

This result is derived primarily from the DMSO-HO hydrogen bond formation requiring access only to the hydroxyl hydrogen; whereas, the formation of an autoassociated chain of OH groups requires access to an unshared pair of oxygen electrons as well as the OH hydrogen. Alcohol autoassociation is thus more susceptible to steric crowding about the OH group than is association with DMSO, as our chemical-shift data clearly indicate.

### Experimental Section

**Materials.** Except where stated otherwise, all alcohol samples were procured from commercial sources, with reagent grade alcohols being obtained wherever possible. Each alcohol sample was analyzed for purity by glpc on either a Carbowax 20M or Carbowax 1540 column. Where necessary, the alcohol samples were distilled through either a 24-in. column packed with glass helices or a 1-m column packed with iron mesh, with literature boiling points being obtained in all cases. Glpc analysis revealed all alcohol samples employed for spectral work to be of >99% purity except for 1-hexanol, where the purity was >98%, and 1-pentanol, where the purity was >95%. No irregularities were found in the pmr spectra of either of these two alcohols.

2,2,4,4-Tetramethyl-3-pentanol was prepared by reduction of hexamethylacetone with sodium borohydride. To hexamethylacetone (5.0 g) in 95% ethanol was added a 20% *M* excess of sodium borohydride in 0.039 *N* aqueous sodium hydroxide and the mixture refluxed 30 min. After stripping off the EtOH from the reaction mixture, distilled water (30 ml) was added and the mixture extracted with three 30-ml aliquots of ether which were combined and dried overnight over Drierite. Following solvent removal, the residue was distilled to give 3.0 g of product (bp 163°). Upon cooling the product gave mp 46–48° (lit.<sup>47</sup> 50°).

Androsterone and *cis*- and *trans*-4-*t*-butylcyclohexanols were obtained from a previous study in these laboratories.<sup>6</sup> Dibenzobicyclo[2.2.2]octyl systems it is concluded that the title cation is classical. Some dramatic examples of the low-field chemical shifts of bridgehead norbornyl hydrogens are described.

(47) "Dictionary of Organic Compounds," Vol. 5, 4th ed, Oxford University Press, New York, N. Y., 1965, p 3025.

(48) N. L. Bauld and Y. S. Rim, *J. Am. Chem. Soc.*, **89**, 179 (1967). The author is extremely grateful to Professor Bauld for unpublished information concerning this preparation.

hexane-acetone (2:1) the product gave mp 136–137°. Its infrared and pmr spectra were in agreement with the structure VIII, the pmr spectrum being identical with that previously reported.<sup>8,48</sup>

Reagent grade dimethyl sulfoxide solvent was redistilled and stored over activated Linde Type 4A Molecular Sieve. Tetramethylurea solvent was redistilled through a 1-m column packed with iron mesh, giving a constant boiling distillate (bp 178°). Spectroquality carbon tetrachloride solvent was dried with P<sub>2</sub>O<sub>5</sub>, shaken with anhydrous Na<sub>2</sub>CO<sub>3</sub>, passed through an alumina column and then stored over silica gel. Reagent grade benzene solvent was shaken with anhydrous Na<sub>2</sub>CO<sub>3</sub> and then stored over a mixture of alumina and silica gel. Spectroquality cyclohexane solvent was shaken with a mixture of Na<sub>2</sub>CO<sub>3</sub>, silica gel, and activated alumina and then stored over this mixture. Reagent grade chloroform solvent was used without further purification.

**Proton Magnetic Resonance Spectra.** All pmr spectra were taken with a Varian A-60 spectrometer at a probe temperature of 39° unless noted otherwise. Probe temperature was monitored by the peak separation of the two peaks of neat ethylene glycol. Pmr measurements were taken only after the sample had been in the probe for a minimum of 10 min and was at thermal equilibrium.

$J_{\text{HCOH}}$  values were measured with a 50-Hz sweep width, the average of a minimum of five sweeps in different directions being taken. To correct for minor day-to-day variations in the sweep width, the vicinal coupling constant of a standard sample of acetaldehyde was measured either immediately before or after the  $J_{\text{HCOH}}$  scans were made on the alcohol sample. The measured  $J_{\text{HCOH}}$  for the alcohol was then corrected to a standard value in direct proportion to an acetaldehyde coupling constant of 2.83 Hz.<sup>49</sup> Our  $J_{\text{HCOH}}$  values may thus be considered accurate within 1%.

In dimethyl sulfoxide, hydroxyl-carbinol coupling was readily observed for the various alcohols. In some of the neat alcohols the peaks of the hydroxyl proton multiplet were either only partially resolved, or a broadened singlet was obtained. The addition of a small amount of adsorption alumina to the sample tube or the passage of the alcohol through a small chromatographic column of alumina directly into the sample tube gave a well resolved OH proton multiplet from which  $J_{\text{HCOH}}$  could be accurately measured. Only in the case of neat methanol were we unable to obtain sufficient splitting of the OH proton multiplet to permit the measurement of  $J_{\text{HCOH}}$  at probe temperature (39°), in spite of numerous attempts with various techniques.

(49) (a) J. G. Powles and J. H. Strange, *Mol. Phys.*, **5**, 329 (1961); (b) see Powles and Strange, Table I, footnote b.

## Proton Nuclear Magnetic Resonance Analysis of the Stable, Classical 2-Phenyl-2-norbornyl and Related Cations

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**Abstract:** The 100-Mc nmr spectrum of the 2-phenyl-2-norbornyl cation has been analyzed with the aid of deuterium labeling, spin decoupling, and computer simulation. From a comparison with several related norbornyl and bicyclo[2.2.2]octyl systems it is concluded that the title cation is classical. Some dramatic examples of the low-field chemical shifts of bridgehead norbornyl hydrogens are described.

It has been suggested by some workers that tertiary 2-norbornyl cations (1), are classical, especially where R = Ph.<sup>1</sup> Because of our interest in the structural analysis of stable carbonium ions,<sup>2</sup> we undertook a

(1) H. C. Brown and K. Takeuchi, *J. Am. Chem. Soc.*, **90**, 2693 (1968), and earlier papers; P. von R. Schleyer, *ibid.*, **89**, 699, 701 (1967).

(2) (a) D. G. Farnum, *ibid.*, **89**, 2970 (1967); (b) D. G. Farnum and C. F. Wilcox, *ibid.*, **89**, 5379 (1967).

reanalysis of the nmr spectra of the 2-phenyl-2-norbornyl cation<sup>3</sup> (1, R = Ph) and several model compounds. It was our expectation that the results

(3) This cation has already been observed and its nmr spectrum determined by Schleyer.<sup>4</sup>

(4) P. von R. Schleyer, D. C. Kleinfelter, and H. G. Richey, Jr., *J. Am. Chem. Soc.*, **85**, 479 (1963); N. C. Deno, P. von R. Schleyer, and D. C. Kleinfelter, *Tetrahedron Letters*, No. 12, 414 (1961).

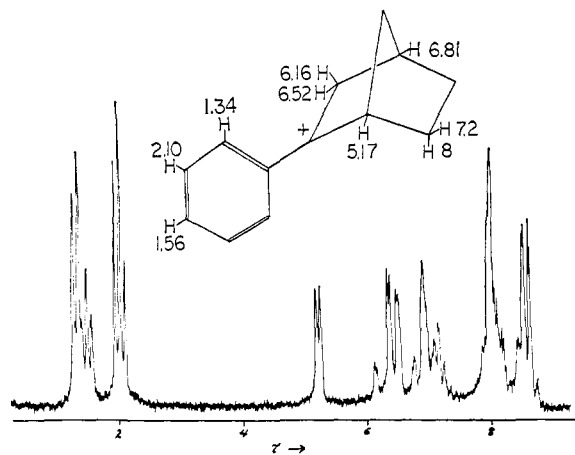


Figure 1. 100-Mc nmr spectrum and chemical shift assignments ( $\tau$  values) for the 2-phenyl-2-norbornyl cation in fluorosulfuric acid at room temperature.

would provide additional evidence on the classical or nonclassical character of the ground-state ion<sup>5</sup> as well as provide another well-studied model compound in the norbornyl cation series for future reference. This paper describes the results of this reanalysis, from which we conclude that the 2-phenyl-2-norbornyl cation (**1**, R = Ph) has no nonclassical leakage of positive charge to the C(1) position detectable by proton nmr.

## Results

The fact that 2-phenyl-2-norbornanol can be dissolved in some strong acids to give stable solutions of **1** (R = Ph) for nmr analysis has already been noted by Schleyer.<sup>4</sup> We find that nmr spectra of solutions made up at low temperature in fluorosulfuric acid are very well resolved (Figure 1). The assignments given in Figure 1 can be deduced by a combination of deuterium labeling, spin decoupling, and computer simulation. Thus, the aromatic protons were assigned by comparison with a computer simulated spectrum.<sup>2a</sup> The AB quartet at  $\tau$  6.16 and 6.52, assigned to the protons of the C(3) methylene group is not present in the 3,3-dideuterio cation prepared from 3,3-dideuterio-2-norbornanone.<sup>6</sup> These signals were also the first to disappear in deuteriosulfuric acid, although the dideuterio cation exchanges only slowly in fluorosulfuric acid. The nmr spectrum of the 6-*exo*-deuterio cation, prepared from 6-*exo*-deuterio-2-norbornanone,<sup>7</sup> was free from the small multiplet at  $\tau$  7.2, while that of the 6-*endo*-deuterio cation (prepared similarly from 6-*endo*-deuterio-2-norbornanone)<sup>7</sup> gave one less proton upon integration of the broad multiplet at  $\tau$  8.0. Similarly, the 7-*syn*-deuterio cation (0.7 atom of deuterium per molecule), prepared from 7-*syn*-deuterio-2-norbornanone,<sup>8</sup> gave approximately one less proton upon integration in the same region. The doublet signal at  $\tau$  5.17 clearly had its origin in the C(1) proton

(5) Previous conclusions have been based upon kinetic studies and are thus strictly applicable only to the presence or absence or nonclassical character in the transition state, not the ion.

(6) Cf. D. S. Weinberg and C. Djerassi, *J. Org. Chem.*, **31**, 115 (1966).

(7) A. Nickon, J. L. Lambert, R. O. Williams, and N. H. Werstiuk, *J. Am. Chem. Soc.*, **88**, 3354 (1966). We thank Professor Nickon for his generous provision of samples of the 6-deuterionorbornanes.

(8) Cf. K. Tori, K. Aono, Y. Hata, R. Muneyuki, T. Tsuji, and H. Tanida, *Tetrahedron Letters*, 9 (1966).

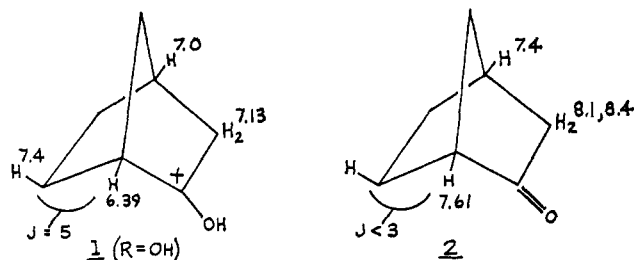


Figure 2. Chemical shift assignments ( $\tau$  values) for 2-norbornanone and its conjugate acid.

since it collapsed to a singlet in the 6-*exo*-deuterio cation or upon saturation of the  $\tau$  7.2 signal. The broad singlet at  $\tau$  6.81 must originate in the remaining bridgehead proton at C(4), since, if its origin were any other remaining proton in the system it would be a part of an AB quartet with a large coupling constant.<sup>9,10</sup> Finally, the highest field AB quartet at  $\tau$  8.6 must be assigned to the remaining methylene protons at C(5). All determined coupling constants in the system are normal with the exception of the C(1) proton-C(6) *exo*-proton value of 6.5 cps, which is much larger than normal.<sup>10</sup>

It was considered desirable to have several model compounds for comparison with cation **1** (R = Ph). Thus the spectra of 2-norbornanone (**2**) in Freon 114B and in fluorosulfuric acid were determined in order to examine systems with very similar geometry but different degrees of positive charge at C(2). A similar series of compounds was examined related to the bicyclo[2.2.2]octyl cation **3** (R = H) in order to have reference ions with similar geometry and charge, but less propensity toward the stereochemical retention, clean rearrangement, and large rate enhancements usually associated with nonclassical character in the norbornyl system.<sup>11,12</sup> The 1-phenylcyclohexyl and 1-phenylcyclopentyl cations were also examined since the parent cations have often been used as models for the norbornyl and bicyclo[2.2.2]octyl cations. The nmr chemical shifts of 2-norbornanone (**2**) and its conjugate acid (**1**, R = OH)<sup>13</sup> are summarized in Figure 2.

The spectrum of 2-norbornanone (**2**) has been determined and tentatively analyzed previously.<sup>14</sup> We have confirmed and extended that analysis by deuterium-labeling studies. An immediately striking feature of the nmr spectrum of ketone **2** is the appearance of two broad, one-proton signals at low field ( $\tau$  7.43, 7.61) instead of the three-proton signal one might expect for the three hydrogens  $\alpha$  to the carbonyl group. Corey<sup>14</sup> has suggested that these two low-field signals are due to the bridgehead hydrogens in accord with the known deshielding of bridgehead hydrogens in norbornane derivatives.<sup>15</sup> Our analysis not only confirms this

(9) Thus, for example, if it were the 7-*anti* proton, it would be coupled to the upfield 7-*syn* proton with a coupling constant near 8 cps.<sup>10</sup>

(10) P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1171 (1964).

(11) J. A. Berson and P. Reynolds-Warnhoff, *ibid.*, **86**, 595 (1964); J. A. Berson and D. Willner, *ibid.*, **86**, 609 (1964).

(12) D. Bethell and V. Gold, "Carbonium Ions," Academic Press, New York, N. Y., 1967, pp 279, 280.

(13) The conjugate acid is written in this way only to emphasize the increased positive charge compared with the ketone. We do not intend to imply that this is the more important resonance contributor.

(14) E. J. Corey, J. Casanova, Jr., P. A. Vatakencherry, and R. Winter, *J. Am. Chem. Soc.*, **85**, 169 (1963).

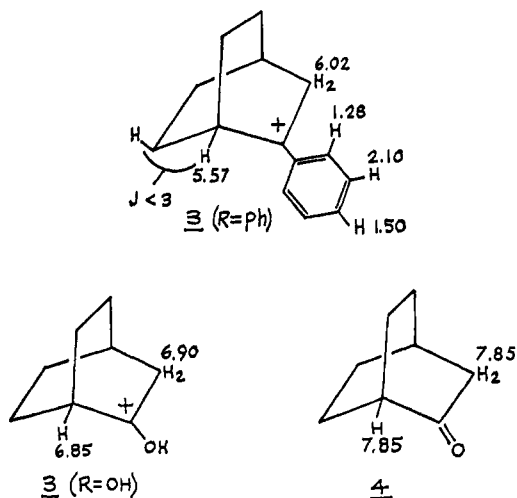


Figure 3. Chemical shift assignments ( $\tau$  values) for some [2.2.2] bicyclooctyl derivatives.

suggestion but leads to the surprising conclusion that the lower singlet arises from the C(4) proton further from the carbonyl group. Thus, the higher field signal, which appears as a doublet ( $J = 2$  cps) becomes a sharp singlet in the spectrum of 6-*exo*-deuterio-2-norbornanone,<sup>7</sup> identifying it as originating from the C(1) proton. The two proton multiplet centered at  $\tau$  8.24 disappears in the spectrum of 3,3-dideuterio-2-norbornanone.<sup>6</sup> The one-proton broad singlet signal at  $\tau$  7.43 can only be assigned to the remaining bridgehead proton, since any other proton in the system should give rise to a well-split doublet. The remainder of the spectrum was not sufficiently well resolved, even at 100 Mc, to make assignments.

The nmr spectrum of solutions of 2-norbornanone in fluorosulfuric acid was similarly analyzed to give the results indicated in Figure 2. Thus the lowest field doublet ( $\tau$  6.39,  $J = 5.5$  cps) was identified with the bridgehead hydrogen at C(1), since it appeared as a singlet in the 6-*exo*-deuterio cation (**1**, R = OH). The two proton multiplet signal at  $\tau$  7.13 was assigned to the methylene protons at C(3), since it disappeared in the 3,3-dideuterio cation. The broad multiplet centered at  $\tau$  7.4 disappeared in the 6-*exo*-deuterio cation, hence was clearly assignable to the 6-*exo* proton. Finally, the broad singlet signal at  $\tau$  7.0 was assignable to the bridgehead proton at C(4) by the same reasoning as above. The remainder of the spectrum was not analyzed.

Chemical shift values for the compounds in the bicyclo[2.2.2]octanone (**4**) series are indicated in Figure 3. The nmr spectrum of ketone **4** is quite simple, exhibiting only two peaks (width at half height *ca.* 5 cps) at  $\tau$  7.85 and 8.27 in area ratio 1:2. The lower field peak apparently is a composite signal due to the C(3) methylene and the two bridgehead protons and is halved in relative area in the 3,3-dideuterio compound. In fluorosulfuric acid, the spectrum is much more complicated, but a low-field three proton multiplet stands out at  $\tau$  6.9. The remainder of the spectrum is a nine-proton multiplet extending from  $\tau$  7.3 to 8.6. The low-field multiplet becomes a poorly resolved one-proton multiplet in the protonated 3,3-

(15) P. von R. Schleyer, private communication. See also ref 8.

dideuterio compound. This low-field multiplet is assigned to the proton at C(1) by analogy with 2-norbornanone.

Moderately stable solutions of the 2-phenylbicyclo[2.2.2]oct-2-yl cation (**3**, R = Ph) could be prepared by solution of 2-phenylbicyclo[2.2.2]octene in fluorosulfuric acid at low temperature. The chemical shifts of the spectra of such solutions. Again the phenyl proton assignments were made by comparison with computed spectra.<sup>2a</sup> A one proton broad singlet at  $\tau$  5.57 (width at half-height 9 cps) was assigned to the bridgehead proton at C(1) and a two proton broad singlet at  $\tau$  6.02 (width at half-height 8 cps) was assigned to the methylene protons at C(3) by analogy with cation **1** (R = Ph). The rest of the spectrum was a broad unanalyzed multiplet extending from  $\tau$  6.9 to 8.6.

The 1-phenylcyclopentyl and 1-phenylcyclohexyl cations were less stable than those examined thus far, but it was possible to obtain reasonable spectra at 0° or less on solutions of the cations dissolved in fluorosulfuric acid. The chemical shift assignments for these cations were straightforward and are given in Figure 4. The slightly different *para* proton resonances at  $\tau$  1.50 and 1.54 for the cyclohexyl and cyclopentyl cations, respectively, are of special interest to the subsequent discussion.

## Discussion

A cursory glance at the chemical shifts for the 2-phenyl-2-norbornyl cation (**1**, R = Ph) shown in Figure 1 reveals some unusual features that demand explanation. Thus, the 1.15-ppm average difference in chemical shift between the proton at C(1) ( $\tau$  5.17) and those at C(3) ( $\tau$  6.12, 6.52), all  $\alpha$  to the carbonium ion, is unusually large. Also, the coupling constant of 6.5 cps between H(1) and H(6) is unusually large. Both of these features are consistent with nonclassical leakage of charge to C(1) with resultant distortion of the geometry of the molecule. However, other factors, such as the anisotropy of the benzene ring and unusual hybridization at the bridgehead positions in norbornyl systems might also be involved. The subsequent discussion attempts to show, from the key information presented in Table I, that these other factors, whatever

Table I. Comparison of H(1)–H(3) Chemical Shift Differences in Some Norbornyl and Bicyclooctyl Systems

Compound	$\Delta\tau^a = \tau_{(H3)} - \tau_{(H1)}$		$\Delta\Delta\tau^a$
	Norbornyl	Bicyclooctyl	
Ketones <b>2</b> and <b>4</b>	0.64	0.00	0.64
<b>1</b> and <b>3</b> (R = OH)	0.74	0.05	0.69
<b>1</b> and <b>3</b> (R = Ph)	1.14	0.45	0.70

<sup>a</sup> For explanation see text.

their nature, are sufficient to account for the chemical shifts in **1** (R = Ph), and that there is not sufficient nonclassical leakage of charge to C(1) to influence the proton nmr chemical shifts.

Cation **1** (R = Ph) was chosen for examination in part because there would be no significant contribution of the isomeric 1-phenyl-2-norbornyl cation (**5**) to a potential classical equilibrium. Thus, Brown has

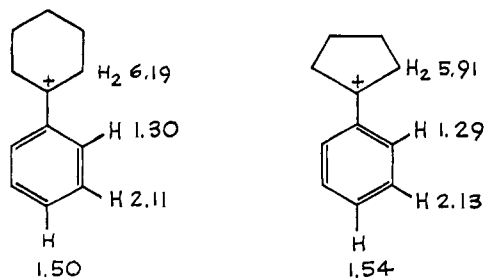


Figure 4. Chemical shift assignments ( $\tau$  values) for 1-phenylcyclohexyl and 1-phenylcyclopentyl cations.

shown<sup>16</sup> that the solvolysis of 2-phenyl-2-*exo*-norbornyl chloride is  $10^7$  times faster than that of 1-phenyl-2-*exo*-norbornyl chloride, suggesting an energy difference near 10 kcal in the transition states. Although other

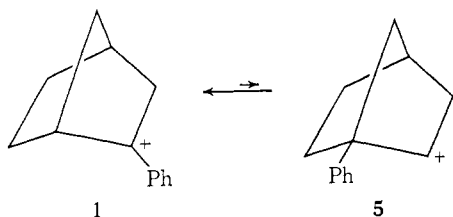


Figure 5. Plot of the *para* proton chemical shift ( $\tau_{para}$ ) vs. the log of the delocalization energy ( $\log DE$ ) for a number of carbonium ions: (a) phenyldimethylcarbonium ion, (b) diphenylcarbonium ion, (c) triphenylcarbonium ion, (d) diphenylcyclopropenium ion, (e) triphenylcyclopropenium ion. The values for  $DE$  are taken from the  $\Delta M$  values given in A. Streitwieser, "Molecular Orbital Theory for Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961, p 365, or calculated from the values given by S. L. Manatt and J. D. Roberts, *J. Org. Chem.*, **24**, 1336 (1965). They represent the difference between the delocalization energies of the cation and the covalent hydrocarbon from which it is derived.

factors, such as ground-state energy differences, may account for a part of this gap, it still seems likely that electron delocalization onto the phenyl group must account for some 5 kcal.<sup>17</sup> This represents a minimum energy difference between the idealized classical cations, since electron delocalization onto the phenyl group in **1** ( $R = Ph$ ) with a fully developed vacant orbital would be greater than that in the transition state for its formation. We therefore conclude that, if ion **1** ( $R = Ph$ ) is classical, its nmr spectrum will be that of the 2-phenyl-2-norbornyl cation.

In an earlier paper<sup>2a</sup> we established the intuitively reasonable qualitative principle that the *para* proton resonance provides a measure of the extent of dispersion of positive charge onto the phenyl group of a phenylcarbonium ion. Thus, any other factor tending to stabilize the positive charge will result in less charge on the phenyl and an upfield shift of the *para* proton resonance. If cation **1** ( $R = Ph$ ) were nonclassical, we would expect the *para* proton resonance to be upfield relative to some "suitable model." From the data presented in Figures 1, 3, and 4, this does not seem to be the case, at least, within the limits of reliability of the technique. The 1-phenylcyclohexyl and 2-phenyl-2-bicyclo[2.2.2]octyl cations show the same *para* proton chemical shifts ( $\tau$  1.50), as expected, while the difference between 1-phenylcyclopentyl ( $\tau$  1.54) and **1** ( $R = Ph$ ) ( $\tau$  1.56) is just outside the limits of error of measurement. Although it is not entirely clear whether either cyclopentyl or cyclohexyl cation is a suitable model for **1** in solvolysis reactions, it seems likely that cyclopentyl cation will approach **1** in ground-state stability much more closely than will cyclohexyl cation.

In an empirical attempt to give some quantitative meaning to these measurements, we have plotted the

(16) H. C. Brown, F. J. Chloupek, and M. Rei, *J. Am. Chem. Soc.*, **86**, 1248 (1964).

(17) Brown<sup>16</sup> concludes that ground-state energy differences are not "a major factor in the observed *exo-endo* rate ratio."

log of the delocalization energies ( $\log DE$ ) for a number of phenylcarbonium ions against the *para* proton chemical shifts in Figure 5. The linearity of the plot probably has no special significance, since at infinite delocalization energy (*i.e.*, complete dispersion of the charge), the *para* proton resonance should asymptotically approach the value for benzene, while at zero delocalization energy ( $\log DE = -\infty$ ) the *para* proton resonance should approach some finite lower limit. Thus, the straight line is just the central segment of a flattened S-shaped curve. However, the plot does serve to indicate the relative insensitivity of the *para* proton resonance to the stabilization energy of the carbonium ion. All of the points in Figure 5 lie within 0.02 ppm of the line. Thus, for these several phenylcarbonium ions, we can guess that a change of 0.02 ppm in the *para* proton resonance is just significant. For the less stable carbonium ions, such as benzyl, at the left of the plot, a change in  $\pi$  delocalization energy of  $0.035\beta$  or perhaps 1 kcal is necessary to cause this chemical shift. For the more stable, such as triphenylcyclopropenium ion, at the right side of the plot, a change of  $0.15\beta$  or perhaps 4 kcal is necessary. We thus conclude that, barring other indeterminable factors causing chemical shift changes of 0.02 ppm, a difference in stability of one to several kilocalories in carbonium ions is barely detectable by this method. This energy requirement is too large to detect the subtle differences expected for partial nonclassical stabilization. Furthermore, Taft has found that <sup>19</sup>F chemical shifts are orders of magnitude more sensitive to the same kind of effect.<sup>18</sup> We will therefore defer judgment on the significance of the 0.04 ppm difference between the *para* proton resonances of 1-phenylcyclohexyl and 1-phenylcyclopentyl cations until the <sup>19</sup>F spectra of the *para* fluorophenyl analogs have been determined.

We now ask whether the abnormally low-field chemical shift ( $\tau$  5.17) of the C(1) proton in **1** ( $R = Ph$ ) reflects *nonclassical* leakage of charge to C(1) or arises

(18) R. W. Taft, E. Prince, J. R. Fox, P. C. Louis, K. K. Anderson, and G. T. Davis, *J. Am. Chem. Soc.*, **85**, 3146 (1963).

from some other factor characteristic of the *classical* norbornyl cation. The data presented in Table I allow a choice between these alternatives. The values  $\Delta\tau$  in Table I are the differences between the C(1) and C(3)  $\alpha$  proton chemical shifts in the several norbornyl and bicyclo[2.2.2]octyl systems. These are the key numbers requiring explanation either in terms of nonclassical or classical factors. The values  $\Delta\Delta\tau$  are the differences in  $\Delta\tau$  for the corresponding norbornyl and bicyclooctyl systems. Thus the C(1) and C(3)  $\alpha$  protons in bicyclooctanone both come at  $\tau$  7.85, therefore  $\Delta\tau$  is 0. The O(1) and C(3) protons in 2-norbornanone appear at 7.61 and 8.25, therefore  $\Delta\tau$  is 0.64. The separation in 2-norbornanone, then is 0.64 ppm greater than that in bicyclooctanone, yielding  $\Delta\Delta\tau = 0.64$ . There are three cases to be considered: (1) all of the separation,  $\Delta\tau$ , is the result of nonclassical leakage of charge to C(1), (2) part of  $\Delta\tau$  is the result of nonclassical leakage of charge to C(1), and (3) none of  $\Delta\tau$  is the result of nonclassical leakage of charge to C(1).

Case 1 can be rejected since, if we choose bicyclo[2.2.2]octanone as our classical model with  $\Delta\tau = 0$ , then 2-norbornanone,  $\Delta\tau = 0.64$ , must have significant nonclassical leakage of charge to C(1), indeed one-half as much as cation **1** ( $R = Ph$ ). This conclusion is inconsistent with the known properties of 2-norbornanone. If we assume the absence of nonclassical leakage of charge to C(1) in both ketones, then we come to case 2. Norbornanone,  $\Delta\tau = 0.64$  is taken as the classical model for the cations, and the increase in  $\Delta\tau$  for the protonated ketone (0.1 ppm) and the cation **1** ( $R = Ph$ ) (0.51 ppm) is taken to represent the nonclassical leakage of charge to C(1) as a result of increased electron demand at C(2). However, since the same effect is quantitatively reproduced in the bicyclooctyl series, *i.e.*,  $\Delta\Delta\tau$  remains essentially constant, we must then conclude that there is the same extent of leakage of positive charge to C(1) in the bicyclo[2.2.2]octyl cations as in the norbornyl cations. Since the available evidence has generally been interpreted to indicate less nonclassical participation in bicyclo[2.2.2]octyl systems than in norbornyl systems,<sup>11,12</sup> we reject this case as well.

We are left, then, with none of the systems exhibiting nonclassical leakage of charge to C(1), provided that we accept the two reasonable, though not rigorous assumptions that 2-norbornanone has no nonclassical leakage of charge to C(1), and the bicyclo[2.2.2]octyl cations, if nonclassical at all, would have less leakage of charge to C(1) than the corresponding 2-norbornyl cations. The unusual chemical shifts of the C(1) protons in the norbornyl series must then find their explanation in some other factor, as must the unusually large coupling constants.

One factor which could affect the chemical shift difference between the C(1) and C(3) protons is the anisotropy of the phenyl group. This can be approximated by determining the coordinates of these protons with respect to the center of the benzene ring from models, and obtaining chemical shift values from the Johnson-Bovey tables<sup>19</sup> or a modification of them.<sup>2b</sup> For a planar cation **1** ( $R = Ph$ ), H(1) experiences a downfield shift of about 0.5 ppm, while H(3) *exo* and *endo* each experience a downfield shift of about 0.3 ppm

(19) C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

yielding  $\Delta\tau = 0.2$  ppm. For a planar cation **3** ( $R = Ph$ ), the downfield shift of H(1) is 0.6 ppm, while that of H(3) is 0.3 ppm yielding  $\Delta\tau = 0.3$  ppm. For nonplanar cations, the numbers are different, but invariably smaller. Thus the differences, though significant, do not account for all of the downfield shift at C(1). Nor do they account for the consistent difference,  $\Delta\Delta\tau$ , between the norbornyl and bicyclooctyl systems.

The search for an explanation inevitably settles on some special characteristic of the bridgehead C-H bond in the strained norbornyl system as evidenced by the low-field chemical shift of the C(4) proton of norbornanone ( $\tau$  7.4). Perhaps excess s character and abnormal polarizability in the bridgehead bonding orbital is responsible. The H(1), H(6) *exo*-coupling constant of 6.5 cps, larger than the 4 cps or less usually observed,<sup>20</sup> may find a similar explanation. Although the effect of the positive charge on coupling constants in this system cannot be predicted with certainty, Olah has found coupling constants in carbonium ions<sup>21</sup> to be within 50% of their normal values. Therefore it seems likely that some special effect is operating in the norbornyl system.

## Experimental Section

The proton nmr spectra were determined at 60 and 100 Mc on a Jeol C-60H or a Varian HA-100 instrument. Chemical shifts are reported relative to tetramethylammonium fluoroborate ( $\tau$  6.87) used as an internal standard.<sup>2a</sup> Carbonium ion solutions (7–10% concentration) were made by rapid dispersion of a Freon 114-B solution of the carbinol or olefin into vigorously stirred  $FSO_3H$  solution at  $-60^\circ$  under an  $N_2$  blanket. The acid layer was drawn off for use. In all cases 40–60% recovery of the starting carbinol or olefin was realized on quenching the carbonium ion in ice cold base.

1-Phenylcyclopentanol, 1-phenylcyclohexanol, 6-*exo*- and *endo*-deuterionorbornan-2-ones,<sup>7</sup> 2-phenylnorbornanol,<sup>22</sup> bicyclo[2.2.2]octan-2-one,<sup>23</sup> and 2-phenylbicyclo[2.2.2]oct-2-ene<sup>24</sup> were prepared according to reported procedures, purified by distillation or crystallization, and characterized by ir and nmr prior to use.

6-*exo*- and *endo*-deuterio-2-phenylnorbornan-2-ols, 3,3'-dideuterio-2-phenylnorbornan-2-ols, and 3,3'-dideuterio-2-phenylbicyclo[2.2.2]octan-2-ol were prepared by the addition of phenylmagnesium bromide to the corresponding ketones. They were also purified and characterized as above.

**3,3'-Dideuterionorbornan-2-one.**<sup>6</sup> Norbornan-2-one (2.2 g, 0.02 mol), trifluorodeuterioacetic acid (2.3 g, 0.2 mol), and  $D_2O$  (18 ml, 1 mol) were heated in a sealed tube for 4 days at  $140^\circ$ . The reaction mixture was neutralized with sodium carbonate, extracted with pentane (two 30-ml portions), washed with  $D_2O$  (two 10-ml portions), and dried over anhydrous  $Na_2SO_4$ . Removal of solvent and sublimation furnished 3,3-dideuterionorbornan-2-one (1.86 g), mp  $93-95^\circ$ . A mass spectrum indicated the incorporation of 95%  $d_2$  and 5%  $d_1$ . The difficulty encountered by Thomas and Willhalm<sup>25</sup> in the dideuteration of norcamphor was thus eliminated.

**3,3-Dideuteriobicyclo[2.2.2]octan-2-one.** Bicyclo[2.2.2]octan-2-one (1.25 g, 0.01 mol), trifluorodeuterioacetic acid (1.15 g, 0.1 mol), and  $D_2O$  (9 ml, 0.5 mol) were mixed and heated at  $150^\circ$  in a sealed tube for 48 hr. The reaction mixture was neutralized with sodium carbonate and extracted with pentane (two 20-ml portions), washed with  $D_2O$  (two 10-ml portions), dried over anhydrous  $Na_2SO_4$ , and freed of solvent. The solid residue was sublimed at  $25^\circ$  to furnish 3,3-dideuteriobicyclo[2.2.2]octan-2-one (1.01 g), mp  $91-92^\circ$ . Mass spectral analysis showed 86%  $d_2$  and 14%  $d_1$  incorporation.

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**7-syn-Deuterionorbornan-2-one.**<sup>8</sup> Norbornene (2 g) was heated with D<sub>2</sub>SO<sub>4</sub> (9 ml) and D<sub>2</sub>O (1 ml) at 80° for 4 hr. Dilution with D<sub>2</sub>O (25 ml) and extraction with pentane (two 20-ml portions) gave a mixture of 7-syn-deuterionorbornan-2-ol and 3-deuterionorbornanol (1.91 g). This material was oxidized with Jones<sup>26</sup> reagent to furnish a mixture of 7-syn-deuterionorbornan-2-one and 3-deuterionorbornanone (1.01 g), mp 89–91°. Repeated washings with 10% potassium hydroxide removed the label from the enolizable position of norbornan-2-one. The resulting 7-syn-deuterio-

norbornan-2-one was sublimed, mp 94–95°, to furnish material containing 70% d<sub>1</sub> as determined by mass spectral analysis.

**7-syn-Deuterio-2-phenylnorbornan-2-ol.** 7-syn-Deuterionorbornan-2-one (0.01 mol) was treated with a small excess of phenylmagnesium bromide (0.015 mol) to furnish 7-syn-deuterio-2-phenylnorbornan-2-ol in 91% yield, mp 43–44°.

**Acknowledgment.** The authors are grateful to Professor Paul von R. Schleyer for helpful criticisms during early vacillating stages of the work. We also thank the National Science Foundation for support of this research under Grants GP 6378 and 8192.

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## Chemistry in Super Acids. III.<sup>1a</sup> Protonation of Alkanes and the Intermediacy of Alkanonium Ions, Pentacoordinated Carbon Cations of the CH<sub>5</sub><sup>+</sup> Type. Hydrogen Exchange, Protolytic Cleavage, Hydrogen Abstraction, and Polycondensation of Methane, Ethane, 2,2-Dimethylpropane (Neopentane), and 2,2,3,3-Tetramethylbutane in FSO<sub>3</sub>H–SbF<sub>5</sub> (“Magic Acid”) Solution<sup>1b</sup>

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**Abstract:** Alkanes undergo hydrogen exchange, protolytic cleavage, and hydrogen abstraction followed by polycondensation in the super acid system, FSO<sub>3</sub>H–SbF<sub>5</sub>. Methane and ethane undergo both hydrogen exchange and polycondensation to produce *t*-butyl cation, *t*-hexyl cations, or higher analogous tertiary alkylcarbonium ions. Neopentane undergoes hydrogen exchange, protolytic fragmentation to trimethylcarbonium ion and methane, and hydrogen abstraction followed by fast rearrangement of the *t*-amyl cation. 2,2,3,3-Tetramethylbutane cleaves to produce the trimethylcarbonium ion. Structures of the intermediate protonated alkane ions (alkanonium ions, of the CH<sub>5</sub><sup>+</sup> type) formed in these reactions were calculated using an all-valence-electron SCF method.

In previous studies we reported that the extremely strong acid FSO<sub>3</sub>H–SbF<sub>5</sub> is capable of forming stable alkylcarbonium ions from alkanes *via* protonation followed by hydrogen abstraction.<sup>3</sup> It was found that even neopentane is sufficiently basic to undergo reaction in “magic acid.” At room temperature neopentane reacted in neat acid solution to yield the trimethylcarbonium ion (*t*-butyl cation) and methane. When treated with FSO<sub>3</sub>H–SbF<sub>5</sub> diluted with SO<sub>2</sub>ClF, the dimethylethylcarbonium ion (*t*-amyl cation) was formed through rapid rearrangement of the intermediate neopentyl cation. Hogeveen and Bickel made similar observations on the protolytic cleavage and hydrogen exchange of neopentane in the related acid system HF–SbF<sub>5</sub>.<sup>4</sup> Although the surprising solubility of methane in sulfuric acid solution was observed 70 years ago,<sup>5</sup>

this observation has since lain dormant. Having observed the solubility of methane in super acid solution, like FSO<sub>3</sub>H–SbF<sub>5</sub>, we started a systematic investigation of methane and related hydrocarbons in strong acid solution. In a preliminary communication we reported that methane undergoes protonation followed by hydrogen abstraction in “magic acid” solution to yield tertiary alkylcarbonium ions. We now wish to report in full our studies relating to the behavior of methane, ethane, neopentane, and 2,2,3,3-tetramethylbutane in the super acid solutions.

### Results

Methane (≥99.5%) when treated either at 150° in an autoclave with tenfold excess of 1:1 FSO<sub>3</sub>H–SbF<sub>5</sub> solution or at 140° under atmospheric pressure, gave primarily the stable trimethylcarbonium ion and insoluble (in SO<sub>2</sub>) polymeric products. In an autoclave at a reaction temperature kept at or below 80°, a mixture of trimethylcarbonium with some *t*-hexyl and *t*-heptyl cations and higher homologous tertiary carbonium ions was formed along with insoluble polymer. Hydrogen gas is liberated in these reactions, but as reported previously,<sup>3</sup> it at least partially reduces the acid. Thus,

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