The Chemistry of Methylnorbornyl Cations. VI. The Stereochemistry of Vicinal Hydride Shift. Evidence for the Nonclassical Structure of 3-Methyl-2-norbornyl Cations[1]

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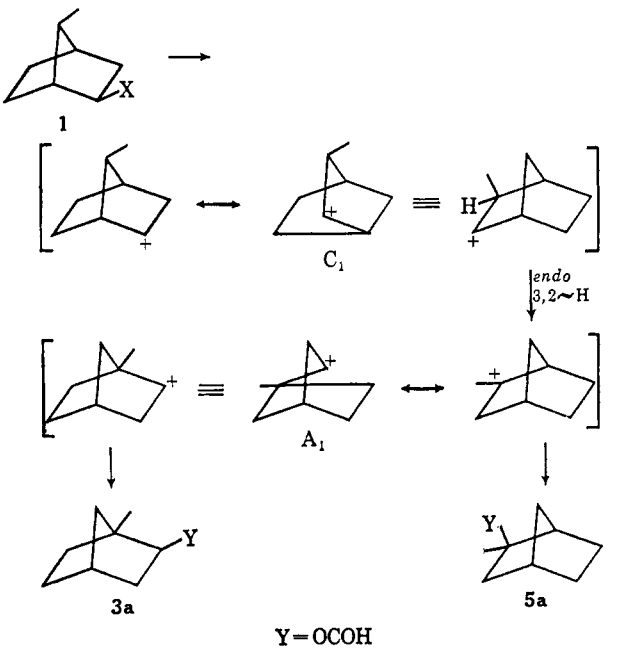
Abstract: The 3-*exo*-methyl-2-norbornyl cation scrupulously avoids rearrangement to the 2-methyl-2-norbornyl cation by *endo*-3,2-hydride shift, despite the large thermodynamic driving force of the reaction. Instead, it takes a more circuitous route involving preliminary 6,2-hydride shift to the 7-*anti*-methyl-2-norbornyl–3-*endo*-methyl-2-norbornyl system, which then suffers *exo*-3,2-hydride shift. The mechanism is elucidated with optically active reactants, since the competing paths lead to enantiomeric forms of 2-methyl-2-norbornyl product. The more circuitous path involving *exo*-3,2 shift is at least 100 times as efficient as the direct one relative to solvent capture and 6,2 shift. Comparison with the results in the 3-*endo*-methyl series shows that the preference for *exo*-3,2 shift inheres in a faster rate for this process rather than in extraneous factors proposed for other systems. Pinacolic rearrangement of 3-*endo*-methyl-2,3-*exo*-norbornanediol gives exclusively 3-*endo*-methyl-2-norbornanone. A number of other examples of vicinal shifts reported in the literature are examined, and the possibility of an alternative mechanism for the longifolene–isolongifolene rearrangement is pointed out. The extension of simple quantum mechanical arguments from primitive three-center displacements to four- and five-center openings of mesomeric bridges is discussed. The experimental findings are fully in accord with a nonclassical structure for 3-methyl-2-norbornyl cation.

One of the characteristic features of norbornyl cation chemistry is the highly stereospecific capture of external nucleophiles from the *exo* direction, even when *endo* attack is sterically about as favorable or more so. This behavior was[4] and still is[5,6] one of the major reasons for assigning nonclassical structures to the product-forming intermediates in such systems. A reasonable corollary of the nonclassical cation hypothesis suggests that *internal* nucleophiles, such as the migrating vicinal groups in Nametkin rearrangements, might also show a large *exo* preference.[5,7-9] The present paper reports a test that confirms this idea.

The formolysis of *syn*-7-methyl-2-*exo*-norbornyl acid phthalate (**1**) had been reported[10] to give 5-*exo*-methyl-2-*exo*- (**2**) and 1-methyl-2-*exo*- (**3**) norbornyl formates. The latter product was of particular interest, since the mechanism proposed[10] for its formation (Scheme I)

Scheme I



(1) (a) Support of part 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. (b) Presented in part at the Anniversary Meeting of the Chemical Society, Birmingham, England, April 1964, Abstracts, p 19; *Proc. Chem. Soc.*, 204 (1964). (c) A preliminary version appeared: J. A. Berson, J. H. Hammons, A. W. McRowe, R. G. Bergman, A. Remanick, and D. Houston, *J. Am. Chem. Soc.*, **87**, 3248 (1965).

(2) (a) To whom inquiries should be directed; (b) University of Wisconsin; (c) University of Southern California.

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

(4) T. P. Nevell, E. de Salas, and C. L. Wilson, *J. Chem. Soc.*, 1188 (1939).

(5) (a) J. A. Berson in "Molecular Rearrangements," Part 3, Vol. I, P. de Mayo Ed., Interscience Publishers, Inc., New York, N. Y., 1963. (b) B. Capon, M. J. Perkins, and C. W. Rees in "Organic Reaction Mechanisms, 1965," Interscience Publishers, Inc., London, 1966, p 14, ascribe to one of us[5a] the view that in reactions of norbornyl derivatives, "kinetics alone give no information on the structure of the cationic intermediate" and conclude that adoption of this view necessitates abandonment of the *exo*:*endo* product ratio as a criterion also. However, the quoted passage[5c] is irrelevant, since it refers to an outline of the complex kinetic problems of hydrogen chloride catalysis of the camphene hydrochloride–isobornyl chloride rearrangement, not to the question of *exo*:*endo* solvolysis rate comparisons. Our position on the connection between solvolysis rate and cation structure is expressed in the introduction to an extensive discussion of the matter: "Mesomerism stabilizes a bridged cationic intermediate relative to the corresponding "classical" carbonium ion...the transition state...benefits energetically from similar mesomerism; it is therefore expected that a solvolysis in which bridging and heterolysis occur simultaneously will be accelerated relative to some standard solvolysis lacking such a feature."[5d] (c) Reference 5a, p 118. (d) Reference 5a, p 175.

(6) R. Howe, E. C. Friedrich, and S. Winstein, *J. Am. Chem. Soc.*, **87**, 379 (1965).

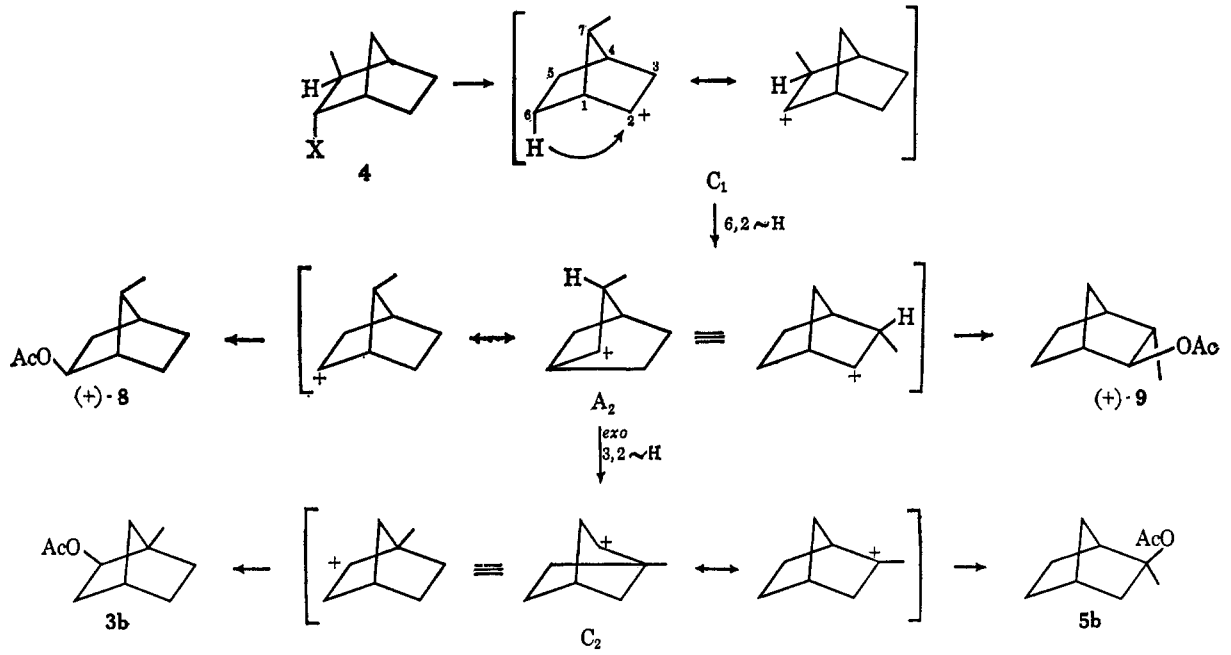
(7) J. D. Roberts and J. A. Yancey, *ibid.*, **75**, 3165 (1953).

(8) P. D. Bartlett, E. R. Webster, C. E. Dills, and H. G. Richey, *Ann.*, **623**, 217 (1959).

(9) D. C. Kleinfelter and P. von R. Schleyer, *J. Am. Chem. Soc.*, **83**, 2329 (1961).

(10) S. Beckmann and G. Eder, *Chem. Ber.*, **91**, 2878 (1958).

Scheme II

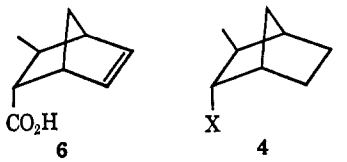


involved an *endo*-vicinal hydride shift in the cationic intermediate C_1,[11] which violates the stereoelectronically anticipated[5,7-9] prohibition. An alternative but more complex mechanism (Scheme II) employing only *exo*-vicinal shifts is possible in principle, however.[5] This involves a preliminary 6,2-hydride shift converting cation C_1 to cation A_2, followed by an *exo*-vicinal 3,2-hydride shift to produce cation C_2, which is enantiomeric with A_1. The mechanisms are clearly distinguishable in the optically active series once the relative configurations of the starting material and product are established.

For a number of reasons, it is preferable to modify the raw form of the problem, first by entrance to the carbonium ion scheme (see paper I[12]) at C_1 *via* a 3-*exo*-methyl (**4**) rather than a 7-*syn*-methyl (**1**) precursor, and second by capture of the rearranged tertiary–secondary cation (A_1 or C_2) as tertiary product (**5a** or **5b**) rather than secondary (**3a** or **3b**). The first change is dictated by expediency, synthetic routes to optically active **1** and configurational correlation with **3** or **5** being unattractive and/or difficult. The second is a response to bitter experience. Secondary product, the 1-methyl-2-*exo*-norbornyl ester (**3**), is formed in appreciable amounts from either **1** or **4** only under conditions of reversible carbonium ion formation, that is, when the acid that accumulates during formolysis or acetolysis is not consumed by an added buffer. Under these conditions, there is danger of racemization by 6,2-hydride shift and/or reversible formation of 1-methylnortricyclene,[13] and in fact, attempted acetolysis of **4** in the absence of sodium acetate leads to completely racemic **3**. In the presence of sodium acetate as buffer, optical activity is preserved, but the kinetically controlled product mixture contains only 2.3% of the desired tertiary ester **5a** or **5b**. Despite the experimentally uninviting prospect of dealing with such a small amount of material, it was nevertheless clear that this product was of theoretical significance and did not represent a minor side path, since its Wagner–Meerwein relative **3** is a major product under reversible conditions. The low yield of **5a** or **5b** under kinetically controlled conditions results merely from irreversible capture of the bulk of the material at earlier points in the complex mechanism of the rearrangement. Since control experiments show that tertiary product **5a** or **5b** is not formed from the other acetates under the solvolysis conditions, this material represents carbonium ions that elude such capture.

Stereochemical Correlations. A distinction between the mechanisms involving *endo*-[10] and *exo*-hydride[5] shifts thus rests upon the configurational correlation of 3-*exo*-methyl-2-*endo*-norbornyl starting material (**4**) and 2-*endo*-methyl-2-*exo*-norbornyl product (**5a** or **5b**).

(+)-3-*exo*-Methyl-2-*endo*-norborneol (**4**, X = OH) is prepared *via* the "acid → acetate" sequence from (+)-3-*exo*-methyl-2-*endo*-norbornanecarboxylic acid[14] (**4**, X = CO_2H), the acid chloride (**4**, X = COCl), and the methyl ketone (**4**, X = $COCH_3$), Bayer–Villiger oxidation of the latter to the acetate (**4**, X = OAc), and lithium aluminum hydride cleavage. The active acid (**4**, X = CO_2H) is derived by hydrogenation of the unsaturated acid **6**,[14] which is readily optically activated by fractional crystallization of the quinidine salt.



To minimize the accumulation of errors that inevitably accompanies a rotational correlation using two different relay compounds, it is desirable to correlate starting alcohol **4** (X = OH) with camphenilone (**7**), the same

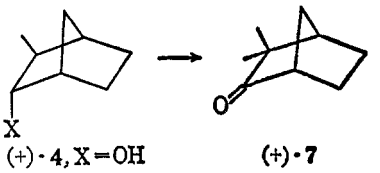
(11) The nomenclature of the cationic intermediates is that given in paper I[12] and retained throughout this series.

(12) J. A. Berson, J. H. Hammons, A. W. McRowe, R. G. Bergman, A. Remanick, and D. Houston, *J. Am. Chem. Soc.*, **89**, 2561 (1967).

(13) J. A. Berson, J. S. Walia, A. Remanick, S. Suzuki, P. Reynolds-Warnhoff, and D. Willner, *ibid.*, **83**, 3986 (1961).

(14) The racemic substance is reported by G. Komppa and S. Beckmann, *Ann.*, **523**, 68 (1936).

substance that had already served[15] as reference in the correlation of product alcohol **5a** or **5b**. This is accomplished by oxidation and methylation of (+)-**4** (X = OH), $[\alpha]_D$ +14.4° (carbon tetrachloride), to (+)-**7**, $[\alpha]_D$ +33.4° (benzene).



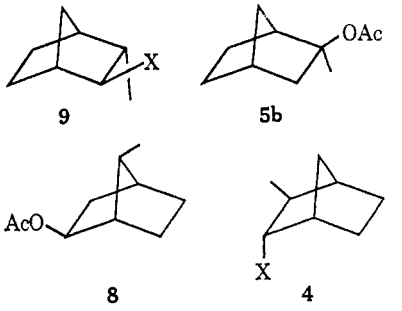
(+)-4, X=OH (+)-7

Acetolysis of Optically Active 3-*exo*-Methyl-2-*endo*-norbornyl *p*-Bromobenzenesulfonate (4, X = OBs). From the product mixture formed by sodium acetate buffered acetolysis of **4**, X = OBs, prepared from (+)-**4**, X = OH, $[\alpha]_D$ +19.9° (carbon tetrachloride), 62.4% optically pure, one can isolate by vapor chromatography (+)-3-*endo*-methyl-2-*exo*-norbornyl acetate (**9**), $[\alpha]_D$ +5.29° (absolute ethanol), and (+)-7-*anti*-methyl-2-*exo*-norbornyl acetate (**8**), $[\alpha]_D$ +9.18° (95% ethanol). Since **9** of $[\alpha]_D$ −1.85° has the same optical purity as **7** of $[\alpha]_D$ +16.5°,[15] whereas the starting alcohol **4**, X = OH, corresponds to **7** of $[\alpha]_D$ (19.9/14.4) × 33.4 = 46.1°, the rotation calculated for **9** isolated from the solvolysis with complete retention of optical purity is (46.1/16.5) × 1.85° = 5.18°. The observed value of 5.29° thus corresponds to 102% retention. Similarly, **8** has[15b] 1.72 times the rotation of **9** of equal optical purity in the indicated solvents. The calculated value of 1.72 × 5.18° = 8.91° is matched by the observed value 9.18°, corresponding to 103% retention. The configurations are as shown[15a,b] and are those expected for a Wagner–Meerwein related pair of products derived from cation A_2 which is in turn formed by 6,2-hydride shift in cation C_1 (Scheme II). The complete preservation of optical purity in these products generated from entry *via* cation C_1 in the present work and *via* cation A_2 in the previous work[15c] shows that vicinal (3,2) secondary–secondary shift of hydrogen or methyl, whether *endo* or *exo*, is very slow relative to 6,2 shift and solvent capture. This is a desirable feature of the experimental system. It eliminates one conceivable source of racemization which, if it had occurred, could have complicated the issue, since it would have been superimposed upon any racemization caused by competition between Schemes I and II.

The optical purity of **8** and **9** (X = OAc) also excludes the possibility of another formally conceivable (although *a priori* unlikely) racemizing mechanism involving 5,2-hydride shift. In cation C_1, this would produce either the 6-methyl-2-norbornyl cation (products from which are not observed[15a,b]) or the enantiomer of A_2. Hence if 5,2 shift were slower than 6,2 shift, the competition would cause some racemization in products **8** and **9**; if the relative rates were in the opposite order, the configurations of **8** and **9** would be enantiomeric with those observed.

The tertiary product 2-*endo*-methyl-2-*exo*-norbornyl acetate is very difficult to isolate from the product mixture. It is present in small amounts and emerges in the early fraction from vapor chromatographic columns with a retention time very close to those of 1-methyl-2-*exo*-norbornyl acetate and 2-*exo*-methyl-2-*endo*-norbornyl acetate, which also are present. The rotation of this three-component mixture, which is readily separable from all the other products by vpc, shows that the 2-*endo*-methyl-2-*exo*-norbornyl acetate in it is (+) (see Experimental Section) and hence that it has configuration **5b**, consistent with its formation at least predominantly by Scheme II. Unfortunately, acetate **5b** is not completely stable on the vpc columns (tricyanoethoxypropane stationary phase) most efficient for its separation from the remaining two contaminants unless extreme care is taken to deacidify the column and injector surfaces by injection of ammonia between passes. With considerable labor, (+)-2-*endo*-methyl-2-*exo*-norbornyl acetate (**5b**) can be obtained free of the other two persistently adhering isomers but now contaminated with decomposition products from the column stationary phase. The rotation of this material is $[\alpha]_{365}$ +6.18° (chloroform), which confirms the configuration as **5b** and represents 75% retention of optical purity.[15a,b] This is a minimum value because of the presence of inert diluents, but still demonstrates that the more circuitous mechanism of Scheme II, involving only *exo*-3,2-hydride shift, accounts for at least 87.5% of the tertiary product acetate.

That this estimate is actually much too conservative is indicated by a comparison of the product ratios from the acetolysis of 3-*exo*-methyl-2-*endo*-norbornyl substrate (**4**, X = OBs) with those from the 3-*endo*-methyl-2-*exo*-norbornyl series **9** (X = OBs).[15] In the latter



9 5b

8 4

case, the ratios of tertiary product 2-*endo*-methyl-2-*exo*-norbornyl acetate (**5b**) to secondary products **9** (X = OAc) and **8** are 0.242 and 0.229.[16] These ratios represent the partition of cation A_2 between solvent capture and *exo* tertiary–secondary 3,2-hydride shift to give cation C_2. Scheme II postulates that all of the tertiary product **5b** from 3-*exo*-methyl substrate **4** (X = OBs) arises from C_2 which is derived solely from the same cation, A_2. If this is correct, the corresponding product ratios from **4** (X = OBs) should be identical with those from **9** (X = OBs). Any tertiary product **5a** formed by direct *endo*-3,2-hydride shift in the alternative mechanism (Scheme I) would make the product ratios **5**:**9** and **5**:**8** from **4** (X = OBs) higher than those from **9** (X = OBs). In fact, since tertiary cation C_2 (or its enantiomeric A_1) gives essentially all tertiary product under the acetolysis conditions,[16] the excess of tertiary product from **4** (X = OBs) over that predicted by the **5b**:**9** and **5b**:**8** product ratios from **9** (X = OBs)

(15) (a) Paper V: J. A. Berson, R. G. Bergman, J. H. Hammons, and A. W. McRowe, *J. Am. Chem. Soc.*, **89**, 2581 (1967); (b) paper III: J. A. Berson and R. G. Bergman, *ibid.*, **89**, 2569 (1967); (c) actual experiment[15a] in the enantiomeric series.

(16) Paper IV: J. A. Berson, A. W. McRowe, and R. G. Bergman, *J. Am. Chem. Soc.*, **89**, 2573 (1967).

is a direct measure of the incursion of any extra path, such as the *endo*-shift mechanism of Scheme I, by which tertiary product might be formed.

Experimentally, these ratios can be determined to about ±1% accuracy by direct capillary vapor chromatographic comparisons of peak areas.[16] The determination is much more accurate than that involved in estimation of the yield of a minor constituent of a multicomponent mixture, where summations of experimental errors become important. In the calculation of "tertiary product" from **4** (X = OBs), the 1-methyl-2-*exo* (**3b**) and 2-*exo*-methyl-2-*endo* (**10**) acetate products are combined with **5b** since control experiments show that they are artefacts derived from it by prolonged exposure to the solvolysis conditions.[16] In the case of the much

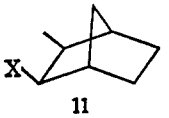
3b **10**

more reactive substrate **9** (X = OBs), **3b** and **10** are not found since complete solvolysis is achieved in a shorter time.[15]

The ratios of "tertiary product" to **9** and **8** from **4** (X = OBs) are 0.247 and 0.233, which are in both cases identical within experimental error with those found from **9** (X = OBs).[16] Thus, a maximum of 2% of the "tertiary product" can have been formed by the *endo*-shift path of Scheme I.

A more revealing estimate of the stringency of the interdiction against *endo*-3,2 shift is given by comparison of the relative importance of *exo*-3,2 shift in A_2 (Scheme II) with the relative importance of *endo*-3,2 shift in C_1 (Scheme I). Cation A_2 gives rise to 7% yield of tertiary product **5b**, of which 100% comes from *exo*-3,2-hydride shift.[15] Cation C_1 gives rise to 3.4% yield of "tertiary product" (**5b** + **3b** + **10**[16]) of which at most 2% comes from *endo*-3,2-hydride shift. Thus, relative to the competing processes 6,2-hydride shift and solvent capture, *exo*-3,2-hydride shift in A_2 is at least 100 times as efficient as is *endo*-3,2 shift in C_1.

Demonstration that *exo*-Vicinal Hydride Shift is Much Faster than *endo* ($k_7 \gg k_5$). In interpreting the high selectivity implied by these observations *on two separate molecules*, one must establish that they are attributable to an intrinsically greater rate of *exo*-hydride migration in cation A_2 than of *endo*-hydride migration in cation C_1 and not to some extraneous cause irrelevant to the test at issue. The misleading effects of failure to do this can be illustrated with the help of Scheme III, which shows the "core" cycle[12] of cations C_1, A_2, and B_3 interconnected by 6,2-hydride shifts. Entry or exit is effected *via* any of the cations from the structurally related substances: C_1 is connected with **4** (X = OBs) and with **1** and **11** (X = OAc), A_2 with **9** (X = OBs) and with **9** and **8** (X = OAc), and B_3 with **12** and **13** (X = OBs or OAc).[16] Schemes I and II,



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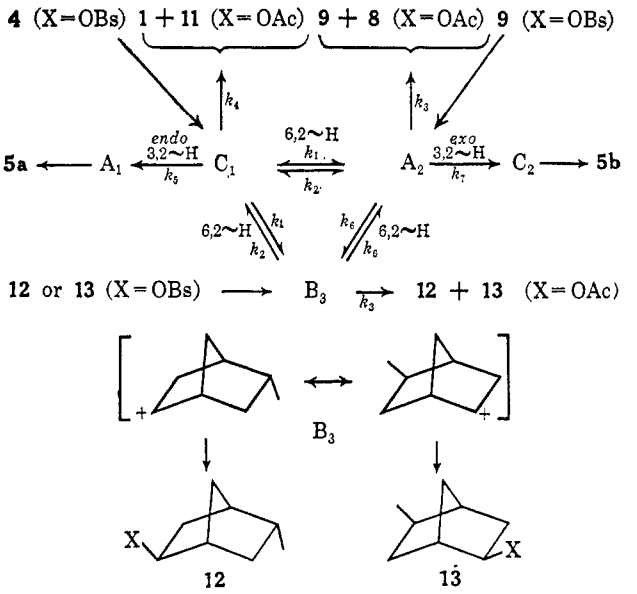
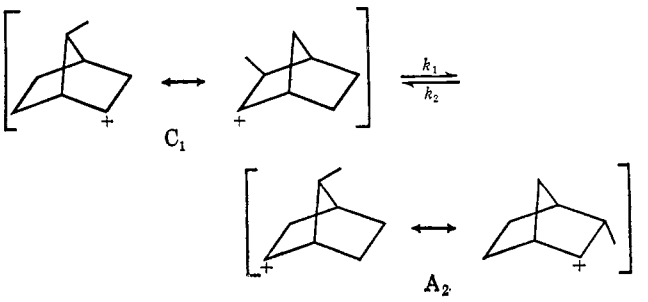
which involve cations C_1 and A_2, respectively, are excerpts from Scheme III. Escape from the "core" cycle

Scheme III



to the "periphery" ($A_2 \rightarrow C_2$) has been shown to be essentially irreversible.[16]

The experiments of the present and preceding[15] paper demonstrate that the ratio of product **5b** derived from the sequence of cations $A_2 \rightarrow C_2$ by *exo*-hydride shift to product **5a** from the sequence $C_1 \rightarrow A_1$ by *endo*-hydride shift is always high, regardless of the point of entry into the scheme. Although this result is consistent with the interpretation that the rate of *exo* shift is intrinsically much greater than that of *endo* shift ($k_7 >> k_5$), in itself it does not require it. An alternative explanation would permit $k_7 \cong k_5$ but would attribute the predominance of *exo*-hydride shift to an entirely unrelated cause, namely a large discrepancy in stability between the "core" cations C_1 and A_2. If A_2 were in fact much more stable than C_1 ($k_1 >> k_2$), the "core" cycle would have a built-in mechanistic gradient, so that points entering the energy surface at A_2 would have difficulty climbing to C_1 at a rate competitive with exit to product, and points entering at C_1 might slide down to A_2 fast enough to preclude appreciable competition from *endo* shift. Furthermore, it would not be difficult to construct a physically reasonable case for the idea that cation A_2 is more stable than cation C_1. For example, one might argue that the two sites of positive charge in the latter are shielded by the methyl group and hence perhaps the solvation energy is less. In fact, a similar argument has been invoked[17] to account for certain behavior of 2-aryl-3-hydroxynorbornyl cations. We shall return to a discussion of these



(17) D. C. Kleinfelter and T. E. Dye, *J. Am. Chem. Soc.*, 88, 3174 (1966).

cases but point out here that in principle the argument does not depend upon the assumption[17] that 6,2-hydride shift is very fast relative to 3,2 shift (which clearly is not the case in our system[16]) but merely requires $k_1 >> k_2$.

It can be shown that the requirements of the alternative explanation ($k_1 >> k_2$ and $k_7 \cong k_5$) cannot be fitted to the rest of the product distribution in the present case and hence that the alternative is excluded. In particular, it is intuitively obvious by inspection that if A_2 and B_3 do not differ appreciably in energy (as seems reasonable), $k_1 >> k_2$ requires that entry at A_2 preclude the formation of any appreciable amounts of products 3-*exo*-methyl-2-norbornyl acetate (**11**, X = OAc) and 7-*syn*-methyl-2-*exo*-norbornyl acetate (**1**, X = OAc), derived from C_1. This can be shown analytically by a steady-state treatment of the cations of Scheme III, from which the product ratio **5b**:**5a** from 3-*exo*-methyl-2-*endo*-norbornyl starting material (**4**, X = OBs) is given by eq 1.

$$(\mathbf{5b}:\mathbf{5a})_4 = \frac{k_7}{k_5}\left[\frac{k_1(2k_6 + k_2 + k_3)}{(k_2 + k_3)(2k_6 + k_2 + k_3) + k_7(k_6 + k_2 + k_3)}\right] \quad (1)$$

Since this ratio is experimentally at least 50, it follows from eq 1 that if the vicinal shift ratio $k_7:k_5$ is about unity, k_1 must be at least $50k_2$.

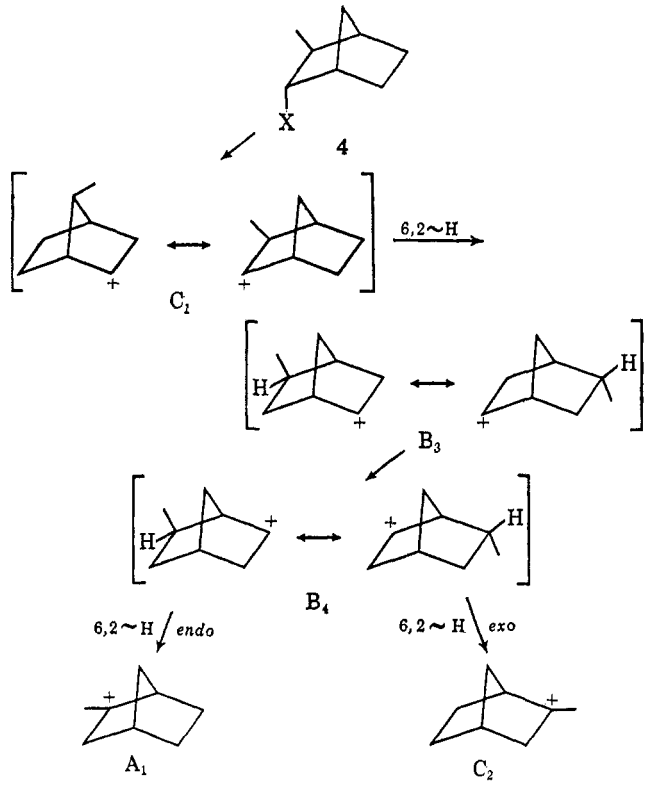
Equation 2 expresses the ratio of products **1** and **11** (derived from cation C_1) relative to **12**, **13**, **9**, and **8** (derived from cations B_3 and A_2) when the core cycle is entered at A_2 *via* **9** (X = OBs) starting material. Since

$$[(\mathbf{1} + \mathbf{11})/(\mathbf{8} + \mathbf{9} + \mathbf{12} + \mathbf{13})]_9 = k_2k_4/[2k_1k_3 + k_3(k_4 + k_5)] \quad (2)$$

the rate constants for capture of the hindered cation C_1 at the two Wagner–Meerwein-related sites are in the ratio of about 5:1,[16] it seems quite reasonable to suppose that a factor about half this large favors attack on unhindered cation A_2 relative to that on C_1, *i.e.*, $k_3/k_4 \sim 2.5$. Experimental support for this assumption is given by the detailed product distributions,[16] which show that capture of C_1 must be considerably slower than capture of A_2. With $k_1/k_2 \geqslant 50$, the maximum permissible value for the product ratio of eq 2 is thus 0.004. That is, *syn*-7-methyl-2-*exo* (**1**) and 3-*exo*-methyl 2-*exo* (**11**) products could not be formed from 3-*endo*-methyl-2-*exo* starting material (**9**, X = OBs) in any amount greater than 0.4% of the total of products **12**, **13**, **8**, and **9** (X = OAc). But the experimentally determined[16] product distribution is 9.2%. Thus, entry into the "core" cycle at cation A_2 produces much more product from cation C_1 than would be permitted if the equilibrium constant favoring A_2 over C_1 (k_1/k_2) were large enough to ensure the observed exclusive *exo*-hydride shift. Of course, as eq 1 shows, $k_1 > k_2$ reinforces $k_7 > k_5$; that is, the thermodynamic bias in question would increase the selectivity. However, even taking this into account, one cannot avoid having $k_7 >> k_5$. Thus, with $k_3/k_4 \sim 2.5$, in order for the term k_7k_1/k_5k_2 to be greater than 50 (see eq 1) the experimental product ratio can be fitted in eq 2 only by values of $k_7/k_5 \geqslant 23$. The heavy predominance of 3,2-*exo*- over 3,2-*endo*-hydride shifted product therefore signifies a large difference in the rates of the two processes themselves.

Elimination of a Hypothetical Alternative. In a purely formal sense, the stereochemical outcome of Scheme II (**4** → C_2 → **5b**) can be duplicated by a hypothetical alternative mechanism (Scheme IV). This involves 3,2-hydride shift in cation B_3 to produce the 6-methyl cation B_4, followed by *exo–exo* hydride shift to give C_2 rather than *endo–endo* shift to give A_1. This path is readily ruled out on the grounds that, first, the required exclusive *exo–exo* 6,2 shift (B_4 → C_2) is highly implausible, since closely related cases of 6,2 shift are exclusively *endo–endo*,[18] and, second, the required 3,2 secondary–secondary shift B_3 → B_4 does not occur under the reaction conditions.[16]

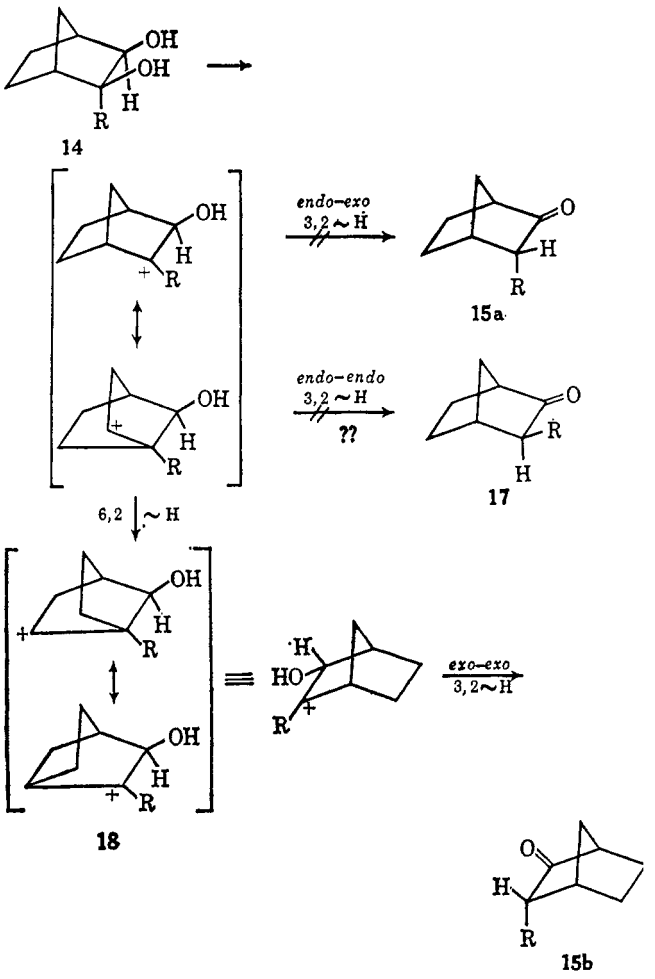
Scheme IV



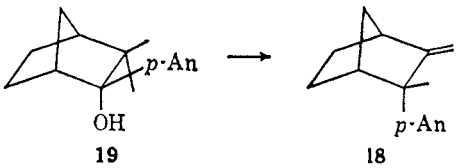
Comparison with Other Systems. An investigation based upon the observed[19] rearrangement of 2-*endo*-phenyl-2,3-*cis*,*exo*-norbornanediol (**14**, R = C_6H_5) to 3-*endo*-phenyl-2-norbornanone (**15a** or **b**, R = C_6H_5) showed[20a] that the reaction in the optically active series did not give **15a**, the product of direct 3,2-hydride shift, but instead proceeded by way of preliminary 6,2-hydride shift (**16** → **18**) followed by *exo–exo* 3,2-hydride shift to give **15b**, enantiomeric with **15a**. The formation of **15b** thus uses a mechanism similar to that by which 3-*exo*-methyl-2-*endo*-norbornyl starting material (**4**, X = OBs) gives 2-*endo*-methyl-2-*exo*-norbornyl product **5b** instead of its enantiomer **5a**. The preference for *exo–exo* 3,2 shift is not quantitatively evaluable from this result since, in the system generated from **14**, the products of the two competing kinds of 3,2-hydride shift *are different substances* (**17** and **15b**), and a measure of the relative importance of the two processes depends on the product composition, **15b**:**17**, not the enantio-

(18) (a) J. A. Berson and P. W. Grubb, *J. Am. Chem. Soc.*, **87**, 4016 (1965); (b) B. M. Benjamin and C. J. Collins, *ibid.*, **88**, 1556 (1966).
(19) D. C. Kleinfelter and P. von R. Schleyer, *ibid.*, **83**, 2329 (1961).
(20) (a) C. J. Collins, Z. K. Cheema, R. G. Werth, and B. M. Benjamin, *ibid.*, **86**, 4913 (1964); (b) C. J. Collins, personal communication.

meric composition, **15a**:**15b**. The **15b**:**17** ratio previously[20a] was implied to be large and now is estimated[20b] as $\geqslant 200$.



It is difficult to evaluate the selectivity that obtains in the related case[17] of 2-*endo*-*p*-anisyl-2,3-*cis*,*exo*-norbornanediol (**14**, R = *p*-$MeOC_6H_4$), where the authors,[17] on the basis of the observation that "the only nonacidic compound isolable was 3-*endo*-*p*-anisylnorbornanone in *ca.* 50% yield," concluded that a large preference for *exo*-3,2 shift existed in their system. Such a preference may well exist but is not demonstrated by the facts disclosed. Similarly, the isolation[8] of olefin **18** from *p*-anisylcamphenilol (**19**) does not of itself indicate a large preference for *exo*-3,2-methyl migration, and in fact was not so interpreted.[8] Brown,[21] in discussing the effect of substitution at the migration terminus on the stereoselectivity of 3,2 shift in norbornyl cation, has referred to the above examples (**14**,



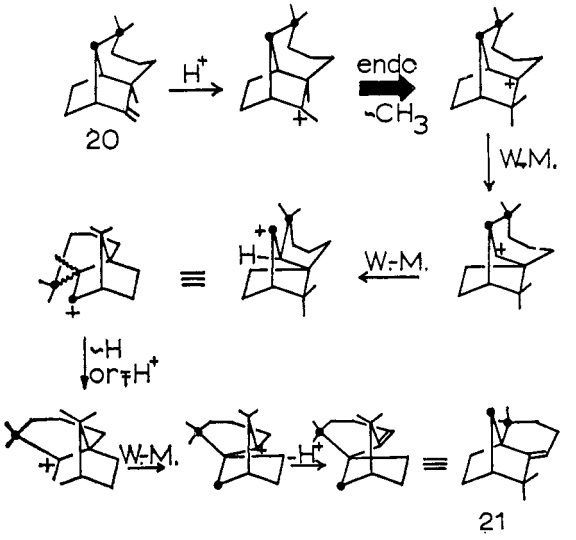
R = C_6H_5, and **19**) as demonstrating highly selective *exo*-3,2 shift and has stated that "the insensitivity of the stereoselectivity to the stability of the cationic center, even with a group as stabilizing as *p*-anisyl, suggests that the steric interpretation is to be preferred" (to the nonclassical interpretation). Regardless of what such invariance might mean if it *were* eventually established (as may well turn out to be the case), it is clear that in the light of the above discussion, an experimental basis for the argument is not yet available.

One must also keep in mind the more general admonition that any evaluation of "invariance" or "insensitivity" is on weak grounds if based upon a set of experimental data all of which show "complete" preference for one path over another. Wide variations in actual sensitivity may hide beneath an apparent "insensitivity" which is attributable to nothing more than a choice of systems that *all* have selectivities so high that they lie at the extreme edge of the available experimental techniques and thus cannot be ranked. Of course, even worse confusion results if one insists that actually observed variations are to be ignored. Thus, the observation[22] that sodium borohydride attacks the 2-*p*-anisylbornyl cation with an *exo*:*endo* preference of 6.5 has been taken[22] to represent "no major change" in selectivity as compared to the attack of acetic acid on norbornyl cation, which shows[23] an *exo*:*endo* preference of 9140.

A large preference for *exo*-3,2-methyl migration *is* demonstrated in the 2,3,3-trimethylnorbornyl,[24a,b] 2,3,3-trimethyl-1-hydroxynorbornyl,[24c] and 2,3-dimethyl-3-β-carboxyethylnorbornyl[24d] cations since in those cases, like the 3-methylnorbornyl case reported here, *enantiomeric composition* is directly translated into product composition, and analysis for structurally isomeric substances is unnecessary. The trimethylnorbornyl cases,[24a-c] which involve *intramolecular* competition between migrating groups, are also free of any ambiguity arising from built-in mechanistic bias caused by a large difference in stability between two different cationic intermediates.

We can now provide an additional example of the two-product type in the case of 3-*endo*-methyl-*cis*,*exo*-2,3-norbornanediol (**14**, R = Me), which rearranges

Scheme V



(21) H. C. Brown, *Chem. Brit.*, **2**, 199 (1966).

(22) H. M. Bell and H. C. Brown, *J. Am. Chem. Soc.*, **86**, 5007 (1964).

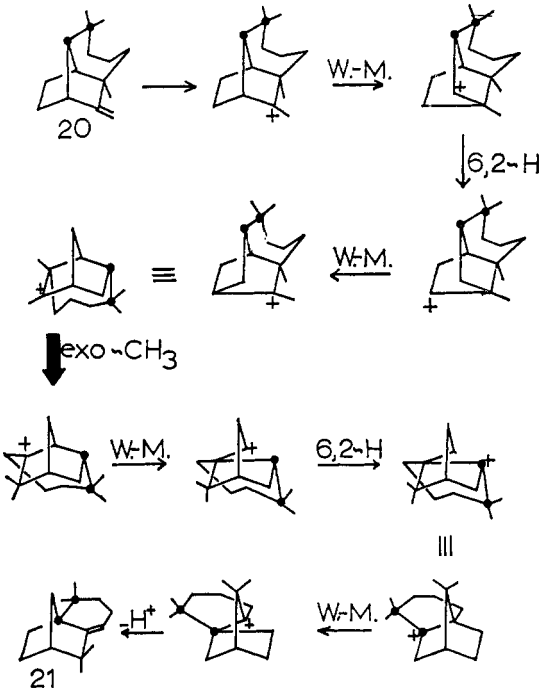
(23) H. L. Goering and C. B. Schewene, *ibid.*, **87**, 3516 (1965).

(24) (a) P. Hirsjärvi, K. Heinonen, and L. Pirilä, *Suomen Kemistilehti*, **B37**, 77 (1964); (b) W. R. Vaughan, C. T. Goetschel, M. H. Goodrow, and C. I. Warren, *J. Am. Chem. Soc.*, **85**, 2282 (1963); (c) A. M. T. Finch, Jr., and W. R. Vaughan, *ibid.*, **87**, 5520 (1965); (d) G. E. Gream and D. Wege, *Tetrahedron*, **22**, 2583 (1966).

in aqueous sulfuric acid to give exclusively 3-*endo*-methyl-2-norbornanone (**15b**, R = Me). This substance is readily separable by capillary vpc from its *exo* epimer (**17**), the presence of which to the extent of 0.03% would have been detectable. Although we have no direct evidence that the rearrangement is intramolecular and involves the route **14** → **16** → **18** → **15b** demonstrated[20] for the phenyl case, adoption of such an assumption means that the *exo–exo* shift path is preferred to the *endo–endo* by a factor of at least 3300.

The acid-catalyzed rearrangement of the sesquiterpene hydrocarbon longifolene (**20**) to isolongifolene (**21**)[25] has been formulated[26] as in Scheme V with an *endo*-3,2-methyl shift (heavy arrow). In the present context, however, it would be plausible to postulate as an at least equally probable alternative the mechanism shown in Scheme VI, which employs a more cir-

Scheme VI

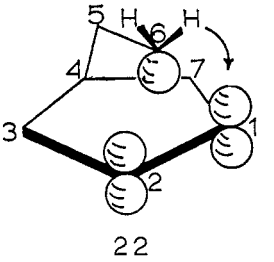


cuitous sequence involving instead an *exo*-3,2-methyl shift (heavy arrow). The two mechanisms are not distinguishable by ordinary methods of configurational correlation since both produce the same enantiomer of the rearranged product **21** from a given enantiomer of the starting material **20**. They differ most directly in the relationship of the two carbon atoms indicated with heavy dots. These remain contiguous in Scheme VI but assume a 1,3 relationship in the product of Scheme V.

Contrasting Stereochemistry of 6,2- and 3,2-Hydride Shifts. The transition state or intermediate for the exclusively *endo–endo* 6,2- (or 6,1-) hydride shift observed in the known examples[18] is readily achieved by a very minor adjustment of atomic positions in the norbornyl nonclassical ion **22**. Thus, a slight movement of a C-6 hydrogen in the indicated direction produces the theoretically favorable[27] edge-protonated cyclopropane species and results in *endo–endo* shift stereochemistry.

(25) J. R. Prahlad, R. Ranganathan, U. R. Nayak, T. S. Santhanakrishnan, and S. Dev, *Tetrahedron Letters*, 417 (1964).
(26) G. Ourisson, *Proc. Chem. Soc.*, 274 (1964).
(27) (a) *Cf.* references cited by A. Colter, E. C. Friedrich, N. J. Holness, and S. Winstein, *J. Am. Chem. Soc.*, **87**, 378 (1965); (b) R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964); (c) see also A. A. Aboderin and R. L. Baird, *J. Am. Chem. Soc.*, **86**, 2300 (1964); (d) C. C. Lee, J. E. Kruger, and E. C. Wong, *ibid.*, **87**, 3985 (1965); (e) C. C. Lee and J. E. Kruger, *ibid.*, **87**, 3986 (1965); (f) G. J. Karabatsos, C. E. Orzech, Jr., and S. Meyerson, *ibid.*, **87**, 4394 (1965).

Brown[22] comments that it is "remarkable" that 6,2 shift is fast enough to compete with solvent capture, since "normally it is considered that the nonclassical structure protects the ion from such attack in the *endo* direction." However, since the ground states of the *intramolecular* 6,2 shift and the *intermolecular* solvent capture are entirely different, a comparison of the rates of the two processes is difficultly interpretable.



22

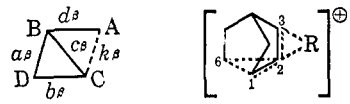
Significance of the Preference for *exo*-3,2 Shift. The present demonstration that *exo*-3,2 shift is highly preferred to *endo* is completely in accord with the behavior expected of a nonclassical ion. Although opening of the mesomeric bridge with inversion by an external or internal nucleophile usually has been rationalized by stereochemical analogy to simpler nucleophilic displacements (SN2), there are also strong quantum mechanical reasons for expecting this behavior. The argument can be given as an adaptation of one already put forward in another connection.[28] The transition state for the substitution reaction in its most primitive form is a three-center problem which can be treated by simple LCAO methods. Regardless of what orbitals are chosen for the basis set, the idealized case will be one with equal bond integrals (β) between the central atom and its two attached groups. For the linear (or approximately linear), inversion-producing relationship of these centers, A–B–C, one can assume a zero A–C integral, which leads to one bonding, one nonbonding, and one antibonding level, as has previously been noted.[29] For the retention-producing orientation, with an acute A–B–C angle, the A–C integral becomes finite ($k\beta$) and the system becomes cyclic. This has the consequences that the energy of the bonding level of the primitive linear case is lowered but that of the nonbonding level is raised (to antibonding) *by a greater amount.* Therefore, the four-electron (nucleophilic) system will prefer the linear geometry, but the two-electron (electrophilic) system will prefer the bent.[30] The assumptions of simple LCAO theory are so severe that one should not be surprised if other factors exert a large enough influence to cause occasional contraventions of the predicted behavior. Nevertheless, the underlying quantum mechanical effects are inescapably present.

An extension of the argument to nucleophilic attack on a nonclassical carbonium ion intermediate would treat the system as a four-electron, four-center case **23**, with nonclassical bonding in the three-membered cycle

(28) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965, p 483.
(29) A. Streitwieser, *Chem. Rev.*, **56**, 571 (1956).
(30) Crudely, the linear system is related to allyl whereas the bent is related to cyclopropenyl.

BDC, and partial bonds A–B and B–C representing the onset of attachment of the nucleophile (A) to one terminus (B) and detachment of the bridging atom (C) from B. The inversion mode would correspond to the linear SN2 case, with no A–C interaction ($k = 0$), but the retention mode would have $k > 0$. Simple LCAO calculations on this four-center problem give results qualitatively similar to those for the three-center case. (The system **23** with $c = 0$ is essentially the same used[28] to discuss the stereochemistry of additions to olefins or eliminations forming them). Over reasonable variations of the parameters *a*, *b*, *c*, and *d* of **23**, the four-electron (nucleophilic) system is always destabilized by inclusion of a front-side interaction ($k > 0$).

Similarly, 3,2 shift in a norbornyl cation may be treated as a five-center, four-electron case **24**. Migration of R on the *endo* side of the cation will correspond to front-side opening of the C-6–C-1–C-2 mesomeric



23 **24**

bridge and will introduce a C-6–R interaction which will be absent in *exo* migration. Again, simple LCAO calculations show this interaction to have a net destabilizing effect in the four-electron case. On this basis, *exo* migration should be favored, as is found experimentally.[31]

The preference for *exo*-3,2 shift is inexplicable in terms of the windshield-wiper effect, which has been postulated[32] to account for *exo* capture of norbornyl cations by *external* nucleophiles.[33] This effect is supposed to operate by the rapid back-and-forth motion of C-6 between C-1 and C-2, which produces an abnormally low nucleophile concentration in the *endo* direction.[32] In the case of 3,2 shift, however, the nucleophile, migrating hydride, is intramolecular and its "concentration" cannot be affected by the rapid motion. The present observations therefore require some other explanation.

One could argue[21] that the results are caused by purely steric factors in the classical ion rather than stereoelectronic factors in the nonclassical one. Some such postulate is needed whether the classical ions are the dominant intermediates in solution[21] or only present in small concentration.[31b] However, it is not obvious that *exo* stereochemistry then should be heavily favored. Although the transition state for *endo* migration is thought to place the migrating hydrogen close to the 5,6-ethylene bridge,[21] the transition state for *exo* migration would force the migrating hydrogen to brush past the *syn*-7-hydrogen. These effects presumably would be offset to some unknown extent by diminution of certain ground-state repulsive forces. The interactions relieved would include a 3,5 interaction in the *endo* case (similar to a 1,3-diaxial interaction in boat cyclohexanes) and a 3,4 interaction in the *exo* (similar to a 1,2-diequatorial interaction). At present, a reliable way to estimate the balance of these factors is lacking. It seems to us preferable, therefore, to employ the nonclassical formulation, which predicts the observations.[33g]

(31) (a) Arguments[31b] favoring the nonclassical structure for norbornyl cation based on the slower rate of 3,2 shift compared to vicinal shift in open-chain systems are debatable, since the alignment of either of the C–H bonds at C-3 in a hypothetical classical norbornyl cation may be much less favorable than that accessible in a more or less freely rotating open-chain case. (b) F. R. Jensen and B. H. Beck, *Tetrahedron Letters*, 4287 (1966).

(32) (a) H. C. Brown, "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, pp 140–157, 176–178. (b) *Cf.* H. C. Brown, J. K. Morgan, and F. J. Chloupek, *J. Am. Chem. Soc.*, **87**, 2137 (1965), for this proposal applied to other systems.

(33) For experimental and theoretical objections to the windshield-wiper effect, see: (a) J. A. Berson and P. Reynolds-Warnhoff, *ibid.*, **86**, 595 (1964); J. A. Berson and D. Willner, *ibid.*, **86**, 609 (1964); (b) S. Winstein, *ibid.*, **87**, 381 (1965); (c) M. J. S. Dewar and A. P. Marchand, *Ann. Rev. Phys. Chem.*, **16**, 321 (1965); (d) G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966); (e) G. E. Gream, *Rev. Pure Appl. Chem.*, **16**, 25 (1966); (f) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965, pp 525.

Experimental Section

Optical Activation of 3-*exo*-Methyl-5-norbornene-2-*endo*-carboxylic Acid. Combination of quinidine alkaloid in absolute ethanol with 1.15 molar equiv of the acid and storage of the resulting solution gave a precipitate of the mixed salts. If smaller proportions of acid were used, the free alkaloid tended to crystallize out. Three recrystallizations gave material from which 40% of the original weight of acid could be obtained with $[\alpha]_D$ −129° (95% ethanol). Seven further recrystallizations from methanol gave material of $[\alpha]_D$ −151°. Dextrorotatory acid was obtained from the mother liquors. The resolution was not pressed further.

(−)-Methyl 3-*exo*-Methyl-5-norbornene-2-*endo*-carboxylate. The ester was obtained by treatment of a distilled sample of the corresponding acid with ethereal diazomethane. Distillation gave ester that was homogeneous on column L and had an infrared spectrum identical with that of the racemate. Acid of $[\alpha]_D$ −130.4°, $[\alpha]_{365}$ −434.1°, gave ester of $[\alpha]_D$ −134.2°, $[\alpha]_{365}$ −446.2° (*c* 5.7, 95% ethanol).

Correlation with 3-*exo*-Methyl-2-*endo*-norbornanecarboxylic Acid. The above unsaturated acid, $[\alpha]_D$ −130.4°, was dissolved in methanol and hydrogenated at 40–20 psi with platinum oxide catalyst. Shaking in the Parr apparatus for 5 min was sufficient to complete the reaction. The saturated acid was distilled bulb to bulb at reduced pressure to produce a crystalline mass. The infrared spectrum in carbon disulfide was identical with that of the pure racemic compound. The rotation was obtained from an aliquot taken from a molten, homogeneous product, $[\alpha]^{24}_D$ −40.5°; $[\alpha]^{24}_{365}$ −110° (*c* 10.8, 95% ethanol).

A homogeneous sample of the above acid, $[\alpha]_D$ −40.5°, was quantitatively converted to its methyl ester with ethereal diazomethane. The distilled product, pure on columns L and N, had an infrared spectrum identical with that of the pure racemic compound and $[\alpha]^{23}_D$ −38.2°; $[\alpha]^{23}_{365}$ −103° (*c* 5.9, 95% ethanol).

Optically Active 3-*exo*-Methyl-2-*endo*-acetylnorbornane (4, X = $COCH_3$). Pure 3-*exo*-methyl-2-*endo*-norbornanecarboxylic acid, $[\alpha]^{25}_D$ +31.4° (*c* 4.6, 95% ethanol), was converted to the acid chloride with thionyl chloride and distilled in 93.4% yield. The acid chloride was immediately converted to the methyl ketone *via* the methylcadmium reagent in ether and distilled to give a 91% yield. The product had infrared spectrum and retention times on vpc (columns L and N) identical with those of the racemic com-

(33g) NOTE ADDED IN PROOF. Although both steric and torsional effects have been proposed as alternative explanations for *exo* attack of nucleophiles [by H. C. Brown, *Chem. Eng. News*, **45**, 87 (1967), and by P. von R. Schleyer, *J. Am. Chem. Soc.*, **89**, 701 (1967), respectively], it is questionable whether quantitative estimates of the magnitudes of these effects can be given. For example, both Brown and Schleyer have used them to explain the reported demonstration [A. F. Thomas and B. Willhalm, *Tetrahedron Letters*, 1309 (1965); A. F. Thomas, R. A. Schneider, and J. Meinwald, *J. Am. Chem, Soc.*, **89**, 68 (1967)], by an nmr method, that camphor exchange its 3-*exo*-hydrogen for deuterium much more rapidly than its 3-*endo*-hydrogen. Brown and Schleyer have argued that the preferred *exo* stereochemistry of carbonium ion capture, by analogy, does not demand a nonclassical explanation. However, additional observations on the exchange require quite a different interpretation. Thomas, *et al.*, report, without further comment, mass spectrometric data which show that camphor-3,3-d_2, 97% dideuterated, exchanges with water to give a mixture of 21% d_2, 64% d_1, and 15% d_0 camphor. This composition is incompatible with a large difference in exchange rate for the 3-*exo*- and 3-*endo*-deuteriums. Since steric and torsional effects previously were postulated to be consistent in direction and magnitude with the reported highly stereospecific *exo* exchange, the observed low stereospecificity now necessitates a revision of the basis for quantitative estimation of the proposed effects.

pound, which had been prepared in the same way.[34] Less than 0.5% impurity was detected, $[\alpha]^{24}D$ −10.8°; $[\alpha]^{24}_{365}$ −224° (*c* 4.6 chloroform).

Optically Active 3-*exo*-Methyl-2-*endo*-norbornyl Acetate. Methyl ketone **4**, X = $COCH_3$, $[\alpha]D$ −7.59° (*c* 4.8, chloroform), was treated with a chloroform solution of peroxybenzoic acid with a catalytic amount of boron trifluoride etherate added. After 1 week, the mixture, consisting of 70% acetate **4**, X = OAc, and 30% starting ketone, was worked up and resubjected to the same reagents for another 10 days to give 97% of the desired acetate and 3% unreacted ketone. The acetate was purified by preparative vpc on column C to yield homogeneous product (columns L and N) in a 58% over-all yield from ketone. Retention times on vpc and the infrared spectrum of this material were identical with those of the pure racemic material; $[\alpha]^{24}D$ +19.1° (*c* 6.8, carbon tetrachloride); $[\alpha]^{24.5}D$ +25.6° (*c* 5.4, chloroform).

Optically Active 3-*exo*-Methyl-2-*endo*-norbornanol (4, X = OH). Chemically pure acetate **4**, X = OAc, $[\alpha]D$ + 35.5° (chloroform), was reduced in high yield with lithium aluminum hydride to the alcohol whose infrared spectrum in carbon tetrachloride was identical with that of the racemic material.[34] The material, which was pure by vpc (columns L and N), was solid at 0°, but became partially liquid at room temperature; rotations from a molten, homogeneous sample: $[\alpha]^{24.5}D$ +19.87 ± 0.09° (*c* 4.5–5.3, carbon tetrachloride).

Correlation of 3-*exo*-Methyl-2-*endo*-norbornanol with Camphenilone [(+)−7]. A solution of 85 ml of acetone, reagent grade, and 3.51 g (27.8 mmoles) of alcohol **4**, X = OH, $[\alpha]^{24}D$ +14.4° (*c* 5.0, carbon tetrachloride), was oxidized with a slight excess of Jones reagent. The reaction mixture was diluted with 350 ml of saturated brine and extracted six times with a total of 500 ml of pentane. The combined organic layers were washed twice with saturated brine and dried successively over sodium sulfate and calcium sulfate. The solvent was carefully distilled off through a short Vigreux column and the residue was distilled at 60–61° (10 mm). The yield was 2.38 g (69%) of product consisting of 96% 3-*exo*-methyl-2-norbornanone and 4% the *endo*-methyl isomer.

The above ketone mixture (*ca.* 19 mmoles) was directly taken up in 45 ml of dry tetrahydrofuran and heated with vigorous stirring for 12 hr with approximately 1.0 g of sodium hydride (pearls, not a fine dispersion). The addition of 13 ml (*ca.* 0.2 mole) of distilled methyl iodide was effected over 2 hr, and the stirring and refluxing were continued another 3 hr. On cooling, 50 ml of water was added, and the two resulting layers were extracted six times with a total of 200 ml of pentane. The combined organic layers were dried successively over sodium sulfate and calcium sulfate. The solvent was carefully distilled off, and the residue was distilled at 60° (10 mm) to yield 2.3 g (90%) of a waxy solid. Analysis on capillary column L indicated approximately 5% high-boiling hydrocarbon impurity; the remainder was camphenilone. Purification was achieved by preparative vpc on column C. The pure product (columns L and N) had an infrared spectrum and retention times on capillary vpc identical with those of pure commercial camphenilone (Light, Ltd., London); $[\alpha]^{21}D$ +33.4° (*c* 7.7, benzene).

Optically Active 3-*exo*-Methyl-2-*endo*-norbornyl *p*-Bromobenzenesulfonate (4, X = OBs). To a sample of 18.0 g (0.1428 mole) of alcohol **4**, X = OH, $[\alpha]D$ +19.87° (carbon tetrachloride), dissolved in 100 ml of pure, dried pyridine, was added 36.5 g (0.1428 mole) of *p*-bromobenzenesulfonyl chloride, freshly recrystallized. The solution was allowed to stand at +5° for 4 days and then worked up with 1.5 l. of ether and 150 ml of water and ice. The ethereal solution was washed once with ice-cold 5% hydrochloric acid and thrice with saturated brine. The solution was dried twice over sodium sulfate and concentrated on a rotary evaporator to give a colorless residue containing pyridine. The residue was held under vacuum (0.2 mm) for 54 hr at room temperature. Besides pyridine, approximately 0.6 g of alcohol was recovered from the cold traps. The white, crystalline sulfonate had an infrared spectrum in carbon disulfide identical with that of the authentic material from the racemic series. No hydroxyl absorptions were present. The yield was 46.28 g (94%).

Preparative Solvolysis of Optically Active 3-*exo*-Methyl-2-*endo*-norbornyl *p*-Bromobenzenesulfonate. The above optically active *p*-bromobenzenesulfonate prepared from alcohol, $[\alpha]D$ +19.87° (carbon tetrachloride), was washed into a 1-l. flask with dry acetic acid (650 ml) and 26.0 g (0.317 mole) of anhydrous sodium acetate. Under a reflux condenser and drying tube, the flask was plunged into an oil bath at 100°; the temperature of the stirred solution had risen to 98° within 1 hr. The temperature was maintained at 98–100° for an additional 9.5 hr.

At the end of this time, the reaction mixture was poured into 2.5 l. of water and ice and extracted six times with a total of 2 l. of pentane. The combined organic layers were washed with successive 150-ml portions or water, saturated sodium bicarbonate solution, and twice with saturated brine. The light yellow solution was successively dried over two portions of sodium sulfate and one of calcium sulfate with a little Norit. The clear solution was filtered and carefully fractionated through a Vigreux column. An intense infrared spectrum of a neat sample of the clear yellow residue contained none of absorptions of the arenesulfonate or hydroxyl compounds. The yield of crude product, which contained less that 2% each of solvent and unidentified olefins (column N), was 22.3 g (99%).

The crude acetate mixture was dissolved in 70 ml of ether and reduced with 3.2 g (0.084 mole) of lithium aluminum hydride in 100 ml of ether in a 1-l., three-necked flask equipped with a Dry Ice condenser. The excess reagent and alkoxide salts were decomposed with a freshly prepared saturated solution of anhydrous sodium sulfate. The clear solution was decanted from the granular precipitate and the latter washed with 1 l. of ether. The ethereal solution was dried over sodium sulfate and carefully concentrated to yield a clear colorless residue. The white granular salts were dissolved in ice-cold hydrochloric acid, but yielded no extractable material.

Enough ether and absolute ethanol were added to completely dissolve the total, combined alcohol mixture obtained from concentration of the ether solution. Analysis on capillary column N indicated at least eight alcohols were present, of which the "tertiary alcohol mixture," consisting of 1-methyl-2-*exo*-norbornanol (**3b**), 2-*exo*-methyl-2-*endo*-norbornanol (**10**), and 2-*endo*-methyl-2-*exo*-norbornanol (**5b**), was present as a group eluting well ahead of the bulk of the alcohol mixture. This "tertiary alcohol mixture" consisted of 3.4% of the total alcohols.

The "tertiary alcohol mixture" was separated from the main bulk by preparative vpc (column A) under conditions separately shown in control experiments not to cause any interconversion or racemization of the alcohols of concern. The first eluted material was distilled bulb to bulb at room temperature (0.03 mm) to remove eluted column packing.

Analysis of the "Tertiary Alcohol Mixture." This alcohol mixture was shown to be contaminated with less than 0.3% of the alcohols of longer retention time which, as a group, were present in the same proportions as in the original solvolysis mixture. Of the two major alcohol peaks, 1-methyl-2-*exo*-norbornanol (**3b**) was 13.0 ± 0.7% of the mixture as determined on capillary columns L and N. The standard deviation is given for four trials.

Two aliquots for the determination of the specific rotation of this mixture were carefully taken from the completely molten material to obviate any optical fractionation. The average specific rotations with the standard deviations were $[\alpha]^{25}D$ −4.51 ± 0.005°; $[\alpha]^{25}_{365}$ −13.93 ± 0.016° (*c* 5.5–6.6, chloroform).

The alcohol mixture was recovered from the rotation solutions, acetylated under the usual conditions, and distilled at 0.03 mm. The analysis of this mixture on capillary columns L and N gave the value for the 2-*endo*-methyl-2-*exo*-norbornyl acetate (**15b**) present as 71.3 ± 0.7% over six determinations. A single determination of the specific rotations of the liquid acetate mixture gave $[\alpha]^{24}D$ −0.15°; $[\alpha]^{24}_{365}$ −0.55° (*c* 5.24, chloroform). With the observed rotation of −0.008 and −0.029°, respectively, the sodium D rotation is hardly useful except to confirm the sign; the accuracy of the mercury 365-mμ rotation is only about 10%.

The composition of the mixture may be calculated from the vpc data on both mixtures: 1-methyl-2-*exo*, 13.0 ± 0.7%; 2-*endo*-methyl-2-*exo*, 71.3 ± 0.7%; and 2-*exo*-methyl-2-*endo*, 15.7 ± 1.0%.

The Isolation of 2-*endo*-Methyl-2-*exo*-norbornyl Acetate (5b) from the "Tertiary Acetate Mixture." Under normal conditions the tertiary *exo*-acetate **5b** was found to decompose to elimination products when passed through preparative vpc columns. It was shown, however, that column A could be conditioned with many large injections of anhydrous ammonia gas to pass this acetate through in relatively good yield and to separate it from 1-methyl-2-*exo*-norbornyl acetate (**3b**) and 2-*exo*-methyl-2-*endo*-norbornyl acetate (**10**). In trials, optically active *t-exo* acetate **5b**-OAc was obtained, after bulb-to-bulb distillation, with the same rotation as that injected. It was found necessary to condition the column with more ammonia after each injecton of acetate **5b**.

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

From the acetylated tertiary alcohol mixture obtained from the acetolysis of optically active 3-*exo*-methyl-2-*endo*-norbornyl *p*-bromobenzenesulfonate, 28.5 mg of the 2-*endo*-methyl-2-*exo*-norbornyl acetate (**5b**-OAc) was obtained after distillation at room temperature (0.03 mm). A small amount of white crystalline material was observed in the colorless liquid acetate. The entire distillate was washed into a volumetric flask for the rotation. From the observed rotation of +0.176° at the mercury 365-mμ line, the specific rotation of $[\alpha]^{25.0}_{365}$ +6.18° (*c* 2.85, chloroform) was calculated. This would be equivalent to *t-exo* alcohol **5b**-OH of $[\alpha]_D$ −5.12° (chloroform), or 46.5% optical purity.[15a,b] While this sample was pure by vpc on capillary column L, containing less than 0.5% of both *t-endo* acetate **10** and 1-methyl-2-*exo* acetate **3b**, it undoubtedly was contaminated with a significant amount of some volatile material from the preparative vpc column resulting from continual treatment of the latter with ammonia. This contamination was evident both from the small amount of crystalline material observed in the sample and from the fact that the infared spectrum of the chloroform solution used for the rotation showed diffuse absorption in the 2.5–3.0-μ range which was not present in the infrared spectrum of a chloroform solution of pure *t-exo* acetate **5b**-OAc; the rest of the spectrum was identical with that of pure **5b**-OAc.

Isolation of 3-*endo*-Methyl-2-*exo*-norbornyl Acetate (9, X = OAc) and 7-*anti*-Methyl-2-*exo*-norbornyl Acetate (8). These two substances emerged first and last, respectively, from the vapor phase chromatogram on column E of the secondary acetate fraction. This fraction was obtained by reacetylation of the alcohols remaining after separation of the "tertiary alcohol mixture" fraction from the solvolysis of optically active *p*-bromobenzenesulfonate. Two passes sufficed to give material that in each case was homogeneous (column L). The infrared and nmr spectra and retention times on capillary vpc (columns L and N) were identical with each sample's respective racemic counterpart.

The specific rotations of the 3-*endo*-methyl-2-*exo*-norbornyl acetate (**9**, X = OAc) were $[\alpha]^{24}_D$ +5.29°; $[\alpha]^{24}_{365}$ +8.52° (*c* 5.2, absolute ethanol); and those of the 7-*anti*-methyl-2-*exo*-norbornyl acetate (**8**) were $[\alpha]^{23}_D$ +9.18°; $[\alpha]^{23}_{365}$ +31.47° (*c* 5.6, 95% ethanol).

A sample of unfractionated secondary acetate mixture, free of solvent, had the specific rotation of $[\alpha]^{23}_D$ −2.80° (*c* 4.8, *l* = 4, chloroform).

The Stability of the Acetolysis Products. A stock solution of 5.88 g (30.9 mmoles) of *p*-toluenesulfonic acid monohydrate, 6.00 g (73.2 mmoles) of anhydrous sodium acetate, and 3.33 g (32.6 mmoles) of acetic anhydride in 150 ml of dried acetic acid was prepared to simulate closely the ionic concentrations at the end of the acetolysis of optically active *p*-bromobenzenesulfonate. Pure 1-methyl-2-*exo* acetate (**3b**), $[\alpha]^{23}_D$ +9.20° (*c* 5.2, chloroform), was heated at 100° for 8 hr in the simulated solvolysis solution. The usual work-up gave back pure **3b**, $[\alpha]^{24}_D$ +8.70° (*c* 6.5, chloroform), a 6% loss of optical activity. Reduction of the acetate thus obtained with lithium aluminum hydride gave the corresponding alcohol which contained less than 0.5% tertiary alcohols **5b**-OH or **10**-OH.

Pure *t-endo* acetate **10**-OAc, $[\alpha]^{25}_{365}$ −51° (*c* 4.9, chloroform), was heated for 8.0 hr at 100° in the simulated solvolysis solution. The reaction mixture was worked up as in the acetolysis experiment. The acetate after bulb-to-bulb distillation (0.03 mm) was analyzed on column N and found to contain 7% *t-exo* acetate **5b**-OAc and just a trace of 1-methyl-2-*exo* acetate **3b**. The specific rotation was $[\alpha]^{25}_{365}$ −47° (*c* 5.1, chloroform), a loss of 8.4% of the original optical activity. Since *t-exo* acetate **5b**-OAc of the same relative configuration has the same sign of rotation, albeit only about 10% of the value of **10**-OAc, a small amount of the *t-endo* acetate **10**-OAc might also be racemized.

Similarly, pure *t-exo* acetate **5b**-OAc, $[\alpha]^{25}_D$ −1.67°; $[\alpha]^{25}_{365}$ −5.29° (*c* 4.9, chloroform), was subjected to the simulated solvolysis conditions for 8.25 hr at 100°. The distilled product was analyzed on column L and shown to contain 58.7% starting material **5b**-OAc.

The acetate mixture was reduced with lithium aluminum hydride to alcohols in the usual manner. The alcohol mixture, when analyzed on column L, contained 22.9% 1-methyl-2-*exo* alcohol **3b**-OH. The calculated concentration of the *t-endo* alcohol **10**-OH was therefore 18.4%. The specific rotations of the alcohol mixture were: $[\alpha]^{25}_D$ +1.79°; $[\alpha]^{25}_{365}$ +4.55° (*c* 6.0, chloroform). The unfractionated secondary acetate mixture obtained from the separation of the tertiary alcohols from the acetolysis products was subjected to the simulated solvolysis conditions for 10 hr at 100°. The isolated acetate mixture was unchanged in composition as determined on capillary vpc columns L and N. No tertiary related material was detected (less than 0.1% of the total mixture would be observable). The specific rotation was unchanged from that of the original.

Acetolysis of 3-*exo*-Methyl-2-*endo*-norbornyl *p*-Bromobenzenesulfonate in Acetic Acid-O-D. Acetic acid-O-D was prepared from 99.8% deuterium oxide and slight excess of acetic anhydride by stirring at room temperature for 24 hr and distillation. A sample of 5.74 g (16.6 mmoles) of the pure *p*-bromobenzenesulfonate was added to 80 ml of acetic acid-O-D containing 3.22 g (39.3 mmoles) of sodium acetate. The reaction mixture was stirred at 100° for 10.0 hr and worked up in the usual manner. Analysis of the acetate mixture on capillary column L indicated the presence of 18.4% *t-endo* acetate and 1-methyl-2-*exo* acetate with 81.6% *t-exo* acetate in the "tertiary product mixture." The acetate mixture was reduced to alcohols with lithium aluminum hydride. The concentration of 1-methyl-2-*exo* alcohol **3b**-OH was not determinable at that time because of capillary column degeneration. That some was present was evident from the preparative isolation. The tertiary alcohols were separated from the main solvolysis components on preparative vpc column E. The tertiary alcohol mixture contained 10.05 atom % excess deuterium as determined by the falling drop method, equivalent to 1.4 deuterium atoms per molecule. The components with longer retention time contained less than 0.03 deterium atom per molecule. Deuterium analyses by the falling drop method were performed by Mr. J. Nemeth, Urbana, Ill.

Acetolysis of 3-*exo*-Methyl-2-*endo*-norbornyl-*p*-Bromobenzenesulfonate in the Presence of 2-*exo*-Methyl-2-*exo*-norbornyl Acetate in Acetic Acid-O-D. About 0.14 g (1.1 mmoles) of *t-exo* acetate **5b**-OAc, 0.074 g (0.9 mmole) of sodium acetate, and 0.13 g (0.37 mmole) of *p*-bromobenzenesulfonate were added to 2.0 ml of dry acetic acid-O-D and heated at 100° for 10.0 hr. The usual work-up yielded acetates which were reduced to alcohols with lithium aluminum hydride. The tertiary alcohol mixture was separated from the alcohol mixture of longer retention time on column E and analyzed by the falling drop method. There was 12.70 atom % excess deuterium present, equivalent to 1.78 deuterium atoms per molecule. Since the tertiary products from the solvolysis of the *p*-bromobenzenesulfonate normally amount to only *ca.* 3% of the total mixture, the tertiary alcohols isolated from this particular run would be expected to be contaminated by only 1% of solvolysis product. Thus, deuterium incorporation clearly can occur after the formation of tertiary solvolysis product.

Optically active 2-*exo*-methyl-2-*endo*-norbornanol (10-OH) was prepared by adding an ether solution of norbornanone, $[\alpha]_D$ −7.95° (chloroform), to ethereal methylmagnesium bromide. The ketone was prepared by Jones oxidation[13] of active norbornanol.[35] The product **10**-OH had infrared spectrum and retention times on vpc identical with those of an authentic sample[36] of the racemate. The alcohol had $[\alpha]_D$ −6.45°, $[\alpha]_{365}$ −17.4° (*c* 4.3, chloroform).

Acetylation of the active alcohol with acetic anhydride in pyridine gave a quantitative yield of **10**-OAc with infrared spectrum and retention times on vpc identical with those of the racemate. The sample, which contained 0.05% of **5**-OAc, had $[\alpha]_D$ −12.1°; $[\alpha]_{365}$ −36.8° (*c* 6.0–7.8, chloroform). Lithium aluminum hydride reduction regenerated **10**-OH with undiminished rotation.

Optically Active 2-*endo*-Methyl-2-*exo*-norbornanol (5-OH). Following a procedure worked out in the racemic series,[36] a homogeneous sample of *t-endo* alcohol **10**-OH, $[\alpha]_D$ −12.1° (chloroform), 3.00 g (0.024 mmole), was stirred with 15 ml of concentrated hydrochloric acid for 2 hr at room temperature. The chloride was extracted with pentane and the organic solution washed with saturated brine. The solvent was distilled off in a 100-ml flask. The colorless residue was homogeneous on capillary columns L and N with the exception of a small amount of residual solvent.

The chloride was stirred at 95° with 35 ml of 1 *N* sodium hydroxide for 4 days. The cooled mixture was extracted four times with pentane; the combined organic layers were washed twice with saturated brine and dried over sodium sulfate, and the solvent was distilled off. The clear, colorless residue crystallized immediately on cooling to room temperature and was completely sublimed at 85° (10 mm). The yield was 2.36 g (80%) of material whose rotations were: $[\alpha]^{26}_D$ +2.78°; $[\alpha]^{26}_{365}$ +8.38° (*c* 5.0–5.3, chloroform).

(35) H. C. Brown, N. R. Ayyangar, and G. Zweifel, *J. Am. Chem. Soc.*, **86**, 397 (1964).

(36) N. J. Toivonen, E. Siltanen, and K. Ojala, *Ann. Acad. Sci. Fennicae, Ser. AII*, No. 64 (1955).

Optically Active 2-*endo*-Methyl-2-*exo*-norbornyl Acetate (5-OAc). A homogeneous sample of the *t-exo* alcohol, $[\alpha]_D$ +2.78° (chloroform), was acetylated with excess acetic anhydride and pyridine at 100° for 13 hr in the usual manner and distilled to give a 94% yield of acetate **5**-OAc, whose infrared spectrum and retention times on vpc were identical with those of authentic racemic material. Capillary vpc on columns L and N indicated 0.75% *t-endo* acetate **10**-OAc was present; rotations: $[\alpha]^{25}_D$ −1.01°; $[\alpha]^{25}_{365}$ −3.36° (*c* 5.2–5.4, chloroform). This acetate was reduced with lithium aluminum hydride in the usual manner to give alcohol **5**-OH with the same rotation as that of the starting material. Analysis by capillary vpc on column L indicated the absence of 1-methyl-2-*exo* alcohol **3**-OH where less than 0.05% could have been detected.

Optically Active 1-Methyl-2-*exo*-norbornyl Acetate (3-OAc). Following the method previously reported,[13] 6.08 g of *t-endo* alcohol **10**-OH, $[\alpha]_D$ −6.45° (chloroform), was solvolyzed in acetic acid–sulfuric acid for 1.0 hr at 98°. Under these conditions, a few per cent each of *t-exo* acetate **5**-OAc and *t-endo* acetate **10**-OAc were present in addition to **3**-OAc. Preparative vpc on column D using a Wilkens Autoprep 700A with automatic 60-μl injections converted the *t-exo* acetate **5**-OAc to olefins and cleanly separated the desired product **3**-OAc from the *t-endo* acetate **10**-OAc. Distillation of the purified acetate separated it from the eluted column packing and gave 4.08 g (52%) of material whose infrared spectrum and retention times on vpc were identical with those of authentic racemic material. Capillary vpc on column N indicated a total of less than 0.2% of impurities; rotations: $[\alpha]^{25}_D$ +9.29°; $[\alpha]^{25}_{365}$ +28.0° (*c* 5.2–5.4, chloroform).

Optically Active 1-Methyl-2-*exo*-norbornanol (3-OH). The above acetate, $[\alpha]_D$ +9.29°, 0.722 g (4.29 mmoles), was reduced with 0.16 g of lithium aluminum hydride in the usual manner. Complete sublimation of the crude residue yielded 0.47 g (87%) of colorless, crystalline alcohol **3**-OH. The infrared spectrum and retention times on vpc were identical with those of pure, racemic material prepared in a similar manner; rotation: $[\alpha]^{25}_D$ +0.21°; $[\alpha]^{25}_{365}$ −2.11° (*c* 5.8–5.9, chloroform).

The alcohol recovered from the rotations was converted to the acetate with excess pyridine and acetic anhydride at 100° for 24 hr to give product with a rotation identical with that of the starting material.

2-*endo*-Methyl-2,3-*cis*,*exo*-norbornanediol (14). A sample of 2-methyl-2-norbornene[37] (0.20 g) was dissolved in 25 ml of dry ether. A stirred solution of 0.50 g of osmium tetroxide in 25 ml of ether was cooled to 0°, protected by a drying tube, and the olefin solution was added dropwise from a pressure-equalizing dropping funnel. A black solid precipitated during the addition; afterwards the mixture was allowed to stir overnight at room temperature. The black osmate ester was collected by filtration and added to a reaction flask containing 5.0 g of sodium sulfite, 25 ml of ethanol, and 25 ml of water. After heating at reflux for 1 hr on the steam bath, this mixture was filtered, and the filtrates were concentrated to dryness at the aspirator. The solid residue was extracted nine times with methylene chloride, and the organic extracts were combined and dried over magnesium sulfate. After filtration, the solvent was evaporated at the aspirator, leaving a greenish oil which distilled bulb to bulb to give a waxy solid.

This material exhibited an intense, broad O–H band in the infrared as well as a small C=O band due to an unknown contaminant. The diol was characterized by its nmr, which showed a broad signal at δ 4.1 (2 H) assigned to the hydroxyl protons and a slightly broadened absorption at δ 1.3 (about 4 H). Superimposed on the δ 1.3 absorption was a sharp singlet due to the methyl group, deshielded by the *gem*-hydroxyl function.

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.70; H, 9.82.

Rearrangement of 2-*endo*-Methyl-2,3-*cis*,*exo*-norbornanediol (14). A round-bottomed flask was charged with 4 ml of concentrated sulfuric acid and cooled to −8° in an ice–salt bath. The cold solution was stirred rapidly with a magnetic apparatus, and 0.040 g of the solid diol **14** was added and allowed to stir in the acid for 10 min. After this time the yellow reaction mixture was poured onto cracked ice and extracted three times with pentane. The pentane was washed four times with saturated brine and dried over sodium sulfate. Careful removal of the solvent left about 30 mg of material which showed only one peak on capillary vpc column N-1, identical in retention time with 3-*endo*-methyl-2-norbornanone (**15b**). Control experiments showed that (1) less than 0.03% of the *exo*-methyl epimer could have been detected, and (2) both epimeric ketones were stable under the reaction conditions.

(37) K. Alder and H. J. Ache, *Chem. Ber.*, **95**, 503, 511 (1962).

Studies on the Molecular Geometry of the Norbornyl Cation. I. The Synthesis and Acetolysis of the *exo*- and *endo*-4,5-*exo*-Trimethylene-2-norbornyl *p*-Toluenesulfonates

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Abstract: 4,5-*exo*-Trimethylene-2-norbornene (**10**) has been synthesized from a monosubstituted cyclopentadiene **9** using an intramolecular Diels–Alder reaction, and from this intermediate *exo*- and *endo*-4,5-*exo*-trimethylene-2-norbornyl *p*-toluenesulfonates (**11**, R = Ts, and **16**, R = Ts) have been prepared. These sulfonates undergo acetolysis (25°) at relative rates of 8.6:1. The ratio of rate constants (25°) for acetolysis of the *exo*-sulfonate **11**, R = Ts, and 2-*exo*-norbornyl *p*-toluenesulfonate is 1:85, whereas the corresponding ratio for the *endo*-sulfonate **16**, R = Ts, and 2-*endo*-norbornyl *p*-toluenesulfonate is 1:2.5. The depressed rate for the tricyclic *exo*-sulfonate **11**, R = Ts, relative to 2-*exo*-norbornyl *p*-toluenesulfonate is readily explained in terms of bridging of carbon in the transition state for ionization, but seems to be contrary to expectations based on ionization to a localized (classical) carbonium ion. Thus, the present results favor the *bridged-ion* mechanism for acetolysis of 2-*exo*-norbornyl arenesulfonates.

A large body of data relating to the solvolysis reactions of various bicyclo[2.2.1]heptanes holding leaving groups such as halide or arenesulfonate at C_2 is now available.[1,2] It is clear, especially from extensive investigations of the parent 2-norbornyl series, that these reactions exhibit characteristics which sharply differentiate them from simple aliphatic or monocyclic

(1) For an excellent recent review see G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966).

(2) A collection of reprints of key papers in this field along with an authoritative commentary has been provided by P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965.