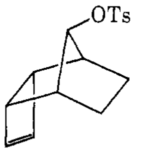
The alcohol mixture was converted to a 55:45 ketone mixture with CrO_3 in ether–water. The retention time of the major ketone was identical with that of authentic tetrahydrobarbaralone (XVI) prepared from barbaralone (XIX). The minor ketone was separated by preparative vpc, and this proved to be identical in ir and nmr spectra with the tetrahydrohomosemibullvalene ketone (XV) which was prepared from the homosemibullvalene ketone (XVIII) available from another investigation.[4]

As regards reactivity in solvolysis, that of the *syn*-X-OTs is essentially the same as that of 7-norbornyl-OTs at 180°. On the other hand, the reactivity of the *anti*-III-OTs, whose configuration is stereoelectronically suitable for edge participation by the cyclobutane ring, is greatly enhanced over that of 7-norbornyl-OTs. At 25°, the rate factor is $10^{4.3}$. The rate enhancement is even greater with the *anti*-VIII-OTs which contains a cyclobutene ring instead of cyclobutane. The rate factor in this case compared to 7-norbornyl-OTs is $10^{5.8}$ at 25°.



VIII-OTs, $10^{5.8}$

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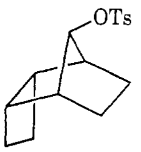

III-OTs, $10^{4.3}$

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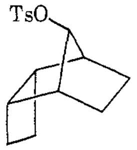

X-OTs, 1.2

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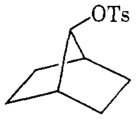

1

It is evident that the anchimeric assistance which a β-cyclobutane ring in III-OTs provides is a substantial fraction of that provided by the cyclopropane ring in II. Since solvolysis of 7-norbornyl-OTs is already somewhat anchimerically assisted,[9] the factor of $10^{4.3}$ between rates of *anti*-III-OTs and 7-norbornyl-OTs is too low a figure for the anchimeric acceleration in III-OTs. On this basis, it is clear that the anchimeric assistance provided by the cyclobutane ring in III-OTs is at least one-third that of the cyclopropane ring in II.[10] The fraction is larger, approaching one-half, in the case of the cyclobutene ring in VIII-OTs. To what extent the increase in anchimeric assistance which is provided by inclusion of the olefinic group in VIII-OTs may be ascribed to increased strain of the ground state or to conjugative stabilization of the transition state is not yet clear.

As regards the course of solvolysis of III-OTs, it is most simply regarded as involving ionization to a trishomocyclopropenyl type cation (XII). On the basis of the observed products, this ion does not give rise to appreciable quantities of product III-OH with retained structure from attack of solvent at C_9. This is analogous to the situation prevailing with the ion from ionization of the cyclopropyl compound[3] II-OTs. Ion XII may be presumed to give rise to the 45% of tetrahydrohomosemibullvalene alcohol (XIV) by attack of solvent at C_2 and C_5. Competitive with this reaction is a Wagner–Meerwein rearrangement to the cyclopropylcarbinyl-type tetrahydrobarbaralyl cation (XIII) which is responsible for formation of the 55% of tetrahydrobarbaralol (XVII).

While solvolysis of III-OTs is most simply described as above, we do not yet have any really crucial evidence regarding the possible intervention of a rearranged classical ion (XIIa) in the formation of tetrahydrosemibullvalene alcohol (XIV) and the Wagner–Meerwein rearrangement to tetrahydrobarbaralyl ion (XIII). This is because we do not yet have evidence as to the epimeric configuration of tetrahydrohomosemibullvalene alcohol (XIV). Since a mixture of epimers might well be expected from classical ion XIIa, and since only one epimer of XIV was observed by analytical vpc, the *endo* configuration, predicted from the trishomocyclopropenyl type ion XII on stereoelectronic grounds, is presumed for XIV. The *endo* configuration of the analogous product is observed in solvolysis of the cyclopropyl system II.[3]

β-Cyclopropane participation has been illustrated in a considerable number of systems; it is now clear that there is a definite, but reduced, tendency for similar participation by the cyclobutane ring. The scope of such participation remains to be explored.

Acknowledgment. We are grateful to Dr. Pommer of the Badische Anilin und Soda-Fabrik in Ludwigshafen, Germany, for generous supplies of cyclooctatetraene.

[9] S. Winstein, F. Gadient, E. T. Stafford, and P. E. Klinedinst, Jr., *J. Amer. Chem. Soc.*, **80**, 5895 (1958).

[10] The importance of the spatial orientation in edge participation of the β-cyclobutyl group is indicated by contrasting the solvolytic behavior of III-OTs with homocubyl-OTs (IX-OTs).[6] In IX-OTs, where the incipient carbonium ion is further removed from the plane of the cyclobutane ring, solvolysis proceeds with a 1,2 C,C participation with no evidence of edge participation.

(11) Deceased Nov 23, 1969.

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Contribution No. 2497, Department of Chemistry
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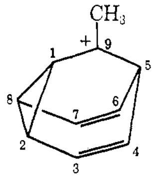
Received February 11, 1970

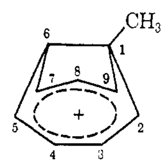
Direct Observation of the Totally Degenerate 9-Barbaralyl Cation and the Bicyclo[4.3.0]nonatrienyl Cation, a 1,4-Bishomotropylium Ion[1]

Sir:

In previous communications[2] we have reported the direct observation of the 9-methyl-9-barbaralyl cation (I), which undergoes a partially degenerate rearrangement, probably involving a series of divinylcyclopropylcarbinyl–divinylcyclopropylcarbinyl rearrangements, as well as the exclusive rearrangement of I to the 1-methylbicyclo[4.3.0]nonatrienyl cation (II), a 1,4-bishomotropylium ion. The interesting 9-barbaralyl cation (V)



I



II

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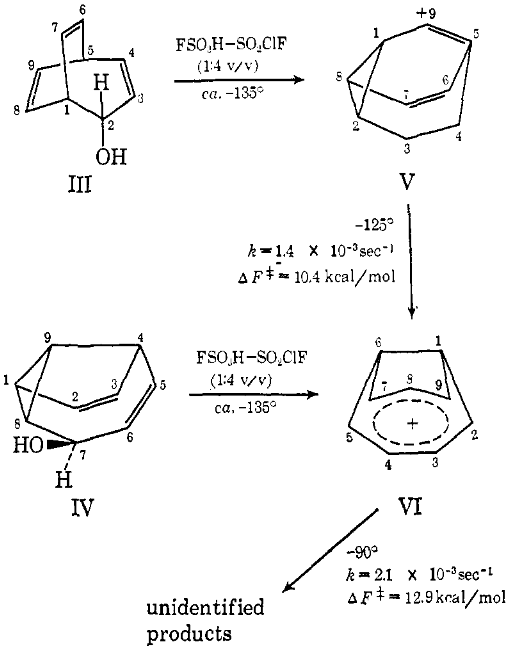
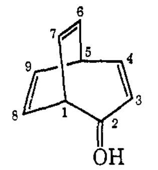
[1] Research supported in part by the National Science Foundation.

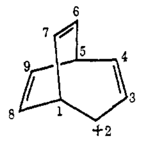
[2] (a) P. Ahlberg, J. B. Grutzner, D. L. Harris, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 3478 (1970); (b) P. Ahlberg, D. L. Harris, and S. Winstein, *ibid.*, **92**, 2146 (1970).

has become the subject of detailed solvolysis studies[3a–c] recently, usually in connection with attempts to investigate the bicyclo[3.2.2]nonatrienyl cation (VIII), a potentially "antibicycloaromatic" species.[4] These studies have revealed the existence of a low-energy, threefold-degenerate rearrangement of cation V,[3a,c] as well as indications of a slower, totally degenerate process.[3a] We now wish to report the successful generation and direct observation of the totally degenerate 9-barbaralyl cation (V) in super acid media, as well as its rearrangement product, the 1,4-bishomotropylium ion, bicyclo[4.3.0]nonatrienyl cation (VI).





VII



VIII

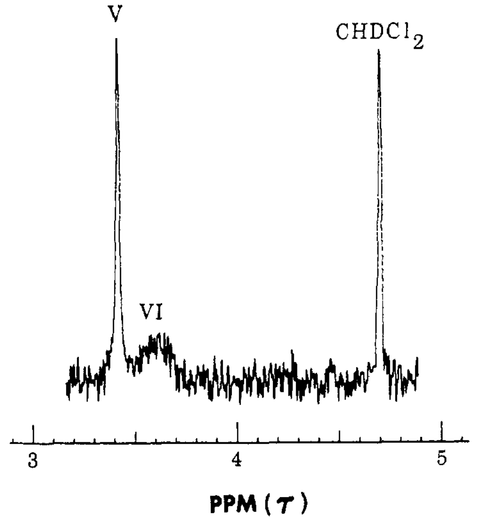
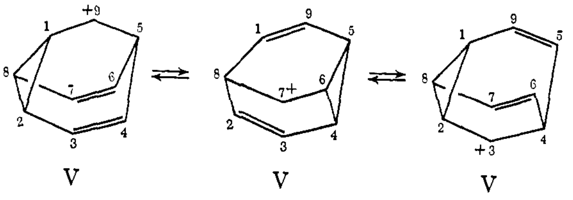


Figure 1. HA-100 nmr spectrum of the 9-barbaralyl cation (V) at −125°. Cation VI appears as an impurity. $CHDCl_2$ internal standard at τ 4.70.

Ion V was prepared by extraction of bicyclo[3.2.2]nona-3,6,8-trien-2-ol (III)[4a] from a CD_2Cl_2 solution into a mixture of FSO_3H–SO_2ClF (1:4 v/v) at *ca.* −135° and observed by nmr at *ca.* −125°. The nmr of V (Figure 1) shows only a sharp singlet at τ 3.41 which indicates that the cation is undergoing very rapid degenerate rearrangements. The ion is inferred to be the 9-barbaralyl cation from the chemical shift of the sharp singlet compared to the nmr data of ion I[2b] and of protonated bicyclo[3.2.2]nona-3,6,8-trien-2-one (VII).[2a] The average chemical shift for the eight protons H_1 to H_8 in ion I is τ 4.28. When the downfield shift observed for the methyl group, which is carrying part of the charge, in I relative to the methyl group in 9-methyl-9-barbaralol is distributed over H_1 to H_8 the new average is τ 3.59. This average is assumed to be closer to the expected value for ion V than τ 4.28.[5a] That the bicyclo[3.2.2]nonatrienyl cation (VIII) is the ion observed is considered unlikely, since the protonated ketone VII exhibits an average chemical shift for the carbon-bound protons of τ 3.27 and the average chemical shift of the cation VIII should be appreciably more downfield.[5b] However, the observed singlet chemical shift is probably a weighted average of those for V and VIII, since these two species are presumed to be in rapid equilibrium (*vide infra*). The divinylcyclopropylcarbinyl–divinylcyclopropylcarbinyl rearrangement suggested to be responsible for the partially degenerate character of ion I[2a] are expected to be present in V with a substantially lower energy barrier. This mechanism (eq 1) leads to a threefold degenerate ion with a presumed nmr of two signals in the ratio 3:6. The total degeneracy observed can be simply rationalized by invoking ion VIII (eq 2). If the rearrangements in eq 2 are very fast a sharp singlet would be observed in the nmr. Thus, the observed total degeneracy of ion V can be accounted for by eq 2 or a combination of eq 1 and 2. An upper limit for the barrier of the total degenerate rearrangement is estimated to be 6 kcal/mol. Thus the suggested mechanism implies that ion VIII is at most 6 kcal/mol less stable than ion V. When III-2-*d* is used as a precursor and the deuterium distribu-



(1)

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[3] (a) J. C. Barborak, J. Daub, D. M. Follweiler, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 7760 (1969); (b) J. C. Barborak and P. v. R. Schleyer, *ibid.*, **92**, 3184 (1970); (c) J. B. Grutzner and S. Winstein, *ibid.*, **92**, 3186 (1970); (d) 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); (e) H. Westberg, Ph.D. Thesis, University of Washington, 1969.

[4] (a) M. J. Goldstein and B. G. Odell, *J. Amer. Chem. Soc.*, **89**, 6356 (1967); (b) M. J. Goldstein, *ibid.*, **89**, 6357 (1967).

[5] (a) An inherent assumption in this type of calculation is that the change in chemical shift with a change in charge is identical for all types of protons, which is not absolutely true. However, our use of this method is intended only to indicate the expected changes in chemical shifts qualitatively; (b) M. Brookhart, Ph.D. Thesis, University of California, Los Angeles, Calif., 1968.

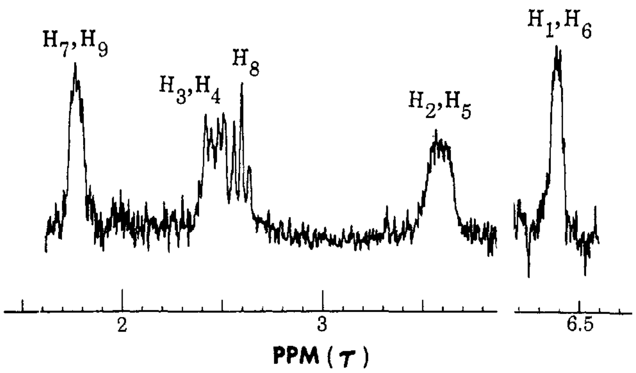
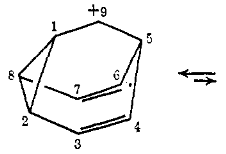
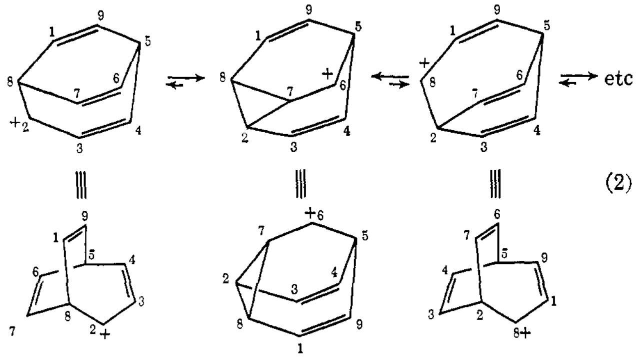


Figure 2. HA-100 nmr spectrum of the bicyclo[4.3.0]nonatrienyl cation (VI) at −125°. $CHDCl_2$ internal standard at τ 4.70.

tion is measured[6] in VI-*d*, it is found that the deuterium is statistically distributed, which is fully consistent with the totally degenerate character of V.



V



(2)

Ion V rearranges exclusively to ion VI which was also generated more directly from *exo*-tricyclo[6.1.0.0^{4,9}]-nona-2,5-dien-7-ol (IV).[7] The structure, bicyclo[4.3.0]-nonatrienyl cation,[8] was assigned to VI on the basis of its nmr data compared to those of 1-methylbicyclo-[4.3.0]nonatrienyl cation (II)[2b] (Table I). The coupling constants of cation VI (Table I) were obtained through a series of double-irradiation experiments (see Figure 2 for undecoupled nmr spectrum) and by analyzing the nmr of protons H_3, H_4, and H_8 obtained after 25 scans with a time-averaging computer while double irradiating both H_1 and H_6. The chemical shifts of VI show that it, like ion II, has substantial homoaromatic character, which possibly contributes to its greater stability relative to the 9-barbaralyl cation.

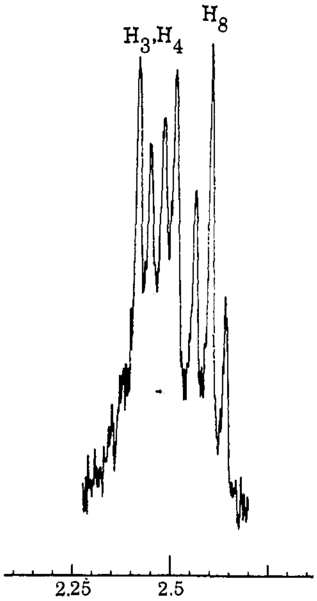
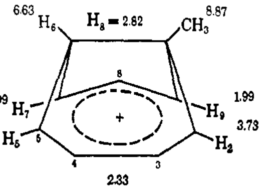


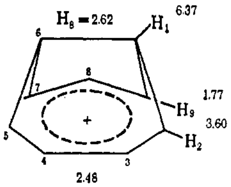
Figure 3. HA-100 nmr spectrum of H_3, H_4, and H_8 in bicyclo[4.3.0]-nonatrienyl cation (VI) (see Figure 2) at −125° after 25 scans with a time-averaging computer while double-irradiating H_1 and H_6. $CHDCl_2$ internal standard at τ 4.70.

Table I



II

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]



VI

J	2,3 (4,5)	2,4 (3,5)	2,5	3,4	7,8 (8,9)	1,3 (4,6)
Hz	8.4	0.9	0.0	6.7	3.9	0.8

[a] Calculated. [b] Measured.

Acknowledgments. For many stimulating discussions and for technical assistance, we wish to thank the members of Professor Winstein's group. 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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(6) The deuterium distribution was estimated by weighing the appropriate recorded nmr signals.

(7) Alcohol IV was prepared by singlet oxygen oxidation of the hydrocarbon and its structure was rigorously proven by nmr spectroscopy: M. Sakai, D. L. Harris, and S. Winstein, to be published.

(8) The great difference between the chemical shifts of H_2, H_5, H_7, and H_9 in ions II and VI and those of typical cyclopropylcarbinyl cations does not justify envisioning these ions as closed tetracyclo-[4.3.0.0^{2,9}.0^{5,7}]non-3-en-8-yl cations, as has been suggested by a referee.

(9) (a) Fritz O. Fernstrom Fellow, 1969–1970; (b) to whom inquiries should be addressed: Chemical Institute, Department of Organic Chemistry, Upsala University, Upsala, Sweden.

(10) Deceased Nov 23, 1969.

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