detectable amount of 3,2-shifted product from norbornyl cation itself, in agreement with experiment.[11]

(14) M. Saunders, P. von R. Schleyer, and G. A. Olah, *J. Am. Chem. Soc.*, 86, 5680 (1964).

(15) P. D. Bartlett and C. E. Dills, unpublished; C. E. Dills, Thesis, Harvard University, 1955.

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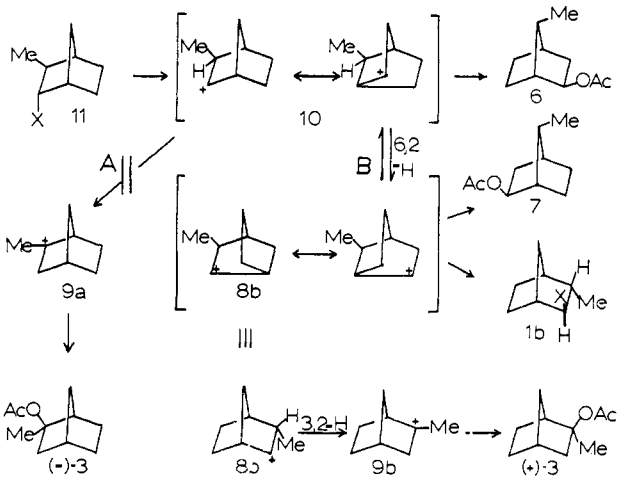
The Stereochemistry of Vicinal Hydride Shift in the 3-Methyl-2-norbornyl Cation. Evidence for the Nonclassical Structure[1]

Sir:

A nonclassical structure for carbonium ions of the 2-norbornyl series would seem to require that 3→2 shift of hydrogen or alkyl occurs only when the migrating group is *exo*.[2-4] It has been suggested[4] that the rearrangement of the 3-*exo*-methyl-2-norbornyl cation (**10**)[5] therefore could not involve the structurally straightforward but mechanistically forbidden *endo*-hydride migration (path A) which would lead to a tertiary cation (**9a**) of the same stereochemical series, but must instead take a more circuitous route. We now report evidence that the rearrangement leads to the enantiomeric series **9b**, thus confirming the mechanism (path B) previously considered[4] the most likely.

(+)-3-*exo*-Methyl-2-*endo*-norborneol (**11**, X = OH)[6] is converted to the *p*-bromobenzenesulfonate (**11**, X = OBs), solvolysis of which in acetic acid–sodium acetate at 100° gives a complex mixture of acetates consisting of several products not yet definitely identified: 3-*exo*-methyl-2-*exo*-norbornyl acetate (6.5%)[8b]; *syn*-7-methyl-2-*exo*-norbornyl acetate (**6**)[8b]; *anti*-7-methyl-2-*exo*-norbornyl acetate (**7**, 16%); (+)-3-*endo*-methyl-2-*exo*-norbornyl acetate (**1b**, X = OAc, 15%)[7]; and (+)-2-*endo*-methyl-2-*exo*-norbornyl acetate (**3**).

Tertiary acetate (+)-**3** constitutes only 3.5% of the acetate products under these conditions[9] and is difficult to isolate pure in substantial quantity. Nevertheless, the sign and magnitude of rotation of a sample obtained by preparative vapor chromatography set a minimum selectivity of 90% in favor of path B over path A. That this number actually is much higher is strongly suggested by the sign and magnitude of rotation[7] of the product (+)-3-*endo*-methyl-2-*exo*-norbornyl acetate (**1b**, X = OAc). This substance, a product of capture of the secondary cation **8b**, which is the immediate precursor of tertiary cation **9b**, is formed with 100.4% retention of optical purity. Further, the product ratios **3**:**1** and **3**:**7**, 0.247 and 0.233, respectively, measure the partitioning of secondary cation **8** between hydride shift to tertiary cation **9** and solvent capture. The agreement of these values with those found[8a] in the acetolysis of **1a**, X = OBs, excludes any appreciable contribution of *direct* formation of tertiary cation **9a** from the first-formed cation **10** *via* path A, since such a process would have caused the ratios **3**:**1** and **3**:**7** to be greater from **11** than from **1a**, X = OBs.



The **3**:**1** and **3**:**7** product ratios suggest that at most about 2% of the tertiary product **3** from cation **10** could have come from path A. On this basis, *exo*-hydride shift in **8** is at least 7.1(100%)/3.5(2%) = 100 times as efficient as *endo*-hydride shift in **10**.

Rapid interconversion of classical ions is postulated[10a] to produce stereochemical consequences which are the same as those now associated with nonclassical ions. In the case of *external* nucleophiles, this is supposed to force *exo* substitution by the "windshield wiper" effect, which produces an abnormally low nucleophile concentration in the *endo* direction.[10a] It is not obvious how one would extend the rapid interconversion hypothesis to the present results, which deal with the *internal* nucleophile, migrating hydrogen. We there-

(1) (a) Presented in part at the Anniversary Meeting of the Chemical Society, Birmingham, England, April 6–9, 1964. See Abstracts, p. 19; *Proc. Chem. Soc.*, 204 (1964). (b) The support of this work by the National Institute of Arthritis and Metabolic Diseases through Grant No. AM-07505, by the American Cancer Society through a grant to the Interdepartmental Research Committee of the University of Southern California, and by the National Science Foundation is gratefully acknowledged.

(2) J. D. Roberts and J. A. Yancey, *J. Am. Chem. Soc.*, 75, 3165 (1953).

(3) (a) P. D. Bartlett, E. R. Webster, C. E. Dills, and H. G. Richey, *Ann.*, 623, 217 (1959); (b) D. C. Kleinfelter and P. von R. Schleyer, *J. Am. Chem. Soc.*, 83, 2329 (1961).

(4) J. A. Berson in "Molecular Rearrangements," Part 3, Vol. I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963.

(5) Or the Wagner-Meerwein related *syn*-7-methyl-2-norbornyl cation studied by S. Beckmann and G. Eder, *Chem. Ber.*, 91, 2878 (1958).

(6) Prepared from the corresponding (+)-carboxylic acid **11**, X = CO_2H (which is derived from (−)-3-*exo*-methyl-2-*endo*-norbornene-5-carboxylic acid obtained by resolution of the quinidine salt) *via* the "acid → acetate" sequence: acid chloride (**11**, X = COCl), methyl ketone (**11**, X = $COCH_3$), Baeyer–Villiger oxidation of the latter to the acetate (**11**, X = OAc), and lithium aluminum hydride cleavage. Stereochemical correlation of (+)-**11**, X = OH, with (+)-camphenilone (**2**)[7] is achieved by oxidation to 3-methylnorbornanone followed by methylation. Satisfactory elemental analyses were obtained on all new compounds.

(7) For configurations and rotations, see ref. 8a.

(8) (a) J. A. Berson, R. G. Bergman, J. H. Hammons, and A. W. McRowe, *J. Am. Chem. Soc.*, 87, 3246 (1965). (b) So far identified only by vapor chromatography.

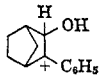
(9) By omitting the buffer, the Wagner–Meerwein relative of **3** (1-methyl-2-*exo*-norbornyl acetate) can be made a major component of the product mixture. Thus, the rearrangement leading to **3** is not a minor side path but lies on the main course of reaction. The low yield of **3** under kinetically controlled conditions results merely from the irreversible escape of the bulk of the material at earlier exits in the mechanism. Since **3** is not formed from the other acetates under the solvolysis conditions, it represents carbonium ions which elude solvent capture at intermediate stages.

(10) (a) H. C. Brown, Special Publication No. 16, The Chemical Society, London, 1962, pp. 140–157, 176–178; H. C. Brown, J. K. Morgan, and F. J. Chloupek, *J. Am. Chem. Soc.*, 87, 2137 (1965). (b) For further discussions, see J. A. Berson and P. Reynolds-Warnhoff, *ibid.*, 86, 595 (1964); J. A. Berson and D. Willner, *ibid.*, 86, 609 (1964); S. Winstein, *ibid.*, 87, 381 (1965).

fore prefer the nonclassical intermediate, which predicts the observations.

The 3-methyl-2-norbornyl (**12**) rearrangements provide the first examples of established 3,2-shift stereochemistry in which the migration terminus is secondary. A tertiary benzyl terminus, as in **13**, apparently produces behavior similar to that of **12**.[11] In contrast, a simple tertiary terminus, as in **14**, is reported[12] to result in only feeble selectivity. The series shown in Table I clearly does not fall into a readily explicable pattern, and further investigation seems necessary.

Table I

Cation	Migrating group	Selectivity, *exo/endo*	Ref.
12 	H	⩾100	Present work
13 	H	High (?)	11
14 	Me	2.6–5.7	12

(11) B. M. Benjamin, C. J. Collins, Z. K. Cheema, and R. Werth, International Symposium on Organic Reaction Mechanisms, Cork, Ireland, July 20–25, 1964, Abstracts, p. 38; C. J. Collins, Z. K. Cheema, R. G. Werth, and B. M. Benjamin, *J. Am. Chem. Soc.*, 86, 4913 (1964). These workers show convincingly that the formation of 3-*endo*-phenyl-2-norbornanone from 3-*endo*-phenyl-2,3-*exo*-norbornanediol involves a circuitous mechanism analogous to path B. Since, however, they do not estimate how little of the *exo*-phenyl isomer can be detected in the product mixture, the selectivity is not clear, although they imply it is high.

(12) W. R. Vaughan, C. T. Goetschel, M. H. Goodrow, and C. L. Warren, *ibid.*, 85, 2283 (1963).

(13) To whom inquiries should be directed at Madison.

(14) National Institutes of Health Predoctoral Fellow, 1964–1965.

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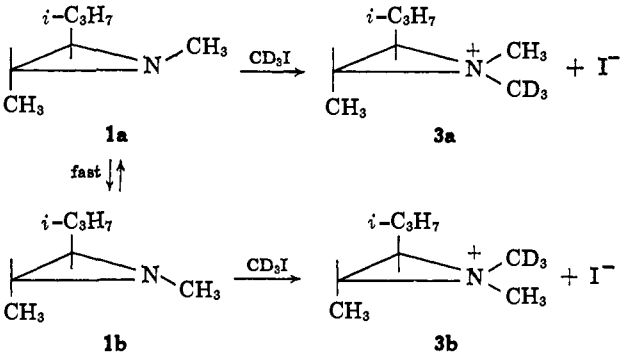
Halide Ion Catalyzed Equilibration of 1,1,2,3-Tetraalkylaziridinium Ions[1]

Sir:

When *trans*-1,2-dimethyl-3-isopropylaziridine (**1**) was quaternized with deuteriomethyl iodide (**2**) in benzene, equal amounts of the diastereomeric aziridinium ions **3a** and **3b** (as iodides) were isolated.[2] Although reasons were given as to why the observed products were likely to be those of a rate-controlled process, we felt uneasy about this conclusion because the observed product composition was identical with the expected equilibrium composition of **3a** and **3b**. We therefore decided to examine the quaternization of **1** with **2** under conditions that would allow direct determination of the stereochemistry of the reaction.

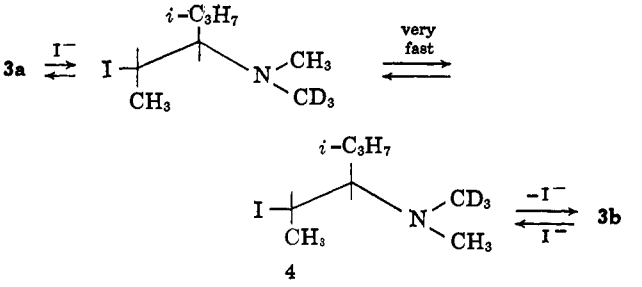
A methanol solution 0.67 *M* in **1** and 0.67 *M* in **2**



was prepared and the changing 60-Mc. n.m.r. spectrum of the solution was observed. As the reaction proceeded, the per cent reaction was determined by comparison of the intensities of the N-methyl bands due to **1** and **3**, and the ratio of the concentrations of **3b** and **3a** was determined by comparison of the intensities of their N-methyl bands.[2,3]

The results obtained showed that the aziridinium ions **3a** and **3b** were equilibrated under the reaction conditions. Thus, after 45 min. at 27°, when the reaction was about 50% complete, the **3b**:**3a** ratio was 2.4; but as the reaction proceeded to >97% completion (>1400 min.), the **3b**:**3a** ratio decreased to unity. That the equilibration of **3a** and **3b** is in fact catalyzed by iodide ion was shown subsequently by the observation that addition of aqueous sodium iodide or potassium iodide to a 2.9:1 mixture of **3b** and **3a** in methanol caused equilibration of the aziridinium ions by a reaction that was first order in iodide ion.

The most reasonable mechanism for iodide ion catalysis of the interconversion of **3a** and **3b** is pictured below.



Reactions of iodide ion with **3a** and **3b** by SN2 attack at C-2 of the aziridinium ring result initially in formation of different rotamers of the same 2-iodoalkylamine **4**. If one accepts the premise that rotation about the C-1–N bond *and* inversion of nitrogen in **4** occur more rapidly than ring closure to an aziridinium ion, the rotamers of **4** formed from **3a** and **3b** become equivalent in that ring closure to either **3a** or **3b** can occur with equal probability. As the principle of microscopic reversibility must be obeyed, interconversion of **3a** and **3b** *via* **4** must occur without disturbance of the steric relationship of the alkyl groups at C-2 and C-3 in the aziridinium ions.

Convincing support for the proposed mechanism has been obtained. The relative rates of iodide ion catalyzed equilibration of several pairs of diastereomeric 1-deuteriomethyl-1,2-dimethyl-3-alkylaziridinium

(1) (a) Structure–Activity Relationships of Ethylenimines. VI. Supported by Grant No. CA-05528 from the National Cancer Institute of the Public Health Service. (b) Part V: A. T. Bottini and R. L. VanEtten, *J. Org. Chem.*, 30, in press.

(2) A. T. Bottini and R. L. VanEtten, *ibid.*, 30, 575 (1965).

(3) (a) Results described in the accompanying communication[3b] allow assignment of the high-field N-methyl band of the aziridinium ions to **3b**. (b) A. T. Bottini, B. F. Dowden, and R. L. VanEtten, *J. Am. Chem. Soc.*, 87, 3250 (1965).