Table I. Percentage of D Remaining at C_9 in the 9-Homocubyl System as a Function of the Number of 1,2-C,C Rearrangements[a]

	No. of rearrangements								
	1	2	3	4	5	6	7	8	∞
% D at C_9, stereospecific process	50	37.5	31.3	27.3	24.8	23.1	22.1	21.4	20.0
% D at C_9, nonstereospecific process	50	37.5	31.3	27.0	23.7	21.2	19.3	17.7	11.1

[a] Kindly calculated by Dr. M. Nomura.

ring opening, good first-order kinetics to three half-lives was observed. The infinity titers were within 7% of the calculated values, and, in preparative solvolyses, about 80–90% yields of 9-homocubyl acetate (V, R = Ac) could be obtained. Analytical capillary gas chromatography failed to reveal the presence of isomers, indicating that hydride shift processes probably were not competitive. The preparative formolysis solutions became even darker, and lower (30–40%) yields of formate V (R = OCH) resulted. Isomers again were not detected.

The acetolysis rate constants and derived thermodynamic values were: 100.0°, $(3.38 \pm 0.09) \times 10^{-4}$ sec^{-1}; 125.0°, $(4.75 \pm 0.03) \times 10^{-3}$ sec^{-1}; $\Delta H^{\pm}$ = 31.2 kcal/mole; $\Delta S^{\pm} = -0.4$ eu (100°). The calculated rate constant at 25°, 8.53×10^{-9} sec^{-1}, was some 400 times faster than that expected from the carbonyl frequency of homocubanone (split peak: 1762 and 1713 cm^{-1}, relative absorbancies 9:1, weighted average position 1757 cm^{-1}).[6] Because of the symmetry of the homocubyl system, this enhanced rate suggests that the 9-homocubyl cation may have a bridged structure.

The demonstration of degeneracy in this 9-cation was accomplished by deuterium labeling, the deuterium being introduced by $LiAlD_4$ reduction of homocubanone (IV, mp 72–73°). The nmr spectrum of tosylate-9-*d* V (R = Ts) indicated the essentially complete absence of the C*H*OR signal, and the course of the rearrangements was followed by the appearance and quantitative integration of this signal in the spectra of the solvolysis products. That no deuterium was lost from the molecule as a whole on solvolysis was confirmed by nmr and mass spectroscopy.

Two mechanistic possibilities for deuterium scrambling need consideration. A stereospecific process involving bridged or rapidly equilibrating species would only equilibrate *five* of the *nine* protons, provided appreciable "leakage" did not occur. Such a process would, in effect, allow the "rotation" of a five-membered ring (C_1,C_6–C_9) above a four-membered one (C_2–C_5). The deuterium label could only be scrambled to the five-membered ring but not to the four-membered ring by means of this mechanism. Of course, a nonstereospecific reaction course would not only allow the eventual equilibration of deuterium to all nine positions, but it would also permit the interchange of all adjacent carbon atoms in a manner now made familiar by the behavior of bullvalene.[1] Table I shows that no difference is to be expected between the two mechanisms until the fourth rearrangement stage.

Our actual results are as follows. In buffered acetic acid at 125° for more than 10 half-lives, 36 ± 4% D remained at C_9 after solvolysis of V (R = Ts). This corresponds to two rearrangements (Table I). In unbuffered medium, under otherwise the same conditions, 22.5 ± 2% D remained at C_9, indicating that more than five rearrangements had occurred. In unbuffered formic acid, at reflux, a medium well known to be favorable for maximizing rearrangement possibilities,[7] only 10 ± 2% D remained at C_9, and the remainder was distributed throughout the molecule. This demonstrates that the expected complete degeneracy of the 9-homocubyl cation can be achieved under these conditions.

Acknowledgments. This work was supported at Princeton University by grants from the National Science Foundation and from the Petroleum Research Fund, administered by the American Chemical Society.

(6) C. S. Foote, *J. Am. Chem. Soc.*, 86, 1853 (1964); P. von R. Schleyer, *ibid.*, 86, 1854, 1856 (1964).

(7) See P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965.

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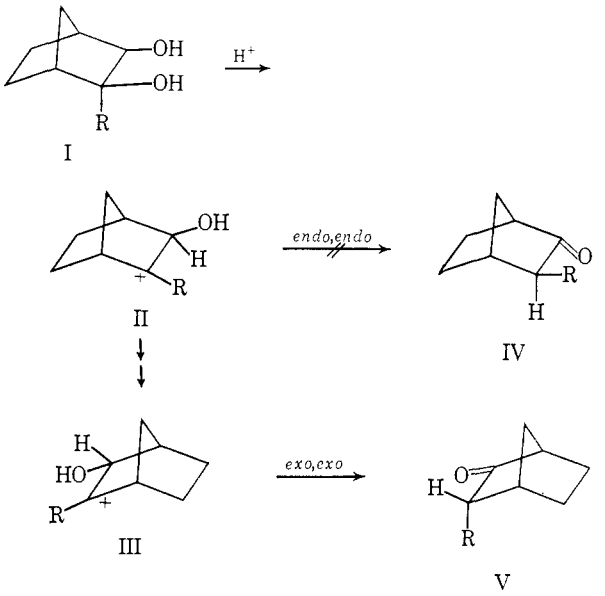
Torsional Effects in Polycyclic Systems. I. The Stereochemistry of 3,2 Shifts in Norbornyl Cations

Sir:

A vexatious problem in norbornane chemistry has been the understanding of the remarkable stereospecificity of the 3,2 shifts.[1-10] These processes involve the migration of a 3-*exo* substituent in preference to a 3-*endo* group to a 2-cation, despite the seemingly similar

(1) P. von R. Schleyer, Ph.D. Thesis, Harvard University, 1956.
(2) J. A. Berson in "Molecular Rearrangements," P. de Mayo, Ed., Part I, Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3.
(3) D. C. Kleinfelter and P. von R. Schleyer, *J. Am. Chem. Soc.*, 83, 2329 (1961).
(4) (a) C. J. Collins, Z. K. Cheema, R. G. Werth, and B. M. Benjamin, *ibid.*, 86, 4913 (1964); (b) B. M. Benjamin and C. J. Collins, *ibid.*, 88, 1556 (1966).
(5) D. C. Kleinfelter and T. E. Dye, *ibid.*, 88, 3174 (1966).
(6) J. A. Berson, J. H. Hammons, A. W. McRowe, R. G. Bergman, A. Remanick, and D. Houston, *ibid.*, in press, papers I–V in the same series, and preliminary communications, especially *ibid.*, 87, 3248 (1965).
(7) W. R. Vaughan, C. T. Goetschel, M. H. Goodrow, and C. L. Warren, *ibid.*, 85, 2282 (1963); A. M. T. Finch, Jr., and W. R. Vaughan, *ibid.*, 87, 5520 (1965).
(8) P. Hirsjärvi, K. Heinonen, and L. Pirilä, *Suomen Kemistilehti*, B37, 77 (1964).
(9) J. D. Roberts and J. A. Yancey, *J. Am. Chem. Soc.*, 75, 3165 (1953); W. R. Vaughan and R. Perry, Jr., *ibid.*, 75, 3168 (1953); see A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 143–144.
(10) P. D. Bartlett, E. R. Webster, C. E. Dills, and H. G. Richey, *Ann.*, 623, 217 (1959).

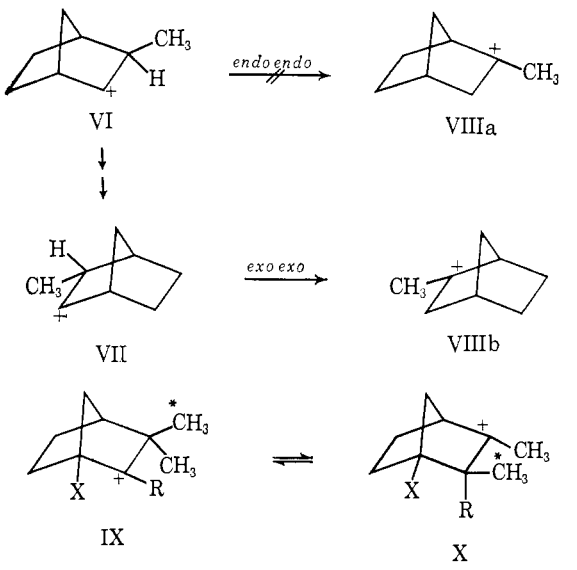
bisected geometrical arrangement along the C_2+–C_3 bond. Illustrative is the pinacol rearrangement of 2-phenylnorbornane-2,3-*cis*,*exo*-diol (I, R = C_6H_5),[3] a reaction whose mechanism has been studied in great detail.[4] Ion II, formed from optically active I in acid, does *not* rearrange by simple 3,2-*endo*,*endo* hydride shift to *exo* ketone IV (R = C_6H_5). Instead of this obvious pathway, a series of Wagner–Meerwein and 6,1-hydride shift steps take place leading to ion III,[4] from which the observed *endo* ketone V (R = C_6H_5) is formed by 3,2-*exo*,*exo* hydride shift. This strange behavior would not appear to be due to thermodynamic causes since V, with an *endo*-phenyl group, has been found[3,4a] to be *less*, not more stable than IV. Also, there seems to be no compelling reason why ion III should be very much more stable than ion II.[5,6] For some reason, 3,2-*exo*,*exo* shifts are much more favorable than the corresponding *endo*,*endo* transformations.[1–10]



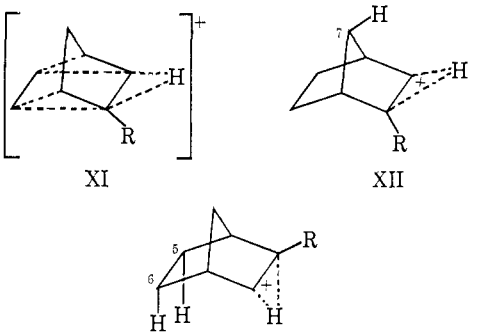
Although reservations can be expressed that the reactions have not been worked out in as much detail,[6] both the *p*-anisyl (I, R = *p*-$CH_3OC_6H_4$)[5] and the methyl (I, R = CH_3)[6] analogs would appear to behave similarly on pinacol rearrangement; only *endo* ketones (V, R = *p*-$CH_3OC_6H_4$ or CH_3) were produced. By gas chromatography 0.03% of the *exo*-methyl ketone IV (R = CH_3) could have been detected, but even so little was not found.[6] In a related example, VI rearranged to VII before the 3,2 shift took place (in the optically active series, the product was VIIIb and not VIIIa).[6] It was estimated that the preference for 3,2-*exo*,*exo* over 3,2-*endo*,*endo* shift was at least 100-fold.[6]

In cations of type IX, direct competition between *exo*,*exo* and *endo*,*endo* 3,2 shifts are possible. In all reported cases, *exo*,*exo* migrations have been found to predominate by large margins.[7–10]

The traditional explanation for this stereospecificity has involved the bridged ion postulate.[1–4,6,8–10] Since a nonclassical norbornyl cation is attacked by external nucleophiles from the *exo* direction, so the argument goes, internal 3,2 rearrangements of the same ion should also favor *exo* migration strongly. Strictly speaking, this means that the extent of charge delocalization in the transition state for *exo*,*exo* 3,2 shifts (as XI)



must be greater than in the *endo*,*endo* transition state (as XIII). If the two transition states were to be best described by XII and XIII, then there would be no apparent electronic reason favoring one over the other. In this case, whether or not the 2-norbornyl cation were bridged would have no relevance to the problem of the 3,2 shifts. Although one may or may not have reservations about postulating species with such extensive charge delocalization as pictured in XI, quantitative organic theory has not yet developed to the point where definitive answers can be given to such matters.



A more serious objection to the bridged ion explanation is the failure of experiment to conform to theoretical expectation. As the substituent R in I is made more and more capable of stabilizing a carbonium ion, the ensuing transition state should become less and less bridged (less like XI and more like XII) and more and more *exo* ketone IV should be produced.[11,12] Yet, even with R = *p*-anisyl, which almost certainly must give a classical ion,[5,13] only *endo* ketone V (R = *p*-$CH_3OC_6H_4$) was found.[5] In fact, most of the cases studied have involved tertiary ions (II, III, IX, X) not expected to have much nonclassical character.[12] Bridging (as in XI) should be even less important in the 3,2-shift transition states involving these ions.

There appear to be grave difficulties with Brown's alternative explanation.[12] The *exo* side of the nor-

(11) J. D. Roberts, quoted in ref 4a.
(12) H. C. Brown, *Chem. Brit.*, 199 (1966).
(13) P. von R. Schleyer, D. C. Kleinfelter, and H. G. Richey, Jr., *J. Am. Chem. Soc.*, **85**, 479 (1963); *cf.*, however, G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966).

bornane molecule is known to be less crowded than the *endo* toward attack by external reagents; therefore, according to Brown,[12] 3,2 shifts should occur preferentially *exo*. Examination of models of the two presumed transition states, XII and XIII, fails to give much support for this steric suggestion. During a 3,2-*exo,exo* shift (XII) the migrating group must pass by the *syn*-7-hydrogen.[6] In the transition state for a 3,2-*endo,endo* shift (XIII) the migrating group is favorably situated *between* the two normally hindering *endo* protons on C_5 and C_6 In addition, when the migrating group is only a small hydrogen atom, the nonbonded distances would appear to be sufficiently large (>2.2 A) so that no crowding should be present. Furthermore, the R group in XIII is *quasi-exo*, which should be favorable, while in XII the R group is *quasi-endo*, a more strained situation. Not only is it not clear which transition state, XII or XIII, should be of lower energy due to nonbonded steric effects, but even more seriously it would not appear possible that the energy differences between XII and XIII could be very large. There appears to be at least a 100-fold preference for *exo,exo* over *endo,endo* 3,2 shifts.[6] One cannot explain such a 3-kcal/mole phenomenon by an effect likely to be of much smaller magnitude.

Torsional effects have been overlooked as a cause of the anomalous behavior often observed in the norbornane series[1,2,12,13] and in other polycyclic systems.[14] The significance of torsional strain to the problem under consideration is easily demonstrated. Molecular models of the presumed 3,2-shift transition states XII and XIII (approximated by the *endo* and *exo* isomers of tricyclo[3.2.1.$0^{2,4}$]octane or of norbornene epoxide) reveal that the arrangements around bonds C_1–C_2 and C_3–C_4 of the *exo* isomer XII are nearly ideally *skewed*. By contrast, in the *endo* conformation XIII the arrangements around the same bonds are almost exactly eclipsed, an energetically unfavorable situation. Since a three-membered ring has little effect in reducing the usual 3-kcal/mole C–C rotation barrier,[15] this means that *endo* transition state XIII (as well as *endo*-bicyclo[3.2.1.$0^{2,4}$]octane and *endo*-norbornene epoxide) should be less stable than the *exo* arrangement XII by up to 6 kcal/mole! This magnitude is more than sufficient to account for the experimentally observed degree of stereospecificity of 3,2 shifts without recourse either to bridging or to nonbonded steric effect arguments. The diverse cations—secondary; methyl-, phenyl-, and anisyl-substituted tertiary—all of which rearrange by stereospecific 3,2-hydride or -methyl shifts, have but one unifying feature: the contrasting torsional arrangements in the isomeric transition states, as XII and XIII. A torsional strain explanation for the stereospecificity of norbornyl 3,2 shifts appears to me to be preferable to both of the alternative current rationalizations.

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(14) Accompanying communication: P. von R. Schleyer, *J. Am. Chem. Soc.*, **89**, 701 (1967).

(15) Propylene oxide, 2.56 kcal/mole: D. R. Herschbach and J. D. Swalen, *J. Chem. Phys.*, **29**, 761 (1958); propylene sulfide, 3.25 kcal mole: W. G. Fateley and F. A. Miller, *Spectrochim. Acta*, **19**, 611 (1963).

Torsional Effects in Polycyclic Systems. II. The Stereochemistry of Attack and Departure in Norbornane Derivatives

Sir:

It has not been possible to understand fully the behavior of norbornane derivatives in terms of ideas presently employed.[1–8] Norbornyl cations have long been regarded as being bridged; the formation of such nonclassical species and their reactions with nucleophiles are believed to occur preferentially *exo*.[1–7] The stereochemistry of reactions not involving bridged transition states is believed to be governed by nonbonded steric effects: the *exo* side of the norbornane molecule is more accessible unless 7,7-dimethyl or similar hindering substituents are present, then the *endo* side is less crowded.[1–8] Although these two basic concepts can account for a large number of reactions involving bicyclo[2.2.1]heptane derivatives, significant exceptions are known, and many of these have been cataloged by Brown.[8] Brown has shown that something is wrong with current theory, but he has not yet supplied a convincing alternative explanation.

I believe that an evaluation of the influence of torsional effects provides a simple solution to many of these problems,[9] and an appreciation of torsional factors will introduce a new dimension of understanding into often complex norbornane chemistry. Such torsional effects should exert an important influence favoring *exo* over *endo* additions and processes involving *exo* bond ruptures. Table I summarizes the predicted

Table I. Favored Transition-State Orientations due to Various Effects

Effect	In norbornane derivatives	In 7,7-dimethyl-norbornane derivatives
Bridged ion	*exo*	*exo*
Steric hindrance	*exo*	*endo*
Torsional strain	*exo*[a]	*exo*[a]

[a] Probably unimportant for processes involving the generation or destruction of exocyclic double bonds. See text.

(1) P. von R. Schleyer, Ph.D. Thesis, Harvard University, 1956.
(2) J. A. Berson in "Molecular Rearrangements," P. de Mayo, Ed., Part I, Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3.
(3) G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966).
(4) G. E. Greame, *Rev. Pure Appl. Chem.*, **16**, 25 (1966).
(5) M. J. S. Dewar and A. P. Marchand, *Ann. Rev. Phys. Chem.*, **16**, 321 (1965).
(6) B. Capon, M. J. Perkins, and C. W. Rees, "Organic Reaction Mechanisms–1965," Interscience Publishers, Inc., New York, N. Y., 1966, Chapter 1.
(7) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965.
(8) H. C. Brown, *Chem. Brit.*, 199 (1966), and references therein summarized.
(9) See accompanying communication: P. von R. Schleyer, *J. Am. Chem. Soc.*, **89**, 699 (1967).