Optically active **3c** also may result from capture of **9** directly at C-2, but the approximate microscopic reverse of this process, **3a** → **9**, does not seem to be important, again since entry into the scheme at **3a** leads only to products **3c** and **4c**, not to **1c** and **2c** (Table I). If escape of some of the cations **9** to racemic intermediates can occur directly and irreversibly (**9** → **7** and/or **6**), cation **10** is superfluous.

The detailed electronic structures of the intermediates **9**, **10**, and **11** are schematic, and this entire pool of optically active cations could be replaced by corresponding sets of classical ions. Rapid equilibration among these (or their replacement by a single nonclassical species, *e.g.*, **12**), however, would predict a product distribution independent of the point of entry into the scheme, in conflict with the results of Table I. In fact, no further economies of representation can be effected, since the data clearly require at least one other intermediate which must be symmetrical (*e.g.*, **6** and/or **7**).

(12) National Institutes of Health Predoctoral Fellow, 1964–1966.

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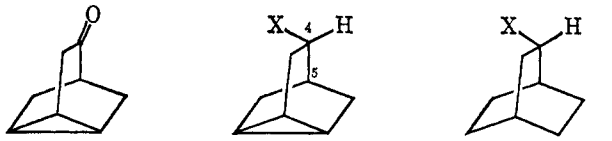
Preferential Formation of a Symmetrical Rather Than an Unsymmetrical Cyclopropylcarbinyl Cation. Vicinal *vs.* Transannular Hydride Shift in the Tricyclo[3.2.1.0^{2,7}]oct-4-yl System[1]

Sir:

As part of a study[2] of cations of the nortricyclylcarbinyl–tricyclooctyl series, we have observed that the pronounced preference for transannular rather than vicinal hydride shift seen in norbornyl cations is reversed in tricyclo[3.2.1.0^{2,7}]oct-4-yl cation.

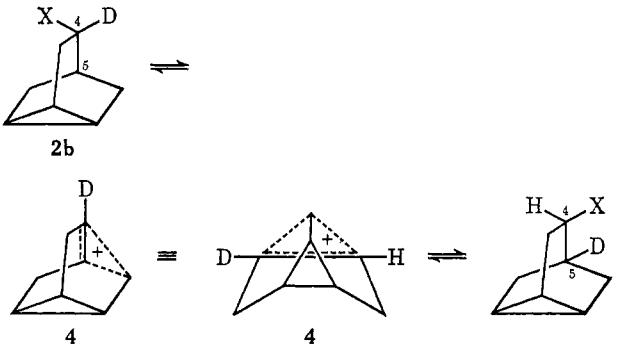
Lithium aluminum hydride reduction of the ketone **1**[3] gives the tricyclic alcohol **2a**, mp 140–141° (lit. mp 124.5–125.5°,[3] 132.5–135°[4]).

Optical activation of the acid phthalate **2c** is achieved by recrystallization of the ephedrine salt. Hydrogenolysis of active alcohol **2a**, $[\alpha]_D$ +6.49° ($CHCl_3$), in acetic acid over platinum oxide gives 2-bicyclo[2.2.2]-octanol (**3a**), mixed with *exo*- and *endo*-2-bicyclo[3.2.1]-octanols. Isolation of **3a** gives material of $[\alpha]_D$ +7.84° ($CHCl_3$). These data combined with the known absolute configuration[5] and approximately known maximum rotation[6] of **3** show that (+)-**2a** has a maximum rotation of about 24.4–31.7° ($CHCl_3$) and the absolute configuration indicated.



1 (+)-**2a**, X = OH; **b**, X = OBs; **c**, X = OPhth; **d**, X = OAc (+)-**3a**, X = OH; **b**, X = OBs

The titrimetrically determined rate constants ($k_t \times 10^4$ sec^{-1}) for acetolysis (NaOAc or KOAc buffer) of **2b** are 0.430 ± 0.005 at 19.90°, 1.67 ± 0.02 at 29.87°, and 6.33 ± 0.16 at 40.16°. The value extrapolated to 25°, 0.871, is *ca.* ten times that for the 2-bicyclo[2.2.2]-octyl analog **3b**.[7,10] The polarimetric rate constant ($k_\alpha \times 10^4$ sec^{-1}) is 1.38 ± 0.03 at 19.90°, about $3.1k_t$; presumably the difference is caused by racemization of **2b** during ion-pair return.[11,12] At least some of this racemization is associated with Wagner–Meerwein rearrangement, since acetolysis of 4-deuterio-**2b** gives **2d** with ~50% of the label at C-4 and ~50% at C-5.[13] The results closely resemble those observed in the *exo*-norbornyl system[11] and are consistent with the formulation of the initial solvolysis intermediate as the symmetrical ion **4**.[14]



2b **4** **4**

Table I shows that the major products of the solvolysis of **2b** are the closely related pair of alcohols **7a** and **8a** (or acetates **7d** and **8d**). Because of the instability of the tricyclic materials **8a** and **8d**, which readily rearrange to the unsaturated isomers **7a** and **7d**, the yield of substances of the structure **7** and **8** in any run are significant only as their sum. The acetate **7d** isolated from solvolysis of optically active **2b** is completely inactive. The derived ketone (maximum $[\alpha]_D$ 883°) also is inactive.

(1) We are grateful for grants in partial support of this work from the National Science Foundation (GP6212X), 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 related papers in this series, 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, D. Wege, G. M. Clarke, and R. G. Bergman, *ibid.*, **90**, 3240 (1968).

(3) J. T. Lumb and G. H. Whitham, *Tetrahedron*, **21**, 499 (1965). We are indebted to Dr. Whitham for a comparison sample of ketone **1**, which was identical with that prepared in our laboratory.

(4) R. R. Sauers, J. A. Beisler, and H. Feilich, *J. Org. Chem.*, **32**, 569 (1967).

(5) J. A. Berson and D. Willner, *J. Am. Chem. Soc.*, **86**, 609 (1964).

(6) Isotopic dilution analyses give 40 ± 4.5[5] and 29.6°.[7] Independent chemical correlations give ≥32[8] and ≥33°.[9]

(7) H. L. Goering and G. Fickes, unpublished; G. Fickes, Ph.D. Thesis, University of Wisconsin, 1965.

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

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

(10) (a) H. M. Walborsky, M. E. Baum, and A. A. Youssef, *J. Am. Chem. Soc.*, **83**, 988 (1961); (b) H. L. Goering and M. F. Sloan, *ibid.*, **83**, 1992 (1961), report the value for the *p*-toluenesulfonate.

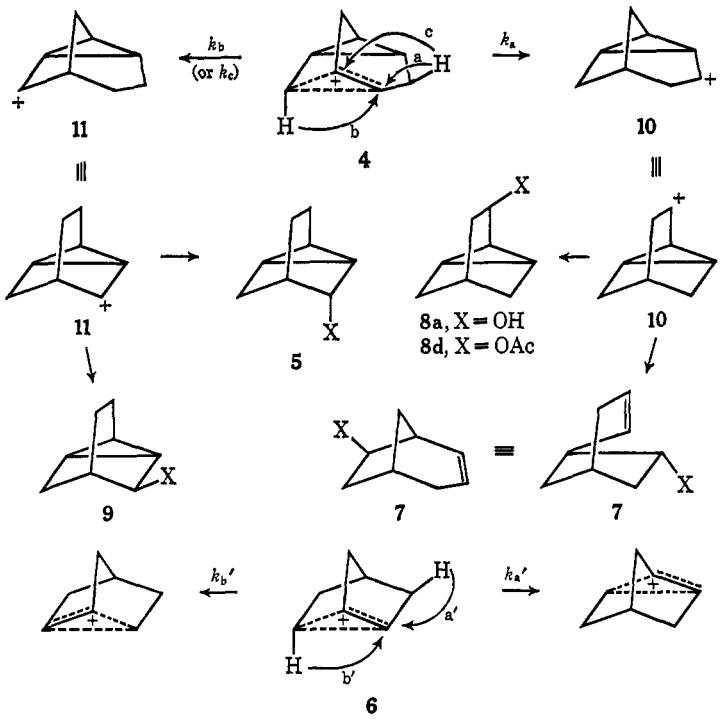
(11) S. Winstein and D. Trifan, *ibid.*, **74**, 1147, 1154 (1952).

(12) S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2165 (1952).

(13) This confirms a previous report of a similar labeling experiment.[4]

(14) A minor competing path appears to result in a small amount of direct displacement which gives 2–4% **2d** of inverted configuration in acetolysis. Small amounts of tricyclo[3.2.1.0^{2,7}]oct-3-ene[15] also are found.

(15) (a) W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 736 (1963); (b) C. A. Grob and J. Hostynek, *Helv. Chim. Acta*, **46**, 1676 (1963).



Products **7** and **8** must arise by vicinal hydride shift in cation **4**, leading to the cyclopropylcarbinyl cation **10**, whereas the minor product **5** results from competing transannular shift to the isomeric cyclopropylcarbinyl cation **11**.

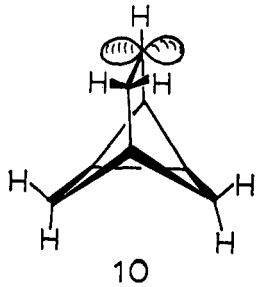
Table I. Products from Solvolyses of Tricyclo[3.2.1.0^{2,7}]oct-4-yl *p*-Bromobenzenesulfonate (**2b**)

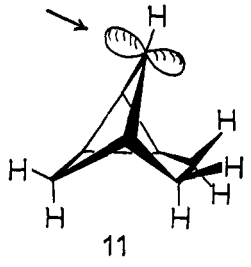
Conditions	—Product, % yield[a]— 2[d]	7[d] 8[c]	5
HOAc, NaOAc, 50°	39	61[e]	~1[a]
HOAc, NaOAc, 100°	35	65[f]	~1[a]
80% aqueous acetone, C_5H_5N, 50°	71	29[f]	*b*
70% aqueous dioxane, C_5H_5N, 100°	58	42[f]	*b*

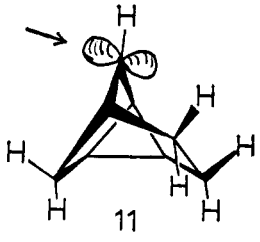
[a] Identified by its retention time and that of the corresponding ketone. [b] Not determinable in this run. [c] Presence of **8** inferred from its retention time. [d] Identified by isolation and spectroscopic comparison with authentic samples. [e] About equal amounts of **7** and **8**. [f] **7** only. [g] In acetolyses, X = OAc (**d**); hydrolyses, X = OH (**a**).

As is the case in norbornyl cation (**6**),[16] hydride shift is competitive in rate with solvent capture and is much diminished in importance in the more strongly nucleophilic aqueous media (Table I), but transannular shift, which in norbornyl cation is very much faster than vicinal shift, becomes subsidiary to it in cation **4**; the k_b'/k_a' ratio is ≥ 14 in norbornyl cation,[17] but the corresponding k_b/k_a ratio is about 1.7×10^{-2} in cation **4**. In fact, the k_b/k_a ratio in **4** could be even lower, since the small amount of product **5** conceivably could result from process c.

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 symmetry of cation **10**, which is the product of vicinal shift in **4**. This cation has the favorable[19] "bisected" cyclopropylcarbinyl geometry, whereas unsymmetrical cation **11**, the result of transannular shift, can only approximate it.[20]







(16) J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **76**, 4501 (1954).

(17) Calculated from the values[18a] $k_b'/k_{SOH} = 0.118$ for norbornyl cation and $k_{SOH}/k_a' \geq 119$ for methylnorbornyl cation and 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°.)

(18) (a) J. A. Berson, R. G. Bergman, J. H. Hammons, and A. W. McRowe, *ibid.*, **87**, 3246 (1965); **89**, 2581 (1967); (b) see also C. J. Collins and M. H. Lietzke, *ibid.*, **89**, 6565 (1967).

(19) *Cf.* 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), and references cited there.

(20) The unsymmetrical structure of **11**, shown here in two conformations, exposes the p lobes to nucleophilic attack unequally; this presumably accounts for the strong preference[21] for kinetically controlled capture from the indicated direction (to give **5** rather than its epimer **9**).

(21) N. A. LeBel and J. E. Huber, *J. Am. Chem. Soc.*, **85**, 3193 (1963).

It seems reasonable to suppose that this difference would be felt in the corresponding transition states. Another example of what may be the same influence is reported in an accompanying paper.[2b]

(22) National Institutes of Health Predoctoral Fellow, 1964–1966.

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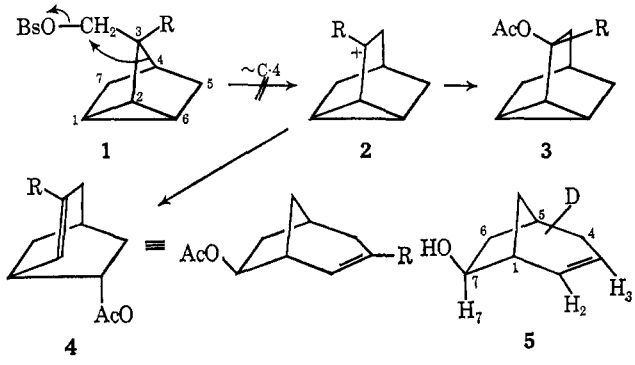
A Circuitous Mechanism for the Formation of a Cyclopropylcarbinyl Cation. On the Anomalous Relative Migratory Aptitude of a Cyclopropyl *vs.* a Cyclopentyl Ring in Nortricyclylcarbinyl Cation[1]

Sir:

Carbonium ion reactions of the nortricyclylcarbinyl system (**1**) produce large amounts of materials derived from the 3-tricyclo[3.2.1.$0^{2,7}$]octyl cation (**2**) which is captured either in the form of the corresponding very sensitive tricyclic product **3** or the closely related unsaturated isomer **4**.[2-4] The most straightforward mechanism imaginable for the **1** → **2** rearrangement involves migration of the cyclopentane ring carbon (C-4) to the methylene side chain, producing the very stable cyclopropylcarbinyl cation **2** directly. Nevertheless, the



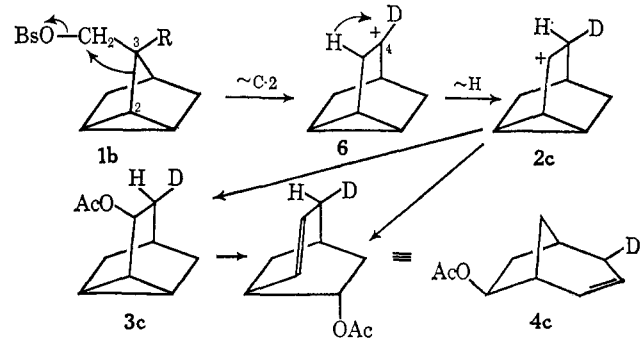
a, R = H; b, R = D

present experiments show that the **1** → **2** rearrangement shuns this path.

3-Nortricyclylcarbinol-3-*d* containing 0.83 D/molecule[5] is formed by lithium aluminum hydride reduction of a mixture of methyl and *t*-butyl esters of 3-nortricyclene carboxylic-3-*d* acid which results from the reaction of methyl 3-nortricyclenecarboxylate with potassium *t*-butoxide in boiling *t*-butyl alcohol-O-d. The location of the deuterium at C-3 follows from the method of synthesis and is confirmed by the nuclear magnetic resonance (nmr) spectrum (solvent CCl_4, tetramethylsilane internal standard, 60 MHz), which shows the signal of the carbinol methylene protons as a singlet at δ 3.34 rather than the doublet characteristic of the undeuterated compound.

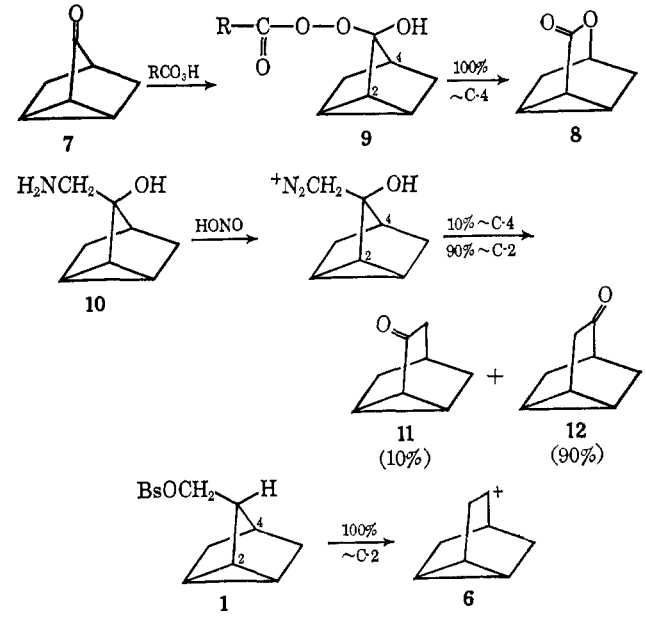
Solvolysis of the deuterated *p*-bromobenzenesulfonate **1b** in acetic acid (sodium acetate buffer) gives a mixture from which, after lithium aluminum hydride reduction and preparative vapor chromatography, bicyclo[3.2.1]oct-2-en-7-ol (**5**) is isolated. This material contains 0.82 D/molecule,[5] and its nmr spectrum shows the O–H and upfield C–H protons as a series of overlapping absorptions of intensity 8. Careful integration of the spectrum of this material (H-2 plus H-3 at δ 5.2–6.0 *vs.* H-7 at δ 4.13) shows the presence of 1.97 ± 0.04 vinyl protons. Therefore, not more than 3–4% of the product **5** is formed from the vinylically deuterated acetate **4b** that would result from the direct cyclopentane migration mechanism.

The results are consistent with a circuitous mechanism in which net cyclopropane ring carbon (C-2) migration gives the tricyclooctyl cation **6** (or a delocalized variant), either directly or through closely related intermediates.[4] The vicinal hydride shift already known[2b,4] to occur in this system then transforms **6** into the C-4-deuterated cyclopropylcarbinyl cation **2c**.



The exclusive cyclopropyl migration observed in **1b** provides a point needed to complete the pattern of structure *vs.* relative migratory aptitude in this series.

Baeyer–Villiger oxidation of nortricyclanone (**7**) gives lactone **8**, resulting from cyclopentyl migration[6] in the intermediate **9**. Nitrous acid deamination of the amino



(1) We are grateful for grants in partial support of this work from the National Science Foundation (GP6212X), the National Institute of Arthritis and Metabolic Diseases (AM-07505), and the Air Force Office of Scientific Research (M2(967)62/1006-66).

(2) (a) R. R. Sauers and J. A. Beisler, *Tetrahedron Letters*, 2181 (1964); (b) R. R. Sauers, J. A. Beisler, and H. Feilich, *J. Org. Chem.*, **32**, 569 (1967).

(3) K. B. Wiberg and G. Wenzinger, *ibid.*, **30**, 2278 (1965).

(4) (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).

(5) Falling-drop analysis by Mr. J. Németh, Urbana, Ill.

(6) (a) R. R. Sauers, *Tetrahedron Letters*, 1015 (1962). (b) The structure is assigned from the nmr spectrum in concentrated sulfuric acid.[6a] Because of the possibility of rearrangement or selective destruction of the lactone that would result from cyclopropyl migration, the extent of the preference for cyclopentyl migration is not firmly established.