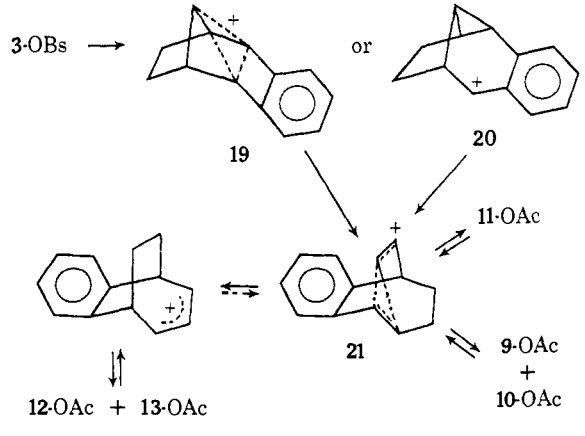
products. The configurations of alcohols **11–13** were established by hydrogenation and examination of the infrared spectra of the saturated alcohols for intramolecular O–H···π absorption.

Since alcohols **12** and **13** appeared to be the products of multiple rearrangements and hence likely of thermodynamic rather than kinetic origin, the stability of the five acetates **9**-OAc–**13**-OAc was examined under the solvolysis conditions (HOAc–NaOAc, 125°, ten half-lives). With the exception of some epimerization at C-2 acetates **12**-OAc and **13**-OAc are largely (85–90%) unscrambled as is acetate **11**-OAc (77 ± 2% recovery). On the other hand **9**-OAc and **10**-OAc are converted to essentially identical mixtures of the five acetates and in almost the same relative proportions as obtained in the original solvolysis of **3**-OBs.

The acetolysis product mixture from *syn*-**4**-OBs (200°, ten half-lives) was exceedingly complex with over 20 components detected by glpc analysis of the crude alcohol product obtained after lithium aluminum hydride reduction. Of the six major alcohol components (69% by peak area) three were separated by preparative glpc and identified as **11** (7%), **12** (8%), and **13** (9%). The remaining three major components, comprising 45% of the total acetolysis product, have not been identified as yet owing to their poor separation by preparative glpc. However, it is clear from their glpc retention times and composite nmr spectra that they are not identical with any other alcohols previously characterized in this study. In any event the forcing conditions (200°) required for the solvolysis of **4**-OBs tend to rule out mechanistic speculation based on product analyses of acetates already shown to be moderately unstable at lower temperatures (125°)

Although critical data regarding the precise nature of the initial ion(s) produced upon ionization of **3**-OBs are not available from this study, homocyclobutylcarbinyl rearrangement to give ion **19** or **20** is clearly implicated. Subsequent rearrangement to the cyclopropylcarbinyl cation **21** followed by solvent attack and/or further rearrangement provides an adequate rationale for the observed products as indicated in Scheme I. Alternatively, the failure to detect products

Scheme I



arising from ion **20** (or **19**) may be attributed to the anticipated reactivity of such benzylic acetates and their facile rearrangement under the imposed conditions. Further clarification of these points is now under investigation.

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(11) Alfred P. Sloan Foundation Fellow, 1967–1969.

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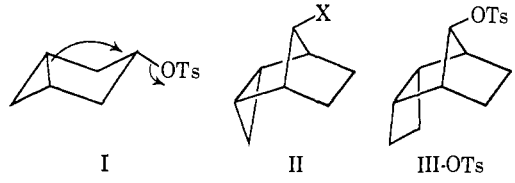
Edge Participation by a β-Cyclobutane Ring in a 7-Norbornyl System[1]

Sir:

Edge participation of a β-cyclopropyl group in solvolysis with formation of a trishomocyclopropenyl cation was first observed with system I.[2] When the cyclopropyl group is placed in a 7-norbornyl system (II), the anchimeric acceleration observed (10^{14}) is most impressive.[3] Similar edge participation by a cyclobutane ring, at least to some degree, can be visualized on theoretical grounds, and this is the subject of the present communication.



I II III-OTs

Since a 7-norbornyl system would appear to be most suitable for disclosing cyclobutane participation if it should prove to be marginal, we have studied the *endo,anti*-III system as well as the epimeric *endo,syn*-X system. The results are reported and discussed in the present communication.

The synthetic route to the III and X systems started most conveniently in these laboratories with the bicyclo[4.2.1]nonatrienol IV, available from another investigation.[4] Irradiation of a 2% solution of alcohol IV in pentane in a Pyrex flask, followed by column chromotography and recrystallization, gave alcohol[5] V, mp 88.0–89.0°, in 50–60% yields. The structure and configuration of V are clear from its chemical properties and nmr spectrum. Conclusive proof of the *endo* fusion of the cyclobutene ring to the norbornene moiety in V is the photochemical conversion of V to homocubyl alcohol[6] IX. Thus, without any attempt to optimize the conversion, irradiation of V in acetone solvent, followed by preparative vpc and recrystallization, led to a 30% yield of homocubyl alcohol, mp 158.0–158.5° (lit.[6b] mp 157°), with nmr and ir spectra

(1) This research was supported in part by the National Science Foundation.

(2) (a) S. Winstein, J. Sonnenberg, and L. de Vries, *J. Amer. Chem. Soc.*, **81**, 6523 (1959); (b) S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3235, 3244 (1961); (c) S. Winstein, E. C. Friedrich, R. Baker, and Y. Lin, *Tetrahedron, Suppl.*, No. 8, Part II, 621 (1966).

(3) (a) H. Tanida, T. Tsuji, and T. Irie, *J. Amer. Chem. Soc.*, **89**, 1953 (1967); (b) M. A. Battiste, C. L. Dreyrup, R. E. Pincock, and J. Haywood-Farmer, *ibid.*, **89**, 1954 (1967); (c) J. Haywood-Farmer and R. E. Pincock, *ibid.*, **91**, 3020 (1969).

(4) M. Sakai and J. B. Smith, unpublished work.

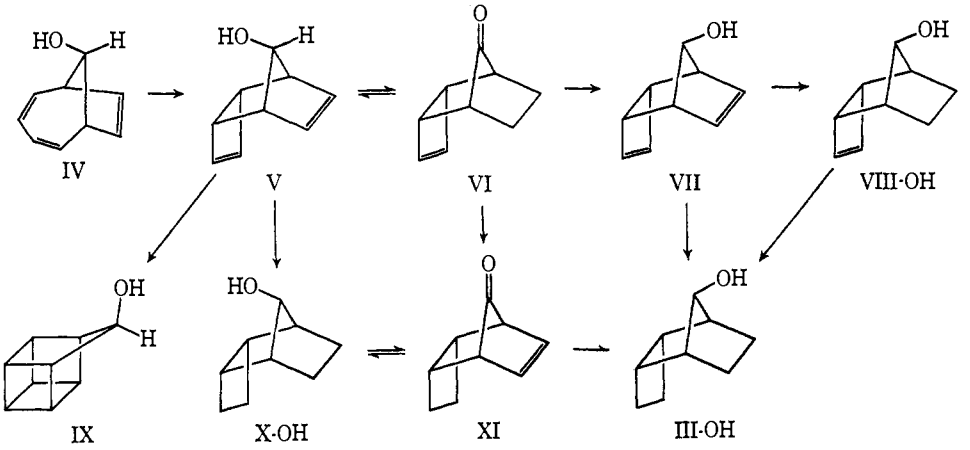
(5) All new compounds reported gave elemental analyses and spectral data in accord with their assigned structures.

(6) (a) W. G. Dauben and D. L. Whalen, *J. Amer. Chem. Soc.*, **88**, 4739 (1966); (b) P. v. R. Schleyer, *et al.*, *ibid.*, **89**, 698 (1967).

identical with those for authentic homocubyl alcohol provided by Dauben.[6a] Conclusive proof of the epimeric configuration of V comes from the comparison with its epimer VII obtained by CrO_3 oxidation of V to the ketone[7] VI, followed by Na in liquid ammonia reduction of the latter to give a 55:45 mixture of V and VII. Column chromotography and recrystallization led to pure VII, mp 41.5–42.5°. The disposition of the hydroxyl group *syn* to the olefinic group in VII was shown by conversion of VII to VIII by treatment with excess lithium aluminum hydride in ether for 15 hr, followed by a water work-up. Recrystallization led to pure VIII, mp 90–92°.

Hydrogenation of V led to the saturated *syn* alcohol X-OH, mp 115–117°. CrO_3 oxidation of the latter led to the saturated ketone XI which was reduced to a roughly 50:50 mixture of the epimeric saturated alcohols X-OH and III-OH by $NaBH_4$, $LiAlH_4$, or $Al(OPr\text{-}i)_3$. These saturated epimeric alcohols were very difficult to separate, so the pure *anti* alcohol III-OH, mp 99.0–100.0°, was prepared by hydrogenation of the unsaturated alcohol VII. The *anti* alcohol III-OH was also obtained from hydrogenation of VIII.

Rates of acetolysis were measured on the tosylate esters III-OTs, mp 71–72°, VIII-OTs, mp 72–73°, and X-OTs, mp 67.5–68.0°, for comparison with the rate of 7-norbornyl tosylate.[8] The results are summarized in Table I. Products of solvolysis have been examined from the saturated *anti*-III-OTs in AcOH–NaOAc at 125°. The product (97% yield) was a mixture of two acetates in 56:44 proportions as given by analytical vpc. Conversion of the acetates to alcohols with lithium aluminum hydride in ether gave a 55:45 mixture of two alcohols. A sample of the major one could be obtained in 95% purity by preparative vpc. Recrystallization of this material from pentane gave white crystals, mp 205–207°, with an ir spectrum identical with that of tetrahydrobarbaralol (XVII), mp 206–207°, prepared from barbaralone (XIX) *via* barbaralol (XX). Attempts to separate the minor alcohol in pure condition have so far been unsuccessful.



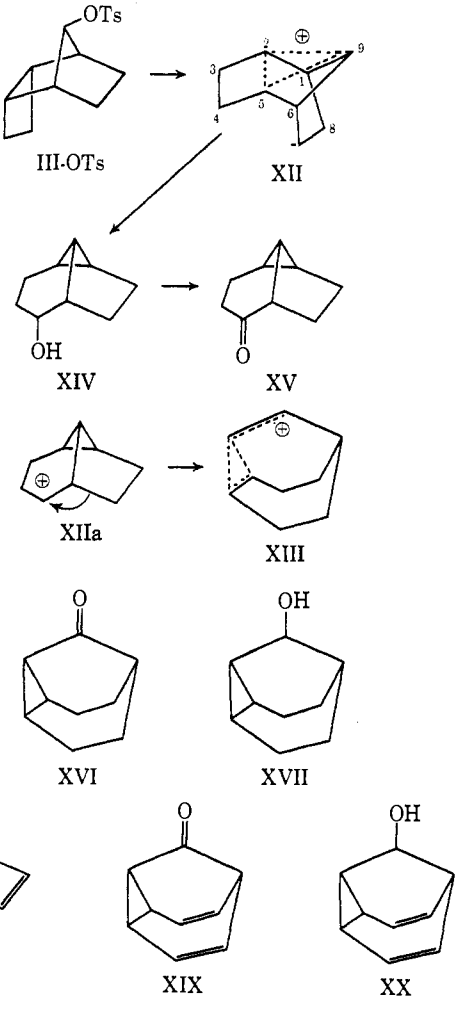


Table I. Acetolysis Rates of Some Toluenesulfonates

ROTs[a]	Temp, °C	10^6k, sec^{-1}	Rel Rate
7-Norbornyl	25.0[b,c]	5.88×10^{-9}	1
	180.0[d]	8.94 ± 0.14	
X-OTs	179.8[d]	10.3 ± 0.6	1.2
III-OTs	25.0[b]	1.22×10^{-4}	20,800
	100.0	4.02 ± 0.09	
	125.0	54.5 ± 0.6	
VIII-OTs	25.0[b]	3.57×10^{-3}	608,000
	100.0	32.0 ± 0.7	
	125.0	313 ± 5	

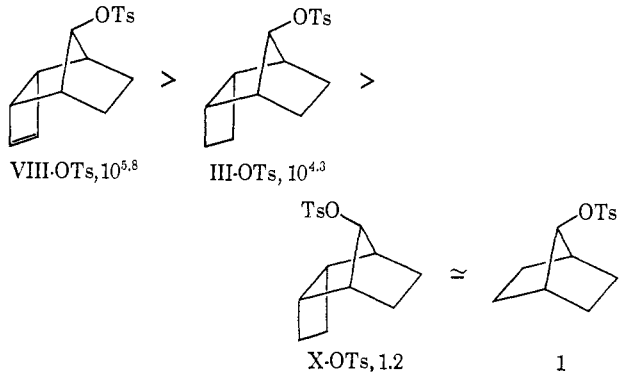
[a] *Ca.* 0.01 *M*. [b] Extrapolated from data at higher temperatures. [c] Extrapolated from the 180.0° point with a $\Delta H^{\ddagger}$ of 35.7 kcal/mol and a $\Delta S^{\ddagger}$ of −3.5 eu previously reported.[8] [d] 0.012 *M* NaOAc.

(7) This ketone is relatively unstable with respect to decarbonylation. Vapor-phase chromatography at a column temperature of 130° yields cyclooctatetraene quantitatively.

(8) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Amer. Chem. Soc.*, 77, 4183 (1955).

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°.



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.

(11) Deceased Nov 23, 1969.

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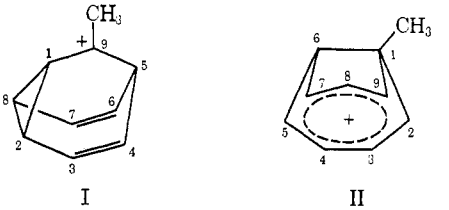
Direct Observation of the Totally Degenerate 9-Barbaralyl Cation and the Bicyclo[4.3.0]nonatrienyl Cation, a 1,4-Bishomotropylium Ion[1]

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

(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.

(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).