and, in partitcular, of adding substantial concentrations of solvent lyate ion in certain solvolyses.[9]

[9] A related example is in methanolysis of isobornyl chloride and camphene hydrochloride, where addition of $NaOCH_3$ does not increase over-all rate but shifts the result from mainly substitution to mainly elimination [P. Beltrame, C. A. Bunton, A. Dunlop, and D. Whittaker, *J. Chem. Soc.*, 658 (1964)].

[10] National Institutes of Health Predoctoral Fellow, 1965–1966.

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Structure of the Nonclassical 7-Norbornenyl Cation[1]

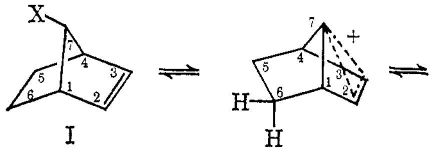
Sir:

In this communication we return to the question of the structure and behavior of the 7-norbornenyl cation. The high rate (10^{11} times 7-norbornyl) and over-all retention of structure and configuration in the solvolysis of *anti*-7-norbornenyl *p*-toluenesulfonate[2] (I-OTs) were previously[2a–c] accounted for on the basis of an intermediate nonclassical "bishomocyclopropenyl"[2e] cation II. This interpretation has been seriously questioned by Brown.[3] Most recently,[3b,c] he has formulated the intermediate as a rapidly equilibrating pair of "classical" tricyclic ions (IVab), and Deno has supported this formulation.[4] We can now report the direct observation of cation II from both σ and π routes[2d] and discuss further its structure and chemical behavior.

Much of the previous discussion of the 7-norbornenyl cation revolved around the nature of the observed products. Thus, in connection with structure IVab for the 7-norbornenyl cation, Brown[3b,c] suggested that the tricyclic alcohol V-OH might well be the chief kinetic control product of neutral hydrolysis of I-OTs, but that it was not isolated because of instability toward the reaction conditions. In the case of methanolysis reported in the previous communication,[2d] where tricyclic V-OCH_3 is now available for control experiments, it is clear that methanol attack at C_2 of the cationic intermediate is very much less important than at C_7. Kinetic control in neutral methanolysis of I-OTs yields 99.7% bicyclic I-OCH_3 and 0.3% tricyclic V-OCH_3.

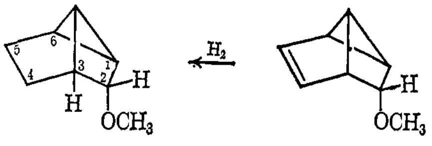
While the C_2:C_7 reactivity ratio is small for methanol, it is much more favorable with nucleophiles such as $^-BH_4$,[2c,3c] ^-CN,[5a] and $^-OCH_3$.[2d] While Brown[3c] found it difficult to rationalize substantial C_2 attack on the basis of the nonclassical structure II, we[2c] found it difficult to rationalize predominant C_7 attack on a classical cation IV. In fact, all the previous and present[2d] information on the gradations in C_7:C_2 product partitioning is well accommodated by the nonclassical formulation II.

Just as stereochemistry at C_7 was previously[2a–c] employed as an argument for the nonclassical structure II instead of the classical structure III, stereochemistry at C_2 (or C_3) can help us decide between structure II and a "classical" tricyclic ion IV. The usual stereoelectronic considerations predict *endo* nucleophilic attack at C_2 or C_3 of ion II; on the other hand, a mixture of *endo* and *exo* products, probably predominantly *exo*, would be expected from a "classical" tricyclic cation IV. The tricyclic ether product from methanolysis of I-OTs in the presence of 4 *M* NaOMe[2d] was separated from I-OCH_3 by vapor phase chromatography, a *ca.* 97% pure fraction of V-OCH_3 being obtained. The nmr spectrum of this material was essentially identical with the one described by Tanida[5b] for the product from hydrogenation of the tricyclic ether VI-OCH_3 from basic methanolysis of 7-norbornadienyl chloride. The C_2 α-proton signal appeared as a clean quartet with vicinal coupling constants (3.8 and 7.4 cps) appropriate for an *endo*-methoxyl group[5b] (*exo* C_2 proton). No evidence of another C_2 α-proton signal was visible even on 60 scans using a Varian C-1024 time-averaging computer (CAT).[6] While further investigation is required to set a lower limit to the *endo*:*exo* ratio in the tricyclic ether, it is already clear that the latter is at least very predominantly *endo* (>97%). Thus, C_2 or C_3 methoxide attack on II is quite highly stereospecific in the *endo* sense. This is true also of attack by ^-CN.[5] Such *endo* specificity is also observed in C_2 or C_3 attack by $^-BH_4$,[7a] $^-AlH_4$,[7a] and $^-OCH_3$[5b] on the 7-norbornadienyl cation VII, an analog of II without the C_5- and C_6-*endo*-protons. Obviously, stereochemistry supports the nonclassical structures implied by II and VII.



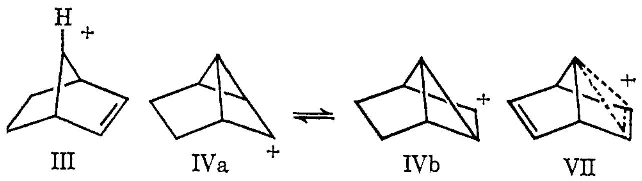
I

II



V-OCH_3

VI—OCH_3



III IVa IVb VII

Cation II may be generated in SO_2–SbF_5–FSO_3H medium[8] at low temperatures by addition of a cold (−50°) CH_2Cl_2–CCl_4 solution of I-OH to a cold SO_2–SbF_5–FSO_3H mixture, followed by vibration and stirring in the cold. The light orange lower layer which separates is the SO_2–SbF_5–FSO_3H solution of the cation containing some CH_2Cl_2 useful as an internal

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[1] Research was supported by the National Science Foundation.

[2] S. Winstein, *et al.*, *J. Am. Chem. Soc.*: (a) **77**, 4183 (1955); (b) **78**, 592 (1956); (c) **85**, 2324 (1963); (d) **88**, 3133 (1966); (e) W. G. Woods, R. A. Carboni, and J. D. Roberts, *ibid.*, **78**, 5653 (1956).

[3] (a) H. C. Brown, "Strained Carbonium Ions," Abstracts, 139th National Meeting of the American Chemical Society, St. Louis, Mo., March 21–30, 1961; (b) H. C. Brown, "Non-Classical Intermediates," Organic Reaction Mechanisms Conference, Brookhaven, N. Y., Sept 5–8, 1962; (c) H. C. Brown and M. Bell, *J. Am. Chem. Soc.*, **85**, 2324 (1963).

[4] N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 159 (1964).

[5] (a) H. Tanida and Y. Hata, *J. Org. Chem.*, **30**, 977 (1965); (b) H. Tanida, T. Tsuji, and T. Irie, *J. Am. Chem. Soc.*, **88**, 864 (1966).

[6] The tricyclic ether fraction shows an additional methyl signal in the nmr spectrum, indicating *ca.* 3% of an impurity whose nature is still not clear.

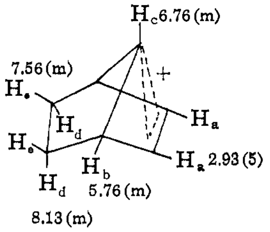
[7] (a) P. R. Story, *et al.*, *J. Am. Chem. Soc.*: (a) **88**, 374 (1966); **83**, 3347 (1961); (b) **84**, 4876 (1962); **85**, 3630 (1963).

[8] G. Olah, *et al.*, *ibid.*, **87**, 2997 (1965).

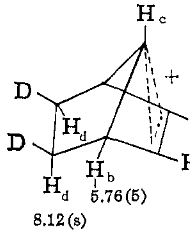
standard for the nmr spectra. These could be recorded at temperatures between −60 and −35°.

The nmr spectrum of ion II is summarized in formula VIII, chemical shifts (relative to internal CH_2Cl_2 taken as τ 4.70) and apparent multiplicities being indicated. Integrations were in good agreement with the expected values, with only a slight disturbance from broad, unresolved signals at τ *ca.* 7 and 8 due to side products formed in amounts varying from run to run. These were even less troublesome with the 5,6-*exo*-dideuterio cation IX, derived from the corresponding labeled I-OH, which in turn was prepared by $LiAlD_4$ reduction of 7-norbornadienyl acetate.[9] For cation IX, the *endo*-H_d proton signal is simplified to a singlet, making easier the separation of the disturbing signal in the integration of the spectrum in the H_d region. Coupling constants were estimated from proton and deuterium decoupling experiments on the deuterated ion at −60° (see IX).[10]

It was possible to store solutions of the cation II salt for long periods of time at liquid nitrogen temperatures. Quenching of such solutions in methanol gave rise to I-OCH_3 in greater than 50% yield. Cation II was also generated from tricyclic V-OCH_3 by the same method employed with I-OH. The same spectrum was obtained as from I-OH, except for somewhat more disturbance from side products. Also, a triplet methyl signal from the generated $CH_3OH_2^+$ species occurs in the region of the bridgehead H_b signal of cation II. This same methyl triplet and an accompanying OH_2 proton quartet are produced in control experiments using CH_3OH as substrate.

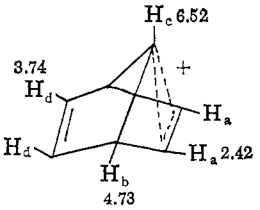


VIII



IX

J_{ac}	J_{bc}	J_{cd}
2.5	2.6	0.8 cps.



X

J_{ac}	J_{bc}	J_{cd}
2.7	2.8	1.0 cps.

As regards chemical shifts and coupling constants, the 7-norbornenyl cation II is quite analogous to the 7-norbornadienyl ion VII, as may be seen from comparing VIII and IX with X^{7b} (VII-BF_4 in liquid SO_2, TMS as internal standard). As regards the protons on the three-center bonded carbon atoms, the H_c proton signal occurs at relatively high field relative to that of the H_a protons in both ions. While the nmr spectra alone do not give an unequivocal answer in favor of the nonclassical structures *vs.* equilibrating classical tricyclic ions such as IVab, they are perfectly consistent with nonclassical ions if we view the C_2–C_7–C_3 part of the structure as a distorted electron-deficient cyclopropane-like arrangement with positive charge considerably greater at C_2 and C_3 than at C_7.

Deno has viewed the 7-norbornenyl and 7-norbornadienyl cations as cyclopropylcarbonium ions and has formulated both species as equilibrating tricyclic ions such as IVab. Specifically in the case of the 7-norbornadienyl species, he has considered the C_7 or H_c proton signal to be too far upfield for a nonclassical formulation and in accord with the tricyclic one. However, such a point of view makes too little allowance for the great variation in charge distribution which results from hybridization changes at individual carbon atoms of a bridged ion such as II. As we have discussed elsewhere,[11] the bridging carbon atom in a bridged ion, *e.g.*, C_7 in II, has considerable tendency to rehybridize from sp^2 toward sp^3. Such rehybridization increases the C_7 Coulomb integral as well as C_7–C_2 and C_7–C_3 orbital overlap. This leads to net stabilization of the bridged ion, and these very features of rehybridization at C_7 tend to diminish the charge on this atom.

If one considers the nmr spectra along with all of the chemical and stereochemical evidence discussed in this and the previous communication,[2d] only a nonclassical formulation such as II for the 7-norbornenyl ion and one akin to VII for the 7-norbornadienyl species will account for all of the facts.[12]

Acknowledgment. We are grateful to Professor F. A. L. Anet for advice and assistance with the decoupling experiments.

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(9) (a) B. Franzus and E. I. Snyder, *J. Am. Chem. Soc.*, **87**, 3423 (1965); (b) P. R. Story, *J. Org. Chem.*, **26**, 287 (1961).

(10) Irradiation of H_b reduced the H_a signal to a doublet (J_{ac} = 2.5 cps) and the H_c signal to an ill-resolved triplet; irradiation of H_a also simplified the H_c signal to an ill-resolved triplet and the H_b signal became a doublet (J_{bc} = 2.6 cps); irradiation of H_d simplifies the H_c signal to a pentuplet; with deuterium decoupling the H_d signal becomes a doublet with J_{cd} = 0.8 cps, and irradiation of the H_c proton gives the H_a signal an A_2X_2 pattern with the separation between the two outer intense lines equal to 8.7 cps ($J_{ab} + J_{ab'}$).

(11) R. J. Piccolini and S. Winstein, *Tetrahedron*, **19**, 423 (1963).

(12) Further support for a symmetrical disposition of C_7 with respect to C_2 and C_3 is provided by extended Hückel calculations [R. Hoffman, *J. Am. Chem. Soc.*, **86**, 1259 (1964)]. A symmetrical structure II is also suggested by comparison with its 7-benzonorbornenyl analog. With the latter system, Tanida has shown the accelerating effects of 4′- and 5′-methoxyl groups to be additive. This indicates a symmetrical ionization transition state and, presumably, therefore, a symmetrical intermediate [H. Tanida, private communication; see *J. Am. Chem. Soc.*, **86**, 4904 (1964)].

(13) National Institutes of Health Predoctoral Fellow, 1965–1966.

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Direct Observation of Norbornenyl Cations

Sir:

This communication reports the nmr spectra of the unsubstituted 7-norbornenyl cation (**1**), the 7-methyl (**2**) and 7-hydroxy (**3**) 7-norbornenyl cations, and the 2-hydroxy-2-norbornenyl cation (**4**). The importance of "homoallylic"[1] interactions in bicyclic systems such as **1**, **5**, and **6** has been evident from studies of rates and

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(1) This word was coined [S. Winstein, H. M. Walborsky, and K. Schreiber, *J. Am. Chem. Soc.*, **72**, 5795 (1950)] to describe interaction between a double bond and a center separated by an intervening carbon atom.