cyclopropyl participation in the transition state for solvolysis, a proposal previously advanced for the similarly structured *endo-anti*-8-tricyclo[3.2.1.$0^{2,4}$]octyl *p*-nitrobenzoate.[17] The solvolysis rate of the latter is reported to be approximately 10 times that of XIII (70% aqueous acetone, 90.2°),[17b] and hence must be roughly 80 times the rate of I-OPNB.

Acknowledgments. We wish to thank R. L. Thrift for the superb pmr and dmr spectra, Professor S. G. Smith for assistance in the kinetic determinations, and the National Institutes of Health for partial financial support.

(24) National Institutes of Health Trainee, 1968.

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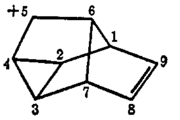
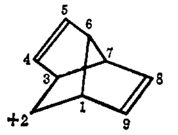
The 5-Tetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$]non-8-enyl Cation. A Curious Case of Nonrearrangement in a $C_9H_9^+$ System[1]

Sir:

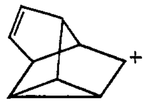
Whole families of interconvertible and potentially degenerate cations of general formula $(CH)_n^+$ (n is odd) are capable of existence, but these have received remarkably little attention, despite their obvious relationship to the well-studied $(CH)_m$ (m is even) hydrocarbons.[2] Many of these hydrocarbons undergo valence isomerization, and the carbonium ions should be even more rearrangement prone. The complete degeneracy of the homocubyl cation has already been demonstrated experimentally;[1,3] we report here the contrasting behavior of a second $C_9H_9^+$ cation, the 5-tetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$]non-8-enyl system (I).



I



II

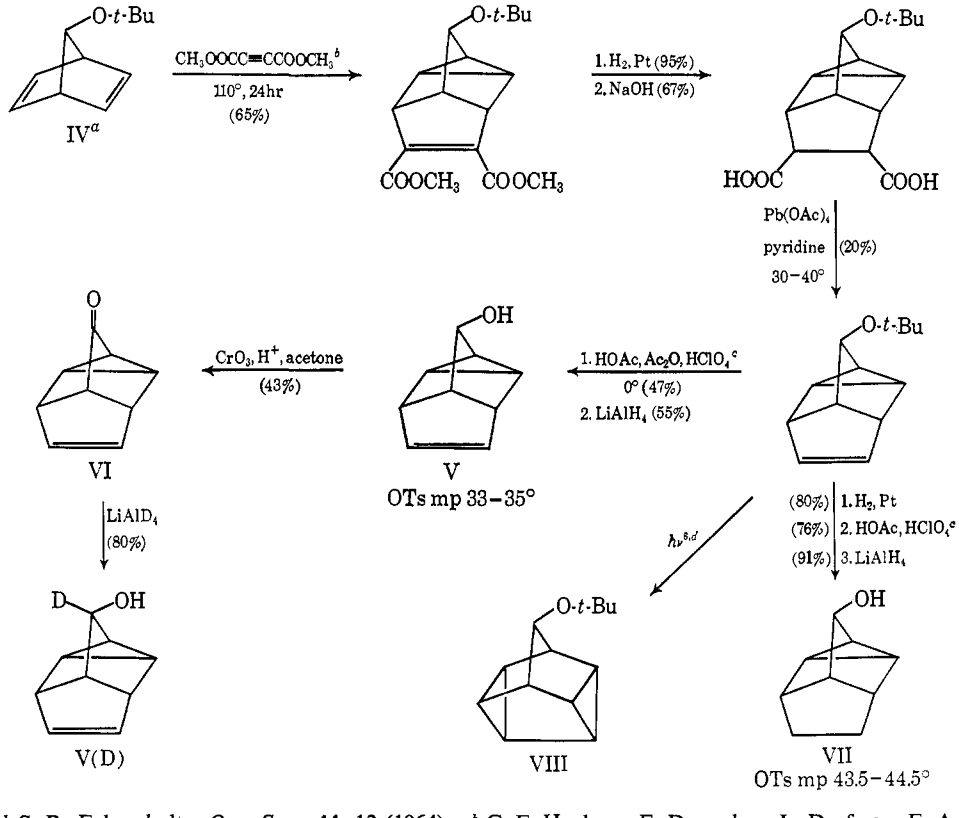


III (≡I)

By cyclopropylcarbinyl–homoallyl rearrangement I might be transformed to II, an unsaturated analog of the tricyclic norbornyl system described by Nickon.[4] II, with a C_2 symmetry axis through C-2 and the midpoint of the C-6–C-7 bond, should be convertible to III or back to I with equal ease, provided no special ion-pair effects are present.[5] By such a mechanism, a deuterium label originally at C-5 can scramble, eventually to the four positions C-4, C-5, C-8, and C-9.

Chart I summarizes our synthetic sequence which was based on the literature precedents cited. Spectral and analytical data are in agreement with the assigned structures. In particular, tetracyclo[4.3.0.$0^{2,4}$.$0^{3,7}$]non-

Chart I



[a] P. R. Story and S. R. Fahrenholtz, *Org. Syn.*, **44**, 12 (1964). [b] C. F. Huebner, E. Donoghue, L. Dorfman, F. A. Stuber, N. Danieli, and E. Wenkert, *Tetrahedron Letters*, 1185 (1966). [c] *Cf.* P. R. Story, *J. Org. Chem.*, **26**, 287 (1961). [d] *Cf.* E. Wiskott and P. von R. Schleyer, *Angew. Chem.*, **79**, 680 (1967); *Angew. Chem. Intern. Ed. Engl.*, **6**, 694 (1967); P. K. Freeman and D. M. Balls, *J. Org. Chem.*, **32**, 2354 (1967).

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(1) Paper II in a series on degenerate and potentially degenerate cations; paper I: P. von R. Schleyer, J. J. Harper, G. L. Dunn, V. J. DiPasquo, and J. R. E. Hoover, *J. Am. Chem. Soc.*, **89**, 698 (1967).

(2) Review: A. T. Balaban, *Rev. Roumaine Chim.*, **11**, 1097 (1966).

(3) J. C. Barborak and R. Pettit, *J. Am. Chem. Soc.*, **89**, 3080 (1967).

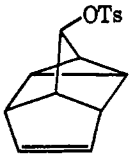
(4) A. Nickon, H. Kwasnik, T. Schwartz, R. O. Williams, and J. B. DiGiorgio, *ibid.*, **87**, 1615 (1965); *cf.* R. S. Bly, R. K. Bly, A. O. Bedenbaugh, and O. R. Vail, *ibid.*, **89**, 880 (1967).

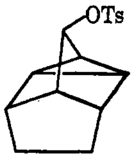
8-en-5-ol (V), bp 56–57° (0.5 mm), gives the following: nmr (δ) 1.35 (d, 2 H), 1.6–1.8 (m, 1 H), 1.85 (bs, 1 H), 2.65 (bs, 1 H), 3.10 (bs, 1 H), 3.90 (s, OH), 4.00 (t, 1 H), 5.85–6.25 (m, 2 H). The spectrum of the deuterated compound V(D) lacks only the signal at δ 4.00. Spectra of V-OH and VI were identical with those of samples prepared by two other independent routes by Coates and Kirkpatrick.[6]

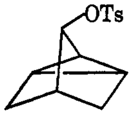
To our great surprise, solvolysis of V(D)-OTs in buffered (10% molar excess of NaOAc) acetic acid at 110° for 3 hr (over 10 half-lives) led to V(D)-OAc as the sole product, *with the deuterium completely* (±*2%*) *unscrambled!* Unfortunately, attempts to study the rearrangement under more vigorous conditions (unbuffered HOAc or HCOOH) were frustrated by solvent addition to the reactive, norbornene-type double bond.[7] Acetolysis of VII-OTs also gave only unrearranged product, VII-OAc.

The double bond in V-OTs also produces a marked rate-depressing effect, as is revealed in the comparison in Chart II.

Chart II







	V-OTs	VII-OTs	IX-OTs
k, sec^{-1} (75°)	1.85×10^{-4}	7.38×10^{-3}	1.62×10^{-3}
k_{rel}	0.11	4.6	1.0
ν_{CO}, cm^{-1}	1755		1762

Although the major product from solvolysis of either 3-nortricyclyl tosylate (IX) or 5-norborn-2-enyl tosylate is 3-nortricyclyl acetate, some 5-norborn-2-enyl acetate also is formed.[7a,8] By analogy, it might have been expected that *some* conversion of I to II and eventually to III might have occurred, with attendant deuterium scrambling.[5] The nonobservance of such scrambling, at least under the conditions employed, shows that "leakage" to II (and to III) did not occur. Not only the unsaturated tosylate V-OTs, but also the saturated analog VII-OTs, failed to produce any detectable homoallylic-type product (*e.g.*, derived from II) on acetolysis. The extra two-carbon bridges in these systems render such opened products unfavorable, possibly because the additional strain introduced by these bridges is greater in the norbornene than in the nortricyclene system.

The double bond in V-OTs produces a 40-fold rate decrease relative to VII-OTs. This decrease seems larger than would be expected on the basis of the inductive effect of such a remote group.[9] A steric effect may be responsible, at least in part. The etheno bridge in I decreases the C-1–C-7 distance. This should depress the solvolysis rate of V-OTs relative to that of IX-OTs.[11]

There is no evidence from either the rate data or the products formed of any participation of the double bond electrons in the ionization of V-OTs. Nevertheless, there is considerable anchimeric assistance in the ionization of V-OTs. From the carbonyl frequency of VI (ν_{CO} band center ~1755 cm^{-1}), an acceleration of 10^5 can be estimated.[10] It would appear that there is considerable stabilization of I due to cyclopropylcarbinyl-type resonance, but without substantial opportunities for structural rearrangements to ions such as II, which might have led to deuterium label scrambling.

Under similar conditions some potentially degenerate carbonium ions rearrange extensively,[1,3,5] while others do not. We are seeking the causes for this disparate behavior, which adds to the variety we are encountering in our continuing studies of $(CH)_n^+$ systems.

Acknowledgments. This research was supported by grants from the National Science Foundation, the National Institutes of Health, and the Petroleum Research Fund, administered by the American Chemical Society.

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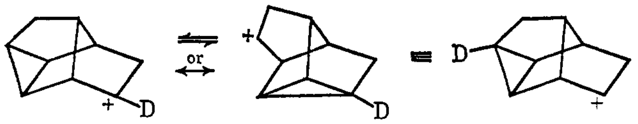
[5] *Cf.* the facile rearrangement observed by P. K. Freeman and D. M. Balls, *Tetrehedron Letters*, 437 (1967).



[6] R. M. Coates and J. L. Kirkpatrick, *J. Am. Chem. Soc.*, **90**, 4162 (1968). This paper deals with the behavior of a related $C_9H_9^+$ system, the 9-pentacyclo[$4.3.0.0^{2,4}.0^{3,8}.0^{5,7}$]nonyl cation. Our own work with this system (*cf.* VIII), entry to which can be gained by irradiation of V-O-*t*-Bu, will be reported in the future. We are grateful to Professor Coates for exchanges of information and for spectral comparisons.

[7] (a) S. J. Cristol, M. K. Seifert, D. W. Johnson, and J. B. Juvale, *J. Am. Chem. Soc.*, **84**, 3918 (1962); (b) S. J. Cristol and G. C. Fusco, *J. Org. Chem.*, **33**, 106 (1968).

[8] J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, 77, 3034 (1955).

[9] The acetolysis rate of norborn-5-en-2-*endo*-yl tosylate is also 40 times slower than that of 2-*endo*-norbornyl tosylate,[10] but the double bond is closer.

[10] P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1854, 1856 (1964); C. S. Foote, *ibid.*, **86**, 1853 (1964).

[11] See P. von R. Schleyer and G. W. Van Dine, *ibid.*, **88**, 2321 (1966).

[12] National Institutes of Health Predoctoral Fellow, 1965–1968.

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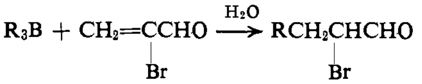
Reaction of Organoboranes with 2-Bromoacrolein. A Facile One-Stage Synthesis of α-Bromo Aldehydes

Sir:

Difficulties inherent in the preparation of the highly reactive α-bromo aldehydes by direct bromination of the corresponding aldehydes have led to the development of indirect synthetic methods, such as the addition of bromine to enol acetates[1] or enamines,[2] followed by hydrolysis of the intermediates. We wish to report that α-bromo aldehydes are now readily accessible by the reaction of organoboranes with 2-bromoacrolein (**1**).



$$R_3B + CH_2{=}\underset{\displaystyle Br}{\underset{|}{C}}CHO \xrightarrow{H_2O} RCH_2\underset{\displaystyle Br}{\underset{|}{C}}HCHO \qquad (1)$$

The products can be isolated from the reaction mixture by distillation at low pressures. However, they are exceedingly reactive and cannot be stored as such for any length of time. In contradiction to reports

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[1] F. Bedoukian, *J. Am. Chem. Soc.*, **66**, 1325 (1944).

[2] R. Tiollais, *et al.*, *Bull. Soc. Chim. France*, 1205 (1964).