The Chemistry of Methylnorbornyl Cations. V. Solvent Capture and Hydride Shift in the 3-*endo*-Methyl Series[1]

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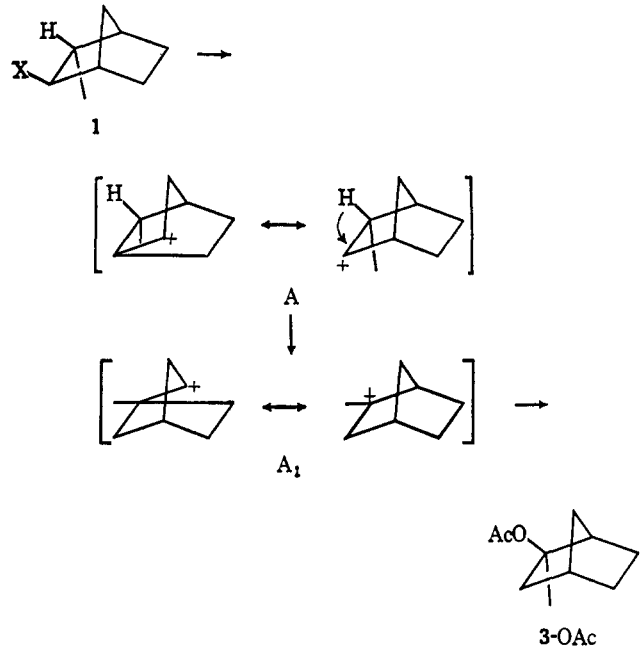
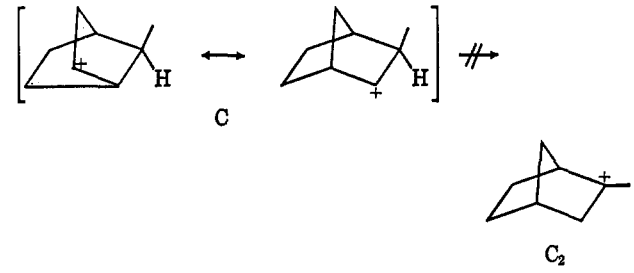
Abstract: By correlations of the configuration and absolute rotation of 3-*endo*-methyl-2-*exo*-norbornyl *p*-bromobenzenesulfonate with those of the corresponding acetate (**1**) and the acetates of *anti*-7-methyl-2-*exo*-norbornanol (**7**) and 2-*endo*-methyl-2-*exo*-norbornanol (**3**) it is established that acetolysis of the sulfonate occurs to give acetates **1**, **7**, and **3** with high retention of optical purity. Acetates **1** and **7** have the configurational relationship of simple Wagner–Meerwein isomers; acetate **3** has the configuration expected of a product derived by direct *exo*-3,2-hydride shift in the 3-*endo*-methyl-2-norbornyl cation. The hydride shifts are intramolecular. From the product distributions and optical purity data, it can be shown that 3,2-hydride shift from a tertiary to a secondary center is at least 14 times as fast as secondary–secondary hydride shift, which in turn is at least 122 times slower than solvent capture in acetic acid at 100°. Previous data in the literature are interpreted to give a competition ratio for secondary–secondary 6,2-hydride shift *vs.* solvent capture (0.27 in acetic acid at 45°). The corresponding ratio for the tertiary–secondary case is evaluated from the product distribution in 6-methylnorbornyl solvolyses as 1.23 in acetic acid at 100°. A method for estimating the temperature correction to be applied and the first estimate of the minimum activation energy for capture of the norbornyl cation in acetic acid (4.65 kcal/mole) are given in the Appendix. The enhancement by methyl substitution of the rate of 6,2-hydride shift is estimated to be between 5- and 15-fold. The weakness of this effect in comparison to that in other systems is attributed to charge distribution in the transition state for the hydride shift, which is reasonably formulated as an edge-protonated cyclopropane.

The 3-*endo*-methyl-2-norbornyl cation (A)[4] can escape from the "core" cycle[4] of 6,2-hydride shifts to a "periphery" system (A_1) by *exo*-vicinal hydride shift. The present paper demonstrates the occurrence of this reaction. The process serves as a standard of comparison for the 3-*exo*-methyl-2-norbornyl case (C), where stringent stereoelectronic prohibition of *endo*-vicinal hydride shift (to C_2) is observed.[5] The chemistry of cation A also provides measures of the competition between solvent capture and vicinal hydride shift and between secondary–secondary and tertiary–secondary vicinal hydride shift.





Configurational Correlations. The stereochemical relationships that provide the experimental basis for this study are established by a set of correlations anchored on (+)-camphenilone (**2**). Although the absolute configuration[6] (as shown) and approximate absolute rotation[7] of camphenilone are known, they become matters of no concern when both starting material (**1**,

(1) (a) Support of part of this work by the National Institute of Arthritis and Metabolic Diseases and by the National Science Foundation is gratefully acknowledged. (b) Presented in part at the Anniversary Meeting of the Chemical Society, Birmingham, England, April 1964, Abstracts, p 19; *Proc. Chem. Soc.*, 204 (1964). A preliminary version appeared: J. A. Berson, R. G. Bergman, J. H. Hammons, and A. W. McRowe, *J. Am. Chem. Soc.*, 87, 3246 (1965).

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

(4) The nomenclature of the various cations follows that of paper I: J. A. Berson, J. H. Hammons, A. W. McRowe, R. G. Bergman, A. Remanick, and D. Houston, *J. Am. Chem. Soc.*, 89, 2561 (1967).

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

(6) A. J. Birch, *Ann. Rept. Progr. Chem.* (Chem. Soc. London), 47, 191 (1950), and references cited therein.

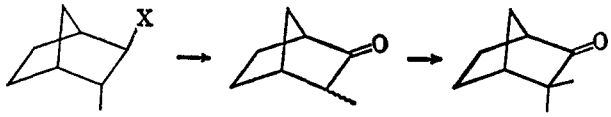
(7) Camphenilone prepared from camphene of $[\alpha]_D$ + 102.5° (ether) has $[\alpha]_D$ + 66.7° (benzene).[8] The highest reported rotation for camphene is 113.5° (ether)[9] and thus, that for camphenilone is 73.8° (benzene).

(8) W. Hückel, W. Doll, S. Eskola, H. Weidner, F. Neumann, and I. Schneider, *Ann.*, 549, 186 (1941).

(9) (a) *Cf.* J. A. Berson, J. S. Walia, A. Remanick, S. Suzuki, P. Reynolds-Warnhoff, and D. Willner, *J. Am. Chem. Soc.*, 83, 3986 (1961); (b) see especially footnote 14 of ref 9a and references cited there.

X = OBs) and product (**3**) are correlated to this ketone as a *common* relay.

Optically active 3-*endo*-methyl-2-*exo*-norbornanol (**1**) (X = OH) is obtained by conversion of the racemic alcohol[10] to the acid phthalate and fractional crystallization of the ephedrine salt from acetone. Ten recrystallizations of the head crop, regeneration of the acid phthalate, and saponification give a 3-*endo*-methyl-2-*exo*-norbornanol (**1**, X = OH) which is converted on one hand to a levorotatory acetate (**1**, X = OAc), $[\alpha]_D$ −1.85° (absolute ethanol), and on the other, by oxidation with chromium trioxide to a mixture of 90% 3-*endo*- and 10% 3-*exo*-methyl-2-norbornanone. Methylation of this mixture (potassium *t*-butoxide, dimethyl sulfoxide, and methyl iodide) gives camphenilone [(+)-**2**], $[\alpha]_D$ +16.5° (benzene), which on the basis of the highest reported rotation[7] is 22% optically pure. Since optical fractionations are carefully avoided

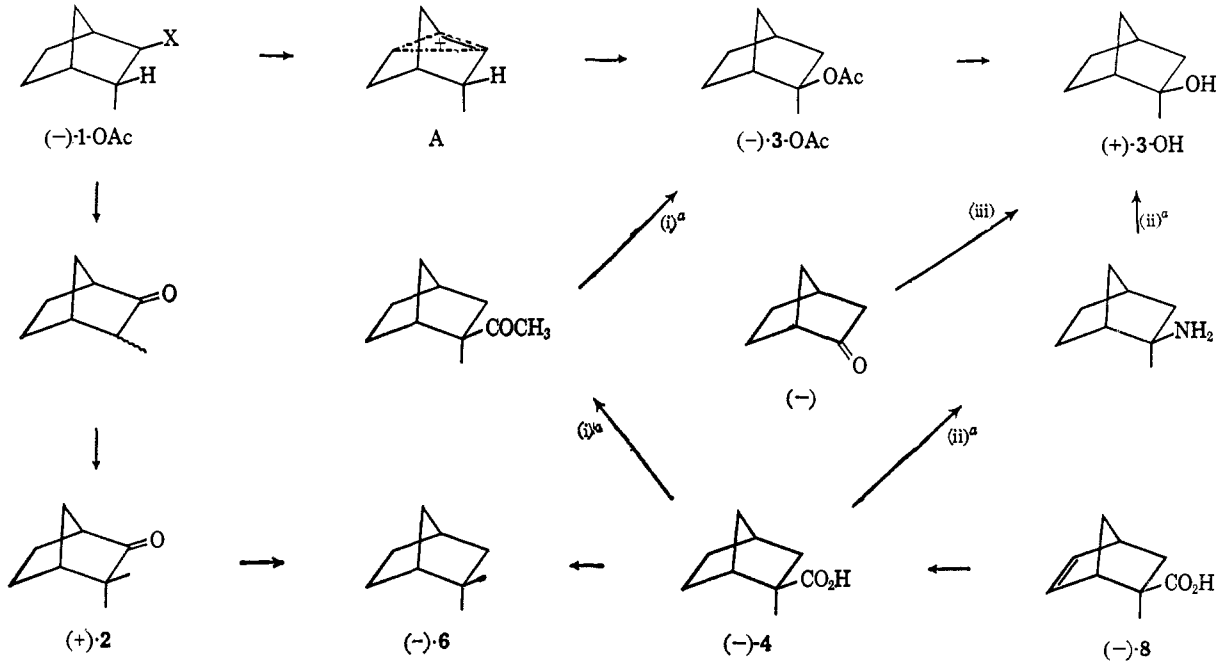


1a (−) when X = OAc (+)-**2**

throughout the sequence, the starting (−)-**1a** (X = OAc), $[\alpha]_D$ −1.85°, has the same optical purity as (+)-**2**, $[\alpha]_D$ +16.5°.

had been obtained[8,11] from (+)-camphenilone (**2**). Acid (−)-**4** now is correlated to (−)-**3** by two sequences (shown for economy of presentation in Scheme I in the series enantiomeric with that in which the experiments were actually performed): (i) by conversion to the methyl ketone and Baeyer–Villiger oxidation; (ii) by conversion to 2-*endo*-methyl-2-*exo*-norbornylamine by the Hofmann rearrangement,[12a] followed by nitrosative deamination[12a] of the latter in aqueous acetic acid to give the tertiary alcohol (+)-**3**-OH corresponding in configuration to (−)-**3**-OAc. The ratio of rotations of the tertiary alcohols (−)-**3**-OH obtained from the two routes is 1.23, in good agreement with the ratio of rotations of the starting acids **4** (i:ii = 1.30). Thus, the deaminatively produced alcohol has lost at most about 5% more optical purity than the oxidatively produced one. The correspondence strongly suggests that both sequences proceed with complete or nearly complete retention of optical purity. It would not have been surprising if the deamination, which probably passes through cation A_1, actually did produce some racemization. At least under equilibrating conditions, this system rapidly loses all optical activity, presumably by intramolecular or intermolecular 6,2-hydride shift.[9a] Under the strongly nucleophilic conditions used in the deamination, however, the cations probably are irreversibly captured, thus suppressing the competing

Scheme I



[a] Experiment actually performed in enantiomeric series.

The tertiary product (**3**) expected from direct 3,2-hydride shift in cation A when the latter has the configuration related to that of (−)-**1a** (X = OAc) (Scheme I) might be derived conceptually from (+)-camphenilone (**2**) by reduction of the CO group to CH_2 and replacement of the *exo*-methyl group with acetoxy. This correlation can be achieved in practice by way of a relay compound, 2-*endo*-methyl-2-*exo*-norbornanecarboxylic acid, (−)-**4**, which had previously been correlated with (−)-camphenilane (**6**), which in turn

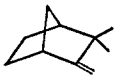
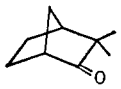
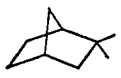
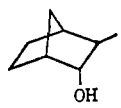
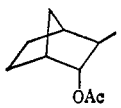
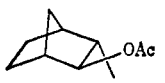
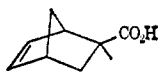
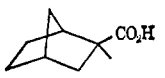
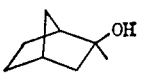
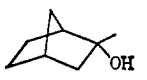
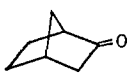
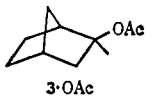
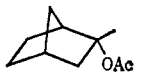
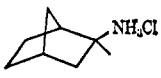
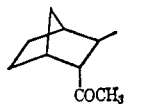
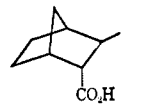
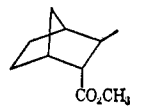
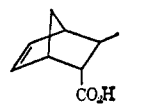
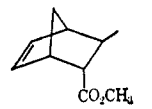
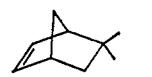
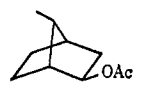
(10) Paper II: J. A. Berson, A. W. McRowe, R. G. Bergman, and D. Houston, *J. Am. Chem. Soc.*, **89**, 2563 (1967).

6,2 shift. Racemizing 6,2 shift is also slow even when cation A_1 is produced under the not completely irreversible conditions in the solvolysis experiments to be

(11) (a) Out of concern that the strongly basic conditions of the Wolff–Kishner reduction[8] might have caused partial racemization of **2** or its hydrazone by homoenolization,[11b] we have confirmed the previous work[8] in both signs and magnitudes of rotation for the (+)-**2** → (−)-**6** correlation using conditions which, although basic, were quite different from the previous ones. The quantitative agreement between the results makes it highly unlikely that any racemization occurs. (b) A. Nickon and J. L. Lambert, *J. Am. Chem. Soc.*, **84**, 4604 (1962); **88**, 1905 (1966).

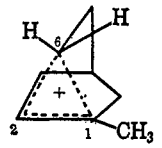
(12) Previously carried out in the racemic series by (a) R. R. Sauers, *ibid.*, **81**, 4873 (1959); (b) N. J. Toivonen, E. Siltanen, and K. Ojala, *Ann. Acad. Sci. Fennicae, Ser. AII*, No. 64 (1955).

Table I. Absolute Configurations and Rotations of Some Norbornane Derivatives

Compound	$[\alpha]_D$, deg	$[\alpha]_{365}$, deg	Solvent	Ref
	−113.5	...	Ether	*a–e*
 (−)-2	−73.8	...	Benzene	*a–e*
	+13.6	...	Benzene	*a,d*
 OH	−31.9	...	CCl_4	*f*
 OAc	−56.8 −42.3	... ...	$CHCl_3$ CCl_4	*f* *f*
	+8.04	...	Abs EtOH	*g*
	+68.6	...	95% EtOH	*a*
	+5.92	...	95% EtOH	*a*
 3-OH	−11.0 −11.8 −11.4	−33.2	$CHCl_3$ CCl_4 Hexane	*g* *g* *g*
	+25.6	+69.1	$CHCl_3$	*g*
	+31.5 +31.3	... ...	$CHCl_3$ $CHCl_3$	*g,h* *i*
 3-OAc	+4.0	+13.3	$CHCl_3$	*g*
	+48.0	+146.3	$CHCl_3$	*g*
	−8.53	...	MeOH	*g*
	+16.8	+347	$CHCl_3$	*j*
	−48.7	−132	95% EtOH	*f*
	−45.9	−124	95% EtOH	*f*
	−157	−521	95% EtOH	*f*
	−162	−536	95% EtOH	*j*
	+48.7	...	Benzene	*a*
	−13.9	...	95% EtOH	*j*

[a] Reference 9a. [b] J. P. Bain, A. H. Best, B. L. Hampton, G. A. Hawkins, and L. J. Kitchen, *J. Am. Chem. Soc.*, **72**, 3124 (1950). [c] For a review, see J. A. Mills and W. Klyne, *Progr. Stereochem.*, **I**, 177 (1954). [d] Reference 8. [e] Reference 6. [f] Reference 5. [g] This work. [h] Correlated with 2-norbornanol, the absolute rotation of which had been established by isotopic dilution analysis of its acid phthalate [J. A. Berson and S. Suzuki, *J. Am. Chem. Soc.*, **81**, 4088 (1959)]. [i] K. Mislow and J. G. Berger, *ibid.*, **84**, 1956 (1962). [j] Reference 17.

described.[5] This behavior contrasts markedly with that of norbornyl cation[13] and a number of substituted derivatives,[14–16] in which 6,2 shift competes with capture of the cations by solvent. An interpretation is offered based on the nonclassical structure, which because of the tendency of the methyl group to localize charge at C-1 has a smaller fraction of the positive charge at C-2 than in the unsubstituted case. This effect would decrease the rate of 6,2-hydride shift. Obviously, a parallel explanation could be given in terms of an interconverting pair of classical ions, one tertiary and the other secondary.



A_1

Correlation of the configuration and rotation of tertiary alcohol (+)-3-OH with those of (−)-norbornanone are also effected (Scheme I, iii) *via* the epimeric tertiary alcohol, which gives (+)-3-OH upon successive treatment with hydrochloric acid and alkali.[12b] The maximum rotation of 3-OH based on norbornanone is 11.0° ($CHCl_3$), the same as that obtained by correlation with camphenilone. Since the norbornanone value (Table I) is ultimately based on an "absolute" method (isotopic dilution), the highest reported value for camphenilone must represent the rotation of optically pure material.

The correlations established in these studies are summarized in Table I, which also lists for easy reference selected data from papers III[17] and VI[5] bearing on the present study.

(13) J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, 76, 4501 (1954).
(14) W. G. Woods, R. A. Carboni, and J. D. Roberts, *ibid.*, 78, 5653 (1956).
(15) A. Colter, E. C. Friedrich, N. J. Holness, and S. Winstein, *ibid.*, 87, 378 (1965), and papers cited therein.
(16) Paper IV: J. A. Berson, A. W. McRowe, and R. G. Bergman, *ibid.*, 89, 2573 (1967).
(17) J. A. Berson and R. G. Bergman, *ibid.*, 89, 2569 (1967).

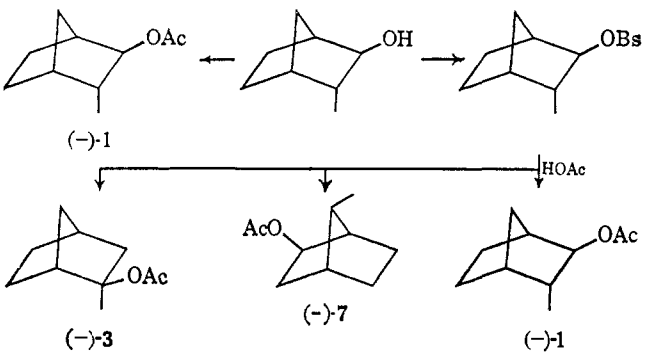
Acetolysis of Optically Active 3-*endo*-Methyl-2-*exo*-norbornyl *p*-Bromobenzenesulfonate. Prepared from the same enantiomer of 3-*endo*-methyl-2-*exo*-norbornanol that gives (−)-**1** (X = OAc) on acetylation, the corresponding *p*-bromobenzenesulfonate (**1**, X = OBs) solvolyzes in sodium acetate buffered acetic acid to give the same mixture of products already described in the racemic series.[16] Three of these acetates are isolated by preparative vapor chromatography with scrupulous precautions to avoid optical fractionation. The acetate of the starting 3-*endo*-methyl-2-norbornyl structure is isolated with the same sign and 99 ± 1% of the magnitude of rotation as that prepared by direct acetylation of the alcohol used to prepare the active substrate **1**, X = OBs. (−)-7-*anti*-Methyl-2-*exo*-norbornyl acetate (**7**), the configuration and absolute rotation of which are established in paper III,[17] is also isolated with complete preservation (101 ± 1%) of optical purity. Finally, the formation of (−)-2-*endo*-methyl-2-*exo*-norbornyl acetate (**3**) with complete retention of optical purity is demonstrated by isolation of the corresponding (+)-tertiary alcohol after lithium aluminum hydride reduction of the solvolysis reaction mixture. The rotation to be expected of the tertiary alcohol can be calculated as follows. The unsaturated acid **8** [(−)-2-*endo*-methyl-2-*exo*-5-norbornenecarboxylic acid] of $[\alpha]_D$ −41.4° has been converted[9a] to (−)-camphenilane of $[\alpha]_D$ −8.20°. In Scheme I, (+)-**8** of $[\alpha]_D$ +24.6° gave (−)-**3**-OH of $[\alpha]_D$ −4.22° by the Baeyer–Villiger route (i), whereas (+)-**8** of $[\alpha]_D$ +32.1° gave (−)-**3**-OH of $[\alpha]_D$ −5.20° by the deamination route (ii). Also, (−)-**1**, X = OAc, $[\alpha]_D$ −1.85°, gave camphenilone (**2**) of $[\alpha]_D$ +16.5°, and **2** of $[\alpha]_D$ +11.6° gave camphenilane (**6**) of $[\alpha]_D$ −2.20°. Using the results of the Baeyer–Villiger route (i), the rotation expected for **3**-OH derived from the *p*-bromobenzenesulfonate corresponding to (−)-**1a**, X = OAc, of $[\alpha]_D$ −1.85° is

$$[\alpha]_{calcd} = -4.22\left(\frac{-41.4}{+24.6}\right)\left(\frac{-2.20}{-8.20}\right)\left(\frac{+16.5}{+11.6}\right) = +2.70°$$

Using the data of the "deamination route" (ii)

$$[\alpha]_{calcd} = -5.20\left(\frac{-41.4}{32.1}\right)\left(\frac{-2.20}{-8.20}\right)\left(\frac{+16.5}{+11.6}\right) = +2.56°$$

If these figures are taken to represent the limits of experimental error, the observed value $[\alpha]_D$ +2.64° corresponds to 100 ± 3% retention.



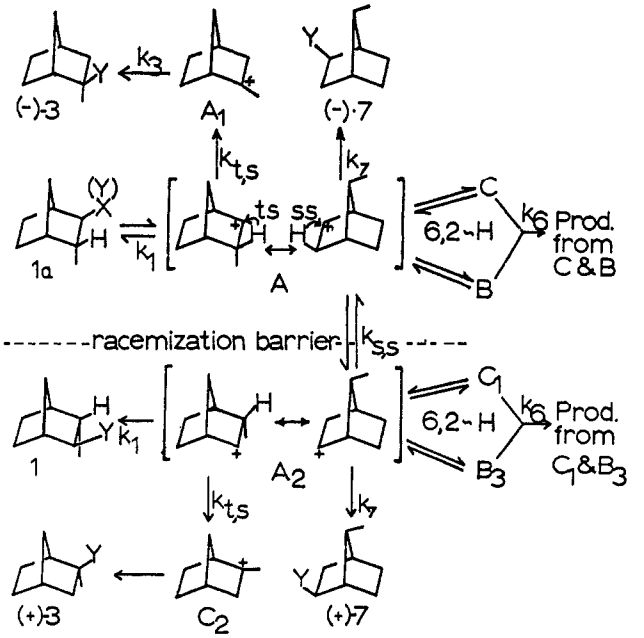
The configuration and optical purity of tertiary product (−)-**3** show that it belongs entirely to the stereochemical series that results from direct *exo*-vicinal hydride shift in cation A. The simplicity of this reaction is in striking contrast to the behavior of the epimeric 3-*exo*-methyl cation C.[5]

The hydride shift that converts secondary cation A to tertiary cation A_1 is at least predominantly intramolecular. Solvolysis of 3-*endo*-methyl-2-*exo*-norbornyl *p*-bromobenzenesulfonate in acetic acid-O-*d* under the same conditions used in the optically active series produces an acetate mixture from which tertiary acetate **3** is isolated containing only 0.23 atom of deuterium per molecule. This small amount of incorporation results from a reaction of the product **3** after its formation, as control experiments show.[5] Thus, in processes that expose it only once, A_1 is formed by essentially completely intramolecular hydride shift. Re-formation of A_1, even in buffered medium, permits incorporation of deuterium,[5] but, fortunately, racemization by 6,2 shift in A_1 is slow enough (see above) to be undetectable.

The 6,2 shifts that lead to the other solvolysis products from **1** (X = OBs)[16] are also entirely intramolecular. The total secondary acetate mixture incorporates only 0.0084 atom of deuterium per molecule.

The uniformly high optical purities of the products from the acetolysis of **1**, X = OBs, demonstrate the absence of secondary–secondary hydride shift and of vicinal methyl shift in cation A, both of which are racemizing events. This allows the construction of Scheme II for use in a more detailed scrutiny of part of the over-all mechanism discussed in paper I.[4] The nomenclature of the cations follows that used there.[4] From the stereochemical results and distributions of products, it is now possible to deduce two important rate constant ratios in terms of Scheme II.

Scheme II



Relative Rates of Vicinal (3,2) Hydride Shift and Solvent Capture. Assume that the concentrations of all of the carbonium ion intermediates can be expressed by steady-state equations. It is known[16] that the con-

version of secondary ion A to its more stable hydride-shifted tertiary isomer A_1[18] is essentially irreversible. The optical purity (P) of product **3** or **1a** (X = OAc) starting with **1a** (X = OBs) is then given by eq 1 and 2. The significance of the rate constants is given in Scheme II except for k'_6, k'_{-6}, and k_6 which refer respectively to summed forward and reverse rate constants for 6,2-hydride shift in cation A (and its enantiomer A_2) and for capture of the hydride-shifted cations C and B (and their enantiomers C_1 and B_3). Rate constants k_1, k_6, and k_7 include solvent concentration terms. The bracketed terms of eq 1 represent steady-state concentrations.

$$v = k_{s,s} + k'_6 + k_{t,s} + k_1 + k_7 - k'_6k'_{-6}/(k_6 + k_{-6}) = k_{ss}[A]/[A_2] \quad (1)$$

$$P = \text{optical purity of } \mathbf{3} \text{ or } \mathbf{1a} = (1 - k_{s,s}/v)/(1 + k_{s,s}/v) \quad (2)$$

The fraction (F) of the total acetate product represented by **3** is given by eq 3.

$$F = k_{t,s}/(v - k_{s,s}) \quad (3)$$

Simple manipulation of eq 2 and 3 gives the ratio of the rate of migration of *exo* hydrogen from a tertiary to a secondary carbon ($k_{t,s}$) to that from a secondary to a secondary carbon ($k_{s,s}$) (eq 4).

$$k_{t,s}/k_{s,s} = (2P/1 - P)F \quad (4)$$

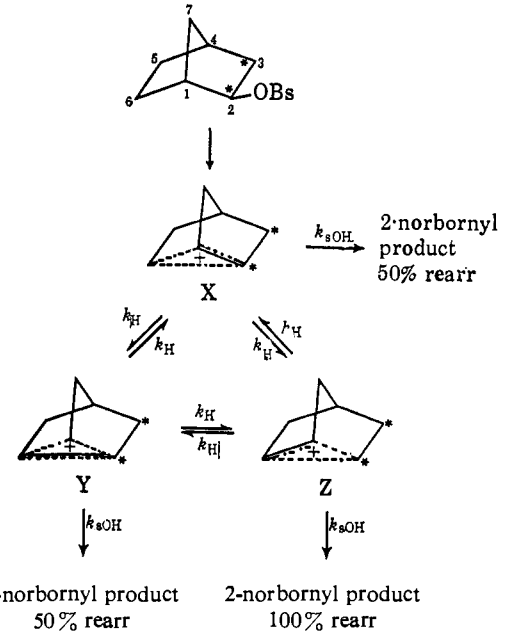
The product distribution[16] gives F as 0.07. The value for P is essentially unity whether determined from the optical purity of **3** or from that of **1**, X = OAc, but the latter is more accurate since it is obtained by direct comparison of the rotations of a single substance. With $P \geqslant 0.99$, $k_{t,s}/k_{s,s}$ has a minimum value of 14.

The ratio of $k_{t,s}$ to the composite rate constant k_{sOH} ($\equiv k_1 + k_7$) measures the competition between tertiary–secondary hydride shift and solvent capture of ion A. It can be evaluated with the previously reported data[16] from the ratio **3**:(**1** + **7**) as 0.074 in aqueous ethanol, 0.049 in aqueous dioxane, 0.18 in formic acid, and 0.115 ± 0.017 (average of ratios from three different modes of entry) in acetic acid. Thus, $k_{sOH}/k_{s,s}$, the competition ratio between solvent capture and secondary–secondary hydride shift in A, is 14:0.115 or at least 122 in acetic acid at 100°. A factor this large would suffice to prevent the formation of a detectable amount of 3,2-shifted product from norbornyl cation itself (2,3-^{14}C-labeled).[13]

Actually, this ratio may be very much larger. As a calibrating rate, we may use 6,2-hydride shift, which is known[13–16] to be competitive with and hence of the same order of magnitude as solvent capture in many norbornyl systems. A direct comparison between 6,2 and secondary–secondary 3,2 shift in norbornyl cation itself is available from the proton magnetic resonance spectrum in solvent SbF_5–SO_2ClF–SO_2 at −120°, which shows[19] that 6,2 shift is at least 8.8 powers of ten faster than 3,2 shift. If this rate ratio were largely due to a difference in activation enthalpy and if it persisted in hydroxylic media, 6,2 shift would be faster than 3,2 shift under the solvolysis conditions (water or acetic acid solvent, 25–100°) by factors in the range 4×10^3–3×10^4. Thus, solvent capture should overwhelm secondary–secondary 3,2 shift by several orders of magnitude. Experimentally, no 3,2 shift was detected[13,20a] in the acetolysis of *exo*-norbornyl *p*-bromobenzenesulfonate-2,3-^{14}C, but Lee and Lam later reported[20b] having found such a process in the acetolysis of the corresponding 2-tritio derivative. These authors interpreted[20b] their data in terms of 1–2% of C-3 tritio product. The total per cent contribution of 3,2 shift would have had to be in the range 7–10% to account for this,[20b] so that 3,2 shift and 6,2 shift, according to this interpretation, cannot differ very much in rate. Furthermore, 3,2 shift seems to be just detectable in formolysis of ^{14}C-labeled material,[13,20,21] although it is not clear whether the distribution there is completely kinetically controlled. If the reports of competitive 3,2 and 6,2 shifts in hydroxylic media are correct, one is forced to the conclusion that the relative and absolute magnitudes of these specific rates can vary by several powers of ten as a function of solvent. Since the rates observed by nmr techniques in nonhydroxylic media are being used as approximations to the rates under solvolytic conditions,[22] it would seem imperative that the discrepancy be resolved. The closely related matter of absolute rates of capture of the cations in solvolytic media is briefly discussed in the Appendix.

Relative Rates of Transannular (6,2) Hydride Shift and Solvent Capture. Estimates of these relative rates for the secondary–secondary case can be made from studies of isotope-position rearrangement in solvolyses of 2,3-^{14}C-norbornyl derivatives[13] or from the more recent experiments in the 2-tritionorbornyl series.[20b] The adjacent diagram (Scheme III) outlines the basis for

Scheme III



(18) Only one resonance form of A_1 is shown here. The argument is not materially changed whether A_1 is considered to be a resonance hybrid tertiary–secondary nonclassical ion or a tertiary classical ion. We are not concerned here or in the sequel[6] with the distinction.

(19) (a) M. Saunders, P. von R. Schleyer, and G. A. Olah, *J. Am. Chem. Soc.*, 86, 5680 (1964); (b) F. R. Jensen and B. H. Beck, *Tetrahedron Letters*, 4287 (1966).

(20) (a) P. D. Bartlett and C. E. Dills, unpublished results; C. E. Dills, Thesis, Harvard University, 1955; (b) C. C. Lee and L. K. M. Lam, *J. Am. Chem. Soc.*, 88, 2831 (1966); (c) *ibid.*, 88, 5355 (1966).

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

(22) S. Winstein, *J. Am. Chem. Soc.*, 87, 381 (1965).

the calculations from the ^{14}C data. Vicinal shift is assumed to be slow.[13b] Kinetic isotope effects in this type of marking are all secondary and are assumed to be small. The tritium-labeling data[20b] must be handled in a different manner, which is described in the Appendix. The total per cent rearrangement of isotope position is given by $F_x(50) + F_y(50) + F_z(100)$, where F_x, F_y, and F_z are the fractions of product formed from cations X, Y, and Z. By symmetry, the steady-state concentrations of Y and Z are equal, and hence $F_y = F_z$. Thus, the total per cent rearrangement may be expressed as in eq 5.

$$F_x(50) + F_y(150) = \text{total } \% \text{ rear} \quad (5)$$

But $F_y = (1 - F_x)/2$, so that eq 5 can be put in the form of eq 6. From the previously derived[16] relationships

$$F_x = 3 - \text{total } \% \text{ rearr}/25 \quad (6)$$

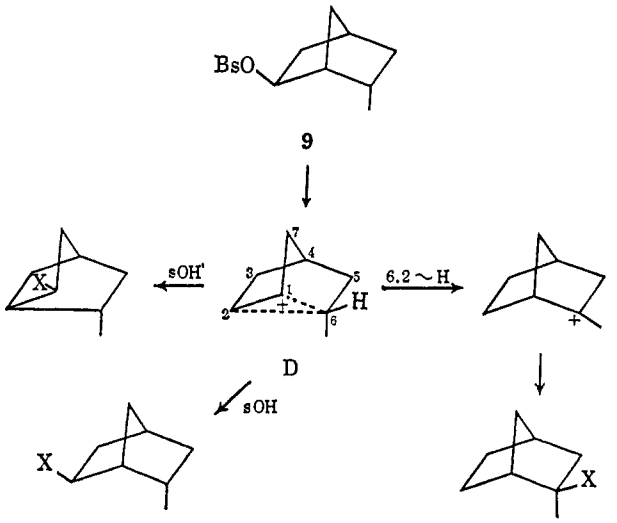
(eq 7 and 8), one obtains eq 9, which permits an experi-

$$F_x = (k_H + k_{sOH})/(3k_H + k_{sOH}) \quad (7)$$

$$F_y + F_z = 2k_H/(3k_H + k_{sOH}) \quad (8)$$

$$k_H/k_{sOH} = (1 - F_x)/(3F_x - 1) \quad (9)$$

mental evaluation of the competition between secondary–secondary 6,2-hydride shift and solvent capture of norbornyl cation. The corresponding competition ratio for a tertiary–secondary case is supplied by the product distribution[16] from 6-*endo*-methyl-2-norbornyl *p*-bromobenzenesulfonate (**9**). Table II summarizes these ratios.



An estimate of the effect of methyl substitution on the absolute rate of 6,2-hydride shift would bear upon the question of charge distribution in the transition state. Although such an estimate based on the data of Table II is at best a rough one, it seems worth making. One should first make some attempt to relate the hydride shift rates to a common solvent capture rate k_{sOH}. It seems reasonable to assume[16] that k_{sOH} would be roughly the same for attack at the favored position[16] (C-1) of the 6-methyl cation (D) as for attack on norbornyl cation. Since attack at C-2 of D is only about one-tenth as fast,[16] k_{sOH} for D can be taken to be roughly one-half k_{sOH} for norbornyl cation. The experimental k_H/k_{sOH} values of Table II for the 6-methylnorbornyl cases are therefore divided by this statistical factor of 2.

Table II. Competition Ratios (6,2-Hydride Shift *vs.* Solvent Capture) for Secondary–Secondary (s,s) and Tertiary–Secondary (t,s) Systems

Structure	Type of shift	Solvent	Temp, °C	k_H/k_{sOH}
Norbornyl	s,s	Aq acetone	45	0.12
Norbornyl	s,s	HOAc	45	0.27
6-Methylnorbornyl	t,s	Aq EtOH	100	0.92 (0.46)[a]
6-Methylnorbornyl	t,s	HOAc	100	2.45 (1.23)[a]

[a] The value in parentheses is an estimate derived from a rough statistical correction of the experimental value (see text).

If 6,2-hydride shift at both the ion-pair and separated-ion stages occurred in the norbornyl cation[23] but not in 6-methylnorbornyl, the norbornyl ratios of Table II, derived upon the assumption of a "single pass" competition, would be too high. It is difficult to guess how much correction should be applied for this,[23] but if it were large, the observed total per cent rearrangement figures would have approached the "equilibrium" value of 66.7%. This is not found to be the case.[13] The change in temperature (45–100°) between the norbornyl and 6-methylnorbornyl experiments might lower the k_H/k_{sOH} ratio in acetic acid by a factor of about 3 (see Appendix).

One concludes that the enhancement of the rate of 6,2-hydride shift by methyl substitution is a factor between about 5 and about 15 in acetic acid. This feeble effect on the removal of "hydride ion" from carbon to the transition state distance contrasts strongly with the enormous change produced by methyl substitution on SN1 solvolyses,[24] where achievement of the transition state involves stretching a halogen–carbon bond. In reactions of bromides, for example, alteration of a secondary structure (isopropyl) to tertiary (*t*-butyl) enhances the solvolysis rate by factors ranging between 10^3 and 10^5. Although ground-state energy differences cannot be ignored, it seems likely that a major cause of the observed weakening of the methyl substituent effect has to do with charge distribution in the transition state. The transition state for halide solvolysis would have a substantial amount of positive charge localized at the reaction site, and its energy would, therefore, be very responsive to alkyl substitution, but the transition state for 6,2-hydride shift if it resembles an edge-protonated cyclopropane,[25] consistent with the known *endo–endo* geometry of the process,[26] might be expected[27] to have relatively little positive charge at the migration origin (C-6) or terminus (C-2). Much of the charge might well be localized on the migrating hydro-

(23) For an earlier discussion, see J. A. Berson and A. Remanick, *J. Am. Chem. Soc.*, **86**, 1749 (1964).
(24) A. Streitwieser, Jr., *Chem. Rev.*, **56**, 571 (1956).
(25) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1154 (1952).
(26) (a) J. A. Berson and P. W. Grubb, *ibid.*, **87**, 4016 (1965). (b) B. M. Benjamin and C. J. Collins, *ibid.*, **88**, 1556 (1966). (c) As has been pointed out,[26a] the possibility cannot be dismissed that substitution may change the 6,2-shift intermediate or transition state from hypothetically face protonated in simple norbornyl cation to edge protonated (or any stereochemical equivalent leading to an *endo–endo* process) in the substituted examples actually studied.[26a,b] However, this is not the equivalent of the statement[26d] that in the substituted cases, "either the edge-protonated or the face-protonated intermediate could produce the same experimental result." In the case of the 1-methyl-7-carboxy-2-norbornyl cation, a single face-protonated intermediate of nominal twofold symmetry was experimentally excluded.[26a] (d) C. J. Collins and B. M. Benjamin, *J. Am. Chem. Soc.*, **89**, 1652 (1967).
(27) R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964).

gen, as extended Hückel calculations suggest is the case with cyclo-$C_3H_7^+$ itself.[27]

Experimental Section

Optical Activation of 3-*endo*-Methyl-2-*exo*-norbornyl Acid Phthalate. A solution of 600 g of the racemic acid phthalate[10] in 1 l. of acetone was brought to boiling on the steam bath and treated with an equimolar amount of ephedrine. After a short while the mixture was homogeneous; it was cooled to room temperature and allowed to stand overnight, after which time a large amount of the amine salt had crystallized from the solution. The white crystals were collected on a Büchner funnel and recrystallized ten times from acetone, yielding 165 g of salt in the head crop. A 50.0-g quantity of this material was stirred rapidly with about 200 g of cracked ice, 30 ml of 35% aqueous HCl, and 75 ml of ether. When solid was no longer visible in the mixture, the phases were separated and the aqueous layer was extracted twice more with ether. The combined ether fractions were washed with 5% hydrochloric acid, water, and brine, and dried over sodium sulfate. They were then decanted and the solvent was evaporated at the aspirator, leaving 30.5 g (quantitative yield) of optically active acid phthalate, which had a specific rotation of $[\alpha]^{24.0}D$ −3.98° ($CHCl_3$).

The optically active acid phthalate was mixed with 40 ml of 15% sodium hydroxide and steam distilled. Optically active 3-*endo*-methyl-2-*exo*-norborneol, **1a**, X = OH, distilled over completely within 10 min and crystallized in the aqueous distillate. To avoid optical fractionation, the alcohol was collected completely by repeated extraction of the distillate with pentane, after saturation of the aqueous phase with salt. The combined pentane extracts were washed with 1% hydrochloric acid and brine and dried over sodium sulfate. The pentane solution was then concentrated to a manageable size, but the alcohol was not allowed to crystallize. An aliquot was removed and concentrated to dryness at the aspirator, and an infrared spectrum taken. It was identicals with that of the pure racemic sample.[10] A second aliquot was removed and converted to optically active 3-*endo*-methyl-2-*exo*-norbornyl acetate, which had an infrared spectrum and retention time on vpc identical with that of the racemic sample. Analysis by capillary vpc showed it to be >99% homogeneous. The rotation was $[\alpha]^{26}D$ −1.85° (absolute ethanol).

Correlation of Optically Active 3-*endo*-Methyl-2-*exo*-norbornyl Acetate ((−)-1a, X = OAc) with (+)-Camphenilone (2). The mixture of 3-methyl-2-norbornanones derived from the above active acetate, $[\alpha]D$ −1.85°, has been described elsewhere.[17] A portion (1.0 g) of the mixed ketones was dissolved in 5 ml of dry dimethyl sulfoxide (previously distilled from lithium aluminum hydride). A three-necked, round-bottomed flask was flamed out under a stream of nitrogen, cooled, and charged with 1.8 g of potassium *t*-butoxide and 40 ml of dry dimethyl sulfoxide. The ketone solution was then added to the flask dropwise from a pressure-equalizing funnel, while the entire system was protected with a nitrogen blanket. During the addition the cloudy, off-white solution turned yellow green.

After the mixture had been stirred for 20 min, 15 ml of freshly distilled methyl iodide was added dropwise while stirring was continued. The cloudiness and color disappeared immediately, and the mixture was allowed to stir for 2 hr at room temperature. Water was then added and the mixture was extracted four times with pentane. The combined pentane extracts were washed repeatedly with water and once with saturated brine, and dried over sodium sulfate. Decantation and evaporation left a greenish oil containing (analysis by capillary vpc) 15% 3-*exo*-methyl-2-norbornanone, 5% of its *endo* epimer, 60% camphenilone (**2**), and the rest low-boiling products. After distillation bulb to bulb, the distillate was chromatographed on column D-1. By this procedure the optically active camphenilone could be obtained in better than 99.0% purity. It had a specific rotation of $[\alpha]^{25.6}D$ +16.5° (benzene).

Conversion of (+)-Camphenilone to (−)-Camphenilane.[8] A sample of optically active camphenilone obtained from Light and Co. ($[\alpha]^{25.5}D$ +11.6°, $CHCl_3$) and weighing 1.0 g was dissolved in 5 ml of 95% ethanol. Semicarbazide hydrochloride (0.9 g) and sodium acetate (1.1 g dissolved in 5 ml of water) were added, and the resulting mixture was heated at reflux for 4 hr on the steam bath under a water condenser. The semicarbazone separated as white needles on cooling; it was extracted with three portions of $CHCl_3$, and the combined organic extracts were washed with saturated sodium chloride and dried over magnesium sulfate. The solution was filtered and an aliquot was taken for an infrared spectrum. The spectrum showed the expected N–H (2.9, 3.0 μ) and C=N (5.92 μ) bands, and a complete absence of C=O absorption (5.72 μ). The solution was therefore concentrated to dryness at the aspirator and all the product (5.5 g, 97% yield) was removed and mixed with 4.5 g of pulverized KOH. This solid mixture was placed in a 100-ml, round-bottomed flask and shaken to ensure homogeneity. A short-path distillation apparatus was attached, and the flask was heated in a Woods' metal bath from 170 to 260°. As the temperature rose, the solid fused and bubbled and a two-phase mixture collected in the receiver. When the distillation was complete, the material in the pot had solidified to a tan mass.

The organic layer was drawn off the top of the distillate with a pipet, a little pentane was added to the aqueous phase, and the pentane layer was drawn off and combined with the first fraction. After a small amount of magnesium sulfate was added to the organic mixture, it was centrifuged and the liquid was separated from the magnesium sulfate. The solid was washed with pentane and the pentane was combined with the rest of the hydrocarbon. As an infrared spectrum of this mixture showed a small C=O band, about 0.060 g of lithium aluminum hydride was added and the material was distilled bulb to bulb at atmospheric pressure. The hydrocarbon (2.5 g, 72% yield) came over as a clear liquid, solidifying in the Dry Ice trap. Chromatography on column D-1 at 135° gave camphenilane (**6**), which was again distilled bulb to bulb and thus obtained better than 99.0% pure by capillary vpc. Its specific rotation was $[\alpha]^{25.5}D$ −2.20° (benzene), and its infrared spectrum was identical with that of a racemic sample.[9a]

Solvolysis of Racemic 3-*endo*-Methyl-2-*exo*-norbornyl *p*-Bromobenzenesulfonate (1a, X = OBs). A 0.1 *M* solution of sodium acetate in acetic acid was heated to thermal equilibrium in an oil bath at 95°. With rapid stirring, a suspension of 12.3 g of the sulfonate[10] in another 50 ml of buffer solution was then added dropwise to the hot solution. The resulting mixture was stirred at this temperature for 15 min, after which time it was allowed to cool to room temperature and poured onto pentane and cracked ice. The phases were separated, the water phase was extracted twice more with pentane, and the combined organic layers were washed with water, saturated sodium bicarbonate solution, and brine, and dried over sodium sulfate. The solution was decanted, and the pentane was distilled away carefully with a Vigreux column, leaving a greenish, sweet-smelling oil. Bulb-to-bulb distillation of this material at 15 mm gave 5.0 g (83%) of acetates as a water-white oil. An analysis of this material by capillary vpc showed that it contained several products, whose identities and relative proportions are given elsewhere.[16]

In another experiment, 0.9 g of the sulfonate was solvolyzed under the same conditions, but for a longer period of time. Aliquots were withdrawn periodically and worked up individually as above. Analysis of these aliquots by vpc indicated that the solvolysis was essentially complete after 5 min at 95°, and the relative proportions of the products remained constant for several hours afterward. At very long reaction times (greater than 4 or 5 hr) small amounts of other products, 1-methyl-2-*exo*-norbornyl acetate and 2-*exo*-methyl-2-*endo*-norbornyl acetate, could be detected.

A solvolysis of 3-*endo*-methyl-2-*exo*-norbornyl *p*-toluenesulfonate was carried out in a manner identical with that of the *p*-bromobenzenesulfonate solvolysis. The product pattern, analyzed by capillary vpc after work-up, was identical with that from the *p*-bromobenzenesulfonate.

Solvolysis of 1a in O-Deuterioacetic Acid. The procedure described for solvolysis of **1a**, X = OBs, and isolation of tertiary product as alcohol **3-OH** in the optically active series was repeated on a sample of racemic *p*-bromobenzenesulfonate, except that O-deuterioacetic acid was employed as solvent. Falling drop analysis on **3-OH** showed it to contain 1.6 atoms % excess deuterium (0.23 atom of deuterium per molecule), and analysis of the remainder of the alcohols showed the mixture to contain 0.06 atom % excess deuterium (0.0084 atom of deuterium per molecule).

Solvolysis of Optically Active 1a, X = OBs. An aliquot of the same pentane solution of 3-*endo*-methyl-2-*exo*-norbornanol (**1a**, X = OH) used to prepare (−)-3-*endo*-methyl-2-*exo*-norbornyl acetate, $[\alpha]D$ −1.85°, contained about 9 g of the alcohol. This was converted to the *p*-bromobenzenesulfonate in a procedure identical with that used to prepare the racemic derivative.[10] The material obtained was identical in spectral properties with the racemic sulfonate, except that the infrared showed the presence of a small amount of residual starting alcohol. A preparative-scale solvolysis on 20.6 g of the optically active sulfonate was carried out under the same conditions as the racemic analog,[16] and 7.6 g (75%) of acetates was obtained from the reaction. The entire mixture was reduced to alcohols with lithium aluminum hydride, and 2-*endo*-

methyl-2-*exo*-norborneol (**3**) was separated from the other products on vpc column B at 135° after bulb-to-bulb distillation of the mixture at 13 mm. The tertiary alcohol was collected as white needles, pure by capillary vpc. After bulb-to-bulb distillation, it had a specific rotation of $[\alpha]^{2.61}D$ +2.64° ($CHCl_3$). Its infrared spectrum was identical with that of a racemic sample.

The remainder of the solvolysis material was collected as a semisolid and reconverted to acetates in the usual way. The two major products, 3-*endo*-methyl-2-*exo*-norbornyl acetate (**1a**, X = OAc) and 7-*anti*-methyl-2-*exo*-norbornyl acetate (**7**), were separated from the rest of the mixture on column E at 175°. Both were recycled on the same column to give acetate **1a** in better than 99.0% purity and **7** in 98.0% purity. Acetate **1a** obtained in this way was identical in infrared spectrum and capillary vpc retention time with authentic **1a**. It was found to have specific rotation $[\alpha]^{25.1}D$ −1.83° (absolute ethanol) and is thus formed with 99 ± 1% retention of configuration. The sample of **7** obtained from this solvolysis was identical in infrared spectrum and retention time on vpc with material obtained from the deamination of 3-*endo*-methyl-2-*exo*-norbornylamine hydrochloride[16] and had a specific rotation of $[\alpha]^{22.9}D$ −3.19° (95% ethanol).

Scheme I. Correlation of 2-*endo*-Methyl-5-norbornene-2-*exo*-carboxylic Acid (8) with 2-*endo*-Methyl-2-*exo*-norbornanol (3-OH). (i) Baeyer–Villiger Route, Racemic Series. Hydrogenation of pure racemic **8**,[28,29] conversion to the acid chloride, and reaction of the latter compound with dimethylcadmium were carried out in the manner described[10] for similar transformations. Racemic **2-*endo*-methyl-2-*exo*-acetylnorbornane** was a liquid, bp 95–98° (25 mm), $n^{22.5}D$ 1.4759.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.60. Found: C, 78.63; H, 10.66.

The **2,4-dinitrophenylhydrazone** was recrystallized from ethanol and had mp 155.5–156°.

Anal. Calcd for $C_{16}H_{20}O_4N_2$: C, 57.82; H, 6.07. Found: C, 57.73; H, 6.19.

The racemic ketone reacted with perbenzoic acid in the usual manner[10] to give 2-*endo*-methyl-2-*exo*-norbornyl acetate.

Optically Active Series. A sample of **8** obtained by resolution[9a] had $[\alpha]D$ +24.6° (95% ethanol). It was hydrogenated over platinum oxide in methanol to the saturated acid which then was converted to the ketone as in the racemic series. The ketone had $[\alpha]D$ +9.25° ($CHCl_3$), $n^{22.5}D$ 1.4751, and was homogeneous by vpc. Its infrared spectum was identical with that of the racemate.

Oxidation with perbenzoic acid as in the racemic series followed by reduction with lithium aluminum hydride gave a mixture of alcohols which was purified by preparative vapor chromatography on column C to give pure 2-*endo*-methyl-2-*exo*-norbornanol (**3-OH**), $[\alpha]D$ −4.22° (CCl_4). This material had mp 84–85°. It was homogeneous on column L, and its infrared spectrum was identical with that of the racemate.

Scheme I. (ii) Deamination Route. A sample of 2-*endo*-methyl-5-norbornene-2-*exo*-carboxylic acid (**8**) obtained by resolution[9a] had $[\alpha]D$ +32.1° (95% ethanol). It was hydrogenated and treated with thionyl chloride to give the corresponding saturated acid chloride. This material was dissolved in dry ether and treated with dry ammonia gas. Filtration of the solid, concentration of the filtrate, washing of the combined solids with water, extraction of the water wash with ether, evaporation of the ether, and drying of the combined solid gave 98.4% of the amide, $[\alpha]D$ +5.65° (methanol).[30] This material was subjected to the Hofmann rearrangement under the conditions reported by Sauers[31] in the racemic series. The resulting amine hydrochloride had an infrared spectrum identical with that of the racemate (kindly supplied by Professor Sauers[31]).

The amine hydrochoride (3.8 g) in a mixture of 10 ml of water and 2.5 ml of acetic acid was treated with a solution of 2.5 g of sodium nitrite in 8 ml of water. The reaction mixture was allowed to stand 3 hr, poured into 150 ml of water, and extracted with pentane. Drying, evaporation of the pentane, lithium aluminum hydride reduction, reacetylation, distillation, and reduction gave 2-*endo*-methyl-2-*exo*-norbornanol, $[\alpha]D$ −5.20° (CCl_4).

Scheme I (iii). Asymmetric hydroboration[32] of norbornene with diisopinocampheylborane (prepared from α-pinene of $[\alpha]D$ −42.7° [*c* 2.3, absolute EtOH], kindly supplied by Dr. H. Enos of Hercules Powder Co.) and acetylation of the crude alcohol obtained after oxidation gave (−)-*exo*-2-norbornyl acetate, α −3.31° (neat, 1 dm), after distillation through a spinning-band column. This material contained less than 5% of the *endo* isomer as estimated by vpc (column N) of the alcohol derived from it by lithium aluminum hydride reduction. Jones oxidation[9a] gave 2-norbornanone, $[\alpha]D$ −7.95° (chloroform), which was homogeneous (columns L and N).

Methyl Grignard reagent was prepared in 150 ml of ether in a 1-l., three-necked flask from 6.90 g (0.28 g-atom) of magnesium turnings and 15.9 ml (at 0°) of methyl bromide (0.29 mole). To this mixture was added a solution of 23.5 g (0.213 mole) of norbornanone, $[\alpha]D$ −7.95° (chloroform), in 100 ml of ether over a 20-min period. The light tan mixture was stirred for 1 hr at room temperature. The excess reagent was destroyed with a saturated solution of ammonium chloride. The solution and salts were cooled to 0° and *almost* all the precipitate was dissolved with 2 *N* hydrochloric acid; the solution was still alkaline as evidenced by the odor of ammonia.

The clear ether layer was separated from the aqueous phase and the latter extracted four times with pentane to give a combined organic solution of *ca.* 650 ml which was twice washed with saturated brine and dried over sodium sulfate. The solvent was carefully fractionated off, to give a slightly yellow oil.

The crude oil was distilled bulb to bulb at 95° (*ca.* 25 mm), to yield a white crystalline solid; the infrared spectrum and retention times on vpc were identical with those of a racemic sample of 2-*exo*-methyl-2-*endo*-norbornanol prepared by the method of Toivonen.[12b] The yield was 25.5 g (95%). A representative sample was taken from the molten alcohol: $[\alpha]^{25}D$ −6.45 ± 0.09°; $[\alpha]^{25}_{365}$ −17.41 ± 0.05° (*c* 4.3, chloroform), average values and standard deviations given for four determinations.

The above alcohol was acetylated with excess acetic anhydride and pyridine at 100° for 24 hr to give, after the usual work-up and distillation, a 100% yield of the acetate, whose infrared spectrum and vpc retention times on vpc were identical with those of the authentic, racemic material. Capillary vpc on column N indicated the presence of *ca.* 0.05% *t-exo* acetate, rotation $[\alpha]^{25}D$ −12.09 ±0.07°, $[\alpha]^{25}_{365}$ −36.84 ± 0.08° (*c* 6–7.8, chloroform). Treatment with lithium aluminum hydride regenerated the starting alcohol with unchanged rotation.

2-*endo*-Methyl-2-*exo*-norbornanol [(+)-3-OH]. A homogeneous sample of 3.00 g of the above optically active 2-*exo*-methyl-2-*endo*-norbornanol was stirred with concentrated hydrochloric acid for 2 hr at room temperature. The chloride was extracted with pentane, washed with brine, and evaporated to give a residue which was homogeneous on columns L and N except for traces of pentane. The crude chloride was stirred at 95° with 35 ml of 1 *N* sodium hydroxide for 4 days and extracted with pentane. Washing with brine, drying over sodium sulfate, removal of solvent, and sublimation gave 2.36 g (80%) of **(+)-3-OH**, infrared spectrum and vpc retention time identical with those of an authentic racemic sample.[12b] The rotations were $[\alpha]D$ +2.78 ± 0.006°; $[\alpha]_{365}$ +8.38 ±0.02° (*c* 5.0–5.3, chloroform).

The corresponding **acetate (−)-3-OAc** prepared in 94% yield from this sample had $[\alpha]D$ −1.01 ± 0.03°; $[\alpha]_{365}$ −3.36 ± 0.01° (*c* 5.2–5.4, chloroform), and contained 0.75% of the epimeric acetate. Lithium aluminum hydride regenerated **(+)-3-OH** with unchanged rotation which contained no 1-methyl-2-*exo*-norbornanol (0.05% could have been detected, column L).

By a previously described procedure,[9a] 2-*exo*-methyl-2-*endo*-norbornanol, $[\alpha]D$ −6.45° (chloroform), was converted to **1-methyl-2-*exo*-norbornyl acetate**, $[\alpha]D$ +9.29 ± 0.03°; $[\alpha]_{365}$ +28.0 ± 0.005° (*c* 5.2–5.4, chloroform), which was reduced with lithium aluminum hydride to **1-methyl-2-*exo*-norbornanol**, $[\alpha]D$ +0.21 ± 0.02°; $[\alpha]_{365}$ −2.11 ± 0.02° (*c* 5.8–5.9, chloroform). Reacetylation gave back the acetate with unchanged rotation.

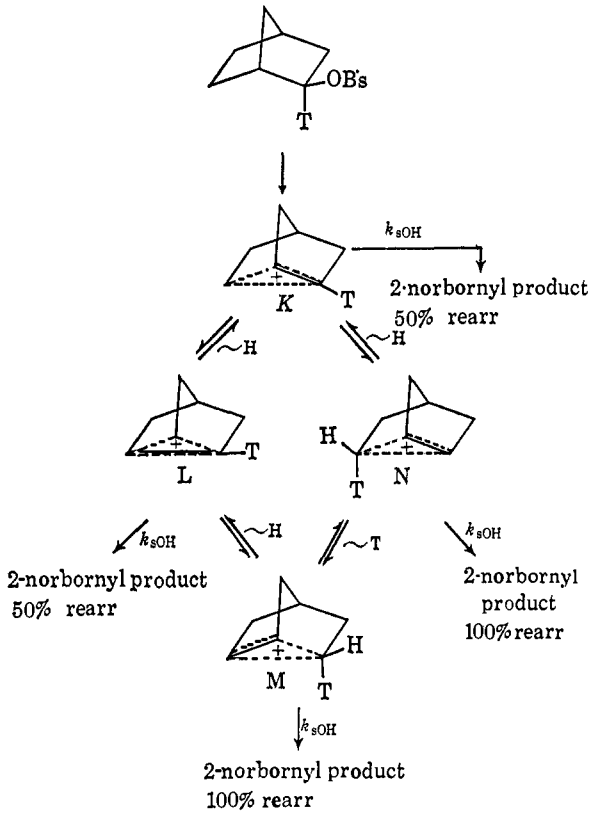
Appendix

6,2-Hydride Shifts in the 2-Norbornyl-2-*t* System. The threefold symmetry properties associated with 6,2-hydride shifts in 2-norbornyl-2,3-^{14}C cations are perturbed in the 2-norbornyl-2-*t* analogs. In the 2,3-^{14}C case (Scheme III), three successive transannular shifts in a given direction suffice to complete the symmetry operation by which the starting cation is trans-

(28) S. Beckmann, R. Schaber, and R. Bamberger, *Chem. Ber.*, **87**, 997 (1954).
(29) J. S. Meek and W. B. Trapp, *J. Am. Chem. Soc.*, 79, 3909 (1957).
(30) For the racemate, see ref 31.
(31) R. R. Sauers, *J. Am. Chem. Soc.*, **81**, 4873 (1959).
(32) H. C. Brown, N. R. Ayyangar, and G. Zweifel, *ibid.*, **86**, 397 (1964).

formed into itself. Although the 2-*t* case has also been discussed as if it were threefold symmetric,[20b] this approach is not really justifiable. The number of successive transannular hydride shifts needed to complete the symmetry operation depends upon the stereochemistry of these shifts. If, as seems likely,[26] these are constrained to be *endo–endo*, *four* successive transannular shifts are required to complete a cycle (Scheme IV). The competition ratio k_{sOH}/k_H can be calculated

Scheme IV



from experimental data by means of eq 10, which is derived by treating all of the cationic intermediates by steady-state methods, assuming no isotope effect ($k_H = k_T$).

$$R_T = (F_M + F_N)/(F_K + F_L) = \frac{4 + (k_{sOH}/k_H)}{4 + 5(k_{sOH}/k_H) + (k_{sOH}/k_H)^2} \quad (10)$$

The quantities F_M, F_N, F_K, and F_L represent the fractions of product formed from each of the four cations, and the quantity R_T is evaluable from the experimental ratio of 5,6-tritiated to 5,6-untritiated product, these two ring positions being inseparable in the degradation scheme. Solution of the quadratic and rejection of the physically insignificant negative root give the desired ratio k_{sOH}/k_H (eq 11).

$$k_{sOH}/k_H = \frac{1 - 5R_T \pm (9R_T^2 + 6R_T + 1)^{1/2}}{2R_T} = (1/R_T) - 1 \quad (11)$$

A cubic relationship (eq 12) is derived from the alternative extreme assumption of a large isotope effect ($k_T = 0$).

$$R_T(k_{sOH}/k_H)^3 + (5R_T - 1)(k_{sOH}/k_H)^2 + (6R_T - 4)(k_{sOH}/k_H) + 2(R_T - 1) = 0 \quad (12)$$

The ratio R_C of 5,6-labeled to 5,6-unlabeled product in the case of 2,3-^{14}C starting material is readily derived from eq 7 and 8 as

$$k_{sOH}/k_H = (1/R_C) - 2 \quad (13)$$

As eq 11, 12, and 13 show, the product distributions from 2,3-^{14}C and 2-*t* starting materials are different functions of the rate constants in question, and the apparent correspondences noted[20b] between the two experiments in terms of "per cent contributions" of C-1, C-2 and C-1, C-2, C-3 equating processes are purely fortuitous. If the same rate constants apply to the two systems, eq 11, 12, and 13 show that, in principle, these "per cent contributions" cannot be the same. Expressed another way, the number of sequential steps required to achieve a given "per cent contribution" differs in the two cases. The proper cross-check is made *via* the rate constants. Thus, from the tritium experiments[20b] and eq 11 one calculates k_{sOH}/k_H = 2.88 in acetic acid at 45°. Using this value and eq 7, 8, and 13, one can calculate R_C and the distribution to be expected in the ^{14}C experiment under the same conditions: C-5, C-6, 17.0%; C-2, C-3, 41.5%; C-1, C-4, 20.8%; and C-7, 20.8%). This is in quite good agreement with the experimental values of 15, 40, 23, and 22%. Conversely, one can calculate R_T from eq 10 and the ^{14}C data, using the value 3.67 for k_{sOH}/k_H obtained from eq 13. This leads to a calculated distribution of 17.6% of tritium at C-5, C-6, which is to be compared with the experimental value[20b] of 20.5%. Although the ratio k_{sOH}/k_H determined from the tritium data is about 20% lower than the ^{14}C value, the distributions calculated in the cross-checks are rather insensitive to the discrepancy. The alternative assumption (eq 12) of a large isotope effect in the tritium experiments leads to k_{sOH}/k_H = 2.7.

The Temperature Effect on the Competition Ratio. An Estimate of the Minimum Activation Energy for the Capture of Norbornyl Cation. From the k_{sOH}/k_H ratios of 2.88 at 45° and 1.76 at 25°, derived from the tritium-labeling data[20b] and eq 11, one can calculate the Arrhenius activation energy difference between the processes of pseudo-unimolecular capture of norbornyl cation by the medium (solvent and/or lyate ion) and 6,2-hydride shift. Solvent capture has the higher activation energy by 4.65 kcal/mole. The k_{sOH}/k_H ratio at 100° is calculated on this basis to be 8.5. The calculation assumes that the observed temperature effect on the tritium distribution is not the result of a temperature-dependent isotope effect.

To the extent that the tritium data (which cover only a narrow temperature range) may be relied upon, the figure 4.65 kcal/mole represents the first estimate of the minimum value of the activation energy for capture of a norbornyl cation in solution. Since this energy is of extreme importance in present discussions of carbonium ion behavior, its confirmation or revision by further experiment would be valuable.