mode of decomposition of unstable triazolines recently described by Logothetis[6] provides guidance in adducing the course of conversion of **13** to the imine tautomers.

(6) A. L. Logothetis, *J. Am. Chem. Soc.*, **87**, 749 (1965).

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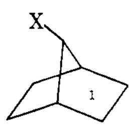
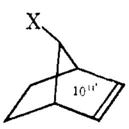
Solvolysis of *endo-anti*-Tricyclo[3.2.1.$0^{2,4}$]octan-8-yl *p*-Nitrobenzoate and Two Routes to Tricyclo[5.1.0.$0^{4,8}$]octane Derivatives

Sir:

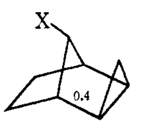
The greatest participation by the double bond has been recorded in the solvolysis of 7-norbornyl derivatives: the ratio of rates in acetolysis of 7-norbornyl (I) and *anti*-7-norbornenyl (II) tosylates[1] is 10^{11}. In this connection, and because a cyclopropyl group displays some properties similar to those of a double bond, the solvolytic behavior of the cyclopropyl compounds III and IV is of considerable interest. However, no effect of the cyclopropyl in III was found.[2]



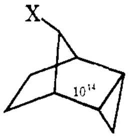
I



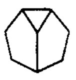
II



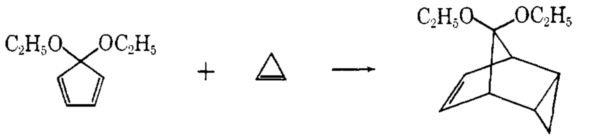
III



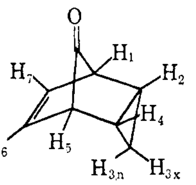
IV


V

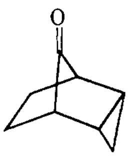
We now report the preparation of the hitherto unavailable IV and its solvolysis rate enhanced by a factor of 10^{14} (a new record for participation). In addition, the study of solvolysis products provides two new synthetic routes to tricyclo[5.1.0.$0^{4,8}$]octane derivatives (V).



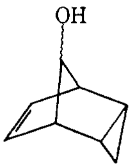
VI



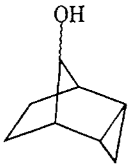
VII



VIII



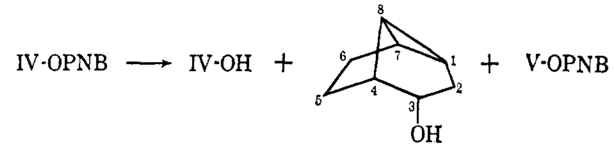
anti, IX-OH
syn, X-OH



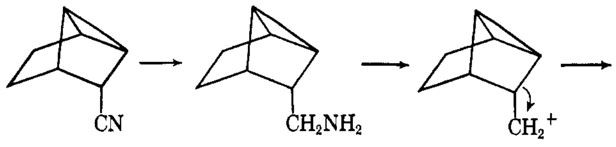
anti, IV-OH
syn, XI-OH

The Diels–Alder reaction of cyclopropene with cyclopentadienone diethyl ketal[3,4] led to the adduct VI boiling at bp 95° (6 mm), which on treatment with dilute $HClO_4$ afforded the unsaturated ketone VII, mp 32–32.5°.[5,6] Catalytic hydrogenation of VI followed by treatment with a weak acid yielded the saturated ketone VIII, mp 71–72°. On standing VII transformed into cycloheptatriene with a half-life of 130 min at 36°, evolving carbon monoxide. The nmr peaks (in CCl_4) of two vinyl H at τ 4.05 (triplet), two H_1, H_5 at 6.92 (quintet), two H_2,H_4 at $\sim$8.6 (multiplet), one H_{3x} at 9.35 (triplet of doublets, $J_{2,3x} = 7$, $J_{3n,3x} = 6.2$ cps), and one H_{3n} at 9.95 (doublet of triplets, $J_{3n,3x} = 6.2$, $J_{2,3n} = 3$ cps) were entirely consistent with the presented structure VII. The observed upfield shift of the vinyl protons relative to those in 7-norbornenone (τ 3.50)[2,4b,7] gives evidence for the *endo* configuration of the cyclopropyl ring. Separable mixtures of *anti*-IV-OH, mp 136–138°, and *syn*-XI-OH, mp 128–130°, were obtained *via* both of the routes: the sodium–liquid ammonia reduction of VII into a mixture of IX-OH and X-OH followed by catalytic hydrogenation and/or the $LiAlH_4$ reduction of VIII. The orientations of hydroxyl groups in IX-OH and X-OH, and thereby in IV-OH and XI-OH, are established by comparison of the infrared spectra; IX-OH showed an association with π-hydrogen bonding, ν_{OH} of IX-OH appearing at 3576 cm^{-1}, whereas that of X-OH was at 3590 cm^{-1}. Further, the infrared and nmr spectra of X-OH and XI-OH were identical with those reported.[2]

The *p*-nitrobenzoate, IV-OPNB, mp 152–153.5°, hydrolyzed with rearrangement and ion-pair return. In 70% aqueous acetone for 4 hr at 90° in the presence of 2 equiv of $NaHCO_3$, the product contained a 1:2 mixture of IV-OPNB and V-OPNB, mp 116–117°, in about 22% yield. Of the remaining 78% product analyzed by vpc, 96% was a 2:8 mixture of IV-OH and V-OH and 4% was a hydrocarbon of unknown structure. That V-OH is a secondary alcohol having a cyclopropyl ring is clear by the infrared (ν 3030, 780, and 760 cm^{-1}) and nmr spectra. Confirmatory evidence for the ring structure in V-OH was obtained by an independent synthesis. Nitrous acid deamination of the methylamine (XII) (prepared from the $LiAlH_4$ reduction of *endo*-2-cyanotricyclo[4.1.0.$0^{3,7}$]heptane[8]) was found by vpc to give a mixture of four products. The most important product, composing about 80% of the mixture, was identified with V-OH. The ring expansion from XII to V is a similar result to that of the carbonium ion reaction of *endo*-2-norbornylcarbinyl derivatives producing predominantly the *endo*-2-bicyclo[3.2.1]octanyl derivative.[9] This result and the



V-OH



XII

V—OH

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

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

(3) P. E. Eaton and R. A. Hudson, *J. Am. Chem. Soc.*, **87**, 2769 (1965).

(4) The same reaction with cyclopentadiene gives the 8-unsubstituted VI. See (a) G. L. Closs and K. D. Krantz, *J. Org. Chem.*, **31**, 638 (1966); (b) K. B. Wiberg and W. J. Bartley, *J. Am. Chem. Soc.*, **82**, 6375 (1960).

(5) Satisfactory analyses were obtained for all compounds described.

(6) In 23% yield from cyclopentanone diethyl ketal, the material for the dienone ketal.[3]

(7) K. Tori and K. Kitahonoki, *J. Am. Chem. Soc.*, **87**, 386 (1965).

(8) Reference 11 in H. Tanida, T. Tsuji, and T. Irie, *ibid.*, **88**, 864 (1966).

(9) J. A. Berson and P. Reynolds-Warnhoff, *ibid.*, **86**, 595 (1964).

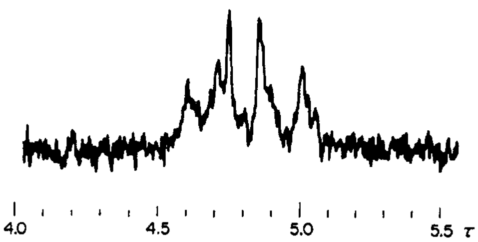

Figure 1. Nmr signal of C*H*OPNB in *endo*-3-tricyclo[5.1.0.0^{4,8}]-octanyl *p*-nitrobenzoate (V-OPNB).

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 C*H*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.

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Received December 6, 1966

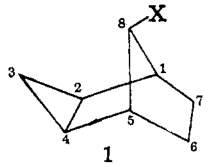
Synthesis and Solvolytic Reactivity of *endo-anti-* and *endo-syn*-8-Tricyclo[3.2.1.0^{2,4}]octane Derivatives. Extensive Homoconjugative Participation by a Cyclopropane Ring

Sir:

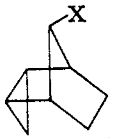
In recent years several examples of cyclopropyl homoconjugative participation at a developing carbonium ion center have been recognized.[1] In some instances the cationic intermediates generated by such participation have been accorded nonclassical tris(homocyclopropenyl) ion structures;[1a,b,e,f,i,2] 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.

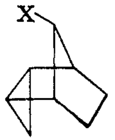
Reaction of 5,5-dimethoxytetrachlorocyclopentadiene with cyclopropene[6] gave the *endo* tricyclic adduct V,[7] mp 70–71° (nmr methoxyl signals at τ 6.37 and 6.48, and an ABX_2 system at τ 8.2, 9.1, and 9.6; $J_{AB} = 7$ cps, $J_{BX} = 7.2$ cps, $J_{AX} = 3.4$ cps). Hydrolysis of this ketal in concentrated 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-



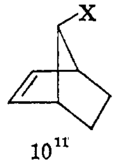
1
I



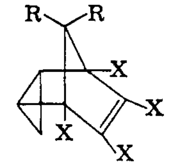
10^{14}-10^{15}
II



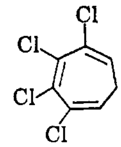
15
III



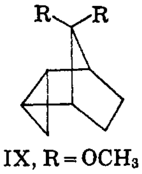
10^{11}
IV



V, R=OMe; X=Cl
VI, R, R=0; X=Cl
VIII, R=OMe; X=H



VII



IX, R=OCH_3
X, R, R=O

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(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.