ions (as well as $C_4H_{10}^+$) at elevated pressures, verifying that the $C_5H_{10}^+$ ions produced in the equilibrium reaction retain the cyclic configuration over the temperature range studied. (c) The equilibrium constant for the reaction c-$C_5D_{10}^+$ + c-C_5H_{10} $\leftrightarrow$ c-$C_5H_{10}^+$ + c-C_5D_{10} was determined at 292 K. The value of 3.2 compares with the value of 4.0 for the analogous equilibrium in the c-C_6D_{12}–c-C_6H_{12} system.[10] (d) The reaction of c-$C_5H_{10}^+$ with NH_3 was also investigated. In contrast with cyclopropane ions, which yield only $CH_2NH_2^+$ and $CH_2NH_3^+$ as the reaction products,[6,11] only 5% of the c-$C_5H_{10}^+$ ions undergo the reaction; c-$C_5H_{10}^+ + NH_3 \rightarrow CH_2NH_2^+ + C_4H_9$ ($\Delta H = -25 \pm 5$ kcal/mol). The major channel (95%) observed was the highly exothermic proton transfer reaction; c-$C_5H_{10}^+ + NH_3 \rightarrow NH_4^+ + C_5H_9$ ($\Delta H = -45 \pm 5$ kcal/mol).

The extent of cyclic retention was also studied in several alkylcyclopentanes (see Figure 1). The results are as follows: methylcyclopentane, ≥90% cyclic, 10.0 + 10.6 eV photons; isopropylcyclopentane, 21% cyclic, 10.6-eV photons and 87% cyclic, 10.0-eV photons; and *n*-propylcyclopentane, ≥91% cyclic, 10.0-eV photons.

It is evident from the past as well as the present results that the degree of decyclization in cyclopentane and alkylcyclopentane ions depends critically upon both the initial internal energy distributions (the method of preparation in mass spectrometric studies) and the time between stabilizing collisions (radiolysis studies carried out at higher densities show that the cyclic structure is retained[4,5]).

On the basis of the data of Figure 1, which indicate that charge exchange becomes effective above 5 mtorr, a lower limit for the lifetime of c-$C_5H_{10}^+$ (10.6-eV photoionization) of approximately 10 μs may be estimated, based on the collision frequency at this pressure and assuming every collision results in stabilization.

Acknowledgment. The support of the Office of Basic Energy Sciences, Department of Energy, is gratefully acknowledged.

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Deuterium Isotope Effect on the Carbon-13 NMR Spectrum of the Bicyclo[2.2.1]heptyl Cation. Nonclassical Norbornyl Cation

Sir:

The norbornyl system is at the center of the "nonclassical ion problem". Both the explanation of the solvolysis kinetics and the structure of the stable norbornyl cation have long been at issue. The argument over the stable cation concerns whether it is a rapidly equilibrating pair of classical ions or rather a symmetric (nonclassical) species. We have recently reported a new method for attacking such problems.[1-4] We now report its application to the problem of the structure of norbornyl cation.

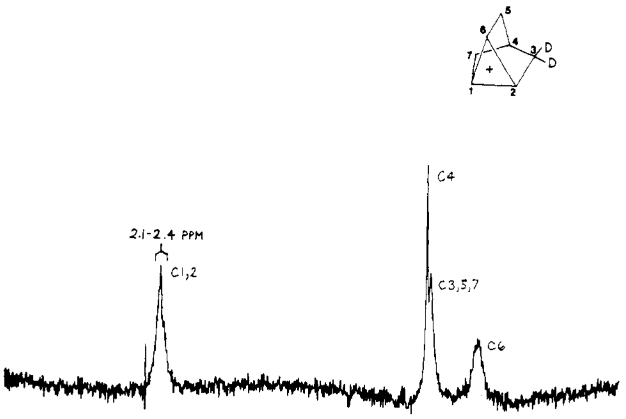
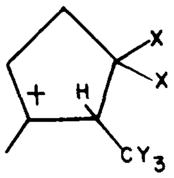


Figure 1. 67.9-MHz ^{13}C NMR spectrum of VIII at about −150 °C.

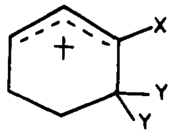
Table I. Isotopic Splitting of the C1,2 Peak in Methylene-Deuterated Analogues of the Norbornyl Cation

cation	temp, °C	isotopic splitting, ppm
I	−130	105.3[1]
IX	−110	23.9[3]
VIII	−150	<2.3

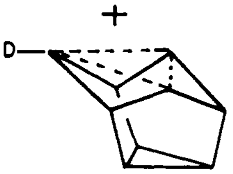
A rapid degenerate rearrangement confers functional symmetry on a carbonium ion, causing averaging of the ^{13}C NMR resonances of carbons which are interchanged by the rearrangement. Deuterium substitution perturbs this symmetry, and thereby induces large splittings in the averaged resonances.[1] The absence of a large splitting is diagnostic for a static structure.[2] Thus, in the ^{13}C NMR spectrum of the dimethylcyclopentyl ion I, the peaks for C1 and C2, which are averaged in the undeuterated ion, are split by 105 ppm at −130 °C,[1] and for II by 82 ppm at −142 °C,[1] whereas for the cyclohexenyl cations III and IV peaks for C1 and C3 are split by 0.33[2] and 0.83[4] ppm, respectively. Similarly, in the 67.9-MHz ^{13}C NMR spectrum of the [9-^2H]9-pentacyclo$[4.3.0.^{2,1}0^{5,7}]$nonyl cation V, the peak corresponding to C6,7,9 is shifted by less than 0.1 ppm, confirming the accepted static, symmetrical structure of the ion.[5] For the bicyclo[2.1.1]hexyl ion VI, a splitting of 1.18 ppm at −115 °C clearly demonstrates a static, bridged structure.[3]



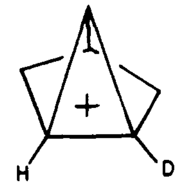
I X = D,Y = H
II X = H,Y = D



III X = D,Y = H
IV X = H,Y = D



V



VI

Both equilibrating[6a,c] and static[6b,c] structures have been proposed for the norbornyl cation. The former is an analogue of I, and its ^{13}C NMR spectrum would therefore show a large splitting of the downfield resonance upon methylene deuteration. A small splitting would argue for the nonclassical structure, by analogy with V and VI.

In the 67.9-MHz ^{13}C NMR spectrum of VIII, deuterium substituted norbornyl, prepared[7] in a mixture of SO_2ClF and

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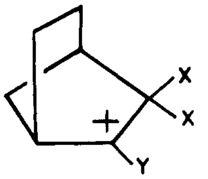
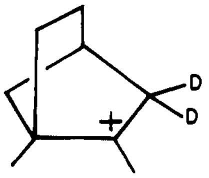
SO_2F_2, at the lowest temperature for which there is no appreciable viscosity broadening (about −150 °C), the 6,2-hydride shift is rapid enough to average the ^{13}C resonances of C3, and C5, and C7 and broaden those of C6 and of C1 and C2, leaving only that of C4 sharp.[8] Figure 1 is the spectrum of VIII, in which the downfield peak (C1 and C2) has a half-height width of about 2.3 ppm. The areas of the peaks show that deuterium is not scrambled. Furthermore, a ^{2}H NMR spectrum of VII at −125 °C taken *after* the ^{13}C spectrum showed negligible deuterium scrambling by the 3,2-hydride shift during preparation of the samples and ^{13}C NMR data acquisition. Thus, 2.3 ppm is an approximate *upper limit* on the isotope splitting.



VII X = D, Y = H
VIII X = H, Y = D



IX

This maximum splitting in VIII is compared with those observed in I and the dimethylnorbornyl cation (IX)[3] in Table I. The value for I would be even larger at −150 °C, so that the effect in VIII is, at most, $^{1}/_{50}$ of that in I. It is even an order of magnitude smaller than that of the partially delocalized IX.[1,3,4,9] *The postulated*[6a,c] *rapid Wagner–Meerwein rearrangement in the norbornyl cation is not consistent with this result. A static, symmetrical structure is.*

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(8) A 25-MHz ^{13}C NMR spectrum was obtained by G. A. Olah, G. Liang, G. D. Mateescu, and J. L. Riemenschneider, *J. Am. Chem. Soc.*, **95**, 8698 (1973).

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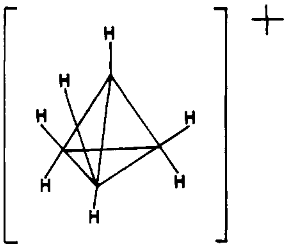
Deuterium Isotope Effects on the Cyclobutyl–Cyclopropylcarbinyl Cation

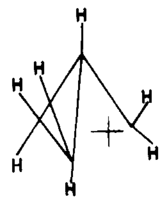
Sir:

Rapid solvolysis rates and ready interconversion of cyclobutyl and cyclopropylcarbinyl derivatives have led to the proposal of common and highly stabilized ionic intermediates.[1] Cyclobutyl or cyclopropylcarbinyl chloride or the corresponding alcohols react with SbF_5 to give stable ion solutions with identical ^{1}H and ^{13}C NMR spectra.[2] These spectra indicate either a threefold symmetric ion, the tricyclobutonium ion I, or a set of *rapidly equilibrating*, less symmetric, ions with the same effective *averaged* symmetry. These could include cyclopropylcarbinyl cations II, bicyclobutonium ions III, or bent cyclobutyl cations IV. Scheme I shows how these ions can interconvert. *Planar* cyclobutyl cation is excluded as a contributor since two peaks of area 3 are present in the proton spectrum, corresponding to *nonequivalent* hydrogens on each methylene. Interconversion of these nonequivalent hydrogens is slow on the NMR time scale.

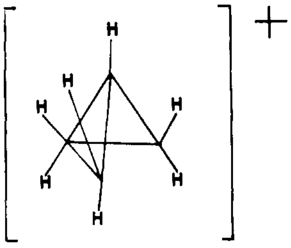
I



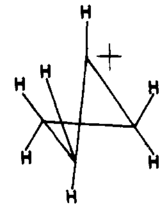
II



III



IV



No conclusive argument for preferring or excluding any of the possibilities I–IV has been presented. Theoretical calculations predict similar energies for II–IV,[4] but indicate that I is less likely. In any case, the exactly symmetric I must be a maximum in energy as a consequence of the Jahn–Teller theorem.[5] The problem appeared suitable for application of the deuterium perturbation method previously used to study the bicyclo[2.1.1]hexyl cation[6] and others.[7,8]

$LiAlD_4$ reduction of cyclopropanecarboxylic acid gave α,α-dideuterated cyclopropylcarbinol which was converted to the cation. A peak, assigned to nondeuterated methylenes, was observed in the ^{13}C NMR spectrum shifted upfield by between 1.77 (−135 °C) and 1.24 ppm (−107 °C) (compared with the *protio* ion), indicating a definite *equilibrium* isotope effect. The upfield ^{1}H NMR peak was also found to be shifted to higher field (relative to the *protio* ion) by between 0.087 (−130 °C) and 0.057 ppm (−80 °C). However, the downfield peak (area = 3) was *unaffected.* This observation can only be rationalized by assuming that equilibrium among nonequivalent methylenes is perturbed by deuterium, but that Δ, the chemical shift difference between the rapidly equilibrating hydrogens if the fast interconversion process could be stopped, is *very different* between the two sets of nonequivalent hydrogens.

Monodeuterated cation was made from α-monodeuterated cyclopropylcarbinol (from reduction of cyclopropanecarboxaldehyde with $LiAlD_4$). This should be a mixture of ions with deuterium at the low-field and high-field methylene positions. As in the dideuterated compound, only the upfield ^{1}H NMR peak showed any perturbation. With deuterium in the downfield methylene position, the upfield peak should be split into a 1:2 doublet. With deuterium in the upfield position, a single peak due to the two remaining upfield hydrogens should appear. The peak of intensity 1 corresponding to the deuterium-substituted carbon goes downfield while the peak of area 2 (the nondeuterated

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