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EVIDENCE FOR SYMMETRICAL BRIDGING IN METHYLATED 7-NORBORNENYL CATIONS

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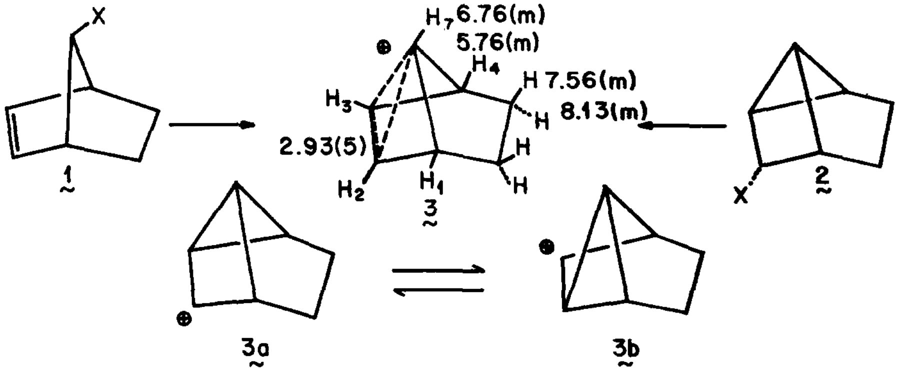
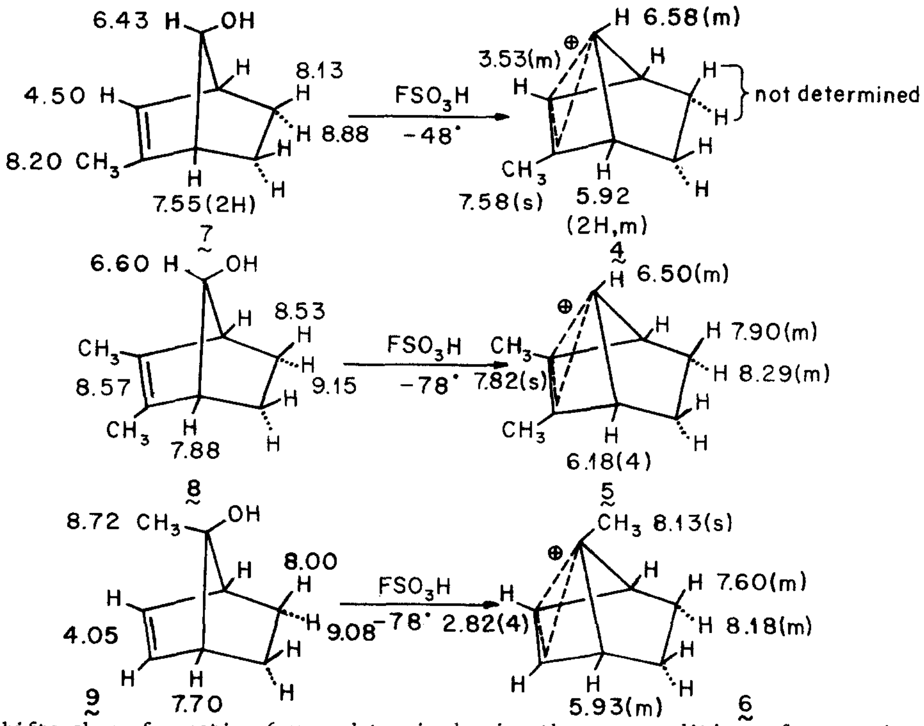
The cationic intermediate in solvolysis of either anti-7-norbornenyl (1) or the isomeric tricyclic (2) derivatives has been described as a symmetrical delocalized species (3) on the basis of rates,[2a,b] products,[2a,b] stereochemistry,[2a] and theoretical calculations.[2a,c] An alternative description of the intermediate as a rapidly equilibrating pair of tricyclic cations (3a $\rightleftharpoons$ 3b) has been offered.[3] Taken alone, the nmr spectrum of the 7-norbornenyl ion[4] serves as a compelling but not conclusive argument in favor of bridged structure 3. However, the argument may be strengthened considerably when the spectrum of the 2-methyl-7-norbornenyl cation (4) is examined. We report here the direct observation by nmr of 4, as well as the 2,3-dimethyl-7-norbornenyl ion (5) and the comparison of their spectra with those of 3 and the 7-methyl ion (6) under comparable conditions.



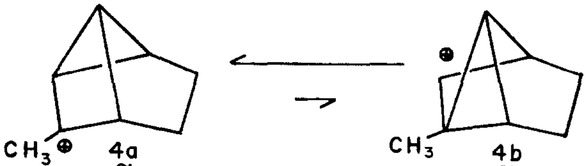
Extraction of a CD_2Cl_2 solution of the monomethyl anti-alcohol 7 into FSO_3H at -48°, followed within 30 seconds by cooling to -78°, resulted in a ca. 50% yield of ion 4.[5] The chemical shift values, given in the figures, are relative to internal CH_2Cl_2 at τ 4.70.[6] Ion 4 is relatively unstable, disappearing at -50° with a half-life of ca. 5 minutes.

Cation **5** was generated in essentially quantitative yield by extraction of **8** into FSO_3H at -78°. The ion is much more stable than **4**, decomposing finally at +49° with k ≅ 2 x 10^{-4} sec^{-1}.[7]



The shifts shown for cation **6** were determined using the same conditions of generation and observation as for ions **3**-**5**, and they agree well with those reported previously.[4b] At +9°, **6** rearranged to an unidentified material with k ≅ 3.1 x 10^{-4} sec^{-1}.

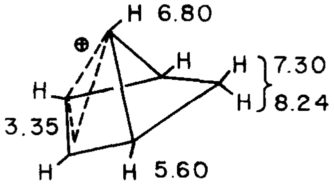
The chemical shifts of ions **3**, **5**, and **6** are such that they could represent time averaged properties of equilibrating tricyclic ions, exemplified by the **3a** ⇌ **3b** equilibrium. However, if the equilibrating tricyclic formulation is applied to **4**, then surely the tertiary ion (**4a**)



will be the predominant species in solution, and the spectrum should be essentially that of **4a**. Spectra of a number of cyclopropylcarbinyl cations are now recorded,[8] and these show signals for the cyclopropane α- and β-protons at similar and relatively high field (ca. τ 7-8). The chemical shift of H_3 in 4 (τ 3.53) is at lower field than H_7 by 3 ppm, and also at lower field than the cyclopropane α-proton in known cyclopropylcarbinyl cations by nearly 3 ppm. It is at higher field than $H_{2,3}$ in the unsubstituted ion (3) or in the 7-methyl ion (6) by only 0.6-0.7 ppm. These results are incompatible with the 4a ⇄ 4b formulation of ion 4. Obviously, the electron distribution in the three-centered cation 3 is insufficiently sensitive to 2-methyl substitution for 3 to be formulated in terms of equilibrating tricyclic structures. Thus a strong nmr argument is added to those based on chemistry and steriochemistry in favor of the nonclassical bridged representation, 3.[9] The relative insensitivity of the olefinic and bridge proton chemical shifts to methyl substitution is in accord with the conclusion that ions 3-6 are stabilized by strong bishomocyclopropenyl resonance.

The present evidence from direct observation of cations 3-5 complements the recent observation that addition of one and then two methyl groups to the double bond of 1 has a cumulative effect on the solvolysis rate.[11] The rate data were best interpreted in terms of symmetrically bridged transition states in solvolysis.

The chemical shifts for H_7 in 3-5, as well as in several 7-norbornadienyl ions,[10] are all quite similar and at high field, as is expected due to the considerable rehybridization at C_7 and delocalization of charge to $C_{2,3}$. The shifts for the protons at $C_{2,3}$ in 3, 4, and 6 are similarly at low field. Recently, the pmr spectra of the bicyclo[2.1.1]hexenyl cation[12] (10) and the "frozen" 2-norbornyl ion (11)[13] have been recorded. In these bridged ions, the shifts of the proton(s) on the bridging carbon are at high field and similar to those reported above for H_7 and the shifts of the "olefinic" protons are at low field and similar to those reported above for the analogous $H_{2,3}$ shifts. It appears that such a three-centered nonclassically bridged interaction may generally be characterized by very similar nmr shift patterns.



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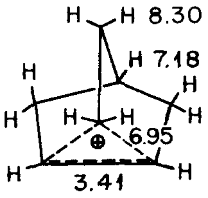

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   b. Deceased November 23, 1969.
   c. Alfred P. Sloan Foundation Research Fellow, 1967-1969.
   d. Goodyear Research Fellow, 1966-1967.

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5. Approximately half of the alcohol is converted to side products, presumably because protonation of the olefinic function is competitive with the desired ionization. Thus, in addition to the signals assigned to 4, the spectrum contains signals at τ ca. 0.0, 4.95, 5.33, 5.92, 7.00, 7.66, and 7.98, with a broad envelope at 6.2-8.9. This competition is temperature dependent since the yield of 4 is less when the precursor alcohol is extracted into FSO_3H at -78°, and essentially none of 4 is formed when the extraction is done at -120° (FSO_3H-SO_2ClF medium).

6. Spectra were recorded at 60 mHz. The shifts for alcohol precursors 7 and 8 are of CD_2Cl_2 solutions with internal CH_2Cl_2 as standard, and those for 9 are of a CCl_4 solution relative to internal TMS.

7. As expected, 2,3-dimethyl-syn-7-norbornenol does not directly yield 5 when extracted into FSO_3H at -78°. However, it appears from the character of the spectra obtained that one or more discrete species is formed and that subsequent nondegradative reaction occurs upon warming.

8. See H. G. Richey, Jr. in "Carbonium Ions", Vol. III, G. A. Olah and P. v.R. Schleyer, Eds., Interscience, New York, to be published.

9. The same argument has been presented for the 7-norbornadienyl system.[10]

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