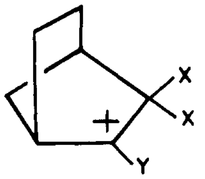
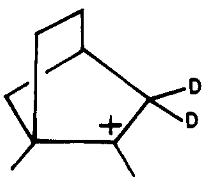
SO$_2$F$_2$, at the lowest temperature for which there is no appreciable viscosity broadening (about −150 °C), the 6,2-hydride shift is rapid enough to average the ^{13}C resonances of C3, and C5, and C7 and broaden those of C6 and of C1 and C2, leaving only that of C4 sharp.[8] Figure 1 is the spectrum 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.*

Acknowledgment. This research was supported by the National Science Foundation. NMR spectra were obtained at the Southern New England High Field NMR Facility, supported by the Biotechnology Resource Program of the National Institutes of Health (RR-798). We are grateful to Professor R. M. Coates for a sample of pentacyclo[4.3.0.^{2,4}0.^{3,8}0^{5,7}]nonan-9-one.

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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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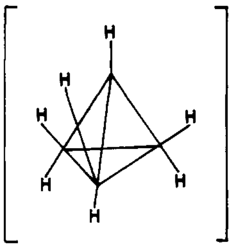
Received May 20, 1980

Deuterium Isotope Effects on the Cyclobutyl–Cyclopropylcarbinyl Cation

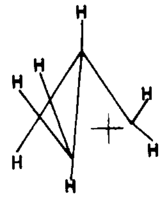
Sir:

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.

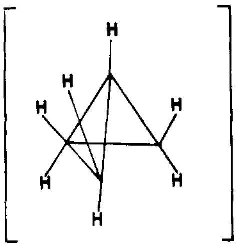
I



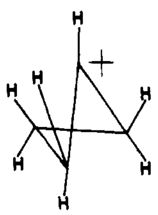
II



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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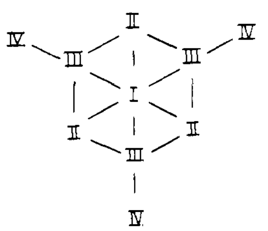
Scheme I



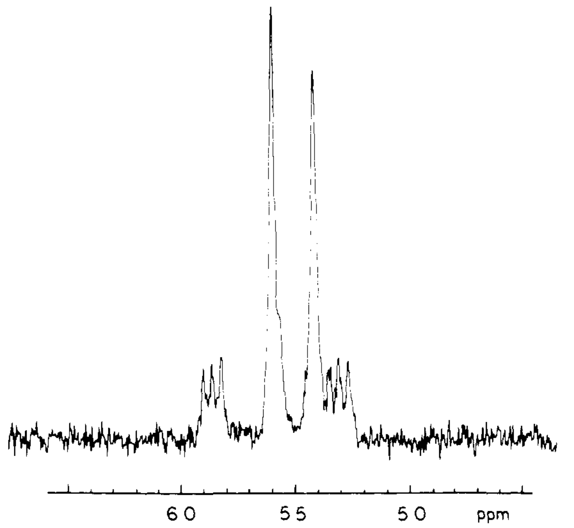


Figure 1. ^{13}C NMR spectrum of the monodeuterated ion.

methylene hydrogens) moves upfield (δ between them = 0.357 at −135 °C). However, a peak of area 2 is also seen closer to the original position but shifted *downfield* ($\delta \sim 0.04$ at −135 °C).

These results indicate that the isotope effects for deuterium in the nonequivalent positions have *opposite signs*. Conclusive confirmation comes from the ^{13}C NMR spectrum of the monodeuterated ion (Figure 1) which shows clearly this remarkable and unanticipated change in the sign of the equilibrium isotope effect. These shifts vary with temperature in the expected fashion for *equilibrium isotope effects*.

Observing *equilibrium* isotope effects indicates that the tricyclobutonium ion I is *not* the main species present. We must therefore consider a degenerate set of rapidly equilibrating ions of lower symmetry (II, III, and IV). The opposite signs of the isotope effects and the large difference in Δ imply that the *differences* both of the chemical shift and of the force constants between the two types of rapidly equilibrating hydrogens are *extremely* different. We would not expect this for either bent cyclobutyl IV or cyclopropylcarbinyl cation II, although delocalization might produce moderate differences. However, the bicyclobutonium ion III has one pentacoordinated carbon which might have two extremely different CH bonds. Pentacoordinated carbons and the attached hydrogens often have very unusual chemical shifts. It might be anticipated that the vibration frequencies of CH groups attached in different positions could also differ considerably. The striking difference in Δ and the equilibrium isotope effects of opposite sign may be due to a large difference in the bonding and, hence, the frequencies and force constants of the two hydrogens on the pentacoordinated carbon of III.

If III is the main species present, the rapid degenerate equilibrium might occur via I, or II, which could represent transition states with the barrier less than ~3 kcal. Bent cyclobutyl cation IV has the same symmetry as bicyclobutonium ion but might be distinguished from it by considering whether bending brings the diagonally related carbons within bonding distance or not.

Roberts and Olah[3] interpreted a small temperature dependence of the ^{13}C NMR spectrum of this ion as indicating a minor species in rapid equilibrium with the major ion. We observed a splitting of 0.4 ppm at −96 °C between the methine peaks of the two isomeric monodeuterated cations which offers strong support to this idea. The minor isomer might correspond to II or, less likely, to a structure similar to I or IV.

Acknowledgment. We acknowledge support of this research by a grant from the National Science Foundation and by a fellowship to H.U.S. by the Deutsche Forschungsgemeinschaft. All NMR spectra were obtained on the HX-270 spectrometer of the Southern New England High Field NMR Facility supported by the BBR office of the NIH.

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Cyclization Dynamics of Polymers. 2. Dynamics and Thermodynamics of End-to-End Cyclization of Polystyrene in a Θ Solvent

Sir:

Since the early part of this century, chemists have been fascinated by the cyclization of flexible chain molecules. The discovery of macrocyclic principles in musk extracts in the 1920's prompted intense interest in the synthesis of medium-sized rings.[1] This interest continues today, spurred by the importance of macrolide antibiotics. In 1934, Kuhn related the cyclization probability, $W(0)$, of a polymer to its other conformational properties.[2] Since then, polymer chemists (most notably Semlyen[3]) have examined ring chain polymerization in detail, comparing measured cyclization equilibrium constants with values calculated from models developed by Jacobsen and Stockmayer[4] and Flory and Semlyen.[5]

A new chapter in this history was opened by Wilemski and Fixman,[6] who examined theoretical models of the *dynamics* of end-to-end cyclization in polymers. These authors related the rate constant for end-to-end cyclization, k_{cy}, to the various relaxation times of both the Rouse–Zimm ball-and-spring model and also the harmonic spring model of long polymer chains. Their work and subsequent papers by Doi[7] emphasize that k_{cy} is related to the slowest normal mode of the polymer. Since this mode is important in other hydrodynamic interaction sensitive properties of polymers, Perico and Cuniberti[8] were able to use intrinsic viscosity data to parameterize the Wilemski–Fixman formalism and predict values for k_{cy}.

These theoretical papers[6-9] have had an important impact on the field of polymer dynamics. Since the formulations involved simplifying assumptions at various stages in the development of the models, further refinements will depend upon experiments which can provide quantitative assessment of the theories. There are many experimental questions which need to be asked. Among them are the following: (1) What are the magnitudes of k_{cy}? (2) What is its chain length dependence? (3) Is there a relationship between k_{cy} and K_{cy}, the equilibrium constant for end-to-end cyclization?

Intramolecular excimer formation between chromophores attached to the ends of a polymer chain provides a tool for answering

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