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SEARCH FOR THE POSSIBLE INTERMEDIACY OF A 1,4-BISHOMOTROPYLIUM ION IN SOLVOLYSIS

D. Cook, A. Diaz,[1a,b] J. P. Dirlam, D. L. Harris, M. Sakai, S. Winstein[1c]
Department of Chemistry, University of California, Los Angeles, California 90024
J. C. Barborak, P. von R. Schleyer[1a]
Department of Chemistry, Princeton University, Princeton, New Jersey 08540

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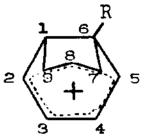
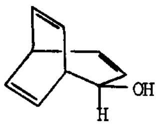
A cation, assigned the bridged 1,4-bishomotropylium structure I (R=H),[2] has been generated in superacid medium from several precursors: bicyclo[3.2.2]nonatrienol (II) (via the barbaralyl cation (III)[2]), exo-7-hydroxy-cis-bicyclo[4.3.0]nonatriene (IV-OH),[2] and exo-3-hydroxytricyclo[4.3.0.0^{2,9}]nona-4,7-diene (V-OH).[3]



I



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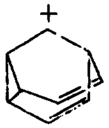

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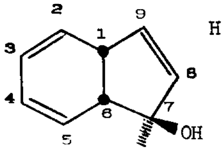
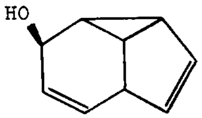
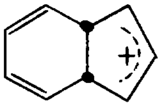


IV-OH



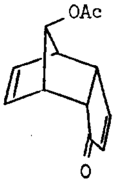
V-OH



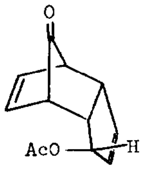
VI

The bishomotropylium structures of I (R=H) and its methyl homolog I (R=CH_3) were suggested by comparison of the pmr chemical shifts with reference allylic systems.[2] Protons attached to C_2 and C_3 resonated further downfield, while the C_7-C_9 proton derivatives gave signals further upfield than expected for the simple allylic cation, VI.[2] However, solvolysis of derivatives of II and III gave only barbaralyl products, and not those derivable from I.[4] We have now examined the solvolysis of the systems IV and V in search of evidence for the intermediacy of I.

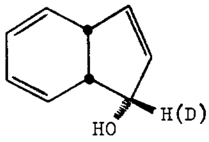
The alcohol, IV-OH, was prepared by solvolysis of the corresponding chloride in 60% aqueous acetone containing $NaHCO_3$.[5,6] The exo-OH stereochemistry of the solvolysis product was established by comparison with the endo isomer IX-OH, synthesized separately. One equivalent of sodium borohydride reduces the nonconjugated ketone function of cyclopentadienone dimer[7] exclusively; acetylation gives VII. The carbonyl group in VIII, expected to exist in thermal equilibrium with VII,[8] is especially labile;[9] pyrolysis of VII at 380° produces directly good yields of IX-OAc.[10] Use of $NaBD_4$ in the initial step of the synthesis provides IX-OH-7-D.[10] Homosemibullvalenyl alcohol, V-OH (m.p. 88.5-89.5°), was obtained by $NaBH_4$ reduction of the hydroperoxide mixture resulting from singlet oxygen oxidation of the corresponding hydrocarbon.[11] The structure of V-OH and its exo-OH stereochemistry have been deduced from nmr spectra and related decoupling experiments.[11] 3,5-Dinitrobenzoate (ODNB) and p-nitrobenzoate (OPNB) derivatives were prepared in the usual manner.



VII



VIII



IX-OH

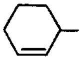
Solvolyses of IV-ODNB and IX-ODNB were carried out in 60% aqueous acetone; rate constants are summarized in the Table and are compared with data for model allylic systems. Both epimers, when solvolyzed under preparative conditions with lutidine as buffer, yielded IV-OH.[12] The only other detectable product,[12] indene, was isolated from solvolysis of IV-ODNB in trace amounts. Under identical conditions, IX-ODNB-7-D gave IV-OH in which 50±5% of the deuterium appeared at C_7, and 50±5% in the remainder of the molecule. No deuterium was found at positions 1 and 6; hence the remaining 50±5% D is olefinic. We presume this D to be at C_9, in agreement with the results of methanolysis of IV-Cl-7-D.[6]

Solvolysis of homosemibullvalenyl p-nitrobenzoate, V-OPNB, in 80% aqueous acetone (NaOAc buffer) gave 67% IV-OH; 33% of the rearranged ester, IV-OPNB; and traces of two unidentified products.[12] The presence of the rearranged ester complicated the kinetics of V-OPNB somewhat, but reasonably good first-order plots could be obtained after correction for the accompanying solvolysis of IV-OPNB (Table).

The exo/endo rate ratio, IV-ODNB/IX-ODNB, is only 8. In addition, neither isomer reacts as fast as cyclopent-2-enyl-ODNB, an allylic model compound. Although the cyclohexadiene moiety of IV and IX may be producing an inductive rate retarding effect, it seems clear that there is no evidence for a marked rate acceleration. While V-OPNB reacts more rapidly, this can reasonably be ascribed to a combination of allylic and cyclopropylcarbinyl resonance in the transition state, as well as relief of ring strain. All precursors, IV-ODNB, IV-OPNB, IX-ODNB, and V-OPNB, gave exo-7-cis-bicyclo[4.3.0]nona-2,4,8-trienyl products (IV-OH and IV-OPNB) almost exclusively,[13] suggesting a common cationic intermediate.

These results provide no definite evidence for the intermediacy of I.[13] The simplest intermediate consistent with the solvolysis results appears to be allylic cation VI (or ion pair), but the bishomotropylium cation cannot be ruled out. The extent to which I may be present as a stable intermediate is not being reflected in the rate determining ionization step, as indicated by the low exo/endo ratio and the lack of marked rate enhancement.

TABLE. KINETIC DATA FOR SOLVOLYSIS OF ALLYLIC ESTERS

	$k \times 10^5$, sec^{-1}						
COMPOUND	60% Acetone		80% Acetone				
	50°	75°	50°	75°	100°	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
 ODNB	57.8[a]	621[a,b]				20.6	-9.9
 ODNB	0.32[a,b]	5.31[a]				24.4	-8.3
IV-ODNB	11.0	99.5				19.9	-15.4
IX-ODNB	0.904	11.5				23.1	-10.5
IV-OPNB			0.033[b]	0.57	6.7	24.7	-11.8
V-OPNB			20[c]	150[c]	863[b]	17.4	-21.9

[a] W. Sliwinski, unpublished results, Princeton University. [b] Calculated values. [c] Based on 67% infinity titer.

References

(1) (a) Address inquiries to these authors. (b) Present address: Department of Chemistry, Revelle College, University of California, La Jolla, California 92037. (c) Deceased Nov. 23, 1969.

(2) P. Ahlberg, D. L. Harris, and S. Winstein, J. Amer.Chem.Soc., 92, 2146, 4454 (1970).

(3) This work; for experimental conditions, see ref. 2.

(4) (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).

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(6) J. C. Barborak, T. M. Su, P. v. R. Schleyer, G. Boche and G. Schneider, ibid., 93, 279 (1971).

(7) C. H. DePuy and B. W. Ponder, ibid., 81, 4629 (1959).

(8) R. B. Woodward and T. J. Katz, Tetrahedron, 5, 70 (1959).

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(10) In exo-IV-OH, $J_{H_6-H_7} = 4$ Hz, while in IX, $J_{H_6-H_7} = 7$ Hz, values consistent with the expected dihedral angles for these isomers.

(11) D. L. Harris, M. Sakai and S. Winstein, to be published.

(12) The presence of small amounts of endo-alcohol IX in these products could not be ruled out on the basis of glc as both epimers were unstable to heating; nmr indicated less than 5% of IX.

(13) A. S. Kende and T. L. Bogard, Tetrahedron Letters, 3383 (1967), drew similar conclusions following their preliminary results for the solvolysis of 1-phenyl-IV-Cl in aqueous methanol.

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