Reactions of the Classical 3-Bicyclo[3.1.0]hexyl Cation. Preparation and Acetolysis of the *endo*- and *exo*-2-Bicyclo[3.1.0]hexyl *p*-Toluenesulfonates[1a,b]

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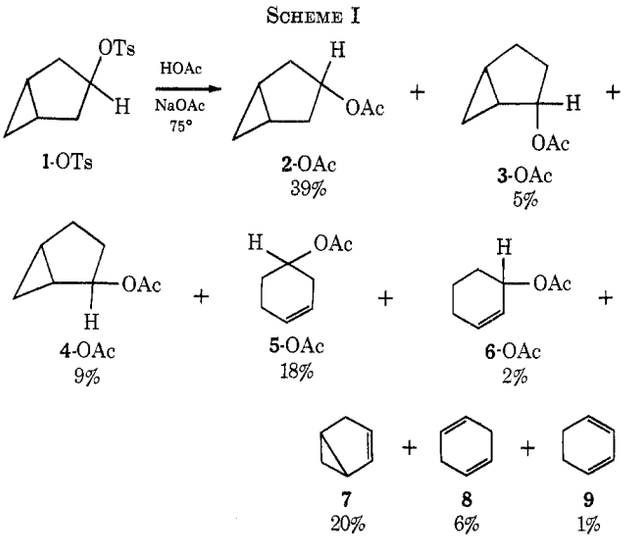
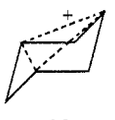
Preparation of the isomeric *endo*- and *exo*-2-bicyclo[3.1.0]hexyl *p*-toluenesulfonates (**3**-OTs and **4**-OTs) and determination of their kinetics and products of acetolysis are described. Both **3**-OTs and **4**-OTs react at similar, high rates, and give within experimental error identical product mixtures consisting of about 16% **3**-OAc, 36% **4**-OAc, and 48% cyclohexen-4-yl acetate at 24°. Using the product results from acetolysis of **3**-OTs and **4**-OTs, together with those reported in the literature for acetolysis of cyclohexen-4-yl *p*-toluenesulfonate, postulation of the nature of the processes involved in formation of the complex mixture of products from acetolysis of *trans*-3-bicyclo[3.1.0]hexyl *p*-toluenesulfonate is made.

In connection with their investigation of the nature and behavior of the unsubstituted trishomocyclopropenyl cation, Winstein and coworkers[3] observed that acetolysis at 75° of *trans*-3-bicyclo[3.1.0]hexyl *p*-toluenesulfonate (**1**-OTs) gave the complex mixture of products shown in Scheme I. On the other hand, acetolysis of *cis*-3-bicyclo[3.1.0]hexyl *p*-toluenesulfonate (**2**-OTs) at 75°, which proceeds primarily *via* formation of the symmetrical trishomocyclopropenyl cation intermediate (**10**), gave only **2**-OAc and **1**-OAc in yields of 99 and 1%, respectively.

SCHEME I





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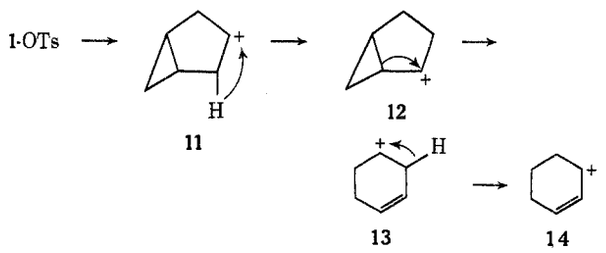
Isotopic labeling studies[3] showed that the 39% yield of **2**-OAc obtained on acetolysis of **1**-OTs must have arisen simply from SN2 displacement by solvent acetic acid on **1**-OTs rather than *via* intermediate formation of **10**. However, the exact natures of the processes leading to the other seven products are not readily apparent, although their formation can be rationalized in simple classical terms by the series of rearrangements yielding the cation intermediates **12** to **14** shown below,



from each of which products are obtained. Thus, to obtain further information regarding the nature of the processes involved in product formation in acetolysis of **1**-OTs, we initiated a study involving direct generation of the 2-bicyclo[3.1.0]hexyl cation (**12**) by acetolysis of the *endo*- and *exo*-2-bicyclo[3.1.0]hexyl *p*-toluenesulfonates (**3**-OTs and **4**-OTs).

Results

Preparation of 3-OTs and 4-OTs.—The *endo*-2-bicyclo[3.1.0]hexanol (**3**-OH) precursor of **3**-OTs was prepared for this study by stereospecific addition of the Simmons–Smith reagent to cyclopenten-3-ol.[4] This was then equilibrated with aluminum isopropoxide in refluxing isopropyl alcohol to a mixture containing 65% of the exo alcohol **4**-OH, which was purified by glpc. Preparation of the *p*-nitrobenzoate or 3,5-dinitrobenzoate ester derivatives of these isomeric alcohols presented no difficulties. However, attempts to prepare the *p*-toluenesulfonate ester derivatives through reaction of **3**-OH or **4**-OH with *p*-toluenesulfonyl chloride by the usual method in pyridine at 0°, or using a special technique[5] at −78°, failed. In these cases only the presumed alkylpyridinium tosylate salts could be isolated.

Both **3**-OTs and **4**-OTs were finally prepared using the technique of Wiberg and coworkers[6] involving reaction of the alcohols with *p*-toluenesulfonyl chloride and powdered potassium hydroxide in ether. Upon addition of pentane and cooling both crystallized as white

(1) (a) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. (b) A portion of the work reported was carried out by E. C. F. while a Postdoctoral Fellow in Chemistry during 1961–1962 at the University of California, Los Angeles. The remainder was taken in part from the Ph.D. Dissertation of M. A. S., University of California, Davis, 1971.

(2) Deceased, November 23, 1969.

(3) S. Winstein, E. C. Friedrich, R. Baker, and Y. Lin, *Tetrahedron, Suppl 8, Part II*, 621 (1966).

(4) W. G. Dauben and G. H. Berezin, *J. Amer. Chem. Soc.*, **85**, 468 (1963).

(5) E. C. Friedrich and S. Winstein, *ibid.*, **86**, 2721 (1964).

(6) K. B. Wiberg, B. R. Lowry, and T. H. Colby, *ibid.*, **83**, 3998 (1961).

solids which, however, after a few minutes at room temperature or a few hours at −25° decomposed to deep blue liquids. These after a few days resolidified to tan solids, which were shown in both cases to consist entirely of cyclohexen-4-yl *p*-toluenesulfonate (**5**-OTs). This is similar to the behavior observed by Wiberg and coworkers[6] for their *endo*-5-bicyclo[2.1.1]hexyl *p*-toluenesulfonate, which also rearranged on standing at room temperature to **5**-OTs *via* melting to a deep blue liquid and resolidification. Thus, because of this extremely low stability of **3**-OTs and **4**-OTs it was not possible to obtain their microanalyses and spectra. Also, it was necessary to store and employ them as solutions in ether for both the kinetic and product studies which follow.

Kinetic Studies.—The rates of acetolysis of **3**-OTs and **4**-OTs were observed to be much too fast to measure using the usual titrimetric techniques even at 25°. Therefore, only "one-point half-life" rate constants could be obtained as described in the Experimental Section. These are shown in Table I. Within experimental error, both **3**-OTs and **4**-OTs underwent acetolysis at the same rate. However, both were highly reactive, as is evidenced by the observation that in acetolysis they are approximately 10^5 times faster than cyclopentyl *p*-toluenesulfonate[7] and 10^4 times faster than nortricyclyl *p*-toluenesulfonate.[8]

Table I
Rates of Acid Production in Acetic Acid and Acetone

ROTs	Solvent	Temp, °C	k_1, sec^{-1}
3-OTs	98% HOAc 2% Et_2O	24.6	$(6.7 \pm 0.2) \times 10^{-2}$ [a]
4-OTs	98% HOA 2% Et_2O	25.1	$(7.0 \pm 0.2) \times 10^{-2}$ [a]
3-OTs	97% Acetone 3% Et_2O	25.0	$(3.53 \times 0.05) \times 10^{-5}$ [b]
4-OTs	97% Acetone 3% Et_2O	25.0	$(2.66 \pm 0.09) \times 10^{-5}$ [c]

[a] Calculated from averages of triplicate "one-point half-life" runs; errors are the maximum deviations from the averages. [b] Infinity is *ca.* 95% of that in acetic acid. [c] Infinity is *ca.* 100% of that in acetic acid.

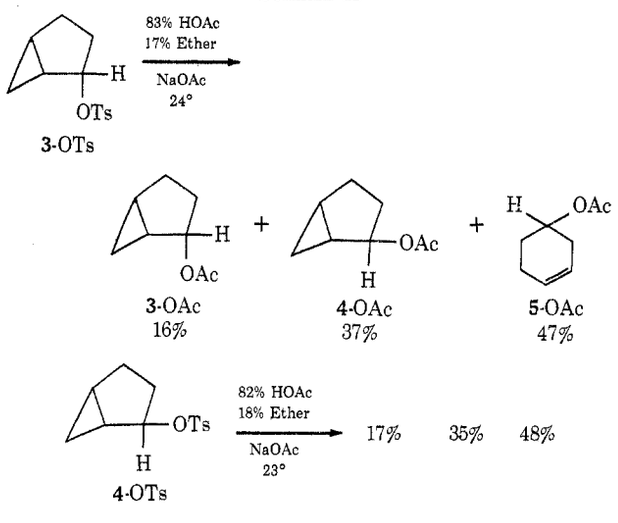
Although the rates of **3**-OTs and **4**-OTs in acetic acid were too fast for highly accurate measurement, they were quite manageable in dry acetone at 25.0°. In this solvent the rates of acid production for both isomers followed good first-order kinetics, with the endo isomer **3**-OTs being 1.3 times faster than the exo isomer **4**-OTs. These results are also shown in Table I.

In connection with the question of whether possible ion-pair return occurs during reaction of **3**-OTs or **4**-OTs to give unreactive **5**-OTs, it is important to note that in the rate runs in the poor ionizing solvent dry acetone the experimental infinities obtained were almost identical with those observed in acetolysis. Thus, it is reasonable to conclude that neither in acetic acid nor in dry acetone is ion-pair return to give unreactive **5**-OTs an important process. This could not be determined directly from experimental infinity titer data, since it was not possible to know the exact concentrations of **3**-OTs or **4**-OTs in the ether stock solution in which they were stored and used.

Although it was not possible to directly prove the structures of **3**-OTs and **4**-OTs by microanalytical and spectral methods, the kinetic results given above clearly show that we are dealing with the correct compounds. In subsequent work it has been found that in the solvolyses of the well-defined *endo*- and *exo*-2-bicyclo[3.1.0]-hexyl 3,5-dinitrobenzoates in 80% aqueous acetone at 80°[9] and the corresponding *N*-methyl-4-oxopyridinium iodides in 80% aqueous ethanol at 86°[10] the endo isomers react at rates approximately 1.2 to 1.3 times faster than the exo isomers, and they are faster in rate by factors of 10^4 to 10^5 over the cyclopentyl derivatives. Also, in neither of these other systems is ion-pair return to unreactive cyclohexen-4-yl derivatives observed.

Product Studies.—For product studies, **3**-OTs and **4**-OTs were allowed to react in acetic acid buffered with sodium acetate at room temperature for about 10 half-lives. Because it was necessary to use the tosylates as solutions in ether, this resulted in 17–18 volume % ether also being present in the acetic acid during the acetolysis product runs. Both **3**-OTs and **4**-OTs gave, within experimental error, by glpc analysis of runs carried out in duplicate, the same mixture of three acetates shown in Scheme II.[11] Less than 1% of any hydrocarbon elimination products were observed. Also, no evidence for any cyclohexen-4-yl tosylate (**5**-OTs) ion-pair return product was obtained. Based on the infinity titers obtained in acetolysis of **3**-OTs and **4**-OTs as a measure of their concentrations in the ether stock solutions in which they were employed, use of internal standards in the glpc analyses showed that the combined yields of **3**-OAc, **4**-OAc, and **5**-OAc were close to theoretical starting with either **3**-OTs or **4**-OTs.

Scheme II



To be able to properly compare the nature and ratio of the acetolysis products obtained from **3**-OTs and **4**-OTs with those obtained from **1**-OTs, it would have

(7) S. Winstein and J. Sonnenberg, *J. Amer. Chem. Soc.*, **83**, 3235 (1961).
(8) Unpublished work of H. J. Schmid and S. Winstein.
(9) (a) E. C. Friedrich and M. A. Saleh, *Tetrahedron Lett.*, 1373 (1971); (b) E. C. Friedrich and M. A. Saleh, *J. Amer. Chem. Soc.*, in press.
(10) G. H. Schmid and A. Brown, *Tetrahedron Lett.*, 4695 (1968).
(11) These product results have already been quoted as unpublished work of Friedrich and Winstein by K. B. Wiberg, R. A. Fenoglio, V. Z. Williams, and R. W. Ubersax, *J. Amer. Chem. Soc.*, **92**, 568 (1970).

been better to also do acetolysis product studies on 3-OTs and 4-OTs in pure acetic acid at 75°, the conditions used in acetolysis of 1-OTs. However, this was not possible owing to the high reactivities of 3-OTs and 4-OTs and the fact that it was necessary to employ them as solutions in ether. Nevertheless, to obtain data of use in telling us something about the effects of solvent and temperature on the nature of the products obtained on acetolysis of the 2-bicyclo[3.1.0]hexyl cation (12), we carried out acetolysis product studies on the 2-bicyclo[3.1.0]hexyl 3,5-dinitrobenzoates 3-ODNB and 4-ODNB at 100°.

Initial controls carried out on the most reactive of the possible acetolysis products 3-OAc showed that it was not stable under the acetolysis reaction conditions at 100°. Heating a pure sample of 3-OAc in acetic acid buffered with sodium acetate and containing 3,5-dinitrobenzoic acid at 100° for 54 hr resulted in 54% rearrangement to give a mixture of 4-OAc and 5-OAc. However, this product instability does not present any serious problems, since on rearrangement only 4-OAc and 5-OAc are obtained and, in any case, direct comparison of the product ratios obtained from 3,5-dinitrobenzoate acetolysis with those obtained from tosylate acetolysis is not possible because of the differences in leaving groups. The primary purpose for doing the 3,5-dinitrobenzoate acetolysis at 100° was to learn something of the effects of temperature on the nature of the products, and this should be relatively independent of the nature of the leaving group.

Thus, samples of 3-ODNB and 4-ODNB were allowed to react in acetic acid buffered with sodium acetate at 100° for 50 hr. This period of time was estimated to be sufficient for approximately 5 half-lives for acetolysis of the dinitrobenzoates at 100°. Both isomeric dinitrobenzoates were found to give, within experimental error, identical product mixtures consisting of approximately 24% 3-OAc, 28% 4-OAc, 37% 5-OAc, 1% 6-OAc, and 10% of ion-pair return product 5-ODNB. It is reasonable that ion-pair return to unreactive 5-ODNB is seen here but is not observed in acetolysis of the *p*-toluenesulfonates, since the 3,5-dinitrobenzoate anion is more nucleophilic than is the *p*-toluenesulfonate anion.

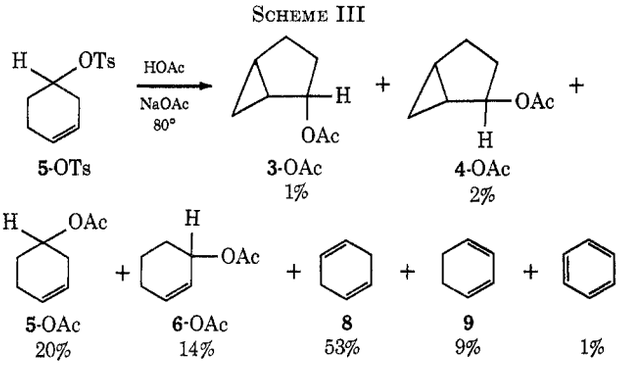
From the results obtained in acetolysis of 3-ODNB and 4-ODNB in acetic acid at 100° several important conclusions may be drawn regarding what might be predicted to be the product-forming behavior of 3-OTs and 4-OTs on acetolysis in pure acetic acid at 75°. First, it is apparent that even at 75° the product mixtures obtained from acetolysis of either 3-OTs or 4-OTs should be identical. Second, one would expect that at 75°, as at 25°, only 3-OAc, 4-OAc, and 5-OAc should be formed in significant yields from acetolysis of 3-OTs or 4-OTs, although the product ratios at 75 and 25° may be different.

Discussion

The kinetic and product results obtained in acetolysis of the *endo*- and *exo*-2-bicyclo[3.1.0]hexyl *p*-toluenesulfonates (3-OTs and 4-OTs) indicate that ionization of these systems must proceed with cyclopropyl participation, and that the 2-bicyclo[3.1.0]hexyl cation intermediate or intermediates involved in product formation must be considerably stabilized *via* charge delocalization from C_2 into the cyclopropane ring. The observation that 3-OTs and 4-OTs on acetolysis reacted at similar rates and gave identical mixtures of products was initially unexpected for stereoelectronic reasons.[12] However, a likely explanation now available for this behavior is that both isomeric tosylates react *via* similar activated complexes and a single bisected bishomoallyl cation intermediate in which delocalization of positive charge on C_2 simultaneously involves both the 1,5 and 1,6 bonds of the cyclopropane ring.[9]

It is readily apparent from the acetolysis product studies on 3-OTs and 4-OTs that the 2-bicyclo[3.1.0]-hexyl cation (12, or better as a charge-delocalized structure) is a reasonable source for the 2-bicyclo-[3.1.0]hexyl acetate (3-OAc and 4-OAc) and at least a portion of the cyclohexen-4-yl acetate (5-OAc) products obtained on acetolysis of 1-OTs. However, another intermediate must be involved in formation of the cyclohexen-3-yl acetate (6-OAc) and the 1,3- and 1,4-cyclohexadiene (9 and 8) products. This intermediate is most likely the cyclohexen-4-yl cation (13), and this conclusion is supported by product studies which have been reported. Thorton and Moore[13] found that acetolysis of cyclohexen-4-yl tosylate (5-OTs) at 80° gives the mixture of products summarized in Scheme III.

SCHEME III



Also, in a similar study carried out independently at 100° by Friedrich, Battiste, and Winstein[14] the substantially identical results 1% 3-OAc, 1% 4-OAc, 22% 5-OAc, 14% 6-OAc, 47% 8, 11% 9, and 4% benzene were obtained.[15]

Thus, if one now makes the reasonable assumption that the nature and ratios of the products obtained *via* acetolysis of the independently generated 2-bicyclo-[3.1.0]hexyl (12) and cyclohexen-4-yl (13) cations are indicative of the nature and ratios of the intermediates involved in formation of the products obtained from acetotysis of the *trans*-3-bicyclo[3.1.0]hexyl tosylate (1-OTs), Scheme IV for the reaction pathway in acetolysis of 1-OTs may be written. Based on this scheme, it may be concluded that, of the products obtained from acetolysis of 1-OTs, 59% arises either *via* the classical

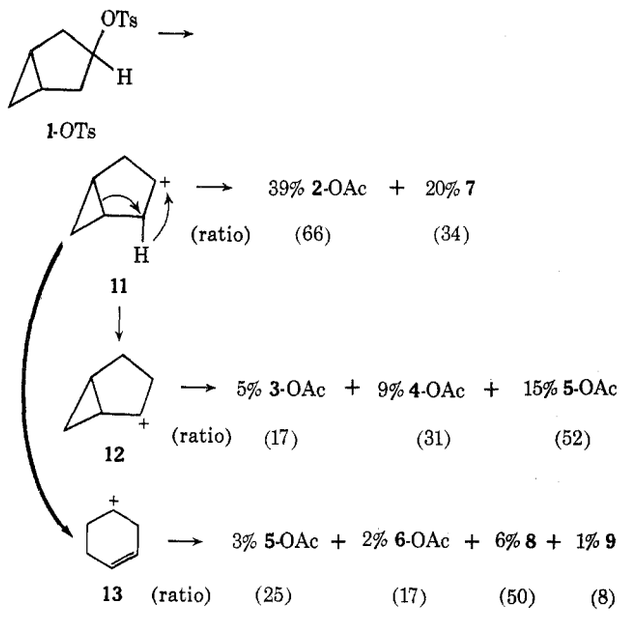
(12) C. D. Poulter, E. C. Friedrich, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 4274 (1970), and references cited therein.

(13) R. L. Thornton, Ph.D. Thesis, Massachusetts Institute of Technology, 1961. Thesis supervisor: W. R. Moore.

(14) Unpublished work of E. C. Friedrich, M. A. Battiste, and S. Winstein.

(15) M. Hanack and W. Keberle, *Chem. Ber.*, **96**, 2937 (1963), also reported obtaining the acetates 3-OAc and 6-OAc in similar ratio from acetolysis of 5-OTs at 70°, but did not investigate the yields or nature of the hydrocarbon products.

Scheme IV



3-bicyclo[3.1.0]hexyl cation (**11**) or *via* Sn2 and E2 reactions by solvent on **1**-OTs, 29% arises from the 2-bicyclo[3.1.0]hexyl cation (**12**), and 12% results from the cyclohexen-4-yl cation (**13**). It is also of interest to note that the reaction scheme requires cyclopropane ring opening to be concerted with 2,3-hydride shift in **11** in giving **13**, since rearrangement of **12** to **13** was not observed. Formation of **12** and **13** may furthermore be concerted with ionization of **1**-OTs, although consideration of the effects of 2-alkyl substituents on the rates of solvolysis of **1**-OTs[16] casts some doubt on the likelihood of this possibility.

Experimental Section

All melting points and boiling points are uncorrected. Elemental analyses were performed by Miss Heather King, University of California, Los Angeles.

endo-**2-Bicyclo[3.1.0]hexanol (3-OH).**—Using a procedure similar to that reported by Dauben and Berezin,[4] 40 g (0.047 mol) of cyclopenten-3-ol was reacted with 88 g (1.33 mol) of zinc–copper couple, 250 g (0.93 mol) of methylene iodide, and 0.4 g of iodine in 600 ml of ether. The product was distilled under vacuum through a 30-cm glass spiral column to obtain, along with about 5 g of unreacted starting material, 20 g of *endo*-2-bicyclo[3.1.0]hexanol, bp 75–76° (20 mm), n^{25}D 1.4771, which was better than 99% pure [lit.[17] bp 76° (17 mm); n^{20}D 1.4788]. The *p*-nitrobenzoate derivative was prepared in the usual manner using a 10% excess of *p*-nitrobenzoyl chloride in cold pyridine and was recrystallized twice from warm methylcyclohexane, mp 81.5–83.0°.

Anal. Calcd for $C_{13}H_{13}NO_4$: C, 63.15; H, 5.30; N, 5.67. Found: C, 63.43; H, 5.27; N, 5.90.

endo-**2-Bicyclo[3.1.0]hexyl *p*-Toluenesulfonate (3-OTs).**—A magnetically stirred solution containing 1.0 g (0.0102 mol) of **3**-OH in about 25 ml of anhydrous ether was cooled in an ice bath and 1.95 g (0.0102 mol) of *p*-toluenesulfonyl chloride was added. After the tosyl chloride dissolved, 2.0 g of powdered potassium hydroxide (95%) was added in 1-g portions. Stirring was then continued for 1 hr at 0°. At the end of this time the odor of tosyl chloride could no longer be detected in the solution. About 1 g of anhydrous potassium carbonate was added and stirring was continued for another 15 min. The reaction mixture was filtered with suction and the solids were washed well with ether. Titration of a 0.5-ml aliquot of the combined ether solutions (*ca.* 40 ml) in 20 ml of acetic acid to a stable bromophenol blue end point required 8.0 ml of 0.01527 *M* sodium acetate in acetic acid. Storage of the ether solution of **3**-OTs was done at −25° over solid potassium carbonate.

Because of the extremely low stability of **3**-OTs, it was impossible to isolate it in pure form for microanalysis or determination of spectra. Concentration of the ether solution, addition of pentane, and cooling to −25° produced white crystals which when filtered melted after a few minutes at room temperature to a deep blue liquid. This again resolidified after a few days to tan crystals melting at 47–49° after recrystallization from methylcyclohexane. Mixture melting point behavior and ir spectrum indicated that this material was pure cyclohexen-4-yl tosylate (**5**-OTs) (lit.[15] mp 50–50.5°).

exo-**2-Bicyclo[3.1.0]hexanol (4-OH).**—A solution of 5.0 g of *endo*-2-bicyclo[3.1.0]hexanol, 5.0 g of freshly distilled aluminum isopropoxide, and 1 ml of dry acetone in 100 ml of anhydrous isopropyl alcohol was heated under reflux for 114 hr. The resulting equilibrium mixture contained 65% **4**-OH and 35% **3**-OH. The reaction mixture was then worked up by the addition of 30 ml of saturated ammonium chloride solution and 150 ml of ether. The ether solution was washed with several 50-ml portions of water, dried over magnesium sulfate, and concentrated. Purification of **4**-OH was accomplished by preparative scale glpc techniques in two passes through a 2 m × 1 in. 30% NMPN on 40/60 mesh firebrick column run at 120°. The *exo*-2-bicyclo[3.1.0]hexanol fraction collected was flash distilled under vacuum to give 1.0 g of **4**-OH, n^{25}D 1.4754, which was contaminated with < 9% **3**-OH [lit.[17] bp 73.5° (17 mm), n^{20}D 1.4801].

Anal. Calcd for $C_6H_{10}O$: C, 73.47; H, 10.20. Found: C, 73.19; H, 10.44.

The *p*-nitrobenzoate derivative of **4**-OH was prepared in the usual manner using a 10% excess of *p*-nitrobenzoyl chloride in cold pyridine and recrystallized twice from warm methylcyclohexane, mp 66.5–68.5°.

Anal. Calcd for $C_{13}H_{13}NO_4$: C, 63.15; H, 5.30; N, 5.67. Found: C, 63.13; H, 5.28; N, 5.88.

exo-**2-Bicyclo[3.1.0]hexyl *p*-Toluenesulfonate (4-OTs).**—An ether solution of **4**-OTs was prepared by the same procedure as that described for **3**-OTs from 1.0 g of **4**-OH, 1.95 g of *p*-toluenesulfonyl chloride, and 2.0 g of powdered potassium hydroxide in about 25 ml of ether. Titration of a 0.5-ml aliquot of the combined ether solutions (*ca.* 40 ml) in acetic acid required 7.8 ml of 0.01527 *M* sodium acetate solution. The tosylate **4**-OTs exhibited the same extremely low stability and melting behavior on isolation as did **3**-OTs.

Tosylate Acetolysis Kinetics.—Anhydrous acetic acid was prepared as previously described.[18] Because the rates of acetolysis of **3**-OTs and **4**-OTs were observed to be much too fast to measure using the usual titrimetric techniques even at 25°, only "one-point half-life" rates could be obtained. As an example of the usual procedure, 2.35 ml of 0.01527 *M* sodium acetate in dry acetic acid was added to 20 ml of dry acetic acid containing 4 drops of bromophenol blue indicator in a 50-ml erlenmeyer flask. Then, while the solution was being vigorously stirred, 0.25 ml of an ether solution of *exo*-2-bicyclo[3.1.0]hexyl tosylate (**4**-OTs) was added rapidly from a hypodermic syringe and the time for the indicator change was measured with a stopwatch. The temperature of the solution was then immediately determined and titration was continued until a stable end point was reached. This end point titer, which had also been previously measured on a separate sample, was 4.70 ml. Runs were always done in triplicate and the average reaction half-lives thus obtained were 10.4 ± 0.2 sec for **3**-OTs at 24.6° and 10.0 ± 0.2 sec for **4**-OTs at 25.1°.

Tosylate Kinetics in Dry Acetone.—Dry acetone was prepared as follows. About 1 l. of 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 glass helices column. Tests for dryness with Karl Fischer reagent showed that it contained less than 1 mg of water per 1 ml. The dried acetone was then stored under dry nitrogen before use. Kinetics were run using the usual sealed ampoule procedure, and titration of aliquotes for acid formed was done rapidly after

(16) T. Norin, *Tetrahedron Lett.*, 37 (1964).
(17) M. Hanack and H. Allmendinger, *Chem. Ber.*, **97**, 1669 (1964).
(18) A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, **78**, 2770 (1956).

dilution in cold, dry acetone using standardized sodium methoxide in methanol to a bromothymol blue endpoint.

Tosylate Acetolysis Products.—As an example of the usual procedure, 1 ml of the ether stock solution of **3**-OTs or **4**-OTs was added rapidly from a hypodermic syringe to 5 ml of rapidly stirred 0.1 *M* sodium acetate in acetic acid containing about 10 mg of benzene internal standard at room temperature. After reacting at room temperature for about 2 min, the reaction mixture was worked up and the acetolysis products were determined by glpc using a similar procedure to that described earlier[3] for analysis of the acetate and olefin products obtained from acetolysis of *trans*-3-bicyclo[3.1.0]hexyl tosylate.

***endo*- and *exo*-2-Bicyclo[3.1.0]hexyl-3,5-Dinitrobenzoates (3-ODNB and 4-ODNB).**—These were samples, mp 122–124° (lit.[17] mp 124–124.8°) and 96–98° (lit.[17] mp 98–98.6°), respectively, prepared as described elsewhere.[9b]

Stability of *endo*-2-Bicyclo[3.1.0]hexyl Acetate (3-OAc) under Acetolysis Conditions at 100°.—A small sample of **3**-OAc was prepared by the reaction of pure **3**-OH with acetic anhydride in pyridine, bp 103–104° (20 mm), n^{25}D 1.4530 [lit.[19] bp 65–68° (15 mm)]. Two separate Pyrex ampoules were made up, each containing about 0.15 g (1.1 mmol) of **3**-OAc, 0.1 g (0.5 mmol) of 3,5-dinitrobenzoic acid, and 0.1 g (1.2 mmol) of sodium acetate dissolved in 5 ml of dry acetic acid. The ampoules were sealed, heated at 100° for periods of 10 and 54 hr, respectively, and then worked up and analyzed by glpc using the procedure described below for studying the acetolysis products of **3**-ODNB and **4**-ODNB at 100°. The mixtures were found to consist of 82% **3**-OAc, 5% **4**-OAc, and 13% **4**-OAc and 46% **3**-OAc, 23% **4**-OAc, and 31% **5**-OAc, respectively.

3,5-Dinitrobenzoate Acetolysis Products.—As an example of the usual procedure, 0.23 g (0.8 mmol) of **3**-ODNB was dissolved in 8 ml of 0.11 *M* sodium acetate in dry acetic acid, sealed in a Pyrex ampoule, and heated at 100° for 50 hr. The ampoule was then opened, and a cyclohexyl acetate internal standard was weighed in. The contents of the ampoule were poured into 40 ml of *n*-pentane, and the pentane solution was washed with water and 5% aqueous sodium carbonate, dried over magnesium sulfate, and concentrated to about 3 ml by careful distillation through a short glass helices column. Cooling the pentane solution in ice caused **5**-ODNB to crystallize out. This was filtered and weighed, and its structure was determined by comparing its melting point and nmr spectrum with those of an authentic sample[20] prepared by us from **5**-OH. The acetate products were then analyzed by glpc on a 4 m × 0.25 in. column packed half with 20% diethylene glycol succinate (DEGS) and half with 20% diglycerol on 60/80 mesh Chromosorb P. The remaining acetates were then reduced in 50 ml of dry ether with 0.3 g of $LiAlH_4$. After work-up by adding saturated NH_4Cl solution, drying over magnesium sulfate, and concentrating the ether solution to about 4 ml, the resulting alcohols were also analyzed on glpc on the column described above. The reasons for this double analysis procedure and the methods used to identify the volatile products are described elsewhere.[9b] It was found that acetolysis of **3**-ODNB gave 24% **3**-OAc, 28% **4**-OAc, 37% **5**-OAc, 1% **6**-OAc, and 10% **5**-ODNB, and acetolysis of **4**-ODNB gave 23% **3**-OAc, 25% **4**-OAc, 41% **5**-OAc, 1% **6**-OAc, and 10% **5**-ODNB.

Registry No.—**3**-OH, 822-58-2; **3**-OH *p*-nitrobenzoate, 37816-89-0; **3**-OTs, 37816-90-3; **3**-OAc, 698-56-6; **3**-ODNB, 34272-26-9; **4**-OH, 822-59-3; **4**-OH *p*-nitrobenzoate, 37816-94-7; **4**-OTs, 37816-95-8; **4**-ODNB, 34272-27-0.

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Monocyclic Allenes. The Synthesis of 3,8,9-Cycloundecatriene-1,6-dione and 12-Oxabicyclo[7.2.1]dodeca-5,6,9,11-tetraen-3-one, a Furanophane Containing an Allene Group

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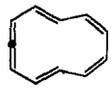
3,8,9-Cycloundecatriene-1,6-dione (**5**) can be prepared from the readily available 4,4,9,9-tetramethoxy-1,6-cyclodecadiene (**2**) *via* the dibromocarbene adduct **3**. The adduct **3** can also be converted into 4,4,10,10-tetramethoxy-6,7-cycloundecadiene-1,2-diol (**8**), which on acid treatment gives 12-oxabicyclo[7.2.1]dodeca-5,6,9,11-tetraen-3-one (**9**), a novel furanophane containing an allene group.

Only a few monocyclic allenes have been prepared in which other functional groups are present. Such molecules are of interest, since the interactions between the functional group and the allene moiety might be unusual. Further, these systems serve as potential precursors of the fully unsaturated monocyclic systems containing an allene group. Heilbronner[1] has suggested that the "Möbius" array of π orbitals in the [4*n*]annulenes might be favored over the "Hückel" array. The introduction of an allene group into a fully conjugated cycle provides an enforced dislocation of the π system. Furthermore, if the allene group is treated as a Möbius array, as suggested by Zimmerman,[2] the possibility exists for a Möbius interaction around the cyclic unsaturated system. The present paper describes the preparation of a number of 11-membered monocyclic allenes containing functional groups, together with a preliminary investigation into methods of converting these molecules into the 12π–11C monocyclic allene **1**.



1

The precursor for the synthesis of the allenes was the bicyclic dibromide **3**. This molecule is obtained[3] by the reaction of dibromocarbene with tetramethoxycyclodecadiene **2**, the latter compound being readily available from naphthalene.[4] Treatment of **3** with methyllithium at −10° gave the allene **4**, mp 75–76°, in 73% yield. The ir spectrum of **4** showed a band at 1980 cm^{-1}, characteristic of an allene,[5] and the nmr

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