

For Ic and IIc (the allylic anions), the system has a net charge of  $-1$  and there will be attractive forces between the methyl group and the *cis*-allylic form. For Ia and IIa (the allylic carbonium ions), the system has a net charge of  $+1$  and in the absence of other factors (*vide infra*) there will be repulsive forces between the dipole of the methyl group and the *cis*-allylic cation. Finally for Ib and IIb, the system has no net charge and neither strong attractive or repulsive forces are expected.

Consideration of these expected dipole interactions leads to the following stability predictions: Ic > IIc; IIa >> Ia; and IIb > Ib. The last prediction evolves from the fact that for the neutral species the thermodynamic stabilities of the several isomers is principally determined by steric repulsive forces in the absence of charge considerations. For this purpose, the parent hydrocarbons serve as a convenient model and, since the stability of simple olefins is *trans* > *cis*, similar isomeric stabilities are expected for the radicals (Ib and IIb).

Data favoring the conclusion that the *cis*-allylic anion is more stable than the *trans* form are outlined in the previous paper.<sup>1</sup> With respect to the cationic species, a test of the proposed scheme is afforded by the silver ion assisted solvolyses of  $\alpha$ -methylallyl chlorides.<sup>2</sup> As expected theoretically, the allylic cations maintain configurational stability. Of greater interest is the fact that "the high predominance of *trans* in the primary alcohol from hydrolysis of  $\alpha$ -methylallyl chloride suggests that  $\alpha$ -methylallyl chloride IS gives rise nearly exclusively to the *trans*-butenyl cation IVT."<sup>2</sup> Additional support is derived from the observation that the order of reactivities of crotyl chlorides is *trans* > *cis*. Insofar as the energetics of the transition states for these reactions accurately reflect the stabilities of the various intermediates, a reasonable assumption, then the *cis*-allylic cation is less stable than the *trans* form.

For the radicals, experimental evidence for the relative stabilities of the *cis* and *trans* form is derived from a study of the allylic chlorination of butenes with *t*-butyl hypochlorite.<sup>3</sup> As is now commonly accepted for these allylic intermediates, the radicals thus formed are configurationally stable. Of direct implication to the concepts in the present work is the observation that, although the *cis* form is statistically favored, the final product has a 1.85:1 preference for the *trans* compound. Significantly the *trans* preference, after correction for the statistical factor, is 3.7:1, which is very similar to that of the parent hydrocarbons (3:1). Thus the available evidence on the stabilities of *cis*- and *trans*-allylic radicals also supports the proposed scheme.

The simple dipole argument presented above is supported by data on the isomeric preferences of the three intermediates. Nevertheless, some consideration of other factors possibly influencing stabilities is warranted. The proposed scheme that charge dipole attractions and repulsions control the isomeric preference neglects significant contributions from induced dipoles, hydrogen bonding, and nonclassical structures. For example, a reasonable case could be made that the

(2) W. G. Young, S. H. Sharman, and S. Winstein, *J. Am. Chem. Soc.*, **82**, 1376 (1960).

(3) C. Walling and W. Thaler, *ibid.*, **83**, 3877 (1961).

*cis*-allylic cation would be favored over the *trans*-if contributions from some or all of these factors were important. Insofar as the stability of the *cis*- and *trans*-allylic cations is successfully derived from simple charge dipole repulsions, these factors must be relegated to secondary roles.

Finally the isomerization of 1-butene over various solid acid catalysts produces ratios of *cis*-2-butene to *trans*-2-butene from 1.5 to 6.5.<sup>4</sup> These results contrast with the ion stabilities outlined in this paper and supported by the solvolyses. Of significant importance, the isomerization of 1-butene in homogeneous acid solution does not exhibit a stereochemical preference to the *cis* olefin.<sup>5</sup> In actual fact the ratios of *cis*- to *trans*-2-butene in dilute sulfuric and phosphoric acids are 1. The *trans*:*cis* ratio of 1 observed in the homogeneous acid-catalyzed isomerization is amply accounted for as proceeding through a 2-butyl cation. Insofar as the stereochemical control is observed only on supported systems and insofar as many possible catalyst surface effects can explain the results, they do not constitute a serious objection to the proposed cation stabilities.

We are currently examining a wide variety of data in the light of the proposed hypothesis. The more detailed description of these results will be published later.

*Acknowledgment.* The author wishes to express his appreciation to Dr. Alan Schriesheim for stimulation and continued interest. He is grateful to the Esso Research and Engineering Co. for permission to publish this research.

(4) (a) P. J. Lucchesi, D. L. Baeder, and J. P. Longwell, *ibid.*, **81**, 3235 (1959); (b) W. O. Haag and H. Pines, *ibid.*, **82**, 2488 (1960).

(5) W. B. Smith and W. B. Watson, Jr., *ibid.*, **84**, 3174 (1962). For possible exception, see, however, ref. 4b.

Shelton Bank

Process Research Division, Esso Research and Engineering Co.  
Linden, New Jersey 07036

Received April 15, 1965

### *exo* Vicinal Hydride Shift in the 3-*endo*-Methyl-2-norbornyl Cation<sup>1</sup>

Sir:

The behavior of the 3-*endo*-methyl-2-norbornyl cation (8) serves as a standard of comparison for the 3-*exo*-methyl-2-norbornyl case, where stringent stereo-electronic prohibition of *endo* vicinal hydride shift is observed.<sup>2</sup> It also provides a measure of the competition between solvent capture and vicinal hydride shift in a norbornyl system.

The racemic alcohol 3-*endo*-methyl-2-*exo*-norborneol (1, X = OH) is prepared (1) from the known<sup>3</sup> 3-*endo*-methyl-2-*exo*-norbornanecarboxylic acid (1, X = CO<sub>2</sub>H) via the "acid  $\rightarrow$  acetate" sequence: 1, X = CO<sub>2</sub>H  $\rightarrow$  1, X = COCl  $\rightarrow$  1, X = COCH<sub>3</sub>  $\rightarrow$  1, X = OAc  $\rightarrow$  1, X = OH; and (2) by hydroboration-oxi-

(1) (a) Presented in part at the Anniversary Meeting of the Chemical Society, Birmingham, England, April 6-9, 1964, Abstracts, p. 19; *Proc. Chem. Soc.*, 204 (1964). (b) Support of part of this work by the National Institutes of Arthritis and Metabolic Diseases through Grant No. AM-07505 is gratefully acknowledged.

(2) J. A. Berson, J. H. Hammons, A. W. McRowe, R. G. Bergman, A. Remanick, and D. Houston, *J. Am. Chem. Soc.*, **87**, 3248 (1965).

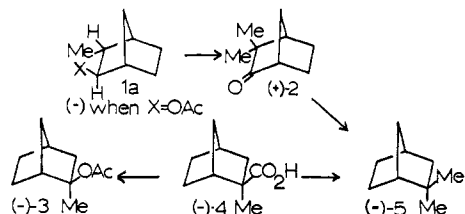
(3) (a) S. Beckmann and R. Mezger, *Chem. Ber.*, **90**, 1559 (1957); (b) G. Komppa and S. Beckmann, *Ann.*, **523**, 69 (1936).

dation<sup>4a</sup> of 2-methyl-2-norbornene.<sup>4b,c</sup> Optically active alcohol **1a**<sup>5</sup> (X = OH), which gives (–)-acetate (**1a**, X = OAc), is obtained by resolution of the ephedrine salt of the acid phthalate and is configurationally correlated with (+)-camphenilone (**2**)<sup>5,6a</sup> by oxidation and methylation.

Alcohol **1a** (X = OH) is converted to a *p*-bromobenzenesulfonate (**1a**, X = OBs), solvolysis of which in acetic acid–sodium acetate at 100° gives a complex mixture of acetates, among which are 14.8% products not yet definitely identified, 29.5% **1a** (X = OAc) of unchanged structure, *syn*- and *anti*-7-methyl-2-*exo*-norbornyl acetate (**6**)<sup>7a,c</sup> and **7** (31.2%),<sup>7a</sup> and 2-*endo*-methyl-2-*exo*-norbornyl acetate<sup>7b</sup> ((–)-**3**, 7.1%). The product ratios **3**:**1a** and **3**:**7**, which measure the competition between vicinal shift and solvent capture in the ion **8**, are 0.242 and 0.229.

Acetate (–)-**1a** (X = OAc) obtained from the solvolysis is identical in sign and magnitude of rotation with material prepared by direct acetylation of alcohol **1a** (X = OH).

The configuration of acetate (–)-**3** from the solvolysis of **1a** (X = OBs) is established by correlation *via* the “acid → acetate” sequence with the previously described<sup>6b</sup> (–)-2-*endo*-methyl-2-*exo*-norbornanecarboxylic acid (**4**). This substance had been converted<sup>6b</sup> to (–)-camphenilane (**5**), which in turn had been obtained<sup>8</sup> from (+)-camphenilone (**2**). Both starting material **1a** (X = OBs) and product (–)-**3** are thus correlated with a *common* reference compound, (+)-camphenilone, and any uncertainties in the assignments to the latter of absolute configuration or maximum rotation have no effect on the assignments of relative configurations or relative optical purities to **1a** (X = OBs) and (–)-**3**.



The sign and magnitude of rotation of tertiary acetate (–)-**3** show that it is formed with  $105 \pm 5\%$  retention of the optical purity of the starting **1a** (X = OBs) and belongs to the stereochemical series that results from direct *exo* vicinal hydride shift in the 3-*endo*-methyl cation **8**. The simplicity of this reaction is to be contrasted with the behavior of the epimeric 3-*exo*-methyl cation.<sup>2</sup>

A lower limit can be calculated for the ratio of the

(4) (a) Cf. H. C. Brown, “Hydroboration,” W. A. Benjamin, Inc., New York, N. Y., 1963; (b) K. Alder and H. J. Ache, *Chem. Ber.*, **93**, 503, 511 (1962); (c) satisfactory elemental analyses were obtained for all new compounds.

(5) The absolute configurations throughout are those shown.

(6) (a) For a summary of references to absolute configurational assignments, see ref. 6b; (b) J. A. Berson, J. S. Walla, A. Remanick, S. Suzuki, P. Reynolds-Warnhoff, and D. Willner, *J. Am. Chem. Soc.*, **83**, 3986 (1961).

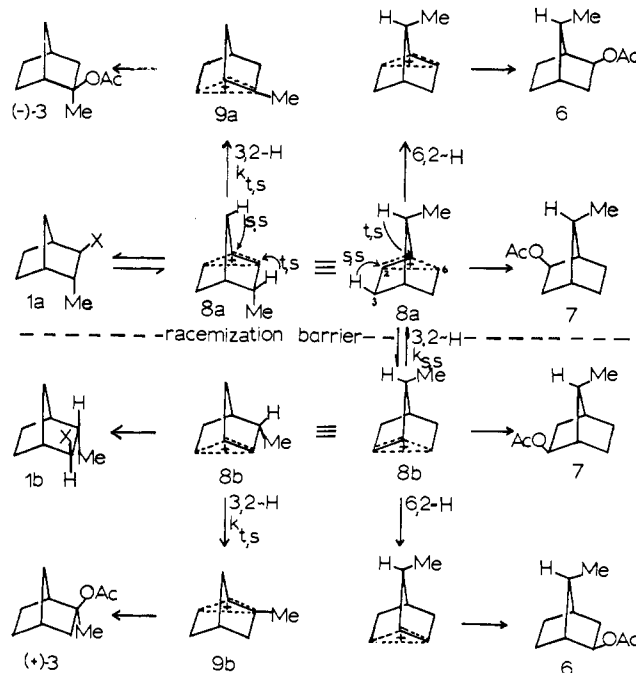
(7) (a) For the racemates, see ref. 3b and S. Beckmann and R. Metzger, *Chem. Ber.*, **89**, 2738 (1956). (b) For the racemate, see N. J. Toivonen, E. Siltanen, and K. Ojala, *Ann. Acad. Sci. Fennicae, Ser. AII*, No. **64** (1955). (c) Quantitative analysis for **6** is presently difficult because of overlap of its vapor chromatographic peak with those of other components.

(8) W. Hüchel, W. Doll, S. Eskola, and H. Weidner, *Ann.*, **549**, 186 (1941). We have reproduced the **2** → **5** correlation and are in full agreement with Hüchel’s results in signs and magnitudes of rotation.

rate of migration of *exo*-hydrogen from a tertiary to a secondary carbon *vs.* that from a secondary to a secondary carbon,  $k_{t,s}:k_{s,s}$ , in **8**, since the symmetry properties of the system make the reaction *s,s* a racemizing event. On the reasonable assumption that the change of the secondary ion **8** to its more stable hydride-shifted tertiary isomer **9** is essentially irreversible, it may be shown that where *P* is the fractional optical purity of **3** or **1** (X = OAc) and *F* is the fraction of product **3** formed, eq. 1 applies. Although *P* for both **3**

$$k_{t,s}/k_{s,s} = (2P/1 - P)F \quad (1)$$

and **1** (X = OAc) is essentially unity, the value for **1** (X = OAc) is more precise since it is obtained by direct comparison of rotations of a single substance. With  $P > 0.99$ ,  $k_{t,s}/k_{s,s}$  has a minimum value of 14. The ratio



$k_{t,s}/k_{s,OH}$ , which measures the competition between tertiary–secondary hydride shift and solvent capture of ion **8**, can be evaluated as 0.118 from the ratio **3**:(**1** + **7**). Thus,  $k_{s,OH}:k_{s,s}$ , the competition ratio between solvent capture and secondary–secondary hydride shift in ion **8**, is at least 119 in acetic acid at 100°. A factor this large<sup>10–14</sup> would suffice to prevent the formation of a

(9) Whether or not *tertiary* ion **9** is nonclassical is not a subject of this or the accompanying paper.<sup>2</sup>

(10) This number actually may be very much larger. In solvent  $SbF_5-SO_2ClF-SO_2$  at  $-120^\circ$  the unsubstituted norbornyl cation experiences 6,2-hydride shift  $10^9$  times faster than 3,2-hydride shift.<sup>14</sup> Since solvent collapse competes in rate with 6,2-shift in hydroxylic media,<sup>11–13</sup> it would overwhelm 3,2-hydride shift by many orders of magnitude if the rate ratio for 6,2- vs. 3,2-shift observed<sup>14</sup> in the nonhydroxylic media persists under solvolytic conditions and at much higher temperature. This seems to be borne out in acetic acid and aqueous solvents, where secondary–secondary 3,2-shift apparently is absent. Nevertheless, 3,2-shift (secondary–secondary) in norbornyl cation seems to be just discernible in formic acid solvent.<sup>11,13,15</sup> Although it is not yet clear how much of this is to be attributed to repeated reformation of the cation, it suggests the possibility that solvents may vary by as much as several powers of ten in the rates at which they react with carbonium ions.

(11) J. D. Roberts and C. C. Lee, *J. Am. Chem. Soc.*, **73**, 5009 (1951); J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *ibid.*, **76**, 4501 (1954).

(12) A. Colter, E. C. Friedrich, N. J. Holness, and S. Winstein, *ibid.*, **87**, 378 (1965), and references therein cited.

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

detectable amount of 3,2-shifted product from norbornyl cation itself, in agreement with experiment.<sup>11</sup>

(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.

Jerome A. Berson, Robert G. Bergman  
James H. Hammons, Arthur W. McRowe

Departments of Chemistry  
University of Wisconsin, Madison, Wisconsin  
University of Southern California, Los Angeles, California  
Received May 5, 1965

### The Stereochemistry of Vicinal Hydride Shift in the 3-Methyl-2-norbornyl Cation. Evidence for the Nonclassical Structure<sup>1</sup>

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*.<sup>2-4</sup> It has been suggested<sup>4</sup> that the rearrangement of the 3-*exo*-methyl-2-norbornyl cation (**10**)<sup>5</sup> 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<sup>4</sup> the most likely.

(+)-3-*exo*-Methyl-2-*endo*-norborneol (**11**, X = OH)<sup>6</sup> 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%)<sup>8b</sup>; *syn*-7-methyl-2-*exo*-norbornyl acetate (**6**)<sup>8b</sup>; *anti*-7-methyl-2-*exo*-norbornyl acetate (**7**, 16%)<sup>7</sup>; (+)-3-*endo*-methyl-2-*exo*-norbornyl acetate (**1b**, X = OAc, 15%)<sup>7</sup>; and (+)-2-*endo*-methyl-2-*exo*-norbornyl acetate (**3**).

Tertiary acetate (+)-**3** constitutes only 3.5% of the

(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.

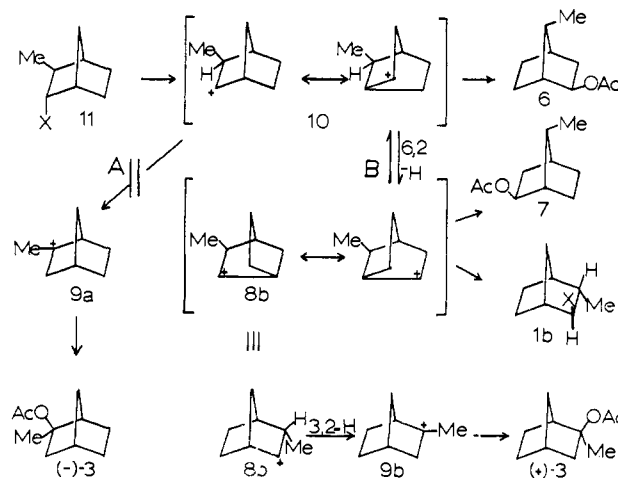
(5) Or the Wagner-Meerwein related *syn*-7-methyl-2-norbornyl cation studied by S. Beckmann and G. Eder, *Chem. Ber.*, **91**, 2878 (1958).

(6) Prepared from the corresponding (+)-carboxylic acid **11**, X = CO<sub>2</sub>H (which is derived from (-)-3-*exo*-methyl-2-*endo*-norborne-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<sub>3</sub>), Baeyer-Villiger oxidation of the latter to the acetate (**11**, X = OAc), and lithium aluminum hydride cleavage. Stereochemical correlation of (+)-**11**, X = OH, with (+)-camphenione (**2**)<sup>7</sup> 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.

acetate products under these conditions<sup>9</sup> 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<sup>7</sup> 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<sup>8a</sup> 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<sup>10a</sup> 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.<sup>10a</sup> 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-

(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).