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(18) Gillette Research Foundation Fellow, 1972-1973

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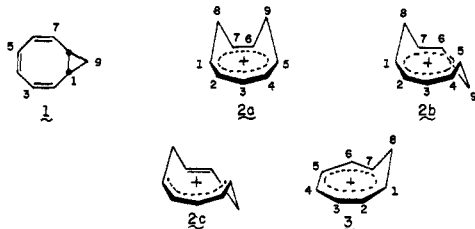
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Protonation of *cis*-Bicyclo[6.1.0]nona-2,4,6-trienes in Supercritical Media. Carbon-13 Nuclear Magnetic Resonance Study of the Mono- and 1,3-Bishomotropylium Ions under Long Life Conditions

Sir:

The facility with which *cis*-bicyclo[6.1.0]nona-2,4,6-triene (**1**) undergoes protonation to yield the parent monocyclic 1,3-bishomotropylium ion was reported in 1971.¹ At that time, several factors were considered to mitigate against the possibility that the resulting cation was transoid (**2b**), and its *cis* conformation (**2a**) was



favored. More recently, however, chlorosulfonyl isocyanate² and tetracyanoethylene additions³ to **1** have been found to occur in a manner which suggests the possible transient involvement of **2b** or the structurally related noninteracting cation **2c**. It was noted that the double-Möbius nature⁴ of **2b** could possibly allow for homoaromatic delocalization, thereby rationalizing the observed charge distribution in **2**. Additionally, kinetically controlled electrophilic attack from the *exo* direction on the folded (rather than extended) conformation of **1** was established.^{2,3}

A more detailed study of the protonation of **1** and its derivatives appeared highly desirable, and we therefore undertook to assess the behavior of these polyenes in superacids under conditions of long life. The high symmetry of **2** was clearly evident in its off-resonance decoupled cmr spectrum obtained in FSO₃H-SO₂ClF solution at -95°. The chemical shifts of the constituent carbon atoms are summarized in Table I where direct comparison with monohomotropylium ion (**3**) (generated under comparable conditions at -60°) is made. Although the ring current effect in **2** is clearly weaker than in **3**,^{1,5} the two spectra are seen to compare favorably.

- (1) P. Warner and S. Winstein, *J. Amer. Chem. Soc.*, **93**, 1284 (1971).
 (2) L. A. Paquette, M. J. Broadhurst, C. Lee, and J. Clardy, *ibid.*, **94**, 630 (1972); L. A. Paquette and M. J. Broadhurst, *ibid.*, **94**, 632 (1972).
 (3) J. Clardy, L. K. Read, M. J. Broadhurst, and L. A. Paquette, *ibid.*, **94**, 2904 (1972).

(4) This term is employed to emphasize the unusual three-dimensional orbital construct of **2b** and refers simply to the π orbital directionality inherent in this cation.

(5) This diminished interaction is also revealed in carbon shift differences. For example, $\Delta\delta^{13}\text{C} = \delta\text{C}_1 + \delta\text{C}_5$ in ion **2** is about +46

Table I. Cmr Data for **2** and **3**^a

C atom in 2	Chem shift, ^b δ	C atom in 3	Chem shift, ^b δ
C ₁ , C ₅	56.7 ^c	C ₁ , C ₇	71.5
C ₂ , C ₄	25.8	C ₂ , C ₆	40.0
C ₃	10.3	C ₃ , C ₅	48.5
C ₆ , C ₇	52.6 ^c	C ₄	49.0
C ₈ , C ₉	162.2	C ₈	150.0

^a A Varian HA-100 instrument was employed and the Fast Fourier Transform (FFT) method was employed. ^b The carbon shifts are cited relative to external CS₂. ^c Interchangeable values.

When the deuteration of **1** in FSO₃D-SO₂ClF at *ca.* -125° was reexamined, distribution of the isotope between the inner and outer positions of C₈ or C₉ was found to be 50:50 within our limits of analysis. Therefore, little if any stereoselectivity obtains in the incorporation of deuterium while proceeding from **1** to **2**.

syn-9-Methyl derivative **4a**, which cannot attain a folded conformation and consequently lacks the ability to achieve good initial overlap of the internal cyclopropane bond with the developing charge center at C₂, gave only broad polymeric-type absorptions upon protonation at -78 to -150°. In contrast, anti isomer **4b** readily gave an nmr spectrum (Figure 1) comparable to that of **2** which, after decoupling clarified all assignments, was consistent only with **5a** or **5b** (Table II).

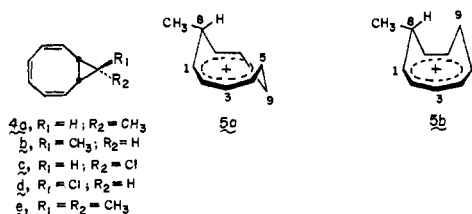


Table II. 100-MHz Pmr Data for Protonated *anti*-9-Methyl-*cis*-bicyclo[6.1.0]nona-2,4,6-triene (**5**) (FSO₃H-SO₂ClF, 1:4 (v/v), *ca.* -130°)

Proton	Chem shift, ^a τ	Coupling constants, Hz
H ₃	0.98	$J_{2,3} \equiv J_{3,4} = 6.0 \pm 0.5$
H ₂	2.05	$J_{1,2} = 9.5 \pm 0.5$
H ₄	2.19	$J_{4,5} = 9.0 \pm 0.5$
H ₅	2.92	$J_{5,9a} = 9.5 \pm 0.5, J_{5,9i} = 11.0 \pm 0.5$
H ₆	2.95	$J_{6,9a} = 10.0 \pm 0.5, J_{6,9i} = ca. 0$
H ₁	3.02	$J_{1,8i} = 11.0 \pm 0.5$
H ₇	3.53	$J_{6,7} = 8.0 \pm 0.5, J_{7,8i} = ca. 0$
H _{9a}	6.06	$J_{9a,9i} = 12.0 \pm 0.5$
H _{8i}	7.86	
H _{9i}	8.30	
CH ₃	8.46	

^a Chemical shifts measured relative to internal CHDCl₂ (τ 4.70).

The remarkable dichotomy in behavior between **4a** and **4b** points again to the fact that protonation of this ring system at C₃ must necessarily occur from the folded conformation to arrive at a homoaromatic species.^{2,3}

ppm, a much larger value than that for the comparable difference in ion **3**, $\Delta\delta^{13}\text{C} = \delta\text{C}_1 - \delta\text{C}_4 = 22.5$ ppm. Equally revealing is the fact that the $\Delta\delta^{13}\text{C}$ values of such homotropylium ions are generally smaller than those in monocyclic pentadienyl cations (54.4-89 ppm).

In the case of **4b**, this process initially places the methyl group on the outside of the ring. For conformational reasons, the initially formed ion must be **5a**. Should the transoid species be the thermodynamically stable conformer under these conditions, then **5a** is considered to be the correct structure since double bridge inversion to place methyl in the sterically less favorable inner position does not operate (*vide infra*). If, on the other hand, the ion is cisoid, the structure must be **5b** (inversion of the methylene bridge) rather than the sterically more demanding ion with the methyl inside. It is important to note that **5** is a static structure and that rapid exchange between **5a** and **5b** is not important. Deuteration of **4b** as before led in this case to stereoselective ($75 \pm 10\%$)⁶ deuterium incorporation at the 9i site.

Numerous attempts to protonate **4c** and **4d** in various media at low temperatures have proved unsuccessful. Not unexpectedly,^{2,3} the 9,9-dimethyl derivative **4e** likewise did not give rise to a bishomotropylum ion.

Comparison of the nmr data for the two 1,3-bishomotropylum ions reveals, *inter alia*, that the average chemical shift of H_{8i} and H_{9i} (τ 8.08) in **5** compares well with that of the corresponding protons in **2** (8.09). The unsymmetrical nature of **5** does, however, reveal for the first time the magnitude of $J_{6,7}$ (8.0 Hz). Although this finding can be readily accommodated by **5a** in which significant twisting of the C_{6,7} bond is necessary to maximize overlap across the methylene bridges, the attendant decrease in C₆-C₇ overlap could so affect J that a clearcut distinction between **5a** and **5b** is unfortunately not possible on this basis.

When consideration is given to the stereochemistry of the deuteration process as revealed by the spectra of the long-lived cations, a greater *net* endo positioning of deuterium is seen in **5**. Unfortunately, the stereoselectivity of H⁺ (or D⁺) attack cannot be determined unambiguously. Consequently, these observations may be satisfied by one of several options: (a) random deuteration to give trans ions **2b** and **5a** with no flipping of either bridge atom, (b) stereoselective exo electrophilic attack followed by a single flip of either bridge in **2b** to give **2a** and by inversion of only the methylene bridge in **5a** with formation of **5b**, (c) in the unsubstituted example, the first inversion (trans \rightarrow cis), when operative, is followed by a rapid flip of the other bridge (cis \rightarrow trans).

Since the type c sequence in the case of **4b** would position methyl in an endo orientation (not reconcilable with the measured coupling constants), operation of this mechanism can be discounted in this instance. Its generality can consequently be questioned. Also, examination of models indicates that the methyl group in **4b** is sufficiently remote from the sites (two equivalent positions are available) of initial electrophilic bonding not to cause the sizable selectivity difference noted upon deuteration of **1** and **4b**. Therefore, ran-

(6) The rather large uncertainty quoted for this inner/outer deuterium ratio arises from several factors. First, partial overlap of the H_{9i} and methyl absorptions renders integration of this peak difficult. The H_{9o} multiplet is clearly separated from all other resonances, but the *total* amount of entering deuterium is unknown (the DSO₃F has 2-3% proton contamination). As a consequence of an unknown isotope effect, the amount of H at C₆ could vary from 1.0 to 1.1. It follows then that if the H_{9o} peak comprises 75% of 1.0 hydrogen, the ratio is 75:25, but if 1.1 hydrogens are present the ratio now becomes 83:17.

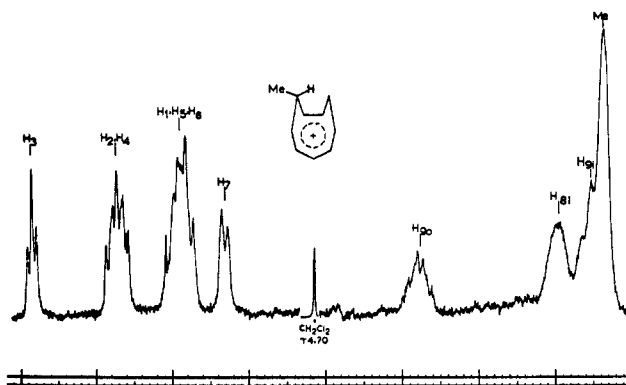


Figure 1. Nmr spectrum of protonated **4b**.

dom deuteration is seemingly not a suitable mechanistic hypothesis.

Thus, the protonation of *cis*-bicyclo[6.1.0]nonatrienes under conditions of long life would appear to involve initial formation of a trans cation which subsequently experiences conformational inversion of a (less substituted) methylene bridge. Molecular models show that the trans ion is reasonably rigid, fairly strain free, and certainly less demanding than a comparable 1,4-bishomotropylum ion.⁷ Nevertheless, although the transoid intermediates are capable of interception under presumed kinetic control conditions,^{2,3} they transmuted to their cis counterparts when thermodynamic control can operate. This can be interpreted to mean that **2b** (or **2c**) resides closer to the transition state for bridge inversion than does **2a**. A number of important questions still remain to be answered about the electronic nature of the trans ion⁸ and about the possible differences which may arise in solvent systems other than superacids.

(7) H. A. Corver and R. F. Childs, *J. Amer. Chem. Soc.*, **94**, 6201 (1972).

(8) Preliminary calculations suggest that **2a** and **2b** may be nearly isoenergetic. However, the lack of strong dependence on molecular geometry requires highly refined calculations before this point may be assessed accurately (J. Clardy, personal communication).

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(10) Considered as publication CXLIII on Stable Carbocations.

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Stable Carbocations. CLV.¹ The Ethylenechloronium and Methylchlorocarbenium Ions

Sir:

Alkenehalonium ions have long been suggested as intermediates in electrophilic halogen addition and

(1) Stable Carbocations. CLIV: G. A. Olah and Y. K. Mo, *J. Org. Chem.*, in press.