The volatile products were examined by vapor phase chromatography using a silicone column at 120°. Separation of the major product gave 0.20 g. (24%) of bromides; at the same time, the ratio of 1-norbornyl acetate to bicyclo[2.1.1]hexane-methyl acetate was found to be 87:13 and the ratio of bromides to acetates was 91:9. Since 1-norbornyl bromide and bicyclo[2.1.1]hexane-1-methyl bromide could not be separated by vapor phase chromatography, the extent of rearrangement was determined by examining the n.m.r. spectrum of the mixture. There was about 25% of unrearranged bromide in the mixture.

Kinetic Experiments. Materials.—Practical grade *m*-cresol was distilled from zinc dust, collecting the portion having b.p. 88–89° at 9 mm. The 40% ethanol was prepared by mixing two volumes of C.P. absolute ethanol with three volumes of carbon dioxide-free distilled water and had $n^{23}D$ 1.3543. The glacial acetic acid used contained 1% acetic anhydride in order to ensure the absence of water.

The chlorides and bromides were purified by vapor phase chromatography followed by redistillation or resublimation. The tosylates were purified by recrystallization.

Solvolysis of Bridgehead Chlorides in *m*-Cresol.—Approximately 0.03 *M* solutions of the chlorides in *m*-cresol were prepared and 5-ml. portions were sealed in ampoules. They were heated for appropriate times in a micro-Carius furnace and the temperature was determined using a thermocouple. After cooling, the contents of a tube was transferred to a beaker using 40 ml. of reagent grade acetone and the chloride was titrated potentiometrically at 0° with standard 80% ethanolic silver nitrate solution (0.01 *N*). At 322°, the rate constant for 1-chlorobicyclo[2.2.1]heptane was $4.9 \pm 1.3 \times 10^{-7}$ sec.$^{-1}$, whereas at 204°, the rate constant for 1-chlorobicyclo[2.1.1]-hexane was $1.25 \pm 0.08 \times 10^{-4}$ sec.$^{-1}$.

Solvolysis of Bridgehead Bromides in 40% Ethanol.—Approximately 0.01 *M* solutions of the bromides in 40% ethanol were prepared and 5-ml. portions were sealed in ampoules. Tubes for a single run were immersed in a bath simultaneously and withdrawn at regular intervals. The samples were titrated with 0.0116 *N* sodium hydroxide solution to a phenolphthalein end point. The rate constants are given in Table IV.

Acetolysis of Bridgehead Carbinyl Tosylates.—Approximately 0.03 *M* solutions of the tosylates in glacial acetic acid were heated at 80.1°, and at regular intervals, 25-ml. aliquots were removed and cooled. Titration with standard sodium acetate in glacial acetic acid (0.05 *N*) was performed to the bromphenol blue end point. The rate constants were given in the Discussion section.

In order to determine the rate of internal return to the 1-norbornyl tosylate, the tosylates were recovered from the aliquots titrated above in the following fashion. The sample was diluted with 75 ml. of ice–water and then extracted with two 50-ml. portions of ether and 25 ml. of pentane. The combined organic extract was washed with cold sodium bicarbonate solution and with ice–water. The organic solution was dried over anhydrous sodium sulfate, and the solvent was removed using a rotary evaporator at room temperature. The acetate was removed by evacuation at 0.1 mm. for 1 hr. The remaining tosylate mixture was dissolved in reagent grade carbon tetrachloride and the composition was determined from the integrated n.m.r. spectrum. There are sufficient differences in spectra between the two compounds to permit an accurate determination of the rate constant.

Ionization Constants of Carboxylic Acids and Amines.—Water was redistilled from alkaline potassium permanganate and protected from atmospheric carbon dioxide by Ascarite tubes. The 50% ethanol was prepared by mixing equal volumes of U.S.I. absolute ethanol and water.

Four buffers were used for standardization of the Beckman model G pH meter: Beckman pH 7.00 and 10.00 prepared buffer solutions; 0.05 *M* potassium acid phthalate (pH 4.01); and 0.01 *M* borax (pH 9.18), all at 25°.

Cyclohexanecarboxylic acid and cyclopropanecarboxylic acid were redistilled before use. Bicyclo[2.1.1]hexane-1-carboxylic acid and bicyclo[2.2.1]heptane-1-carboxylic acid were purified as the β-phenethylamine salt and resublimed.

Reagent grade ammonium chloride was used. The stable amine hydrochlorides (recrystallized from methanol and ethyl acetate) were used in order to avoid the problem of weighing the free amines which are rather susceptible to carbonate formation.

The equivalence points of approximately 0.01 *N* stock solutions of the acid were accurately determined by potentiometric titration. The concentration of amine hydrochloride was determined from the weight of material used. A number of samples of each solution were exactly half neutralized with 0.2114 *N* sodium hydroxide under nitrogen. After reaching equilibrium at 25°, the pH of the solutions was determined. The pH meter was standardized with appropriate buffers before and after each series of measurements. In aqueous solution the pK_a's of acetic, cyclohexanecarboxylic, and cyclopropanecarboxylic acids were found to be 4.72, 4.88, and 4.80, respectively: the reported values are 4.75, 4.90 and 4.83.[5,9] The data are summarized in Tables I and II.

Dipole Moment Measurements.—Analytical reagent grade benzene was shaken with several portions of concentrated sulfuric acid, water, dilute sodium hydroxide solution, and water. After being dried over calcium chloride, it was distilled and a center fraction, b.p. 80–81°, $n^{25}D$ 1.4980, was collected. Chlorobenzene was distilled once before use and had $n^{27}D$ 1.4583. 1-Chlorobicyclo[2.1.1]hexane was distilled immediately before use and had b.p. 121°, $n^{27}D$ 1.4612.

A Dipolemeter DMO1 (Wissenshaftlich Technische Werkstatten), kindly made available by Dr. A. Huitric of the Pharmacy Department, University of Washington, was employed for the measurements. Calibration was carried out in the manner suggested by the manufacturer using cyclohexane, benzene, and di-*n*-butyl ether. The data were treated using the method of Halverstadt and Kumler.[21] The data are summarized in Table III.

(21) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE STATE UNIVERSITY, DETROIT 2, MICH.]

The Tricyclo[2.2.2.0^{2,6}]octan-3-ols and Derivatives. Preparation, Structure, and Reactivity Studies[1]

BY NORMAN A. LEBEL AND JOEL E. HUBER

RECEIVED MAY 28, 1963

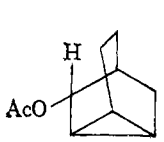
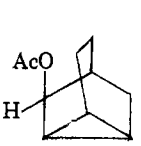
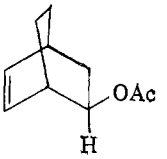
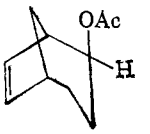
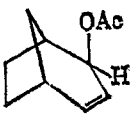
Acetolysis of arenesulfonates of *exo*-bicyclo[2.2.2]oct-5-en-2-ol (**2a**) proceeds with a substantial amount of anchimeric assistance by the double bond. The major product in buffered medium was determined to be *endo*-tricyclo[2.2.2.0^{2,6}]octan-3-yl acetate (**5c**), whereas the minor products were retained acetate **2d** and *axial*-bicyclo[3.2.1]oct-6-en-2-yl acetate (**10**). The results indicate that **2a** and **5a** represent a unique pair of homoallylic isomers, in which the carbonium ion intermediate(s) for their interconversion is attacked from the *exo* direction (retention) at C-5 and from the *opposite side* (steric approach control) at C-2. The epimeric tricyclic alcohol **7a** has been prepared by sodium borohydride reduction of tricyclo[2.2.2.0^{2,6}]octan-3-one (**6**). The stereochemistry of the tricyclanols **5a** and **7a** was determined by equilibration studies, n.m.r. spectral data, and hydrogenolysis. Both tricyclic acetates **5c** and **7c** undergo rapid, quantitative, acid-catalyzed isomerization to bicyclic isomers. Products of the acetolysis of the *p*-nitrobenzoates of **5a** and **7a** have been determined. A convenient preparative route to **5c** is available *via* the lead tetraacetate decarboxylation of *exo*- and *endo*-5-carboxybicyclo[2.2.2]oct-2-ene. The homoallylic isomers in this system are compared to the related cholesteryl and dehydronorbornyl analogs.

In a recent manuscript,[2] we noted that hydrolysis of the monobromide fraction isolated from the reaction of N-bromosuccinimide with bicyclo[2.2.2]oct-2-ene afforded substantial amounts of a tricyclo[2.2.2.0^{2,6}]-octan-3-ol (**1**). This product was postulated as having resulted from solvolysis of *exo*-5-bromobicyclo[2.2.2]-

(1) Presented at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1–5, 1963, p. 52M.

(2) N. A. LeBel, J. E. Huber, and L. Zalkow, *J. Am. Chem. Soc.*, **84**, 2226 (1962).

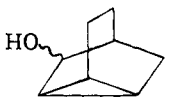
TABLE I

Compound	Conditions	Temp., °C.	Product composition, wt. %[a]				
							
2b	HOAc–NaOAc	25	90	..	7	3	..
2b	H_2O–Li_2CO_3	100	75[b]	..	16[b]	4[b]	5[b]
2b	Et_4NOAc–acetone	56	46	32	10	12	Trace
3 (R = Ts)	Et_4NOAc–acetone	56	..	..	22	..	78
2c	HOAc–NaOAc	25	81	..	17	2	..
			68	3	26	3	..
5b	HOAc–NaOAc	75	81	6	9	4	..
7b	HOAc–NaOAc	109	77[c]	5[c]	9[c]	5[c]	4[c]

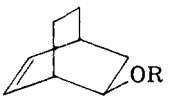
[a] Determined by gas chromatography. The estimated error in analysis is ±2%; the minimum amount of *exo*-tricyclic acetate **7c** that can be detected in the presence of *endo* epimer **5c** is estimated as 3%. [b] The alcohols were analyzed in this run. [c] These values are corrected to account for slight decomposition of **5c** at this temperature.

oct-2-ene. In order to verify the structure and origin of this alcohol and to establish its stereochemistry, we chose to prepare and study the solvolytic reactivity of *exo*-bicyclo[2.2.2]oct-5-en-2-ol (**2a**) and its arenesulfonate esters.

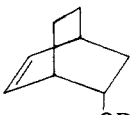
Compound **2a** was most conveniently prepared by careful chromatography of the alcohol mixture from hydrolysis of the Diels–Alder adduct of vinyl acetate and 1,3-cyclohexadiene.[3,4] The mixture contained approximately 14% of **2a** and 86% of its *endo* epimer (**3**, R = H). Prior to chromatography, enrichment to a 1:2 ratio of *exo* and *endo* isomers could be obtained by equilibration with aluminum isopropoxide. The *exo*-alcohol **2a** was obtained as a crystalline solid whose infrared spectrum and *p*-nitrobenzoate derivative were different from those of **3** (R = H).[4] Recently, pure **2a** has been prepared by gas chromatographic separation of the mixture (2:3) of **2a** and **3** obtained by lithium aluminum tri-*t*-butoxyhydride reduction of bicyclo[2.2.2]oct-5-en-2-one,[5] and our results substantiate this report.



1



2a, R = H
b, R = Ts
c, R = Bs
d, R = Ac



3

The *p*-toluenesulfonate (**2b**) and *p*-bromobenzenesulfonate (**2c**) esters of **2a** were prepared. The tosylate was a liquid at room temperature, whereas the brosylate was a solid. Both arenesulfonates were rather unstable and could best be stored for short periods of time in dry pentane solution at 0°.

The hydrolysis of **2b** was carried out with a stirred suspension of lithium carbonate in water. The product was a mixture of alcohols consisting of 75% tricyclic alcohol **1**,[2] 16% of **2a**, 5% of *axial*-bicyclo[3.2.1]oct-3-en-2-ol,[4] and 4% of a product assigned the structure *axial*-bicyclo[3.2.1]oct-6-en-2-ol (see Table I). Acetolysis of the tosylate and brosylate esters at 25° in dry acetic acid, 0.0183 *M* in sodium acetate, followed good first-order kinetics. The calculated specific rate constants were 6.2 ± 0.1 × 10^{-4} sec.$^{-1}$ for **2b**, and 2.4 ± 0.1 × 10^{-3} sec.$^{-1}$ for **2c**. The tosylate **2b** is reported to solvolyze in "100% glacial acetic acid" at 18.2° with a rate constant = 2.4 × 10^{-4} sec.$^{-1}$, and 85% of retained acetate **2d** was the only identified product.[5] Product studies for the solvolyses reported in this investigation are given in Table I.

Ethanolysis of the brosylate **2c** was also carried out. The integrated first-order rate constants for ethanolysis showed a slight downward drift; however, the infinity titer was within 1% of the calculated value. We attribute the downward drift to the reaction of tricyclic ethers formed in the solvolysis with *p*-bromobenzenesulfonic acid to regenerate a certain proportion of **2c**. This might be expected to become more serious as the reaction progresses and would account for the observed downward drift. The ethanolysis rate constant, 6.2 × 10^{-4} sec.$^{-1}$ (Table IV), is given as the initial rate constant obtained by extrapolation.[4] Ethanolysis of **2b** showed good first-order kinetics, and $k_1^{25°}$ = 1.02 ± 0.02 sec.$^{-1}$ Table (II).

The products summarized in Table I were identified by comparison of retention times on gas chromatography with those of known samples, and by saponification to the alcohols and subsequent comparison.

In order to verify that the products were, in fact, those of kinetically-controlled solvolyses, several control experiments were carried out. The acetate of the "tricyclic alcohol" was recovered unchanged after solution in acetic acid–sodium acetate for 24 hr. at 25°. On the other hand, the tricyclic alcohol **1** was nearly quantitatively converted to **2d** after treatment at room temperature with acetic acid containing 5% sulfuric acid. In addition, the tricyclic acetate **5c** *and* its epimer **7c** (see below) were quantitatively isomerized to **2d** (88%) and 12% of another acetate (**10**) after several hours in acetic acid containing one molar equivalent of *p*-toluenesulfonic acid. The structure of **10**, *axial*-bicyclo[3.2.1]oct-6-ene-2-yl acetate,[6] was deduced from the fact that hydrogenation of the mixture of **2d** and **10** gave, after saponification, a mixture of saturated alcohols in the same proportion which had gas chromatographic retention times identical with those of bicyclo[2.2.2]octan-2-ol[4] and *axial*-bicyclo[3.2.1]octan-2-ol.[4] Since **10** was not identical with *axial*-bicyclo[3.2.1]oct-3-en-2-yl acetate, its structure seems correctly assigned. The acetate of the *exo* isomer of the tricyclic alcohol **7c** (see below) was also shown to be stable in buffered acetic acid at 80°.

The tricyclic alcohol **1** is unlike the homologous 3-nortricyclanol in that two epimers are possible. The

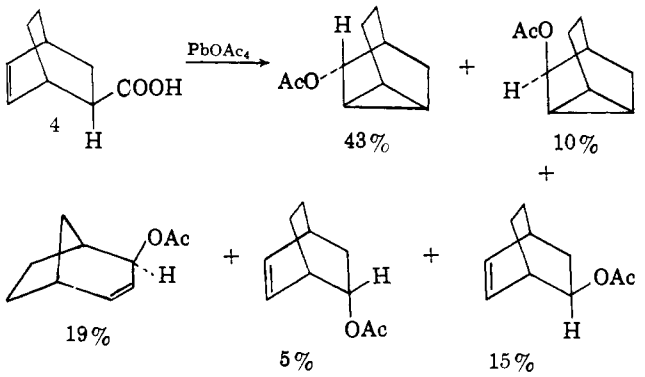
(3) K. Alder and H. Rickert, *Ann.*, **543**, 1 (1940).

(4) H. L. Goering, R. W. Greiner, and M. F. Sloan, *J. Am. Chem. Soc.*, **83**, 1391 (1961).

(5) R. R. Fraser and S. O'Farrell, *Tetrahedron Letters*, 1143 (1962).

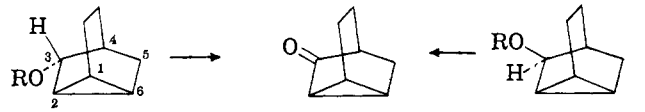
(6) H. K. Hall, Jr., *J. Am. Chem. Soc.*, **82**, 1209 (1960), has reported that Demjanov rearrangement of the adduct of cyclopentadiene and allylamine afforded bicyclo[3.2.1]oct-6-en-2-ol, but the product was not purified.

solvolytic studies described above gave nearly exclusively *one* of these two epimers (as the acetate). In order to obtain sufficient quantities of **1** for stereochemical studies, a lead tetraacetate decarboxylation of *exo*-5-carboxybicyclo[2.2.2]oct-2-ene (**4**) was carried out.[7] This oxidative decarboxylation apparently involves cationic species as intermediates.[7,8] Upon heating the acid **4** with lead tetraacetate in acetic acid containing excess potassium acetate, a 30–38% yield of acetates was obtained. Analysis of this mixture and *also* the mixture of alcohols obtained on saponification by gas chromatography indicated the production of 43% of the acetate of **1**, *ca.* 10% of an epimeric tricyclic acetate, 15% of **2d**, 5% of **3** (R = Ac), 19% of *axial*-bicyclo[3.2.1]oct-3-en-2-yl acetate, and 7% of an unidentified component. It is significant to note that oxidative decarboxylation of a mixture (82:18) of *endo*-



and *exo*-5-carboxybicyclo[2.2.2]oct-2-ene afforded a nearly identical mixture of products.

The stereochemistry of the tricyclic alcohol **1** was deduced as described below, and the structure is assigned that of *endo*-tricyclo[2.2.2.0^{2,6}]octan-3-ol (**5a**).[9] Oxidation afforded a crystalline low-melting ketone **6**[2] in fair yield. This ketone was characterized by its spectral properties (λ_{max}^{EtOH} 281 mμ, ε 63; ν_{max} 1724 cm.$^{-1}$; n.m.r. shows no vinyl hydrogens) and by the preparation of derivatives. Reduction of **6** with sodium borohydride in methanol at 0° (kinetic control) gave a mixture of alcohols. Gas chromatographic analysis showed that this mixture contained <5% of **5a** and >95% of an epimer, **7a**. The *exo*-alcohol **7a** was shown have the tricyclic carbon skeleton by means of n.m.r., elemental



5a, R = H
b, R = $CC_6H_4NO_2$ (O)
c, R = Ac

6

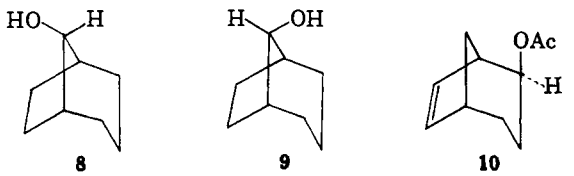
7a, R = H
b, R = $CC_6H_4NO_2$ (O)
c, R = Ac

analysis, and by oxidation to **6**. Examination of a molecular model indicated that the bottom side of this tricyclic system was clearly less hindered, and suggested that equilibration of either **5a** or **7a** should afford a mixture rich in **5a**. When either pure **5a** or nearly pure **7a** was heated for long periods in isopropyl alcohol containing acetone and aluminum isopropoxide, an equilibrium mixture consisting of 80 ± 2% of **5a** and 20 ± 2% of **7a** was obtained. Further evidence for the stereochemical assignments is given by the n.m.r. spectra of the crystalline *p*-nitrobenzoates **5b** and **7b**. The spectrum of the endo isomer **5b** shows the C-3 hydrogen atom at δ = 5.19 p.p.m. as a singlet. Since the dihedral angle between the *exo*-C-3 hydrogen and the hydrogen atoms at C-2 and C-4 is close to 80°, little if any splitting is expected.[10] On the other hand, **7b** shows a pair of overlapping doublets at about δ = 5.36 p.p.m., corresponding to a splitting of the *endo*-C-3 hydrogen by two adjacent hydrogen atoms at C-2 and C-4 (J = 5.3 and 3.4 c.p.s.). The dihedral angle in the latter case is equal to about 40°.

The ultimate proof of the stereochemistry of **5a** and **7a** resides in hydrogenation studies. In the case of **5a**, reductive cleavage of the C-1–C-6 bond would afford *exo*-bicyclo[3.2.1]octan-8-ol (**8**),[11a,b] whereas under similar conditions the bicyclo[3.2.1]octan-8-ol to be obtained from **7a** must be the *endo* isomer **9**.[11b] Hydrogenation of **5a** in acetic acid gave a mixture of alcohols containing 22% of **8**. This product was isolated by gas chromatography and its structure was confirmed by infrared comparisons and by preparation of a derivative. Similarly, **7a** was hydrogenated and **9** (66%) could be separated and identified.

The tosylate of *endo*-tricyclo[2.2.2.0^{2,6}]octan-3-ol (**5a**) could not be isolated. Consequently, the *p*-nitrobenzoate **5b** and the epimeric ester **7b** were solvolyzed in acetic acid. Qualitatively, **5b** was found to be more reactive than **7b**. The products were detected by gas chromatography and are given in Table I.

In order to contrast the relative proportion of acetates obtained from **2b** and **3** (R = Ts) under solvolytic conditions with that from direct SN2 displacement by acetate, we also examined the reactions of these *p*-toluenesulfonates with tetraethylammonium acetate in refluxing acetone. The products are also given in Table I.



8 **9** **10**

Discussion

The solvolytic studies reported herein unequivocally demonstrate that ionization of **2b** and **2c** involves considerable *anchimeric* assistance by the C-2,3 double bond. Some idea as to the magnitude of this acceleration can be appreciated by a comparison of relative rates of acetolysis at 25°, in which it can be shown that cyclohexyl tosylate (1)[12] < bicyclo[2.2.2]-oct-2-yl tosylate (72)[13] < **3** (R = OTs) (330)[13] < **2b** (12,800). Significantly, **2b** undergoes acetolysis at a rate approximately 1.7 times faster than *anti*-7-norbornenyl tosylate.[14] Comparison of our data in sodium acetate buffered media with that reported[5] for solvolysis in "100% acetic acid" indicates that a small "normal" salt effect obtains for the ionization of **2b**. An estimate of the rate of unassisted ionization for **2b** is difficult. It can probably be assumed that internal return[15] is operating and that the rate of ionization is faster than the rate of acetolysis.[16] Employing the

(7) Private communication from G. Büchi and J. Marvel. We wish to thank Prof. G. Büchi for informing us of a suitable procedure.

(8) E. J. Corey and J. Casanova, Jr., *J. Am. Chem. Soc.*, **85**, 165 (1963).

(9) The designation of the *endo* configuration to **5a** is arbitrary and was chosen to conform with the related bicyclo[2.2.2]oct-5-en-2-ols.

(10) See H. Conroy in "Advances in Organic Chemistry," Vol. II, Interscience Publishers, Inc., New York, N. Y., pp. 310–311.

(11) (a) A. C. Cope, S. Moon, C. H. Park, and G. L. Woo, *J. Am. Chem. Soc.*, **84**, 4865 (1962); (b) A. C. Cope, J. M. Grisar, and P. E. Peterson, *ibid.*, **82**, 4299 (1960).

(12) H. C. Brown and G. Ham, *ibid.*, **78**, 2735 (1956).

(13) H. L. Goering and M. F. Sloan, *ibid.*, **83**, 1992 (1961).

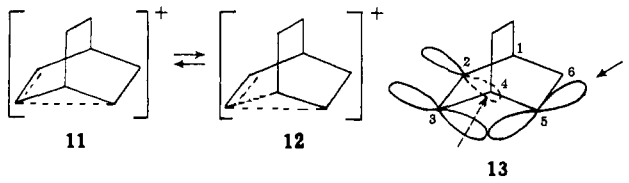
(14) S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956).

(15) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and G. C. Robinson, *ibid.*, **78**, 328 (1956).

(16) Ion pair return would conceivably give rise to starting tosylate **2b** and a tricyclic tosylate; *cf.* footnote 12 in S. J. Cristol, W. K. Seifert, D. W.

endo-dehydronorbornyl system as a model for the unassisted ionization rate of **2b** (or **2c**), an estimated rate enhancement by double bond participation would be at least 4×10^5.

The kinetic results clearly suggest participation by the double bond in the ionization of **2b** and **2c** and are consistent with the direct formation of the unsymmetrical[17] homoallylic ion **11**. This ion accommodates the production of retained acetate **2d** in the solvolyses, since p–σ overlap of the vacant orbital on C-5 with the



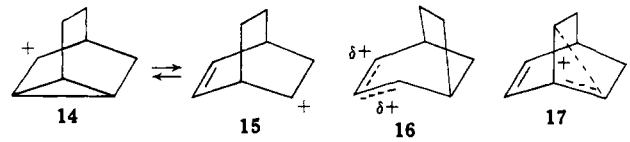
11 **12** **13**

p-orbital at C-3 and partial formation of an *endo* bond necessitates nucleophilic attack at C-2 from the *exo* side (*cf.* 13). Other workers[5] have utilized this same explanation to account for the nearly exclusive production of **2d**; however, their product studies were carried out under conditions which effect the rapid, acid-catalyzed isomerization of both **5c** (the major product of acetolysis of **2b** and **2c**) and **7c** to *exo*-bicyclo[2.2.2]oct-5-en-2-yl acetate (**2d**). The very minor production of *axial*-bicyclo[3.2.1]oct-6-en-2-yl acetate (**10**) suggests some conversion of **11** to the "symmetrical" homoallylic cation **12**. The predominant mode of attack on **11** to give the tricyclic acetate **5c** apparently takes place from the least hindered, or *endo*, side. The net result is, in effect a *cis* addition to the double bond of **2b**. That the observed stereochemical course of formation of **5c**, is reasonable can be recognized by the fact that **13** has a geometry somewhere between that of the tricyclic products and bicyclo[2.2.2]octene; *endo* isomers in both of these systems are more stable than the corresponding *exo* compounds, and it would be expected that attack at C-2 should prefer the *endo* direction.

The nonclassical cation **11** is also unique when compared to the dehydronorbornyl and cholesteryl analogs. In the former, the kinetic solvolysis products are predominantly tricyclic—and these are the thermodynamically more stable.[16-18] With the cholesteryl homoallylic isomers the less stable "cyclo" product results; with, however, the more sterically hindered 6β-isomer formed to the exclusion of the 6α-epimer.[15] There is apparently a stereoelectronic preference for *axial* (β) attack at C-6 in the cholesteryl ion. With the bicyclooctenyl cation **11**, collapse to substitution products occurs from the *exo* or top side at C-5 and mainly from the bottom side at C-2 (*cf.* **13**). To our knowledge, this represents the first documented case in which a pair of homoallylic isomers are produced by opposite directions of nucleophilic attack on a homoallylic cation system.

The data seem to exclude a rationale to account for the production of tricyclic product (**5c**) on the basis of direct nucleophilic attack at C-2 in the arenesulfonates **2b** and **2c** by solvent. In the first place the ratios $k_{HOAc}/k_{EtOH} = 3.8$ and 6.0 suggests little dependence on solvent nucleophilicity. Secondly, analogy with the known stereochemical course[19] of the SN2′ reaction would lead one to expect that attack at C-2 with concerted displacement of the *exo* leaving group at C-5 should occur from the *exo* side. Solvolysis afforded nearly exclusively **5c**. It is significant to note that approach to conditions more favorable to SN2′ displacement—*e.g.*, tetraethylammonium acetate in acetone—leads to substantial amounts of **7c** (see Table I).

In light of recent arguments against the existence of nonclassical cations in certain systems,[20] one must consider the alternate possibility that the products arise from attack on a rapidly equilibrating pair of classical cations **14** and **15**. This explanation can be summarized as: The established *anchimeric* acceleration by the double bond requires cation **14** to be formed initially and attack at C-2 should occur from the bottom side to give **5c**. However, the same argument might predict attack at C-5 from the less hindered bottom side to afford *endo*-bicyclo[2.2.2]oct-5-en-2-yl acetate (**3**, R = Ac). This product *was not detected*. On the other hand, if equilibrium between **14** and **15** is established,



14 **15** **16** **17**

cation **15** may give rise to the substitution products. Steric arguments would again predict *endo* attack. A factor that might account for the observed stereochemical results is that alternating expansion and compression of the C-3–C-5 bond distance as expressed by **14** $\rightleftarrows$ **15** may effectively shield the bottom side of the molecule so that attack at C-5 must occur from the top. This approach presumes that collapse to products must take place at a rate faster than **15** can rearrange to the more stable bicyclo[3.2.1]oct-3-en-2-yl cation (**16**).[13] It may be mechanistically significant that about 5% *axial*-bicyclo[3.2.1]oct-3-en-2-ol was detected among the hydrolysis products of **2b** (see Table I). We are presently studying the stereochemical course of the fission of the three-membered ring of **14** by employing ketone **6** as a model.

Several careful studies have been carried out which convincingly demonstrate that the cationic species generated in the diazotization of amines or the oxidative decarboxylation of acids are of a different nature from those cations from the solvolyses of arenesulfonates, especially where anchimeric assistance is evident in the latter. Of particular interest are the studies with optically active *exo*- and *endo*-2-norbornylamine[21,22] and the lead tetraacetate decarboxylation of the norbornane-2-carboxylic acids.[8] In the present study the lead tetraacetate decarboxylation of *exo*-5-carboxybicyclo[2.2.2]oct-2-ene (**4**) affords a product mixture which can best be explained on the basis of initial generation of the classical cation **14** (probably as an ion pair).[23] This ion is apparently produced from both the *exo* and *endo* isomers of the acid. Several pathways are apparently open to **15**: direct reaction with acetate ion to give **3** (R = Ac) and **2d**; rearrangement to *two* nonclassical cations **11** (and possibly **12**) and **17** can occur; collapse to products from **11** gives the observed acetates **5c**, **2d**, and **7c**, whereas **17** would lead to *axial*-bicyclo[3.2.1]oct-3-en-2-yl acetate.[23a]

Johnson, and J. B. Jurale, *J. Am. Chem. Soc.*, **84**, 3918 (1962). The expected tricyclic tosylate, *endo*-tricyclo[2.2.2.$0^{2,6}$]octan-3-yl tosylate, would solvolyze very rapidly.

(17) *Cf.* S. Winstein and E. M. Kosower, *ibid.*, **81**, 4399 (1959), and earlier references.

(18) J. D. Roberts, C. C. Lee, and W. H. Saunders, *ibid.*, **77**, 3034 (1955).

(19) G. Stork and W. N. White, *ibid.*, **78**, 4609 (1956).

(20) H. C. Brown, Proceedings of the Symposium on "The Transition State," The Chemical Society, Burlington House, London, W. 1, 1962, pp. 140-158, 174-178.

(21) J. A. Berson and D. A. Ben-Efriam, *J. Am. Chem. Soc.*, **81**, 4094 (1959).

(22) E. J. Corey, J. Casanova, Jr., P. A. Vatakencherry, and R. Winter, *ibid.*, **85**, 169 (1963).

(23) The conditions are comparable to those employed for acetolysis except that the temperature is about 60° higher.

(23a) NOTE ADDED IN PROOF.—It has recently been shown (H. L. Goering and D. L. Towns, *J. Am. Chem. Soc.*, **85**, 2295 (1963)) that ionization of **3** (R = Ts) results in the direct formation of **16** and not **17**.

The epimeric *p*-nitrobenzoates **5b** and **7b** were solvolyzed in buffered acetic acid under identical conditions. The product data summarized in Table I show a variation in distribution of the acetates. These results suggest that ionization of the two isomers proceeds initially *via* different cations. Of perhaps notable significance is the low ratio (8.5) of **5c** to **2d** in the solvolysis of **7b** as compared to the value 9 observed for **5b**. This may reflect the more favorable geometry for participation of the C-2–C-6 electron pair in the ionization of the *exo*-*p*-nitrobenzoate group of **7b**. Quite obviously, quantitative data for solvolysis and isomerization of the epimeric tricyclic alcohols would be helpful and such studies are underway.

Experimental[24]

Gas Chromatographic Analysis.—Two standard columns of 6 × 8 mm. Pyrex tubing were employed: column A was packed with 25% by weight of γ-nitro-γ-methylpimelonitrile suspended on 35–80 mesh base-washed firebrick and column B was packed with 15% Dow–Corning Polyglycol 4000 on firebrick. Both columns were preconditioned with several large injections of di-*n*-butylamine and were operated at 145° with helium flow rates of about 130 cc./min. for the analysis of the bicyclic alcohols, acetates, and ketones as described below.

exo-**Bicyclo[2.2.2]oct-5-en-2-ol** (**2a**).—The Diels–Alder reaction between 1,3-cyclohexadiene and vinyl acetate was carried out as described previously.[4] Fractional distillation afforded a mixture of dicyclohexadiene and *endo* and *exo* adducts, b.p. 88–94° (10 mm.), n^{25}D 1.4740–1.5110. Saponification of the acetates with potassium hydroxide in methanol, followed by dilution with water and continuous extraction with pentane, gave a residue from which 23 g. of alcohols could be separated by crystallization from pentane. The mother liquors were chromatographed on alumina. Elution with pentane gave 49 g. of hydrocarbon. Further elution with 15% ether–pentane gave an additional 14 g. of alcohol mixture, total 37.5 g. (22% based on cyclohexadiene). Gas chromatography on column A showed the presence of 14% *exo*- and 86% *endo*-bicyclo[2.2.2]oct-5-en-2-ols, respectively.

This mixture was altered to a ratio of 34:66, respectively, by equilibration with aluminum isopropoxide in isopropyl alcohol containing a few drops of acetone at 80–82° for 36 hr.[25]

A portion of this mixture (9.45 g.) was separated by chromatography on 900 g. of alumina (Fisher). The column was eluted with a 10% ether–pentane mixture and the first 50 l. of eluent contained traces of bicyclo[2.2.2]oct-5-en-2-one. *exo*-Bicyclo[2.2.2]oct-5-en-2-ol (**2a**) (2.73 g.) was collected in the next 29 l. and was shown to be pure by gas chromatography on column B. Recrystallization from pentane and sublimation gave a solid, m.p. 169.8–171° (lit.[5] m.p. 175–176°); infrared spectrum (CS_2): 696 (s), 809 (m), 820 (w), 850 (m), 905 (m), 950(m), 988 (m), 1009 (m), 1047 (s), and 1088 (m) cm.$^{-1}$.

Anal. Calcd. for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.16; H, 9.48.

The *p*-nitrobenzoate was prepared in the usual manner, and melted at 92.0–92.9° after two recrystallizations from pentane.

Anal. Calcd. for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53. Found: C, 65.87; H, 5.49.

The acetate was obtained by reaction with acetyl chloride in pyridine at 0°. Work-up afforded a 77% yield of *exo*-bicyclo[2.2.2]oct-5-en-2-yl acetate (**2d**), b.p. 74–80° (4.2 mm.), n^{25}D 1.4722.

Approximately 1.37 g. of a mixture of alcohols was eluted with the next 9 l. of solvent, at which time the eluent was changed to 75% ether–pentane and 4.5 g. of *endo*-bicyclo[2.2.2]oct-5-en-2-ol (**3**, R = H) was obtained. Recrystallization from pentane and sublimation gave a solid, m.p. 166.4–167.6° (lit.[4] m.p. 167–168.8°). A mixture melting point with the *exo* isomer showed 167.4–168.2°. The *p*-nitrobenzoate melted at 113–114.2° (lit.[4] m.p. 109.8–110.8°) which was depressed to 88–106° upon admixture with the *p*-nitrobenzoate of the *exo*-alcohol.

exo-**Bicyclo[2.2.2]oct-5-en-2-yl *p*-Toluenesulfonate** (**2b**).—A solution of 1.73 g. (13.9 mmoles) of **2a** in 7 ml. of pyridine was allowed to react at −25° with 3.18 g. of *p*-toluenesulfonyl chloride for 1.5 hr. After 2 days at −10°, the mixture was worked up to give 3.56 g. (92%) of crude, liquid tosylate.

exo-**Bicyclo[2.2.2]oct-5-en-2-yl *p*-Bromobenzenesulfonate** (**2c**).—Employing the same procedure as for the tosylate, 620 mg. of **2a** was converted to 1.60 g. (94%) of crude brosylate **2c**. Recrystallization from dry pentane afforded white plates, m.p. 61–63° dec.

endo-**Tricyclo[2.2.2.0^{2,6}]octan-3-ol** (**5a**). **Procedure A.**—The crude tosylate **2b** (3.44 g.) was stirred with 1.70 g. of lithium carbonate in 26 ml. of water at reflux for 20 hr. The aqueous suspension was cooled and was extracted with three 50-ml. portions of ether and one of pentane. After drying, concentration gave 1.49 g. of crude crystalline product (97%), which was shown by gas chromatography on column B to consist of 75% *endo*-tricyclo[2.2.2.0^{2,6}]octan-3-ol (**5a**), 16% of *exo*-bicyclo[2.2.2]-oct-5-en-2-ol (**2a**), and 9% of two bicyclo[3.2.1]octenols.

Procedure B.—Pure *exo*-5-carboxybicyclo[2.2.2]oct-2-ene (4) was prepared by conversion of the *endo* isomer in a mixture containing 58% of *exo*- and 42% of *endo*-acids to the iodolactone as described by Boehme, *et al.*[26] A stirred solution of 15.5 g. (102 mmoles) of the *exo*-acid (m.p. 45–47°, lit.[26] m.p. 46–47°) and 15.0 g. (153 mmoles) of anhydrous potassium acetate in 110 ml. of glacial acetic acid containing 2% of acetic anhydride was heated to 60°. At this time 54.0 g. (122 mmoles) of lead tetraacetate was added and the temperature was raised to 85–87° at which point a slightly exothermic reaction accompanied by the vigorous evolution of carbon dioxide took place. The temperature was not allowed to go above 89° and the mixture was stirred at 86–89° for 1.5 hr. After cooling, the mixture was added to 700 ml. of cold water and the bulk of the acetic acid was neutralized by the careful addition of about 70 g. of sodium carbonate. The crude products were obtained by continuous extraction of the aqueous solution with pentane for 48 hr. and subsequent washing of the pentane solution with several portions of saturated sodium bicarbonate, drying, and concentrating. The high boiling material was distilled to give 6.51 g. (38%) of acetates, b.p. 90–102° (8.5–7.5 mm.), n^{25}D 1.4789. This acetate mixture was saponified in essentially quantitative yield with potassium hydroxide (1.2 equiv.) in absolute methanol at room temperature.

Gas chromatographic analysis of the acetates on column B showed 43% of **5c**, 10% of **7c**, 26% of a mixture of **3** (R = Ac) and *axial*-bicyclo[3.2.1]oct-3-en-2-yl acetate, and 21% of a mixture of **2d** and an unassigned acetate. Analysis of the alcohols on column A indicated 43% of **5a**, 10% of **7a**, 5% of **3** (R = H), 19% of *axial*-bicyclo[3.2.1]oct-3-en-2-ol, 15% of **2a** and 7% of an unassigned alcohol. The retention times of these alcohols are 25.0, 22.8, 20.3, 18.8, 17.5, and 16 min., respectively.

Starting with a 10% *exo*: 90% *endo* ratio of 4, the decarboxylation–acetylation reaction (31% yield) gave, after saponification, the alcoholic mixture: 49% of **5a**, 3% of **7a**, 21% of *axial*-bicyclo[3.2.1]oct-3-en-2-ol, 6% of **3** (R = H), 17% of **2a**, and 3% of the unassigned alcohol.

Separation of **5a** from the mixture could be conveniently effected in the following manner. A column was prepared by the absorption of 80 ml. of an 80% aqueous silver nitrate solution on 240 g. of 100–200 mesh silica gel,[27] followed by drying at 100° for 12 hr. A mixture of alcohols (2.53 g.) containing 71% **5a** and 13% **7a** was chromatographed. Elution with 10% ether–pentane afforded trace amounts of an unidentified alcohol followed by **7a** (200 mg.) in the first fractions and pure **5a** (1.21 g., 67% recovery) in the later fractions. Unsaturated alcohols were eluted only after 5 l. of eluent had been used.

Sublimation of the material from the column (m.p. 125.5–129.0°) raised the melting point to 127.8–129.0° (lit.[2] m.p. 125–127.1°).

The *p*-nitrobenzoate of 5a was prepared and after two recrystallizations from hexane, needles (86%) melting at 91.2–92.0° were obtained.

The acetate 5c, prepared as described above, distilled at 67–70° (2.2 mm.), n^{25}D 1.4789.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 71.97; H, 8.58.

The infrared spectrum (CS_2) of the pure alcohol shows bands at 717 (m), 748 (m), 798 (m), 813 (m), 908 (m), 929 (w), 993 (s), 1008 (s), 1038 (w), 1054 (s), 1064 (s), and 1086 (w) cm.$^{-1}$.

Tricyclo[2.2.2.0^{2,6}]octan-3-one (6).—Oxidation of **5a** to the tricyclic ketone 6 could be effected by either chromium trioxide–pyridine complex[2] or by chromic acid employing a two-phase system.[28] The ketone was separated from unreacted alcohol(s) by chromatography on Merck acid-washed alumina. The retention time of 6 on g.c. with column B was 13.8 min. Pure 6

(24) All melting points are corrected (sealed capillaries were used in the cases of bicyclic alcohols and ketones) and boiling points are uncorrected. The infrared spectra were obtained on a Beckman Model IR-4 recording spectrophotometer with sodium chloride optics. The n.m.r. spectra were obtained with a Varian Associates DP-60 high resolution spectrophotometer. Carbon tetrachloride was used as the solvent and chemical shifts were obtained by the side-band technique with tetramethylsilane as an internal standard. Analyses are by Midwest Microlabs, Inc., Indianapolis, Ind.

(25) It was later shown that a 59% *exo* to 41% *endo* ratio of the alcohols could be obtained in good yield by equilibration with aluminum *t*-butoxide in refluxing benzene containing a trace of fluorenone.

(26) W. R. Boehme, E. Schipper, W. G. Scharpf, and J. Nichols, *J. Am. Chem. Soc.*, **80**, 5488 (1958).

(27) H. L. Goering, W. D. Closson, and A. C. Olson, *ibid.*, **83**, 3507 (1961).

(28) H. C. Brown and C. P. Garig, *ibid.*, **83**, 2952 (1961).

had m.p. 41–44° after sublimation from anhydrous sodium sulfate. The n.m.r. showed no vinyl hydrogens; the cyclopropyl hydrogens were shifted downfield and were masked by the methylene signals.

Anal. Calcd. for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.72; H, 8.55.

The semicarbazone melted at 187.5–188.1° (lit.[2] m.p. 187.5–188.1°).

The 2,4-dinitrophenylhydrazone was prepared by adding two drops of dil. hydrochloric acid to a mixture of reagent and ketone in ethanol. After purification by chromatography, red needles were obtained, m.p. 205–206°, λ_{max}^{EtOH} 371 mμ (ε 24,900).

Anal. Calcd. for $C_{14}H_{14}N_4O$: C, 55.62; H, 4.67; N, 18.54. Found: C, 55.68; H, 4.87; N, 19.06.

The oxidation of the *exo* isomer **7a** under similar conditions also afforded good yields of **6**.

exo-**Tricyclo[2.2.2.0^{2,6}]octan-3-ol** (**7a**).—A solution of 500 mg. (4 mmoles) of the tricyclic ketone in 12 ml. of absolute methanol was treated at −10 to 15° with 309 mg. of sodium borohydride. The mixture was stirred for 30 min. at 0°. After the usual work-up, there was obtained 511 mg. of crude alcohol, m.p. 151.5–156.5°. Gas chromatography on column A showed 95% of *exo*-tricyclic alcohol **7a**. The alcohol was converted to the crude *p*-nitrobenzoate, m.p. 85–91°. The *p*-nitrobenzoate **7b** was recrystallized from pentane, m.p. 99.8–101°.

Anal. Calcd. for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.13. Found: C, 66 18; H, 5.62; N, 5.33.

Saponification of the ester **7b** with potassium hydroxide in methanol and subsequent work-up gave a 68% yield of the pure alcohol, m.p. 156.5–158.2° after sublimation. The infrared spectrum of the alcohol (CS_2) showed bands at 757 (m), 780(m), 802(m), 813(m), 840(m), 918(m), 971(m), 1026(s), 1035(s), 1065(s), and 1075(s) cm.$^{-1}$.

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.38; H, 9.95.

The acetate had b.p. 76–82° (5 mm.), $n^{25}D$ 1.4768.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.56; H, 8.69.

Equilibration of the Tricyclic Alcohols.—A 100-mg. sample of pure *endo*-tricyclo[2.2.2.0^{2,6}]octan-3-ol (**5a**) was equilibrated at reflux temperature with 160 mg. of aluminum isopropoxide in 1.3 ml. of isopropyl alcohol, containing a few drops of acetone, for 3.5 days. Work-up gave 100 mg. of recovered alcohols, which showed 90% *endo* and 10% *exo* on gas chromatography on column A. The equilibration was repeated for an additional 3.5 days. There was recovered 98 mg. of a mixture consisting of 81% *endo* and 19% *exo* tricyclic alcohols. No appreciable change was noted on further equilibration.

A mixture containing approximately 95% *exo*-alcohol **7a** and 5% of **5a** alcohols was equilibrated in the same manner for 5 days. An 81% recovery of alcohols was obtained which analyzed for 80% *endo*- (**5a**) and 20% *exo*-tricyclo[2.2.2.0^{2,6}]octan-3-ol (**7a**).

Kinetic Experiments.—The kinetic procedure for the acetolysis studies was essentially that employed previously.[29] The reactions were carried out at 25° in volumetric flasks and 3-ml. aliquots were quenched by addition to pentane which had been cooled to −80° with Dry Ice–acetone. Titration[13] was carried out at low temperature. Infinity titers were within 2% of the calculated values. The results are summarized in Tables II and III.

TABLE II

SOLVOLYSIS OF *exo*-BICYCLO[2.2.2]OCT-5-EN-2-YL *p*-TOLUENESULFONATE (**2b**) AND *p*-BROMOBENZENESULFONATE (**2c**) AT 25°[a]

Compound	n[b]	10^4k, sec.$^{-1}$
	Acetolysis	
2b	1	0.61
2b	3[c]	0.62 ± 0.01
2c	3[c]	2.40 ± 0.1
	Ethanolysis	
2b	3	0.102 ± 0.02
2c	2	0.635 ± 0.01

[a] Initial concentration of arenesulfonate was 0.026 *M* in most runs. [b] Number of independent kinetic experiments. [c] Contained 0.033 *M* sodium acetate.

The ethanolysis experiments were carried out in the manner described for **3** (R = Ts),[13] except that aliquots were delivered into flasks containing dimethylformamide at −20°. Titration to the brom thymol blue end point with standard sodium methoxide in methanol was also carried out at low temperature.

(29) S. Winstein, C. Hanson, and E. Grunwald, *J. Am. Chem. Soc.*, **70**, 812 (1948).

TABLE III

ACETOLYSIS OF *exo*-BICYCLO[2.2.2]OCT-5-EN-2-YL *p*-TOLUENESULFONATE AT 25.00°[a]

Time, 10^{-2} sec.	]ROTs] (10^2 *M*)	10^4k, sec.$^{-1}$
0	1.94	
2.48	1.66	6.22
3.70	1.55	6.07
5.25	1.40	6.22
7.40	1.23	6.19
12.21	0.91	6.16
19.74	0.57	6.22
	Av.	6.18 ± 0.04

[a] Contains 0.0332 *M* sodium acetate.

TABLE IV

ETHANOLYSIS OF *exo*-BICYCLO[2.2.2]OCT-5-EN-2-YL *p*-BROMOBENZENESULFONATE AT 25.00°

Time, 10^{-2} sec.	]ROTs] (10^2 *M*)	10^4k, sec.$^{-1}$
0	2.885	6.2[a]
0.70	2.765	5.99
2.40	2.507	5.86
6.24	2.031	5.62
13.23	1.437	5.26
27.16	0.703	5.20
49.10	0.259	4.91

[a] By extrapolation to 0% reaction.

Considerable difficulty was encountered in the ethanolysis studies owing to dissolved carbon dioxide and the quenching and titrations had to be done with appropriate precautions. Table IV lists the data for a typical ethanolysis experiment.

Product Stability Studies. A. *exo*-Tricyclo[2.2.2.0^{2,6}]octan-3-yl Acetate (**7c**).—A solution of 0.3 mmole of **7c** in 1.5 ml. of acetic acid, 0.0764 *M* in sodium acetate, was heated at 84° for 20 hr. The acetate was recovered and analysis by gas chromatography indicated 94% **7c** and 6% of its epimer **5c**.

A solution of **7c** in acetic acid containing 1 equivalent of acetic anhydride was treated with 1 equivalent of *p*-toluenesulfonic acid monohydrate, and the solution was allowed to stand at room temperature for 28 hr. After work-up, the crude acetate was analyzed and showed 88% *exo*-bicyclo[2.2.2]oct-5-en-2-yl acetate (**2d**) and 12% of *axial*-bicyclo[3.2.1]oct-6-en-2-yl acetate (**10**). No starting material was detected.

B. ***endo*-Tricyclo[2.2.2.0^{2,6}]octan-3-yl Acetate** (**5c**).—Acetate **5c** (0.23 mmole) was dissolved in 0.8 ml. of 0.0764 *M* sodium acetate–acetic acid containing 2% of acetic anhydride, and the mixture was allowed to stand at room temperature for 24 hr. The recovered acetate was found to be unchanged.

Employing conditions identical to those used with **7c**, the *endo*-acetate **5c** was quantitatively isomerized in 14 hr. upon solution in acetic acid containing *p*-toluenesulfonic acid. The products were identified as 88% **2d** and 12% **10**.

C. ***endo*-Tricyclo[2.2.2.0^{2,6}]octan-3-ol** (**5a**).—A solution of 25 mg. (0.2 mmole) of **5a** in 1 ml. of acetic acid containing 5% by weight of sulfuric acid was allowed to stand at room temperature for 40 hr. After the usual work-up, the crude acetates were analyzed by gas chromatography. There was detected 96% of **2d** and 4% of **10**, and no **5c** was found.

Hydrogenolysis of 5a.—A solution of 500 mg. (4 mmoles) of *endo*-tricyclo[2.2.2.0^{2,6}]octan-3-ol in 15 ml. of glacial acetic acid was hydrogenated in the presence of 500 mg. of platinum oxide until the uptake of hydrogen had ceased (1.5 hr.). The catalyst was removed by filtration and the filtrate was added to water and was continuously extracted with pentane. The extract was washed, dried, and concentrated to give 486 mg. of crystalline product. Gas chromatography on column A showed two peaks in the ratio 22:78 which had retention times identical with those of *exo*-bicyclo[3.2.1]octan-8-ol (**8**) and bicyclo[2.2.2]octan-2-ol, respectively. A portion of this mixture (200 mg.) was partially oxidized with chromic anhydride–pyridine complex and the crude product was isolated and analyzed by g.c. The peak corresponding to unoxidized **8** was collected and reanalyzed to show > 90% pure **8**. The infrared spectrum was nearly identical with that of **8**, and a phenylurethan derivative was prepared. The phenylurethan melted at 122.8–123.5° after several recrystallizations from aqueous ethanol (lit.[11] m.p. 124.8–125.6°). The mixture melting point with an authentic sample of the phenylurethan of **8** was 123.5–124.5°.

Hydrogenolysis of 7a.—A 100-mg. sample of *exo*-tricyclo[2.2.2.0^{2,6}]octan-3-ol was hydrogenated by the procedure described for its epimer. Analysis of the crude product by g.c. on column B showed a major component (66%) with a retention time identical with that of *endo*-bicyclo[3.2.1]octan-8-ol (**9**). A

small sample was separated by g.c. and the infrared spectrum was similar to that of authentic **9**.[11a] A phenylurethan was prepared and recrystallized from pentane, m.p. 133–136° (lit.[11a] 136.7–137°), m.m.p. with the phenylurethan of **8** 119–121°.

Reactions with Tetraethylammonium Acetate. *exo*-Bicyclo[2.2.2]oct-5-ene-2-yl Tosylate (**2b**).—To a cold (−10°) stirred solution of 205 mg. (1.04 mmoles) of tetraethylammonium acetate monohydrate[30] in 0.6 ml. of dry acetone was added 250 mg. (0.90 mmole) of *exo*-tosylate **2b** in 0.6 ml. of dry acetone. The solution was allowed to warm to room temperature and, after stirring for 2 hr. at this temperature, the solution was stirred at reflux for an additional 2 hr. Upon cooling, the reaction mixture was added to 75 ml. of water and the product was extracted with two 25-ml. portions of ethyl ether followed by a 25-ml. portion of pentane. The combined extracts were thoroughly washed with saturated sodium bicarbonate solution and then with water. The dried ether–pentane solution was concentrated by distillation to give 146 mg. of high boiling residue which was shown to consist of a mixture of 46% **5c**, 32% **7c**, 10% **2d**, and 12% **10** by gas chromatography on column B.

endo-Bicyclo[2.2.2]oct-5-en-2-yl Tosylate (**3**, **R** = **Ts**).—*endo*-Tosylate **3** (R = Ts; 184 mg., 0.66 mmole) was added to a stirred solution of 469 mg. (2.38 mmoles) of tetraethylammonium acetate monohydrate in 1.5 ml. of dry acetone. The solution was then stirred at gentle reflux for 30 hr. and, after a similar work-up to that described above, 86 mg. of crude acetates was obtained; g.c. analysis shows the presence of 22% **2d** and 78% *axial*-bicyclo[3.2.1]oct-3-en-2-yl acetate.

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The Stereochemistry of Elimination Reactions. The 2,3-Dihalonorbornanes[1,2]

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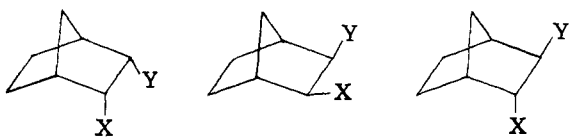
The kinetics of dehydrohalogenation of the three isomeric 2,3-dibromonorbornanes, *endo-cis*-2-bromo-3-chloronorbornane and *exo*-2-bromo-*endo*-3-chloronorbornane, have been examined with sodium pentoxide as the base. The *trans*- and *endo-cis*-dibromides were also studied with potassium *t*-amyloxide. Hydrogen exchange was not detected when the 2,3-dideuterated analogs of the *trans*- and *endo-cis*-dibromides were subjected to conditions of partial elimination. Kinetic isotope effects were measured at 126.7° for the *endo-cis*-dibromide and 96.3° for the *trans*-dibromide and the observed values (k_H/k_D = 3.4 and 3.6, respectively) are considered too large for a two-step mechanism. Both chlorobromides afford nearly exclusively 2-chloro-2-norbornene upon reaction with potassium *t*-butoxide. From reactivity considerations, product studies, and the results of isotopic substitution, elimination reactions of 2,3-dihalonorbornanes are considered to follow a concerted, though probably not synchronous, pathway.

Recently, DePuy and co-workers have suggested that a plot of the rate of bimolecular elimination *vs.* the dihedral angle will show maxima at both 0 and 180° and a minimum at 90°.[5] This generalization was based on observations that the base-promoted *cis* eliminations of a series of *trans*-2-arylcyclopentyl tosylates were of a concerted nature, and that k_{trans}/k_{cis} in the arylcyclopentyl system is only about 14. In addition, the observed favoring of *cis* over *trans* dehydrochlorination in bridged bicyclic dichlorides[6,7] was interpreted in terms of this proposal.

We have been of the opinion that, as a general rule, *cis* coplanar E2 reactions will be faster than *trans* noncoplanar bimolecular eliminations. As the result of another study, we had available the three isomeric 2,3-dibromonorbornanes.[8] A detailed kinetic analysis of the dehydrobromination of these isomers was considered of interest for several reasons. Among these were: (1) a determination of whether coplanar *cis* and noncoplanar *trans* eliminations in this series followed similar mechanisms, (2) a comparison of the activation parameters with those reported for concerted *trans* E2 reactions of simple dihaloethylenes, and (3) a comparison of *trans*-eliminations from *exo-cis*- and *endo-cis*-dihalides.

In the course of these studies, kinetic and product analyses of the dehydrohalogenation of the *endo-cis*- and *exo*-2-bromo-*endo*-3-chloronorbornanes were made, as well as a study of the hydrogen–deuterium isotope effect and exchange phenomena for the *endo-cis*- and *trans*-dibromides.



I, X = Y = Br; II, X = Br, Y = Cl; III, X = Y = Cl

IV, X = Y = Br

V, X = Y = Br; VI, X = Cl, Y = Br; VII, X = Y = Cl

Results

The synthesis of the three dibromides I, IV, and V has been described previously.[8] In the earlier work, the structures of the *cis*-dibromides were based on dipole moment evidence and the fact that the *exo-cis* isomer would be expected from the free radical addition of hydrogen bromide to 2-bromo-2-norbornene. Recently, we had obtained a great deal of additional data which require that the dibromide of m.p. 60.5–61.5° be assigned the *endo-cis* structure I, and the lower melting isomer must have structure IV. The 2,3-dideuterated analogs of I and V were prepared in an analogous manner employing *sym*-dibromodideuterioethylene. The free radical addition of hydrogen bromide to 2-chloro-2-norbornene afforded mixtures of *endo-cis*-2-bromo-3-chloronorbornane (II) and *exo*-2-bromo-*endo*-3-chloronorbornane (VI) in the ratio 3:7, and the isomers were separated by distillation. The structures were assigned by analogy,[8] and are consistent with the nuclear magnetic resonance spectra.[9]

In order to allow a direct comparison with the data that Cristol and Hoegger obtained for the dichlorides III and VII,[6] the dehydrobrominations of dihalides I, II, IV, V, and VI were studied at several different

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(3) A. P. Sloan Foundation Fellow, 1961–1965.

(4) National Science Foundation Cooperative Graduate Fellow, 1962–1963.

(5) C. H. DePuy, R. D. Thurn, and G. F. Morris, *J. Am. Chem. Soc.*, **84**, 1314 (1962).

(6) S. J. Cristol and E. F. Hoegger, *ibid.*, **79**, 3438 (1957).

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(9) The n.m.r. analysis of the 2,3-dihalonorbornanes will be discussed in a later manuscript.