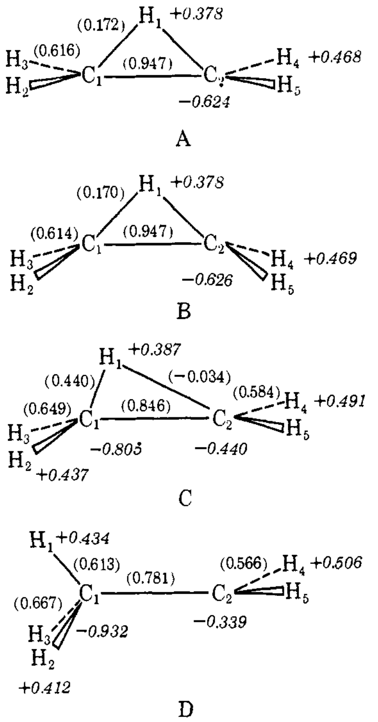


Figure 1. Conformations, charge densities (italicized), and overlap populations (in parentheses) for various bridged and open ethyl cations. See text for details of geometry of each structure.

mation for CH_3^+.[7] As observed by others, when this structure is distorted from strict tetrahedral and trigonal bonding we find that a lower energy is obtained for structure D shown in Figure 1. No attempt has been made to minimize the energy of this structure with respect to bond lengths and bond angles. Instead we have bent the $C_2H_4H_5$ group 3° counterclockwise out of the trigonal plane and bent the $C_1H_1H_2H_3$ group 6° clockwise with respect to the trigonal plane. We find this structure to be approximately 0.5 kcal/mol more stable than the open structure with tetrahedral and trigonal bonding.

For the bridged or nonclassical ethyl cation the "protonated ethylene" structure shown as structure A in Figure 1 was first examined. This structure was optimized with respect to the CC and CH bonds, the HCH angle, and the height of the bridging hydrogen. We find $r_{CC} = 1.483$ Å, $r_{CH} = 1.11$ Å, HCH angle = 120°, and the bridging hydrogen 1.2 Å above the CC bond. The $C_1H_1C_2$ plane is a plane of symmetry for this structure. Additional structures were then examined in which a plane of symmetry bisects the CC bond and passes through H_1. The lowest energy was found for the conformation indicated as structure B in Figure 1. The CC and CH bond lengths and the HCH angle were fixed and the planes of the CH_2 groups were bent away from the bridging hydrogen such that these planes are 3° below an extension of the CC line. Structure B is approximately 0.3 kcal/mol more stable than structure A. The breakdown of the total energy into its components for structures A and B reveals that the stability of the latter is due solely to a decrease in nuclear–nuclear repulsion terms upon bending. The kinetic energy, nuclear–electron attraction, and electron–electron repulsion terms all favor structure A. The population analyses indicate that the overlap populations increase in the C_1C_2 bond and decrease in the C_1H_1 bond of B in comparison to A. The charge densities of Figure 1 also indicate that protonated ethylene is an inappropriate description for the bridged structure. In actuality all of the hydrogens have some deficiency in electronic charge, but the bridging hydrogen is considerably less deficient than the terminal hydrogens H_2,H_3,H_4,H_5. Comparing the charge densities for structures A, B, and D we see that the charge density associated with H_1 increases in going from the open to the bridged form while the charge density associated with H_2 and H_3 decreases from D to B. The charge densities shown in Figure 1 support the conventional viewpoint of describing the open structure as "charge localized" and the bridged structure as "charge delocalized."

In order to determine whether structure B is an activated complex or an intermediate for 1,2 hydride migration we examined many conformations in which the structural parameters of B were slightly altered. The bridging hydrogen, H_1, was first allowed to move a short distance (0.026 Å) toward C_1 while maintaining its 1.2-Å distance above the C_1C_2 bond. No significant change in the energy was observed. The charge density on C_1 was found to increase as does the C_1–H_1 overlap population. Two other structural changes in B were considered: (1) increase in the angle of the $C_1H_2H_3$ plane to 5° below the C_1C_2 bond; (2) restoration of the trigonal conformation of the $C_2H_4H_5$ group. Both of these changes (separately and jointly) led to conformations of higher energy than structure B. We found that lower energy structures could be found if the bridging hydrogen was allowed to migrate to a position 0.26 Å from C_1 (maintaining a height of 1.2 Å above the C_1C_2 bond). If the additional structural changes mentioned above are then carried out the energy is further lowered and we arrive at structure C of Figure 1. The population analysis for structure C shows a large increase in the charge on C_1 compared to structure B. A large decrease in charge is also observed on C_2 in structure C, and our results indicate that the major orbital change is in the $C(2p_y)$ orbitals on both centers. We believe that structure C is a reasonable representation of a point on the reaction path leading from B to D. Our calculations on other structures also indicate that the points on such a reaction path will all be lower in energy than structure B and hence that B represents an activated complex for 1,2-hydride migration in ethyl cation.

Acknowledgments. This work was supported in part by a grant from the National Science Foundation (GP 8703). The computation time was provided by the Ohio University Computer Center which is partially supported by a grant from the National Science Foundation (GJ 352).

Gary V. Pfeiffer, J. G. Jewett
Clippinger Research Laboratories, Department of Chemistry
Ohio University, Athens, Ohio 45701
Received January 31, 1970

---

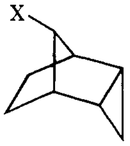
[7] J. E. Williams, Jr., R. Sustmann, L. C. Allen, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 91, 1037 (1969).

Extensive Cyclopropyl Participation at a Remote Carbonium Ion Site

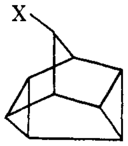
Sir:

The efficacy of cyclopropane as a neighboring group in solvolytic reactions has been probed on a number of occasions in recent years with contrasting results.[1] Thus, whereas the tricyclic and pentacyclic systems I[1d,e] and II[11] display extraordinarily accelerated solvolytic rates, the corresponding rate enhancements observed for the remainder[1a–c,f–k,m] of the systems studied may be described as modest, at best. Apparently the orientation of the cyclopropane ring in I and II is structurally and spatially ideal for participation at the developing carbonium ion center. Recently, evidence suggesting cyclopropyl participation at the more remote primary center in III has been presented;[1m] however, the degree of anchimeric assistance was meager (*ca.* $10^{0.5}$). In sharp contrast with this result, we now report convincing evidence for *extensive* cyclopropyl participation (*ca.* 10^5–10^8) at a similarly remote secondary carbonium site in the trismethanonaphthalene system IV. For both systems, III and IV, the reaction site is four bonds (five atoms) removed from the cyclopropane ring; however, the fixed spatial arrangement in IV considerably enhances the possibilities for participation.

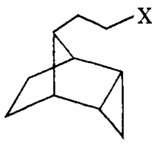
In view of the overwhelming stereochemical preference for *exo* cyclopropanation of the norbornene double bond,[2] it was anticipated that adoption of such procedures to the known[3] unsaturated alcohol V-OH should yield the requisite alcohol IV-OH in isomerically pure form. Synthesis of V-OH was accomplished by the following improved variation of the published route. Reaction of hexachlorocyclopentadiene with *anti*-7-norbornenyl acetate (VI-OAC) gave the expected Diels–Alder adduct VIIa,[4] mp 132–132.5°, which was converted to the hexachloro alcohol VIIb, mp 109–110°, by lithium aluminum hydride reduction. Dechlorination of VIIb with sodium-*t*-butyl alcohol–tetrahydrofuran led to V-OH, mp 107–109°, identical in all respects with the previously reported material.[3]



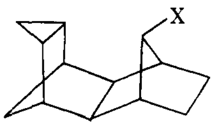
I



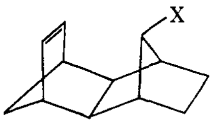
II



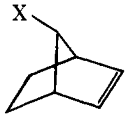
III



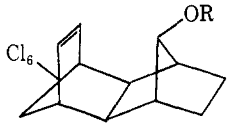
IV



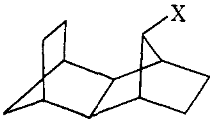
V



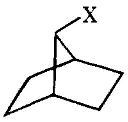
VI



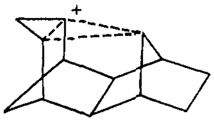
VIIa, R = Ac
b, R = H



VIII



IX



X

Cyclopropanation of V-OH with CH_2N_2–CuCl did in fact give rise to IV-OH, mp 121–122°, but surprisingly large amounts of its methyl ether, IV-OMe, were also formed. Uncontaminated IV-OH was obtained in almost quantitative yield, however, by cyclopropanation of the unsaturated acetate, V-OAc, followed by lithium aluminum hydride reduction. Pentacyclic IV-OH and its derivatives, IV-OMe, IV-OPNB (mp 152.5–152.8°), and IV-OBs (mp 118–119°), were characterized by their nmr spectra which showed a one-proton resonance at *ca.* τ 10.0, the position and pattern of which was typical of *exo*-tricyclo[3.2.1.$0^{2,4}$]octanes.[5]

Although the *p*-nitrobenzoate of IV was stable to conditions under which I-OPNB readily solvolyzed, acetolysis of IV-OBs at several temperatures proceeded smoothly giving good first-order plots through at least two half-lives. The appropriate rate and activation parameters are: 55.20°, $k = 3.57 \times 10^{-5}$ sec^{-1}; 67.65°, $k = 1.55 \times 10^{-4}$ sec^{-1}; 79.60°, $k = 6.49 \times 10^{-4}$ sec^{-1}; 25°, $k = 9.95 \times 10^{-7}$ sec^{-1} (extrapolated); $\Delta H^{\ddagger} = 26.8$ kcal/mol; $\Delta S^{\ddagger} = -2.4$ eu. For comparison, the relative solvolytic reactivities of several bridged norbornyl systems are summarized in Table I. From these data it is clear that the ionization of IV-OBs is accelerated over that for the saturated tetracyclic ester VIII-OBs[6] by nearly 10^5. Since the solvolysis of VIII-OBs proceeds with complete rearrangement and is itself considered to be anchimerically accelerated,[6] a perhaps better measure of the extent of cyclopropyl participation is obtained by comparison with 7-norbornyl brosylate (IX-OBs)[7] leading to an accelerative factor of *ca.* 10^8.

Table I. Relative Solvolytic Rates of Some Bridged Esters

Compound	I[a]	II[b]	IV	V[c]	VI[d]	VIII[e]	IX
Rel k (25°)	10^{14}	10^{12}	$10^{8.2}$	$10^{10.6}$	$10^{11.1}$	$10^{3.6}$	1.0

[a] Reference 1d,e. [b] Reference 11. [c] Reference 3. [d] Reference 7. [e] Reference 6.

The acetolysis product from IV-OBs is saturated and consists of an as yet unidentified mixture of at least eight components, although some are present in very minor amounts. The nmr spectrum of the crude acetolysis mixture clearly revealed the absence of IV-OAc and any brosylate derivatives, rearranged or unrearranged.[8] The

---

[1] (a) S. Winstein, E. C. Friedrich, R. Baker, and Y. Lin, *Tetrahedron Suppl.*, **8**, Part II, 621 (1966), and earlier references; (b) K. B. Wiberg and G. R. Wenzinger, *J. Org. Chem.*, **30**, 2278 (1965); (c) A. K. Colter and R. C. Musso, *ibid.*, **30**, 2462 (1965); (d) H. Tanida, T. Tsuji, and T. Irie, *J. Amer. Chem. Soc.*, **89**, 1953 (1967); (e) M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *ibid.*, **89**, 1954 (1967); (f) P. K. Freeman and D. M. Balls, *Tetrahedron Lett.*, 437 (1967); (g) C. F. Wilcox and R. G. Jesaitis, *ibid.*, 2567 (1967); (h) M. A. Eakin, J. Martin, and W. Parker, *Chem. Commun.*, 955 (1967); (i) M. J. S. Dewar and J. M. Harris, *J. Amer. Chem. Soc.*, **90**, 4468 (1968); (j) Y. E. Rhodes and T. Takio, *ibid.*, **90**, 4469 (1968); (k) G. D. Sargent, R. L. Taylor, and W. H. Demisch, *Tetrahedron Lett.*, 2275 (1968); (l) R. M. Coates and J. L. Kirkpatrick, *J. Amer. Chem. Soc.*, **90**, 4162 (1968); (m) R. Muneyuki, T. Yano, and H. Tanida, *ibid.*, **91**, 2408 (1969).

[2] H. E. Simmons, E. P. Blanchard, and R. D. Smith, *ibid.*, **86**, 1347 (1964); J. Haywood-Farmer, R. E. Pincock, and J. I. Wells, *Tetrahedron*, **22**, 2007 (1966); M. A. Battiste and M. E. Brennan, *Tetrahedron Lett.*, 5857 (1966).

[3] S. Winstein and R. L. Hansen, *ibid.*, No. 25, 4 (1960).

[4] All new compounds reported gave elemental analyses and spectral data in accord with their assigned structures.

[5] *Cf.* J. S. Haywood-Farmer and R. E. Pincock, *J. Amer. Chem. Soc.*, **91**, 3020 (1969), and pertinent references cited therein.

[6] S. Winstein and R. L. Hansen, *ibid.*, **82**, 6206 (1960).

[7] S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *ibid.*, **77**, 4183 (1955).

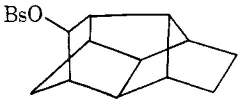
[8] (a) Ionization of V-OBs in acetic acid proceeds with significant ion-pair return to a less reactive sulfonate ester shown to have structure

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.

Acknowledgment. Financial support of this work by the National Science Foundation (Grants No. GP-9412 and GP-6568) is gratefully acknowledged.

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.

Merle A. Battiste,[9a] John Haywood-Farmer
Herbert Malkus
Department of Chemistry, University of Florida
Gainesville, Florida 32601

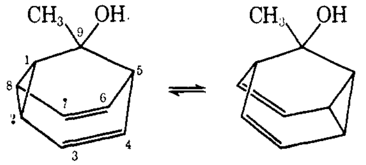
P. Seidl,[9b] S. Winstein
Contribution No. 2496, Department of Chemistry
University of California, Los Angeles, California 90024

Received December 3, 1969

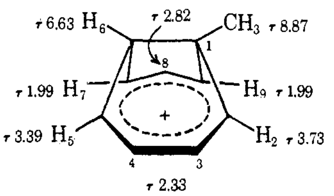
1-Methylbicyclo[4.3.0]nonatrienyl Cation. A 1,4-Bishomotropylium Ion[1]

Sir:

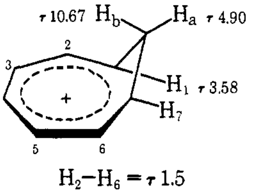
The successful generation and direct observation of the monohomotropylium ion (IV)[2] has inspired much work to show the existence of polyhomotropylium ions.[3] We now wish to report the first successful generation and observation of one in a series of potential bishomotropylium ions, the 1,4-bishomotropylium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



I



III



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 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.

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

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.

(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.