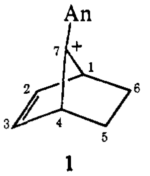
Communications to the Editor

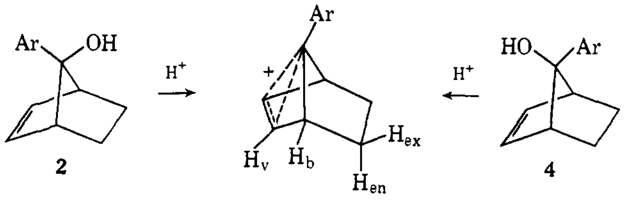
A Classical 7-Norbornenyl Cation. Competition between Aryl and Alkenyl Functions in Stabilizing 7-Aryl-7-norbornenyl Cations

Sir:

An nmr study suggests that classical structure **1** closely approximates the 7-*p*-anisyl-7-norbornenyl cation. In contrast, the interaction of C-7 with C-2



1



2 **3** **4**

and C-3 is significantly greater in a series of 7-aryl-7-norbornenyl cations with aryl substituents at C-7 less efficient than *p*-anisyl at conjugating with a positive carbon. Structures, such as nonclassical structure **3**,[1] that indicate such an interaction must be assigned to these cations. The observation of the properties of an essentially classical 7-norbornenyl cation strengthens previous assignments of structures such as **3** to most other 7-norbornenyl cations.[2]

Four aspects of the nmr observations, summarized in Table I, suggest that the *p*-anisyl cation differs qualitatively from the other aryl cations.[3] (1) The absorptions of H_o and H_m of the *p*-anisyl cation, downfield $\sim$1.2 and $\sim$0.7 ppm, respectively, from the corresponding absorptions of its alcohol precursors (**2a** and **4a**), are typical of α-*p*-anisylcarbonium ions.[4,5] In contrast, the aryl absorptions of the 7-phenyl-7-norbornenyl cation (**3b**)[6] are downfield only $\sim$0.4 ppm from the absorptions of its alcohol precursors (**2b** and **4b**); consequently the absorptions of H_o and H_p of **3b** are much further upfield (and the spread in chemical shifts of the H_o, H_m, and H_p absorptions is much smaller) than observed in spectra of carbonium ions in which an α-phenyl group supports considerable positive charge.[4,7] The aryl H absorptions of the other 7-aryl-7-norbornenyl cations are downfield <0.4 ppm from those of the precursors.[8] It is concluded that considerably more of the charge is delocalized into the aryl substituent in the *p*-anisyl cation than in the other cations. (2) Chemical shifts of the absorptions of the norbornenyl H's of the *p*-anisyl cation, particularly of H_v and H_b, are considerably upfield from those of the other cations. Chemical shifts of comparable absorptions of the other cations (**3b–f**) are remarkably similar, but the small variations are proportional to Brown[9] σ^+ constants.[10] The absorptions of the *p*-anisyl cation are much further upfield than would be predicted by the correlations of chemical shift and σ^+.[11] It is concluded that much less of the charge is at C-2 and C-3 in the *p*-anisyl cation than in the other cations. (3) The similar H_v multiplet patterns exhibited by **3b–g** differ significantly from that exhibited by the *p*-anisyl cation, suggesting that the *p*-anisyl cation differs structurally from the other cations. (4) Solutions of **3b–g**, generated by dissolving SO_2 solutions of the corresponding alcohols (**2b–g**, **4b**, and **4d**) in FSO_3H or SbF_5–FSO_3H–SO_2 at −78°, are stable at low temperatures. However, solutions prepared similarly from **2a** or **4a** furnish a spectrum with a different pattern of absorptions.[12] The absorbing species is an α-*p*-anisylcarbonium ion, but contains no "double bond," probably because of addition of the solvent acid. The "double bond" must be sufficiently incorporated into a conjugated system in **3b–g**, but not in the *p*-anisyl cation (**1**), to preclude rapid addition of such a potent electrophilic reagent as FSO_3H.

It is not surprising that charge distribution in the fully formed 7-norbornenyl cations (that are observed spectrally) is not related linearly to σ^+ over a wide range of substituents. Stabilization due to placement of charge at C-2 and C-3 is offset not only by reduced delocalization into the aryl substituent, incurred by reduction of charge at C-7 and the probable rehybridization[13] of C-7 from sp^2 toward sp^3, but also

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(1) Rapidly equilibrating cyclopropylcarbonium ion structures (in which C-7 is bonded alternately to C-2 and C-3), sometimes considered as alternatives to nonclassical structures for 7-norbornenyl cations, could be used to rationalize the observations reported in this communication. However, since such structures are rendered extremely improbable by other evidence,[2] we have used nonclassical structures (**3**) in discussing our observations.

(2) Previous investigations of 7-norbornenyl cations have been reviewed [S. Winstein, *Quart. Rev. Chem. Soc.*, 23, 141 (1969)]. Recent studies add further evidence that C-2 and C-3 are identical in the 7-norbornenyl cation [P. G. Gassman and D. S. Patton, *J. Amer. Chem. Soc.*, **91**, 2160 (1969); R. K. Lustgarten, M. Brookhart, S. Winstein, P. G. Gassman, D. S. Patton, H. G. Richey, Jr., and J. D. Nichols, *Tetrahedron Lett.*, in press].

(3) Essentially identical spectra were obtained of each ion in solutions differing significantly in acidity, eliminating the possibility that the observed absorptions were averages of those of ions and neutral species in rapid equilibrium in solutions not sufficiently acidic to "fully form" the ions.

(4) H. G. Richey, Jr., and A. S. Kushner, to be published.

(5) H. G. Richey, Jr., and J. D. Nichols, to be published.

(6) The aryl H absorption of **3b** resembles that of the 7-phenyl-7-norbornadienyl cation [M. Brookhart, R. K. Lustgarten, and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 6354 (1967)].

(7) D. G. Farnum, *ibid.*, **89**, 2970 (1967).

(8) Such a comparison cannot be made for ion **3c** because its precursor (**2c**) had a different substituent (*p*-dimethylamino). However, the absorption of H_o of **3c** is 1.34 ppm upfield from that in the *p*-(dimethylammoniumphenyl)dimethylcarbonium ion.[4]

(9) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

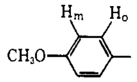
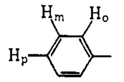
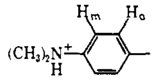
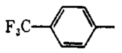
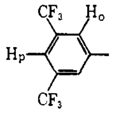
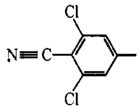
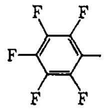
(10) Ion **3g** is not included in this correlation because $\rho\sigma$ treatments generally fail for *ortho* substituents. In fact, the positions of the various absorptions of this ion do not place it consistently in the sequence **3b–f**.

(11) Such a discontinuity between positions of nmr absorptions of a *p*-anisyl ion and of other aryl ions is not general; the *p*-anisyl ion satisfactorily fits a linear relationship between σ^+ and chemical shift of methyl H's that is observed for aryldimethylcarbonium ions.[4]

(12) An almost identical nmr spectrum is exhibited by solutions prepared by dissolving 3-*p*-anisyltricyclo[2.2.1.0^{2,6}]heptan-3-ol in fluorosulfonic or sulfuric acids.[5]

(13) R. J. Piccolini and S. Winstein, *Tetrahedron, Suppl.*, **19** (2), 423 (1963).

Table I. Nuclear Magnetic Resonance Spectra[a] of 7-Aryl-7-norbornenyl Cations (**3**) and σ^+ for the Aryl Groups

	Aryl group	H_v	H_b	H_{ex}	H_{en}	Aryl H's	Other H's	σ^{+b}
a[c]		3.35 (m)[f]	5.84 (m)	7.84 (m)	8.14 (m)	1.55 (d)[j] H_o 2.60 (d)[j] H_m	5.67 (s) OCH_3	−0.78
b[d]		2.58 (m)[g]	5.29 (m)	7.47 (m)	8.07 (m)	2.40 (m)[k]		0.00
c[d]		2.47 (m)[g]	5.25 (m)	7.39 (m)	8.01 (m)	2.27 (s)	6.65 (d)[l] $N(CH_3)_2$	(0.41)[m]
d[d]		2.46 (m)[h]	5.22 (m)	7.37 (m)	8.03 (m)	2.26 (s)		0.61
e[d]		2.39 (m)[h]	5.19 (m)	7.34 (m)	8.00 (m)	1.87 (m) H_p 1.98 (m) H_o		1.04[n]
f[e]		2.33 (m)[i]	5.18 (m)	7.27 (m)	7.94 (m)	2.25 (s)		1.22[o]
g[e]		2.33 (m)[h]	5.20 (m)	7.38 (m)	8.00 (m)			

[a] Chemical shifts are expressed in parts per million on the τ scale. Solutions are 0.2–0.5 *M*. [b] Reference 9. [c] In 5% H_2SO_4–95% CF_3CO_2H (v:v) at 35° calibrated with internal tetramethylsilane. [d] In 50% FSO_3H–50% SO_2 (v:v) at −60° calibrated with internal tetramethylammonium chloride assumed to absorb at τ 6.90. [e] In 25% SbF_5–25% FSO_3H–50% SO_2 (v:v) at −60° calibrated with internal tetramethylammonium chloride assumed to absorb at τ 6.90. [f] Resembles a triplet, spacing between absorptions ~4 Hz. [g] Resembles a triplet, spacing between absorptions ~4 Hz, with the inner absorption split into two lines separated by ~1 Hz. [h] Resembles a triplet, spacing between absorptions ~4 Hz, with the inner absorption broadened. [i] Partially obscured by the aryl H absorption; probably resembles a triplet, spacing between absorptions ~4 Hz. [j] $J = 9$ Hz. [k] Absorption covers a range of ~0.3 ppm. [l] $J = 5$ Hz. [m] This value is for the trimethylammonium substituent. [n] Twice the value for a *m*-trifluoromethyl substituent. [o] P. G. Gassman and A. F. Fentiman, Jr., *Tetrahedron Lett.*, 1021 (1970).

by increased strain incurred on placing C-7 in closer proximity to C-2 and C-3.[14] The balance between delocalization and strain favors distorted geometries that allow considerable charge at C-2 and C-3 and relatively little at C-7 in **3b–g**, but not in the *p*-anisyl cation (**1**),[15] in which the potential for stabilizing charge at C-7 is greater.

Absence of involvement by the double bond when the carbonium ion stabilizing ability of the aryl function exceeds a certain level also is found in solvolysis of a series of 7-aryl-7-norbornenyl *p*-nitrobenzoates; the solvolysis rate of 7-*p*-dimethylaminophenyl-7-norbornenyl *p*-nitrobenzoate (σ^+ of *p*-dimethylamino $\simeq -1.7$)[9] is much too large to fit the excellent $\rho\sigma^+$ plot exhibited by the rates of the *p*-nitrobenzoates of **2a**, **2b**, **2d**, and **2e**.[16] However, the *p*-anisyl ($\sigma^+ = -0.78$) compound adheres to the $\rho\sigma^+$ plot for solvolysis, the loss of double bond participation occurring near its value of σ^+, while the large changes in properties observed in this study occur instead between the *p*-anisyl and phenyl ($\sigma^+ = 0$) cations. The observation that a 7-aryl group eliminates double bond involvement somewhat more readily in a cation that in a transition state for solvolysis indicates that properties of the cations and of the transition states in 7-aryl-7-norbornenyl systems have a somewhat different dependence on σ^+.

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(14) The delocalization and strain energies of the 7-norbornenyl cation have been considered theoretically [ref 13; W. G. Woods, R. A. Carboni, and J. D. Roberts, *J. Amer. Chem. Soc.*, **78**, 5653 (1956); R. Hoffmann, *ibid.*, **86**, 1259 (1964); H. O. Ohorodnyk and D. P. Santry, *ibid.*, **91**, 4711 (1969)].

(15) Some bonding interaction of C-7 with C-2 and C-3, placing charge on C-2 and C-3, will be present even in an undistorted cation (such as represented by **1**).[14]

(16) P. G. Gassman, J. Zeller, and J. T. Lumb, *Chem. Commun.*, 69 (1968); P. G. Gassman and A. F. Fentiman, Jr., *J. Amer. Chem. Soc.*, **91**, 1545 (1969); **92**, 2549 (1970).

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