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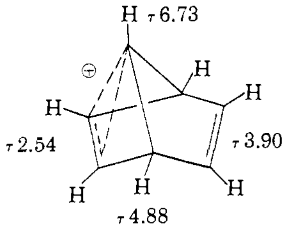
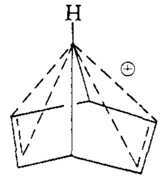
7-Phenyl- and 7-Methoxynorbornadienyl Cations[1]

Sir:

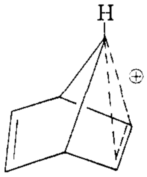
Bridge flipping and other rearrangements of the norbornadienyl cation I and its 7-methyl analog III are reported in the two preceding communications.[2] The large barrier to bridge flipping in I ($\Delta F^{\ddagger} \geqslant 19.6$ kcal/mole) is markedly reduced in the 7-methyl ion III ($\Delta F^{\ddagger} = 12.4$ 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.



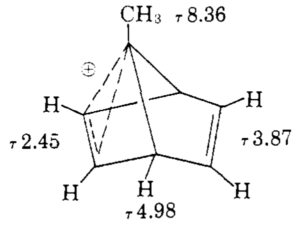
Ia



II



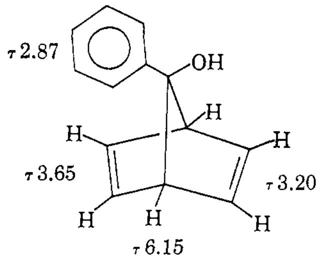
Ib



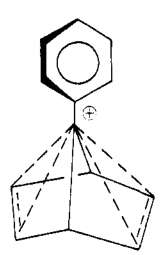
III

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_2Cl_2 into FSO_3H at −78°.

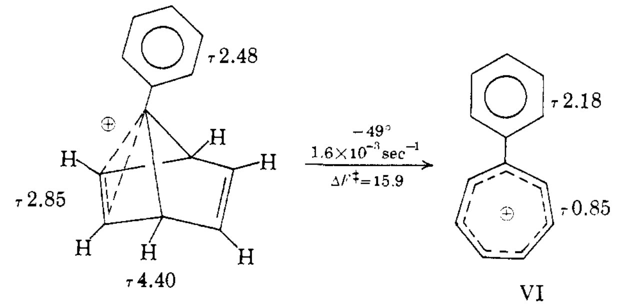
The nmr spectrum[2] of the 7-phenyl cation V in FSO_3H at −70° exhibits a sharp four-proton triplet at τ 2.85 for four equivalent vinyl protons, a two-proton pentuplet at τ 4.40 for the bridgehead protons, and a five-proton broad singlet centered at τ 2.48 for the aromatic protons. Of considerable interest 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_3H 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_3H-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.

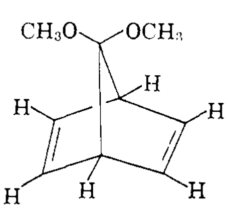
[2] (a) R. Lustgarten, M. Brookhart, and S. Winstein, *J. Am. Chem. Soc.*, **89**, 6350 (1967); (b) M. Brookhart, R. Lustgarten, and S. Winstein, *ibid.*, **89**, 6352 (1967).

[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]

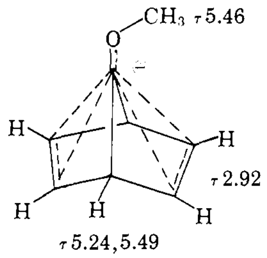
[4] D. M. Lemal, R. A. Lovald, and R. W. Harrington, *Tetrahedron Letters*, 2779 (1965).

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

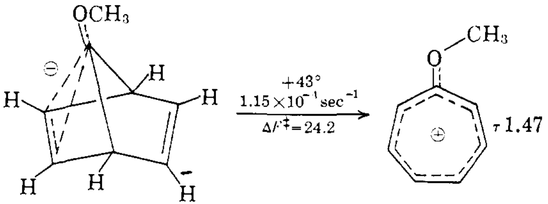
[6] H. J. Dauben, R. B. Medz, and W. R. Gresham, unpublished work; R. B. Medz, Ph.D. Thesis, University of Washington, 1964.



VII



VIIIa



VIIIb

IX

which is held *syn* to one bridgehead proton and *anti* to the other at low temperatures.[7,8b]

Warming of the FSO_3H solution of VIII causes coalescence of the bridgehead proton signals at −44° and at *ca.* 0° sharpening of this resonance to a pentuplet which is partially obscured by the methoxy singlet at τ 5.46. At the coalescence temperature, the rate constant for exchange of the magnetic environments of bridgehead protons is *ca.* 31 sec^{-1}, and $\Delta F^{\ddagger}$ is 11.7 kcal/mole. On warming to higher temperatures, cation VIII rearranges partially to methoxytropylium ion IX, identified by its nmr spectrum. The latter shows a methoxy singlet at τ 5.68 and a six-hydrogen multiplet for the tropylium protons centered at τ 1.47. This latter signal is centered at τ 1.45 in the case of hydroxytropylium ion[9] (protonated tropone), and the multiplet pattern is essentially identical with that for IX. At +43°, conversion to IX is *ca.* 48%, the first-order rate constant for its appearance being 1.15×10^{-4} sec^{-1} ($\Delta F^{\ddagger}$ = 24.2 kcal/mole). Accompanying the methoxytropylium ion is *ca.* 52% of material giving rise to broad high-field signals.

The equivalence of the four vinyl protons in both 7-phenyl and 7-methoxy cations, taken alone without considering other features of the nmr spectra, indicates that these cations are either symmetrical, or they are unsymmetrical and yet bridge flipping rapidly even at −100°. In the latter case, assuming that the chemical shifts of the two sets of vinyls would differ by at least 40 cps, the rate of bridge flip must be greater than 840 sec^{-1}, which leads to a maximum $\Delta F^{\ddagger}$ of 7.6 kcal/mole.

The chemical shifts of the vinyl protons in V and VIII provide essentially no assistance in deciding between the symmetrical and rapidly equilibrating unsymmetrical formulations. This is because the observed chemical shifts of τ 2.85 in V and τ 2.92 in VIII are not so very different from the average chemical shift of bound and unbound vinyl protons in I (τ 3.22) and III (τ 3.16), nor are they unreasonable values for symmetrical ions Va and VIIIa; *e.g.*, the vinyl chemical shitt is at τ 3.4 in the parent norbornadiene.

In the case of the 7-phenyl cation V, an important clue is the chemical shift and signal pattern for the aromatic protons. The spread in chemical shift for the various *ortho*, *meta*, and *para* protons is very small, the whole half-band width being 9 cps. On the other hand, a substantial spread in chemical shift values of the benzene ring protons is observed in carbonium ions where an α-phenyl group is tolerating considerable positive charge.[10] Examples of such cations are cumyl and benzhydryl, where the difference between *meta* and *ortho* chemical shift values is 0.83 and 0.48 ppm, respectively. Not only is the signal pattern for the aromatic protons in V quite narrow, but their chemical shift is at quite high field compared to typical α-phenyl carbonium ions. In fact, the phenyl proton signal even in the extreme case of the phenyltropylium ion VI comes at definitely lower field and has much more of a spread pattern than in cation V. It is thus evident that the phenyl group in V tolerates very little positive charge. Since it would undoubtedly bear a great deal of charge in the symmetrical ion Va, we have a strong argument that V is unsymmetrical and similar to I and III. On this basis, I, III, and V are all three unsymmetrical norbornadienyl cations with flipping barriers of ⩾ 19.6, 12.4, and <7.6 kcal/mole, respectively, in just the sequence expected for 7-H, 7-CH_3, and 7-C_6H_5 substituents.

Ion VIII, with the extremely cation-stabilizing methoxy substituent,[8] can be expected to be strongly disposed toward trigonal hybridization at C_7. The extent to which C_7 may lean away from the symmetrical position in VIIIa is still not clear. The methoxyl chemical shift appears not to be a sensitive probe for charge distribution and, further, values are not yet available for a sufficient number of close models. The barrier for *syn* ⇌ *anti* methoxyl equilibration ($\Delta F^{\ddagger}$ = 11.7 kcal/mole) is smaller than the barrier in related cases, *e.g.*, the methoxybenzenium or methoxypentadienyl cation from protonation of anisole,[11] where the barrier is *ca.* 13.0 kcal/mole. Although data are not yet available for good model systems, one might have anticipated a higher barrier in a symmetrical 7-methoxy cation VIIIa than in a methoxybenzenium ion. This may be an indication that the norbornadienyl part of cation VIII is unsymmetrical in the *syn* ⇌ *anti* equilibration transition state.

The rearrangement of the 7-phenyl cation V to the tropylium ion VI is more rapid than any of the rearrangement processes of the unsubstituted cation I.[2] On the other hand, the rearrangement of the 7-methoxy cation VIII to the tropylium ion IX is even slower than the analogous isomerization of I.[2a] In neither case is any intermediate species detectable. Discussion of these facts is postponed until the mechanisms of the various rearrangements are clarified.

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[7] (a) M. Brookhart, G. Levy, and S. Winstein, *J. Am. Chem. Soc.*, **89**, 1735 (1967). (b) The same phenomenon has been observed with 7-methoxynorbornenyl and 7-methoxyquadricyclyl cations (M. Brookhart, unpublished work).

[8] (a) R. W. Taft, R. H. Martin, and F. W. Lampe, *J. Am. Chem. Soc.*, **87**, 2490 (1965); **88**, 1353 (1966); (b) B. G. Ramsey and R. W. Taft, *ibid.*, **88**, 3058 (1966).

[9] (a) H. J. Dauben and K. M. Harmon, unpublished work; K. M. Harmon, Ph.D. Thesis, University of Washington, 1958; (b) M. Brookhart, M. Ogliaruso, and S. Winstein, *J. Am. Chem. Soc.*, **89**, 1965 (1967).

[10] *E.g.*, D. G. Farnum, *ibid.*, **86**, 934 (1964).

[11] D. M. Brouwer, E. L. Mackor, and C. Maclean, *Rec. Trav. Chim.*, **85**, 114 (1966).

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

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