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SOLVOLYSIS AND DIRECT OBSERVATION STUDIES ON THE *exo*,*exo*-8-TRICYCLO[3.3.1.0^{2,4}] NON-6-ENYL SYSTEM[1]

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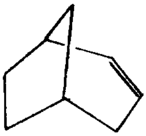
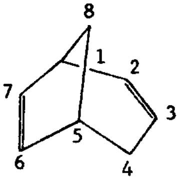
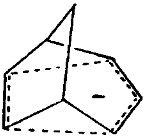
Recent studies on the anionic reactions of bicyclooctadiene, II, strongly suggest the direct involvement of the 6,7-olefinic group with the allylic anion to form the intermediate *bis*-homocyclopentadienyl anion, III, in accord with the bonding interaction predicted by HMO calculations.[4a] Specifically, II is more reactive than bicylooctene, I, in allylic proton-deuterium exchange by a factor of $10^{4.5}$ in DMSO-KOtBu at 50°.[5a] The nmr spectrum of III is also appropriate for the delocalized 6 π-electron *bis*-homoaromatic species with appreciable ring current.[4b,5b]



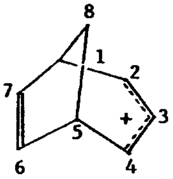
I



II

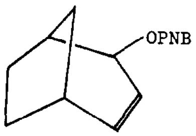


III

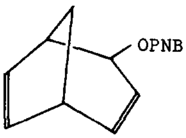


IV

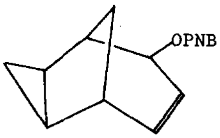
In the carbonium ion analog, IV, HMO calculations predict no stabilizing interaction between the allylic cation and the 6,7-olefinic group to form the 4 π-electron *anti*-homoaromatic *bis*-homocyclopentadienyl species.[6] Solvolysis of the bicyclooctadienyl *p*-nitrobenzoate, VI, in aqueous acetone proceeds 235 times slower than the monoene analog V. The rate retardation is probably even larger than can be ascribed to the rate-retarding inductive effect of the second olefinic group, which is in line with the *anti*-homoaromatic designation for the first intermediate cation formed in the solvolysis of the dienyl *p*-nitrobenzoate VI.[6b]



V - OPNB



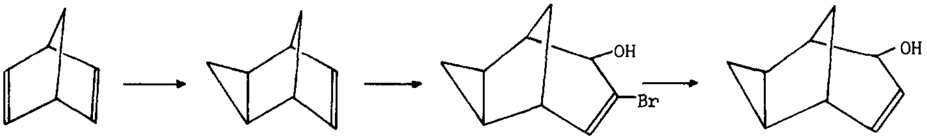
VI - OPNB



VII - OPNB

It is now recognized that edge participation of a β-cyclopropyl group can be more effective than that of olefinic group in the solvolysis of secondary systems. A striking example of this effect is found in comparing the relative rates for the solvolysis of 7-norbornyl (1), *anti*-7-norbonenyl (10^{11})[7] and *endo*, *anti*-8-tricyclo[3.2.1.$0^{2,4}$] octyl toluensulfonates (10^{14}).[8] Therefore, it is of some interest to compare the effect of the β-cyclopropyl group with the olefinic group in the solvolyses of the allylic *p*-nitrobenzoates V-VII. We now report the results of such an investigation in this communication.

The synthetic route to VII-OH started most conveniently by treating norbornadiene with Simmons-Smith reagent to afford a product mixture containing 31% norbornadiene, 61% *exo*-monoadduct and 8% *bis*-adduct. Simple distillation of the recovered product provided an oil containing 81% *exo*-monoadduct which was treated with dibromocarbene without further purification. Hydrolysis of the crude product mixture in 50% aqueous acetone containing $AgNO_3$ afforded VIII-OH, m.p. 85.5-88.0°, in 90% yield. Reduction of the vinyl bromine in VIII-OH with sodium in liquid ammonia provided an 88% yield of *exo*-VII-OH (oil). The corresponding *p*-nitrobenzoate was prepared in the usual manner, m.p. 93.0-95.0°.[9]

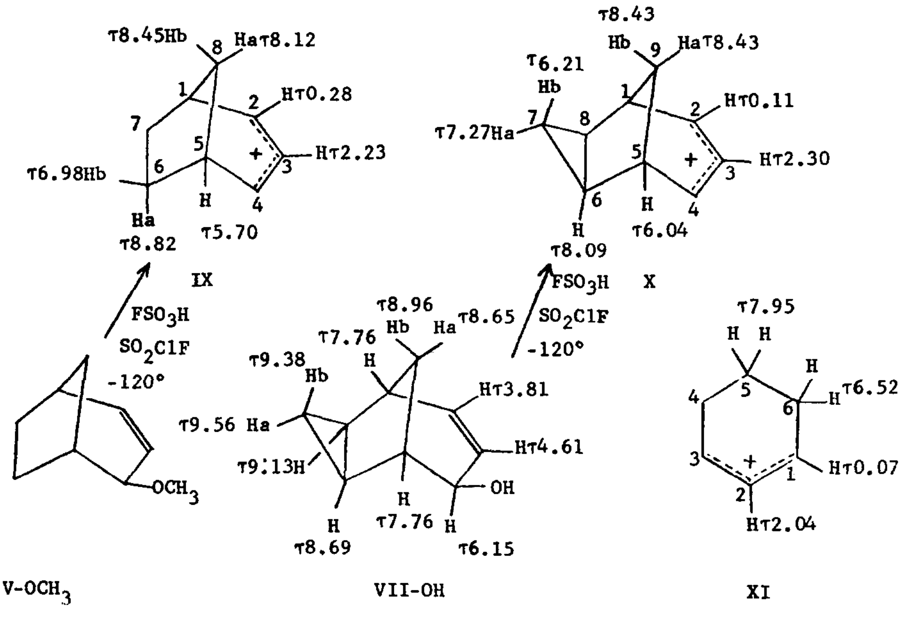


VIII - OH

exo - VII - OH

The solvolysis of VII-OPNB in 80% aqueous acetone at 100° proceeds with good first-order kinetics providing the rate constant $5.63 \pm 0.08 \times 10^{-6}$ sec^{-1}. The infinity titer is ≥98% of the theoretical value. The solvolysis product is largely *exo*-VII-OH, 96.0%, plus 1.82% of a second carbinol tentatively identified as the *endo* epimer.[10] Two additional minor products, produced in 1.03 and 0.66% yield, were detected, but not identified. Similarly, *exo*-V-OPNB solvolyses in 80% aqueous acetone at 100.0° to produce exo-V-OH in 99% yield with a first-order rate constant of 17.6×10^{-6} sec^{-1}.[6b] The absence of significant involvement of the β-cyclopropyl group in the solvolysis of exo-OPNB is evident by the closely similar solvolytic behavior of exo-V-OPNB and exo-VII-OPNB. The solvolytic reactivity of exo-VII-OPNB being 3.1 times less than exo-V-OPNB is appropriate for the rate retarding effect of the β-cyclopropyl group.[11]

Further evidence in support of negligible interaction between the β-cyclopropyl group and the allylic cation segment is provided by direct observation by nmr of the ion produced from exo-VII-OH. The stable carbonium ions IX and X were prepared by mixing a CD_2Cl_2 solution of V-OCH_3 and VII-OH, respectively, into a 1:4 mixture (v:v) and FSO_3H-SO_2ClF at -120°, and were observed at -95°. The difference between the chemical shifts of the allylic protons H_2 and H_3 of X and the corresponding chemical shifts for the model ions IX and XI[12] was less than 0.3 ppm in all cases, which reflects negligible differences in charge density. This similarity of chemical shifts indicates that no charge is removed from the allylic cation moeity of X by homoconjugation.[13] An interesting observation, however, is the substantial deshielding of the cyclopropane protons of X, which is most likely due to the magnetic anisotropy of the allylic cation.[14]



In conclusion, it is clear from the solvolysis data and direct observation of the ions that no significant interaction occurs between the β-cyclopropyl group and the allylic cation to form the four π-electron *anti*-aromatic *tris*-homocyclopentadienyl cation.

REFERENCES

1. Research sponsored by the National Science Foundation.
2. To whom inquires should be addressed: Department of Chemistry, Revelle College, University of California, La Jolla, California 92037.
3. Deceased Nov. 23, 1969.
4. (a) S. Winstein, Chemical Society International Symposium on Aromaticity, Sheffield, England, July 6-8, 1966; Special Publication No. 21, The Chemical Society, London, 1967; (b) S. Winstein, M. Ogliaruso, M. Sakai and J. M. Nicolson, *J. Amer. Chem. Soc.*, **89**, 3656 (1967).
5. (a) J. M. Brown and J. L. Occolowitz, *Chem. Comm.*, 376 (1965); (b) J. M. Brown, *ibid*, 639 (1967).
6. (a) S. Winstein, The Chemical Society 1967 Centenary lecture for the Symposium on "Some Aspects of Organic Reaction Mechanisms", England, October 10-20, 1967; (b) A. F. Diaz, M. Sakai and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 0000 (1970).
7. (a) S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, *J. Amer. Chem. Soc.*, **77**, 4183 (1955); (b) S. Winstein and M. Shatavsky, *ibid*, **78**, 592 (1956); (c) S. Winstein, A. L. Lewin and K. C. Pande, *ibid*, **85**, 2324 (1963).
8. (a) H. Tanida, T. Tsuji and T. Irie, *ibid*, **89**, 1953 (1967); (b) M. A. Battiste, C. L. Deyrup, R. E. Pincock and J. Haywood-Farmer, *ibid*, **89**, 1954 (1967).
9. The compound gave satisfactory carbon and hydrogen analysis; the configuration was assigned on the basis of the usual nmr and chemical criteria.
10. Product analysis by glc at 100° using 2.5% KOH-2.5% carbowax on CW 80/100.
11. A similar rate retardation by a β-cyclopropyl group is observed in the solvolysis of *exo*, *anti*-8-tricyclo[3.2.1.$0^{2,4}$] octyl OTs which solvolyses 2.5 times slower than 7-norbornyl OTs. See Reference 8.
12. P. M. Warner, Ph.D. Thesis, UCLA, 1970.
13. For examples of homoconjugative charge delocalization see: (a) P. Ahlberg, D. L. Harris, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 2146 (1970); (b) P. Ahlberg, D. L. Harris, and S. Winstein, *ibid*, **92**, 4454 (1970); (c) M. Roberts, H. Hamberger, and S. Winstein, submitted for publication; (d) P.Warner and S. Winstein, submitted for publication; (e) reference 12.
14. A similar effect is seen in tricyclo[3.2.2.$0^{7,8}$] non-2-enyl cation;[13c] further evidence in support of the absence of ring opening of the cyclopropyl group in the cation is the near equal coupling constants of the cyclopropyl protons in the ion, X, and the carbinol precursor, VII-OH.