is to be noted that the radical spectra produced by hot fragment attack are better resolved than those produced by radiolysis, and therefore at least as free of contribution from more than one radical.

Comparison with Other Systems. When compounds such as those of Table II are subjected to radiolysis in the gas or liquid, bond rupture is much less selective than in the glassy state.[32,39] It is also of note that the radiolytic radical yield, $G = 1.6$, in 3MP glass is significantly lower than that in liquid 3MP ($G = 7$), which has been demonstrated by scavenger methods.[40] *n*-Alkanes[2,36,41] and doubly branched alkanes such as neopentane,[36] 2,2-dimethylbutane,[2] and 2,3-dimethylpentane,[20] unlike the singly branched compounds discussed in this paper, give rather complex esr spectra following radiolysis at 77°K, suggesting the presence of several radicals.

(39) (a) R. D. Doepker and P. Ausloos, *J. Chem. Phys.*, **41**, 1865 (1964); (b) C. D. Wagner, *J. Phys. Chem.*, **64**, 231 (1960); (c) P. R. Geissler and J. E. Willard, *J. Am. Chem. Soc.*, **84**, 4627 (1962).
(40) E. N. Weber, P. F. Forsyth, and R. H. Schuler, *Radiation Res.*, **3**, 68 (1965).
(41) R. S. Alger, T. H. Anderson, and L. A. Webb, *J. Chem. Phys.*, **30**, 695 (1959).

Radical Production by Iodide Photolysis. The observation that photolysis of any of the 3-methylpentyl iodides in dilute solution in a glassy hydrocarbon produces a radical derived from the hydrocarbon is unexpected. Significant yields of hot-radical abstraction are produced by hot methyl, ethyl, and propyl radicals formed by dissociative electron capture, but these yields decrease with increasing length of the carbon chain.[25] 3-Methylpentyl radicals are sufficiently complex so that it is improbable that they can utilize efficiently either kinetic or vibrational energy for hot processes. Consistent with this expectation, the quantum yield of 2-methylpentyl radicals from the photolysis of a 3-methylpentyl iodide in 2MP is less than 10^{-4}.[42] Possibly this yield results not from hot-radical attack, but from attack by hot H atoms from the photolysis of HI, formed by a disproportionation reaction in the photolysis of $C_6H_{13}I$. The absence of radicals corresponding to the 3-methylpentyl iodide results from caging effects which maximize the recombination of sibling partners.

(42) Estimated by comparing the radical yield from the photolysis of HI (which has been reported to be 0.1–0.2 in 3MP glass[8]) with the radical yield from the 3-methylpentyl iodide.

Synthesis and Solvolytic Reactivity of 8-Tricyclo[3.2.1.$0^{2,4}$]octane Derivatives[1]

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Contribution from the Department of Chemistry, The University of British Columbia, Vancouver 8, British Columbia, Canada. *Received November 19, 1968.*

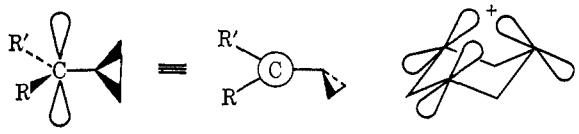
Abstract: To investigate the stereochemical influence of a cyclopropyl group on carbonium ion formation in a homoallylic position, the four stereoisomers (*i.e.*, *exo-anti*, *exo-syn*, *endo-anti*, and *endo-syn*) of tricyclo[3.2.1.$0^{2,4}$]-octan-8-ol were synthesized and their *p*-nitrobenzoates (*p*-NB) or *p*-bromobenzenesulfonates (brosylates) were solvolyzed. Reaction of 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene with cyclopropene gave the *endo* Diels–Alder adduct which was dechlorinated with Na–*t*-butyl alcohol and catalytically hydrogenated to give *endo*-8,8-dimethoxytricyclo[3.2.1.$0^{2,4}$]octane. This ketal was hydrolyzed to the *endo* 8-ketone which reduced ($LiAlH_4$ or Pt–H_2) to a mixture of *endo-syn* and *endo-anti* alcohols separated by gas–liquid partition chromatography. The *exo* 8-ketone, available from CuCl-catalyzed addition of diazomethane to 7,7-dimethoxynorbornene followed by hydrolysis, was reduced by $LiAlH_4$ to *exo-syn* alcohol. The kinetics of acetolysis of *endo-syn* brosylate was studied at 165–185° and the *exo-syn* isomer at 95–115°; first-order rate constants at 100° were calculated as 1.9×10^{-7} and 7.0×10^{-5} sec^{-1}, respectively. Products of both compounds were complex and extensively rearranged. As the brosylate of *endo-anti* alcohol was too reactive for isolation, the *p*-nitrobenzoate derivative was solvolyzed in 70% aqueous dioxane and compared to the rate of solvolysis of *anti*-7-norbornenyl *p*-nitrobenzoate; at 100° the rate constants are 2.4×10^{-4} and 1.9×10^{-7} sec^{-1}, respectively. The relative rates for brosylate acetolysis of *exo-anti*, *endo-syn*, *exo-syn*, and *endo-anti* structures are calculated to be $1:10:10^4:10^{12}$ at 100°, with the *endo-anti* compound 10^3 times more reactive than the already very reactive 7-norbornenyl brosylate. Highly favorable homoconjugative interaction involving considerable σ-type interaction of sp^5-cyclopropyl and *p*-carbonium ion orbitals is demonstrated by these ratios. The two solvolysis products from *endo-anti p*-nitrobenzoate (*i.e.*, the rearranged *endo*-tricyclo[3.3.0.$0^{4,6}$]oct-2-yl alcohol and its *p*-nitrobenzoate) correspond, respectively, to stereospecific hydrolysis and ion-pair return of an intermediate ion which shows characteristics expected of a nonclassical 2,4-ethanotrishomocyclopropenyl cation.

The allylic interaction of cyclopropyl ring orbitals with directly adjacent carbonium ion centers, as in solvolysis of cyclopropylcarbinyl derivatives, is well known to result in relatively great chemical reactivities[3] and highly stable cyclopropylcarbinyl cations.[4] Such

(1) Research sponsored by the U. S. Air Force Office of Scientific Research, Grant No. AFOSR 1102-66, the Petroleum Research Fund administered by the American Chemical Society, and the National Research Council of Canada.

(2) Alfred P. Sloan Foundation Fellow.
(3) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951); H. Hart and P. A. Law, *ibid.*, **84**, 2462 (1962); **86**, 1957 (1964).
(4) C. U. Pittman and G. A. Olah, *ibid.*, **87**, 2998, 5123 (1965); G. A. Olah, *Chem. Eng. News*, **45** (14), 76 (1967); N. C. Deno, H. G. Richey,

studies have shown that the cyclopropyl group interacts to give stabilized ions (I) where the electron-deficient p orbital is parallel to the plane of the cyclopropyl ring.[3-5] The olefinlike cyclopropyl ring orbitals[6] then interact symmetrically with the p orbital of the carbinyl atom.

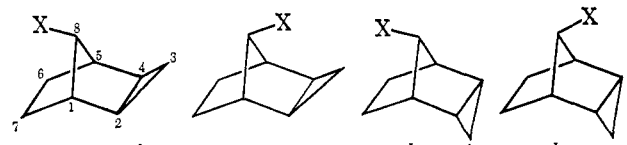


I II

The general influence of a cyclopropyl group on the development of a positive charge at still greater distance is less well established and subject to considerable controversy. Winstein, Sonnenberg, and de Vries[7] have studied the solvolysis of *cis*- and *trans*-3-bicyclo[3.1.0]-hexyl tosylates and concluded from the observed relative rate ratio (*cis*/*trans* = 36 in acetolysis), high stereospecificity of product formation (*cis* → *cis* product, *trans* → complex mixture), ion-pair return, and rearrangement of deuterio-labeled *cis* compound that solvolysis of *cis* isomer led directly to stabilized trishomocyclopropenyl cation II.

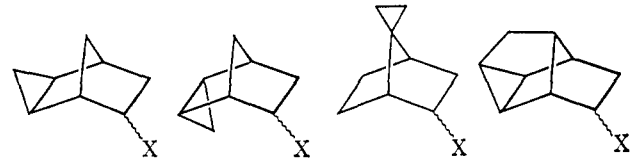
Homoallylic interaction giving rise to such a nonclassical intermediate ion has been questioned by Brown[8] and by Corey, Uda, and Dawson[9] who showed that high stereospecificity of product formation did not generally occur, and that 1,5-diphenyl substitution in this ring system resulted in essential elimination of a relative *cis* to *trans* rate difference. These observations have recently been reviewed by Winstein[10] who suggested that the chair form required for development of ion II is not the stable conformation in this ring system and it is even less readily attained in the diphenyl derivative than in the unsubstituted compound. Ionization therefore proceeds in both *cis*- and *trans*-1,5-phenyl-substituted isomers to give classical boat-shaped ions. Other studies[11] of 3-substituted *cis*- and *trans*-bicyclo[3.1.0]hexyl derivatives have given experimental results generally interpreted in terms of ionic intermediates like structure II.

To investigate any potential homoallylic effect (in structures free from conformational flexibility) of a cyclopropyl group on carbonium ion formation, we have studied the stereoisomers of 8-substituted tricyclo[3.2.1.0^{2,4}]octanes III–VI.[12] These structures pos-



exo-anti *exo-syn* *endo-anti* *endo-syn*
III IV V VI

sess four different rigid arrangements of a cyclopropyl group with respect to leaving group at C-8, and the inplane olefinic characteristics of cyclopropyl takes up two distinct orientations (chair-form *endo* V and VI; boat-form *exo* III and IV) with respect to a carbonium ion created at C-8. These arrangements, however, are basically different from that in cyclopropylcarbinyl cations. Both the *exo*- and *endo*-cyclopropyl configurations in III–VI have a "perpendicular" rather than parallel relationship of cyclopropyl ring to carbonium ion p orbital at C-8. Nevertheless, they all possess double-bond character in the C-2–C-4 cyclopropyl bond at a homoallylic position with respect to C-8. In analogy to the highly activating influence of a double bond in solvolysis of 7-norbornenyl derivatives,[13] any long-range interaction of the cyclopropyl group in these compounds can be expected to show in their relative rates and in specificities of product formation. Potential homoallylic cyclopropyl–carbonium ion interactions have recently been studied in the related rigid structures VII–X.[14-16a] The ratios of solvolysis rates



VII VIII IX X

for *exo* and *endo* leaving groups have been similar to that for unsubstituted *exo*- and *endo*-2-norbornyl derivatives and little or no accelerating effect of cyclopropyl in these positions has been indicated.[16b-d]

Results

Synthesis Studies. Our earlier attempts to obtain stereoisomers related to structures III–VI by the addition of methylene units (from CH_2N_2–CuCl) to 7-norbornadienyl acetate or to 7-norbornenol resulted in formation of *exo-syn* and *endo-syn*, and of *exo-anti* isomers, respectively.[17] Very little of the *endo-syn* and none of the *endo-anti* isomer is available by this

J. S. Liu, D. N. Lincoln, and J. O. Turner, *J. Am. Chem. Soc.*, **87**, 4533 (1965); H. G. Richey and J. M. Richey, *ibid.*, **88**, 4971 (1966).

(5) *Cf.* K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968); M. Hanack and H.-J. Schneider, *Angew. Chem. Intern. Ed. Engl.*, **6**, 666 (1967).

(6) *Cf.* W. A. Bernett, *J. Chem. Educ.*, **44**, 17 (1967); F. J. Weigert and J. D. Roberts, *J. Am. Chem. Soc.*, **89**, 5962 (1967).

(7) S. Winstein, J. Sonnenberg, and L. de Vries, *ibid.*, **81**, 6523 (1959); **83**, 3235, 3244 (1961); S. Winstein, E. C. Friedrich, R. Baker, and Y. Lin, *Tetrahedron*, **22** (Suppl 8, part II), 621 (1966).

(8) Private communication to authors from Professor H. C. Brown.

(9) E. J. Corey and H. Uda, *J. Am. Chem. Soc.*, **85**, 1788 (1963); E. J. Corey and R. L. Dawson, *ibid.*, **85**, 1782 (1963).

(10) S. Winstein, Special Publication No. 21, The Chemical Society, London, 1967; see also G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966).

(11) W. J. le Noble, B. L. Yates, and A. W. Scaplehorn, *J. Am. Chem. Soc.*, **89**, 3751 (1967); T. Norin, *Tetrahedron Letters*, 37 (1964); see also P. J. Kropp, *J. Am. Chem. Soc.*, **88**, 4926 (1966); S. Winstein, P. Bruck, P. Radlick, and R. Baker, *ibid.*, **86**, 1867 (1964); R. F. Childs and S. Winstein, *ibid.*, **89**, 6348 (1967); P. G. Gassman and F. V. Zalar, *ibid.*, **88**, 2252 (1966), and ref 10.

(12) Both Dr. H. Tanida, Professor M. Battiste, and their associates have reported similar studies of this system: see (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); (c) see also S. C. Clarke and B. L. Johnson, *Tetrahedron Letters*, 617 (1967).

(13) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955); S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956).

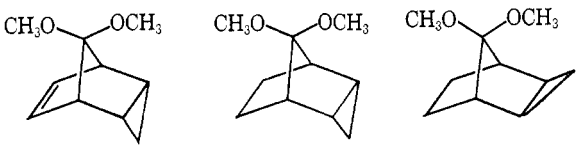
(14) K. B. Wiberg and G. R. Wenzinger, *J. Org. Chem.*, **30**, 2278 (1965); A. K. Colter and R. C. Musso, *ibid.*, **30**, 2462 (1965).

(15) C. F. Wilcox, Jr., and R. G. Jesaitis, *Tetrahedron Letters*, 2567 (1967).

(16) (a) P. K. Freeman and D. M. Balls, *ibid.*, 437 (1967). (b) Possible interaction of cyclopropyl groups with remote ionizing centers has recently been studied by M. A. Eakin, J. Martin, and W. Parker, *Chem. Commun.*, 955 (1967), and by G. D. Sargent, R. L. Taylor, and W. H. Demisch, *Tetrahedron Letters*, 2275 (1968). Little or no rate enhancement by a cyclopropyl group in 2-cyclopropylethyl brosylate solvolysis has been reported by (c) Y. E. Rhodes and T. Takio, *J. Am. Chem. Soc.*, **90**, 4469 (1968), and by (d) M. J. S. Dewar and J. M. Harris, *ibid.*, **90**, 4468 (1968).

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

method. Fortunately, the exclusive formation of *endo* addition product from Diels–Alder reaction of cyclopropene and cyclopentadiene[18] indicated a stereospecific route to compounds with *endo*-cyclopropyl configuration.[12c] Utilizing the convenient source described by Closs and Krantz,[19] a stream of cyclopropene gas was led through a solution of 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene at 0° to give a 95% yield of crystalline adduct. Dechlorination of this Diels–Alder adduct using metallic sodium in THF–*t*-butyl alcohol[20] gave the ketal olefin XI characterized by its nmr spectrum. The *endo* configuration of the cyclopropyl group, expected from its mode of formation, was confirmed in XI by the relatively high-field signal for olefinic protons at τ 4.43. The anisotropic field effect of a cyclopropane ring shifts the olefinic triplet of norbornenes (*ca.* τ 4.0) to shielded positions (*ca.* τ 4.3) in *endo* isomers and to deshielded positions (*ca.* τ 3.6) in *exo* isomers.[17,18,21]



XI XII XIII

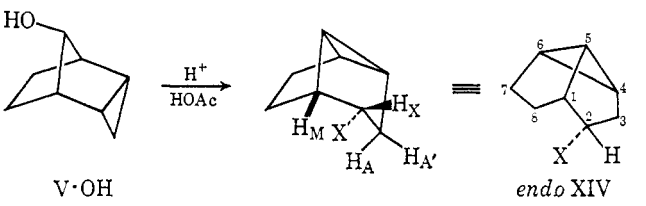
Further evidence of *endo* structure in XI stems from its hydrogenation to give a saturated ketal different from an isomer previously assigned[17] the *exo* structure XIII. Interestingly, in the *endo* compound XII the field effect of the cyclopropyl group results in magnetic nonequivalence of the two methyl protons (singlets at τ 6.82 and 6.93), while *exo* isomer has one nmr methyl peak at τ 6.88. This chemical shift difference (0.11 ppm) of the methyl groups in *endo* XII is even larger than the corresponding shift (0.07 ppm) arising from the presence of a double bond in 7,7-dimethoxynorbornene.

Acid hydrolysis of the *exo* and *endo* ketals XIII and XII (the former available from stereospecific methylene addition to 7,7-dimethoxynorbornene)[17] gave the corresponding ketones. Lithium aluminum hydride reduction of the *exo* ketone resulted in exclusive formation of *exo-syn* alcohol IV-OH, while $LiAlH_4$ reduction of *endo* ketone gave a 67:33 mixture of *endo-syn* and *endo-anti* alcohols VI-OH and V-OH. Catalytic hydrogenation of *endo* ketone gave a 33:67 ratio of these alcohols, respectively. Therefore, in contrast to the stereoexclusive reduction of the *exo* ketone (which is apparently controlled by a steric effect), there is little steric or electronic preference for attack on the two sides of the carbonyl group in *endo* ketone.

The mixture of two isomeric *endo* alcohols VI-OH and V-OH could be separated by preparative gas–liquid partition chromatography. The *endo-syn* isomer was identified by spectral comparisons with a sample previously prepared through the reaction of diazomethane with 7-norbornadienyl acetate; the *endo-anti* isomer was the only previously unknown isomer of the tricyclo[3.2.1.$0^{2,4}$]octan-8-ols.[22a]

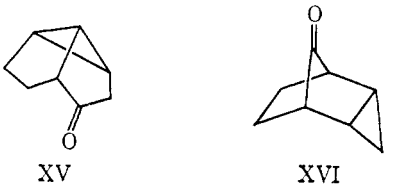
Treatment of the four isomeric octanols III–VI with acetic anhydride in pyridine gave the corresponding acetates. Similar treatment of the *exo-anti*, *exo-syn*, and *endo-syn* alcohols with *p*-bromobenzenesulfonyl chloride in pyridine gave the corresponding brosylates, but all attempts to prepare the *endo-anti* brosylate V-Bs resulted in rearranged material (see below). For solvolysis studies the *p*-nitrobenzoate (*p*-NB) of this *endo-anti* alcohol (V) was prepared, and, for comparison in rates of reaction, the *p*-nitrobenzoates of the *endo-syn* alcohol VI and of *anti-7*-norbornenol were also prepared.

The *endo-anti* alcohol V-OH was especially sensitive toward rearrangement; the *p*-toluenesulfonic acid catalyzed rearrangement in acetic acid produced a 95% yield of an acetate which displayed a six-peak, one-proton signal for *H*COAc around τ 5.1. This splitting corresponded to the X part of an AA'MX system consistent with an expected product of simple cyclopropyl rearrangement, *i.e.*, the acetate of tricyclo-[3.3.0.$0^{4,6}$]octan-2-ol (XIV).[22b] Although we have obtained only one of the two possible (2-*exo* and 2-*endo*) isomers, the magnitude of the observed coupling constants, $J_{AX} = J_{A'X} = 9.0$ cps and $J_{MX} = 6.6$ cps, seems most consistent with an *endo* configuration of the 2-acetate group (*i.e.*, *exo* configuration of 2-hydrogen). This assignment is also that of Tanida[23] who synthesized and compared both of the 2 isomers.



V-OH *endo* XIV

Oxidation of the *endo* alcohol XIV by chromium trioxide in pyridine gave the ketone, tricyclo[3.3.0.$0^{4,6}$]-octan-2-one (XV). In contrast to the *endo* ketone of the [3.2.1.$0^{2,4}$] structure[24] XVI, the isomeric compound XV showed ir and uv carbonyl absorptions more typical of an unstrained five-membered-ring ketone. Reduction of XV with $LiAlH_4$ gave back *ca.* 90% of alcohol containing the initial *endo* alcohol as the only detectable product. Thus this ketone appears to be highly hindered from attack on the *endo* side and it gives rise to *endo* alcohol XIV-OH by *exo* approach of hydride.



XV XVI

With a number of derivatives of the four stereoisomeric alcohols available, a comparison of their nmr spectra is possible. The cyclopropyl protons of tricyclo[3.2.1.$0^{2,4}$]octanes show signals characteristic of

(18) K. B. Wiberg and W. J. Bartley, *J. Am. Chem. Soc.*, **82**, 6375 (1960).
(19) G. L. Closs and K. D. Krantz, *J. Org. Chem.*, **31**, 638 (1966).
(20) P. G. Gassman and P. G. Pape, *ibid.*, **29**, 160 (1964).
(21) R. R. Sauers and P. E. Sonnet, *Chem. Ind.* (London), 786 (1963).
(22) (a) These results confirm both the previous structural assignments and the suggested[17] *syn-exo* and *syn-endo* stereochemistry of addition of methylene to 7-norbornadienyl acetate. (b) A referee has pointed out this correct name for the tricyclic structure XIV (see J. Meinwald and J. K. Crandall, *J. Am. Chem. Soc.*, **88**, 1292 (1966)). Other names have involved a tricyclo[3.2.1.$0^{4,6}$]- or a -[5.1.0.$0^{4,6}$]octyl numbering system.
(23) Private communication from Dr. H. Tanida.
(24) R. E. Pincock and J. Haywood-Farmer, *Tetrahedron Letters*, 4759 (1967).

exo configuration; in all the saturated[25] *exo* compounds there appeared a signal at about τ 10 which integrated for one proton. The hydrogen responsible appears to be the one at C-3 *cis* to the equivalent cyclopropyl hydrogens at C-2 and C-4. This assignment is based on the peak widths of the signals due to the two 3-methylene hydrogens. The high-field signals had widths of about 25 cps; those for the other geminal hydrogens, where measurable, had widths of about 15 cps. Since J_{cis} is generally larger than J_{trans} for cyclopropanes, the broadest signal corresponds to the *cis* hydrogen.[26] The 3-*trans* hydrogen appears at about τ 9.5 in the *exo-anti* derivatives, but is shifted to about τ 9.1 in the *exo-syn* derivatives.[27]

Kinetic Studies. The brosylates of *exo-syn* (IV-Bs) and *endo-syn* (VI-Bs) alcohols, like that of the *exo-anti* isomer III-Bs previously reported,[17] were solvolyzed in 0.1 *N* NaOAc–HOAc (Table I). Inability to isolate the

Table I. Observed Rate Constants for Acetolysis of *endo-syn* (VI) and *exo-syn* (IV) *p*-Bromobenzenesulfonates[a]

Temp, °C	$k_1 \times 10^5$ sec^{-1}	Temp, °C	$k_1 \times 10^5$ sec^{-1}
	endo-syn Brosylate VI-Bs[b]		
165.0	5.25	175.0	11.4
165.0	5.11[c]	185.0	27.8
175.0	11.1	185.0	26.6
	exo-syn Brosylate IV-Bs[b]		
95.0	3.09	105.0	11.3[c]
95.0	3.25	115.0	30.6
105.0	11.5	115.0	30.2

[a] 0.098 *M* NaOAc in acetic acid. [b] 0.04 *M* brosylate unless noted. [c] 0.02 *M* brosylate.

endo-anti brosylate V-Bs made it necessary to compare the solvolysis of a less reactive compound; the *p*-nitrobenzoate V-*p*-NB was studied in 70% aqueous dioxane. To establish a rate relationship with the reactivities of brosylates, the *p*-nitrobenzoates of *anti*-7-norbornenol was also hydrolyzed in this solvent (see Table II).

Table II. Observed Rate Constants for Solvolysis of *p*-Nitrobenzoates of *endo-anti* Alcohol V and of *anti*-7-Norbornenol in 70% Aqueous Dioxane

Temp, °C	$k_1 \times 10^5$ sec^{-1}	Temp, °C	$k_1 \times 10^5$ sec^{-1}
	endo-anti p-Nitrobenzoate (V-*p*-NB)[a]		
90.0	8.69	100.0	24.6[b]
90.0	9.72	110.0	61.6
100.0	23.3	110.0	65.0
	anti-7-Norbornenyl *p*-Nitrobenzoate[a]		
170.0	4.89	185.0	15.2[b]
170.0	5.07	195.0	24.7
185.0	13.8	195.0	24.7

[a] 0.01 *M* ester unless noted. [b] 0.005 *M* ester.

(25) *exo* compounds containing a double bond did not show such a high-field signal.

(26) This assignment is different from that of D. T. Longone and A. H. Miller, *Chem. Commun.*, 447 (1967), who suggest in general that the highest field signal in 1,2-dialkyl-substituted cyclopropanes is due to the hydrogens *trans* to the 1,2-hydrogen atoms. It may be that the constrained [3.2.1.0^{2,4}]octyl ring system here provides a net deshielding of C-3 *trans*-hydrogen which is in close proximity to C-8 groups.[27]

(27) This effect is like that reported by M. A. Battiste and M. E. Brennan, *Tetrahedron Letters*, 5857 (1966), except the deshielding effect is greater with their compounds.

In calculating the relative rates of solvolysis of these compounds (with respect to acetolysis of 7-norbornyl brosylate as unity) it was assumed that the relative rates of solvolysis of brosylates and *p*-nitrobenzoates are the same, *i.e.*, *endo-anti p*-nitrobenzoate solvolyzed 10^3 times faster than *anti*-7-norbornenyl *p*-nitrobenzoate at 100°, and, as the calculated rate of acetolysis of *anti*-7-norbornenyl brosylate is 10^9 times greater than that of 7-norbornyl brosylate at this temperature,[28] the hypothetical *endo-anti* brosylate was assigned an acetolysis rate of 10^{12} relative to 7-norbornyl brosylate. These calculated relative rates are given in Table III.

Table III. Comparison of Solvolytic Rates

Compd	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu	k, sec^{-1} at 100°	k rel to 7-norbornyl brosylate
endo-anti V	26.7[a]	−4.0	2.4×10^{-4} [a]	*Ca.* 10^{12}
anti-7-Norbornenyl	25.6[a]	−21.2	1.9×10^{-7} [a]	10^9
exo-syn IV	27.1[b]	−5.4	7.0×10^{-5} [b]	10^4
endo-syn VI	31.8[b]	−6.3	1.9×10^{-7} [b]	10
exo-anti III	29.4[b]	−17.1	8.4×10^{-9} [b]	1

[a] *p*-Nitrobenzoate solvolysis in 70% aqueous dioxane. [b] *p*-Bromobenzenesulfonate solvolysis in 0.1 *N* NaOAc–HOAc.

With solvolysis of *endo-anti p*-nitrobenzoate and *exo-syn* brosylate the observed infinity titers were less than the theoretical ones due to rearrangements yielding unreactive esters. The *endo-anti p*-nitrobenzoate gave *ca.* 30% of *endo*-tricyclo[3.3.0.0^{4,6}]oct-2-yl *p*-nitrobenzoate (XIV-*p*-NB), and the *exo-syn* brosylate gave *ca.* 20% of an unidentified solid brosylate. This was not the very unreactive *exo-anti* brosylate which would have been produced from simple inversion around the ionic center. In any case, the observed infinity titers were used in first-order kinetic plots and the observed rate constants from slopes of the resulting straight lines correspond to the sum of rate constants for rearrangement and solvolysis, *i.e.*, $k_{obsd} = k_{rear} + k_{solv}$.[29] Both the rearrangement as well as solvolysis products probably arise from a common ionization process and the observed rate constants are therefore the best measurement of rates of ion formation.

Carbonium ion formation (rather than simple ester hydrolysis) from the *endo-anti* (V) and *anti*-7-norbornenyl *p*-nitrobenzoates was indicated by product studies (see below). Also control experiments on *endo-syn* and 7-norbornyl *p*-nitrobenzoates showed that ester hydrolysis of these similar compounds was very slow in 70% aqueous dioxane under the conditions of the kinetic studies used with *endo-anti* (V) or with *anti*-7-norbornenyl *p*-nitrobenzoates.[30]

(28) Calculated from data of ref 13 and assuming a rate of brosylate solvolysis three times greater than tosylate solvolysis.

(29) *Cf.* K. L. Servis and J. D. Roberts, *Tetrahedron Letters*, 1369 (1967).

(30) However, all four *p*-nitrobenzoate esters hydrolyzed rapidly under basic conditions (0.01 *N* NaOH or $NaHCO_3$) in this solvent.[31]

(31) With the addition of 1 equiv of $NaHCO_3$ to the solvolysis media the *endo-anti p*-nitrobenzoate V gave an alcohol portion consisting of a 14:86 mixture of unrearranged *endo-anti* alcohol V and rearranged *endo* alcohol XIV. Tanida, *et al.*,[12a] report a 20:80 ratio of these alcohols from solvolysis of *endo-anti p*-nitrobenzoate in 70% aqueous acetone in the presence of 2 equiv of $NaHCO_3$. A simple base-promoted ester hydrolysis accounts for the appearance of *endo-anti* alcohol V under these conditions.[23] See ref 26 in H. Tanida, *Accounts Chem. Res.*, 1, 239 (1968).

Product Studies. Two compounds were found as products of solvolysis of the very reactive *endo-anti* *p*-nitrobenzoate (V) after ten half-lives under kinetic conditions (0.01 *M* ester in 70% aqueous dioxane at 100°). The crude extracted products contained only the solid rearranged *p*-nitrobenzoate (*endo* XIV-*p*-NB) and the corresponding alcohol (*endo* XIV-OH). No other products were detected by capillary column gas–liquid partition chromatography; specifically, the *endo-syn* (VI-OH) and *endo-anti* (V-OH) alcohols were not found under conditions where a 1% mixture of either of these in the presence of rearranged alcohol (XIV-OH) was readily detectable.[31]

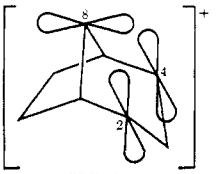
The possibility that unrearranged *endo-anti* alcohol was an initial product (either from a carbonium ion reaction or from ester hydrolysis) but that it was then catalytically rearranged by *p*-nitrobenzoic acid to the final alcohol XIV-OH was investigated by control experiments. Treatment of an equimolar 0.01 *M* solution of *endo-anti* alcohol V-OH and *p*-nitrobenzoic acid under kinetic conditions (for a time corresponding to 20 half-lives for the solvolysis of V-*p*-NB) gave a 1:4 mixture of rearranged (XIV-OH) and unrearranged (V-OH) alcohols. The *endo-anti* alcohol V is then only slowly rearranged under the conditions of the product and kinetic studies described above. This experiment shows that if *endo-anti* alcohol had been formed in solvolysis of *endo-anti* *p*-NB it would have been sufficiently stable to survive, be extracted by the separation procedure, and detected by the analytical method.[32]

Because of lower importance and higher complexity not as much attention was paid to the products of acetolysis of *exo-syn* (IV-Bs) and *endo-syn* (VI-Bs) brosylates. Under kinetic conditions (0.04 *M* in 0.1 *M* NaOAc–HOAc at 115 and 185°, respectively, for five half-lives) different complex mixtures of rearranged acetates were obtained. Reduction of the mixtures with $LiAlH_4$ gave alcohols partially separable by gas–liquid partition chromatography. The *exo-syn* brosylate gave at least five alcohol components (one major); the *endo-syn* brosylate gave at least ten products on a capillary column (four major ones). No further attempts were made to identify these products.

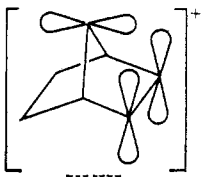
Discussion

Cyclopropyl Participation. As compounds III–VI are rigid structures each possessing only one "conformation," the results of Table III require no modification for conformation equilibria, and direct comparisons of relative rates with cyclopropyl configurations are possible. The order of observed reactivity is *endo-anti* $\gg$ *exo-syn* > *endo-syn* > *exo-anti* with rate ratios $10^{12}:10^{4}:10:1$, respectively. The tremendous difference of 10^{12} leaves little room for disagreement with the idea[7] that a suitably oriented cyclopropyl bond can participate very effectively in homoallylic formation of a carbonium ion. The *endo-anti* and *endo-syn* isomers V and VI possess essentially identical steric, inductive, and angular environments around the ionizing center, yet their rates differ by a factor of 10^{11}. Backside participation by the cyclopropyl group during ionization of the rigid chair form *endo-anti* isomer seems to be the unique explanation.

The orientation required for such participation is unlike the parallel π alignment of orbitals in cyclopropylcarbinyl cations,[4,5,33] but rather a relationship which allows more σ-type interaction of the electronically difficient ionic center with the sp^5 orbitals of cyclopropane (as in the ion II suggested by Winstein[7]). The situation is analogous to homoallylic participation by double bonds; at relatively great distances σ overlap is more effective than π overlap.[34] In addition, since the relative rate of *endo-anti* *p*-nitrobenzoate is 10^3 times greater than that of *anti*-7-norbornenyl *p*-nitrobenzoate, overlap of cyclopropyl orbitals during ionization of XVII appears to be even more favorable than overlap of double-bond orbitals in XVIII. Compared with the p orbitals of double bond in XVIII, the p-like orbitals of cyclopropyl in XVII are pointed



XVII



XVIII

more directly at the initial cationic center. Calculations[35] have indicated greater stability from the orbital interaction shown in XVII than from that in XVIII.

Generally there is little influence of cyclopropyl at a variety of homoallylic positions as in compounds VII–X.[14–16] This might be due to more stringent configurational requirements for homocyclopropylcation interaction,[16,36a] *e.g.*, conditions which are met only with the *endo-anti* structure V, such as equal participation by both ends of a cyclopropyl bond. It may also be that in solvolysis of *endo-anti* *p*-nitrobenzoate the release of strain contributes to high reactivity[16c,d] (see below). However, the orientation of orbitals as in XVII remains a necessary condition for this activity.

Structure of the Intermediate. Although carbonium ion formation from *endo-anti* *p*-nitrobenzoate V must at least begin with equal participation of p-like cyclopropyl orbitals at C-2 and C-4, there is considerable uncertainty on what type of intermediate this leads to. Equal contributions from C-2 and C-4 may continue and a nonclassical ion with bonding similar to XVII may exist, or, the bonding contributions from one of C-2

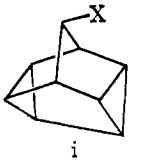
(32) It was at one time believed that *endo-anti* alcohol V was a product of carbonium ion reaction in solvolysis of V-*p*-NB.[12] The absence of this product makes suggestions[12b] of a nonclassical ion somewhat less viable (however, see Discussion).

(33) An interesting example of parallel overlap of a cyclopropyl "banana" bond with developing adjacent orbitals has been presented by B. Halton, M. A. Battiste, R. Rehberg, C. L. Deyrup, and M. E. Brennan, *J. Am. Chem. Soc.*, **89**, 5964 (1967).

(34) M. Simmonetta and S. Winstein, *ibid.*, **76**, 18 (1954).

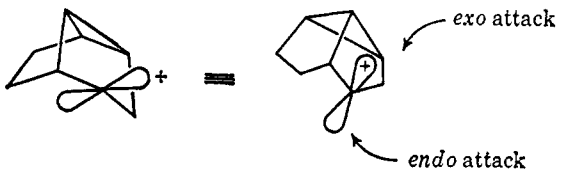
(35) R. Hoffmann, *Tetrahedron Letters*, 3819 (1965).

(36) (a) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965, p 298; (b) R. M. Coates and J. L. Kirkpatrick, *J. Am. Chem. Soc.*, **90**, 4162 (1968), have recently presented a very interesting study of compound i. They pointed out that the large observed solvolytic rate of i (10^{12} faster than the corresponding 7-norbornyl compound) cannot be attributed to an over-all relief of strain. The ring structure of the major solvolysis product remains the same as that of i although a triply degenerate rearrangement occurs.



i

and C-4 may decrease while the other increases and the resulting rearranged classical ion XIV may be the only intermediate.



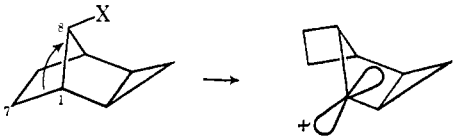
XIV

A large relative rate of solvolysis has often been interpreted to indicate formation of a nonclassical intermediate, stabilized by special overlap of nonadjacent orbitals. But the *endo-anti*-tricyclo[3.2.1.$0^{2,4}$]-oct-8-yl structure V rearranges completely to the tricyclo[3.3.0.$0^{4,6}$]oct-2-yl structure XIV (which, judging from carbonyl stretching frequencies of ketones XVI and XV, is less strained), so therefore an especially great reactivity does not require an especially unusual explanation. The release in strain in moving from ring system V toward ring system XIV may contribute to a high reactivity whether the transition state resembles XVII or XIV. A direct measurement or estimate of the energy change in conversion of these ring structures would be desirable.[36b]

In any case, solvolytic kinetic studies are less important in arguments concerning the structure of an intermediate than are product studies. With simple "double-hump" reaction paths, involving a single carbonium ion intermediate, the activation energy for formation of the intermediate is much greater than that for formation of any product from the intermediate. Assuming that a small energy change is indicative of a small structural change, the transition states for product formation are closer in structure to the intermediate than is the transition state for intermediate formation. The nature and variety of products are then better measures of the intermediate structure than are ordinary kinetic studies. The formation of only rearranged product from *endo-anti p*-nitrobenzoate suggests that the positive charge of the intermediate resides predominately at C-2(C-4) rather than at C-8 (see XVII).[37] The presence of *ca.* 30% rearranged *p*-nitrobenzoate (*endo* XIV-*p*-NB), the product of ion pair return, suggests the existence of a relatively stable and long-lived ion, one able to survive long enough in 67 mole % water to allow a *p*-nitrobenzoate anion to approach from a new direction. These characteristics can perhaps be as much expected from a nonclassical ion XVII as from classical ion XIV.

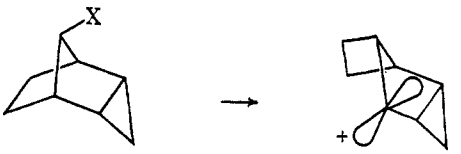
Most indicative of an intermediate like XVII is the stereospecificity in forming only *endo* product XIV-OH or -*p*-NB. In structurally similar bicyclo[3.2.1]-octyl compounds, the reaction of a C-2 cation with a nucleophile occurs with considerable *exo* approach.[38] *exo* attack of nucleophilic reagent occurs in the hydride reduction of tricyclo[3.3.0.$0^{4,6}$]octan-2-one (XV) but does not occur in the solvolysis of *endo-anti p*-nitrobenzoate which yields only products of *endo* attack (see diagram XIV above). The formation of *endo* solvolysis product is consistent with an electronic effect which shields the *exo* side and directs the nucleophilic agent to the sterically more hindered *endo* side. Thus, in product formation, the expected properties of possible intermediate ions XVII and XIV lead to divergent predictions and the experimental result supports the nonclassical ion XVII.

Stereospecific formation of few products, lack of extensive rearrangement, and relatively greater rates of solvolysis have all been supporting evidence for a nonclassical ion (II) in the closely related case of *cis*-bicyclo[3.1.0]hex-2-yl tosylate solvolysis.[7] These properties correspond to those found in solvolysis of *endo-anti p*-nitrobenzoate V, but are generally different than those found in solvolysis of the *exo-anti* III, *exo-syn* IV, and *endo-syn* VI brosylates. Acetolysis of *endo-syn* brosylate VI proceeds at a rate little over ten times that of 7-norbornyl brosylate and produces many products. *exo-syn* brosylate IV is considerably more reactive, however, with a relative rate of 10^4. Here the departure of leaving group may be sterically aided by the very close methylene group of the *exo*-cyclopropyl group. Another possibility is a concerted C-1 to C-8 rearrangement of the C-7 atom *trans* to the leaving group. Such concerted rearrangement in a *syn* structure corresponds to that occurring in solvolysis of *syn*-7-norbornenyl tosylate which gives rise to a stabilized allyl cation.[39] The resulting ion from *exo-syn* IV would be a stabilized cyclopropylcarbinyl cation with parallel orientation of ring and adjacent carbonium ion orbital. While a similar arrangement of *endo-syn*



exo-syn

VI isomer (relative rate 10) gives a carbonium ion center adjacent to a cyclopropyl group, there would not initially be stabilization by a parallel alignment of orbitals.



endo-syn

Finally, the most unreactive of the four isomers, the *exo-anti* isomer III, cannot undergo a concerted *trans* rearrangement to a cyclopropylcarbinyl cation and, of course, has a rigid boat conformation which prevents homoallylic cyclopropyl participation.

In summary, the close similarity of cyclopropyl and olefinic bonding is well illustrated in properties and reactions of the stereoisomers of the rigid tricyclo-[3.2.1.$0^{2,4}$]oct-8-yl system. A suitably oriented cyclopropyl group can interact from homoallylic positions and cause great solvolytic rate differences as well as changes in electronic and nmr spectra.[24] The origin of the interaction is the in-plane, p-electron-donating

(37) This is analogous to the charge distribution in the ion from *anti*-7-norbornenyl derivatives. The positive charge is predominately on C-2 (C-3). See M. Brookhart, A. Diaz, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 3135 (1966); H. R. Richey, Jr., and R. K. Lustgarten, *ibid.*, **88**, 3136 (1966).

(38) J. A. Berson and P. Reynolds-Warnhoff, *ibid.*, **84**, 682 (1962); **86**, 595 (1964); R. T. LaLonde, J. Ding, and M. A. Tobias, *ibid.*, **89**, 6651 (1967); H. L. Goering and U. Mayer, *ibid.*, **86**, 3753 (1964); H. L. Goering and M. F. Sloan, *ibid.*, **83**, 1398 (1961).

(39) S. Winstein and E. T. Stafford, *ibid.*, **79**, 505 (1957).

properties of cyclopropyl orbitals, which in solvolysis of *endo-anti p*-nitrobenzoate V may directly give a nonclassical cationic intermediate, the 2,4-ethanotrishomocyclopropenyl cation XVII.

Experimental Section[40,41]

***endo*-8,8-Dimethoxy-1,5,6,7-tetrachlorotricyclo[3.2.1^{2,4}]oct-6-ene.** Cyclopropene[19] was carried by a slow stream of nitrogen to a 50-ml, two-necked flask fitted with a short condenser cooled to −5°. The gas was bubbled through a solution of 17.6 g of 5,5-dimethoxytetrachlorocyclopentadiene at 0° in 25 ml of petroleum ether (bp 30–60°). After the diene was treated with cyclopropene over *ca.* 10 hr, the reddish solid which had formed in the flask was filtered off and the solvent was removed by rotary evaporation at 50° (15 mm) to give 20.1 g (95%) of reddish crystals. Recrystallization from methanol–water gave an analytical sample, mp 70–71°. The nmr spectrum ($CDCl_3$) showed singlets at τ 6.37 and 6.49 (methoxyl protons), a pair of doublets at 8.18 (two equivalent cyclopropyl protons, J_{cis} = 7.0 cps, J_{trans} = 3.5 cps), a pair of triplets at 9.08 (*cis*-cyclopropyl proton, J_{cis} = 7.4 cps, J_{gem} = 6.8 cps), and a pair of triplets at 9.58 (*trans*-cyclopropyl proton, J_{trans} = 3.5 cps, J_{gem} = 7.5 cps).

Anal. Calcd for $C_{10}H_{10}Cl_4O_2$: C, 39.51; H, 3.32; Cl, 46.61. Found: C, 39.42; H, 3.30; Cl, 46.51.

***endo*-8,8-Dimethoxytricyclo[3.2.1.0^{2,4}]oct-6-ene (XI).** *endo*-8,8-Dimethoxy-1,5,6,7-tetrachlorotricyclo[3.2.1.0^{2,4}]oct-6-ene (33.4 g) was dissolved in a mixture of 90 g of *t*-butyl alcohol and 525 ml of freshly distilled tetrahydrofuran under nitrogen in a 2-l., three-necked flask fitted with a gas-inlet tube, a mechanical stirrer, and a reflux condenser.[20] Finely cut sodium (60 g) was then added with stirring. The mixture was heated to initiate the reaction and refluxed gently with stirring for 8 hr. The reaction mixture was cooled to 0°, and 500 ml of methanol slowly was added to destroy the excess sodium and poured into 2 l. of water. The aqueous solution was extracted and the combined ether extracts were washed with brine and dried over Mg_2SO_4. Vacuum distillation provided 13.8 g (76%) of product, bp 103–105° (33.5 mm). The nmr spectrum (CCl_4, $CDCl_3$) showed a triplet at τ 4.43 (olefinic protons), singlets at 6.89 and 7.02 (methoxyl protons), a multiplet at 7.28 (bridgehead protons), a multiplet at 8.90 (two cyclopropyl protons), and a multiplet at 9.65 (two cyclopropyl protons).

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.05; H, 8.34.

***endo*-8,8-Dimethoxytricyclo[3.2.1.0^{2,4}]octane (XII).** The octene XI (22.75 g) was dissolved in 200 ml of ethanol and hydrogenated at room temperature in the presence of 10 g of sodium carbonate and 2.0 g of 10% palladium on charcoal. Vacuum distillation gave 21.1 g (92%) of product, bp 96–98° (16 mm). The nmr spectrum (CCl_4), $CDCl_3$) showed a pair of singlets at τ 6.82 and 6.93 (methoxyl protons), a multiplet at 8.01 (bridgehead protons), and a multiplet between 8.35 and 9.63 (*exo*, *endo*, and cyclopropyl protons).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.33; H, 9.39.

***endo*-Tricyclo[3.2.1.0^{2,4}]octan-8-one (XVI).** The ketal XII (18.0 g) was dissolved in 135 ml of glacial acetic acid and the mixture was stirred at 70° for 24 hr. After the reaction mixture had been cooled to 0°, it was diluted with about 100 ml of pentane and the acetic acid was neutralized by carefully adding 108 g of sodium hydroxide in 360 ml of water. About 100 ml of water was added and the aqueous layer was extracted with three 300-ml portions of pentane. After drying, the solvent was removed by rotary evaporation at 40° (40 mm) to give 13.5 g (103%) of a slightly yellowish oil. This oil was estimated to be about 90% product XVI by glpc. A small portion was purified by cooling the oil to about −40° and filtering it on a sintered-glass funnel as it warmed up to room temperature. The solid thus obtained was sublimed at 50–60° (20 mm) to give product: mp 66.5–69°, lit.[12a] mp 71–72°; ν_{max} (cm^{-1}) 1858 w, 1818 m, 1772 m, 1760 s, 1725 w in CCl_4. The nmr spectrum ($CDCl_3$) showed a multiplet at τ 7.93 (bridgehead protons), a multiplet at 8.44 (*exo* protons), a multiplet at 8.81 (*endo* protons), a multiplet at 9.01 (two equivalent cyclopropyl protons and *cis*-cyclopropyl protons), and a pair of triplets at 9.32 (*trans*-cyclopropyl proton, J_{trans} = 3.4 cps, J_{gem} = 6.8 cps). The ultraviolet spectrum showed an n → π^* band at λ_{max}^{EtOH} 276 mμ (ε 40.5) and an end absorption at 215 mμ (ε 495).[24] The mass spectrum showed *m/e* 122 (12.82), 94 (39.49), 79 (100.00). *Anal.* Calcd for $C_8H_{10}O$: *m/e* 122.073. Found: *m/e* 122.072. Carbon and hydrogen analysis gave consistently low carbon probably due to loss of CO.

***endo-syn*- and *endo-anti*-Tricyclo[3.2.1.0^{2,4}]octan-8-ols (VI-OH and V-OH). Method I.** To a stirred suspension of 0.3 g of lithium aluminum hydride in 15 ml of anhydrous ether was added a solution of 0.95 g of *endo* ketone in 10 ml of anhydrous ether. The mixture was stirred at room temperature for 0.5 hr and then refluxed gently for 1 hr. After cooling, addition of water, ether extraction, and drying, the solvent was removed by rotary evaporation at 40° (30 mm) to give 0.82 g (85%) of a yellowish, slushy oil. Glpc showed that the product consisted of two major compounds in the ratio of about 2:1. The major component was identified as the previously reported[17] *endo-syn* isomer, mp 131–132°, lit.[12a] mp 128–130°. The nmr spectrum ($CDCl_3$) showed a broad singlet at τ 5.76 (bridge proton), a sharp singlet at 7.05 (hydroxyl proton), a broad singlet at 7.97 (bridgehead protons), and a multiplet between 8.20 and 9.20 (*exo*, *endo*, and cyclopropyl protons). The mass spectrum showed *m/e* 124 (4.42), 107 (6.90), 106 (39.56), 78 (100.00), 70 (93.81).

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74; O, 12.88; *m/e* 124.089. Found: C, 77.60, 77.29; H, 9.70, 10.10; O, 12.61; *m/e* 124.089.

The minor component was the previously[17] unknown *endo-anti* isomer, mp 140–141°, lit.[12a] mp 136–138°. The nmr spectrum ($CDCl_3$) showed a broad singlet at τ 5.91 (bridge proton), a sharp singlet at 7.08 (hydroxyl proton), a broad singlet at 7.92 (bridgehead protons), a multiplet at 8.36 (*exo* protons), a multiplet at 8.93, and a multiplet at 9.35 (*endo* protons and cyclopropyl protons). The mass spectrum showed *m/e* 124 (3.23), 107 (4.72), 106 (31.23), 78 (55.87), 70 (100.00).

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74; *m/e* 124.089. Found: C, 77.27; H, 9.77; *m/e* 124.089.

Method II. *endo* ketone XVI (4.9 g) was dissolved in 150 ml of 95% ethanol and exposed for 1.5 hr to hydrogen gas at 4 atm in the presence of 3 g of sodium carbonate and 0.4 g of platinum oxide. The sodium carbonate and platinum were removed by filtration and the solvent was distilled until about 10 ml of a yellowish stillpot residue containing a white precipitate remained. The residue was treated with charcoal and filtered to give a clear yellowish solution which was shown by glpc to contain a 1:2 mixture of *endo-syn* alcohol and *endo-anti* alcohol. The solution was separated by preparative glpc on a preparative Carbowax column at 200° to give 0.59 g of the *syn* isomer and 0.98 g of the *anti* isomer (31.5% total yield). It was later found that the yield could be doubled if the glpc collectors were packed with glass wool and saturated with ether.

***p*-Bromobenzenesulfonates.** The brosylates were prepared from the corresponding alcohol and *p*-bromobenzenesulfonyl chloride in pyridine at 0° over a few hours. *exo-syn* brosylate IX-Bs from alcohol IX-OH[17] was recrystallized from methanol and gave mp 95.2–96°. *Anal.* Calcd for $C_{14}H_{15}SO_3Br$: C, 48.99; H, 4.40; S, 9.34; Br, 23.21. Found: C, 49.17; H, 4.44; S, 9.45; Br, 23.17.

endo-syn brosylate VI-Bs was recrystallized from methanol and gave mp 107.2–107.6°. *Anal.* Calcd for $C_{14}H_{15}SO_3Br$: C, 48.99; H, 4.40; S, 9.34. Found: C, 48.87; H, 4.62; S, 9.61.

Attempts to prepare *endo-anti* brosylate V failed.[40]

***p*-Nitrobenzoates** were prepared from equimolar alcohol and acid chloride in boiling pyridine for *ca.* 1 min. *endo-anti p*-nitrobenzoate V-*p*-NB was recrystallized from methanol and had mp 150.1–151.5°, lit.[12a] 152–153.5°. *Anal.* Calcd for $C_{15}H_{15}NO_4$: C, 65.93; H, 5.53; N, 5.13. Found: C, 65.70; H, 5.60; N, 5.19.

endo-syn p-nitrobenzoate VI-*p*-NB, mp 108–109°, was recrystallized from methanol. *Anal.* Calcd for $C_{15}H_{15}NO_4$: C, 65.93; H, 5.53; N, 5.13. Found: C, 65.97; H, 5.32; N, 4.56.

anti-7-Norbornenyl *p*-nitrobenzoate recrystallized from 95%

(40) Further details, especially on synthetic procedures, infrared, mass, and nmr spectra, and kinetic data can be obtained from the Ph.D. thesis of J. A. Haywood-Farmer, University of British Columbia, 1967. Available on microfilm through the National Library of Canada, Ottawa.

(41) Infrared absorption relative intensities are expressed as w = weak, m = medium, and s = strong. Nuclear magnetic resonance (nmr) spectra were recorded on a Varian A-60 spectrometer. Resonance peaks are given in τ units, samples were 15–20% (w/v). Mass spectra were obtained on an Associated Electronic Industries MS9 instrument using a windowless photoionization source.[42] The source employed was the 584-Å He line. The masses and relative intensities of pertinent peaks are given. Gas–liquid partition chromatography (glpc) was carried out with Aerograph 90-P, A-700 Autoprep, and Perkin-Elmer Model 226 (capillary column) chromatographs.

(42) C. E. Brion, *Anal. Chem.*, **38**, 1941 (1966).

ethanol had mp 118–119°. *Anal.* Calcd for $C_{14}H_{13}NO_4$: C, 64.86; H, 5.05; N, 5.40. Found: C, 64.71; H, 5.17; N, 5.60.

***endo*-Tricyclo[3.3.0.0^{4,6}]oct-2-yl *p*-Nitrobenzoate (XIV-*p*-NB).** *endo-anti* *p*-nitrobenzoate V-*p*-NB (216 mg) was dissolved in 70 ml of 70% aqueous dioxane held in a 100-ml flask with a constricted neck. The flask was flushed with nitrogen, sealed, and heated at 100° for 8.5 hr. After cooling, the flask was opened and the contents was diluted with 100 ml of water. The mixture was extracted with four 125-ml portions of pentane and the combined pentane solutions were washed with three 100-ml portions of water and 100 ml of 10% aqueous sodium carbonate solution. After drying, the solvent was removed by rotary evaporation to give 147 mg of a slushy yellowish solid. Sublimation of this solid at 80° (10 mm) for 5 hr left 108 mg (50%) of a yellowish residue which was washed twice with small volumes of cold pentane to give a pure sample of *endo*-tricyclo[3.3.0.0^{4,6}]oct-2-yl-*p*-nitrobenzoate, mp 113–114°, lit.[12a] mp 116–117°. The nmr spectrum ($CDCl_3$) showed a singlet at τ 1.79 (aromatic protons), a pair of overlapping triplets at 4.76 (H-2, $J_{2,3}$ = 9.0 cps, $J_{1,2}$ = 6.5 cps), and complex multiplets between 7.0 and 9.0.

Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.93; H, 5.53; N, 5.13. Found: C, 65.79; H, 5.52; N, 5.28.

***endo*-Tricyclo[3.3.0.0^{4,6}]oct-2-yl Acetate (XIV-OAc).** *endo-anti* alcohol V-OH (417 mg) was treated at room temperature for 22 hr with 3.5 ml of 0.04 *M* *p*-toluenesulfonic acid in glacial acetic acid. About 70 ml of water was added to the solution which was then extracted with three 50-ml portions of pentane. The combined pentane portions were washed with three 25-ml portions of water, 25 ml of 10% aqueous sodium carbonate solution, and 25 ml of brine. After drying, the pentane was removed to give 487 mg (87%) of crude yellowish acetate. Glpc on an acid-washed Carbowax column at 145° gave the pure ester. The nmr spectrum ($CDCl_3$) showed a pair of triplets at 5.15 (H-2, $J_{2,3}$ = 9.0 cps, $J_{1,2}$ = 6.6 cps), a singlet at 8.12 (acetate protons), and an unresolvable multiplet between 7.30 and 9.20 (aliphatic and cyclopropyl protons). *Anal.* Calcd for $C_{10}H_{14}O_2$: *m/e* 166.099. Found: *m/e* 166.099.

***endo*-Tricyclo[3.3.0.0^{4,6}]octan-2-ol (XIV-OH).** The acetate XIV-OAc (525 mg) was reduced with 250 mg of $LiAlH_4$ in 10 ml of anhydrous ether. Normal work-up gave 390 mg (98%) of a yellowish, slushy oil. Glpc on the acid-washed Carbowax column at 145° provided an analytical sample of the alcohol, mp 77–79.5°. The nmr spectrum ($CDCl_3$) showed a pair of triplets at τ 5.83 (H-2, $J_{2,3}$ = 8.9 cps, $J_{1,2}$ = 6.4 cps), a singlet at 7.44 (hydroxyl proton), and a complex unresolvable multiplet between 7.50 and 9.25 (aliphatic and cyclopropyl protons). *Anal.* Calcd for $C_8H_{12}O$: *m/e* 124.089. Found: *m/e* 124.089.

Tricyclo[3.3.0.0^{4,6}]octan-3-one (XV). Chromium trioxide (1.8 g, 0.018 mole) was slowly added to 10 ml of ice-cooled pyridine. To this mixture was added a solution of 400 mg (3.2 mmoles) of *endo* alcohol XIV-OH in 10 ml of pyridine over about 10 min. After the addition was complete, the stirring was continued for a further 20 min. The very dark reaction mixture was allowed to stand at room temperature for 24 hr and then 20 ml of water was slowly added with stirring. After dilution to about 200 ml with water, the suspension was extracted with five 80-ml portions of pentane. The combined extracts were washed with 80 ml of water, 100 ml of 10% aqueous hydrochloric acid solution, 200 ml of water, and brine and dried over magnesium sulfate. After the drying agent had been removed by filtration, the solvent was removed to give 260 mg (66%) of a yellowish oil. Glpc on an acid-washed Carbowax column at 145° gave an analytical sample of the liquid ketone. Its infrared spectrum in CCl_4 showed a sharp carbonyl peak at 1741 cm^{-1}. The nmr spectrum ($CDCl_3$) showed a complex multiplet between τ 7.30 and 9.00. The ultraviolet spectrum showed an n $\rightarrow$ π^* band at λ_{max}^{EtOH} 292 mμ (ϵ 29) and an end absorption at 215 mμ (ϵ 150).

Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25; *m/e* 122.073. Found: C, 78.59; H, 8.35; *m/e* 122.073.

This ketone was reduced with $LiAlH_4$ in ether. Sublimation of the product gave a sample whose nmr and infrared spectra were identical with those of *endo* alcohol XIV-OH although its mp 66–77.5° was lower. This melting point was undepressed on mixing with alcohol XIV, mp 77–79.5°, which had been purified by glcp (see above). The product of reduction showed only *endo* alcohol XIV on TCEP and Carbowax columns and on a UCON LB 550X capillary column.

***exo*-Tricyclo[3.2.1.0^{2,4}]octan-8-one.** *exo* ketal XIII[17] (3.8 g) was dissolved in 28 ml (0.49 mole) of glacial acetic acid and the mixture stirred at 70° for 24 hr. The solution was cooled in ice and dissolved in about 75 ml of pentane and the acetic acid was removed by slowly adding a cooled solution of 23 g (0.575 mole) of sodium hydroxide in 80 ml of water. The pentane layer was separated and the aqueous layer was extracted with three 50-ml portions of pentane. The pentane solutions were dried and distilled to give product (2.2 g, 80%), bp 83–84° (17 mm). This ketone in CCl_4 showed infrared absorption at (cm^{-1}) 1859 w, 1813 w, 1775 s, 1743 m, and 1724 w. The nmr spectrum (CCl_4, $CDCl_3$) showed a broad singlet, at τ 8.04 (bridgehead protons), a broad singlet at 8.23 (*exo* and *endo* protons), a quartet at 8.85 (two equivalent cyclopropyl protons, J_{cis} = 6.8 cps, J_{trans} = 3.4 cps), a pair of triplets overlapping to a quartet at 9.50 (*cis*-cyclopropyl proton, J_{cis} = 6.7 cps, J_{gem} = 6.7 cps), and a pair of triplets overlapping to a quintet at 9.87 (*trans*-cyclopropyl proton, J_{trans} = 3.4 cps, J_{gem} = 6.8 cps). The two equivalent cyclopropyl protons were also coupled to the bridgehead protons, J = 0.8 cps. This small coupling was removed by irradiation of the bridgehead protons giving a sharp quartet for the equivalent cyclopropyl proton signal. The ultraviolet spectrum showed an n $\rightarrow$ π^* band at λ_{max}^{EtOH} 293 mμ (ϵ 22) and an end absorption at 215 mμ (ϵ 63).[24] The mass spectrum showed *m/e* 122 (2.77), 94 (41.74), 79 (100.00). *Anal.* Calcd for $C_8H_{10}O$: *m/e* 122.073. Found: *m/e* 122.074. Repeated carbon and hydrogen analyses failed to give the calculated amount of carbon possibly due to loss of CO.

This *exo* ketone was reduced with $LiAlH_4$ in ether to yield *exo-syn* alcohol IV-OH. The crude product was distilled, bp 96–105° (15 mm), and sublimed at 65° (10 mm) to give a sample, mp 46.5–48°, lit.[17] mp 44–46°.

Kinetic Studies. Rates of acetolysis of *p*-bromobenzenesulfonates were obtained in 0.098 *N* sodium acetate–acetic acid, using the common procedure.[43] Samples were titrated with 0.02 *N* perchloric acid–acetic acid to the bromophenol blue end point.

The solvolyses of the *p*-nitrobenzoates were followed[44] by titrating the acid formed from 0.01 *M* ester in dioxane–water (70:30 by vol). The initial ester solution was divided equally among *ca.* ten glass tubes which were then flushed thoroughly with nitrogen and sealed. The infinity samples for the *endo-anti* *p*-nitrobenzoate were taken after at least ten half-lives. Theoretical infinity values were used for the olefinic *p*-nitrobenzoate because solvent oxidation caused an excess acid titer to appear after several hours at 170–195°. This was not a problem at 90–110°.

Product Studies. *endo-anti* V-*p*-NB in 70% Aqueous Dioxane. *endo-anti*-Tricyclo[3.2.1.0^{2,4}]oct-8-yl *p*-nitrobenzoate (216 mg) was dissolved in 70 ml of 70% aqueous dioxane in a 100-ml flask with a constricted neck. The flask was flushed with nitrogen, sealed, and heated for 8.5 hr (10.2 half-lives) at 100°. The solution was cooled to room temperature, the flask was opened, and the contents was poured into 100 ml of water. The cloudy mixture was extracted with four 125-ml portions of pentane. The combined pentane solutions were washed with three 100-ml portions of water, 100 ml of 10% aqueous sodium carbonate solution, and brine. The solution was dried over $MgSO_4$, filtered, and evaporated to give a slushy white solid. This solid was sublimed for 2 hr at 65° (16 mm) to give 35.6 mg (36.3%) of white sublimate and 108.0 mg (50%) of yellowish residue. Further sublimation at 80° (10 mm) for 3 hr resulted in no further loss of weight from the residue. The sublimate was examined by glpc (UCON LB 550X capillary column at 115°) and showed a peak for only *endo*-tricyclo[3.3.0.0^{4,6}]octan-2-ol (XIV-OH). The *endo-syn*- and *endo-anti*-tricyclo[3.2.1.0^{2,4}]octan-8-ols (VI and V) were shown to be absent. A 1% mixture of either of these two alcohols in *endo*-tricyclo[3.3.0.0^{4,6}]octan-2-ol was readily detectable by the glpc analysis. The solid residue was shown by infrared analysis to contain almost pure *endo*-tricyclo-[3.3.0.0^{4,6}]oct-2-yl *p*-nitrobenzoate (XIV-*p*-NB).

***endo-anti* V-*p*-NB in 70% Aqueous Dioxane with $NaHCO_3$.** *endo-anti*-Tricyclo[3.2.1.0^{2,4}]oct-8-yl *p*-nitrobenzoate (85.5 mg, 0.313 mmole) and 32.1 mg (0.382 mmole) of sodium bicarbonate were placed in 31 ml of 70% aqueous dioxane in a 100-ml flask with a constricted neck. The flask was flushed with nitrogen, sealed, and heated at 100° for 1.75 hr (2.1 normal half-lives). Work-up similar to that above gave 50 mg of a yellowish white solid. Glpc (acid-washed Carbowax column at 145°) of an ether solution of this solid showed only one major peak. A sample was collected and was shown by infrared to be mainly *endo*-tricyclo[3.3.0.0^{4,6}]-octan-2-ol (XIV) with a small amount of *endo-anti*-tricyclo-

(43) Similar to that described by P. D. Bartlett and W. P. Giddings, *J. Am. Chem. Soc.*, **82**, 1240 (1960), and reference therein; see also ref 40.

(44) *Cf.* H. L. Goering, M. M. Pombo, and K. D. McMichael, *ibid.*, **85**, 965 (1963); P. D. Bartlett and E. B. Lefferts, *ibid.*, **77**, 2804 (1955).

[3.2.1.$0^{2,4}$]octan-8-ol (V) present. Glpc on the UCON LB 550X capillary column at 115° showed that the minor component was present as 14 ± 3% of the mixture.

endo-anti **Alcohol V in the presence of *p*-Nitrobenzoic Acid.** *endo-anti*-Tricyclo[3.2.1.$0^{2,4}$]octan-8-ol (53.4 mg, 0.43 mmole) and 73.8 mg (0.44 mmole) of *p*-nitrobenzoic acid were dissolved in 42 ml of 70% aqueous dioxane in a 50-ml flask with a constricted neck. The flask was flushed with nitrogen, sealed, and heated at 100° for 16 hr. Extraction with pentane, washing with 10% aqueous Na_2CO_3 solution, drying, and removal of solvent (see above work-up) gave 48 mg (90%) of a white solid. Glpc on the UCON LB 550X capillary column at 115° showed that the product was a 1:4 mixture of *endo*-tricyclo[3.3.0.$0^{4,6}$]octan-2-ol and *endo-anti*-tricyclo[3.2.1.$0^{2,4}$]octan-8-ol. *endo-anti* alcohol V is only slowly rearranged under the product study conditions given above.

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On the Mechanism of the Free-Radical Reactions of Cyanogen and Cyanogen Chloride with Hydrocarbon Substrates[1]

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Abstract: Both the free-radical reactions of cyanogen chloride and cyanogen with hydrocarbon substrates proceed by chain mechanisms involving intermediate imidyl radicals. In the reaction of cyanogen with 2,3-dimethylbutane the imidyl radical was found to be the chain-carrying species while in the reactions of cyanogen chloride with a variety of hydrocarbons, the imidyl intermediate undergoes a β-scission reaction producing the alkyl cyanide plus a chlorine atom which then carries the chain. The mechanism of the cyanation reaction of cyanogen chloride has been shown to proceed through a chain sequence of reactions in which each step was demonstrated to be reversible. The high selectivity observed in these cyanations was found to be due to the reversible reaction of the alkyl radicals formed with the hydrogen chloride produced in the reactions.

The photochemical reaction between cyanogen chloride and certain hydrocarbons has recently been reported by Müller and Huber.[3] Moderate yields of cyclohexyl cyanide (10%) were obtained from the reaction between cyanogen chloride and cyclohexane, while in the presence of acetyl chloride[3a] or free chlorine[3c] the yield was much improved.

$$C_6H_{12} + ClCN \xrightarrow{h\nu} C_6H_{11}CN + HCl \quad (1)$$

The authors proposed a radical chain mechanism in which the chain-propagating step was the abstraction of hydrogen by chlorine atoms. The radicals so formed then underwent a radical displacement upon the carbon of cyanogen chloride, a rare if not unique reaction[4] (Scheme I), to give the alkyl cyanide.

Scheme I

$$Cl\cdot + RH \longrightarrow HCl + R\cdot \quad (2)$$

$$R\cdot + ClCN \longrightarrow RCN + Cl\cdot \quad (3)$$

Although there are a few reports in the patent literature of the reactions of cyanogen chloride with alkanes[5] and alkenes[6-8] these involved very drastic temperatures and were very unselective reactions.

There are also reports of the reaction of cyanogen chloride with ethyl vinyl ether to give 2-ethoxy-3-chloroproprionitrile[9] and with saturated alkanes to give alkyl cyanides[10] both of which required the presence of peroxy compounds as radical initiators.

Because of the novelty of the chain-transfer reaction (eq 3) and because of the potential synthetic utility of a free-radical cyanation process, a detailed investigation of the mechanism of the reaction was undertaken.

Results and Discussion

Peroxide-Initiated Cyanation. The chain nature of the cyanation was established by initiation of the reaction with benzoyl peroxide. By treating cyanogen chloride (0.8 *M*) with various hydrocarbons in the presence of benzoyl peroxide (3 mole %), and determining the yield of alkyl cyanides, an approximate chain length of 6–15 units, depending on the substrate, was found. The efficiency for benzoyl peroxide initiation was taken, in these calculations,[11] to be 0.5. When 2,3-dimethylbutane was the substrate, minor amounts of alkyl chlorides were also formed. At higher initiator concentrations the ratio of alkyl

(1) Presented in part at the Division of Organic Chemistry, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968.

(2) University of Alberta, Killam Memorial Post-Doctoral Fellow, 1967–1969.

(3) (a) E. Müller and H. Huber, *Chem. Ber.*, **96**, 670 (1963); (b) *ibid.*, **96**, 2319 (1963); (c) German Patent 1,129,157 (1962); *Chem. Abstr.*, **57**, 13627*g* (1962).

(4) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 32.

(5) J. K. Dixon, U. S. Patents 2,553,404 (1951), 2,553,406 (1951); *Chem. Abstr.*, **45**, 9081 (1951).

(6) W. L. Kohlhase and T. F. Martens, U. S. Patents 2,848,476 (1958), 2,848,477 (1958); *Chem. Abstr.*, **53**, 2093*i* (1959).

(7) J. K. Dixon, U. S. Patent 2,745,864 (1956); *Chem. Abstr.*, **51**, 2019*b* (1957).

(8) H. Brendlein, U. S. Patent 2,833,808 (1958); *Chem. Abstr.*, **52**, 14659*c* (1958).

(9) E. I. Vasil'eva, B. I. Keda, and R. Kh. Freidlina, *Dokl. Akad. Nauk, SSSR*, **154**, 129 (1964).

(10) R. Graf, German Patent 848,947 (1952); *Chem. Abstr.*, **47**, 5425*b* (1953).

(11) Reference 4, pp 73–80.