Memory Effects in Multiple Carbonium Ion Rearrangements. IV. Solvolytic Studies of the Tricyclo[3.2.1.0^{2,7}]oct-4-yl System[1,2]

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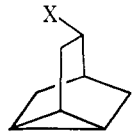
Abstract: The major products of solvolyses of tricyclo[3.2.1.0^{2,7}]oct-4-yl *p*-bromobenzenesulfonate are the corresponding tricyclic product and the bicyclic unsaturated material derived by vicinal hydride shift, a bicyclo[3.2.1]oct-2-en-6-*exo*-yl derivative. The hydride shift is solvent dependent, being much suppressed in aqueous medium. Isotopic labeling experiments and a comparison of polarimetric and titrimetric rates show that solvolysis is accompanied by Wagner–Meerwein rearrangement and ion-pair return. The major portion of the solvolysis seems to proceed through a nonclassical ion or its stereochemical equivalent. A small amount of transannular hydride shift is observed, but the ratio of vicinal to transannular shift is 800-fold higher in tricyclo[3.2.1.0^{2,7}]oct-4-yl cation than in norbornyl cation. This effect is attributable in part to the relatively unfavorable orbital geometry in the cyclopropylcarbinyl-type of cation (tricyclo[3.2.1.0^{2,7}]oct-6-yl) that results from transannular hydride shift in the present system.

Titrimetric and Polarimetric Solvolysis Rates in the Tricyclo[3.2.1.0^{2,7}]oct-4-yl Cation System. As a guide to the behavior of the cations from ring expansion of nortricyclylcarbinyl derivatives,[4] it is instructive to examine the solvolysis of tricyclo[3.2.1.0^{2,7}]oct-4-yl *p*-bromobenzenesulfonate (**1**-OBs). This material, prepared from the corresponding alcohol[5] **1**-OH, can be obtained as a crystalline solid which is unstable upon storage at room temperature. The structure is confirmed by the nuclear magnetic resonance (nmr) spectrum, by lithium–ammonia cleavage,[6] which regenerates the original alcohol **1**-OH, uncontaminated by other isomers, and by solvolysis, which liberates the theoretical quantity of *p*-bromobenzenesulfonic acid.



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Optical activation of alcohol **1**-OH is achieved by recrystallization of the ephedrine salt of the acid phthalate, although the brucine salt seems[7] to be more convenient.

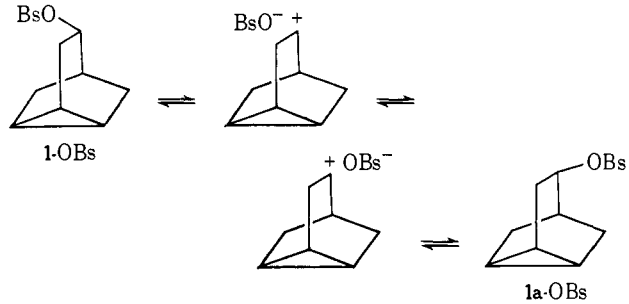
Acetolysis rates for **1**-OBs are followed both by titration of *p*-bromobenzenesulfonic acid and by decline of optical activity. In both procedures, the reaction obeys first-order kinetics, but the polarimetric rate constant (k_α) is 3.1 times the titrimetric one (k_t) at 19.90° (Table I). Ion-pair return, which can cause racemization of the sulfonate ester without liberation of acid, provides the simplest explanation of the discrepancy.

Table I. Rate Constants for Acetolysis of **1**-OBs

Method	Temp, °C	$k \times 10^4$, sec^{-1}
Titrimetric[a,b]	19.89	0.430 ± 0.005
Titrimetric[d,e]	19.90	0.452
Titrimetric[a,c]	29.87	1.67 ± 0.02
Titrimetric[a,c]	40.16	6.33 ± 0.16
Titrimetric[f]	25.00	0.871
Polarimetric[c,e]	19.90	1.38 ± 0.03

[a] In 0.026 *M* NaOAc–HOAc; initial concentration 0.024 *M* **1**-OBs. [b] Mean of two runs. [c] Mean of three runs. [d] Single run. [e] In 0.09840 *M* KOAc–HOAc; initial concentration 0.092–0.098 *M* **1**-OBs. [f] Interpolated.

There are two conceivable detailed mechanisms for this. The first involves migration of OBs$^-$ ion from one face to another of the carbon to which it was originally attached (**1**-OBs → **1a**-OBs). The second associates ion-pair return with Wagner–Meerwein rearrangement, as in the case of *exo*-2-norbornyl derivatives.[8] In principle, these two mechanisms are distinguishable by an isotopic labeling experiment, since by intervention of the symmetrical Wagner–Meerwein intermediate **2**, a deuterium label initially at C-4 in **1**-OBs-*d* would be parti-



(1) This work was supported in part by grants from the National Science Foundation (GP 6212X), the National Institute of Arthritis and Metabolic Diseases (AM 07505), and the Air Force Office of Scientific Research (M2(967)62/1006-66).

(2) For preliminary reports, see (a) J. A. Berson, R. G. Bergman, G. M. Clarke, and D. Wege, *J. Am. Chem. Soc.*, **90**, 3236 (1968); (b) J. A. Berson, G. M. Clarke, D. Wege, and R. G. Bergman, *ibid.*, **90**, 3238 (1968); (c) J. A. Berson, D. Wege, G. M. Clarke, and R. G. Bergman, *ibid.*, **90**, 3240 (1968).

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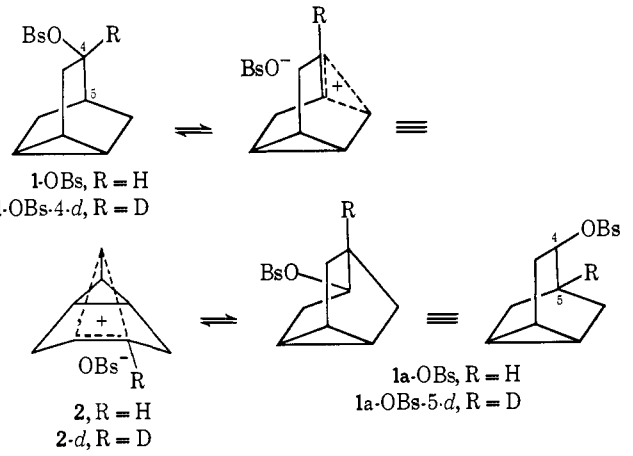
(4) J. A. Berson, R. G. Bergman, G. M. Clarke, and D. Wege, *J. Am. Chem. Soc.*, 91, 5601 (1969).

(5) J. T. Lumb and G. H. Whitham, *Tetrahedron*, 21, 499 (1965).

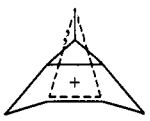
(6) (a) W. D. Closson, P. Wriede, and S. Bank, *J. Am. Chem. Soc.*, **88**, 1581 (1966), and references cited there; (b) H. L. Goering and R. W. Thies, *ibid.*, **90**, 2967 (1968).

(7) G. N. Fickes, personal communication, describes this resolution. His solvolyses of 1-OTs give results very similar to those we find for **1**-OBs.

(8) (a) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, 74, 1147, 1154 (1952); (b) S. Winstein and K. C. Schreiber, *ibid.*, 74, 2165 (1952).



tioned equally between C-4 and C-5 in that portion of the *p*-bromobenzenesulfonate which had returned from the ion pair to the covalent condition. This experiment is difficult to carry out because the instability of **1**-OBs makes it inconvenient to reisolate it from partial solvolyses, but strong presumptive evidence that at least part of the "excess" racemization of **1**-OBs occurs by the Wagner–Meerwein path comes from the deuterium distribution in the acetate product from acetolysis of **1**-OBs-4-*d*. This labeled substrate is prepared from **1**-OH-4-*d*, which results from the corresponding ketone[5] upon lithium aluminum deuteride reduction. The nmr spectrum of the product **1**-OAc isolated from acetolysis shows the α-acetoxy (C-4) proton region as a broadened doublet of doublets centered about τ 5.4–5.55 with an intensity corresponding quite accurately to 0.5/13 of the total integral. Since the C-4 proton in the undeuterated analog **1**-OAc accounts for $^1/_{14}$ of the total integral of the nmr spectrum of that compound, it is clear that half of the deuterium label in the acetolysis product from **1**-OBs-4-*d* is at C-4.[9,10] (The precise location of the remaining 0.5 D is assumed to be at C-5 but cannot be determined from the nmr spectrum.) Wagner–Meerwein rearrangement involving symmetrical species **3**,



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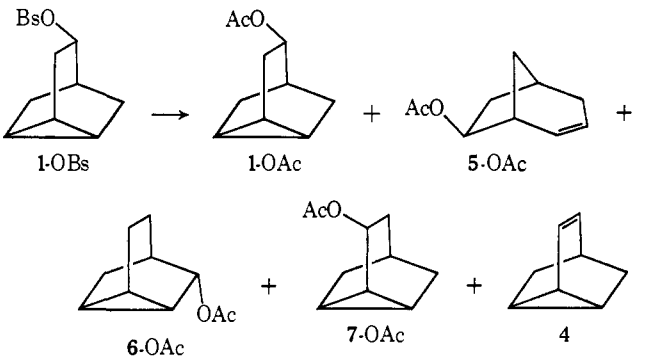
either as a transition state or an intermediate, thus occurs in the actual solvolysis. It is reasonable to assume that the ion-pair counterpart involving symmetrical species **2** is a likely path for the "excess" racemization of **1**-OBs.

The titrimetric acetolysis rate constant interpolated to 25° (Table I) is 9.6 times that reported[11] for bicyclo[2.2.2]oct-2-yl *p*-bromobenzenesulfonate. Since it is concluded[12,13] that solvolysis in the bicyclo[2.2.2]octyl system probably does not receive much anchimeric assistance, we hesitate to interpret the modest additional rate enhancement in the tricyclic case (**1**-OBs) as strong evidence for σ-bond participation in the rate-determining step.

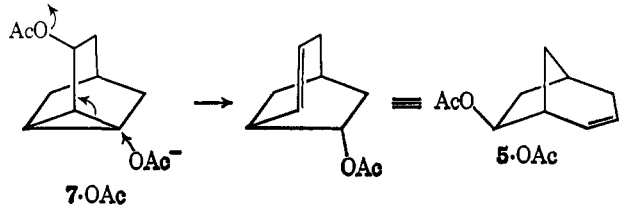
With the anchimerically assisted process apparently being only slightly favored in the present system, it would not be surprising to find some nonrearranging solvolysis taking place in competition with the process leading through the symmetrical species **2**. The first indication that this may be the case is the finding that the "infinity" readings in the polarimetric rate runs are not exactly zero but always show a small rotation opposite in sign to that of the starting *p*-bromobenzenesulfonate **1**-OBs. More definitive evidence on the origin of this rotation and on the over-all solvolysis mechanism comes from a study of the products.

Acetolysis of tricyclic substrates **1**-OBs at 100° gives 5–10% of a hydrocarbon, tricyclo[3.2.1.$0^{2,7}$]oct-3-ene (**4**) and a mixture of acetates, of which the bicyclic unsaturated one, **5**-OAc, is the major component (65%). The remainder of the acetate product mixture is almost entirely the acetate of the starting tricyclic structure **1**-OAc. There is an additional small peak in the vapor chromatogram (vpc) which has the same retention time as that of an isomeric tricyclic substance, *exo*-tricyclo[3.2.1.$0^{2,7}$]6-yl acetate (**6**), but there is no indication of another peak that might correspond to another tricyclic secondary isomer, tricyclo[3.2.1.$0^{2,7}$]oct-3-yl acetate (**7**). However, control experiments show that this material



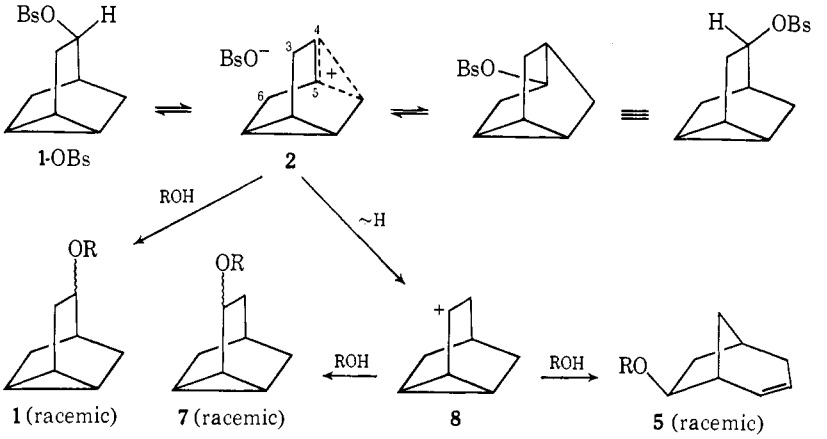
is very unstable, as has already been foreshadowed by the observation[10] that attempted acetylation (acetic anhydride–sodium acetate) of tricyclo[3.2.1.$0^{2,7}$]octan-3-ol (7-OH) gave only unsaturated acetate **5**-OAc. We find that acetic anhydride–pyridine acetylation of 7-OH gives an acetate, presumably 7-OAc, which has the correct nmr spectrum for this structure, but the substance is very reactive. In sodium acetate buffered acetic acid at 100°, it is converted quantitatively in 15 min to the unsaturated bicyclic acetate **5**-OAc. The tricyclic acetate **7** decomposes on most vpc columns to give mainly **5**-OAc, identified by retention time and isolation, but it does pass through a 100-ft Apiezon L coated capillary at 95° with a retention time different from that of **5**-OAc.

These observations show that tricyclic acetate 7-OAc would not survive the solvolysis conditions. They leave some question of whether unsaturated acetate **5**-OAc is



(9) This confirms a previous report[10] of a similar labeling experiment.
(10) R. R. Sauers, J. A. Beisler, and H. Feilich, *J. Org. Chem.*, **32**, 569 (1967).
(11) H. M. Walborsky, M. E. Baum, and A. A. Youssef, *J. Am. Chem. Soc.*, **83**, 988 (1961).
(12) H. L. Goering and G. N. Fickes, *ibid.*, **90**, 2856 (1968).
(13) H. L. Goering and M. F. Sloan, *ibid.*, **83**, 1992 (1961).

Scheme I. Solvolysis of Tricyclo[3.2.1.0^{2,7}]oct-4-yl *p*-Bromobenzenesulfonate (**1**-OBs)



a true kinetically controlled product of carbonium ion capture or whether all of it results from isomerization of **7**-OAc. The formal changes needed to effect the rearrangement are those shown, but the reaction may actually involve regeneration of a carbonium ion from **7**-OAc.

Under less strenuous conditions in buffered acetic acid at 50°, tricyclic acetate **7**-OAc can be detected as a product. The amount of acetate product of the starting structure, **1**-OAc, remains nearly the same as at 100°, and virtually all of the unstable tricyclic acetate **7**-OAc is formed at the expense of the unsaturated acetate **5**-OAc (Table II). This is most simply interpreted to mean that the distribution of carbonium ion reaction paths as between **1**-OAc-forming cations and **5**-**7**-OAc-forming cations is not a sensitive function of temperature. The variation in the relative amounts of **5**-OAc and **7**-OAc does not represent major shifts in the partition ratio for capture of the cations, but rather is largely an artifact resulting from the instability of **7**-OAc.

Table II. Products of Solvolyses of Tricyclo[3.2.1.0^{2,7}]oct-4-yl *p*-Bromobenzenesulfonate (**1**-OBs)

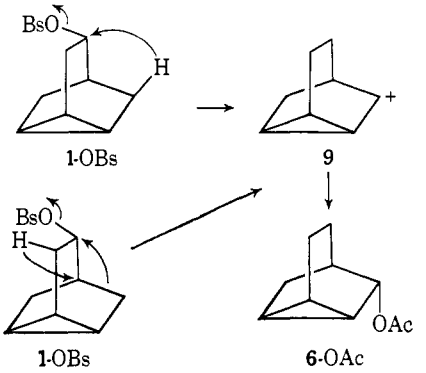
Conditions	Product, % yield[e]			
	1[d]	**5**[d]	**7**[c]	**6**[a]
HOAc, NaOAc, 50°	39	31	30	~1
HOAc, NaOAc, 100°[f]	35	65	0	~1
80% aq acetone, C_5H_5N, 50°	71	29	0	*b*
70% aq dioxane, C_5H_5N, 100°	58	42	0	*b*

[a] Identified by its retention time and that of the corresponding ketone. [b] Not determinable in this run. [c] Identified by retention time. [d] Identified by isolation and spectroscopic comparison with authentic samples. [e] Per cent of acetate or alcohol product. In acetolyses, X = OAc; in hydrolyses, X = OH. [f] About 5% of tricyclo[3.2.1.0^{2,7}]oct-3-ene is formed.

In aqueous media (Table II), there are significant changes in the product distribution. The product of the starting structure **1**-OH now becomes predominant.

These effects are compatible with the simplest mechanism that can be written for the major portion of the solvolysis of **1**-OBs (Scheme I). The relative amounts of products **1** and **5** (**7**) depend upon the competition between nucleophilic capture of the ion pair **2** (or solvated ion **3** resulting from it) and the irreversible 3,4 (or 6,5) hydride shift to produce cation **8**.[14] The ratio of the two rates should be strongly solvent dependent by virtue of the greater sensitivity of the extramolecular capture reaction to the nucleophilic power of the solvent. The observed suppression of the hydride-shifted products **7** and **5** in the more nucleophilic aqueous solvents parallels similar findings in other systems.[15]

Scheme I, which shows only symmetrical product-forming intermediates, is deficient in that it cannot account for the small amount of optical activity that survives even the "infinite"-time solvolysis of optically active **1**-OBs. One possible source of this activity might be the small amount of tricyclo[3.2.1.0^{2,7}]oct-6-yl acetate (**6**-OAc) formed. Two conceivable nonvicinal hydride shifts before symmetrization might be imagined as sources of optically active cation **9**, the precursor of



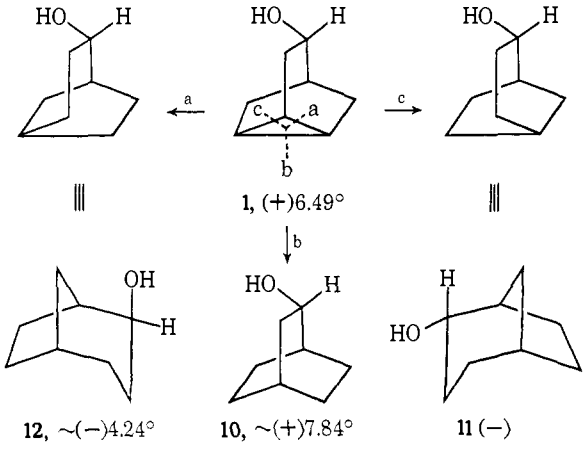
6-OAc. These are shown as occurring directly from **1**-OBs, but the same result would be obtained if the shift took place from a hypothetical unsymmetrical ion pair. In fact, however, a careful examination of the products from the solvolysis argues against this interpretation and implicates as the active component a small amount of unrearranged **1**-OAc of configuration inverted relative to starting **1**-OBs.

Products from the Acetolysis of Optically Active 1-OBs. The absolute configuration and a rough value for the maximum rotation of the starting alcohol **1**-OH can be obtained by hydrogenolysis to a ternary mixture of 2-bicyclo[2.2.2]octanol (**10**), *endo*-2-bicyclo[3.2.1]-octanol (**11**), and *exo*-2-bicyclo[3.2.1]octanol (**12**). The rotations shown in Scheme II refer to chloroform solu-

(14) The details of the structure of cyclopropylcarbinyl cation **8** are not implied and are of no direct concern here. Any cation with over-all reflection symmetry and with the capability of giving **7** and **5** will serve the conceptual function of **8** in Scheme I.

(15) (a) *Cf. inter alia* J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, 76, 4501 (1954); (b) J. A. Berson in "Molecular Rearrangements," Vol. 1, Part 3, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963.

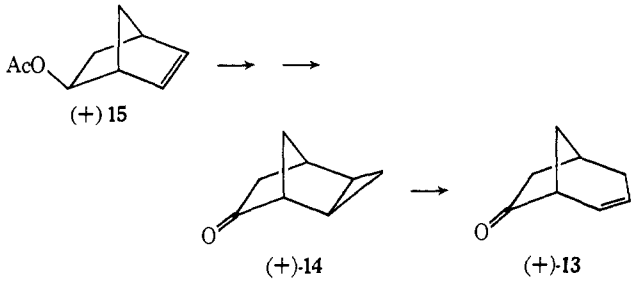
Scheme II



tions of starting material **1** and products, the latter being isolated by a difficult preparative vpc separation. Products **11** and **12** are of no particular interest in the present study, and only **12** of this epimeric pair is isolated.[16b] The correlation of **11** and **12** is described elsewhere[16a] in another connection.

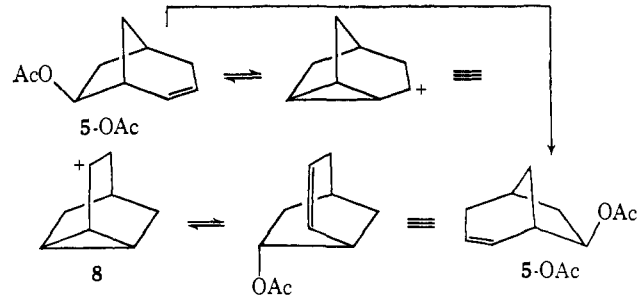
The known absolute configuration[17] and approximately known maximum rotation[18-21] of 2-bicyclo[2.2.2]octanol (**10**) combined with the data of Scheme II show that (+)-**1**-OH has a maximum rotation of about 24–32° ($CHCl_3$) and the absolute configuration indicated.

Conversion of the active (+)-alcohol **1**-OH to the *p*-bromobenzenesulfonate **1**-OBs and acetolysis without further purification of the derivative give a mixture of products which is separated by preparative vpc. The unsaturated acetate **5**-OAc is isolated optically inactive from two separate experiments using samples of **1**-OH of differing rotations. Lithium aluminum hydride cleavage of the acetate **5**-OAc to the alcohol **5**-OH and oxidation give a ketone **13** that is also inactive. This substance can be prepared independently (the actual experiment is in the enantiomeric series) in optically active form from (+)-*exo*-norbornenyl acetate (**15**) *via* the



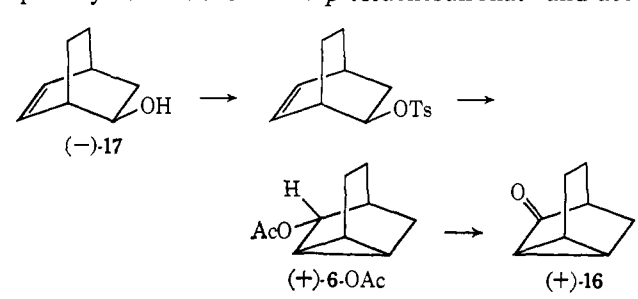
tricyclic ketone **14**. Boron trifluoride or an acidic ion-exchange resin at 100° convert (+)-**14** to (+)-**13**. From the known maximum rotation[22] of **15** and the above correlation with **13**, values of $[\alpha]_D$ ~856°, $[\alpha]_{365}$ ~4980° (in methanol) can be calculated for the maximum rotation of unsaturated ketone **13** (see Experimental Section). With the intrinsic rotation of **13** providing so sensitive a test, the observed inactivity of ketone **13** obtained from acetolysis product means that racemization in acetolysis is complete to within a few parts in ten thousand.

A mild reservation on this conclusion is needed since a control experiment on the behavior of optically active acetate **5**-OAc under the reaction conditions is not available. Because most reduction methods applied to ketone **13** give mainly the unwanted *endo* epimer of *exo*-alcohol **5**-OH, we have so far been unable to obtain a sufficient quantity of active *exo*-acetate **5**-OAc for test. In any case, if racemization occurs by reversible carbonium ion formation after the kinetically controlled capture of an optically active intermediate, there must be an extremely readily accessible racemizing pathway. This presumably would merely involve Wagner–Meerwein rearrangement of **5**-OAc, plausibly but not necessarily *via* symmetrical ion **8**.



Tricyclic acetate **1**-OAc, isolated by preparative vapor chromatography from the mixture of products resulting from acetolysis of optically active **1**-OBs, has a small activity which corresponds in sign and magnitude to 3–4% net inversion of configuration relative to the starting material. One possible spurious source for the rotation is the tricyclic acetate **6**-OAc resulting from transannular hydride shift. This material is only barely resolved from **1**-OAc even on capillary columns under the best vpc conditions, and it still contaminates the **1**-OAc isolated with a packed column under preparative separation conditions.

To check this possibility, the maximum rotation of **6**-OAc and of the corresponding ketone tricyclo[3.2.1.$0^{2,7}$]octan-6-one **6** (which has a substantially higher rotation) are established by correlations with bicyclo[2.2.2]oct-5-en-6-*exo*-ol (**17**-OH), the maximum rotation of which is known approximately by hydrogenation[22] to bicyclo[2.2.2]octan-2-ol (**10**-OH).[17] Conversion of optically active **17**-OH to a *p*-toluenesulfonate and ace-



(16) (a) J. A. Berson and P. Reynolds-Warnhoff, *J. Am. Chem. Soc.*, **84**, 682 (1962); **86**, 595 (1964). (b) The correlation in rotatory powers between **12** and **10** implied by Scheme II is only approximate because of isolation difficulties described in the Experimental Section.

(17) J. A. Berson and D. Willner, *J. Am. Chem. Soc.*, **84**, 575 (1962); **86**, 609 (1964).

(18) Isotopic dilution analyses give 40 ± 4.5[17] and 29.6.[19] Independent chemical correlations give ⩾ 32[20] and ⩾ 33°.[21]

(19) H. L. Goering and G. Fickes, *J. Am. Chem. Soc.*, **90**, 2862 (1968).

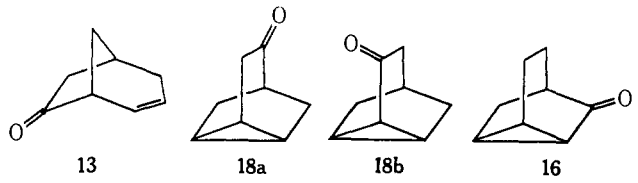
(20) J. A. Berson and N. Kundu, unpublished. N. Kundu, Ph.D. Thesis, University of Wisconsin, 1966.

(21) J. A. Berson and E. J. Walsh, Jr., unpublished; E. J. Walsh, Jr., Ph.D. Thesis, University of Wisconsin, 1968.

(22) K. Mislow and J. G. Berger, *J. Am. Chem. Soc.*, **84**, 1956 (1962).

tolysis, following experiments already carried out in the racemic series,[23] give optically active **6**-OAc, which is converted to ketone **16**.

The slightly active acetolysis product mixture from active **1**-OBs is converted successively to alcohols and then to a mixture of ketones consisting mainly of **13** and **18a**, which correspond to the major acetate products **5**-OAc and **1**-OAc. Small amounts of ketones **18b** and



13 18a 18b 16

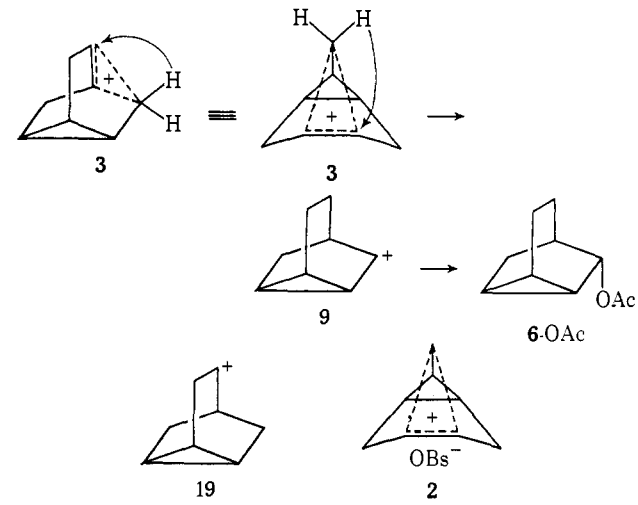
16 also are present. Ketone **13** is known to be inactive from the experiments already described, and both **18a** and **18b** are necessarily inactive by symmetry. From the known enantiomeric purity of the starting **1**-OBs and the amount of ketone **16** in the mixture, it can be calculated that if ketone **16** were formed with over-all complete preservation of enantiomeric purity, the ketone mixture should have $\alpha_{obsd} \sim -0.06°$, a value readily observable with the instrument at our disposal. In fact, the observed rotation is quite accurately zero ($\alpha_{obsd} = 0.000 \pm 0.002°$). There is no ready escape from the implications of this, for example, by the postulate that partial racemization occurs and depresses the rotation to an unobservably low value. In that case, the mixture of acetates from solvolysis should also be optically inactive, in conflict with experiment.

Barring the presence of an unknown impurity, the only hypothesis consistent with all the data is that the slight activity in the **1**-OAc product arises from about 3–4% net excess of **1**-OAc with configuration inverted relative to the starting **1**-OBs. The finding that a detectable part of the acetolysis proceeds by a conventional inversion mechanism is consistent with the earlier suggestion that at least in acetic acid, anchimeric assistance does not appear to produce a large rate enhancement in this system.

Hydride Shifts. Since tricyclo[3.2.1.$0^{2,7}$]oct-*exo*-6-yl product **6**-OAc seems to be formed optically inactive, the transannular hydride shift leading to it must occur *after* the system has passed through a symmetrical stage. This is most simply formulated as a reaction of either of the symmetrical cations **3** or **19** or of the symmetrical ion pair **2**. Hydride shift thus follows rather than runs parallel to carbon rearrangement or ionization.

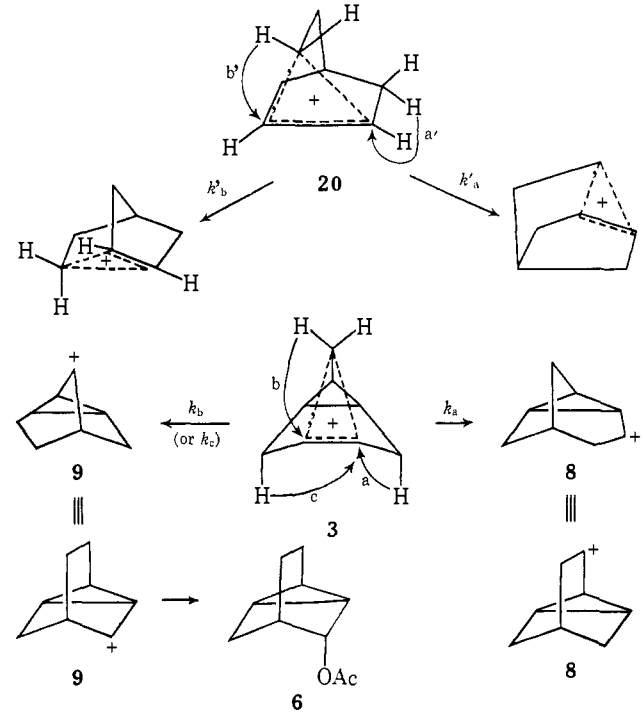
The result is similar to those in norbornyl cationic systems, where the evidence also favors sequential rather than competitive carbon and hydrogen shifts.[15,24,25]

There is, however, a striking difference from the behavior of norbornyl systems in the relative rates of vicinal and transannular hydride shift. In norbornyl cation **20**, the ratio of rates of transannular and vicinal hydride shift (k_b'/k_a') is at least 14,[26-28] but the corresponding ratio k_b/k_a in cation **3** is about 1.7×10^{-2} (Table II). In fact, the k_b/k_a ratio in **3** could be even lower, since the small amount of product **6**-OAc conceivably could result from the alternative hydride shift c.



3 3 9 6-OAc 19 2

This greater than 800-fold change in the relative rates may result from a number of factors, among which are bond angle strains associated with the incorporation of the trigonal carbon in rings of different sizes, but it is tempting to assign a large part of the effect to the sym-



20 9 3 8 9 6 8

(23) N. A. LeBel and J. E. Huber, *J. Am. Chem. Soc.*, **85**, 3193 (1963).
(24) A. Colter, E. C. Friedrich, N. J. Holness, and S. Winstein, *ibid.*, **87**, 378 (1965).
(25) (a) J. A. Berson, A. W. McRowe, and R. G. Bergman, *ibid.*, **89**, 2573 (1967). (b) Note that analogy to norbornyl systems implies the likelihood of stereospecificity for both vicinal[25c,d] and transannular[25e,f] hydride shifts. No experimental evidence on this is available for the present system. (c) J. A. Berson, J. H. Hammons, A. W. McRowe, R. G. Bergman, A. Remanick, and D. Houston, *ibid.*, **87**, 3248 (1965); **89**, 2590 (1967); (d) C. J. Collins, Z. K. Cheema, R. G. Werth, and B. M. Benjamin, *ibid.*, **86**, 4913 (1964); (e) J. A. Berson and P. W. Grubb, *ibid.*, **87**, 4016 (1965); (f) B. M. Benjamin and C. J. Collins, *ibid.*, **88**, 1556 (1966).

(26) Calculated from the values[27,28] $k_b'/k_{SOH} = 0.118$ for norbornyl cation and $k_{SOH}/k_a' \geq 119$ for methylnorbornyl cation and from the assumption that the latter ratio is applicable to norbornyl cation. The rate constant k_b' refers to transannular shift, k_a' to vicinal shift, and k_{SOH} to solvent capture, all in acetic acid at 100°.
(27) J. A. Berson, R. G. Bergman, J. H. Hammons, and A. W. McRowe, *J. Am. Chem. Soc.*, **89**, 2581 (1967).
(28) See also C. J. Collins and M. H. Lietzke, *ibid.*, **89**, 6565 (1967).
(29) For collections of the many references to this question, see *inter alia* L. Birladeanu, T. Hanafusa, B. Johnson, and S. Winstein, *ibid.*, **88**, 2316 (1966); P. von R. Schleyer and G. W. van Dine, *ibid.*, **88**, 2321 (1966).

metry of cation **8**, which is the product of vicinal shift in **3**. Cation **8** has the favorable[29] "bisected" cyclopropylcarbinyl geometry, whereas unsymmetrical cation **9**, the product of transannular shift, can only approximate it.[30]

It seems reasonable to suppose that this difference would be felt in the corresponding transition states. Another example of what may be the same effect is reported in an accompanying paper.[4]

Experimental Section[31]

The vpc columns used in this work are listed in Table III.

Table III. Vapor Chromatographic Columns[e]

Column	Dimensions (ft × in.)	Stationary phase
A	250 × 0.01[a]	UCON 50LB550X
B	250 × 0.01[a]	TCEP[b]
C	100 × 0.01[a]	TCEP[b]
D	100 × 0.01[a]	Apiezon L
E	10 × 0.25	Ethylene glycol succinate
F	10 × 0.375	Carbowax 20M
G	20 × 0.25	UCON 50LB550X
H (H-I)	10 × 0.375 (20 × 0.375)	TCEP
I	3 × 0.25	UCON 50LB550X
J	20 × 0.375	UCON 50HB2000
K	20 × 0.375	Carbowax 20M
L	6 × 0.25	*c*
M	27 × 0.25	Carbowax 20M
N	20 × 0.375	FFAP[d]
O	100 × 0.01[a]	UCON 50HB2000

[a] Stainless steel capillary. [b] Tri(β-cyanoethoxy)propane. [c] γ-Nitro-γ-methylpimelonitrile. [d] Varian's "free fatty acid phase." [e] Support for the stationary phase in the packed columns was Chromosorb P.

Tricyclo[3.2.1.0^{2,7}]octan-4-ol (1-OH) was obtained in 95% yield by the lithium aluminum hydride reduction of the corresponding ketone, which in turn was prepared by the procedure of Lumb and Whitham[6] and identified by comparison with an authentic sample of ketone kindly supplied by Dr. Whitham. After sublimation, **1-OH** had mp 140–141° (lit. mp 124.5–125.5°,[5] 132.5–135°[10]). The nmr spectrum (CCl_4) showed a broad multiplet centered at δ 3.60 (1 H, C*H*OH), a singlet at 2.14 (O-*H*) superimposed on complex absorption between 0.40 and 2.30 (11 H).

The ***p*-bromobenzenesulfonate (1-OBs)** was formed when a cold solution of **1-OH** (910 mg, 7.4 mmol) in pyridine (10 ml) was treated with *p*-bromobenzenesulfonyl chloride (2.12 g, 8.3 mmol). After 16 hr at 0°, the mixture was added to ice-cold dilute hydrochloric acid, extracted with ether, and dried. Filtration and evaporation gave 2.12 g of an oil which crystallized on cooling. Recrystallization from petroleum ether, (bp 30–60°) with minimal heating gave 1.72 g (68%) of colorless needles, mp 50–52°. The nmr spectrum (CCl_4) showed a singlet at δ 7.65 (4 H, aromatic), a complex multiplet centered at 4.45 (1 H, C*H*OBs), and a complex pattern between 2.30 and 0.40 (10 H). The substance could be stored at −10° but rapidly decomposed at room temperature to a black tar.

Lithium–Ammonia Reduction of 1-OBs. To about 30 ml of liquid ammonia (distilled from sodium) in a three-necked flask equipped with a condenser cooled with solid carbon dioxide–acetone was added 500 mg of lithium metal. The resulting blue solution was stirred for 10 min and treated with a solution of 241 mg of **1-OBs** in 3 ml of dry tetrahydrofuran and 0.5 ml of dry methanol. The syringe was rinsed with 1 ml of dry tetrahydrofuran, and the rinsings were added to the reaction mixture. After having been stirred for 1 hr at −78°, the mixture was treated with methanol until the blue color disappeared. The ammonia was allowed to evaporate overnight, and the mixture was treated with water and extracted with pentane. The pentane extract was washed with brine, dried, and evaporated to give 86 mg of a waxy solid, which was identified by its infrared spectrum and vpc as pure **1-OH**.

Kinetic Measurements. Titrimetric rates were determined by an ampoule technique.[32] A solution of **1-OBs** (*ca.* 0.023 *M*) in standard sodium acetate–acetic acid (0.02570 *M*, containing 1% w/w acetic anhydride) was distributed in approximately 5.5-ml portions among a series of Pyrex ampoules, which then were cooled in ice and sealed. The ampoules were placed in a thermostat bath and allowed to reach bath temperature (10–20 min). The time of withdrawal of the first ampoule is called zero time. Each ampoule was opened, and with a calibrated pipet, a 4.913-ml aliquot was withdrawn and titrated to a bromophenol blue end point with a standard solution of perchloric acid in acetic acid. The normality of the perchloric acid solution was determined by titration in acetic acid against a primary standard, potassium hydrogen phthalate. The normality of the sodium acetate solution was checked by titration against the standard perchloric acid.

Infinity titers were obtained after at least 10 half-lives and generally were within 2% of the theoretical values.

Rate constants were determined graphically from the slope of plots of log $(V_t - V_\infty)$ *vs.* time, where V_t = titer at time *t*, and V_∞ = titer at "infinite" time. Good first-order behavior was observed through each run. Polarimetric rate constants were determined in a center-filling 4.03-dm all-glass-jacketed polarimeter tube of 23-ml capacity. The potassium acetate–acetic acid stock solution was equilibrated at 19.90 ± 0.01° overnight, and water from the constant-temperature bath also was circulated through the jacket of the empty polarimeter tube overnight. A weighed amount of optically active **1-OBs** was made up to 25.0 ml with the equilibrated stock solution, and the resulting solution was quickly transferred to the polarimeter tube. Readings at known time intervals were taken with the Rudolph Series 200 photoelectric polarimeter, using the mercury 365-mμ source. The data are collected in Table I.

Preparative solvolyses of 1-OBs were carried out under the conditions given in Table II. Typical details of the individual runs follow.

Acetolysis. A solution of sodium acetate (67.8 mg, 0.82 mmol) in dry acetic acid (30 ml) was equilibrated at 50° for 30 min. A sample of **1-OBs** (251 mg, 0.73 mmol) was added, and the mixture was stirred at 50° for 1 hr, cooled, poured into water, saturated with sodium chloride, and extracted four times with pentane. The pentane extract was washed with sodium bicarbonate solution and then with brine, dried over calcium sulfate, and evaporated through an 18-in. Vigreux column. Bulb-to-bulb distillation gave 110 mg (91%) of an acetate mixture, which was analyzed on column D at 95°. Under these conditions, tricyclic acetate **7-OAc** was stable and emerged just before acetate **1-OAc**. The two peaks overlapped, but the peak corresponding to unsaturated acetate **5-OAc** was well resolved. The composition was found to be 31% **5-OAc** and 69% **7-OAc** plus **1-OAc**. A sample of the solvolysis product (23 mg) in 1 ml of acetic acid was heated at 100° for 15 min to convert tricyclic acetate **7-OAc** to unsaturated acetate **5-OAc**. Work-up as before and analysis on vpc column A showed 61% **5-OAc** and 39% **1-OAc**. Hence, the composition of the original solvolysis product was that given in Table II (31% **5-OAc**, 30% **7-OAc**, and 39% **1-OAc**).

A similar acetolysis was carried out at 100°, conditions under which control experiments (see below) show that tricyclic acetate **7-OAc** is unstable. The product mixture consisted of 65% unsaturated acetate **5-OAc** and 35% tricyclic acetate **1-OAc**. About 5% of a hydrocarbon was also present. This was identified as tricyclo[3.2.1.0^{2,7}]oct-3-ene[33,34] by isolation (vpc on column F at 165°) and comparison of the infrared spectrum with that reported.[34]

(30) The unsymmetrical structure of **9** exposes the p lobes to nucleophilic attack unequally; this may well be part of the basis for the strong preference[23] for kinetically controlled capture from the indicated direction (to give products of the *exo* series 6 rather than the *endo* epimers).

(31) Optical rotations refer to measurements at fixed wavelength with the Rudolf Series **200** photoelectric polarimeter equipped with oscillating polarizer. Optical rotatory dispersion curves derive from measurements with a Cary Model **60** instrument kindly made available to us by Professor T. Higuchi, School of Pharmacy. The nmr spectra were taken with a Varian A-60-A spectrometer. We are indebted to Mr. Kenneth Breslauer for help with some of the experiments. Microanalyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich. Standard reaction procedures are described in paper I of this series [J. A. Berson, J. J. Gajewski, and D. S. Donald, *J. Am. Chem. Soc.*, **91**, 5550 (1969)].

(32) *Cf.* S. Winstein, E. Grunwald, and L. L. Ingraham, *ibid.*, **70**, 821 (1948).

(33) C. A. Grob and J. Hostynek, *Helv. Chim. Acta*, **46**, 1676 (1963).

(34) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 736 (1963).

Bicyclo[3.2.1]oct-2-en-7-yl acetate (5-OAc)[10,35] was collected from the same chromatogram as a clear oil, homogeneous by capillary vpc. Its nmr spectrum in carbon tetrachloride showed complex absorption at δ 6.04–5.27 (2 H, vinyl), a multiplet centered at 4.96 (1 H, C*H*OAc), complex absorption at 2.67 (11 H), and a sharp singlet at 1.93 (acetate). Further characterization is described below in connection with experiments in the optically active series.

Tricyclo[3.2.1.0^{2,7}]oct-4-yl acetate (1-OAc) emerged last from the chromatogram. Its infrared spectrum was identical with that of an authentic sample obtained by acetylation of the corresponding alcohol **1-OH**.[5]

Hydrolysis. A solution of pyridine (257 mg, 3.25 mmol) in 175 ml of 20% water–80% acetone (v/v) was equilibrated at 50° for 45 min and treated with 1.013 g (2.96 mmol) of **1-OBs**. After 1 hr at 50°, the volume of the mixture was reduced to *ca.* 50 ml by distillation of most of the acetone at 30° under aspirator pressure. The solution was saturated with sodium chloride and extracted with five portions of pentane. After having been washed with 2% hydrochloric acid and brine, the pentane extracts were dried and evaporated to give 271 mg of a waxy solid. Capillary vpc analysis on column B showed two peaks, but tailing prevented an accurate analysis of the components. The nmr spectrum showed C*H*OH signals at δ 3.58 and 4.13 in the ratio 70:30, representing the relative amounts of alcohols **1-OH** and **5-OH**. Part of the product was acetylated with acetic anhydride–pyridine. Analysis of the product on column A showed 70% tricyclo[3.2.1.0^{2,7}]oct-4-yl acetate (**1-OAc**) and 30% unsaturated acetate **5-OAc**. Analysis on column D under conditions where tricyclo[3.2.1.0^{2,7}]oct-3-yl adetate **7-OAc** is stable (see below) showed that this material was not present, and controls (see below) showed that **7-OH** was converted to **5-OH** under the hydrolysis conditions.

Control Experiments on Tricyclo[3.2.1.0^{2,7}]octan-3-ol and Its Acetate (7-OH and 7-OAc). The alcohol **7-OH** was unstable on column F. A sample that produced one peak in capillary vpc analysis on column B at 118° was passed through column F at 187°. The collected material showed two peaks on column B, one corresponding to **7-OH** and the other to unsaturated alcohol **5-OH**. The infrared spectrum also showed the presence of these two alcohols. On column E at 140° (injector block at 180°), **7-OH** gave a large peak emerging just after the solvent (benzene) which was probably attributable to olefin. Only a small amount (~15%) of the original sample emerged as an alcohol, identified as **5-OH** by its nmr spectrum.

Acetylation of **7-OH** with acetic anhydride–pyridine gave an acetate which showed no vinyl proton absorptions in the nmr, a complex multiplet near δ 5.1 (1 H, C*H*OAc), and a complex pattern between 0.8 and 2.0 with a singlet (C*H*$_3$CO) superimposed at 1.95 (total about 13 H). This is consistent with the structure of tricyclo[3.2.1.0^{2,7}]oct-3-yl acetate (**7-OAc**).

The substance is extremely unstable to vpc. On columns A and B, the patterns observed depended upon conditions but were always complex. A total of 100 μl in 20-μl portions was injected onto column E at 135° (injector block at 170°). The eluate consisted of material (67 mg) from a single peak, which was identified by its capillary vpc retention time and nmr spectrum as unsaturated acetate **5-OAc**, bicyclo[3.2.1]oct-2-en-*6-exo*-yl acetate. The *endo* epimer (see below) was not present (<0.5%).

Acetate **7-OAc** passed through the Apiezon L capillary column (column D) at 95° with little decomposition. Its retention time was different from that of the bicyclic unsaturated acetate **5-OAc**.

When acetate **7-OAc** (28 mg) was heated for 15 min at 100 in acetic acid (2 ml) buffered with sodium acetate (60 mg) and the mixture poured into water, extracted with pentane, washed with sodium bicarbonate and then with brine, dried over sodium sulfate, and evaporated, the residual oil showed one peak on vpc and had an infrared spectrum identical with that of unsaturated acetate **5-OAc**.

A solution of tricyclic alcohol **7-OH** (228 mg) in acetic acid (5 ml) was heated at 100° for 45 min. Dilution with water, extraction with ether, and conventional work-up gave 280 mg of an oil showing one peak on capillary vpc. The product was identified by its nmr spectrum as **5-OAc**.

Optical Activation of Tricyclo[3.2.1.0^{2,7}]oct-4-yl Acid Phthalate. The acid phthalate was prepared in virtually quantitative yield by heating equimolar quantities of **1-OH** and acid-free phthalic anhydride in solution in about twice their combined weight of pyridine for 4 hr. The solution was diluted sevenfold with benzene, washed twice with dilute sulfuric acid and then with water. After having been dried over sodium sulfate, the solution was evaporated to give a white solid which was used without further purification.

A solution of ephedrine (8.0 g) in dry ether was added to a solution of 11.7 g of the crude acid phthalate in dry ether. Crystals separated in about 1 min. Four recrystallizations from acetone gave material from which acid phthalate was regenerated by shaking with ether and 10% hydrochloric acid. The ether layer was dried over magnesium sulfate and evaporated to give 1.7 g of oily product. This material was dissolved in 50 ml of 10% potassium hydroxide solution, and the mixture was steam distilled until 200 ml of distillate had been collected. Extraction with ether, drying with magnesium sulfate, and evaporation gave a residue which was sublimed at 0.2 mm. The sublimate, 700 mg of white crystals, had $[\alpha]^{21}$D −3.06° (*c* 10.4, *l* 1, chloroform). The dextrorotatory form could be obtained from the mother liquors. A number of samples from different small-scale resolutions were used during the subsequent work. The degree of optical purity varied between 10 and 20%. The configurations and optical rotatory powers of **1-OH** and **1-OAc** were established by acetylation of **1-OH** of $[\alpha]$D −3.1° (*c* 10.4, *l* 1, chloroform) to **1-OAc** of $[\alpha]$D −2.4° (*c* 9, *l* 1, chloroform). Lithium aluminum hydride cleavage of the latter gave back **1-OH** of $[\alpha]$D −3.2°.

A sample of **1-OH** having $[\alpha]$D +3.08°, $[\alpha]_{365}$ +9.14° (*c* 10.4, *l* 1, methanol), was converted to the *p*-bromobenzenesulfonate as in the racemic series. The crude **1-OBs** had no OH absorption in the infrared spectrum and showed $[\alpha]$D +0.64° (*c* 11, *l* 1, chloroform). To avoid the possibility of optical fractionation, it was used without crystallization. Acetolysis of the sample (0.20 *M*) in the presence of 0.22 *M* sodium acetate at 100° for 1 hr gave an acetate product which was separated on column E at 140° into two fractions.

Fraction 1 (404 mg) was pure unsaturated acetate **5-OAc**, which showed $[\alpha]$D 0.000, $[\alpha]_{365}$ 0.000 (*c* 26.7, *l* 1, chloroform). Lithium aluminum hydride cleavage of this acetate gave alcohol which was also inactive (*c* 10.9, *l* 1, methanol). In another experiment, acetolysis of **1-OBs** prepared from **1-OH** of $[\alpha]$D +6.30° (*v* 4.3 *l* 1, chloroform) gave (after the same processing already described) unsaturated alcohol **5-OH** which was oxidized by chromic oxide–pyridine to bicyclo[3.2.1]oct-2-en-6-one (**13**) which was also inactive at both the sodium D and mercury 365-mμ lines (*c* 1.70, *l* 1, isooctane).

Fraction 2 (157 mg) was shown by analysis on column A to consist of 4% **5-OAc**, 93.5% tricyclo[3.2.1.0^{2,7}]oct-4-yl acetate (**1-OAc**), and 2.5% tricyclo[3.2.1.0^{2,7}]oct-*endo*-8-yl acetate (**6-OAc**). This mixture showed $[\alpha]$D −0.10°, $[\alpha]_{365}$ −0.28° (*c* 12.9, *l* 1, chloroform). The alcohol mixture obtained from this by lithium aluminum hydride cleavage showed $[\alpha]$D −0.10°, $[\alpha]_{365}$ −0.36° (*c* 10.1, *l* 1, methanol). These values corresponded to 3–4% inversion of configuration in **1-OAc**. That the rotations were not due to alcohol **6-OH** or acetate **6-OAc** was checked as follows.

The acetate solutions from the three polarimetric rate determinations using **1-OBs** of initial optical purity about 20% showed infinity readings of −0.009, −0.019, and −0.015°. These solutions were combined and the acetates were isolated by ether extraction and bulb-to-bulb distillation at a bath temperature 120° and aspirator pressure. The acetate mixture contained 65% unsaturated acetate **5-OAc** and 35% **1-OAc**. The product of transannular hydride shift **6-OAc** could not be resolved due to some deterioration of column A. The mixture showed $[\alpha]$D −0.25°, $[\alpha]_{365}$ −0.84° (*c* 3.46, *l* 1, ether). The acetates were cleaved with lithium aluminum hydride and the resulting alcohols (620 mg) oxidized with CrO_3 (1.45 g) in pyridine (25 ml) at room temperature for 20 hr. The product isolated by ether extraction and bulb-to-bulb distillation was a clear oil, which was shown by vpc on column C to consist of 0.9% unknown material of low retention time, 64.8% bicyclo[3.2.1]oct-2-en-6-one (**13**), 31.6% tricyclo[3.2.1.0^{2,7}]octan-4-one (**18a**), 0.7% tricyclo[3.2.1.0^{2,7}]octan-6-one (**16**), and 2.0% tricyclo[3.2.1.0^{2,7}]octan-3-one (**18b**). Since the starting **1-OBs** was 20% optically pure, and the correlation to be described gives the value $[\alpha]$D 212° (chloroform) as the rotation of enantiomerically pure **16**, the rotation to be expected from the 0.7% **16** in the ketone mixture was $[\alpha]$D −1.48°. Under the conditions of measurement, αD(obsd) should have been − 0.059° if the only source of activity was **16** of undiminished enantiomeric purity. The observed value was αD(obsd) 0.000° (*c* 5.1, *l* 4, chloroform).

Correlation of Configurations and Optical Rotatory Powers of Tricyclo[3.2.1.0^{2,7}]octan-6-one (16) and Tricyclo[3.2.1.0^{2,7}]oct-6-*endo*-yl Acetate (6-OAc) with Those of Bicyclo[2.2.2]oct-5-en-2-*exo*-ol (17-OH). A sample of **17-OH** (189 mg), $[\alpha]$D −5.70° (*c*

(35) K. B. Wiberg and G. R. Wenzinger, *J. Org. Chem.*, 30, 2278 (1965).

0.87, *l* 1, chloroform), kindly supplied by Dr. E. J. Walsh, Jr.,[21] gave on oxidation with chromic oxide–pyridine a sample of bicyclo[2.2.2]oct-5-en-2-one of $[\alpha]_D$ −65.1° (*c* 1.2, *l* 1, chloroform) and hence is about 10% optically pure.[1,7,18,22] The alcohol **17-OH** was converted to a *p*-toluenesulfonate **17-OTs**[23] in the usual way, and the latter was subjected to acetolysis in the presence of sodium acetate buffer for 24 hr. Conventional work-up and isolation of the tricyclo[3.2.1.0^{2,7}]oct-6-*endo*-yl acetate **6-OAc** by vpc on column I gave **6-OAc** with $[\alpha]_D$ +3.46° (*c* 5, *l* 1, in chloroform). Lithium aluminum hydride reduction followed by chromic oxide–pyridine oxidation and isolation by vpc on column I gave ketone **16**, $[\alpha]_D$ +20.6° (*c* 1.7, *l* 1, chloroform). Enantiomerically pure material thus has a maximum rotation of about 212°. This figure is subject to the same uncertainty as that for **10-OH**.[18] The ketone was homogeneous on column C, and its retention times on columns A and C were identical with that of one of the ketones in the ketone mixture obtained from the acetolysis products of **1-OBs**.

Correlation of Configurations and Optical Rotatory Powers of Tricyclo[3.2.1.0^{2,7}]octan-4-ol (1-OH) with those of Bicyclo[2.2.2]-octanol (10) and Bicyclo[3.2.1]octan-2-*exo*-ol (12). A sample (200 mg) of **1-OH**, $[\alpha]_D$ +6.49° (*c* 3.0, *l* 1, chloroform), was dissolved in 2 ml of acetic acid, treated with 150 mg of platinum oxide, and placed in a long-necked flask, which was shaken in a Parr shaker at 40 psi pressure of hydrogen for 27 hr. The solution was neutralized with sodium bicarbonate and extracted with pentane. After having been washed with brine and dried with magnesium sulfate, the pentane extract was evaporated, and the residual material was separated by vpc on column L. (In a separate experiment, the hydrogenation was interrupted before completion, and starting material of undiminished rotation was recovered.) The hydrogenation products were eluted in the order **12-OH**, **10-OH**, and **11-OH**.

The sample consisting largely of bicyclo[2.2.2]octan-2-ol (**10-OH**) was sublimed and then showed $[\alpha]_D$ +7.60°, $[\alpha]_{365}$ +21.3° (*c* 2.6, *l* 1, chloroform). Capillary vpc on column B showed this sample (called I) to contain 2% bicyclo[3.2.1]octan-2-*exo*-ol (**12-OH**) and 98% **10-OH**. The infrared spectrum was identical with that of an authentic sample.

The vpc fraction of **12-OH** was sublimed to remove some column packing material, whereupon it showed $[\alpha]_D$ −3.50° (*c* 3.1, *l* 1, chloroform). Capillary vpc on column B showed the presence in this sample (called II) of a small amount (~5%) of **10-OH** as well as about 4% of an unknown contaminant. For the purposes of the following calculations, it is assumed that the unknown substance is optically inactive.

If the specific rotation of chemically homogeneous **10-OH** and **12-OH** are called α_{10} and α_{12}, the observed specific rotations of samples I and II (α_I and α_{II}) may be represented by eq 1 and 2. Solution of simultaneous eq 1 and 2 gives the values α_{10} = +7.84°

$$\alpha_I = +7.60° = 0.98\alpha_{10} - 0.02\alpha_{12} \quad (1)$$

$$\alpha_{II} = -3.65° = 0.05\alpha_{10} + 0.95\alpha_{12} \quad (2)$$

and α_{12} = −4.24°. Using the maximum rotation of 17.4° for **12-OH**,[19] the optical purity of the **12-OH** isolated from hydrogenolysis of **1-OH** may be calculated as 24%. Using the maximum rotation of 29.6–40° for **10-OH**,[18] the optical purity of the **10-OH** isolated from hydrogenolysis of **1-OH** may be calculated as 20–26%. This value corresponds to **1-OH** of $[\alpha]_D$ 6.49°, so that enantiomerically pure **1-OH** has $[\alpha]_D$ 24–32° (chloroform).

Memory Effects in Multiple Carbonium Ion Rearrangements. V. Nucleophilic Capture of an Asymmetric Tricyclooctyl Cationic Intermediate in the Ring Expansion of the Nortricyclylcarbinyl System[1,2]

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Abstract: A memory effect is observed in the capture of the first ring-expanded cation in reactions of optically active nortricyclylcarbinyl derivatives. This nucleophilic capture leads to tricyclo[3.2.1.0^{2,7}]oct-4-yl derivatives with partial (*ca.* 30%) survival of the original enantiomeric purity. Configurational correlations show that capture occurs predominantly from the same side as that occupied by the leaving group. The complex series of rearrangements also can be entered from the tricyclo[3.2.1.0^{2,4}]oct-6-yl side, with about the same degree of retention of enantiomeric purity. The intermediate responsible for these results cannot be the same as the cation generated in solvolysis of tricyclo[3.2.1.0^{2,7}]oct-4-yl derivatives, since that is shown in an accompanying paper to behave quite differently. The nortricyclylcarbinyl and tricyclo[3.2.1.0^{2,4}]oct-6-yl products are formed with essentially complete preservation of enantiomeric purity. These results require the postulation of at least two cationic intermediates as precursors of the tricyclo[3.2.1.0^{2,7}]oct-4-yl products, and taken together with the detailed product distributions and other evidence, they lead to the formulation of the mechanism of the whole set of interconnected processes.

Ring-expansions of norbornylcarbinyl derivatives in carbonium ion reactions quite generally produce once-rearranged intermediates that behave unsymmetrically.[4] In the 2-norbornylcarbinyl system, although most of these intermediates **3** and **4** formed from both *endo*[5] and *exo*[6] substrates (**1** and **2**) suffer further

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(2) For preliminary reports, see (a) J. A. Berson, R. G. Bergman, G. M. Clarke, and D. Wege, *J. Am. Chem. Soc.*, **90**, 3236 (1968); (b) J. A. Berson, G. M. Clarke, D. Wege, and R. G. Bergman, *ibid.*, **90**, 3238 (1968); (c) J. A. Berson, D. Wege, G. M. Clarke, and R. G. Bergman, *ibid.*, **90**, 3240 (1968).

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(4) For a review, see J. A. Berson, *Angew. Chem.*, **80**, 765 (1968); *Angew. Chem. Intern. Ed. Engl.*, 7, 779 (1968).

(5) J. A. Berson and P. Reynolds-Warnhoff, *J. Am. Chem. Soc.*, **84**, 682 (1962); **86**, 595 (1964).

(6) J. A. Berson and D. Willner, *ibid.*, **84**, 675 (1962); **86**, 609 (1964).