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FINE STRUCTURE IN THE NMR SPECTRUM OF THE NORBORNYL CATION

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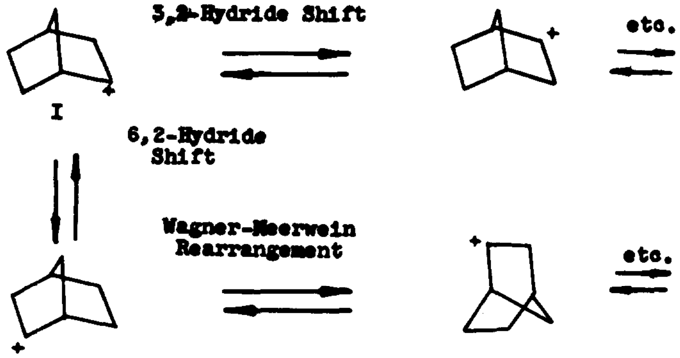
The structure of the 2-norbornyl cation has attracted considerable attention because of the possibility that it is stabilized by σ-bond delocalization and exists in a "non-classical" structure. Recently the direct observation of the NMR spectrum of this ion has been reported (1). The results reported here confirm their findings, but in addition, fine structure of the cation was observed at low temperature which gives added confidence to the structural assignments.

Spin-spin splitting was observed with 2-norbornyl bromide and several Lewis acid-solvent systems, but the best defined spectra were obtained with gallium tribromide as the Lewis acid and sulfur dioxide as solvent. The samples were prepared in the NMR tubes utilizing carefully purified reagents and taking necessary precautions to ensure that the contents were entirely anhydrous and oxygen free. The tubes were then sealed under high vacuum.

The cation undergoes sufficiently rapid hydride transfers and Wagner-Meerwein rearrangements at 25° that its NMR spectrum consists of a single peak located at δ 3.3 ppm (downfield from TMS in a sealed capillary). Thus, all eleven protons are equivalent at this temperature on the "NMR time scale". In Fig. 1, the hydride shifts and alkyl rearrangements which lead to the equivalency of the protons are pictured for convenience in terms of classical structures, but the observed spectra are explained more satisfactorily as arising from rapidly equilibrating electron-delocalized structures.

FIG. 1

Classical Ion Representation of Proton Equivalence Achieved by Hydride- and Alkyl-Shifts.

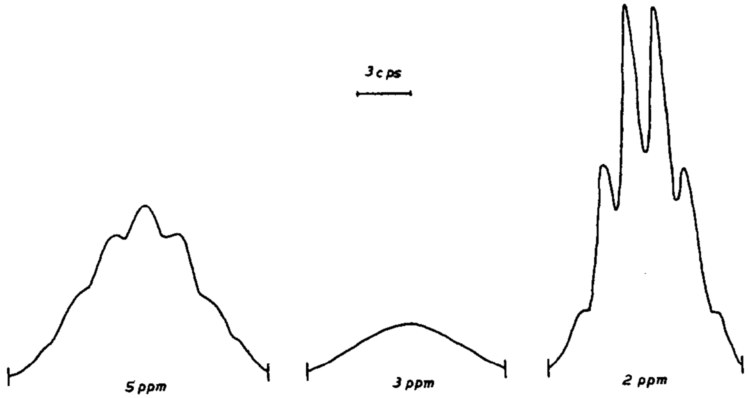


Upon cooling the sample, the single peak broadens and separates into three separate resonances at δ of 5.2, 3.1, and 2.1 with relative areas of 4:1:6 respectively. These results indicate that on the NMR time scale the 3,2-hydride shifts are slow, but the 1,2-alkyl rearrangements and 6,2-hydride shifts are fast. At low temperature, the six protons at the 3, 5, and 7 positions become equivalent as do the four protons at the 1, 2, and 6 positions. The peak whose relative intensity is one is the bridgehead hydrogen at the 4-position. These results are similar to those obtained by the previous workers (1,2).

However, whereas no fine structure was observed by Saunders, Schleyer, and Olah (3) to temperatures as low as -143°, spin-spin splitting appeared in the spectrum soon after the three resonances became sharp. The coupling constants for this splitting are small and can only be observed when the field is carefully tuned. In well-resolved spectra, obtained at -80°, the high field signal is split into a clear sextet with J = 1.5 cps. Although the signal at δ 3.1 shows no fine structure, the low field signal at δ 5.2 appears as a poorly resolved septet with J = 1.5 cps. Each of the outermost peaks of a septet occupy only 1.5% of the total area of the band, and are often difficult to discern in the spectrum. Confirmation of this assignment is found in analyzing the shape of the envelope. Thus, the spectrum consists of resonances at δ 5.2, 3.1 and 2.1 with relative intensities of 4:1:6 and observed multiplicities of 7, 1, and 6 respectively.

FIG. 2

NMR Spectrum of the Norbornyl Cation at -80°



The simplest explanation for this pattern is that the sextet at δ of 2.1 arises from coupling with the four protons at δ of 5.2 and the one at δ of 3.1 with J = 1.5 cps in each case. As expected, the peak at δ 5.2 is split into a septet by the six protons at δ 2.1. The broadness of these septet peaks is not due to slow exchange but likely arises from coupling ($J \sim \frac{1}{4}$ cps) with the resonance at δ 3.1. This splits each of the main peaks of the septet into a doublet, the result of which broadens the peaks. The lack of fine structure in the resonance at δ 3.1 (one proton) is in accord with this explanation. Spin-spin splitting with the six (δ 2.1) protons converts it into a septet with J = 1.5 cps, but the four (δ 5.2) protons split each of these peaks into a quintet ($J \sim \frac{1}{4}$ cps) with the result that only a broad peak is observed. In accord with this postulate, the half-width of this peak is about 6 cps.

Three structures for the norbornyl cation appear to deserve serious consideration (3,4). The principal form (most stable form) of the ion observed in the NMR studies must have structural features which allow carbon scrambling, exceedingly rapid exchange on the 1,2, and 6 hydrogens ($\Delta F^{\ddagger} \leq 5.5$ kcal/mole), and slow 3,2-hydride shifts ($\Delta F^{\ddagger} \sim 11$ kcal/mole). The latter piece of datum is especially important since α,β-secondary, secondary-hydride shifts occur in open chain carbonium ions with about the same activation energy ($\Delta F^{\ddagger} \sim 2$ kcal/mole) as ion capture by solvent (5).

From NMR studies, the 6,2-hydride shifts have been shown to occur at a rate at least 10^9 times faster than the 3,2-shifts (2). However, in solvolysis studies of labeled 2-norbornyl derivatives, the scrambling of the label in products indicated that the 6,2- and 3,2-hydride shifts do not exhibit so large a difference in rates (4), and in some instances 3,2-hydride shifts compete with reaction by solvent. The simplest explanation for this difference in behavior is that in solvolysis experiments an intermediate is formed (perhaps only initially) which allows rapid 3,2-hydride shifts.

The observed slow 3,2-hydride shifts ($\Delta F^{\ddagger} \sim 11$ kcal/mole) do not appear to be consistent with a classical ion (I) being the stable species in the system used in the NMR studies, since the secondary,secondary-hydride shifts are expected to occur in this ion with a very low activation energy. Using the activation energy for the shifts in open chain systems one calculates that the stable species is $11 - 2 = 9$ kcal/mole (maximum) more stable than the classical ion.* However, as is discussed below, it is reasonable that

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* The argument can be advanced that 3,2-hydride shifts would be less favorable in the bicyclic structure because of the instability of norbornene or norbornene-like structures, but it seems unlikely that this difference could result in an energy elevation of more than 3 or 4 kcal/mole.

the 3,2-shifts do occur from classical ions formed in low equilibrium concentration with more stable forms, and as a result occur slowly.

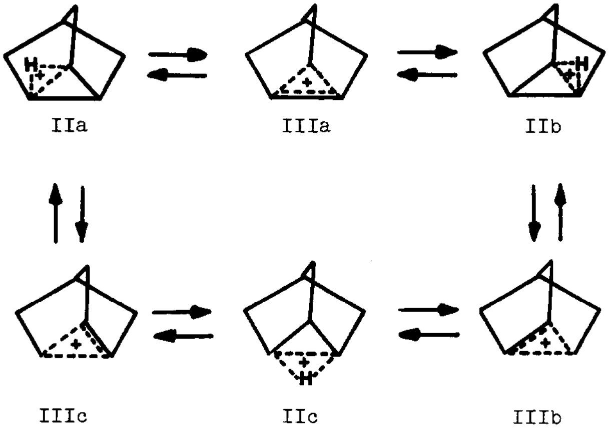
From this line of reasoning it follows that the 6,2-hydride shifts and the 1,2-alkyl shifts do not occur through the classical ion as an intermediate because the energy requirement for this pathway would be too high.

The observed spectra and rates of proton exchange can be adequately accounted for on the basis that alkyl- and hydrogen- bridged ions occur in the system as stable forms, or one of these two forms is a transition state and the other a stable species (6). For example (Fig. 3), proton shift and alkyl rearrangement may occur between edge protonated-cyclopropane (IIa) and edge protonated-cyclopropane (IIb) with the alkyl-bridged form (IIIa) serving as a transition state; alternately proton and alkyl exchange may occur between alkyl-bridged forms IIIa and IIIb with edge protonated-cyclopropane IIb as a transition state, and finally. the edge protonated-cyclopropanes (II) and the alkyl-bridged species (III) may be of comparable energy

FIG. 3

Proton and Alkyl Shifts Which Occur With

$\leq$ 5.5 kcal/mole Activation Energy



with suitable transition states (7), thus providing systems in which the observed 6,2-hydride shifts and 1,2-alkyl shifts are expected to readily occur. However, since product studies under solvolysis conditions indicate that 1,2-alkyl shifts occur more rapidly than 6,2 hydride shifts, the scheme with the alkyl-bridged transition state seems unlikely. In addition, it is reasonable to expect that 3,2-hydride shifts do not readily occur between forms of these types, but rather these shifts result from classical ions present in small equilibrium concentration (8).

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2. M. Saunders, P. von R. Schleyer, and G. A. Olah, ibid., **86**, 5680 (1964).
3. A face protonated cyclopropane intermediate has also been proposed, but this fourth form is not discussed here since there is no established structural analogy. J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., J. Am. Chem. Soc., **76**, 4501 (1954); J. D. Roberts and C. C. Lee, ibid., **73**, 5009 (1951).
4. For an excellent review of the norbornyl cation problem, see Chapter 3 by J. A. Berson in, "Molecular Rearrangement", P. DeMayo, Ed., Interscience Publishers, New York, 1963.
5. Private communication from Professor G. J. Karabatsos.
6. S. Winstein, E. Clippinger, R. Howe and E. Vogelfanger, J. Am. Chem. Soc., **87**, 377 (1965).
7. Although protonated cyclopropanes have been proposed as reaction intermediates for many years, compelling evidence for their existence has been only recently developed. R. L. Baird and A. A. Aborderin, ibid., **86**, 252 (1964); G. J. Karabatsos, C. E. Orzech, Jr., and S. Meyerson, ibid., **87**, 4394 (1965).
8. One might propose that the anion in some manner interacts with the cation and causes the rates of 3,2-hydride shifts to be slow. However, it is difficult to formulate structrual features which might be responsible for such a phenomenon.