minimum figure for the rate constant for V → I is 10^{-2} sec^{-1} at $-78°$, and the rate constant for I → V at this temperature may be estimated as 1.5×10^{-6} sec^{-1} from the available data. Thus, a minimum figure for the equilibrium constant for $V \rightleftharpoons I$ is 7000 at $-78°$.

[10] (a) National Institutes of Health Postdoctoral Fellow, 1966–1967; (b) National Institutes of Health Predoctoral Fellow, 1965–1967.

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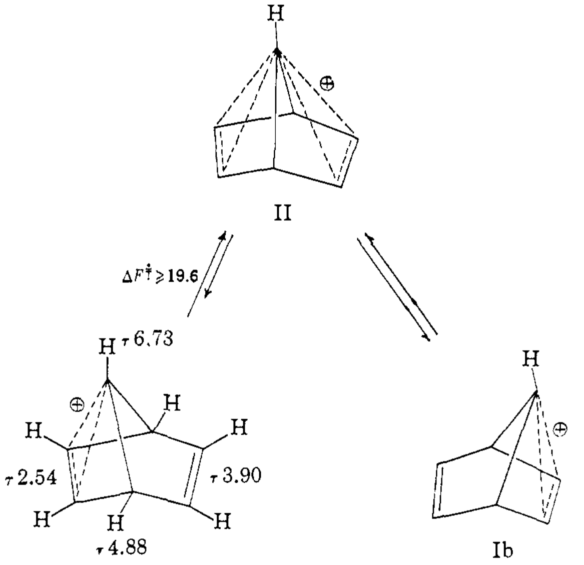
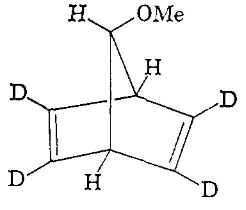
Bridge Flipping and Rearrangement of Norbornadienyl and 7-Methylnorbornadienyl Cations[1]

Sir:

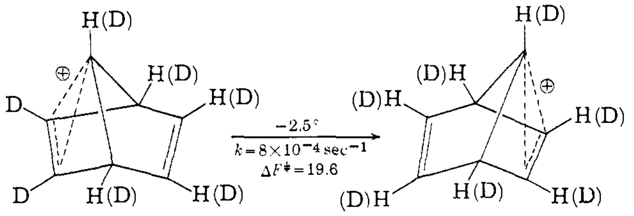
The 7-norbornadienyl cation from anchimerically assisted ionization of 7-norbornadienyl derivatives was first studied solvolytically by Winstein and Ordronneau.[2] Of the possible nonclassical structures visualized by them, the unsymmetrical one represented by I[3] can be chosen on the basis of the nmr spectrum of the ion observed by Story and Saunders.[4a] A symmetrical structure represented by II[3] was also envisioned, and this is clearly less stable than I. Even at +45°, the vinyl proton signals for the "bound" and "unbound" vinyl groups in I are sharp,[4a,5] thus showing that there is a substantial barrier to "bridge flipping" (Ia ⇌ Ib) *via* symmetrical II as a transition state (>17 kcal/mole). On the other hand, extended Hückel calculations[6] predict a relatively low value for this barrier (8 kcal; 0.35 ev). The magnitude of this barrier is one of the subjects of this communication. Methyl substituent effects on the size of the barrier, and on nmr spectra as well, can be quite illuminating, and these are illustrated by means of the 7- and 2-methylnorbornadienyl cations.



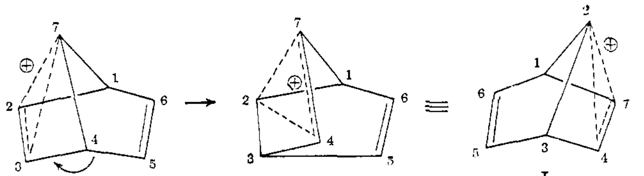
It was possible to study the equilibration of bound and unbound vinyl groups in I by observing the labeled cation Ic derived from the precursor III-OMe as a result of degenerate five-carbon scrambling.[5] Cation Ic has a deuterium atom at each bound vinyl position but only $^2/_5$ of a deuterium atom at each unbound vinyl position. At *ca.* 0° protium incorporation into the bound vinyl positions is indeed observed, the bound and unbound vinyl signals approaching equal intensities. At $-2.5°$, $k = 8 \times 10^{-4}$ sec^{-1} and thus $\Delta F^{\ddagger}$ is 19.6 kcal/mole, some 3 kcal greater than $\Delta F^{\ddagger}$ for five-carbon scrambling.[5]



III-OMe



The value of 19.6 kcal/mole is actually a lower limit to the free-energy difference between the symmetrical (II) and unsymmetrical (I) structures of the 7-norbornadienyl cation. This is because bridge flipping is not the only possible mechanism for exchange of vinyl groups. For example, another plausible mechanism involves 1,2 shifts of an unbound vinyl carbon atom[7] from C_1 to C_2, or C_4 to C_3. Such shifts, *e.g.*, I → Ie, move the bound vinyl group around so as to scramble C_1, C_2, C_3, C_4, and C_7. Coupled with the more rapid degenerate five-carbon rearrangement reported previously,[5] all seven carbon atoms of I become scrambled.[8]



As the precursor to the 7-methyl cation V we employed alcohol IV. This was prepared by addition of methyl Grignard to quadricyclanone and subsequent isomerization of the 7-methylquadricyclanol to bicyclic IV with a correct C and H analysis and an appropriate nmr spectrum in CS_2. Extraction of IV from CD_2Cl_2 into FSO_3H at $-78°$ yielded an FSO_3H solution of V

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[1] Research supported by the National Science Foundation.

[2] S. Winstein and C. Ordronneau, *J. Am. Chem. Soc.*, **82**, 2084 (1960).

[3] These representations are employed for simplicity. Molecular orbital calculations suggest greater electron delocalization than is indicated: (a) R. J. Piccolini and S. Winstein, *Tetrahedron Suppl.*, **2**, 423 (1963); (b) W. G. Woods, Ph.D. Thesis, California Institute of Technology, 1957.

[4] (a) P. R. Story and M. Saunders, *J. Am. Chem. Soc.*, **84**, 4876 (1962); P. R. Story, *et al.*, *ibid.*, **85**, 3630 (1963); (b) H. G. Richey, Jr., and R. K. Lustgarten, *ibid.*, **88**, 3136 (1966), have reported observation of I in FSO_3H.

[5] R. K. Lustgarten, M. Brookhart, and S. Winstein, *ibid.*, **89**, 6350 (1967).

[6] R. Hoffmann, *ibid.*, **86**, 1259 (1964).

[7] Any involvement of the "unbound" vinyl group in the electron delocalization of I[3] would provide some predisposition to such a shift.

[8] Still another conceivable mechanism involves the kind of ring contraction occurring in the five-carbon scrambling[5] but, instead of the bound vinyl migrating, it is now the less favored unbound vinyl. Ring contraction involving the unbound vinyl group, followed by the conventional ring expansion, results in an exchange of roles between bound and unbound vinyl groups.

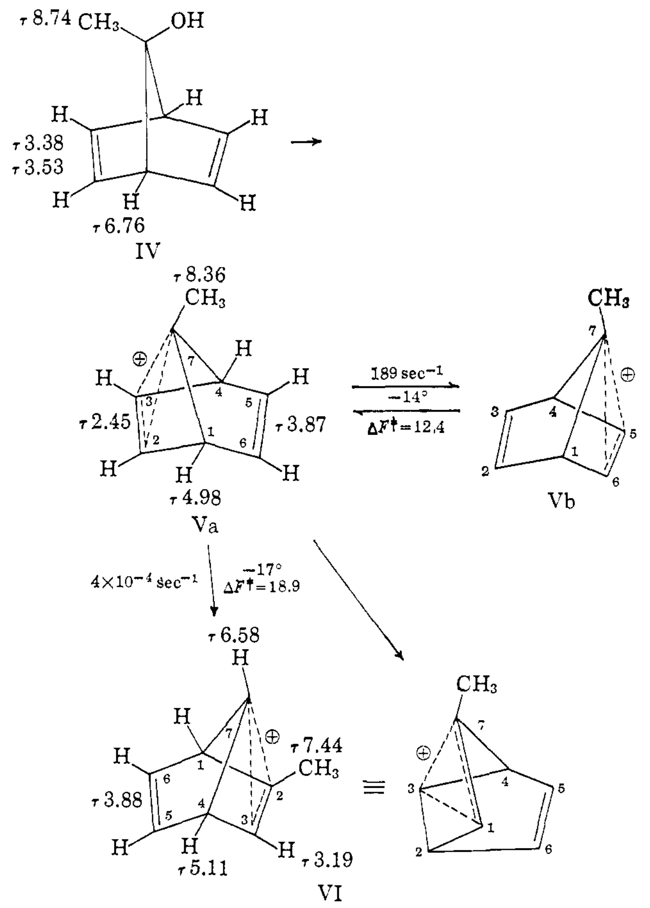
whose nmr spectrum[5] below −45° corresponds to an unsymmetrical structure V.[3] This spectrum consists of a two-proton bound vinyl quartet at τ 2.45, a broad two-proton unbound vinyl singlet at τ 3.87, a two-proton bridgehead multiplet at τ 4.98, and a methyl singlet at τ 8.36.

As the temperature is raised, the vinyl signals of V begin to broaden and eventually coalesce at −14°, while the bridgehead signal sharpens to a pentuplet and the methyl peak remains sharp. The fact that the bridgehead signal actually sharpens indicates that only the magnetic environments of the vinyl protons are being averaged, so this must occur by bridge flipping (Va $\rightleftharpoons$ Vb). At the coalescence temperature, the first-order rate constant for bridge flip is 189 sec^{-1}, and $\Delta F^{\ddagger}$ is 12.4 kcal/mole.

Above *ca.* −5°, V rearranges quite rapidly to a more stable species, the 2-methyl ion VI.[3] This is formed at −17° in *ca.* 60% yield with a rate constant of 4×10^{-4} sec^{-1} ($\Delta F^{\ddagger}$ = 18.9 kcal/mole.) As regards conceivable mechanisms of the V → VI rearrangement, the simplest[9] is by way of a $C_1 \rightarrow C_2$ shift of the unbound vinyl carbon C_6 in V, producing VI directly. Upon further heating of VI, decomposition occurs with no detectable formation of methyltropylium ion.

The 2-methyl ion VI was identified by its nmr spectrum and the results of quenching it in MeOH. In the nmr spectrum of VI, signals appear at τ 3.19, 3.88, 5.11, 6.58, and 7.44 for bound vinyl, unbound vinyl, bridgehead, bridge, and methyl protons, respectively. From quenching the FSO_3H solution of VI in MeOH there was isolated the corresponding *anti*-methyl ether with a correct analysis and an appropriate nmr spectrum summarized in VII (solvent CS_2).

The chemical shifts of the C_7, C_2, and C_3 protons in I, and in the *anti*-7-norbornenyl ion as well, were previously explained[10b] on the basis that C_7, where considerable rehybridization from trigonal toward sp^3 is expected,[3a] bears very little of the plus charge, while C_2 and C_3 carry most of it. This interpretation is strongly supported by the nmr spectra of V and VI. Thus, in the nmr spectrum of the 7-methyl cation V, the chemical shifts at C_2 and C_3 (and C_5 and C_6, also) are nearly the same as for I[11] and the 7-CH_3 chemical shift is nearly as high as in covalent IV. Thus, a 7-CH_3 group, on a carbon atom bearing very little positive charge, interacts very little with the cationic electronic system and perturbs the charge distribution negligibly. As expected, however, the 2-CH_3 group in VI does interact very appreciably with the cationic electronic system. Thus, in the nmr spectrum of VI, the chemical shift of the 2-CH_3 group is shifted downfield by 0.92 ppm and that of the 3-proton is shifted upfield by 0.74 ppm relative to the values in V. One would expect VI to be the most stable of the monomethylnorbornadienyl cations, and this is in line with the observed substantial equilibrium constant for V $\rightleftharpoons$ VI.

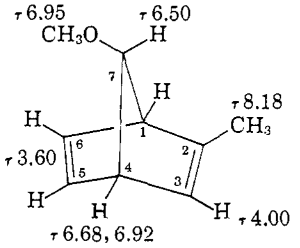


IV

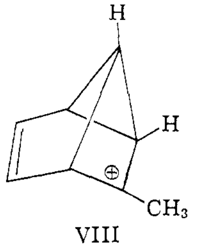
Va

Vb

VI



VII



VIII

The large barrier to bridge flipping in I ($\Delta F^{\ddagger} \geqslant$ 19.6 kcal/mole) discloses the enormous gain in stability when C_7 in symmetrical II is at least partially rehybridized and the geometry is distorted to that of unsymmetrical I where the interaction of C_7 is entirely with one of the two available olefinic groups. While a 7-methyl group has little effect on unsymmetrical I, it would be expected to have a strongly stabilizing effect on symmetrical II, where olefinic electron involvement is much less, and much more positive charge resides at C_7. On this basis one can understand the substantial reduction in the bridge-flipping barrier in V relative to I by an amount equal to or greater than 7.2 kcal/mole.

The nmr spectrum of VI is of interest in connection with Brown's and Deno's formulation[12a,b] of I, and the 7-norbornenyl cation as well, as a pair of rapidly equilibrating tricyclic ions. On such a basis, the equilibrating tricyclic 2-methyl cation would surely be nearly exclusively tertiary, and the nmr spectrum would be that of VIII. Spectra of a number of cyclopropylcarbinyl cations are now recorded,[13] and these show signals

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[9] Other conceivable mechanisms involve the five-carbon rearrangement observed with I, followed by bridge flip or "wrong-way" ring contraction[8] of the ion containing an unbound vinyl methyl group. This matter is being investigated. Neither the ion with an unbound vinyl methyl group nor a cation with a bridgehead methyl is observed during rearrangement, so their proportions must remain below *ca.* 3%.

[10] (a) A. Diaz, M. Brookhart, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 3133 (1966); (b) M. Brookhart, A. Diaz, and S. Winstein, *ibid.*, **88**, 3135 (1966).

[11] The same relationship has been observed between the 7-norbornenyl cation and its 7-methyl analog.[4b]

[12] (a) H. C. Brown and M. Bell, *J. Am. Chem. Soc.*, **85**, 2324 (1963); (b) N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 129 (1964).

[13] *E.g.*, C. U. Pittman and G. A. Olah, *J. Am. Chem. Soc.*, **87**, 5123 (1965).

for the cyclopropane α and β protons at similar and very high field (τ *ca.* 7). Contrary to this, the chemical shift of the 3-proton in the 2-methyl cation VI (τ 3.19) is at lower field than the 7-proton by 3.4 ppm, and also at lower field than the cyclopropane α-proton in known cyclopropylcarbinyl cations[13] by at least 3 ppm. Thus, we can add a strong nmr argument to those based on chemistry and stereochemistry[10] against the equilibrating tricyclic ion formulation.

[14] (a) National Institutes of Health Predoctoral Fellow, 1965–1967; (b) National Institutes of Health Postdoctoral Fellow, 1966–1967.

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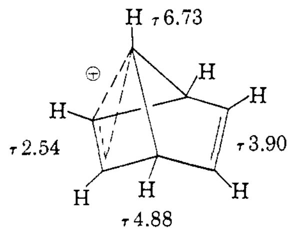
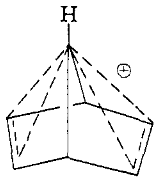
7-Phenyl- and 7-Methoxynorbornadienyl Cations[1]

Sir:

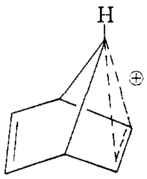
Bridge flipping and other rearrangements of the norbornadienyl cation I and its 7-methyl analog III are reported in the two preceding communications.[2] The large barrier to bridge flipping in I ($\Delta F^{\ddagger} \geqslant 19.6$ kcal/mole) is markedly reduced in the 7-methyl ion III ($\Delta F^{\ddagger} = 12.4$ kcal/mole), since a 7-methyl group stabilizes the symmetrical cation II substantially, but has no appreciable effect on unsymmetrical I.[2b] Since one would expect progressively greater stabilization of the symmetrical structure relative to the unsymmetrical one by 7-phenyl and 7-methoxyl groups, we have investigated the 7-phenyl- and 7-methoxynorbornadienyl cations. The direct observation of these species and their rearrangements to substituted tropylium ions are reported in the present communication.



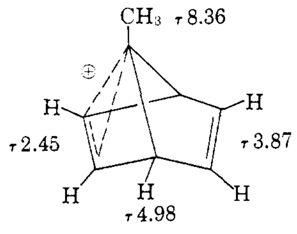
Ia



II



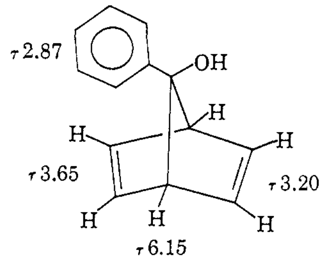
Ib



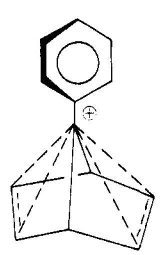
III

The precursor to the 7-phenyl cation, 7-phenyl-7-norbornadienol (IV), was prepared using the synthetic method of Dauben and Breazeale, involving phenyl Grignard addition to quadricyclanone to give the tertiary 7-quadricyclic alcohol and subsequent isomerization of the latter in CCl$_4$ to the corresponding 7-dienyl alcohol.[3] The 7-phenyl-7-norbornadienol, whose nmr spectrum (CCl$_4$) is summarized in IV, was identical with that previously prepared by Dauben and Breazeale.[5] The precursor of the 7-methoxy cation was the known 7,7-dimethoxynorbornadiene[4] (VII). Carbonium ion solutions were generated[2] by extraction of the precursors from CD$_2$Cl$_2$ into FSO$_3$H at −78°.

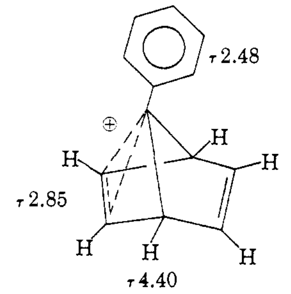
The nmr spectrum[2] of the 7-phenyl cation V in FSO$_3$H at −70° exhibits a sharp four-proton triplet at τ 2.85 for four equivalent vinyl protons, a two-proton pentuplet at τ 4.40 for the bridgehead protons, and a five-proton broad singlet centered at τ 2.48 for the aromatic protons. Of considerable interest is the relative width of the aromatic proton signal, being only *ca.* 9 cps at half-height. When the acid solution is diluted with SO$_2$, spectra may be recorded as low as −100° without viscosity broadening. Even at this temperature V still exhibits a vinyl triplet broadened less than 3 cps.



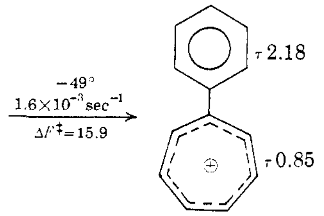
IV



Va



V



VI

When the temperature of the FSO$_3$H solution is raised, cation V undergoes a clean rearrangement to phenyltropylium ion VI. The first-order rate constant for appearance of phenyltropylium ion at −49° is 1.6×10^{-3} sec^{-1}, corresponding to a $\Delta F^{\ddagger}$ of 15.9 kcal/mole. Ion VI was identified by its nmr spectrum which exhibits a six-proton multiplet at τ 0.85 and a five-proton multiplet centered at τ 2.18. The nmr spectrum was identical with that of authentic phenyltropylium fluoroborate.[6]

The nmr spectrum of the 7-methoxy cation VIII at −65° shows a triplet at τ 2.92 for four equivalent vinyl protons, a methoxy singlet at τ 5.46, and multiplets at τ 5.24 and 5.49 for nonequivalent bridgehead protons. The vinyl triplet remains unbroadened (<3 cps) down to −100° in FSO$_3$H–SO$_2$. The nonequivalence of the bridgehead protons is due to the difference in magnetic environments caused by the methoxyl methyl group

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[1] Research was supported by the National Science Foundation.

[2] (a) R. Lustgarten, M. Brookhart, and S. Winstein, *J. Am. Chem. Soc.*, **89**, 6350 (1967); (b) M. Brookhart, R. Lustgarten, and S. Winstein, *ibid.*, **89**, 6352 (1967).

[3] The quadricyclic alcohol in CCl$_4$ was isomerized in nmr tubes previously washed with a chromic acid cleaning solution. The rates of these isomerizations were erratic and nonreproducible. Such isomerizations, obviously catalyzed and not thermal, have been similarly commented on by Lemal.[4]

[4] D. M. Lemal, R. A. Lovald, and R. W. Harrington, *Tetrahedron Letters*, 2779 (1965).

[5] (a) H. J. Dauben and A. F. Breazeale, unpublished work; (b) A. F. Breazeale, Ph.D. Thesis, University of Washington, 1965.

[6] H. J. Dauben, R. B. Medz, and W. R. Gresham, unpublished work; R. B. Medz, Ph.D. Thesis, University of Washington, 1964.