Organic and Biological Chemistry

The Chemistry of Methylnorbornyl Cations. I. Introduction and General Survey[1]

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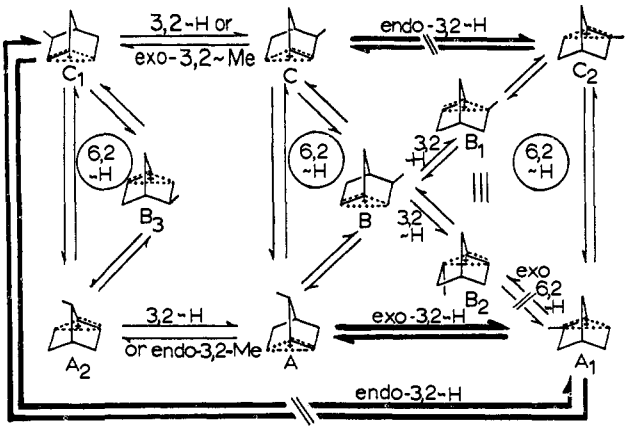
Abstract: A scheme is presented summarizing the structural and mechanistic relationships among the nine methylnorbornyl cations. References are given to the accompanying papers which detail experimental evidence supporting the scheme.

In the accompanying papers[4-8] we report the results of several investigations of the behavior of carbonium ions of the norbornyl series labeled with methyl groups. These studies supplement extensive previous work on norbornyl cations[9] and, in particular, permit examination of several aspects of the chemistry of these species not readily visible heretofore. These include the relative rates of vicinal *vs.* transannular hydride shifts, the relative rates of hydride shift and capture by solvent, the stereochemistry of vicinal hydride shifts, and the quantitative evaluation of transition-state steric effects in solvolysis and product formation. The results bear on the vexatious question of the precise formulation (classical *vs.* nonclassical) of the structure of such intermediates and provide experimental evidence that the "windshield-wiper effect" cannot be the cause of all of their special stereochemical behavior (paper VI[8]).

Scheme I is intended as a guide to the complex maze of structural and mechanistic relationships embodied in this work. In the papers that follow, experimental evidence is presented in support of the various parts of the scheme.

Interconversions of nine different Wagner–Meerwein pairs of cations are involved in Scheme I. The pairs are shown in full below but for economy of space are shown in Scheme I in nonclassical notation without implications as to the electronic structure. (Mechanistically,

Scheme I



ten cations should be considered, but the B_1–B_2 set is structurally and stereochemically degenerate.) At the core of the scheme are the parent cations A, B, and C, which are mutually interconvertible by transannular "6,2"-hydride shifts. On the periphery lies another set of 6,2-hydride shifts which in principle might interconvert six pairs of cations. Access from the core to the periphery (or *vice versa*) is by way of vicinal "3,2"-hydride and/or methyl shifts, which interconvert either a pair of secondary cations (light arrows) or a tertiary with a secondary cation (heavy arrows). The scheme is oversimplified in the sense that additional intermediates describing ion-pair return processes should be included. Although it seems entirely probable that such processes do occur, their influence on the product patterns does not seem to be significant (papers IV, V, and VI[6-8]).

The cyclic series of rearrangements can be entered *via* solvolyses of several methyl-substituted norbornyl derivatives. The location of the methyl group relative to the positive charge at C-2 in the resulting first intermediate is 3-*endo*:7-*anti* (cation A, paper V[7]), 3-*exo*:7-*syn* (cation C, paper VI[8]), 5-*exo*:5-*endo* (cation B, paper IV[6]), and 6-*exo*:6-*endo* (cation $B_1 = B_2$, paper IV[6]). Under kinetically controlled conditions, the six products from the inner core set of cations A, B, and C are observed regardless of which entry into the cycle

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(4) Paper II: J. A. Berson, A. W. McRowe, R. G. Bergman, and D. Houston, *J. Am. Chem. Soc.*, **89**, 2563 (1967).

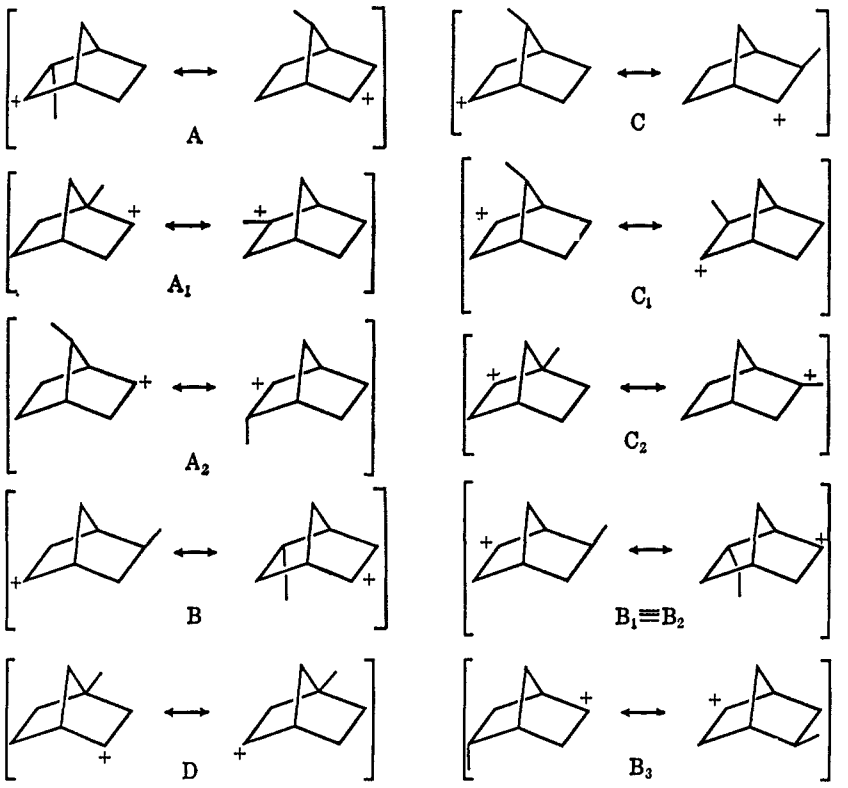
(5) Paper III: J. A. Berson and R. G. Bergman, *ibid.*, **89**, 2569 (1967).

(6) Paper IV: J. A. Berson, A. W. McRowe, and R. G. Bergman, *ibid.*, **89**, 2573 (1967).

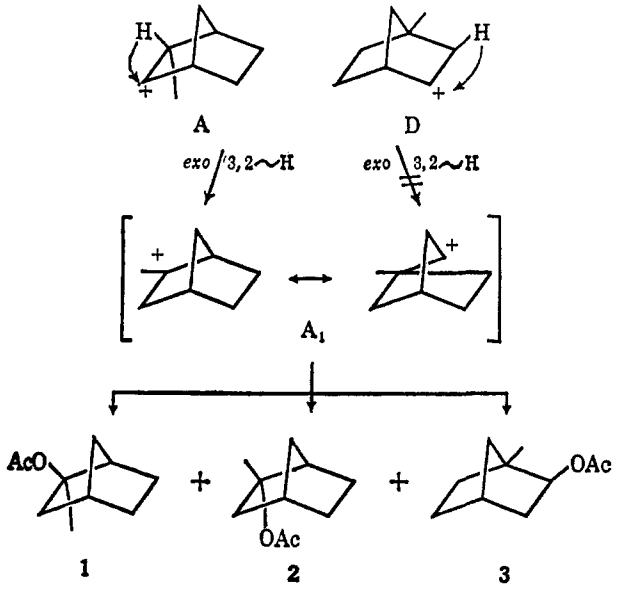
(7) Paper V: J. A. Berson, R. G. Bergman, J. H. Hammons, and A. W. McRowe, *ibid.*, **89**, 2581 (1967).

(8) Paper VI: J. A. Berson, J. H. Hammons, A. W. McRowe, R. G. Bergman, A. Remanick, and D. Houston, *ibid.*, **89**, 2590 (1967).

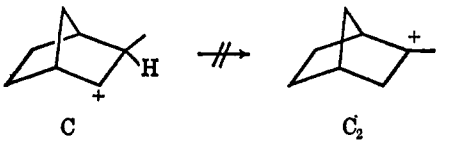
(9) For a review, see J. A. Berson in "Molecular Rearrangements," Part 3, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963.



is used. The influence of solvent and point of entry on the distribution of these products gives some information on relative rates of hydride shift and nucleophilic capture. The steric effect of a methyl group in



various positions of the norbornyl system also is elucidated from the product distributions (paper IV[6]). Three additional products, **1**, **2**, and **3**, are observed. These are derived from the vicinal *exo*-hydride shift which converts secondary cation A to tertiary cation A_1. Vicinal hydride and/or methyl shift which interconverts two secondary ions (B → B_1, C → C_1, A → A_2) is slow. Even the stability associated with tertiary cation A_1 is insufficient to force vicinal hydride shift (D → A_1) when the migrating hydrogen departs from a secondary center (papers IV and V[6,7]). Direct vicinal shift of an *endo*-hydride, even when tertiary–secondary (C → C_2), does not occur (blocked heavy arrow of Scheme I). Thus, entry into the core cycle at cation C eventually does give products **1**, **2**, and **3** derived from a tertiary cation, *but only by a circuitous route*. This involves conversion of C to A followed by exit *via* cation A_1, the enantiomer of C_2. The distinction is made on the basis of stereochemical correlations given in papers III,[5] V,[7] and VI.[8]



The preference for *exo*-3,2-hydride shift is not attributable to a large thermodynamic bias favoring cation A over cation C but rather to an intrinsically faster rate for *exo* than for *endo* migration (paper VI[8]). This behavior is consistent with the formulation of the cationic intermediates with nonclassical structures.