sodium methoxide in methanol using 3 drops of a 1% methanolic solution of bromothymol blue as the indicator. Infinity titers were determined in duplicate after about 10 half-lives for reaction. All runs were carried out in duplicate, and the reported values are the averages of two runs. The rate constants and thermodynamic values given in Table I are the most probable values calculated by computer by Professor L. E. Friedrich of the University of Rochester using a general least-squares program and an Eyring calculation, respectively. The values given in Table II were calculated by hand.

Hydrolysis Products of 1-ODNB and 2-ODNB. Approximately 0.2 g of the 3,5-dinitrobenzoate, dissolved in 5 ml of 80% aqueous acetone, was placed in a Pyrex ampoule. To this was added 0.2 g of finely powdered calcium carbonate, and the ampoule was sealed and heated at 99.6° for about 5 half-lives. The ampoule was then opened and an appropriate quantity of cyclohexanol was weighed in to serve as an internal standard in later glpc analyses. After work-up, the alcoholic products were analyzed by glpc on a 4 m × 0.25 in. column operated at 100° consisting of 2 m of 20% by weight diethylene glycol succinate (DEGS) and 2 m of 20% diglycerol on 60–80 mesh Chromosorb P. The remaining alcohol products were then converted into the corresponding acetates by reaction with 0.2 ml of acetic anhydride in 5 ml of pyridine for 24 hr at 0°. After work-up, the acetates were also analyzed on the 4-m DEGS–diglycerol column. This double analysis procedure was necessary because the *exo*-2-bicyclo[3.1.0]hexanol and cyclohexen-4-ol were not well separated by glpc. However, cyclohexen-4-yl acetate was well separated from the other products as their acetates, although the *endo*- and *exo*-2-bicyclo[3.1.0]hexyl acetates were not well separated. The identities of the alcohol products and their acetates, except for the minor cyclohexen-3-ol and its acetate, were determined by isolation by glpc and nmr examination. In all cases they were also determined by coinjection with authentic samples. The authentic samples of cyclohexen-3-ol and cyclohexen-4-ol were prepared using methods similar to those described by Burgstahler and Nordin[18] and Zelinsky and Titowa,[19] respectively. Small samples of the acetates needed for glpc retention time comparisons were prepared from the corresponding alcohols using acetic anhydride in pyridine.

The lack of significant amounts of olefinic hydrocarbon products was shown by the fact that the total yields of alcohols were close to theoretical, based on calculations using the internal standard and by separate injection of the initial product mixtures after work-up but before concentration onto a 2-m 20% NMPN column operated at 50°.

(18) A. W. Burgstahler and I. C. Nordin, *J. Amer. Chem. Soc.*, **83**, 198 (1961).

(19) N. D. Zelinsky and A. N. Titowa, *Ber.*, **64**, 1339 (1931).

Stability of *endo*-2-Bicyclo[3.1.0]hexanol under Hydrolysis Conditions. A 0.1-g sample of pure *endo*-2-bicyclo[3.1.0]hexanol was dissolved in 5 ml of 80% aqueous acetone containing 0.08 g of 3,5-dinitrobenzoic acid and 0.2 g of calcium carbonate, sealed in a Pyrex ampoule and heated in a 100° bath. After 100 hr reaction time, glpc analysis showed that the alcohol had rearranged to the extent of only about 5% to a mixture of *exo*-2-bicyclo[3.1.0]hexanol and cyclohexen-4-ol.

Recovery of the *endo*- and *exo*-2-Bicyclo[3.1.0]hexyl 3,5-Dinitrobenzoates. Approximately 0.3-g samples of the dinitrobenzoates were dissolved in 30 ml of 80% aqueous acetone containing a $CaCO_3$ buffer, sealed in Pyrex ampoules, and heated at 100° for periods of time sufficient for approximately 65% acid production. The unreacted dinitrobenzoates were isolated by removal of the acetone under reduced pressure, dissolving the remaining solids in ether, and washing the ether solutions with 10% sodium bicarbonate. Removal of the ether gave solids whose nmr spectra showed that no isomerization or interconversion of the dinitrobenzoates *via* ion-pair return had occurred during the course of the reactions. Also, after crude nonfractional crystallizations, the isolated dinitrobenzoates were found to have melting points close to those of the respective starting materials.

Deuterium Scrambling Studies in Hydrolysis. Samples (*ca.* 0.8 g) of the 2-deuterio-*endo*- and -*exo*-2-bicyclo[3.1.0]hexyl 3,5-dinitrobenzoates were dissolved in 25 ml of 80% aqueous acetone containing a calcium carbonate buffer and heated for about 10 half-lives. After work-up, the alcoholic products were separated into an *exo*-2-bicyclo[3.1.0]hexanol plus cyclohexen-4-ol fraction and an *endo*-2-bicyclo[3.1.0]hexanol fraction by glpc on a 4-m 20% DEGS–diglycerol column. The amount of deuterium at various locations in the hydrolysis products contained in the above fractions was determined by nmr as follows. The per cent vinylic deuterium in the cyclohexen-4-ol product was calculated using the ratio of the H_4 to the vinylic proton absorptions and assuming no loss of deuterium in the solvolysis. For the *endo*- and *exo*-2-bicyclo[3.1.0]hexanol products, the per cent deuterium at their 2 positions was determined using their cyclopropyl methylene protons as internal standards. Duplicate runs were carried out in each case.

Deuterium Scrambling Studies by Perchloric Acid Catalyzed Rearrangement in Acetic Acid. The samples of 2-deuterio-*endo*-2-bicyclo[3.1.0]hexanol and 2-deuterio-*exo*-2-bicyclo[3.1.0]hexyl acetate (approximately 0.5 g) were each dissolved in 5 ml of glacial acetic acid containing 0.5 wt % of 70% aqueous perchloric acid and heated at 50° for 30 min in sealed Pyrex ampoules. The resulting dark blue solutions were worked up by pouring into 35 ml of *n*-pentane, and washing with water and 10% sodium bicarbonate solutions. After drying and concentration by distillation through a short glass helices column, samples of the pure cyclohexen-4-yl acetate products were separated by glpc on the 4-m 20% DEGS–diethylene glycol column for nmr examination for per cent vinylic deuterium.

Hydrolysis Products of 8-ODNB. A 1.0-g sample of 5-methyl-*endo*-2-bicyclo[3.1.0]hexyl 3,5-dinitrobenzoate (**8**-ODNB) was dissolved in 25 ml of 80% aqueous acetone containing a $CaCO_3$ buffer, placed in a Pyrex ampoule, sealed, and heated at 100° for 5 hr. After work-up, analysis by glpc on a 2-m 20% DEGS column on 80–100 mesh Chromosorb W showed that the product was almost entirely 4-methylcyclohexen-4-ol, accompanied by less than 10% of other alcoholic products: nmr (CCl_4) δ 1.0 (s, 2, CH_2), 1.4 (m, 4), 2.0 (s, 3, CH_3), 3.65 (s, 1, OH), and 5.5 (s, 2, *vinylic*). The mass spectrum at 70 eV showed a parent peak at *m/e* 112. A sample collected by glpc was submitted for microanalysis and gave satisfactory results for % carbon but unsatisfactory results (off by 0.77% from theory) for % hydrogen. Unfortunately, insufficient material was available for further purification from column packing materials to obtain a better analysis.

A control run for the stability of 5-methyl-*endo*-2-bicyclo[3.1.0]-hexanol (**8**-OH) under the same conditions as the product run, and with added 3,5-dinitrobenzoic acid, showed the rearrangement of only about 15% of the **8**-OH to 4-methylcyclohexen-4-ol.

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