

bilities: (i) either hydride attacks the halogen atom directly to yield the appropriate carbanion which then can capture environmental hydrogen, or (ii) less plausibly, the Lewis acid properties of LiAlH_4 engender the formation of what is tantamount to an incipient carbenium ion which is then attacked as soon as it is formed by hydride in a front-side manner.²⁰

Experiments are under way to decide between these mechanisms. From the synthetic standpoint, it can be predicted that LiAlH_4 will, with the correct choice of solvent, effect reductive dehalogenation of any alkyl halide regardless of functional type.

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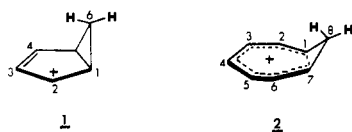
(20) A similar mechanism has been proposed to account for the stereospecific reduction of *gem*-bromofluorocyclopropanes (H. Yamana, T. Yagi, K. Teramura, and T. Ando, *Chem. Commun.*, 380 (1971)).

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Homotropylium-4-d Ion. On the Energy Barrier to a Non-Least-Motion Circumambulatory Rearrangement¹

Sir:

Orbital symmetry allowed² degenerate rearrangements, in which a cyclopropane ring suprafacially circumambulates the periphery of a cyclic polyene³ or polyenylium ion,⁴ should show alternating stereochemical behavior. In the cation series, the migrating group should invert configuration in $1,n$ rearrangements ($n = 4, 8, 12 \dots$) and retain it in $1,m$ rearrangements ($m = 2, 6, 10, 14 \dots$). The $1,n$ rearrangements, which use a "least-motion" pathway with relatively little distortion of normal atomic coordinates, should be stereochemically facile, and a number of examples in the bicyclo[3.1.0]-hex-3-enyl system ($n = 4$),⁴ including the parent ion **1**,^{4f} are known. The "allowed" migration in **1** preserves the original endo and exo nature of the 6-hydrogens at each step and occurs with $\Delta F^\ddagger = 15$ kcal/mol.^{4f}



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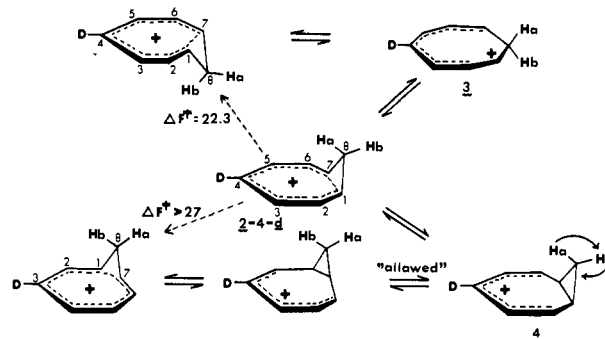
(2) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1969, pp 124-140.

(3) (a) J. A. Berson and M. R. Willcott, III, *J. Amer. Chem. Soc.*, **87**, 2751, 2752 (1965); **88**, 2494 (1966); *Rec. Chem. Progr.*, **27**, 139 (1966); (b) J. A. Berson, P. W. Grubb, R. A. Clark, D. R. Hartter, and M. R. Willcott, III, *J. Amer. Chem. Soc.*, **89**, 4076 (1967); (c) J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968).

(4) (a) R. F. Childs and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 7146 (1968); (b) R. F. Childs, M. Sakai, and S. Winstein, *ibid.*, **90**, 7144 (1968); (c) R. F. Childs and B. Parrington, *Chem. Commun.*, 1540 (1970); (d) V. H. Koptuyug, L. I. Kuzubova, I. S. Isaev, and V. I. Manatyuk, *ibid.*, 389 (1969); (e) D. W. Swatton and H. Hart, *J. Amer. Chem. Soc.*, **89**, 5075 (1967); (f) P. Vogel, M. Saunders, N. M. Hasty, Jr., and J. A. Berson, *J. Amer. Chem. Soc.*, **93**, 1551 (1971).

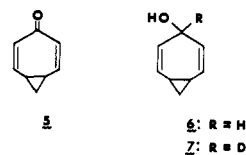
The next higher vinyllog, homotropylium ion (**2**),⁵⁻⁷ is a $1,m$ system, rearrangement of which by a suprafacial "allowed" pathway would require an interchange of the 8-endo and 8-exo hydrogens at each step. Winstein, *et al.*,^{5,8} already have noted that **2-8-endo-d** upon storage at $32-37^\circ$ is converted with $\Delta F^\ddagger = 22.3$ kcal/mol to an equimolar mixture of **2-8-endo-d** and **2-8-exo-d**. Although this equilibration was ascribed⁵ to a conformational ring inversion passing through the planar, classical cyclooctatrienyl cation **3**, it is evident that the "allowed" circumambulatory reaction would provide an alternative account of the observation (Scheme I, ΔF^\ddagger values in kilocalories per mole). A

Scheme I



ring-labeling experiment is required to distinguish the rearrangement (endo-exo interchange coupled with label scrambling) from the conformational inversion (endo-exo interchange only). The present paper reports the preparation of homotropylium-4-d ion and the minimum value $\Delta F^\ddagger > 27$ kcal/mol for its rearrangement.

4,5-Homotropone (**5**)⁹ is reduced in high yield to the dienol **6** at 0° with diisobutylaluminum hydride¹⁰ or to the corresponding 4-deuterio analog **7** with diisobutyl-



aluminum deuteride.¹¹ The dienol, upon extraction from CD_2Cl_2 with $\text{FSO}_3\text{H}-\text{SO}_2\text{ClF}$ at -120° ¹² or upon treatment with concentrated H_2SO_4 at -78° and slow warming to room temperature, gives stable preparations of homotropylium ion (**2** from **6** and **2-4-d** from **7**). The nuclear magnetic resonance (nmr) spectrum of **2** so obtained is the same as that previously

(5) S. Winstein, C. G. Kreiter, and J. I. Brauman, *ibid.*, **88**, 2047 (1966).

(6) (a) J. L. von Rosenberg, J. E. Mahler, and R. Pettit, *ibid.*, **84**, 2842 (1962); (b) S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *ibid.*, **87**, 3267 (1965).

(7) P. Warner, D. L. Harris, C. H. Bradley, and S. Winstein, *Tetrahedron Lett.*, 4013 (1970).

(8) For a similar observation on 8-chlorohomotropylium ion, see G. Boche, W. Hechtel, H. Huber, and R. Huisgen, *J. Amer. Chem. Soc.*, **89**, 3344 (1967).

(9) O. L. Chapman and R. A. Fugiel, *ibid.*, **91**, 215 (1969).

(10) Attempted reductions with LiAlH_4 give products resulting largely from saturation of the olefinic bonds. Comparable experiences have been reported by K. E. Wilson, R. T. Seidner, and S. Masamune, *Chem. Commun.*, 213 (1970).

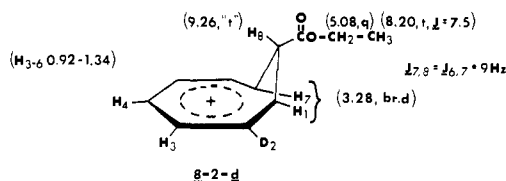
(11) Prepared from diisobutylaluminum chloride and LiD [cf. G. Wilke and H. Müller, *Justus Liebigs Ann. Chem.*, **618**, 267 (1958)].

(12) We thank Dr. Pierre Vogel for instruction in this procedure.

reported⁵⁻⁷ for **2** prepared by protonation of cyclooctatetraene. The spectrum of the deuterio analog **2-4-d** is again identical except for the absorptions at lowest field (near τ 1.5) due to H_{2-6} . The intensity of this group decreases from 5 units in the spectrum of **2** to 4 in the spectrum of **2-4-d**, and the multiplicity is simplified to a sharp five-line pattern (doublet + pseudotriplet). Spin decoupling by irradiation at τ 3.6, where absorption due to $H_{1,7}$ occurs, causes the H_{2-6} multiplet of **2-4-d** to collapse to an AB quartet ($\Delta\tau_{2,3} = 0.18$ ppm; $J_{2,3} \sim 8.6$ Hz), in agreement with values found⁷ on the undeuterated cation **2** by analysis of the 251-MHz nmr spectrum.

At equilibrium, after a large number of sequential circumambulatory steps, the rearrangement shown in Scheme I would have spread the deuterium label equally over sites 1-7. Thus, in the H_{1-7} absorption region, the nmr proton spectrum would be six-sevenths as intense as that of the undeuterated analog **2**, but more significantly, the clean doublet + pseudotriplet pattern of H_{2-6} of **2-4-d** would have returned to the unsymmetrical multiplet pattern of **2** (slightly broadened because of deuterium coupling). The latter multiplet contains strong lines that occur in absorption "windows" of the **2-4-d** pattern and thus provides a means to detect scrambling significantly in excess of a few per cent. The conservative estimate that 50% scrambling would not escape notice, and the observation that the τ 1.5 multiplet remains unchanged even when solutions of **2-4-d** are heated almost to complete destruction of the cation (75 min at 65° in FSO_3H , 75 min at 80° in H_2SO_4), place a lower limit of 26-27 kcal/mol on ΔF^\ddagger for the rearrangement. By exclusion, the most likely mechanism for the 8-endo-8-exo hydrogen interchange ($\Delta F^\ddagger = 22.3$ kcal/mol) is the previously postulated⁵ conformational isomerization.

The ring-deuterated 8-*exo*-carboethoxyhomotropylum ion (**8-2-d**) (nmr chemical shifts shown in τ units), prepared from the known¹³ 8-*exo*-carboethoxybicyclo[5.1.0]octa-3,5-dien-2-one, does not rearrange after 100 min at 60° in FSO_3H-SO_2ClF , so that again $\Delta F^\ddagger > 26$ kcal/mol.



The billion-fold retardation of circumambulatory rearrangement in homotropylum ion **2** as compared to bicyclo[3.1.0]hexenyl ion **1** presumably results from two causes. The first operates in the ground state, which must sacrifice its homoaromaticity in order to cyclize (**2-4-d** \rightarrow **4**, Scheme I) in preparation for rearrangement. This factor, anticipated on qualitative grounds, also is suggested by *ab initio* molecular orbital calculations.¹⁴ The second is the rather inefficient orbital overlap which would be imposed upon the transition state by the twisting motion of the migrating

carbon in the "allowed" pathway. The relative importance of these factors is not known.

(15) National Science Foundation Postdoctoral Fellow, 1970-1971.

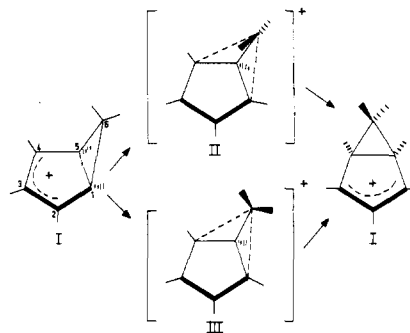
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Circumambulatory Degenerate Rearrangements in Polyenyl Cations

Sir:

The bicyclo[3.1.0]hex-3-en-2-yl cation **1** undergoes facile degenerate rearrangement in which the three-membered ring circumambulates above the cyclic polyene¹ (Scheme I). The positional identity of the

Scheme I



polyene is completely lost as a result of such a process, but the two methylene hydrogens retain their endo-exo integrity, implying first that the rearrangement proceeds through a bisected **II** (as opposed to eclipsed **III**) transition state or intermediate, in accordance with orbital symmetry considerations for a suprafacial [1,4N] ($N = 1$) sigmatropic shift,² and second that inversion through a planar benzenium ion (and hence scrambling of the endo-exo hydrogens) is not energetically competitive. As pointed out in the work of Berson and Jenkins,³ however, the situation is entirely different for the corresponding [1,4N + 2] ($N = 1$) degenerate rearrangement in the homotropylum ion **IV** (Scheme II). No scrambling of the polyene skeletal positions is observed, suggesting that neither the symmetry "forbidden" bisected **V** nor the "allowed" eclipsed **VI** transition states (intermediates) are energetically realizable. A low-energy pathway to scrambling of the methylene hydrogens is available, presumably through the planar cyclooctatrienyl cation.⁴

In this communication we report our preliminary

(1) (a) D. W. Swatton and H. Hart, *J. Amer. Chem. Soc.*, **89**, 5075 (1967); (b) R. F. Childs, M. Sakai, and S. Winstein, *ibid.*, **90**, 7144 (1968); (c) R. F. Childs and S. Winstein, *ibid.*, **90**, 7146 (1968); (d) V. H. Koptiug, L. I. Kuzubova, I. S. Isaev, and V. I. Manatyuk, *Chem. Commun.*, 389 (1969); (e) R. F. Childs and B. Parrington, *ibid.*, 1540 (1969); (f) P. Vogel, M. Saunders, N. M. Hasty, Jr., and J. A. Berson, *J. Amer. Chem. Soc.*, **93**, 1551 (1971); (g) for a discussion of these and related systems see R. E. Leone and P. v. R. Schleyer, *Angew. Chem., Int. Ed. Engl.*, **9**, 860 (1970).

(2) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1969.

(3) J. A. Berson and J. A. Jenkins, *J. Amer. Chem. Soc.*, **94**, 8907 (1972).

(4) (a) S. Winstein, C. G. Kreiter, and J. I. Brauman, *ibid.*, **88**, 2047 (1966); (b) G. Boche, W. Hechtel, H. Huber, and R. Huisgen, *ibid.*, **89**, 3344 (1967); (c) S. Winstein, *Quart. Rev., Chem. Soc.*, **23**, 141 (1969).

(13) Y. Sugimura and N. Soma, *Tetrahedron Lett.*, 1721 (1970).

(14) W. J. Hehre, *J. Amer. Chem. Soc.*, **94**, 8908 (1972). We thank Dr. Hehre for keeping us informed of the progress of his calculations and for helpful exchanges of correspondence.