

nmr (CDCl₃, TMS) τ 5.81 (2 H, m), 6.98 (3 H, s), 7.18 (2 H, m), 7.4–8.3 (8 H, m).

Anal. Calcd for C₁₁H₁₅N₃O₂: C, 59.7; H, 6.85; N, 19.0. Found: C, 59.9; H, 6.79; N, 19.1.

(d) **Cyclobutylazoxyalkane 13**. See *cis*-azoxyalkanes, Method B, and Table IV. For computations *cf.* ref. 42 for the CNDO parameterization.

Azoxymethane (27a–b) and 2,3-Diazabicyclo[2.1.1]-hexene 2-N-Oxide (28). For the two conformations of *trans*-azoxymethane, 27a and 27b, five simplifying structural assumptions have been made: (i) $r(\text{CH}) = 1.09 \text{ \AA}$, (ii) tetrahedral carbon angles (109.47°), (iii) $\angle \text{N}_2\text{N}_1\text{C}_4 = \angle \text{N}_1\text{N}_2\text{C}_5$,⁵⁰ (iv) $r(\text{N}_1\text{C}_4) = r(\text{N}_2\text{C}_5)$,⁵⁰ and (v) planarity for all atoms except the four methyl hydrogens H-7, H-8, H-10, and H-11. Remaining bond lengths and angles have been

(50) Separately minimized NNC bond angles fall within the very narrow range $117 \pm 2.4^\circ$.³⁹ This compares well with the 115.5 and 117.7° angles for 27a and 27b obtained by using assumption iii. Likewise separately minimized $r(\text{NC})$ distances fall within the limits $1.384 \pm 0.007 \text{ \AA}$.³⁹

derived by minimization of the bonding energy with respect to molecular geometry (27a/27b): $r(\text{NN}) = 1.220/1.220 \text{ \AA}$, $r(\text{NO}) = 1.267/1.272 \text{ \AA}$, $r(\text{NC}) = 1.383/1.388 \text{ \AA}$, $\angle \text{NNO} = 125.8/126.7^\circ$, $\angle \text{NNC} = 117.7/115.5^\circ$. A fixed geometry calculation for *N*-oxide (28) made use of the following input: $r(\text{NN}) = 1.23 \text{ \AA}$, $r(\text{NO}) = 1.25 \text{ \AA}$, $r(\text{NC}) = 1.53 \text{ \AA}$, $r(\text{CH}) = 1.10 \text{ \AA}$, $\angle \text{NNO} = 121.4^\circ$.

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A Proton Nuclear Magnetic Resonance Study of 2-Aryl-2-norbornyl Cations. The Onset of "Nonclassical" Stabilization¹

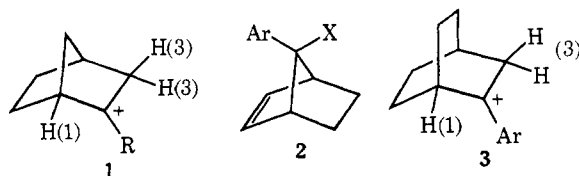
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Abstract: A plot of the nmr chemical shifts of H(1) *vs.* H(3) (average) for a series of substituted 2-aryl-2-norbornyl cations shows a marked deviation from linearity for substituents on the aryl group more electron withdrawing than hydrogen. A similar plot for 2-arylbicyclooctyl cations is very closely linear over a wider range of substituents although some deviation is apparent for *p*-trifluoromethylphenyl. Calculation of the maximum concentration of rearranged classical ion that could be in equilibrium with unrearranged classical ion indicates that a rapid equilibration between classical ions accounts for no more than 1% of the deviation for the norbornyl cations. The results are consistent with the onset of C(1)–C(6) σ bond delocalization or "nonclassical" stabilization in those norbornyl cations more electron demanding than the 2-phenylnorbornyl cation. A rearrangement which exchanges H(1) and H(6) *endo* but not H(6) *exo* is detected in these cations by the "double irradiation spin saturation transfer" (DISST) technique. This experiment also reveals a large nuclear Overhauser effect (*ca.* 50% enhancement) for geminal hydrogens H(6) *exo* and *endo*.

Searching for nonclassical character in the norbornyl cation (1, R = H) has been a favorite pastime for hosts of chemists for many years. The often elusive, and sometimes recalcitrant, nature of the problem has extracted an enormous expenditure of time and energy, has trained a generation (perhaps two) of physical-organic chemists in the difficult art of casting subtle structural questions in experimental form, and has resulted in a mind-boggling flood of literature. To contribute to the flood at this point may seem curious, or even superfluous, but we enjoy making our ripple as much as the next man, and, because we had so much to learn, we learned much from the effort. Most of the literature has been reviewed recently,² and in an earnest

desire to avoid confusing both ourselves and our readers, we have chosen to restrict ourselves to a brief discussion of the two contributions which seem to delineate most clearly the limited aspect of the nonclassical ion problem to which we want to direct our attention. We will try to avoid a pitfall of this approach, unrecognized bias, by stating our bias where it seems important and we are able.



From an extensive study of the stable norbornyl cation (1, R = H) in solution in powerful acids, Olah

(1) Abstracted in part from the Ph.D. thesis of Anthony D. Wolf, Michigan State University, 1972. Supported by the National Science Foundation under Grants GP 10734 and GP 27994.

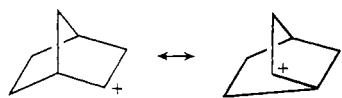
(2) H. C. Brown, *Chem. Brit.*, 199 (1966), *Chem. Eng. News.*, 45, 87 (1967); G. D. Sargent, *Quart. Rev., Chem. Soc.*, 20, 299 (1966); P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, New York, N. Y., 1965; T. D. Swartz, "Solvolytic Studies of Brendyl, Brexyl, and Norbornyl Systems," Ph.D. Thesis, Johns Hopkins University, Baltimore,

Maryland, 1966; G. D. Sargent in "Carbonium Ions," Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1972, p 1099.

has concluded that the ion under these conditions is nonclassical.³ We, too, are convinced that his data, especially the cnmr and esca spectra of the ion, are not compatible with a pair of rapidly equilibrating classical ions and require some change in hybridization at C(1) not ordinarily found in classical carbonium ions.

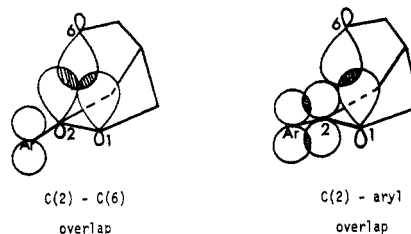
From a thorough investigation of the solvolysis of 2-aryl-2-norbornyl derivatives, Brown has concluded that there is no evidence for nonclassical participation in the transition states leading to the cationic intermediates⁴ (1, R = aryl). Thus, the solvolysis rate constants show a linear free energy relationship over the range of substituents from *p*-methoxyphenyl to *p*-trifluoromethylphenyl, about 60% of the difference in activation energy between 2-*p*-methoxyphenylnorbornyl and norbornyl derivatives. The onset of nonclassical participation would be expected to result in a change of slope in the linear free energy relationship. We find Brown's arguments here quite convincing, particularly in view of the application of a similar approach by Gassman, Richey, and Winstein to 7-aryl-7-norbornenyl derivatives (2).⁵ Gassman and Fentiman found that the linear free energy relationship changed slope sharply at the *p*-methoxyphenyl derivative. They concluded that the transition state for the *p*-methoxyphenyl derivative was just classical, while those for the other derivatives were nonclassical. This conclusion was consistent with the collaborative observation that the nmr spectrum of the 7-*p*-methoxyphenyl-7-norbornenyl cation was qualitatively different from those for the other ions. The observation of a clear case in which nonclassical participation does result in a sharp change in slope for the linear free energy relationship strengthens Brown's claim that the absence of such a deviation in the 2-arylnorbornyl systems indicates the absence of nonclassical participation.

We can now phrase in terms of the above experiments the question which we felt we could answer. Thus, if the transition states to the several 2-aryl-2-norbornyl cations studied by Brown are clearly classical, and the 2-norbornyl cation in fluorosulfonic acid-antimony pentafluoride studied by Olah is clearly "nonclassical,"⁶



then where between these limits of electron demand at C(2) does nonclassical participation become detectable?⁷ Since our analysis and comparison of the nmr spectrum of the 2-phenyl-2-norbornyl cation (1, R = C₆H₅) with those of model compounds had con-

vinced us that the ion was classical,⁸ we chose to examine the nmr spectra of ions with more and less electron demanding substituents than phenyl to try to detect the onset of nonclassical character. It seemed likely that, if all the ions were classical, a plot of the chemical shifts of the key protons H(1) and H(3) against one another would be linear (*i.e.*, both would be affected proportionately by the positive charge at C(2)), while, if there were a nonclassical mechanism for leakage of charge to C(1), its onset would be manifested by a change in the slope of the plot.⁹ We felt we could



use the plot of H(1) *vs.* H(3) for the 2-aryl-2-bicyclo-octyl cations (3) as a model for classical behavior (or at least, more nearly classical behavior) to provide an independent check on our assumptions. We discuss here the results of this examination which lead us to conclude that, for aryl substituents more electron demanding than phenyl, nonclassical leakage of charge to C(1) is detected by our probe.¹¹

Results

Determination of the Chemical Shifts. Standard procedures were used to prepare the cations in strong

(8) D. G. Farnum and G. Mehta, *J. Amer. Chem. Soc.*, **91**, 3256 (1969).

(9) If nonclassical leakage of charge to C(1) and delocalization of charge onto the aryl group were independently additive, then a plot of H(1) *vs.* H(3) would be linear over the whole range of substituents whether or not nonclassical leakage was present; *i.e.*, such a plot would be the sum of two independent linear plots. That such a situation is not likely is shown both by Gassman and Richey's results with the 7-aryl-7-norbornenyl cations and by the following arguments. Since nonclassical leakage of charge results in rehybridization about trigonal C(2), and sp² hybridization is preferred at C(2) for delocalization of charge onto the aryl group, nonclassical leakage of charge results in less effective delocalization of charge onto the aryl group. Also, since an MO description of the mixing of the C(2) and C(6) orbitals in the nonclassical ion requires a different symmetry than an MO description of the mixing of C(2) with the p orbitals of the aryl group, these cannot be additive. In pictorial terms, an increase in bonding overlap between the "endo" lobes at C(2) and C(6) can occur only at the expense of bonding overlap between the "exo" lobe of C(2) and the aryl group p orbitals. Conversely, bonding overlap between C(2) and the aryl group p orbitals can occur only at the expense of bonding overlap between C(6) and the "endo" lobe of C(2) (see structures below). It is not clear to us that "vertical stabilization" as proposed by Traylor¹⁰ as an explanation for the solvolytic behavior of the norbornyl system would result in a change in slope of the correlation line. Since it does not require rehybridization to be effective, it might well be independently additive with aryl delocalization and give a linear correlation over the whole range.

(10) T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *J. Amer. Chem. Soc.*, **93**, 5715 (1971).

(11) We have restricted ourselves to the 2-aryl derivatives in order to minimize the effects of changing the magnetic anisotropy of the substituent at C(2) on the chemical shifts of H(1) and H(3). It is true that rapid equilibration between a classical 2-aryl-2-norbornyl and a classical 1-aryl-2-norbornyl cation provides a mechanism for leakage of charge to C(1). However, given the expected relative energies of the two ions (ref 4 and 8), we were convinced that the 1-aryl-2-norbornyl cation could not contribute sufficiently to the equilibrium to affect the chemical shifts. We were also convinced intuitively that a classical equilibration would only impose another linear relationship on the plot and result in a new straight line of different slope, rather than a sharp change in slope (see ref 9). It was unnecessary to explore this intuition more analytically since a fortunate circumstance gave us a simpler way to rule out equilibrating classical ions as a quantitatively acceptable explanation of our data (see Discussion).

(3) G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *J. Amer. Chem. Soc.*, **92**, 4627 (1970).

(4) (a) H. C. Brown and K. Takeuchi, *J. Amer. Chem. Soc.*, **90**, 2691 (1970); (b) K. Takeuchi and H. C. Brown, *ibid.*, **90**, 2694 (1970).

(5) P. G. Gassman and A. F. Fentiman, Jr., *J. Amer. Chem. Soc.*, **92**, 2549 (1970); H. G. Richey, Jr., J. D. Nichols, P. G. Gassman, A. F. Fentiman, Jr., S. Winstein, M. Brookhart, and R. K. Lustgarten, *ibid.*, **92**, 3783 (1970).

(6) We take the term "nonclassical" to mean any "significant" reorganization of the geometry which results in an increase in bonding between C(2) and C(6), a decrease in bonding between C(1) and C(6), and dispersal of charge to C(1) from C(2); *i.e.*, the ion is better represented by the following resonance hybrid of two (not necessarily equal) contributors rather than by either one of them alone.

(7) The absence of nonclassical character in the transition state for formation of an ion does not necessarily mean, of course, the absence of nonclassical character in the more electron demanding ion itself (see Discussion).

acid solution for this study. The details are presented in the Experimental Section. The chemical shifts of the protons of interest, *i.e.*, H(1) and H(3) in cations **1** and **3** at 100 MHz, are listed in Tables I and II, respectively.

Table I. H(1) and H(3)^a Chemical Shifts^b in 2-Aryl-2-norbornyl Cations^c

Cations 1	Aryl group	H(1)	H(3)	$\Delta\nu$, Hz
a ^e	<i>p</i> -CH ₃ OC ₆ H ₄	5.68–5.71	6.72	br s ^d
b	<i>p</i> -HOC ₆ H ₄	5.64	6.69	br s ^d
c	3,4-(CH ₃) ₂ C ₆ H ₃	5.34	6.48	9
d	<i>p</i> -CH ₃ C ₆ H ₄	5.32	6.46	10
e	<i>p</i> -FC ₆ H ₄	5.27	6.42	11
f	<i>p</i> -ClC ₆ H ₄	5.22	6.38	14
g	<i>p</i> -BrC ₆ H ₄	5.22	6.47	19
h	<i>p</i> -IC ₆ H ₄	5.25	6.63	28
i ^f	C ₆ H ₅	5.17	6.34	14
j	<i>m</i> -BrC ₆ H ₄	5.09	6.32	16
k	<i>m</i> -ClC ₆ H ₄	5.08	6.32	17
m	<i>p</i> -CF ₃ C ₆ H ₄	4.93	6.25	22
n	3,5-(CF ₃) ₂ C ₆ H ₃	4.75	6.20	26
p	3,5-(Cl) ₂ -4-N ⁺ (CD ₃) ₂ H	4.63	6.34	

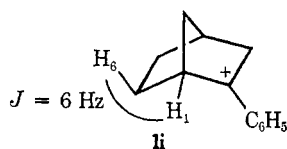
^a Average chemical shift of H(3) exo and H(3) endo. ^b τ values relative to internal standard of tetramethylammonium tetrafluoroborate (τ 6.87).⁸ ^c Determined at -60° unless otherwise indicated. ^d Center of H(3) exo, H(3) endo multiplet. ^e **1a** (30°), **1p** (-100°). ^f Literature values.

Table II. H(1) and H(3) Chemical Shifts^a in 2-Aryl-2-bicyclo[2.2.2]octyl Cations^b

Cations 3	Aryl group	H(1)	H(3)
a	<i>p</i> -CH ₃ OC ₆ H ₄	6.03	6.42
b	3,4-(CH ₃) ₂ C ₆ H ₃	5.75	6.17
c	<i>p</i> -CH ₃ C ₆ H ₄	5.74	6.15
d	<i>p</i> -FC ₆ H ₄	5.68	6.09
e	<i>p</i> -ClC ₆ H ₄	5.66	6.09
f	<i>p</i> -BrC ₆ H ₄	5.65	6.19
g	<i>p</i> -IC ₆ H ₄	5.66	6.36
h ^c	C ₆ H ₅	5.57	6.02
i	<i>m</i> -BrC ₆ H ₄	5.53	5.96
j	<i>m</i> -ClC ₆ H ₄	5.52	5.95
k ^d	<i>p</i> -CF ₃ C ₆ H ₄	5.33	5.83
m	3,5-(CF ₃) ₂ C ₆ H ₃	5.15–5.29	5.78

^a τ values relative to internal standard of tetramethylammonium tetrafluoroborate (τ 6.87).⁸ ^b Determined at -60° unless otherwise indicated. ^c Literature values. ^d **3k** (-90°).

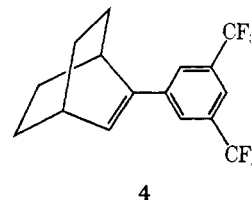
The chemical shift of proton H(1) in cation **1a** is reported as a range of values τ 5.68–5.71 because this resonance appeared as a shoulder (actually the lower field portion of a broad doublet) of the methyl resonance of the *p*-methoxy group. That this assignment was correct was verified by decoupling experiments. It was reported previously that in 2-phenyl-2-norbornyl cation **1i**, H(1) is coupled to H(6) exo with an unusually large coupling constant.⁸



When **1** was irradiated in the region in which H(6) exo was expected to absorb, the shoulder due to H(1) collapsed under the *p*-CH₃O resonance thereby confirming the assignment. The range τ 5.68–5.71 is the limit

over which the center of the H(1) resonance could be found.

The chemical shift of H(1) in cation **3m** is also reported as a range of values albeit for a completely different reason. Careful ionization of olefin **4** in fluoro-

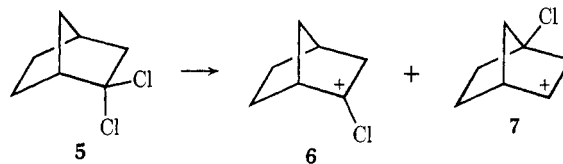


sulfonic acid-sulfuryl chlorofluoride to which was added antimony pentafluoride (to ensure complete ionization) at -120° gave a mixture of cations as noted by the nmr spectrum at -100° . Since the cation of interest was a minor component of the mixture, precise identification of H(1) was not possible. However, the range of τ values within which H(1) could absorb is reported. The broad singlet (2 H) for H(3) in **3m** (τ 5.78) could be identified.¹²

All chemical shifts are reported at -60° for cations **1** and **3** with the exceptions of cations **1i**, **3h** (literature values⁸), **1a**, **1p**, and **3k**. The chemical shifts of cation **1a** are reported at -30° , since at this temperature H(1) is better resolved from the *p*-CH₃O resonance. At -60° resolution of H(1) is quite poor because of viscosity broadening by fluorosulfonic acid. The chemical shifts of cation **3k** are reported at -90° , since at -60° this cation is rapidly converted to a mixture of cations in which **3k** is a minor component.¹³ The activation energy for rearrangement of **3k** is greater than it is for cation **3m**; thus we were able to determine its chemical shifts prior to rearrangement.

Cation **1p** undergoes a rapid Wagner-Meerwein-6,2-shift^{14,15}-Wagner-Meerwein rearrangement. Thus, at -60° the H(1) and H(3) resonances are broadened due to averaging with other protons in the system. This interesting rearrangement will be discussed in detail in a later section.

It has been reported that under some conditions of ionization 2,2-dichloronorbornane (**5**) yields a mixture



of both 2-chloronorbornyl cation **6** and protonated 4-chloro-2-norbornyl cation **7**.¹⁶ We have never been able to observe cation **1q**. Ionization of olefin **8** in fluorosulfonic acid-antimony pentafluoride-sulfuryl chlorofluoride even at temperatures lower than -100° produced cation **9**. This assignment was based on a

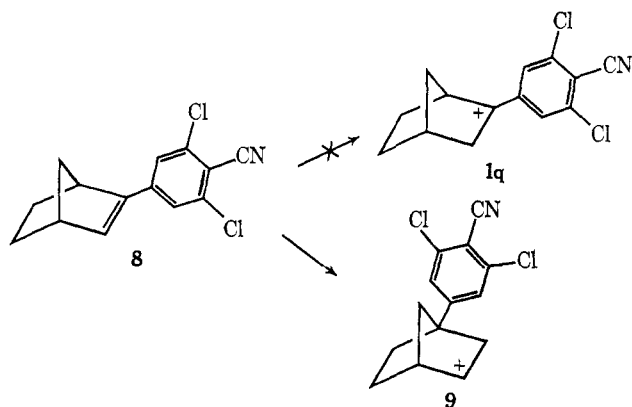
(12) The observation that a mixture of cations results on ionization of **4** has led us to make a thorough study of the equilibration that occurs among certain arylbicyclooctyl cation isomers. We have reported these results elsewhere.¹³

(13) D. G. Farnum and A. D. Wolf, *J. Amer. Chem. Soc.*, **96**, 5175 (1974).

(14) J. A. Berson and P. W. Grubb, *J. Amer. Chem. Soc.*, **87**, 4016 (1965).

(15) B. M. Benjamin and C. J. Collins, *J. Amer. Chem. Soc.*, **88**, 1556 (1966).

(16) G. A. Olah, P. R. Clifford, and C. L. Jewell, *J. Amer. Chem. Soc.*, **92**, 5531 (1970).



comparison of the nmr spectrum of 9 with that reported for 7 and the 2-norbornyl cation 1 (R = H) (Table III).¹⁶ There is a broad singlet (2 H) at τ 2.14 which is

Table III. Proton Chemical Shifts (τ Values) in Related 2-Norbornyl Cations

Cation	H(1), H(2), H ₆ exo, H ₆ endo	H(3), H(5), H(7)	H(4)	Ar
7 ^a	4.70	7.58		
1 (R = H) ^a	4.65	7.80	6.85	
9 ^b	4.62	7.52		2.14

^a Chemical shift relative to capillary tetramethylsilane.^{3,16}

^b Chemical shift relative to internal tetramethylammonium tetrafluoroborate.

assigned to the two aromatic protons.¹⁷ There is another broad singlet (4 H) at lower field which is assigned to H(1), H(2), H(6) exo, and H(6) endo. These protons are equivalent as a result of a rapid 6,1,2-hydride shift.¹⁶ As a result of this same rearrangement H₃, H₅, and H₇ are also equivalent. Thus this spectrum is consistent with the assigned structure and analogous to those of 7 and 1 (R = H) which have already been characterized.¹⁶

Since we found it necessary to report some of the data at temperatures other than -60° and since the chemical shift difference between H(1) and H(3) for 1 and 3 is important to the interpretation of our data, we determined the change in these chemical shifts over a 100° temperature range (-60 to $+40^\circ$). These data are reported in Table IV.

There is a distinct shift to higher field for protons H(1) and H(3) in every cation in Table IV when the temperature is raised 100° . The explanation for this observation is not clear. What is clear, however, is that this effect is operating to the same magnitude and in the same direction (*i.e.*, higher field with increasing temperature) for both H(1) and H(3). Thus the chemical shift difference between protons H(1) and H(3) is constant over a wide temperature range and our interpretation of the data in Table I should not be signifi-

(17) We do not know for certain if the CN group in 9 is protonated. The chemical shift of the aromatic protons in 9 is 0.51 ppm to lower field compared to the aromatic protons in olefin 8 and 0.21 ppm to lower field compared to the corresponding 2-aryl-2-*endo*-norbornanol. Olah and coworkers have reported that alkyl nitriles are completely protonated in $\text{FSO}_3\text{H}/\text{SbF}_5/\text{SO}_2$.¹⁸ This report coupled with the shift of the aromatic protons to lower field compared to starting materials suggests that the CN group is protonated.

(18) G. A. Olah and T. E. Klousky, *J. Amer. Chem. Soc.*, **90**, 4666 (1968).

Table IV. The Effect of a 100° Temperature Difference (-60 to $+40^\circ$) on the Chemical Shifts of H(1) and H(3) in 1

Cation	H(1) (-60°)	H(3) ^a (-60°)	H(1) ($+40^\circ$)	H(3) ^a ($+40^\circ$)	$\Delta H(1)$, ^b ppm	$\Delta H(3)$, ^c ppm
1a		6.75		6.72		0.03
1d	5.33	6.46	5.37	6.51	0.04	0.05
1e	5.27	6.42	5.32	6.47	0.05	0.05
1f	5.22	6.41	5.28	6.46	0.06	0.05
1g	5.22	6.47	5.29	6.54	0.07	0.07
1h	5.25	5.63	5.31	6.70	0.06	0.07
1i	5.16	6.35	5.19	6.39	0.03	0.04

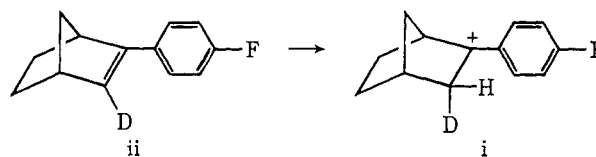
^a Average chemical shift of H(3) exo and H(3) endo. ^b H(1)($+40^\circ$) - H(1)(-60°). ^c H(3)($+40^\circ$) - H(3)(-60°).

cantly affected by any temperature variation. It is interesting nevertheless that the magnitude of this effect is variable from one cation to another. We will return to this point when we discuss the para-halogen cations.

The chemical shifts observed for H(3) exo and H(3) endo in cation 1 deserve some comment. As mentioned earlier we reported the average chemical shift here since an AB quartet having a variable chemical shift difference is observed. For example, in cation 1a and 1b the H(3) exo and H(3) endo protons give a broad singlet in the nmr spectrum. However, in all the other cations of the arylnorbornyl series, the H(3) endo proton is the lower field component of an AB quartet having a chemical shift difference dependent upon the magnitude of the positive charge at C(2)¹⁹ (except for cations 1f, 1g, and 1h which will be discussed). As more potent electron withdrawing aryl groups are placed at C(2), the magnitude of the chemical shift difference $\Delta\nu$ between H(3) exo and H(3) endo increases as shown in Table I.²⁰

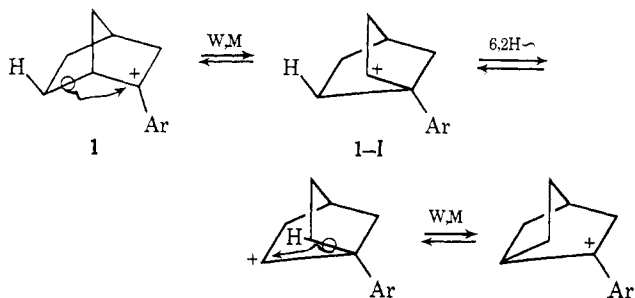
Hydride Shifts in 2-Aryl-2-norbornyl Cations. Among the interesting phenomena encountered in this study is the Wagner-Meerwein-6,2-hydride shift-Wagner-Meerwein rearrangement (W,M-6,2 H \sim W,M) which we have observed for a number of cations in the norbornyl series 1. This degenerate rearrangement is formally depicted in Scheme I. A considerable simplification of the nmr spectrum is observed because of the symmetrization which is imposed when the hydride shift in 1-I is rapid on an nmr time scale as shown below for cation 1m at 20° . The complicated multiplets at higher field for protons on C(5) and C(7) collapse to an AB quartet centered at τ 7.95, while the aromatic protons and H(4) remain invariant. The

(19) In the earlier work⁴ the assignment of H(3) exo and endo for 2-phenyl-2-norbornyl cation was not secured and should be interchanged. This is based on the observation that in the nmr spectrum of cation i produced from partially deuterated olefin ii the higher field

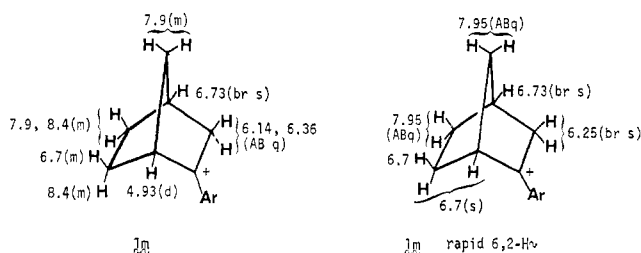


portion of the AB quartet due to H(3) exo and H(3) endo has collapsed and is of greater intensity than the lower field component of the quartet. Assuming exo protonation by FSO_3H , H(3) endo must be at lower field. In extending this assignment to the other cations in series 1 (except 1f, 1g, and 1h which we are not assigning) it is assumed that no factors are operating that would interchange H(3) exo and H(3) endo.

(20) We will show later that this effect is independent of charge leakage to C(1).



H(3) exo and H(3) endo AB quartet collapses to a singlet. H(6) endo and H(1) average to a singlet with the same chemical shift as H(6) exo. Thus it was not possible to tell whether H(6) endo, H(1), and H(6) exo were all exchanging or if only H(6) endo and H(1) were exchanging, while H(6) exo was remaining invariant. We were able to distinguish between these two possibilities by using the double irradiation spin saturation transfer (DISST) technique that was applied recently by Sorensen, Huang, and Ranganayakulu to methyl-substituted norbornyl cations.²¹



The success of the DISSST technique depends upon the half-life for chemical exchange being shorter than the half-life for proton relaxation. At -10° the coupling of H(6) exo to H(1) in cation **1m** is nearly wiped out as a result of the onset of chemical exchange. If H(1) is irradiated at this temperature (exchange is slow), the two-proton multiplet at highest field decreases by 25% (or 50% of the integrated intensity of H(6) endo).²² The integral in the region in which H(6) exo and H(4) absorb is increased²³ by 25% which corresponds to an increase of approximately 50% for H(6) exo! Presumably this represents an increase in the intensity of H(6) exo rather than H(4). Thus H(6) exo is not exchanging with H(1) or H(6) endo. H(6) exo also increases in intensity by 45–50% on irradiation of H(6) endo under slow chemical exchange. This large positive nuclear Overhauser effect is the maximum enhancement predicted for geminal protons.²³

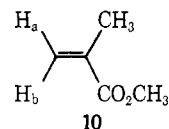
A recent review^{23a} cites many examples of chemical systems in which the nuclear Overhauser effect (NOE) has been observed. However, there were no cases of molecules cited having geminal methylene hydrogens exhibiting an NOE enhancement. This may simply be a result of a practical problem. A substantial chemical shift difference between the observed and irradiated protons (25 Hz)^{23b} is necessary for a successful determination of an NOE enhancement. In most structures

(21) E. Huang, K. Ranganayakulu, and T. A. Sorensen, *J. Amer. Chem. Soc.*, **94**, 1779, 1781 (1972).

(22) This observation allows us to assign the chemical shift of H(6) endo.

(23) (a) J. H. Nogle and R. E. Schirmer, "The Nuclear Overhauser Effect," Academic Press, New York, N. Y., 1971; (b) R. A. Bell and J. K. Saunders, *Can. J. Chem.*, **48**, 1114 (1970).

having geminal methylene protons the chemical shift difference between these protons is small. In 2-substituted norbornyl cations, however, the chemical shift difference between the geminal protons at C(6) can be substantial. For example, in cation **1m** the difference between H(6) exo and H(6) endo is 170 Hz. The closest analogs reported in the literature are structures having geminal methylenide protons. In these cases the protons are also very close together (in space, as are geminal methylene protons) and the NOE enhancements are large. For example, in methyl methacrylate (**10**) ir-



radiation of H_a gives rise to a 48% increase in the integrated intensity of H_b .³⁷

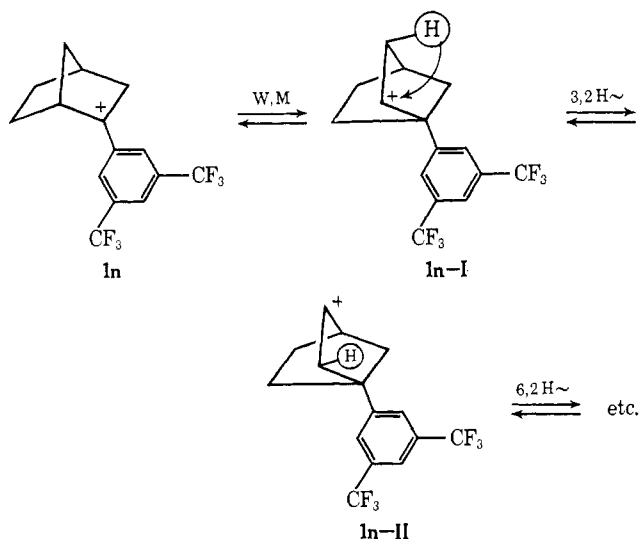
Table V summarizes the approximate coalescence

Table V. Data on Hydride Shifts in **1** at 100 MHz

Cation	6,2 H \sim , ^a deg	3,2 H \sim , deg
1j	+40	
1k	+80	
1m	+20	+60 ^b
1n	-40	+70 ^c
1p	-40-0	+30 to +40 ^b

^a Approximately lowest temperature for which complete coalescence is observed as a result of 6.2 H \sim . ^b Temperature at which broadening is observed as a result of 3.2 H \sim . ^c See text.

temperatures for the 6,2 H~ in several cations. Cation **1q** presumably would have a 6,2 H~ with a coalescence temperature nearer that of norbornyl cation.³ We also list in Table V the temperature for which we observe the onset of a second reversible process. We believe that this broadening is a result of a 3,2-hydride shift completely analogous to the 3,2 H~ in norbornyl cation.²⁴ The cations decompose, however, before this process results in complete coalescence. Thus cation **1n**, al-



ready undergoing rapid 6,2 H~ at +69°, undergoes further changes due to a 3,2 H~. The Ab quartet due

(24) M. Saunders, P. v. R. Schleyer, and G. A. Olah, *J. Amer. Chem. Soc.*, **86**, 5680 (1964).

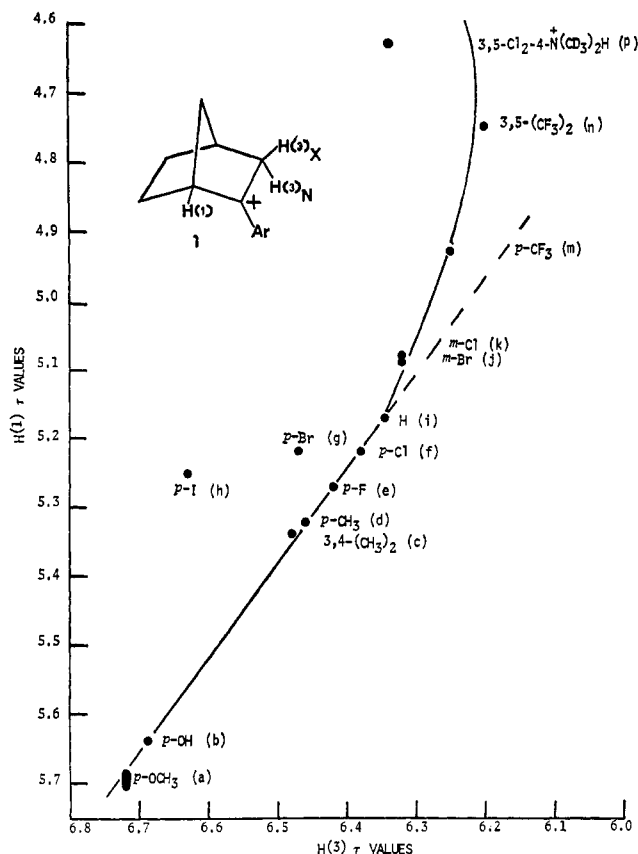


Figure 1. Plot of H(1) vs. H(3) chemical shifts in 2-aryl-2-norbornyl cations, **1**.

to protons on C(5) and C(7) collapses to a very broad signal (58-Hz width at half-height). At lower field the signals due to protons on C(1), C(3), C(4), and C(6) collapse to a broad singlet also. This process is reversible. The expected singlet which would result from total exchange of all protons in the system is not observed, since the sample decomposes.

Discussion

Figures 1 and 2 contain in graphic form the information presented in Tables I and II, respectively. Before discussing the meaning of the data we will first note several features which are apparent from the graphs. First the ordering of the points in general follows the σ^+ values for these substituents.²⁵ A strong electron releasing group places relatively little positive charge at C(2); hence, the nmr chemical shifts of protons H(1) and H(3) occur at relatively high field, while a strong electron withdrawing group places relatively more positive charge at C(2); hence, the nmr chemical shifts of H(1) and H(3) occur at relatively lower field. There are several exceptions to this trend which are noteworthy. For example, in the arylnorbornyl series of cations (Figure 1) a *p*-methoxy substituent stabilizes a positive charge better than a *p*-hydroxy group. This is opposite to what would be expected on the basis of σ^+ values.²⁵ One possible explanation involves a rapid protonation equilibrium between cations **1b** and **1b-I**. Since it would be expected that **1b-I** would have H(1) and H(3) chemical shifts at considerably lower field

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

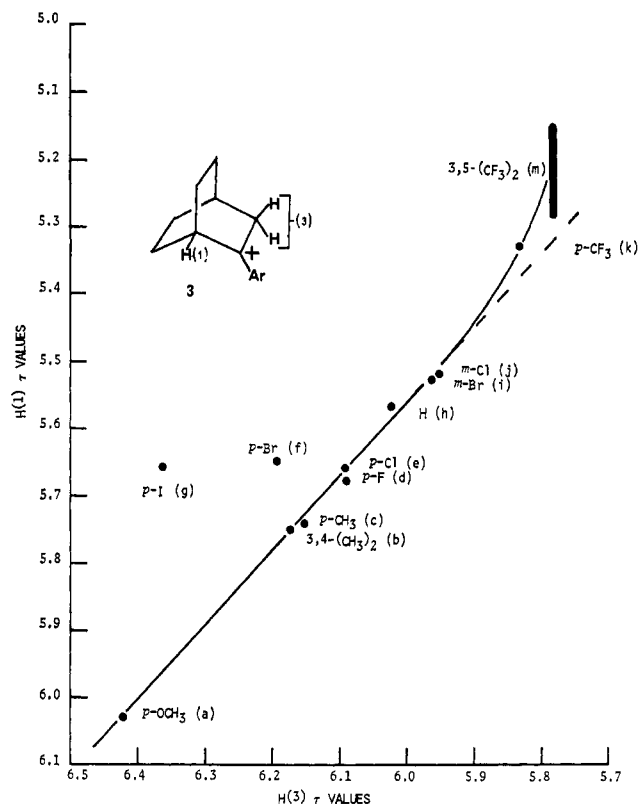
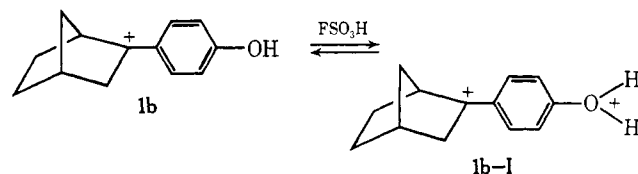


Figure 2. Plot of H(1) vs. H(3) chemical shifts in 2-aryl-2-bicyclo[2.2.2]octyl cations, **3**.



than **1b**, the averaging due to the rapid equilibrium would cause the observed values of H(1) and H(3) for **1b** to be at lower field than expected.²⁶ This argument will hold as long as the extent of protonation of cation **1b** is greater than it is for **1a**. It is not at all clear, however, that this should be the case.

A second possible explanation lies in the origin of the σ^+ values. Brown and Okamoto²⁵ have reported σ^+ values for *p*-HO and *p*-CH₃O substituents which they have calculated from the data of various reactions. These results are shown in Table VI.

Table VI. σ^+ Values Calculated from Various Reactions²⁵

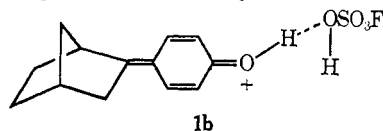
Reaction	A ^a	B ^b	C ^c
<i>p</i>	-12.14	-4.32	-3.44
<i>p</i> -HO	-0.969	-0.933	-0.833
<i>p</i> -CH ₃ O	-0.826	-0.736	-0.721

^a Uncatalyzed bromination of aromatic derivatives in acetic acid at 25°. ^b Protonolysis of substituted triphenylmethylsilanes by perchloric acid in aqueous methanol at 51.2°. ^c Ionization of triphenylcarbinols in aqueous sulfuric acid: N. C. Deno and A. Schriesheim, *J. Amer. Chem. Soc.*, **77**, 3051 (1955); N. C. Deno and W. L. Evans, *ibid.*, **79**, 5804 (1957).

(26) As long as charge leakage to C(1) is not extensive in cation **1b-I**, the net effect of the rapid equilibrium would be a displacement of the point for the *p*-HOC₆H₄ derivative to lower field along the straight line portion of the curve shown in Figure 1.

(27) (a) P. B. D. de la Mare, *J. Chem. Soc., London*, 4450 (1954). (b) C. Earborn, *J. Chem. Soc., London*, 4858 (1956).

In the case of reaction A it has been postulated that the observed substituent effects simply reflect more effective hyperconjugation by H *vs.* CH₃.^{27a} On the other hand, to explain the results in reaction B, Earborn has claimed that equally important to any hyperconjugative effect would be a hydrogen bonding interaction between solvent and hydroxyl group in determining the relative σ^+ values for *p*-HO and *p*-CH₃O.^{27b} Thus it is possible that weakening of the protonated oxygen-hydrogen bond in **1b** by the weak base fluoro-



sulfonic acid would be much less important than it would be for the more basic solvents used in the determination of σ^+ values in Table VI. Thus there might be a reversal of these two σ^+ values in fluorosulfonic acid.

A curved line²⁸ in the case of Figure 1 and a line with less curvature in the case of Figure 2 satisfactorily accommodate the bulk of the data in Tables I and II, respectively. There is some unusual effect which is present in the case of the para-halogen substituted cations, however, which causes these points to fall "off the line" in both the arylnorbornyl and arylbicyclooctyl series. From σ^+ values we can estimate that the para-halogen derivatives should fall between phenyl ($\sigma^+ = 0$)²⁵ and *m*-bromo ($\sigma^+ = 0.405$)²⁵ and would have H(1) and H(3) chemical shifts at about τ 5.12 and 5.32, respectively. The approximate chemical shift differences between observed and expected values are shown in Table VII²⁹ along with the chemical shift differences

Table VII. Chemical Shift Deviations in Para-Halogen Cations

Para-halogen		σ^+ ^a	$\Delta H(1)$, Hz ^b	$\Delta H(3)$, Hz ^c	$\Delta\nu$, ^d Hz
<i>p</i> -Cl	1f	0.114	9	5	14
<i>p</i> -Br	1g	0.150	9	15	19
<i>p</i> -I	1h	0.135	12	31	28

^a Values from ref 25. ^b τ H(1) observed - τ H(1) expected. ^c τ H(3) observed - τ H(3) expected. ^d Chemical shift difference between H(3) exo and H(3) endo.

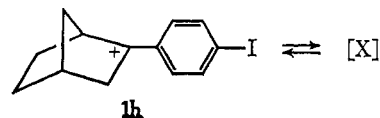
between H(3) exo and H(3) endo. While H(1) is relatively constant, H(3) is variable and in the case of the *p*-iodo derivatives the magnitude (31 Hz) is rather dramatic. We have also included the chemical shift difference between H(3) exo and H(3) endo ($\Delta\nu$) to point out further that there is some unusual effect operating in the para-halogen derivatives. We noted earlier that $\Delta\nu$ increased with increasing positive charge at C(2). A comparison of the para-halogen derivatives with the other data given in Table I indicates that for *p*-Br and *p*-I $\Delta\nu$ is larger than expected. This does not

(28) We have not included the point for **1p** in the curve, since the chemical shift of H(3) is not known with complete certainty. Labeling experiments are necessary to verify this assignment. The present assignment is based on the fact that at -100° the 6.2 H \sim in **1p** is slow on an nmr time scale, but H(3) exo, H(3) endo, and H(6) exo are indistinguishable. At higher temperatures a broad singlet is formed at τ 6.34 before H(1) (and presumably H(6) endo) coalesces to a broad singlet in the same region of the spectrum. This singlet is probably due to the averaged H(3) exo and H(3) endo protons.

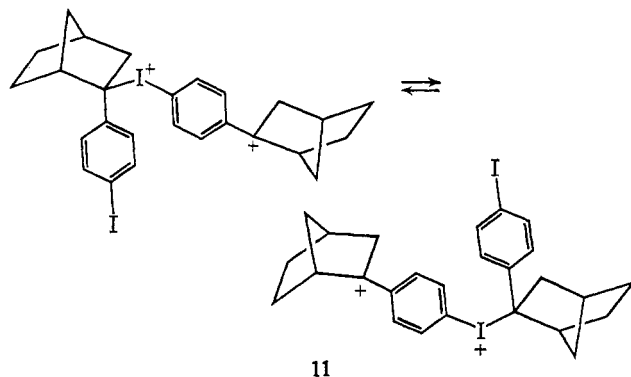
(29) The chemical shift difference between observed and expected values for H(1) and H(3) in the para halogen bicyclooctyl analogs is of about the same magnitude as it is for the norbornyl series. For simplicity only the norbornyl derivatives are discussed.

mean that there is more positive charge at C-2 in these ions, since the chemical shifts for H(1) and H(3) are at higher field than expected. Although the general features of the para-halogen cation nmr spectra are typical of other 2-aryl-2-norbornyl cations, the temperature effects on chemical shifts in cations **1f**, **1g**, and **1h** were larger than for the other derivatives studied (see above).

While we have not discovered the nature of the effect causing the deviations observed in the para-halogen cations, the above observations point to a temperature-dependent equilibrium which favors the para-halogen cation (or its nmr equivalent): The other species [X]



in the equilibrium in the case of **1b**, for example, should have the effect of decreasing charge at C(2) so that H(1) and H(3) appear at higher field than expected while at the same time $\Delta\nu$ should be larger than expected on the basis of σ^+ values and the trend set for $\Delta\nu$ by the other cations in Table I. Furthermore, the equilibrium contribution of [X] should be much less important for the meta-halogen derivatives.³⁰ A possible structure for [X] (though not an entirely satisfying one) is the "equilibrating dimer" **11**. We have investigated this pos-



sibility by a dilution study. Over a 50-fold change in concentration there was only a 2-Hz shift of H(1) and H(3) to lower field. Thus, if **11** is the species present, it is not in equilibrium with significant amounts of monomer at these concentrations.

Deno has calculated σ^+ values for a number of substituents from four independent reaction series and he has noted that σ^+ values calculated for para-halogens do not show good agreement.³¹ Thus unusual behavior for para-halogen derivatives is not unique for the aryl-norbornyl and arylbicyclooctyl cations.

We suggested in the introduction that charge leakage to C(1) would be detectable in a series of 2-aryl-2-norbornyl cations (**1** (R = aryl) by nonlinear behavior in a graph of H(1) *vs.* H(3) chemical shifts. Figure 1 illustrates just this relationship. The fractional distribution of charge at C(2) remains constant from 2-*p*-methoxyphenyl through 2-phenylnorbornyl cation.³² Substituents more electron withdrawing than phenyl,

(30) The chemical shifts for the meta-halogen derivatives in both series 1 and 3 cannot be largely different from their true values. (See Figures 1 and 2.)

(31) N. C. Deno and W. L. Evans, *J. Amer. Chem. Soc.*, **79**, 5804 (1957).

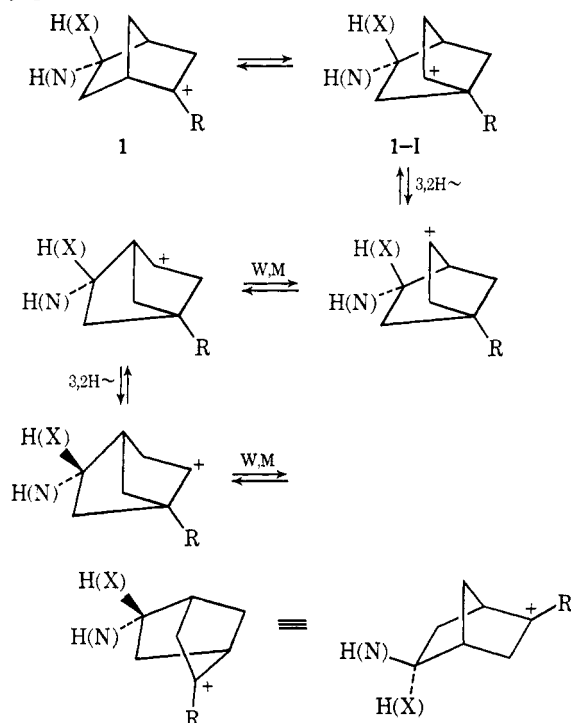
(32) We have made a least-squares fit of this portion of the data (except cations **1a**, **1g**, and **1h**). For a given value of H(1), H(3) was fitted by a least-squares method. The standard deviation for 6 points was 0.005 ppm. The slope was 0.74.

however, lead to a "break" in the linear relationship between H(1) and H(3). This effect is rather dramatic in the case of cations **1m** and **1n**. For H(1) chemical shifts of 4.93 and 4.75, the H(3) chemical shifts should be within 0.005 ppm of the straight line. They are off the line by 0.08 and 0.17 ppm, respectively.

By contrast the behavior of H(1) and H(3) chemical shifts in 2-aryl-2-bicyclooctyl cations **3** with increasing positive charge is linear from *p*-methoxyphenyl through *m*-chlorophenyl. With cation **3k** it seems possible that we are observing the onset of charge leakage to C(1). This effect is not nearly so dramatic in this case as it is in the norbornyl system. H(1) at τ 5.33 should have H(3) within 0.01 ppm of the line.³⁸ H(3) is 0.04 ppm from the line. Due to the uncertainty in the H(1) chemical shift of **3m**, the data do not permit any further conclusions concerning the electronic structure of these cations.

We must now turn to the critical question which has so often rendered contributions to this problem ambiguous; can these results be accommodated by a rapidly equilibrating pair of classical ions **1** \rightleftharpoons **1-I** (Scheme II)?

Scheme II



There are reasons for rejecting this possibility *a priori* (see ref 11), but the fortunate observation that the H(5) exo and H(5) endo AB quartet did not collapse to a singlet below 70° for cations **1** (R = aryl) allowed a simple, rigorous rejection of the equilibrating classical ion explanation. Thus, if there were any ion **1-I** in equilibrium with **1**, than a mechanism for exchange of H(5) exo and H(5) endo through a rate-controlling 3,2 hydride shift in **1-I** would be available as in Scheme II. The observed rate (k_r) of this process in hertz for the equilibrium population **1** \rightleftharpoons **1-I** would be the product of the rate constant for the 3,2 hydride shift in **1-I** (k) and the mole fraction of **1-I** in the equilibrium mixture (X), $k_r = kX$. An upper limit to k_r of 71 sec⁻¹ at 70° can be established for cation **1n** by the observation that, at

(33) A least-squares fit of the points for cations **3a**–**3e** and **3h** has a slope of 0.87. The standard deviation of these points is 0.01 ppm.

70°, the AB quartet in the nmr for H(5) exo and endo is just coalescing to a broad singlet.³⁴ A lower limit to k of 6.5×10^5 sec⁻¹ at 70° can be established by extrapolation of the data for the 3,2 hydride shift in the norbornyl cation in powerful acids.³⁶ It seems likely that the 3,2-hydride shift in a classical cation **1-I** would be at least as fast as that in the nonclassical cation **1** (R = H).³⁷ We can now calculate the maximum mole fraction, $X = k_r/k$, of **1-I** in equilibrium with **1n** as approximately 10⁻⁴. The effect of **1-I** on the nmr chemical shift of H(1) can be estimated to be approximately 10 ppm downfield, since it places a full positive charge at C(1).³⁹ Therefore, a contribution of 10⁻⁴ to the equilibrium mixture would cause a downfield shift of 0.001 ppm, *i.e.*, not detectable. In fact, the observed downfield deviation of the chemical shift of H(1) from the classical cation line in Figure 1 is 0.2 ppm, a factor of 200 greater.⁴⁰ We therefore conclude that equilibrating classical cations cannot account for our data.

Our data, then, require some mechanism for leakage of positive charge to C(1) in cations **1** (R = aryl) not ordinarily found in classical carbonium ions. Whatever electronic description is ultimately settled upon for this charge dispersal, it is clear that its effect is detectable in the cations before it is detectable in the transition states to them in the solvolysis reactions studied by Brown.⁴ It seems reasonable that the more electron demanding cations would benefit more than the transition states from electron donation from nearby bonds. In fact, a similar phenomenon has been observed by Gassman and Richey in their study of the 7-aryl-7-norbornenyl cations (**2**) referred to earlier.⁵

We have incidentally observed a remarkable effect on the shift of H(6) exo protons in cations **1**. For example, in **1a** H(6) exo appears at τ 7.47, while in **1n** it appears at τ 6.5. The chemical shift difference between them of 1 ppm is the same as that for H(1) in these two systems. While it is difficult to identify the shift of H(6) endo with precision, it is close to τ 8.4, and changes less than 0.4 ppm in these two systems. The differential effect of the charge at C(2) on H(6) exo and endo may simply reflect the difference in angle between the charge vector and the bond vector as discussed by Musher, although the difference seems too large.⁴¹

(34) The value is obtained by substitution of $\Delta\nu = 32$ Hz for the AB quartet in the expression $k = \pi\Delta\nu/\sqrt{2}$,³⁶ where k is the exchange frequency.

(35) J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, p 64.

(36) G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *J. Amer. Chem. Soc.*, **92**, 4627 (1970).

(37) Any steric influence of the aryl group at C(1) on the rate of 3,2 hydride shift in **1-I** should only accelerate it in terms of Schleyer's torsional effects.³⁸

(38) P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 701 (1967).

(39) G. Fraenkel and D. G. Farnum in "Carbonium Ions," Vol. 1, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1968, p 237.

(40) For simplicity we make the reasonable assumption that the influence of leakage of charge to C(1) is felt predominantly at H(1) rather than H(3). Even if the influence is distributed equally, the deviation is still 0.1 ppm or 100-fold greater.

(41) J. I. Musher, *J. Chem. Phys.*, **37**, 34 (1962). The magnitude of the effect of the charge at C(2) on the chemical shifts of H(6) exo and endo calculated from Musher's equations is critically dependent on the precise geometry taken for the norbornyl cation, since the H(6) endo bond vector is so nearly perpendicular to the charge vector (*i.e.*, small changes in geometry result in large changes in Musher's $\cos \theta$ term). Nonetheless, the effect on H(6) exo was not more than 0.5 ppm greater (downfield) than that on H(6) endo for a number of reasonable geometries. The observed difference is 1–2 ppm.

Table VIII. Preparation of 2-Aryl-2-endo-norbornanols^{a,b}

Aryl Group	yld	Mp or bp, deg	Molecular formula	C, %		H, %		X ^a		N, %		Mass spec (parent peak)	
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	m/e (calcd)	m/e (found)
<i>p</i> -CH ₃ OC ₆ H ₄ ^{c,d}	40	46.5–47.0 ^e	C ₁₄ H ₁₆ O										
<i>p</i> -HOC ₆ H ₄ ^e	38	146–147.5	C ₁₂ H ₁₆ O ₂	76.42	76.25	7.90	7.68					204	204
3,4-(CH ₃) ₂ C ₆ H ₃ ^f	55.8	130–145 ^g (0.6–1 mm)	C ₁₅ H ₂₀ O	83.28	83.62	9.32	8.93					216	216
<i>p</i> -CH ₃ C ₆ H ₄ ^{d,h}	69.2	46–47	C ₁₄ H ₁₆ O	83.12	83.70	8.97	8.91					202	202
<i>p</i> -IC ₆ H ₄ ⁱ	61.2	98–99	C ₁₃ H ₁₅ IO	49.68	49.80	4.81	4.85	40.41	40.36			314	314
<i>p</i> -BrC ₆ H ₄	70.2	93–94.5	C ₁₃ H ₁₅ BrO	58.42	58.38	5.66	5.62	29.92	29.94			268, 266	268, 266
<i>p</i> -ClC ₆ H ₄ ^d	68.8	85–86.5	C ₁₃ H ₁₅ ClO	70.09	69.90	6.79	7.12	15.92	15.85			224, 222	224, 222
<i>p</i> -FC ₆ H ₄	45.2	63–64	C ₁₃ H ₁₅ FO	75.66	75.86	7.38	7.44	9.21	9.18			206	206
C ₆ H ₅ ^{h,i}	70.0	41–42	C ₁₃ H ₁₆ O										
<i>m</i> -ClC ₆ H ₄ ^k	27	42–43.5	C ₁₃ H ₁₅ ClO	70.36		6.73		15.79				224, 222	224, 222
<i>m</i> -BrC ₆ H ₄	40.2	54.5–56.5	C ₁₃ H ₁₅ BrO	58.42	58.47	5.66	5.68	29.92	29.90			268, 266	268, 266
<i>p</i> -CF ₃ C ₆ H ₄	32.6	64.0–65.5	C ₁₄ H ₁₅ F ₃ O	65.58	65.79	5.94	5.97	22.23	22.27			256	256
3,5-(CF ₃) ₂ C ₆ H ₃	54.5	75.0–76.5	C ₁₅ H ₁₄ F ₆ O	55.56	55.67	4.35	4.40	35.15	35.08			324	324
3,5-(Cl) ₂ -4-N(CH ₃) ₂ C ₆ H ₂ ^l	59.9	152–158 (0.3 mm)	C ₁₅ H ₁₉ Cl ₂ NO	59.98		6.43		23.61		4.66	4.89	301, 299	301, 299
3,5-(Cl) ₂ -4-CNC ₆ H ₂ ^m	24.4	102.5–103.0	C ₁₄ H ₁₃ Cl ₂ NO	59.59	59.59	4.64	4.61	25.13	25.18	4.96	4.89	283, 281	283, 281

^a Endo alcohol unless otherwise indicated. ^b The organometallic reagent was prepared by the halogen-metal interconversion reaction unless otherwise indicated. ^c Olefin. ^d See ref 45. ^e The lithium reagent was prepared at 0°. It was then refluxed for 2.5 hr prior to the addition of 2-norbornanone (at the reflux temperature). ^f The lithium reagent was prepared at 0°. It was then stirred at room temperature for 2 hr prior to the addition of 2-norbornanone (at room temperature). ^g Short-path distillation. ^h The organometallic reagent was prepared by the Grignard reaction. ⁱ Butyllithium in hexane was added to *p*-diiodobenzene at –20°. The temperature was then raised to +10°. After all of the *p*-diiodobenzene dissolved the temperature was lowered to –20°. 2-Norbornanone was then added. ^j See ref 45. ^k Not analyzed. ^l Satisfactory elemental analysis was not obtained. ^m The lithium reagent was prepared by adding the aryl bromide to butyllithium below –60°. The ketone was then added. At all times the reaction was kept below –60°. ⁿ X refers to the appropriate halogen atom.

In any event, it is curious that H(6) exo and endo isotope effects on solvolysis rates in norbornyl systems are reported to be the same.⁴²

Experimental Section

Melting points (uncorrected) were measured on a Thomas-Hoover capillary melting point apparatus. Infrared spectra were taken on a Perkin-Elmer 137 instrument. Nmr spectra were measured at 60 MHz on a Varian T-60 or A 56/60 D or at 100 MHz on a Varian HA-100 instrument. (Tetramethylammonium tetrafluoroborate (τ 6.87)⁸ was used as an internal standard for carbonium ion spectra.) Mass spectra were measured on a Hitachi Perkin-Elmer RMU-6 instrument. Combustion analyses were performed by Spang Microanalytical Laboratories.

Preparation of Carbocations. The acid to be used was chosen so as to ensure complete ionization of the carbocation precursor; essentially identical spectra were obtained in acids differing significantly in acidity. The carbocations were formed by solution of the precursor in a suitable solvent and then slow dropwise addition to rapidly stirred acid (under N₂ atmosphere). For example, CFCl₃ was a convenient solvent for many of the precursors when FSO₃H was used. If very low temperatures were desired and/or any SbF₅ was added to the FSO₃H, then SO₂ClF (25–75%) and/or SO₂F₂ (25–75%) was used as the solvent for the precursor. About a 5 wt % final solution concentration of the carbocation was found to be ideal in most cases. The sample was then transferred to the nmr tube.

Carbocation Precursors. The alcohols used for this study were formed by the reaction of the desired organometallic reagent with the appropriate ketone 2-norbornanone or bicyclo[2.2.2]octan-2-one.^{43,44} The organometallic reagent was formed by the Gri-

gnard reaction⁴⁵ or the halogen-metal interconversion reaction⁴⁶ (HMIR).

General Procedure for Alcohol Synthesis Using the HMIR. Ether was distilled into a dried 50-ml three-neck flask containing a weighed amount of the desired aryl halide. The flask was equipped with a low-temperature thermometer, a magnetic stirring bar, N₂ inlet, and 15-ml constant pressure addition funnel. About a 10–30% by volume solution of the aryl halide in ether was used. The solution was cooled to about –40° using a Dry Ice-acetone bath. To this solution was added dropwise a 10% molar excess (over the halide) of commercial *n*-butyllithium in hexane. The reaction was kept between –30 and –40° during the addition and then allowed to warm to –10° for about 5 min. After the addition of the butyllithium was complete, the temperature of the reaction mixture was again lowered to –40°. A solution of the ketone (1 equiv) in anhydrous ether was added at a rate such that the temperature of the reaction mixture did not rise above –30°. Following the addition of the ketone, the Dry Ice-acetone bath was removed and the temperature of the reaction mixture was allowed to warm slowly to room temperature. The reaction mixture was then hydrolyzed with saturated aqueous NH₄Cl solution and extracted with ether. Drying the ether solution with MgSO₄ followed by evaporation of the ether led to a crude oil or solid which was then purified.

The desired organometallic reagent was formed from the aryl bromide except in the case of *p*-iodophenyllithium. In this case *p*-diiodobenzene was used. All the aryl halides were commercially available with the exception of 4-bromo-2,6-dichlorobenzonitrile and 4-bromo-2,6-dichloro-*N,N*-dimethylaminobenzene. The latter compound was prepared in 95% yield by methylation of 2,6-dichloro-4-bromoaniline⁴⁷ with dimethyl sulfate. 4-Bromo-2,6-dichlorobenzonitrile was prepared according to the procedures of Gassman and Fentiman.⁴⁷

Tables VIII and IX are a summary of the pertinent data on compounds prepared by the methods mentioned above.

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Table IX. Preparation of 2-Aryl-2-bicyclo[2.2.2]octanols^a

Aryl group	% yield	Mp or bp, deg	Molecular formula	C, %		H, %		X, %		Mass spec (parent peak)	
				Calcd	Found	Calcd	Found	Calcd	Found	m/e (calcd)	m/e (found)
<i>p</i> -CH ₃ OC ₆ H ₄ ^{b-d}	18.5	56.5–58.0 ^b	C ₁₅ H ₁₈ O							214	214
3,4-(CH ₃) ₂ C ₆ H ₃ ^e	70.4	60–100 (0.3 mm) ^f	C ₁₅ H ₂₂ O							230	230
<i>p</i> -CH ₃ C ₆ H ₄ ^{b,d,g}	76	100 (0.33 mm) ^b	C ₁₅ H ₁₈	90.85	89.45	9.15	9.07			198	198
<i>p</i> -IC ₆ H ₄ ^{b-i}	60	100 (0.2–0.4 mm) ^f	C ₁₄ H ₁₇ IO							328	328
<i>p</i> -BrC ₆ H ₄ ⁱ		120 (5–10 mm) ^k	C ₁₄ H ₁₇ BrO							282, 280	
<i>p</i> -ClC ₆ H ₄ ^{i,j}	40–60	125–145 (3 mm) ^k	C ₁₄ H ₁₇ ClO							238, 236	238, 236
<i>p</i> -FC ₆ H ₄ ⁱ	8.6 ^l	55–56	C ₁₄ H ₁₇ FO	76.29	76.10	7.84	7.78	8.62	8.62	220	220
C ₆ H ₅ ^m	45.4	135–152 (15 mm)	C ₁₄ H ₁₈ O								
<i>m</i> -BrC ₆ H ₄ ⁱ	55	60 (0.25 mm) ^f	C ₁₄ H ₁₇ BrO	59.78	59.75	6.10	6.06	28.43	28.43	282, 280	282, 280
<i>m</i> -ClC ₆ H ₄ ⁱ	24	60 (0.3 mm) ^f	C ₁₄ H ₁₇ ClO							238, 236	238, 236
<i>p</i> -CF ₃ C ₆ H ₄ ^{b,n}	25.5	90 (10 mm) ^{b,j}	C ₁₅ H ₁₅ F ₃	71.38	70.98	6.04	6.04	22.58		252	252
3,5-(CF ₃) ₂ C ₆ H ₃ ^{b,n}	19.8	98–99 ^b	C ₁₅ H ₁₄ F ₆	60.00	59.55	4.41	4.24	35.59	36.17	320	320

^a Alcohol unless otherwise indicated. Alcohols were prepared by the halogen-metal interconversion reaction unless otherwise indicated.

^b Olefin. ^c Dehydrated with KHSO₄ during distillation (see ref 45). ^d The organometallic reagent was prepared by the Grignard reaction. ^e The lithium reagent was prepared at 0°. It was then stirred at room temperature for 2 hr prior to the addition of bicyclo[2.2.2]octan-2-one (at room temperature). ^f Molecular distillation. ^g Dehydrated by overheating the alcohol. ^h Butyllithium in hexane was added to *p*-diiodobenzene at –20°. The temperature was then raised to +10°. After all the *p*-diiodobenzene dissolved the temperature was lowered to –20°. Bicyclo[2.2.2]octan-2-one was then added. ⁱ Not analyzed. ^j Partial dehydration during distillation. ^k Short-path distillation. ^l The yield of crude product was actually much greater than this value. Molecular distillation of the crude product produced a mixture of alcohol and olefin from which the alcohol was obtained pure after three recrystallizations from hexane. The yield of pure product was reduced in the fractional crystallizations. ^m See ref 8. ⁿ The alcohol was dehydrated in the presence of H₂SO₄ by heating to the boiling point under reduced pressure. ^o X refers to the appropriate halogen atom.

The nmr and ir spectra of the alcohols and olefins in the norbornyl and bicyclooctyl series of compounds were consistent with the assigned structures. The following are typical nmr spectra for an alcohol and olefin in each series of compounds.

Norbornyl System. 2-*p*-Iodophenyl-2-*endo*-norbornanol: nmr (CCl₄) τ 2.51 (AA'BB', $\Delta\nu$ = 26 Hz, J_{AB} = 9 Hz, 4 H), 7.70 (m, 4 H), 8.43 (m, 7 H). 2-*p*-Methoxyphenyl-2-norbornene: nmr (CCl₄) τ 3.04 (AA'BB', $\Delta\nu$ = 31 Hz, J_{AB} = 9 Hz, 4 H), 3.96 (d, J = 3.5 Hz, 1 H), 6.28 (s, 3 H), 6.76 (br s, 1 H), 7.06 (br s, 1 H), 8.12–9.0 (m, 6 H).

Bicyclooctyl System. 2-*p*-Fluorophenylbicyclo[2.2.2]octan-2-ol: nmr (CCl₄) τ 2.58 (m, 2 H), 3.09 (m, 2 H), 7.5–8.8 (m, 13 H). 2-*p*-Methoxyphenylbicyclo[2.2.2]oct-2-ene: nmr (CCl₄) τ 2.98 (AA'BB', $\Delta\nu$ = 31 Hz, J_{AB} = 9 Hz, 4 H), 3.62 (dd, J = 7 Hz, 2 H, 1

H), 6.22 (s, 3 H), 6.98 (br s, 1 H), 7.38 (br d, J = 7 Hz, 1 H), 8.52 (AB q, $\Delta\nu$ = 17 Hz, J = 9 Hz, 8 H).⁴⁸

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(48) Decoupling experiments showed that the 2-Hz coupling at 3.62 is between the olefinic proton and the broad singlet at 6.98. Comparison of a 100-MHz spectrum with a 60-MHz spectrum of this compound indicates that the absorption centered at 8.52 is indeed an AB quartet (or two overlapping AB quartets with similar chemical shifts).

Fluorine-19 and Hydrogen-1 Nuclear Magnetic Resonance Study of an Equilibrium among Arylbicyclooctyl Cations¹

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Abstract: The following cations were characterized at –90° by a ¹H nmr study: 2-*p*-trifluoromethylphenyl-2-bicyclo[2.2.2]octyl cation (**2a**), 2-*p*-trifluoromethylphenyl-2-bicyclo[3.2.1]octyl cation (**9a**), and 6-*p*-trifluoromethylphenyl-6-bicyclo[3.2.1]octyl cation (**11a**). Warming any of these cations to –60° produced the same equilibrium mixture. By ¹⁹F nmr the order of stability was found to be **11a** > **2a** >> **9a**. The equilibrium constant between **2a** and **11a** at –80° is 3.2. Other thermodynamic parameters are presented and a mechanism for the equilibrium is discussed.

Recently we have found it desirable to examine certain chemical shifts in a series of 2-aryl-2-norbornyl cations **1** and 2-aryl-2-bicyclo[2.2.2]octyl cations

2.^{1b} During the course of this study we observed that upon ionization of their respective precursors at –78°, cations of type **2** in which X was a strongly withdrawing substituent (e.g., **2a**, X = *p*-CF₃) gave proton nmr spectra substantially different from cations in which X was electron donating (e.g., **2b**, X = *p*-F).^{1b} Since

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