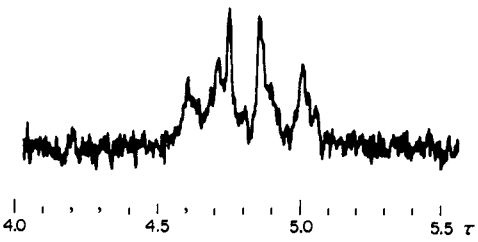


Figure 1. Nmr signal of *CH*OPNB in *endo*-3-tricyclo[5.1.0.0^{4,8}]-octanyl *p*-nitrobenzoate (V-OPNB).

mechanistic consideration of the rearrangement from IV-OPNB to V-OH, perhaps with the fact that V-OPNB is less reactive than IV-OPNB, support that the hydroxyl group in V-OH is at C_3, but not at C_2 (if so, this cyclopropylcarbinol derivative would be more reactive than IV-OPNB). The large $W_{1/2}$ of the nmr signal due to *CH*OPNB in V-OPNB, as shown in Figure 1, suggests the predominantly *endo* configuration of the ester group.

Solvolysis of IV-OPNB in 60% aqueous dioxane at 100.0° resulted in the formation of about 0.77 equiv of *p*-nitrobenzoic acid by a clean first-order process. The reaction was followed by titration of forming nitrobenzoic acid. The first-order rate constant thus obtained was 6.75×10^{-4} sec^{-1}.[10] In the same solvent, the constants of II-OPNB were 9.35×10^{-5} sec^{-1} at 161.2° and 8.89×10^{-6} sec^{-1} at 130.0°, leading to an extrapolated value of 6.39×10^{-7} sec^{-1} at 100.0°. Thus, the reactivity of IV is some 10^3 times that of II and, therefore, roughly 10^{14} times that of I.

The striking difference in the reactivities of III and IV indicates that participation of the cyclopropyl is dependent upon the stereochemistry. Combined with the theory of Woodward and Hoffman[11] and with the view of DePuy and Cristol in the cyclopropyl ring opening,[12] our results suggest that the C_2–C_4 bond cleavage and, perhaps, similar phenomena in the related systems occur in an upward disrotatory process. The inertness of III is in agreement with this hypothesis since such a rotation would lead to a severe steric interaction between the *endo* H_2 and H_4.

(10) For calculation of rate constants for solvolysis of this kind involving ion-pair return to an unreactive isomer, refer to H. Hart and J. M. Sandri, *J. Am. Chem. Soc.*, **81**, 320 (1959).

(11) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965).

(12) C. H. DePuy, L. G. Schnack, and J. W. Hausser, *ibid.*, **88**, 3343 (1966), and references cited therein.

Hiroshi Tanida, Teruji Tsuji, Tadashi Irie
Shionogi Research Laboratory, Shionogi & Co., Ltd.
Fukushima-ku, Osaka, Japan
Received December 6, 1966

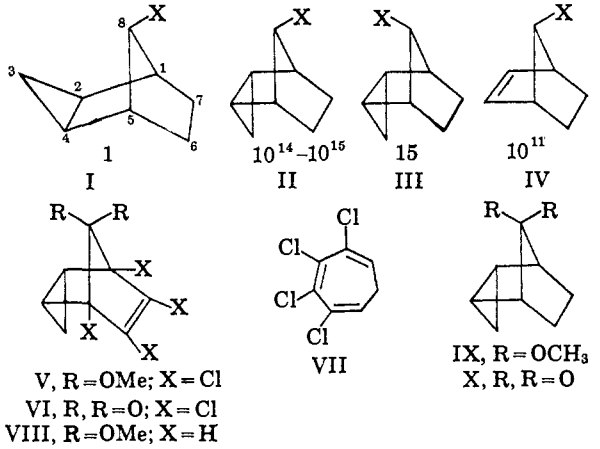
Synthesis and Solvolytic Reactivity of *endo-anti-* and *endo-syn*-8-Tricyclo[3.2.1.0^{2,4}]octane Derivatives. Extensive Homoconjugative Participation by a Cyclopropane Ring

Sir:

In recent years several examples of cyclopropyl homoconjugative participation at a developing carbonium ion center have been recognized.[1] In some instances the cationic intermediates generated by such participation have been accorded nonclassical tris-(homocyclopropenyl) ion structures;[1a,b,e,f,i,2] however, the rate enhancements observed in these cyclopropyl systems are disturbingly low (10^1–10^3) compared to those obtained in other nonclassical systems. Although this could be taken as evidence for a relatively weak participating effect by cyclopropane bonding electrons, it may more likely reflect the special geometrical requirements for this interaction. With regard to this question, the solvolytic reactivities of the *exo-anti-*, *endo-anti-*, and *endo-syn*-8-tricyclo[3.2.1.0^{2,4}]-octyl derivatives I, II, and III, respectively, are of particular interest in view of the very large rate enhancement to ionization (*ca.* 10^{11}) provided by the double bond p orbitals in the *anti*-7-norbornenyl system IV.[3]

As previously reported,[4] the acetolysis of the *exo-anti* *p*-bromobenzenesulfonate (I-OBs) is even slower, by a factor of 3, than the acetolysis of the already notably "slow" 7-norbornyl *p*-bromobenzenesulfonate.[5] We now wish to report the synthesis of the epimeric *endo* alcohols II-OH and III-OH and a solvolytic reactivity ratio of 1:15:10^{14} for derivatives of I, III, and II, respectively.

Reaction of 5,5-dimethoxytetrachlorocyclopentadiene with cyclopropene[6] gave the *endo* tricyclic adduct V,[7] mp 70–71° (nmr methoxyl signals at τ 6.37 and 6.48, and an ABX_2 system at τ 8.2, 9.1, and 9.6; J_{AB} = 7 cps, J_{BX} = 7.2 cps, J_{AX} = 3.4 cps). Hydrolysis of this ketal in concentrated sulfuric acid at 0° yielded the chlorinated ketone VI,[7] mp 107–108° (frothing), $\nu_{C=O}$ 1815 cm^{-1}. The nmr spectrum of VI revealed only cyclopropyl protons with a lower field quartet at τ 8.1 (2 H) and two higher field doublet of triplets at τ 8.8 (1 H) and 9.7 (1 H). On warming the deuterio-



(1) (a) S. Winstein, J. Sonnenberg, and L. DeVries, *J. Am. Chem. Soc.*, **81**, 6523 (1959); (b) S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3235, 3244 (1961); (c) D. H. R. Barton, R. Bernasconi, and J. Klein, *J. Chem. Soc.*, 511 (1960); (d) A. C. Cope, S. Moon, and C. H. Park, *J. Am. Chem. Soc.*, **84**, 4850 (1962); (e) T. Norin, *Tetrahedron Letters*, 37 (1964); (f) S. Winstein, P. Bruck, P. Radlick, and R. Baker, *J. Am Chem. Soc.*, **86**, 1867 (1964); (g) K. B. Wiberg and G. R. Wenzinger, *J. Org. Chem.*, **30**, 2278 (1965); (h) A. K. Colter and R. C. Musso, *ibid.*, **30**, 2462 (1965); (i) S. Winstein and Y. Lin, unpublished work cited in ref 2.

(2) S. Winstein, Lecture at The Chemical Society International Symposium on Aromaticity, Sheffield, England, July 6, 1966. We wish to thank Professor Winstein for a printed copy of this lecture.

(3) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, 77, 4183 (1955); S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, **85**, 2324 (1963).

(4) J. Haywood-Farmer, R. E. Pincock, and J. I. Wells, *Tetrahedron*, **22**, 2007 (1966).

(5) S. Winstein and M. Shatavsky, *J. Am. Chem. Soc.*, **78**, 592 (1956).

(6) G. L. Closs and K. D. Krantz, *J. Org. Chem.*, **31**, 638 (1966).

(7) Satisfactory carbon and hydrogen analyses were obtained for all new compounds reported here.

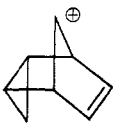
chloroform solution of VI, this complex cyclopropyl spectrum was destroyed and replaced by a pair of equally intense triplets at τ 4.04 and 7.55, corresponding to decarbonylation of VI and formation of 2,3,4,5-tetrachlorocyclohepta-1,3,5-triene (VII).[8]

Dechlorination of V with sodium–THF–*t*-butyl alcohol[9] afforded the unsaturated ketal VIII[7] in 70% yield. The nmr spectrum of this compound showed relatively shielded olefinic protons at τ 4.30, characteristic of the *endo*-tricyclo[3.2.1.$0^{2,4}$]octene system.[4,10] In addition, the spectrum did not reveal any unusual deshielding of a cyclopropyl methylene hydrogen by the bridge methoxyls which would be expected of an *exo* configuration.[11] Catalytic hydrogenation of VIII gave the saturated ketal IX[7] which, on treatment with pH 4 buffered aqueous solution at 60°, yielded the corresponding ketone X, mp 58–61°, $\nu_{C=O}$ 1760 cm^{-1}; semicarbazone[7] mp 224–226°. Sodium borohydride reduction of X afforded a 1:1 mixture of isomeric alcohols II-OH and III-OH. Separation by preparative vpc and vacuum sublimation gave vpc homogeneous samples of *endo-anti*-II-OH,[7] mp 137–139°, and *endo-syn*-III-OH,[7,12] mp 128–130°.

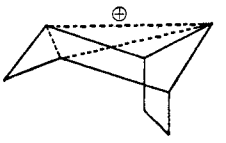
Although the *p*-bromobenzenesulfonate III-OBs,[7] mp 108–109°, was prepared in a normal manner for the *endo-syn* alcohol, attempts in both laboratories to prepare the *endo-anti* brosylate II-OBs have so far resulted in mainly rearranged materials. For solvolytic comparisons the appropriate *p*-nitrobenzoates II-OPNB,[7] mp 153–154°, III-OPNB,[7] mp 111–112°, and IV-OPNB,[7] mp 118–119°, were prepared by standard methods.

In 70% aqueous dioxane the *endo-anti-p*-nitrobenzoate II-OPNB solvolyzes with initial liberation of *ca.* 60% of the theoretical *p*-nitrobenzoic acid and with a decreasing first-order rate constant characteristic of ion-pair return to a much less reactive ester. The *initial* rate constant at 100° is $k = 16.3 \times 10^{-5}$ sec^{-1}. The olefinic ester IV-OPNB displayed good first-order kinetics in the same solvent system, giving rate constants of $k = 13.8 \times 10^{-5}$ sec^{-1} at 185° and $k = 4.89 \times 10^{-5}$ sec^{-1} at 170°. On this basis the *endo-anti* cyclopropyl derivative is 1.3×10^{3} times more reactive than the *anti*-7-norbornenyl compound. A more direct comparison with the olefinic norbornyl derivatives was made in 70% aqueous acetone. In this solvent II-OPNB solvolyzed with an *initial* first-order rate constant of $k_{90.2°} = 13.4 \times 10^{-5}$ sec^{-1}, whereas 7-norbonadienyl *p*-nitrobenzoate[13] solvolyzed at only one-tenth this rate ($k_{90.2°} = 1.31 \times 10^{-5}$ sec^{-1}). Thus, from previously established reactivity ratios in the norbornyl series[3,5,13] a rate enhancement of 10^{14}–10^{15} is obtained for the *endo-anti* cyclopropyl system II compared to the *exo-anti* system I and 7-norbornyl itself. On the other hand, the *endo-syn* brosylate III-OBs was found to be only 15-fold more reactive in acetolysis than *exo-anti* brosylate I-OBs (for acetolysis of III-OBs, $k_{165°} = 5.25 \times 10^{-5}$ sec^{-1}, $k_{175°} = 11.1 \times 10^{-5}$ sec^{-1}; for acetolysis of I-OBs, $k_{163°} = 2.94 \times 10^{-6}$ sec^{-1}).

Among the saturated or olefinic derivatives of the 7-norbornyl ring system considered here the *exo-anti* system I exhibits an extreme of solvolytic stability while the *endo-anti* isomer II presents an extreme of solvolytic reactivity. Ionization of II-OPNB must proceed with extensive backside participation by the cyclopropane C_2–C_4 bonding electrons which, in the *endo* configuration, are ideally oriented for interaction at the bridge position.[14] No corresponding interaction is possible with the *exo-anti* or *endo-syn* *p*-nitrobenzoates. Furthermore, it seems clear that as a participating group in solvolytic reactions cyclopropane is more effective than vinyl. This is not totally unexpected since extended Hückel calculations on the tricyclooctenyl cation XI definitely indicated primary stabilization of the bridge cation from interaction with the cyclopropane ring rather than the double bond.[15] The kinetic results presented here are in striking agreement with this prediction and further suggest that ionization of II-OPNB proceeds directly to the uniquely



XI



XII

stable tris(homocyclopropenyl) ion XII.[16]

(8) (a) In the course of studies relating to the dienophilic reactivity of cyclopropenes[8b] we have prepared a number of *endo*-8-tricyclo[3.2.1.$0^{2,4}$]-octenone derivatives, and each was observed to undergo facile decarbonylation at unusually low temperatures (<100°), the expected cycloheptatrienes being formed in almost quantitative yield. By contrast, the corresponding *exo* ketones that have been examined are quite resistant to decarbonylation. In their ease of decarbonylation the *endo* ketones resemble the bicyclo[2.2.1]heptadienones which spontaneously decarbonylate to the appropriate benzene derivative. Here again cyclopropane exhibits intermediate double bond–single bond character, but only when in the *endo* configuration where proper orbital overlap is possible between the developing new π centers. (b) M. A. Battiste, *Chem. Ind.* (London), 550 (1961); *J. Am. Chem. Soc.*, **85**, 2175 (1963); T. J. Barton, Ph.D. Dissertation, University of Florida (1966).

(9) *Cf.* P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964).

(10) K. B. Wiberg and W. J. Bartley, *J. Am. Chem. Soc.*, **82**, 6375 (1960); R. R. Sauers and P. E. Sonnet, *Chem. Ind.* (London), 786 (1963).

(11) M. A. Battiste and M. E. Brennan, *Tetrahedron Letters*, 5857 (1966).

(12) The *endo-syn* alcohol III-OH showed infrared and nmr spectra identical with those of a sample prepared by another method.[4]

(13) S. Winstein and C. Ordronneau, *J. Am. Chem. Soc.*, **82**, 2084 (1960).

(14) To account for the large rate enhancement in the *endo-anti* tricyclic system II as compared to that observed in the *cis*-3-bicyclo-[3.1.0]hexyl system (*ca.* 40)[1b] it is instructive to view II as a bicyclohexyl system which is locked in the chair form by a 2,4-bridging ethanol group. The five-membered ring is severely puckered in this rigid structure and C_3 (actually C_8 by the real numbering) is nearer to the edge of the cyclopropane ring than it is in the unbridged case. In fact, considerable strain energy is required to bend the rather flat five-membered ring of the latter system into a chairlike form for the best possible interaction with the cyclopropane electrons. The amount of this strain energy may be considered to represent a ground-state contribution to the lowered activation energy for solvolysis of II.

(15) R. Hoffmann, *Tetrahedron Letters*, 3819 (1965).

(16) The accompanying communication by H. Tanida, T. Tsuji, and T. Irie (*J. Am. Chem. Soc.*, **89**, 1953 (1967)) reports similar independent results on the tricyclo[3.2.1.$0^{2,4}$]octyl system. We wish to thank Dr. Tanida for graciously delaying publication of his results so that the work from the three laboratories might appear simultaneously.

(17) Support of this research by the National Science Foundation and the Air Force Office of Scientific Research is gratefully acknowledged.

(18) This work was supported by grants from the National Research Council of Canada and from the Petroleum Research Fund administered by the American Chemical Society. We thank the National Research Council for a Studentship, 1965–1967, to J. H.-F.

Merle A. Battiste, Cynthia L. Deyrup[17]
Department of Chemistry, University of Florida
Gainesville, Florida

Richard E. Pincock, John Haywood-Farmer[18]
Department of Chemistry, University of British Columbia
Vancouver, British Columbia, Canada

Received February 3, 1967