

Figure 2. Two views of the thermal transition state.

heptadienyl anions X^{9a} and XI.¹⁰ Heating solutions of these anions to 150° for 30 min gave no change; above this temperature, gradual decomposition occurred which did not appear to involve anion equilibration. To check that the geometry of this system permitted *suprafacial* 1,6-hydrogen shifts, anions X and XI were irradiated in quartz at 0° using a high-pressure mercury lamp. After 1 week of irradiation, X was virtually unchanged, but XI had been quantitatively converted into a new anion, XII, presumably via a photochemical *suprafacial* hydrogen shift. These stereochemical results are consistent with the Woodward–Hoffmann rules.

Although other factors are certainly involved, the relative rates of the thermal isomerizations observed thus far correlate well with the number of alkyl substituents in the positions bearing R's in Figure 2. The slowing effect of an alkyl substituent is considerably greater than the statistical factor expected due to the decrease of one in the number of hydrogens available to migrate, and is presumably due to nonbonded steric interactions in the transition state. Observed activation energies are: I → II, 18 kcal/mol (no R's); IV → V, 20 kcal/mol (one R); III → V and VI → VIII, 26 kcal/mol (two R's on same carbon); and VIII → IX, 27 kcal/mol (two R's on different carbons). Presumably with three or four R's, the reaction will be slower still.

The relative thermodynamic stabilities of four sets of thermally equilibrated pentadienyl anions are shown by the percentages in Figure 1. The results can be rationalized as follows: VIII is >3 kcal/mol less stable than IX (and the other acyclic anions in the equilibrium) because of the extra carbon–carbon σ bond in VIII; I, IV, and VI are the least stable anions in their respective sets because of their greater degree of alkyl substitution on carbons 1, 3, and 5 of the pentadienyl system, which bear nearly all of the negative charge; V is favored over III by 1.6 kcal/mol largely because of nonbonded steric interactions due to a trisubstituted sp^3 -hybridized carbon in the latter (this same factor favors VI over VII, but is outweighed by the previous factor in this case).

These thermal rearrangements should increase considerably the utility of acyclic pentadienyl anions in synthesis. By keeping the temperature low, they can be avoided. On heating, equilibration occurs, sometimes quantitatively (e.g., IV → V at 35°, and VIII → IX).

Acknowledgments. We gratefully acknowledge financial support from the Petroleum Research Fund, administered by the American Chemical Society, the Sloan Foundation (Fellowship to R. B. B.), the NDEA (Fellowship to W. H. D.), Ethyl Corp. (Fellowship to

(10) Prepared in 24% yield from cycloheptadienyllithium^{9a} by treatment with methyl iodide, preparative glpc purification, and the addition of butyllithium in THF–hexane.

D. E. P.), and the National Science Foundation (Grants No. GU-1534 and GP-21115).

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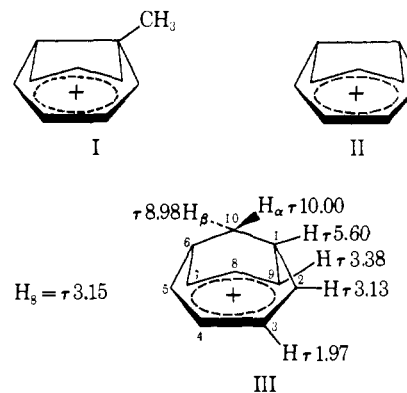
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Received July 27, 1970

The Bicyclo[4.3.1]deca-2,4,7-trienyl Cation. A Homoconjugative Protonation Route to a 1,4-Bishomotropylium Ion¹

Sir:

The study of polyhomotropylium ions has received increased interest in the past few years.² The first reported bishomotropylium ions, I^{2d} and II,^{2e} showed some evidence for ring current, but this aromatic character was largely deduced from the observed charge delocalization. During our attempts to prepare by more conventional methods the more informative bicyclo[4.3.1] skeleton, we discovered a protonation reaction which we have successfully applied to the preparation of III, a 1,4-bishomotropylium ion.³ III contains two methylene hydrogens which lie over the face of the potentially aromatic ring system, thus offering a means of observing the shielding effects of a ring current.



The prototype of the reaction used to generate III was first observed in the protonation of bicyclo[4.2.1]nona-2,4,7-triene (IV),⁴ which was extracted from a

Table I. Coupling Constants for Ion V

J	1,2	2,3	3,4	4,5	5,6 _{exo}	5,6 _{endo}	$\frac{ \delta_{\text{exo}} - \delta_{\text{endo}} }{6}$	1,7	2,4
Hz	9	9	9	9	8	0	16	6	Small

(1) Research supported in part by the National Science Foundation.
(2) (a) S. Winstein, *Quart. Rev., Chem. Soc.*, **23**, 141 (1969); (b) A. S. Kende and T. L. Bogard, *Tetrahedron Lett.*, 3383 (1967); (c) J. C. Baborak, J. Daub, D. M. Follweiler, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 7760 (1969); (d) P. Ahlberg, D. L. Harris, and S. Winstein, *ibid.*, **92**, 2146 (1970); (e) P. Ahlberg, D. L. Harris, and S. Winstein, *ibid.*, **92**, 4454 (1970); (f) Schröder has recently reported the methoxymercuration of VI and has considered a bishomotropylium ion intermediate: H. P. Löffler and G. Schröder, *Tetrahedron Lett.*, 2119 (1970). Subsequent to the submission of this communication, Professor Schröder informed us of similar results from the protonation of bicyclo[4.2.2]deca-2,4,7,9-tetraene.

(3) This nomenclature is defined in ref 2a, p 147.

(4) (a) W. Grimme, *Chem. Ber.*, **100**, 113 (1967); (b) L. G. Cannell, *Tetrahedron Lett.*, **48**, 5967 (1966).

Table II. Coupling Constants for Ion III

J Hz	1,2	1,9	1,10 α	1,10 β	2,3	2,4	2,5	3,4	2,10 β	7,10 α	$ 10\alpha,10\beta $
	$\sim 4^b$	5.9 ^b	0.0 ^b	4.5 ^b	+9.9 ^a	+1.2 ^a	0.0 ^a	+9.4 ^a	$\sim 1^b$	Small	14.2

^a Calculated. ^b Measured.

CD₂Cl₂ solution into a mixture of FSO₃H and SO₂ClF (1:4, v/v) at *ca.* -120° . The resulting ion was observed at -90° (see Figure 1) and was assigned the structure V on the basis of its nmr data. Some of the coupling constants were obtained from double irradiation experiments and are listed in Table I. Protons H₂, H₃, and H₄ are all triplets appearing at τ 0.35, 2.16, and 1.37, respectively ($J_{1,2}$, $J_{2,3}$, and $J_{4,5}$ are all 9 Hz). H₁ is a complex multiplet which appears at

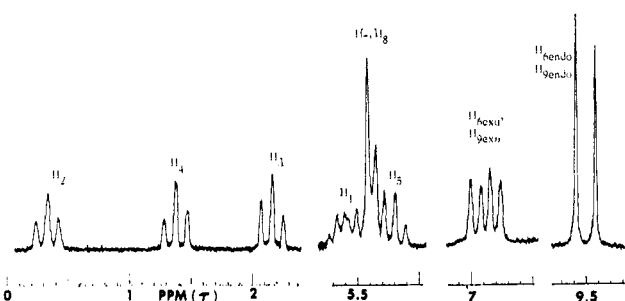
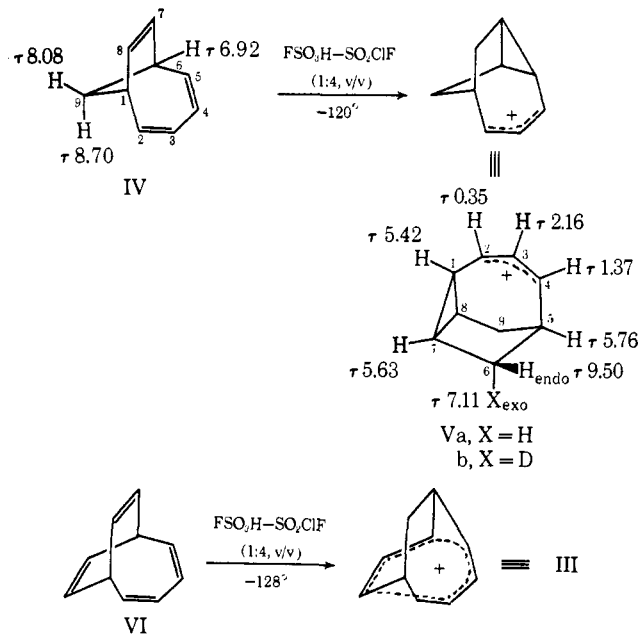


Figure 1. Nmr spectrum (100 MHz) of tricyclo[3.2.2.0⁸]non-2-enyl cation (V) in FSO₃H-SO₂ClF (1:4, v/v) at -90° . CDHCl₂ was used as internal standard, τ 4.70.

τ 5.42. Irradiation of H₂ collapses H₁ to a triplet, H₃ to a doublet, and causes H₄ to sharpen. Irradiation of H₃ collapses both H₂ and H₄ into doublets. Irradiation of H₄ causes collapse of H₃ to a doublet and H₅ (τ 5.76) to a triplet. Protons H₇ and H₈ (τ 5.63) appear as a doublet and are coupled to H₁ ($J_{1,7} = 6$ Hz). Protons H_{6endo} and H_{9endo} (τ 9.50) appear as a



sharp doublet and are coupled only to H_{6exo} and H_{9exo} (τ 7.11), respectively ($|J_{gem}| = 16$ Hz). Deuteration of IV yielded Vb with $\geq 95\%$ deuterium incorporation exo to the allylic moiety.

It is evident from the nmr data that ion V has a plane of symmetry through carbons C₁-C₅. Furthermore, it is apparent that some of the charge on the allylic moiety is delocalized into the cyclopropane ring. The stereoselective homoconjugative⁵ protonation of hydrocarbon IV is best explained in terms of electrophilic attack by H⁺ at C₈ with anchimeric assistance from the π electrons on C₅. The ion thus formed is a cyclopropylallyl cation, which should be the most stable product. Quenching experiments of V were unsuccessful.

By analogy to the protonation of IV, it seemed probable that bicyclo[4.2.2]deca-2,4,7,9-tetraene⁶ (VI) would protonate to give bicyclo[4.3.1]deca-2,4,7-trienyl cation (III). Hydrocarbon VI was extracted into super acid medium at *ca.* -128° . The ion III was first observed at -110° and remained unchanged at $+20^\circ$ (see Figure 2 and Table II). III was quenched in

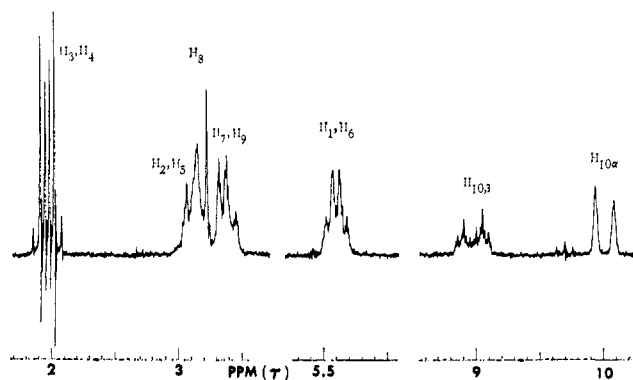


Figure 2. Nmr spectrum (100 MHz) of bicyclo[4.3.1]deca-2,4,7-trienyl cation (III) in FSO₃H-SO₂ClF (1:4, v/v) at -30° . CDHCl₂ was used as an internal standard, τ 4.70.

saturated NaOCH₃-CH₃OH at -78° to give *exo*-7-methoxybicyclo[4.3.1]deca-2,4,8-triene.^{2f} The bridgehead protons, H₁ and H₆ (τ 5.60), appear as a complex multiplet which collapses upon irradiation of H₂ and H₅ (τ 3.13, $J_{1,2} = \sim 4$ Hz) and of H₇ and H₉ (τ 3.38, $J_{1,9} = 5.9$ Hz). The methylene bridge protons, H_{10 α} (τ 10.00) and H_{10 β} (τ 8.98), show a geminal coupling constant of $|J_{gem}| = 14.2$ Hz. H_{10 β} is a complex multiplet which collapses to a doublet containing triplet fine structure upon irradiation of H₁ and H₆ ($J_{1,10\beta} = 4.5$ Hz). Irradiation of H₂ and H₅ removes this fine structure ($J_{2,10\beta} = \sim 1$ Hz). H_{10 α} appears as a sharp doublet which further sharpens upon irradiation of H₇ and H₉. Irradiation of H₁ and H₆ does not affect H_{10 α} . Protons H₃ and H₄ (τ 1.97) appear as one-half of an AA'XX' pattern which collapses to a singlet upon irradiation of H₂ and H₅. The coupling constants

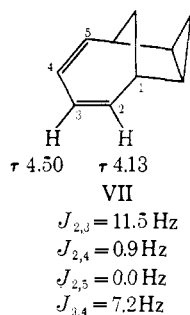
(5) S. Winstein and M. Shatavsky, *Chem. Ind. (London)*, 56 (1956).

(6) (a) E. Vedejs, *J. Amer. Chem. Soc.*, **90**, 4751 (1968); (b) M. Jones, Jr., S. D. Reich, and T. L. Scott, *ibid.*, **92**, 3118 (1970); (c) S. Masamune, R. T. Seidner, H. Zenda, M. Wiesel, N. Nakatsuka, and G. Bigam, *ibid.*, **90**, 5286 (1968); W. von E. Doering and J. W. Rosenthal, *Tetrahedron Lett.*, 349 (1967).

within the AA'XX' pattern can be easily calculated⁷ and are listed in Table II. Protons H₇ and H₉ appear as a complex multiplet and collapse to a doublet upon irradiation of H₁ and H₆. Proton H₈ is a triplet ($J_{7,8} = 7.8$ Hz). Due to the small shift difference of protons H₇, H₈, and H₉ it was impossible to observe decoupling effects among them.

The assigned structure of III is consistent with the coupling constants listed in Table II. $J_{7,8}$ is 7.8 Hz, which, when compared to cyclohexenyl cation⁸ ($J_{1,2} = 7.0 \pm 0.5$ Hz), indicates that carbons C₇–C₉ are a part of a six-membered ring. For cyclohexenyl cation, protons H₁ and H₃ appear at τ 0.07 and H₂ at τ 2.04 while for ion III, protons H₇ and H₉ are at τ 3.38 and H₈ at τ 3.15. The average chemical shift for the allylic protons on ion III is 2.53 ppm upfield from that of cyclohexenyl cation, indicating that considerable charge has been delocalized away from these three carbons.

In considering the four-spin system, H₂–H₅, we have chosen as a model tricyclo[4.3.1.0^{7,9}]deca-2,4-diene⁹ (VII). The coupling constants shown have been calculated for the AA'XX' pattern in the same manner as for III. The average vicinal coupling constant for VII is 9.4 Hz while that for III is 9.7 Hz. The aromatic character of III tends to average these coupling constants as can be seen by comparing $J_{2,3}$ and $J_{3,4}$ for the two systems. The average chemical shift for the four-spin system of III is 1.77 ppm downfield from that in VII. This indicates that much of the charge on III is delocalized from the allylic into the butadiene moiety.



An important aspect of ion III is that it contains two methylene protons, which lie above the plane of the seven-carbon tropylium ring (C₂–C₅, C₇–C₉). If one compares the average chemical shift of H_{10 α} and H_{10 β} ($\tau_{av} = 9.49$) with the average methylene shift of hydrocarbon IV ($\tau_{av} = 8.39$)⁴ the resulting difference is approximately a 1-ppm upfield shift for ion III. A probable explanation is that this difference is due in part to a shielding of the methylene protons by a ring current in the tropylium skeleton. Consistent with this ring current effect is the fact that the bridgehead protons, H₁ and H₆, appear at 1.3 ppm lower field than the bridgehead protons on IV (τ 6.92).⁴ If a ring current were present these protons would indeed be deshielded, since they project outside the tropylium ring. These effects are analogous to those observed in monohomotropylium ion.¹⁰ These features, combined

(7) E. D. Becker, "High Resolution NMR," Academic Press, New York, N. Y., 1969, p 166.

(8) P. M. Warner, Ph.D. Thesis, University of California at Los Angeles, Los Angeles, Calif., 1970.

(9) This hydrocarbon was chosen in preference to bicyclo[4.2.1]nona-2,4,7-triene because of its much simpler vinyl nmr region.

with the evidence for charge delocalization, strongly support the bishomoaromatic character of ion III.

Work is being continued in these laboratories on the ¹H and ¹³C spectra of these and related polyhomoaromatic carbonium ions.

Acknowledgments. We wish to thank Drs. D. Harris and P. Ahlberg for assistance in obtaining and interpreting nmr spectra. H. H. is grateful to the Max Kade Foundation for support during 1969–1970. We are grateful to Badische Anilin und Sodafabrik for gifts of cyclooctatetraene.

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

(11) Deceased November 23, 1969.

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Received July 22, 1970

The Conformational Dependence of β -Fluorine Coupling Constants

Sir:

The conformational dependence and the origin of β -fluorine coupling constants have not been well elucidated and a number of contradictory proposals have been reported.^{1–3} Previously we have shown^{4,5} that the direction of the maximum principal element of the β -fluorine coupling tensor of $-\text{OOC}-\dot{\text{C}}\text{FCF}_2-\text{COO}^-$ determined by Rogers and Whiffen⁶ in a single crystal quantitatively coincides with the direction of the maximum overlap of the fluorine $2p\pi$ orbital ($F_{2p\pi}$) with the half-filled carbon $2p\pi$ orbital ($C_{2p\pi}$). This strongly suggests that the spin density in the $F_{2p\pi}$ orbital is transferred from the $C_{2p\pi}$ orbital by direct overlap. We have also found^{4,5} that the conformational dependence of the overlap integral between $F_{2p\pi}$ and $C_{2p\pi}$ gives the so-called $\cos^2 \theta$ rule such as $B_0 + B \cos^2 \theta$ with a fairly large value for B_0 .

Recently, Kosman and Stock⁷ have obtained the experimental coupling value for $\theta = 90^\circ$ conformation and reached a similar conclusion based on the magnitudes of the overlap integral. According to their report,⁷ a_F with $\theta = 90^\circ$ in semiquinone derivatives is 0.85 G and a_F for the freely rotating CF_3 group in the same derivatives is 2.77 G. The ratio $a_F(\text{CF}_3)/a_F$ ($\theta = 90^\circ$) is 3.2, while the predicted ratio from their conformational dependence of the overlap integral was about 2. However, we have found that our numerical value for the overlap integral is quite different from theirs⁸ and that ours is more consistent with their experimental results, giving the predicted ratio of 3.1. Accordingly, it would be of interest to see the results

(1) E. T. Strom and A. L. Bluhm, *Chem. Commun.*, 115 (1966).

(2) J. L. Gerlaock and E. G. Janzen, *J. Phys. Chem.*, **72**, 1832 (1968).

(3) K. Morokuma, *J. Amer. Chem. Soc.*, **91**, 5412 (1969).

(4) M. Iwasaki, Abstracts, 7th Electron Spin Resonance Symposium, Sapporo, Japan, 1968, p 31.

(5) M. Iwasaki, *Fluorine Chem. Rev.*, in press.

(6) M. T. Rogers and D. H. Whiffen, *J. Chem. Phys.*, **40**, 2662 (1964).

(7) D. Kosman and L. M. Stock, *J. Amer. Chem. Soc.*, **92**, 409 (1970).

(8) It seems that they used Table XXI rather than Table XX in ref 9.

(9) R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).