

of tetramethylethylene using a microwave discharge,¹⁶ Corey and Taylor⁶ were unable to observe this oxidation using a similar source. It is conceivable that the "ene" reaction, which requires relocation of a hydrogen atom, is more sensitive to the differences between gas-phase and solution conditions than is the diene reaction. This could lead to a different order of reactivities for gas-phase and solution singlet oxygen oxidations.

In a separate experiment the adduct was permitted to decompose so that the product gas passed through a column of silica gel which had been impregnated with leuco malachite green and was protected from light by aluminum foil. The initial color of the adsorbed dye was pale blue even when carefully prepared. After decomposition of the adduct, the bottom portion of the column had turned dark blue-green in color, presumably due to the formation of the oxidation product.¹⁷

Control experiments in which a pressure rise comparable to that obtained by decomposition of the adduct was produced by the introduction of ground-state O₂ gave none of the oxidation products from the olefins nor caused a color change in the adsorbed dye experiment.

The phosphite-ozone adduct is representative of a large number of potential singlet oxygen sources in ozone chemistry. The possibility, suggested by the results reported here, that these sources can be responsible for gas-phase reactions of singlet oxygen is of particular significance to the air pollution problem. That singlet oxygen may play an important role in air pollution was discussed recently by Khan, Pitts, and Smith.¹⁸ These authors suggest that singlet oxygen, to be used in accomplishing the important conversion of NO to NO₂ in smog production, is produced by photosensitization of ground-state O₂. They have proposed that polynuclear aromatic hydrocarbons, present as atmospheric contaminants, may act as one such type of photosensitizer.

The results reported here coupled with the known high concentrations of ozone in polluted atmospheres suggest that the required singlet oxygen¹⁸ may be produced by reactions of ozone with other atmospheric contaminants. Such contaminants could include tertiary amines, sulfides, sulfoxides, phosphines, phosphites, and some olefins, all of which are known to react with O₃ in such a way that one oxygen atom is retained in the oxidized product. The other product is molecular oxygen which it now appears is almost certainly in an excited singlet state.¹⁹

(16) A. M. Winer and K. D. Bayes, *J. Phys. Chem.*, **70**, 302 (1966).

(17) H. Kautsky, *Trans. Faraday Soc.*, **35**, 216 (1939).

(18) A. U. Khan, J. N. Pitts, Jr., and E. P. Smith, *Environ. Sci. Technol.*, **1**, 656 (1967).

(19) NOTE ADDED IN PROOF. We have also observed the conversion of α -terpinene to ascaridole by singlet oxygen in the gas phase.

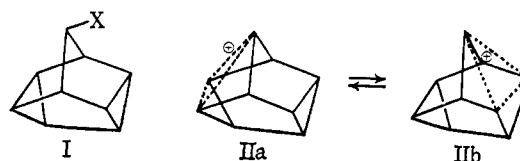
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Reactivity and Degenerate Rearrangement in the Solvolysis of 9-Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane *p*-Nitrobenzoate

Sir:

The carbonium ion produced by solvolysis of the 9-pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane derivative I has

unique structural and symmetry properties which could result in multiple degeneracy. Since I is a polycyclic analog of *cis*-3-bicyclo[3.1.0]hexyl tosylate, the carbonium ion is capable of threefold degeneracy by means of a homocyclopropyl carbonyl rearrangement (I \rightarrow IIa).¹ In addition, there is the possibility of a bridge-flip rearrangement (*e.g.*, IIa \rightleftharpoons IIb) which again regenerates a cation identical with the original. If both processes were to operate concurrently, all positions become interchangeable and, hence, all nine carbon atoms could become equivalent. We now report the synthesis of the functionalized pentacycle I² and the results of a preliminary study on its solvolytic reactions.



The key intermediate in our synthetic plan was the unsaturated, tetracyclic alcohol III since a photochemical bond reorganization of III homologous to the norbornadiene-quadracyclene transformation³ should produce I-OH.^{2,4} Epoxide V⁵ was secured from the readily available hydrocarbon IV (deltacyclene)⁶ by perbenzoic acid treatment (30 min at 0°, 78%). The reaction of V in chloroform with 48% hydrobromic acid produces mainly the rearranged bromohydrin VI [48%; mp 73–74°; τ 5.82 (2 d, $J = 3$ and 7 Hz) and 5.75 (s, $h_{1/2} = 4$ Hz)] in addition to lesser amounts of the *exo,exo* vicinal isomer VII [31%; mp 50–51°; τ 5.40 (d, $J = 6$ Hz) and 5.90 (d, $J = 6$ Hz)].⁸ With anhydrous hydrogen bromide in ether, however, the reaction proceeds with little rearrangement, VII and its *exo,endo* isomer VIII [mp 82–83°, τ 5.70 (2 d, $J = 1.5$ and 4 Hz) and 5.90 (d, $J = 1.5$ Hz)] being the major products. Dehydrobromination of VI (KO-*t*-Bu-DMSO, 3 hr at 25°) gives rise to 8-tetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonen-5-ol (III) [83%, bp 74–78° (2 mm); ν_{\max} 700 cm⁻¹; τ 4.08 (m, 2 H) and 6.04 (t, $J = 2$ Hz, 1 H)].⁹

The structure of III has been confirmed by an independent synthesis. The diazo ketone IX, obtained from 7-norbornadienecarboxylic acid,¹⁰ affords (Cu-THF, reflux 2 hr) the tetracyclic ketone X [\sim 50%; ν_{\max} 1750 and 1764 cm⁻¹; τ 3.80 (t, $J = 2$ Hz, 2 H)]⁹ also

(1) S. Winstein, E. C. Friedrich, R. Baker, and Y. Lin, *Tetrahedron Suppl.*, **8** [II], 621 (1966), and references cited.

(2) The parent hydrocarbon I (X = H) has recently been synthesized by three different routes: (a) H. Prinzbach and D. Hunkler, *Angew. Chem. Intern. Ed. Engl.*, **6**, 247 (1967); (b) P. K. Freeman and D. M. Balls, *J. Org. Chem.*, **32**, 2354 (1967); (c) E. Wiskott and P. von R. Schleyer, *Angew. Chem. Intern. Ed. Engl.*, **6**, 694 (1967).

(3) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1961); G. S. Hammond, N. J. Turro, and A. Fischer, *J. Am. Chem. Soc.*, **83**, 4674 (1961).

(4) C. F. Huebner, E. Donoghue, L. Dorfman, E. Wenkert, W. E. Streth, and S. W. Donnelly, *Chem. Commun.*, 419 (1966).

(5) All new compounds have been fully characterized by satisfactory spectral and microanalytical data (IX, spectra only).

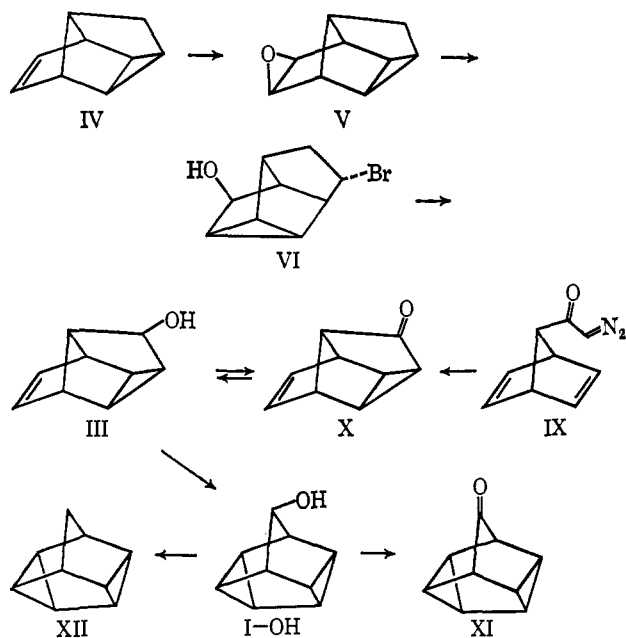
(6) Prepared (62%) from the norbornadiene dimers⁷ by the method of L. G. Cannell, *Tetrahedron Letters*, 5967 (1966).

(7) J. J. Mrowca and T. J. Katz, *J. Am. Chem. Soc.*, **88**, 4012 (1966).

(8) For similar homocyclopropyl rearrangements, *cf.* P. K. Freeman and D. M. Balls, *Tetrahedron Letters*, 437 (1967); R. R. Sauters, J. A. Beisler, and H. Feilich, *J. Org. Chem.*, **32**, 569 (1967).

(9) Professor P. von R. Schleyer has informed us that III (and X) has also been prepared in his research. Comparison of the nmr spectra of III and X, kindly proffered by Professor Schleyer, has established the identity of the compounds from both laboratories.

(10) G. W. Klump and F. Bickelhaupt, *Tetrahedron Letters*, 865 (1966).



available from III by oxidation (H_2CrO_4 -acetone, 79%). Ultraviolet irradiation (450-W medium-pressure Hanovia lamp, quartz immersion well) of III in 50% aqueous *t*-butyl alcohol induces valence isomerization to I-OH [$\sim 10\%$; mp 132 – 133° ; mol wt 134 (mass spectrum); τ 5.75 (quartet, $J = 2$ Hz, 1 H),¹¹ 7.55 (sextet, $J = 2$ Hz, 2 H), 7.67 (m, 1 H), 7.90 (m, 2 H), ~ 8.05 (m, 1 H), and 8.23 (m, 2 H)].^{12,13} The novel pentacyclic ketone XI [mp 87 – 88° ; mol wt 132 (mass spectrum); ν_{max} 3055, 3017, and 1770 cm^{-1} ; τ 7.5 (m, 4 H) and 8.0 (m, 4 H)]¹² can be obtained from I-OH by chromic acid oxidation. The structure for I-OH is supported by the spectral data cited, the photochemical analogy with IV,^{2b,c} and chemical conversion (SOCl_2 - Et_2O , then LiAlH_4 -THF)¹⁴ to the parent hydrocarbon XII ($\sim 70\%$; ir, nmr, and glpc comparison), a substance of well-established constitution.²

The solvolysis of the *p*-nitrobenzoate (I-OPNB, mp 153.5 – 154.5°) of I-OH in 65% aqueous acetone at 125.0° exhibits good first-order kinetics with a rate constant of $(7.0 \pm 0.2) \times 10^{-5}\text{ sec}^{-1}$.¹⁵ Under these same conditions 7-norbornadienyl *p*-nitrobenzoate (XIII)¹⁶ solvolyzed with a first-order rate constant of $(5.8 \pm 0.1 \times 10^{-4})\text{ sec}^{-1}$,¹⁵ i.e., $k_{\text{I-OPNB}}/k_{\text{XIII}} = 0.12$. Thus, the solvolysis of I-OPNB is enhanced by approximately 10^{12} over that of 7-norbornyl derivatives by the usual comparisons.¹⁷

Solvolysis of I-OPNB having a deuterium label at position 9¹⁸ for 4–5 half-lives regenerates I-OH¹⁹

(11) There is apparently long-range coupling (through five bonds) between the carbonyl proton and the single *anti*-cyclopropyl hydrogen (C-5): K. Tori and M. Ohtsuro, *Chem. Commun.*, 886 (1966).

(12) Nmr data obtained with a Varian HA-100 instrument.

(13) Professors W. G. Dauben and P. von R. Schleyer have informed us of their independent syntheses of I. We thank them for this exchange of information.

(14) The possibility of skeletal change during this two-step sequence seems unlikely since solvolysis of I, although proceeding with rearrangement, gives back I-OH in high yield (see below).

(15) Determined by titration of *p*-nitrobenzoic acid as a function of time; average of three separate runs.

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

(17) (a) H. Tanida, T. Tsuji, and I. Irie, *ibid.*, **89**, 1953 (1967); (b) M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *ibid.*, **89**, 1954 (1967).

(18) The label was introduced by reduction (LiAlD_4) of X. The nmr

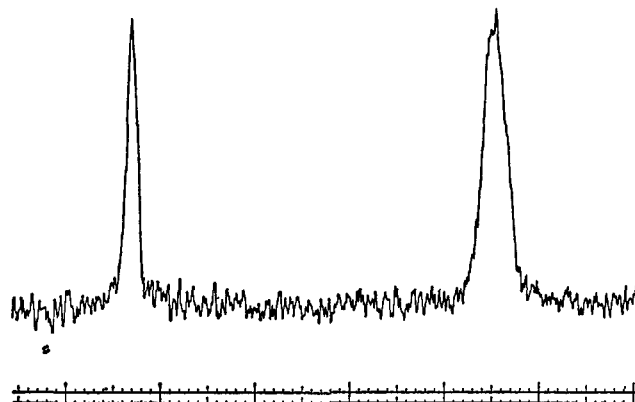


Figure 1. Dmr spectrum of scrambled I-OH (28 mg) determined at 15.35 MHz by computer average of 100 scans.

in which carbonyl nmr absorption has reappeared. The extent of the scrambling is conveniently and accurately determined from the deuterium nmr (dmr) spectrum of the product (see Figure 1). Two peaks at τ 5.8 and 8.2²⁰ are observed in a ratio 1:2.05 (± 0.08) (average of two separate runs). Thus one-third of the deuterium label remains at the carbonyl position while the other two-thirds is distributed between two other equivalent positions. This result constitutes strong evidence for the intervention of the triply degenerate carbonium ion intermediate IIa (or its rapidly equilibrating equivalent). Further rearrangement, although possible by the bridge-flip process, does not occur to a significant extent under these conditions.^{21,22}

Corroborative data are obtained from the pmr spectra of scrambled I-OH. Quantitative integration of the carbonyl region indicates the presence of 0.67 ± 0.02 (average of two separate runs) proton (calculated 0.67 for IIa, 0.89 for complete scrambling). Furthermore, the absorption at τ 8.2 is reduced from an area of 2 to 1.3 ± 0.1 protons while the remainder of the spectrum is essentially unchanged (the sextet at τ 7.55 reduces to a quintet). These observations again require partial label distribution and are consistent with the trishomocyclopropenyl formulation IIa (or its rapidly equilibrating equivalent).

It is worth noting that the large rate enhancement observed with I-OPNB cannot be attributed to an overall relief of strain²³ since I-OH is the major product of the reaction. The acceleration is presumably the result of a geometry in I particularly favorable for homo-

spectra of labeled I-OH and I-OPNB showed $<1\%$ of one hydrogen in the carbonyl region.

(19) The recovery is 46% of the starting I-OPNB. With 1.5 equiv of 2,6-lutidine added, the recovery is $\sim 70\%$.

(20) These chemical shifts are relative to internal CDCl_3 assuming $\tau_{\text{CDCl}_3} = \tau_{\text{CHCl}_3} = 2.73$. Dmr chemical shifts are usually within 0.05 ppm of the corresponding pmr value: P. Diehl and T. Leipert, *Helv. Chim. Acta*, **47**, 545 (1964).

(21) Product I-OH undergoes some scrambling ($32 \pm 2\%$ of solvolytic scrambling) after 4.5 half-lives in the presence of *p*-nitrobenzoic acid. With 1.5 equiv of 2,6-lutidine added, this decreases to $\sim 4 \pm 2\%$. The presence of 2,6-lutidine does not alter the degree of scrambling in the solvolysis. Recovery of unreacted I-OPNB after one half-life indicates a minor amount ($\sim 4 \pm 2\%$) of scrambling prior to product formation.

(22) Another case in which the interconversion of equivalent trishomocyclopropenyl cation intermediates is possible but not in fact observed is the acetolysis of 3-tricyclo[7.1.0.0^{5,7}]decyl *p*-toluenesulfonate: S. Winstein, P. Bruck, P. Radlick, and R. Baker, *J. Am. Chem. Soc.*, **86**, 1867 (1964).

(23) W. G. Dauben, J. L. Chitwood, and K. V. Scherer, *ibid.*, **90**, 1014 (1968).

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.

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(24) National Institutes of Health Trainee, 1968.

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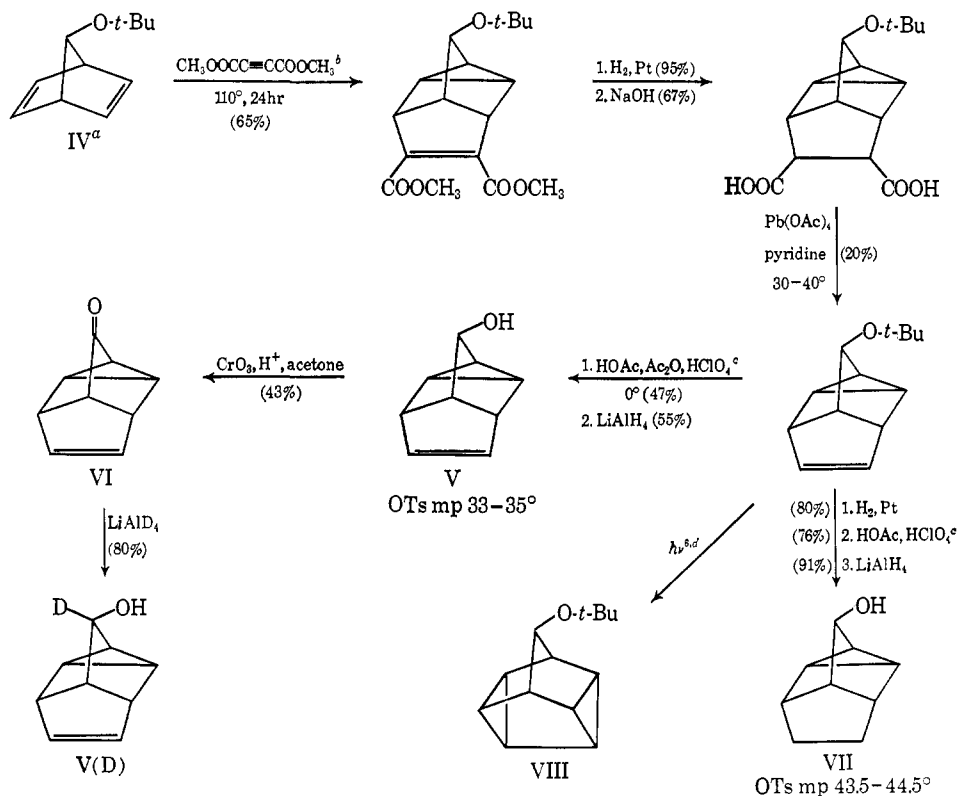
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The 5-Tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-enyl Cation. A Curious Case of Nonrearrangement in a C₉H₉⁺ System¹

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

Chart I

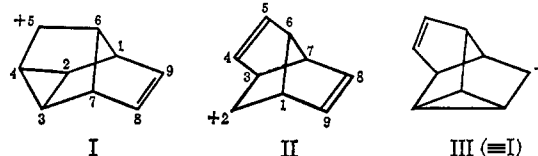


^a P. R. Story and S. R. Fahrenholtz, *Org. Syn.*, **44**, 12 (1964). ^b C. F. Huebner, E. Donoghue, L. Dorfman, F. A. Stuber, N. Danielli, and E. Wenkert, *Tetrahedron Letters*, 1185 (1966). ^c Cf. P. R. Story, *J. Org. Chem.*, **26**, 287 (1961). ^d Cf. E. Wiskott and P. von R. Schleyer, *Angew. Chem.*,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

remarkably little attention, despite their obvious relationship to the well-studied (CH)_{*m*} (*m* is even) hydro-

(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).

carbons.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 C₉H₉⁺ cation, the 5-tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-enyl system (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 C₂ 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-

(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).