absence from the product mixture of unrearranged acetate or any related acetate product containing geminal cyclopropyl protons is consistent with cyclopropyl participation and suggests that nonclassical ion X, probably formed initially, experiences further rearrangement before solvent capture at C-10; however, a complete structure analysis of the products is required before anything definite can be inferred about the nature of the ionic intermediate(s) involved.

While it is clear that ionization of IV-OBs is extensively accelerated, the degree of assistance provided by the cyclopropyl ring is substantially lower than that provided by the double bond in V.[3] This result is in striking contrast to the previous observation[1d,e] in the norbornyl series (compare relative reactivities of I and VI). Since V and VI are of comparable reactivity one can estimate that cyclopropyl assistance to ionization in IV is some 10^5 less efficient than in *endo-anti*-I. Of the several possible rationalizations of this curious anomaly, the explanation which we prefer is that based on a simple examination of molecular models. Thus for I the σ-orbital plane of the cyclopropyl ring is more favorably oriented toward the developing carbonium ion center than is the π-orbital plane of the double bond in VI. Just the opposite relationship is observed when molecular models of IV and V are compared. The participating π orbital of V is oriented directly toward the reaction center whereas the corresponding cyclopropyl orbital is directed into the cavity region between the two bridges. The latter orientation would lead to less favorable interaction in the early stages of ionization. An additional factor which may be of relevance here is the often-argued[1h-k] relief of ground-state strain involved in the opening of the *endo*-cyclopropyl ring of I. The *exo* geometry of the cyclopropane ring precludes such arguments in the case of IV.

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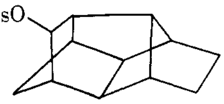
i. The failure to observe similar products of ion-pair return from



i

IV-OBs is not unexpected since the possible rearranged esters should be comparable in reactivity to the starting ester.[8b] (b) H. L. Goering and M. F. Sloan, *J. Amer. Chem. Soc.*, **83**, 1992 (1961).

(9) (a) Alfred P. Sloan Foundation Fellow, 1967–1969; (b) Organization of American States Predoctoral Fellow, 1968–1969.

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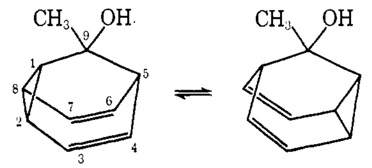
Received December 3, 1969

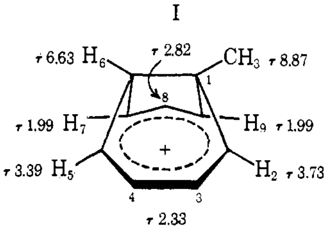
1-Methylbicyclo[4.3.0]nonatrienyl Cation. A 1,4-Bishomotropylium Ion[1]

Sir:

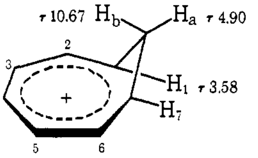
The successful generation and direct observation of the monohomotropylium ion (IV)[2] has inspired much work to show the existence of polyhomotropylium ions.[3] We now wish to report the first successful generation and observation of one in a series of potential bishomotropylium ions, the 1,4-bishomotropylium ion (III).[4]



I



III



H_2–H_6 = τ 1.5

IV

9-Methyltricyclo[3.3.1.$0^{2,8}$]nona-3,6-dien-9-ol (I),[5] prepared from barbaralone[6] and methyllithium, was extracted from a CD_2Cl_2 solution into a mixture of FSO_3H

$$\mathrm{I}\ \xrightarrow[-135^\circ]{\substack{\mathrm{FSO_3H\text{-}SO_2ClF}\\ (1:3\ v/v)}}\ \mathrm{II}\ \xrightarrow[-116^\circ]{k\,=\,2.2\,\times\,10^{-3}\ \mathrm{sec}^{-1}}\ \mathrm{III}\ \xrightarrow[-50^\circ]{}\ \text{unidentified products}$$

and SO_2ClF (1:3 v/v) at *ca.* −135° and observed by nmr at −116°. The first ion observed, the 9-methyl-9-barbaralyl cation[7] (II), rearranged exclusively to III at −116° with a rate constant of 2.2×10^{-3} sec^{-1} ($\Delta F^* = 11.0$ kcal/mol). Ion III was found to be stable over a relatively large temperature interval which allowed extensive nmr work to be done with the ion at −80°. Quenching experiments on ion III were not successful.

The structure 1-methylbicyclo[4.3.0]nonatrienyl cation was assigned to III on the basis of its nmr data. Some of the coupling constants were obtained from the following double irradiation experiments. Proton H_6 (τ 6.63) appears as a complex multiplet which, on irradiation of H_5 (τ 3.39), collapses into a doublet ($J_{6,7} = 2.0$ Hz) that has fine structure. Also, on irradiation of H_7 and H_9 (τ 1.99), H_6 collapses into a doublet ($J_{5,6} = 4.9$ Hz). Protons H_7 and H_9, which have accidental chemical shift equivalence, appear as a doublet further complexed by small coupling. On irradiation of either H_2 (τ 3.73) or H_5, protons H_7 and H_9 collapse into a doublet ($J_{7,8} = J_{8,9} = 4.0$ Hz). It was impossible to irradiate either H_2 or H_5 without simultaneously irradiating the other.

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(1) Research supported in part by the National Science Foundation.

(2) (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).

(3) S. Winstein, *Quart. Rev. Chem. Soc.*, **23**, 141 (1969).

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

(5) Satisfactory ir, nmr, and analytical data were obtained.

(6) W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, **23**, 3943 (1967).

(7) P. Ahlberg, J. B. Grutzner, D. L. Harris, and S. Winstein, submitted for publication.

Proton H_8 (τ 2.82) appears as a triplet which collapses into a singlet on irradiation of H_7 and H_9. Protons H_3 and H_4 (τ 2.33), which accidentally have the same chemical shift, appear as a complex multiplet. On irradiation of H_2 or H_5, protons H_3 and H_4 collapse into a doublet with some further fine structure. Irradiation of H_6 causes a slight change in the center of the H_3–H_4 multiplet. Proton H_2 appears as a complex multiplet which is somewhat simplified on irradiation of H_7 and H_9. Irradiation of H_6 gives no detectable simplification of the H_2 multiplet. Irradiation of H_3 and H_4 changes H_2 into a singlet; however, H_7 and H_9 probably were irradiated at the same time. On irradiation of H_6 or protons H_7 and H_9, the H_5 complex multiplet collapses somewhat, and on irradiation of H_3 and H_4, the H_5 multiplet collapses into a doublet.

In view of the complexity of the nmr spectrum, a computer simulation was carried out in order to obtain some of the coupling constants. From the decoupling experiments described above, it is clear that the group of four protons (H_2–H_5) are coupled only slightly to the group of three protons (H_7–H_9). Therefore, the two groups can be treated separately, with H_6 decoupled, in order to simplify the calculation. The four-spin system was simulated using the computer program LAME[8] (LAOCN3 with magnetic equivalence), and the results are given in Table I.

Table I

J	2,3	2,4	2,5	2,9	3,4	3,5	3,6
Hz	8.9[a]	0.1[a]	0.0[a]	Small[b]	6.7[a]	1.7[a]	Small[b]
J	4,5	4,6	5,6	5,7	6,7	7,8	8.9
Hz	7.7[a]	Small[b]	4.9[b]	Small[b]	2.0[b]	4.0[b]	4.0[b]

[a] Calculated. [b] Measured.

The coupling constants in Table I clearly indicate the structure of ion III. Hence, $J_{7,8}$ and $J_{8,9}$ are both 4.0 Hz, which, when compared to $J_{1,2}$ = 3.8 Hz in cyclopentenyl cation,[9] indicates that carbons C_7–C_9 are part of a five-membered ring. Furthermore, the coupling constants observed in the four-spin group, H_2–H_5, closely resemble those of naphthalene[10] ($J_{1,2}$ = 8.3, $J_{1,3}$ = 1.3, $J_{2,3}$ = 6.5 Hz) and those of 1,3-cyclohexadiene[11] ($J_{1,2}$ = 9.42, $J_{1,3}$ = 1.06, $J_{1,4}$ = 0.91, $J_{2,3}$ = 5.14 Hz), which indicates that C_2–C_5 comprise part of a six-membered ring.

Delocalization of charge is indicated by the proton chemical shifts in ion III. The protons H_7–H_9 in III are shifted considerably upfield relative to H_3 (τ 1.54) and H_4 (τ −1.10) in cyclopentenyl cation.[9] This demonstrates that C_7–C_9 in III are not part of an isolated allylic ion. The average shift of protons H_2–H_5 in III is τ 2.95, whereas that of the olefinic protons in 1,3-cyclohexadiene is τ 4.22 and that of naphthalene is τ 2.45. The deshielding of H_2–H_5 in III compared to H_1–H_4 in 1,3-cyclohexadiene indicates delocalization of positive charge onto C_2–C_5. This evidence for charge delocalization over the seven carbons C_2–C_5 and C_7–C_9 suggests the presence of homointeraction between C_2 and C_9, and between C_5 and C_7. In the transformation of ion II to ion III, four protons including the bridgehead, H_6, and the methyl protons are shifted upfield a total of *ca.* 13.1 ppm, and the other seven downfield *ca.* 16.6 ppm. The deshielding of the seven peripheral protons indicates the presence of a ring current in a seven-membered ring in analogy to that observed in monohomotropylium ion IV.[2] This, together with the evidence for charge delocalization, demonstrates substantial homoaromatic character in cation III.

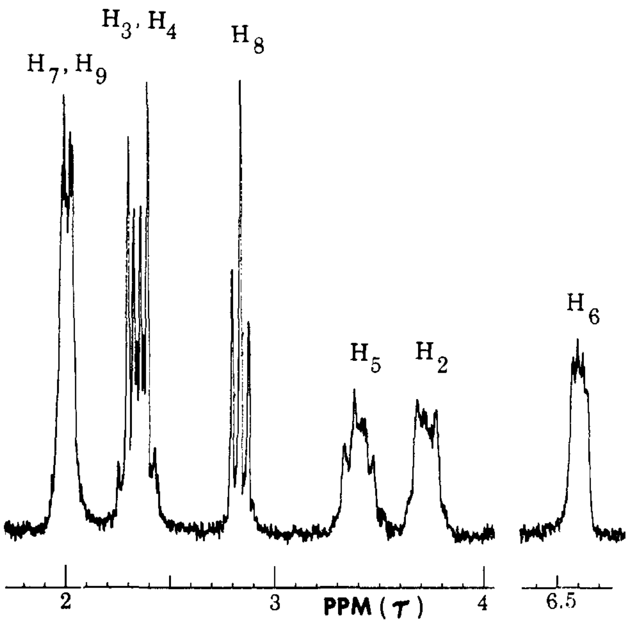

Figure 1. Nmr spectrum (100 MHz) of 1-methylbicyclo[4.3.0]-nonatrienyl cation(III) in FSO_3H-SO_2ClF (1:3 v/v) at −85° (the methyl absorption is not shown). $CDHCl_2$ was used as an internal standard, τ 4.70.

Work on the generation and observation of other bishomotropylium ions is in progress in these laboratories.

Acknowledgments. We wish to acknowledge the assistance of Dr. William D. Larson with the computer program LAME. Computing assistance was obtained from the Health Science Computing Facility, University of California at Los Angeles, sponsored by National Institute of Health Grant FR-3. P. A. is grateful for travel grants from Wallenberg's Travel Fund at Umeå University, Umeå, Sweden, and The Swedish Natural Science Research Council.

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(8) Private communication from Dr. B. Kaptein to Dr. F. A. L. Anet.

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(11) C. Ganter and J. D. Roberts, *J Amer. Chem. Soc.*, **88**, 741 (1966).

(12) Fritz O. Fernstrom Fellow, 1969–1970.

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Flash Vacuum Pyrolysis. VII.[1] Fulvenallene. The Ring Contraction and Expansion of Phenylcarbene

Sir:

It now appears that the high-temperature fragmentation of aromatic intermediates such as **1a–c** to cyclo-

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(1) Part VI: E. Hedaya, I. S. Krull, R. D. Miller, M. E. Kent,