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DIRECT OBSERVATION OF SUBSTITUTED QUADRICYCLYL CATIONS AND THEIR REARRANGEMENTS[1a]

M. Brookhart,[1b,c] R. K. Lustgarten[1d]

David L. Harris, S. Winstein[1e]

Department of Chemistry, University of California, Los Angeles, California 90024

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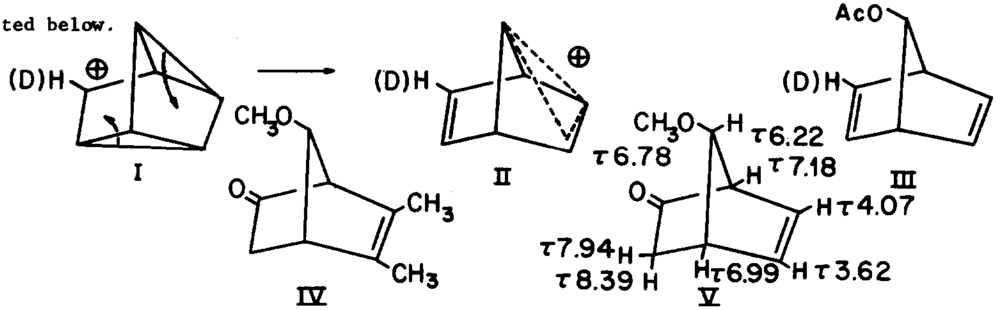
The rearrangement of the unsubstituted 7-quadricyclyl cation, I, to the 7-norbornadienyl cation, II, was first reported by Richey[2] who observed that acetolysis of 7-quadricyclyl β-naphthalenesulfonate in acetic acid led to both 7-quadricyclyl acetate and 7-norbornadienyl acetate. Similar solvolytic observations, as well as hydride trapping experiments, were also reported by Story.[3] The mechanism postulated[2,3] to account for this rearrangement is illustrated below.

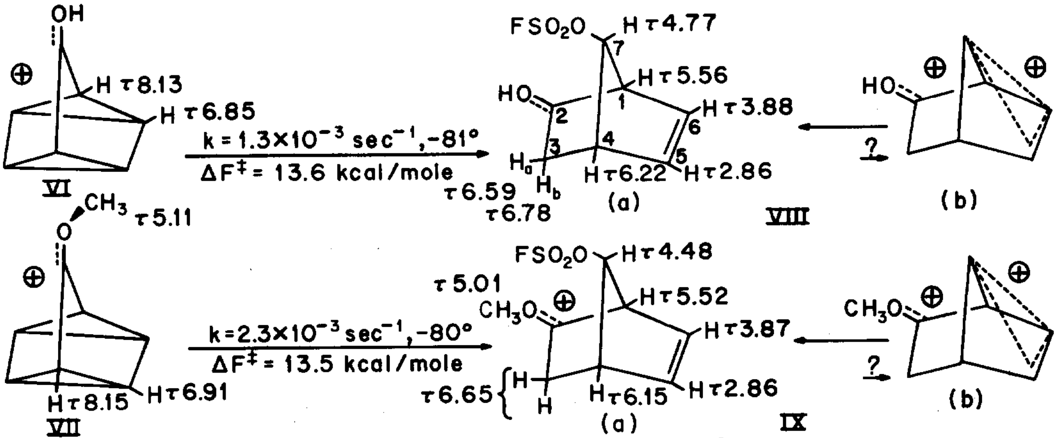


I II III IV V

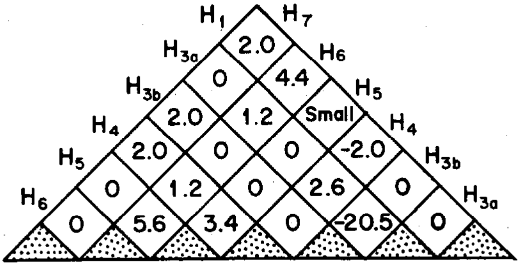
In support of this mechanism, Story[3b] showed that solvolysis of 7-deuterio-7-quadricyclyl p-toluenesulfonate leads to the dienyl acetate, III, containing the deuterium exclusively <u>syn</u> (>95%) to the acetoxy group. In a related study, Gassman[4] has reported that acid catalyzed rearrangement of 2,3-dimethyl-7,7-dimethoxyquadricyclane in methanol yields keto ether IV,[4a,b] while under similar conditions both quadricyclanone and 7,7-dimethoxyquadricyclane yield keto ether V in addition to products derived from protonation of the cyclopropane ring.[4c]

In this communication we report the first direct spectroscopic observation at low temperatures of 7-quadricyclyl cations, specifically the 7-hydroxy and 7-methoxy ions, and the rates and products of rearrangement of these ions. The 7-OH ion, VI, was prepared by protonation of quadricyclanone (CD_2Cl_2 solution) at -80° in FSO_3H-SO_2 while the 7-OCH_3 ion, VII, was prepared by extracting 7,7 dimethoxyquadricyclane[5] from CD_2Cl_2 into FSO_3H-SO_2 at -80°.

The nmr data[6] for these ions recorded at -80° in FSO_3H-SO_2 is summarized below. The 7-OH ion, VI, exhibits a two proton triplet (J=3.7 Hz) at τ 8.13 for the α protons and a four proton doublet (J=3.7 Hz) at τ 6.85 for the β hydrogens. The OH proton is unobserved due to rapid exchange with solvent acid protons.[7] The 7-OCH_3 ion, VII, shows a two proton multiplet at τ 8.15 and a four proton multiplet at τ 6.91 for the α and β hydrogens[8], respectively, and a three proton methoxyl singlet at τ 5.11.



Proton-proton coupling constants for Ion VIII[a]



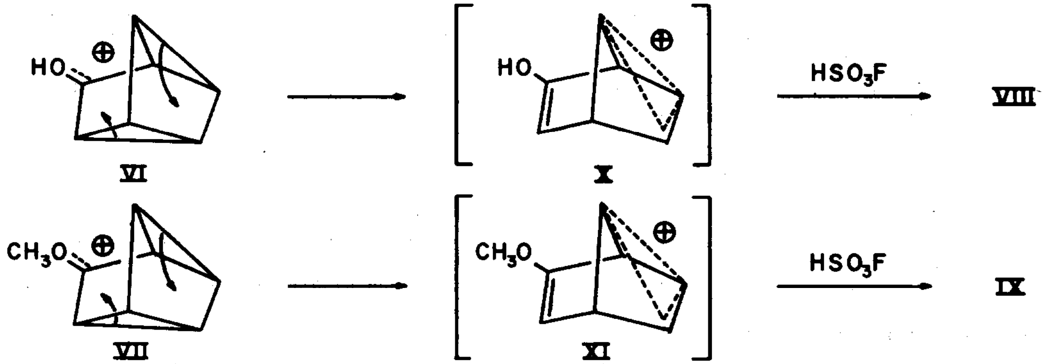
	H₇	H₆	H₅	H₄	H₃b	H₃a
H₁	2.0	4.4	Small	-2.0	0	0
H₃a	0	1.2	0	2.6	-20.5	
H₃b	2.0	0	0	3.4		
H₄	2.0	1.2	5.6			
H₅	0	0				
H₆	0					

[a] In Hz determined at -30° C in FSO_3H-SO_2ClF(1:3/v:v) by double and triple resonance experiments on a Varian HA-100 NMR spectrometer

Each of these ions, VI and VII, rearranges at -80° to species assigned structures VIII(a) and IX(a), respectively. The first order rate constant for disappearance of VI is ca. 1.3 X 10^{-3} sec^{-1} at -81°(ΔF‡=13.6 kcal/mole) while that for VII is ca. 2.3 X 10^{-3} sec^{-1} at -80° C (ΔF‡=13.5 kcal/mole). Structures were assigned on the basis of the following data. When solutions of VIII are quenched in $CH_3OH-NaHCO_3$ at -78°, a 60% yield of known keto ether V[4c] is isolated, confirming the rearrangement product as either VIII(a) or dication VIII(b). Several features of the nmr spectra, however, lead us to favor monocation structures VIII(a) and IX(a). The splitting patterns of the nmr signals of VIII and V are nearly identical, and from the chemical shifts of V the observed order of shifts in the cation is predictable. In addition, the vinyl hydrogens H_6 and H_5, exhibit chemical shifts and splitting patterns nearly identical to the vinyl hydrogens of protonated 2-norbornenone[9] which serves as a good model for VIII(a) and IX(a). Further evidence against VIII(b) and IX(b) is that the H_7-H_5 and H_7-H_6 coupling constants are 0 (see Table 1). In the dication structures these coupling constants would be expected to be ca. 2.5 Hz[10].

The presence of a strongly electron-withdrawing substituent at C_7 is indicated by the chemical shift of H_7. This substituent is apparently FSO_3- since the same nmr spectrum is obtained in pure FSO_3H. The fluorosulfonate is assigned the anti configuration from the observed coupling of 2.0 Hz between H_7 and H_3 endo.[11,4] Although no signals consistent with VIIb or VIIIb are observed, it cannot be ruled out that the observed spectra depict rapid equilibria between structures a and b, heavily weighted toward a.

The rearrangements of VI and VII are readily accommodated by the Richey-Story mechanism.[2,3] These ions probably rearrange initially to species X and XI and subsequently add FSO_3H to give VIII and IX, respectively.[12]



VI X VII XI

Data are now available for the rates of rearrangement of several quadricyclyl cations to norbornadienyl ions via the Richey-Story mechanism. Since the rearrangement of the unsubstituted quadricyclyl ion competes with solvent collapse in acetic acid,[2,13] $\Delta F^{\ddagger}$ for rearrangement is probably in the range of 4-6 kcal/mole.[14] Only the rearranged ion is observed when 7-methyl-7-quadricyclanol is extracted into FSO_3H-SO_2ClF at -125° and observed at -100° within two minutes,[15] indicating that $\Delta F^{\ddagger}$ for rearrangement of the 7-methyl-7-quadricyclyl ion must be less than ca. 11.5 kcal/mole. (The lower limit to $\Delta F^{\ddagger}$ is probably also in the range 4-6 kcal/mole, since the 7-methyl ion is expected to be longer lived than the unsubstituted ion.) Experiments similar to those reported here indicate that $\Delta F^{\ddagger}$ for rearrangement of the 7-phenyl-7-quadricyclyl ion must be $\leq$10.5 kcal/mole.[16] The highly stabilized 7-hydroxy and 7-methoxy ions are thus far the only quadricyclyl ions with sufficiently long lifetimes to allow direct nmr observation. Clearly, charge stabilizing substituents at C_7 stabilize the ground states of quadricyclyl ions relative to the charge-dispersed transition states for rearrangements to 7-norbornadienyl cations.

References

1. (a)Research supported in part by the National Science Foundation; (b)National Science Foundation Postdoctoral Fellow; (c)To whom inquiries should be addressed, Department of Chemistry, University of North Carolina, Chapel Hill, N. C. 27514; (d)National Institutes of Health Postdoctoral Fellow, present address: Dept. of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213; (e)Deceased November 23, 1969.
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3. (a)P. R. Story and S. R. Fahrenholt, *ibid.*, *86*, 527, (1964); (b)P. R. Story and S. R. Fahrenholt, *ibid.*, *88*, 374 (1966).
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5. D. M. Lemal, R. A. Lovald, and R. W. Harrington, *Tetrahedron Letters*, No. 32, 2779 (1965).
6. Chemical shifts in FSO_3H-SO_2 are in τ relative to internal CH_2Cl_2 taken as τ 4.70.
7. The O-H signal could be successfully observed in FSO_3H-SbF_5-SO_2 at -80° C. We will report later on the implications of this observation with respect to the structure of the ion.
8. The observation of these bands as multiplets rather than a doublet and triplet as in VI arises because restricted rotation around the C-O band causes the α and β protons on each side of the ion to be nonequivalent.
9. (a)H. G. Richey, Jr. and R. K. Lustgarten, *ibid.*, *88*, 3136 (1966); (b)Dr. D. L. Harris has made a complete analysis of the proton chemical shifts and proton-proton coupling constants (unpublished results).
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12. The VI to VIII rearrangement proceeds in essentially 100% yield but during the rearrangement an intermediate is seen, the most clear indication of which is a τ 2.37 signal which is observed initially, builds to a maximum concentration, then disappears. This can tentatively be assigned to X. No intermediate is observed in the rearrangement of VII, possibly because XI is more rapidly protonated than X.
13. The ratio of norbornadienyl to quadricyclyl acetates from acetolysis of quadricyclyl tosylate is 50:50 at 25° C.[3b] When the tosylate is solvolyzed in formic acid-sodium formate at ambient room temperature, the ratio of the corresponding formates is 60:40 (R. Lustgarten, unpublished result).
14. S. Winstein, Special Publication No. 21, The Chemical Society, London, 1967.
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