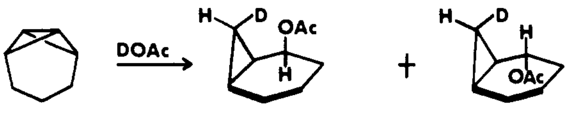
product **10** and some product **11** (in the ratio 62:12) but, significantly, no products of exo deuteration. If this behavior is taken as a model for the stereochemistry of additions of hydroxylic reagents to bicyclobutanes, the present observations are readily rationalized with benzvalene (**5**) as the key intermediate in the photolytic hydration of benzene.



9 **10 (62%)** **11 (12%)**

Acknowledgment. We thank Professor S. Masamune for spectra of authentic samples of **7**-OAc and **8**-OAc.[14a]

(14) (a) S. Masamune, N. Nakatsuka, R. Vukov, and E. N. Cain, *J. Amer. Chem. Soc.*, **91**, 4322 (1969). (b) Supported by NIH Fellowship No. 5-FO1-GM-38,024-02.

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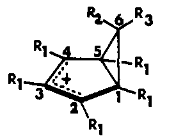
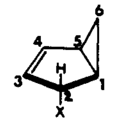
Bicyclo[3.1.0]hex-3-en-2-yl Cation[1]

Sir:

Recently developed synthetic procedures[2] for specific introduction of deuterium at the 2- and 6-endo positions of the parent bicyclo[3.1.0]hex-3-en-2-yl cation **1** make possible the study of the properties of this species by nuclear magnetic resonance (nmr) spectroscopy of its solutions in strongly acidic media. These spectra reveal a slow sigmatropic rearrangement not observable in the unlabeled compound. They also serve as probes for the special electronic effects anticipated for **1**, a potentially "homoantiaromatic" relative of cyclopentadienylium cation.[3] The results provide instructive comparisons with those obtained for the heptamethyl (**2**),[4] hexamethyl (**3** and **4**),[4,5] pentamethyl (**5**),[6a] tetramethyl,[6b] and hydroxy substituted[7] derivatives.





1: $R_1, R_2, R_3 = H$
2: $R_1, R_2, R_3 = CH_3$
3: $R_1, R_3 = CH_3$; $R_2 = H$
4: $R_1, R_2 = CH_3$; $R_3 = H$
5: $R_1 = CH_3$; $R_2, R_3 = H$

6: X = Cl
7: X = OH

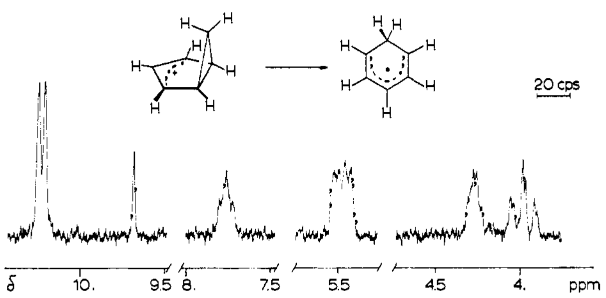


Figure 1. Nmr spectrum (100 MHz) of the bicyclo[3.1.0]hex-2-enyl cation **1** at −63° in SbF_5–SO_2ClF with external tetramethylsilane reference. The sharp singlet at δ 9.68 is the spectrum of the benzenonium ion, the protons of which suffer rapid exchange under these conditions and thereby have averaged chemical shifts [*cf.* G. Olah, R. H. Schlosberg, D. P. Kelly, and G. D. Mateescu, *J. Amer. Chem. Soc.*, **92**, 2546 (1970)]. The rest of the spectrum is interpreted in Table I. The chemical shifts are converted to those of Table I (internal CH_2Cl_2 reference) by subtraction of 0.25 unit from each δ value.

Distillation under vacuum of 2-chlorobicyclo[3.1.0]hex-3-ene (**6**) in SO_2ClF into a mixture of SbF_5–SO_2ClF kept at −100° gives dilute solutions of cation **1**, which has the proton nmr spectrum shown in Figure 1 and interpreted in Table I. An alternative preparation is achieved by extraction of a solution of 2-hydroxybicyclo[3.1.0]hex-3-ene (**7**) in CD_2Cl_2 with FSO_3H–SO_2ClF at −120°. The cation solutions obtained in this way are more concentrated but less stable than those generated by the first procedure.

Table I. Nmr Spectral Assignments of Protons of Bicyclo[3.1.0]hex-3-en-2-yl Cation (**1**)

Position	Rel intensity	Chemical shift, δ^a	Coupling constant, Hz	
H_2, H_4	2	9.97	$J_{1,2}$	<1
H_3	1	7.49	$J_{2,3}$	3.5
H_5, H_1	2	5.27	$J_{1,6}$ (endo)	3.5
H_6 (endo)	1	4.03	$J_{1,6}$ (exo)	7
H_6 (exo)	1	3.73	$J_{3,6}$	>0
			J_6 (endo), J_6 (exo)	~2

[a] In parts per million relative to internal CH_2Cl_2. Chemical shifts relative to external tetramethylsilane (Figure 1) lie 0.25 ppm downfield from those given here.

The assignments of the absorptions at δ 4.03 and 3.73 respectively to the 6-endo and 6-exo protons follow from the disappearance of the lower field (δ 4.03) band from the spectrum of the 6-endo-deuterio cation, prepared from 6-*endo*-deuterio-2-chlorobicyclo[3.1.0]hex-3-ene.[2] The small difference in chemical shift ($\delta_{endo} - \delta_{exo} = +0.30$ ppm) of the 6 protons of **1** is in striking contrast to that ($\delta_{endo} - \delta_{exo} = -5.8$ ppm) of the 8 protons of the bicyclo[5.1.0]octa-2,4-dienyl ("homotropylium") cation, one resonance structure of which is **8**.[8,9] This presumably results

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(2) J. A. Berson and N. M, Hasty, Jr., *J, Amer. Chem. Soc.*, **93**, 1549 (1971).

(3) For the properties of some cyclopentadienylium derivatives, see R. Breslow, R. Hill, and E. Wasserman, *ibid.*, **86**, 5349 (1964); R. Breslow, H. W. Chang, R. Hill, and E. Wasserman, *ibid.*, **89**, 1112 (1967).

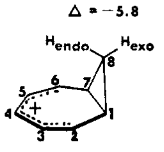
(4) R. F. Childs and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 7146 (1968).

(5) V. H. Koptyug, L. I. Kuzubova, I. S. Isaev, and V. I. Manatyuk, *Chem. Commun.*, 389 (1969).

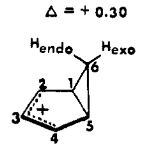
(6) (a) R. F. Childs, M. Sakai, and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 7144 (1968); (b) R. F. Childs and B. Parrington, *Chem. Commun.*, 1540 (1970).

(7) D. W. Swatton and H. Hart, *J. Amer. Chem. Soc.*, **89**, 5075 (1967).

at least in part from ring-current effects in opposing directions,[10] the endo proton being located in **8** over a six-electron homoaromatic system[8,9] and in **1** over a four-electron system, which, to the extent that the C_1–C_5 bond electrons conjugate, is homoantiaromatic. Moreover, the resonances of both of the 6 protons of cation **1** occur at substantially lower field than those of its pentamethyl analog **5** (δ 2.45 and 3.37[6a]). This is in accord with the conclusion based on chemical observations that C_6 bears a large burden of positive charge in **1** and in the solvolysis transition state leading to **1**.[11] It is reasonable that methyl substitution on the five-membered ring should drain off some of this charge and thus produce an upfield shift of the C_6 proton resonances.



8

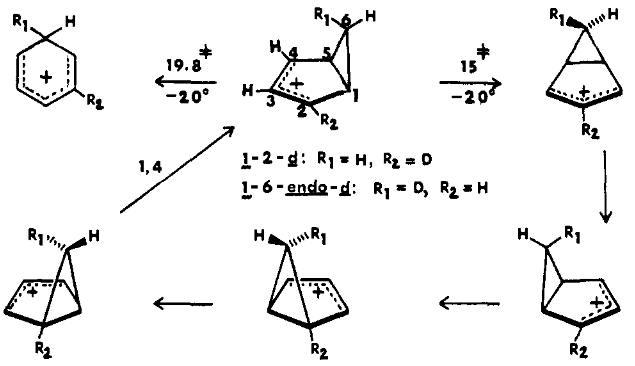


1

The sharp fluctuations in chemical shifts of the 2 (4) and 3 protons along the allyl chain of **1** (δ 9.97, 7.49) contrast strongly with the nearly uniform chemical shifts of the 2 (6), 3 (5), and 4 protons along the pentadienyl chain of **8** (δ 8.39, 8.57, and 8.27[9]). Similarly, the methylene geminal coupling constants ($J_{8,8}$ = 7.2 Hz in **8**, $J_{6,6} \sim 2$ Hz in **1**) differ drastically. These observations are consistent with the view that cation **8** has a rather "open" cyclopropane ring, which conjugates with the pentadienyl system in homoaromatic fashion principally by use of the C_1–C_7 bond,[8,9] but that **1** has a "closed" cyclopropane ring, which conjugates with the allyl system principally with the C_1–C_6 and C_5–C_6 bonds, thus minimizing insofar as possible the homoantiaromatic conjugation by way of the C_1–C_5 bond.

Storage of the solutions of cation **1** at −20° results in irreversible decomposition to unidentifiable products and, at a rate about 20–30% as fast, ring opening with $\Delta F^{\ddagger}$ = 19.8 kcal/mol to benzenonium ion (Figure 1). Sigmatropic rearrangements of **1** by 1,4 or successive 1,3 migrations, if rapid on the nmr time scale, would average the chemical shifts of $H_{1,5}$, $H_{2,4}$, and H_3 (Scheme I), but the spectral line broadening that would signify this process is not observed between −96 and −15°. This places a lower limit of 13–14 kcal/mol (at −15°) on the $\Delta F^{\ddagger}$ of the rearrangement. It nevertheless can be observed by conventional labeling as a slow process in the 2-deuterio cation **1**-*2-d* (Scheme I). This species can be prepared from alcohol **7**-*2-d*[2] at −90° with the label incompletely equilibrated. Upon storage at −90°, the spectrum gradually achieves the proton ratio ($H_{1,5}$:$H_{2,4}$:H_3:$H_{6_{endo}}$:$H_{6_{exo}}$) of 1.6:1.6:0.8:1:1, consistent with a statistical distribution of the deuterium and the hydrogens attached to C_1–C_5. The activation energy for the sigmatropic rearrangement, $\Delta F^{\ddagger}$ = 15 ± 1 kcal/mol at −90°, is substantially higher than that ($\Delta F^{\ddagger}$ = 9 kcal/mol at −89°) reported[4] for the heptamethyl ion **2**.

Scheme I



‡ΔF‡, kcal./mole

Experiments with the 6-endo-deuterated cation **1**-*6-endo-d* show that under conditions where the formation of benzenonium ion by ring opening has gone through approximately one half-life, no detectable (<5%) increase in the intensity of the 6-endo proton region of the spectrum of cation **1** occurs. The rate of ring opening then serves as a standard to which the degenerate rearrangement and 6-endo–6-exo exchange rates may be referred. The ratio of rates of sigmatropic rearrangement and loss of stereochemical integrity has a minimum value in the range of 10^4–10^6, in agreement with the previous estimate[4] of $>5 \times 10^4$ for this ratio in the heptamethyl cation **2**.

It is tempting to interpret these and other[4,12] examples of highly stereospecific inversion of configuration in the migrating group of 1,4-sigmatropic rearrangements as occurring under orbital symmetry constraints.[13] However, one should keep in mind that in all these cases the alternative process with retention of configuration would require much more complex distortions of atomic positions than does the observed inversion, which involves a "least-motion" pathway. Qualitatively, inversion therefore would be expected, even in the absence of orbital symmetry factors.

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[8] J. L. von Rosenberg, J. E. Mahler, and R. Pettit, *J. Amer. Chem. Soc.*, **84**, 2842 (1962).

[9] P. Warner, D. L. Harris, C. H. Bradley, and S. Winstein, *Tetrahedron Lett.*, 4013 (1970), and references cited therein.

[10] (a) H. C. Longuet-Higgins, *Chem. Soc., Spec. Publ.*, No. 21, 109 (1967); (b) J. A. Pople and K. G. Untch, *J. Amer. Chem. Soc.*, **88**, 4811 (1966).

[11] The rate of hydrolysis of bicyclo[3.1.0]hex-3-en-2-*exo*-yl chloride (6) in 70% aqueous acetone at 0° is retarded by a factor of 6 × 10^4 by substitution of an *exo*-carbomethoxy group at C_6. This corresponds to a ρ^+ value of −8.6.

[12] (a) H. E. Zimmerman and D. S. Crumrine, *J. Amer. Chem. Soc.*, **90**, 5612 (1968); (b) T. M. Brennan and R. K. Hill, *ibid.*, **90**, 5614 (1968); (c) H. Hart, T. R. Rogers, and J. Griffiths, *ibid.*, **91**, 754 (1969).

[13] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1969, p 128.

[14] Supported by the Stiftung für Stipendien auf dem Gebiete der Chemie, Basel, Switzerland.

[15] National Institute of General Medical Sciences Predoctoral Fellow, 1967–1970 (5-FO1-GM-38,024-02).