formations containing *an odd number of Grignard displacement steps* (asterisked in Chart I).

The optical stability[11] and rotatory dispersion characteristics[5] of **1** are under investigation.

---

(11) D. R. Rayner, E. G. Miller, P. Bickart, A. J. Gordon, and K. Mislow, *J. Am. Chem. Soc.*, **88**, 3138 (1966).

(12) National Aeronautics and Space Administration Fellow, 1965–1967.

(13) National Aeronautics and Space Administration Fellow, 1964–1966.

(14) Public Health Service Postdoctoral Fellow, 1966–1967.

Paul Bickart,[12] Michael Axelrod,[13] John Jacobus,[14] Kurt Mislow
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

Received December 12, 1966

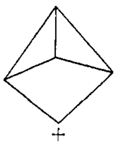
The Degenerate 9-Homocubyl Cation

Sir:

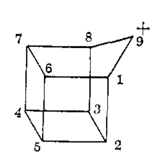
Intriguing rearrangement processes are possible whereby individual atoms and bonds become interchanged, but only lead to products of the same gross structure as that of the starting materials. Such transformations can only be followed by special techniques, as the loss of optical activity, the dispersal of an isotopic label, or the observation of equivalency by nmr. The most interesting of these degenerate rearrangements are those capable of mixing *all* atoms of a given kind completely. Bullvalene is the best known organic molecule of this type: every Cope rearrangement returns to bullvalene and at temperatures somewhat above ambient all H and all C atoms become equivalent on the nmr time scale.[1]

Carbonium ions are particularly prone toward rearrangement, and it is expected that further degenerate examples might be found within this class of species. At room temperature the nmr spectrum of the 2-norbornyl cation shows but a single proton resonance, indicating the time-average equivalence of all 11 hydrogens present.[2] This equivalence is not achieved simply, from a mechanistic viewpoint. Three types of rearrangements are necessary, Wagner–Meerwein, 6,2-(6,1-) hydride shifts, and 3,2-hydride shifts. Each of these lead from one 2-norbornyl cation to another, but all three processes are needed to achieve the observed equivalence.

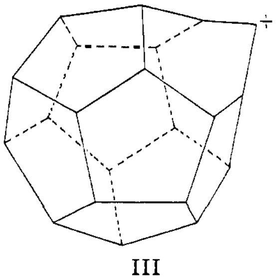
More elegant conceptually is the degeneracy which might be achieved in the homolog ions of regular polyhedra, *e.g.*, the homotetrahedryl cation I,[3] the homocubyl cation II, and the homododecahedryl cation III.[4] In these three systems only one kind of rearrangement process—a simple 1,2-C,C shift—should not only produce eventual equivalence of all H and all C atoms in each of these ions, but should also permit the positional exchange of all C–H units in a manner similar to that of bullvalene.[1] Were each of the C–H units somehow to be uniquely identified, a vast number of different arrangements would be possible in each of the three ions: homotetrahedryl (I) $5!/2 = 60$; homocubyl (II) $9!/2 = 181{,}440$; and homododecahedryl (III) $21!/2 = 2.56 \times 10^{19}$.



I



II

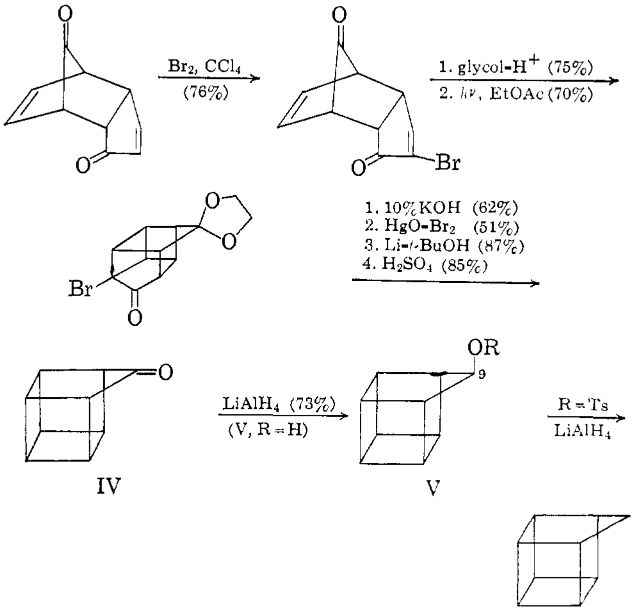


III

We report here the preliminary results of a study of one of these ions, the 9-homocubyl cation (II), which demonstrate that the predicted degeneracy can be achieved under solvolytic conditions.

A number of synthetic approaches to the homocubane (pentacyclo[4.3.0.0^{2,5}.0^{3,8}.0^{4,7}]nonane) ring systen have been described.[5] The desired starting material, 9-homocubyl tosylate (V, R = Ts), mp 73–73.5°, was prepared by a sequence similar to that of Eaton and Cole[5a,c] and summarized in Chart I. The nmr spectra of all compounds were entirely consistent with the structures assigned and with expectation based on previous findings.[5] In particular, 9-homocubanol (V, R = H), mp 157°, and its tosylate, acetate, and formate derivatives all gave similar basic three-peak spectra, integrating for one (C*H*OR; δ = 4–5 ppm), two ($\delta \sim$ 3.5–3.7 ppm), and six protons ($\delta \sim$ 3.2–3.3 ppm).

Chart I



VI[5c, d]

The kinetic acetolysis of V (R = Ts) was carried out in unbuffered media. Despite darkening of the solution at longer reaction times, indicative, perhaps, of

---

(1) W. von E. Doering and W. Roth, *Tetrahedron*, **19**, 715 (1963); J. F. M. Oth, R. Merényi, G. Engel, and G. Schröder, *Tetrahedron Letters*, 3377 (1966); G. Schröder, J. F. M. Oth, and R. Merényi, *Angew. Chem. Intern. Ed. Engl.*, **4**, 752 (1965).

(2) P. von R. Schleyer, W. E. Watts, R. C. Fort, Jr., M. B. Comisarow, and G. A. Olah, *J. Am. Chem. Soc.*, **86**, 5679 (1964); M. Saunders, P. von R. Schleyer, and G. A. Olah, *ibid.*, **86**, 5680 (1964); F. R. Jensen and B. H. Beck, *Tetrahedron Letters*, 4287 (1966).

(3) S. Masamune, K. Fukumoto, Y. Yasunari, and D. Darwish, *ibid.*, 193 (1966).

(4) For an approach to dodecahedrane, see R. B. Woodward, T. Fukunaga, and R. C. Kelly, *J. Am. Chem. Soc.*, **86**, 3162 (1964).

(5) (a) P. E. Eaton and T. W. Cole, Jr., *ibid.*, **86**, 962, 3157 (1964); (b) K. V. Scherer, Jr., R. S. Lunt, III, and G. A. Ungefug, *Tetrahedron Letters*, 1199 (1965); (c) G. L. Dunn, V. J. DiPasquo, and J. R. E. Hoover, *ibid.*, 3737 (1966); (d) W. G. Dauben and D. L. Whalen, *ibid.*, 3743 (1966); (e) C. G. Chin, H. W. Cuts, and S. Masamune, *Chem. Commun.*, 880 (1966).

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}; $\Delta H^{\ddagger} = 31.2$ kcal/mole; $\Delta S^{\ddagger} = -0.4$ 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.

Paul von R. Schleyer, Jon J. Harper
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

George L. Dunn, Vincent J. DiPasquo, J. R. E. Hoover
Research and Development Division
Smith Kline and French Laboratories
Philadelphia, Pennsylvania 19101

Received December 30, 1966

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).