Stable Carbonium Ions. C.[1a]
The Structure of the Norbornyl Cation[1b]

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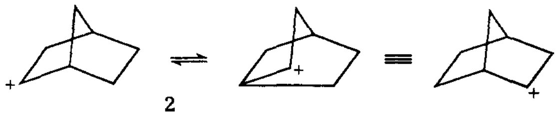
Abstract: The structure of the stable, long-lived 2-norbornyl cation as well as those of the related 2-methyl-, 2-ethyl-, and 2-phenylnorbornylcations were studied in SbF_5-SO_2 (SO_2ClF, SO_2F_2) and FSO_3H-SbF_5-SO_2 (SO_2ClF) solution by ^1H and ^{13}C nmr and laser Raman spectroscopy. The "frozen out" 2-norbornyl cation displays, at −154° in SbF_5–SO_2ClF–SO_2F_2, ^1H and ^{13}C nmr spectra compatible only with a nonclassical structure. The norbornyl cation was found to be identical with corner-protonated nortricyclene and was thus shown to contain a pentacoordinated bridging carbon atom involved in three-center bond formation. The Raman spectrum of the norbornyl cation also indicates nortricyclene and not norbornane-type skeletal symmetry. Quenching in tertiary base at −78° yields nearly exclusively nortricyclene. The rate of the 3,2- and 6,1,2-hydrogen shifts and the corresponding activation parameters were measured by nmr temperature-dependence studies of the ions and are discussed. The tertiary 2-methyl- and 2-ethylnorbornyl cations show, based on the Raman spectra and the ^1H and ^{13}C nmr studies, structural correlations indicative of partial 6,2-σ delocalization without, however, a nortricyclene-type skeleton. Very little or no σ delocalization is found in the basically classical 2-phenylnorbornyl cations. For comparison with ^{13}C nmr spectra obtained for the norbornyl cation, we also studied the ^{13}C nmr spectra of the nonclassical 7-norbornenyl and 7-norbornadienyl cations. The close relationship of the bridging pentacoordinated carbon in these ions with that in the 2-norbornyl cation is evident. It is concluded that these studies give a definitive answer to the controversial question of the nature of the long-lived norbornyl cation showing without doubt that it is the σ-delocalized, nonclassical ion.

A considerable effort has been directed in the past two decades toward the elucidation of the structure of the 2-norbornyl and related cations.[3] In 1949 Winstein suggested the symmetrically bridged, nonclassical structure which is generally depicted as structure **1**.[3a] (We, however, prefer to leave out the third dashed line in representations of the nonclassical 2-norbornyl cation, as in **1b**, for reasons given in the subsequent discussion.) Winstein, Roberts, and numerous subsequent investigators have presented evidence supporting this conception. On the other hand, Brown[3b] advanced the view that the ion is a classical, secondary carbonium ion which achieves pseudosymmetry *via* fast Wagner–Meerwein 1,2-alkyl rearrangements as depicted in **2**.


1a


1b


2

Kinetic data for solvolysis reactions give only information about the transition state preceding ion formation and subsequent solvent capture. While the transition state should reflect the structure of the ion intermediate such extrapolation has inevitably lent itself to varied interpretation.

The possibility of observing the norbornyl cation as a stable, long-lived species in solution[4] presented a unique and challenging opportunity for clarification of the nature of this most controversial ion. Elucidation of the structure of the stable ion was complicated by the fact that the distinction between the alternative formulations of the ion is a subtle one and therefore sensitive probes were needed to resolve the problem. Our first approach with Schleyer and Saunders using proton nuclear magnetic resonance spectroscopy[4a,b] failed to distinguish between the two limiting structural possibilities since, due to the relatively long time scale of the experiment, it could be argued that a rapid Wagner–Meerwein rearrangement (as in **2**) in the classical ion would give a spectrum indistinguishable from that of the nonclassical ion. Further, in these early experiments it was found that rapid equilibration of the 6, 1, and 2 protons renders them equivalent on the nmr time scale (at least down to −120°) leading to a pmr spectrum with only three absorptions being observed. Two further approaches were therefore subsequently tried to resolve this problem: the use of vibrational spectroscopy[5] to overcome the time-scale limitation and the application of ^{13}C nmr spectroscopy.[6]

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[1] (a) Part IC: G. A. Olah, R. H. Schlosberg, D. P. Kelly, and G. D. Mateescu, *J. Amer. Chem. Soc.*, **92**, 2546 (1970); (b) for a preliminary communication see G. A. Olah, *et al.*, *ibid.*, **91**, 3882, 3954, 3956, 3958, 6883 (1969); see also (c) P. von R. Schleyer, W. E. Watts, R. C. Fort, Jr., M. B. Comisarow, and G. A. Olah, *ibid.*, **86**, 5679 (1964); (d) M. Saunders, P. von R. Schleyer, and G. A. Olah, *ibid.*, **86**, 5680 (1964); (e) presented in part at the 21st National Organic Chemistry Symposium of the American Chemical Society, Salt Lake City, Utah, June 1969.

[2] (a) Postdoctoral Research Associate; (b) Nato Postdoctoral Fellow from the University of Montpellier, France, 1968.

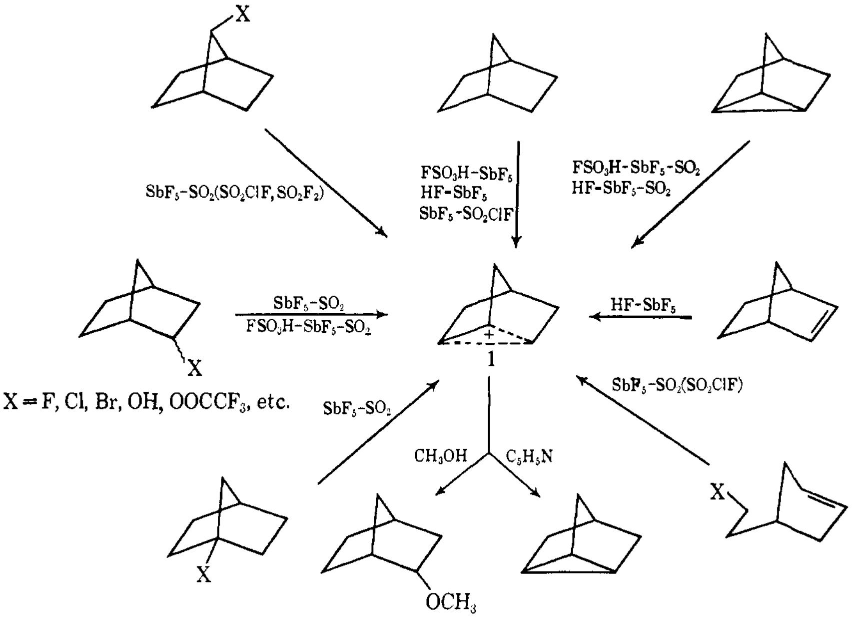
[3] (a) S. Winstein and D. S. Trifan, *J. Amer. Chem. Soc.*, **71**, 2935 (1949). For reviews and leading references see, P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, New York, N. Y., 1965; G. D. Sargent, *Quart. Rev. Chem. Soc.*, **20**, 299 (1966); G. E. Gream, *Rev. Pure Appl. Chem.*, **16**, 25 (1966); M. J. S. Dewar and A. P. Marchand, *Annu. Rev. Phys. Chem.*, **16**, 321 (1965); B. Capon in "Organic Reaction Mechanisms, 1967," B. Capon, M. J. Perkins, and C. W. Rees, Ed., Wiley-Interscience, New York, N. Y., 1968; (b) for a summary and references see H. C. Brown, *Chem. Brit.*, 199 (1966); *Chem. Eng. News*, **45**, 87 (Feb 13, 1967).

[4] (a) See ref 1c; (b) see ref 1d; (c) F. R. Jensen and B. H. Beck, *Tetrahedron Lett.*, 4287 (1966).

[5] G. A. Olah, A. Commeyras, and C. Y. Lui, *J. Amer. Chem. Soc.*, **90**, 3882 (1968).

The latter method, in spite of its having almost the same time-scale limitations as proton nmr spectroscopy, has been demonstrated to be well suited to differentiate between rapidly equilibrating or bridged ions by virtue of the sensitivity of the carbon chemical shifts to the charge distribution in carbonium ions.[6c]

In this paper we present in full the results of our studies including all three approaches which when taken *in toto* show that the stable, long-lived 2-norbornyl cation has the nonclassical structure **1**. Our studies further give detailed information on the stability of the ion and on the rates and mechanisms of the intramolecular rearrangements which the ion has been found to undergo. In addition we report the results of concurrent studies on norbornyl ions substituted in the 2 position where we have found it possible to observe carbonium ions with a degree of σ participation. We have also studied the 7-norbornenyl and 7-norbornadienyl cations with particular reference to the comparison of the bridging, pentacoordinated carbon atoms in these ions to that in the 2-norbornyl cation.

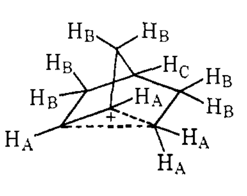


Results

A. The Norbornyl Cation. (1) Preparation and Quenching. The norbornyl cation can be generated in solution from a variety of precursors.[4] The ion has been prepared from *exo*- or *endo*-2-norbornyl halides (F, Cl, and Br) and 1-chloro- and 7-chloronorbornane in SbF_5, SbF_5–SO_2, SbF_5–SO_2ClF, and SbF_5–SO_2ClF–SO_2F_2 solution, from *exo*-2-norborneol in FSO_3H–SbF_5 (SO_2, SO_2ClF) and in SbF_5–SO_2 (SO_2ClF), from norbornane, norbornylene, or nortricyclene in FSO_3H–SbF_5 or HF–SbF_5 (SO_2, SO_2ClF), from norbornane in SbF_5–SO_2ClF, from β-(cyclopentenyl)ethyl halides in SbF_5–SO_2, SbF_5–ClF (SO_2F_2) solution. Jensen and Beck[4c] have also prepared the ion from *exo*-2-norbornyl chloride in $GaBr_3$–SO_2. In our hands, the method of choice (giving the highest resolution nmr spectra) was preparation from *exo*-2-norbornyl chloride in SbF_5–SO_2 solution at −78°, as described in the Experimental Section.

The product obtained on quenching solutions (in FSO_3H–SbF_5–SO_2) of the ion depends on the nucleophile and on the efficiency of neutralization of the acid solution.[5] With $MeOH$–$NaHCO_3$ or $Na^+{}^-OCH_3$–$MeOH$, a mixture of nortricyclene and *exo*-2-norbornyl methyl ether is obtained (with some norbornylene as by-product). The proportions of each vary according to the procedure used. Quenching solutions with pyridine on the other hand gave nortricyclene as the only identifiable product, 80% yield overall (from vpc analysis). When the acid solution of the ion is quenched with methanol with no methoxide base present, the product is *exo*-2-norbornyl methyl ether (with some norbornylene) with no detectable amount of nortricyclene formed.

2. ^{1}H Nuclear Magnetic Resonance Study. At −80° solutions of the norbornyl cation in SbF_5–SO_2 give the spectrum shown in Figure 1 with peaks at δ 1.86 (sextet, area 6), 2.82 (broadened pentuplet, area 1), and 5.01 (broadened septuplet, area 4).[7] Proton–proton decoupling was used to obtain the coupling constants. Irradiation of the low-field, 4-proton multiplet caused the peak at δ 2.82 to sharpen, the coupling constant between the protons responsible for these peaks being 0.4 Hz (see inset to Figure 1). At the same time the high-field peak collapsed from a sextet to a doublet with a coupling constant of 1.6 Hz (Figure 2B). Finally irradiation of the 1-proton multiplet caused the high-field peak to collapse to a pentuplet (Figure 2C) with a coupling of 1.4 Hz. The assignments of these protons are shown with the equivalence of the protons indicated being the result of a rapid, degenerate 6,1,2-hydride shift.



$\delta_{H_A} = 5.01$ ppm
$\delta_{H_B} = 1.86$ ppm
$\delta_{H_C} = 2.82$ ppm
$J_{H_AH_B} = 1.4$ Hz
$J_{H_BH_C} = 1.6$ Hz
$J_{H_AH_C} = 0.4$ Hz

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(6) (a) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3954 (1969); (b) *ibid.*, **91**, 3956 (1969); (c) *ibid.*, **91**, 5801 (1969).

(7) The fine structure in the spectrum was first reported by Jensen and Beck (ref 4c) in $GaBr_3$–SO_2 solution. We have obtained well-resolved spectra in SbF_5–SO_2 solution. This fine structure cannot be observed above −70° (at 100 MHz) due to incursion of the 3,2-hydride shift.

Figure 1. Proton spectrum (100 MHz) of the norbornyl cation in SbF$_5$–SO$_2$ solution at −80°. The insert shows the effect of irradiating the low-field septuplet on the one-proton peak at δ 2.82. A is the spectrum without irradiation and B is with irradiation.

Preparation of the ion in FSO$_3$D–SbF$_5$–SO$_2$ solution from nortricyclene shows only one deterium incorporated,[5] resulting in the area of the low-field peak being reduced from relative area 4 to 3. No further inter- or intramolecular scrambling of the deuterium is observed at −80° (at least initially as monitored for 1 hr after sample preparation).

In the temperature range −50 to +20° (studied at 60 MHz) collapse of the nmr spectrum is observed leading to a single peak at δ 3.10. This reversible collapse is attributable to the 3,2-hydride shift (*vide infra*) and using a multisite shape analysis[4b] the rates shown in Table I were calculated. The activation energy, from the usual Arrhenius plot, is E_a = 10.8 ± 0.6 kcal/mol^{-1}, the preexponential factor being $A = 10^{12.3}$ sec^{-1}. (It should be mentioned that at higher temperature irreversible opening of the bicycloheptyl skeleton takes place in acid solution giving 1-methylcyclohexyl cation and also dimethylcyclopentyl cations.)

Table I. Calculated Rates of the 3,2- and 6,1,2-Hydride Shifts in the 2-Norbornyl Cation

3,2-Hydride shift		6,1,2-Hydride shift	
Temp, °C	k, sec^{-1}	Temp, °C	k, sec^{-1}
+12.9	10,000	−125.0	10,000
+7.0	6,000	−128.5	5,000
+3.8	5,500	−131.5	3,300
−2.0	2,900	−133.8	2,500
−6.5	2,600	−135.8	1,700
−11.2	1,550	−137.5	1,250
−16.2	1,200	−138.5	1,000
−19.3	850	−141.0	670
−25.5	525	−143.8	500
−29.0	375	−145.0	400
−30.2	325	−146.0	330
−33.5	225	−147.8	250
−35.9	175	−150.0	125
−38.2	150	−152.0	100
−44.5	75		
−46.0	72		

Other changes are observed in the temperature range −130 to −154°, spectra being obtained at 100 MHz in an SbF$_5$–SO$_2$ClF–SO$_2$F$_2$ solution[6b] as described in the Experimental Section. At −154° the low-field four-proton resonance is completely separated into two peaks (each with a relative area of two) at δ 3.05 and 6.59 (Figure 3). The high-field resonance also broadens, developing a shoulder at δ 1.70. The single proton resonance at δ 2.82 remains unchanged and since TMS cannot be used as a reference at these temperatures this peak was used as an internal standard for shift calibration. A line shape analysis (Figure 4) of the low-field proton resonance gave rates for the exchange process (attributable to the 6,1,2-hydride shift) as shown in Table I and from an Arrhenius plot an activation energy of 5.9 ± 0.2 kcal/mol was obtained with $A = 10^{12.7}$ sec^{-1}.

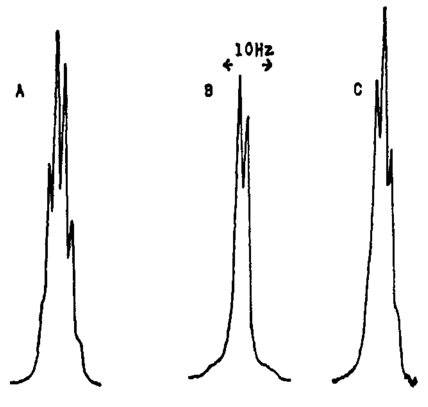


Figure 2. A shows the δ 1.86 six-proton multiplet recorded under the same conditions as in Figure 1. Irradiation of the low field from proton multiplet causes collapse to a doublet (B) while irradiation of the one-proton multiplet causes collapse to a pentuplet (C).

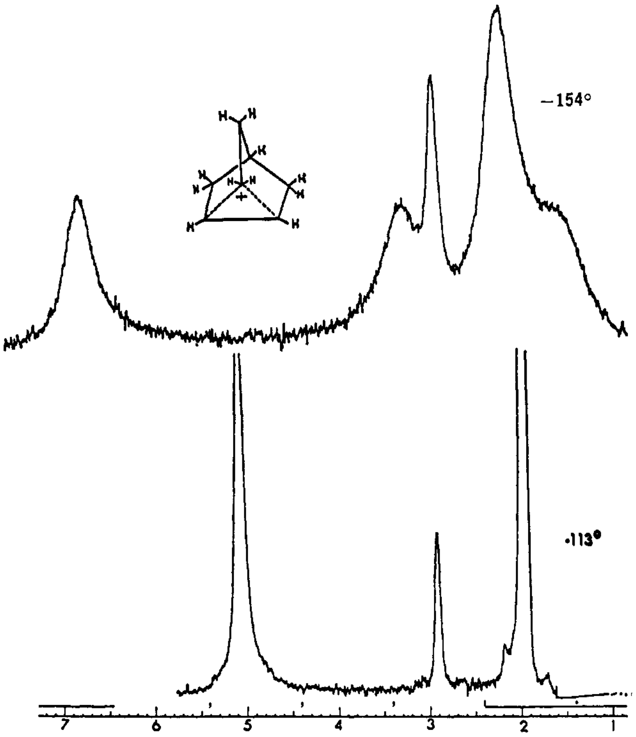


Figure 3. Proton nmr spectra (100 MHz) of the "norbornyl cation" in SbF$_5$–SO$_2$ClF–SO$_2$F$_2$ solution at temperatures between −113 and −154°.

3. Carbon-13 Nuclear Magnetic Resonance Spectroscopic Study. The ^{13}C nmr spectrum of the ion (in SbF$_5$–SO$_2$ solution at −70°) was obtained in natural

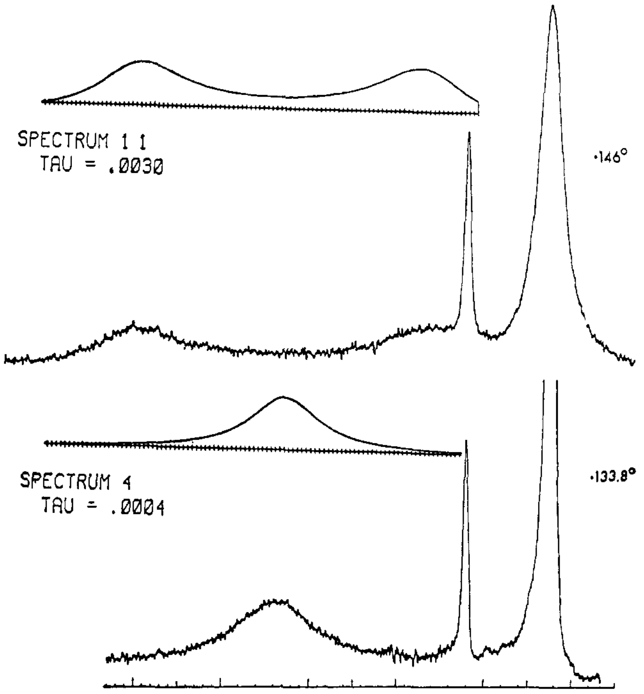
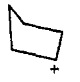
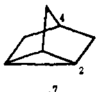
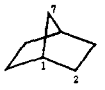
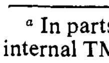


Figure 4. Computer-simulated and experimental spectra of the "norbornyl cation" for two temperatures before and after coalescence. The values of τ indicated refer to the mean lifetime in seconds.

abundance by the indor method.[6a] This technique involves observation of the ^{13}C satellites in the proton spectrum of the ion at 100 MHz and locating connected ^{13}C transitions by irradiation at 25.1 MHz and thus has the great advantage of giving directly the relationship of the carbons to the protons in the molecule being studied. The low-field proton resonance satellites give a ^{13}C indor spectrum (Figure 5) comprised of a 53 Hz pentuplet at +101.8 ppm from $^{13}CS_2$. Satellites of the proton peak at δ 2.82 give a doublet at +156.1 ppm in the ^{13}C spectrum (J_{CH} = 153 Hz) and the remaining high-field proton peak gives a triplet (J_{CH} = 140.2 Hz) at +162.5 ppm. Both ^1H and ^{13}C shifts and coupling constants are summarized and assigned in Table II together with data for the model compounds: the cyclopentyl cation, norbornane, and nortricyclene.

Table II. ^{13}C and ^1H Nuclear Magnetic Resonance Chemical Shifts and Coupling Constants in the Norbornyl Cation, Cyclopentyl Cation, Nortricyclene, and Norbornane

Δ	Solvent	$\delta_{^{13}C}$[a]	$\delta_{^1H}$[b]	J_{CH}[c]
	SbF_5–SO_2	C_2 +101.8	5.01	53.3
	−70°	C_3 +162.5	1.86	140.2
		C_4 +156.1	2.82	153
	SbF_5–SO_2ClF–SO_2F_2	C_1 +173	3.05	*d*
	−154°	C_2 +70	6.59	*d*
	SbF_5–SO_2ClF	C_2 +95.4	4.48	28.5
	−70°			
		C_2 +183.6	0.99	175
	CCl_4	C_3 +161.8	1.19	133
	35°	C_4 +165.2	1.89	148
		C_2 +164.2	1.30	(130 ± 2)
	CCl_4	C_7 +155.4	2.10	(130 ± 2)
	35°	C_1 +157.6	2.18	140

[a] In parts per million from $^{13}CS_2$. [b] In parts per million (δ) from internal TMS. [c] In hertz. [d] Was not obtainable in natural carbon abundance samples.

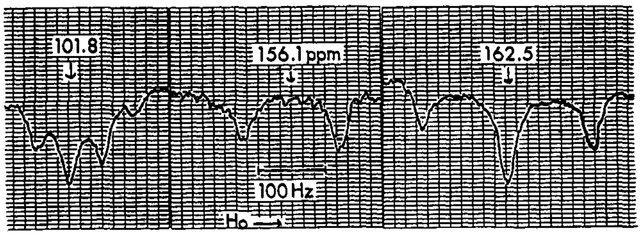


Figure 5. ^{13}C indor spectrum of the norbornyl cation generated in SbF_5–SO_2 solution from *exo*-2-chloronorbornane and recorded at −70°. The spectrum was obtained by observing the ^{13}C satellites in the proton spectrum at 100 MHz while irradiating the sample with a swept 25-MHz frequency. ^{13}C shifts indicated are with respect to $^{13}CS_2$.

The ^{13}C spectrum of the ion was also obtained at room temperature in SbF_5 solution by time-averaging the direct ^{13}C resonance spectrum (with proton decoupling).[8] The resultant spectrum is a single broad line (peak width at one-half height, 50 Hz) centered at +134 ppm. This shift represents the averaged shift of all carbons in the ion (due to rapid 3,2- and 6,1,2-hydride shifts and Wagner–Meerwein rearrangements at ambient temperatures) and can be computed on the basis of the assignments in Table I from the −70° indor spectrum. The value obtained in this manner is $[(101.8 \times 3) + (162.5 \times 3) + 156.1]/7 = 135.6$ ppm, in good agreement with the experimentally observed average shift.

More difficulty was encountered in obtaining the ^{13}C spectrum of the "frozen out" ion at −150°. The satellites in the proton spectrum could not be detected due to a poor signal-to-noise ratio at this temperature; however, enhancement of the ^{13}C proton resonance (due to collapse of the ^{13}C satellites and possibly a nuclear Overhauser enhancement) was observed on irradiation at 25.1 MHz. The low-field proton resonance (at δ 6.59) was enhanced on irradiation at +70 ± 2 ppm while the higher field proton resonance (δ 3.05) was enhanced by irradiation at +173 ± 2 ppm. The "main peak" ^{13}C indor experiment obviously does not give the ^{13}CH coupling constants and peak multiplicities. However, since the average of the two shifts obtained from the resolved signals has to give rise to the three-carbon resonance at 101.8 ppm (observed at −70°) the 70-ppm shift has to be assigned to two carbons and the 173 ppm to one carbon, *i.e.*, $[(2 \times 70) + 173]/3 = 104$ ppm.

B. Preparation and Quenching of 2-Alkyl(aryl)norbornyl Cations. The 2-methyl-, 2-ethyl-, and 2-phenylnorbornyl cations were prepared by ionization of the corresponding 2-alkyl(aryl)-2-chloro or 2-hydroxy precursor using acid media identical with those described above for the 2-norbornyl cation. Cations obtained upon ionization of 1-alkyl(aryl)-2-halonorbornanes were identical in every respect with those generated from the 2-substituted derivatives.

When superacid solutions of 2-substituted norbornyl cations were quenched with nucleophiles like sodium methoxide in methanol, 2-*exo*-2-alkyl(aryl)norbornane methyl ethers were obtained as the only identifiable products (30% yield overall).

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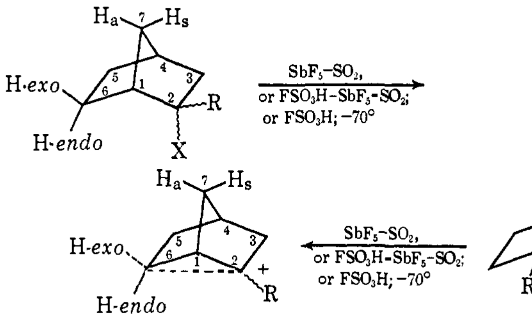
(8) We are grateful to Professor J. D. Roberts and Dr. F. J. Weingart for obtaining this spectrum.

Table III. Pmr Parameters (δ) of 2-Methyl-, 2-Ethyl-, and 2-Phenylnorbornyl Cations at 100 MHz in $FSO_3H-SbF_5-SO_2$ Solution at −60°[a]

Ion	CH_3	CH_3CH_2	H_1	H_6 *exo*	H_3 *exo*, *endo*	H_4	H_7	H_5 *exo*, *endo*	H_6 *endo*
2-CH_3	3.00 (J = 3 tr)		4.64 (J = 6.5 d)	3.28 (br, m)	2.70	2.70	1.71	1.47	1.09
2-C_2H_5	1.28 (tr)	3.46 (m)	4.41 (J = 6.5 d)	3.46 (br, m)	2.82	2.82	1.78	1.60	1.28
2-C_6H_5[b]			4.83 (J = 6.5 d)	2.81 (br, m)	3.49	3.20	2.04	1.41	2.00

[a] d = doublet; tr = triplet; br = broad; m = multiplet. J values in hertz. [b] In FSO_3H, as reported by Farnum and Mehta.[9]

^{1}H Nuclear Magnetic Resonance Spectroscopic Study. The 100 MHz pmr spectrum of the 2-methylnorbornyl cation recorded at −80° in SbF_5-SO_2 is shown in Figure 6. Table III summarizes the 100 MHz pmr spectra obtained for the 2-methyl-, 2-ethyl-, and 2-phenylnorbornyl cations either in neat FSO_3H or in SbF_5-SO_2 at −60°. The most significant and well-defined signal in the spectrum of each cation is the low-field one-proton doublet assigned to the H_1 bridgehead proton. Each of the doublets displays coupling constants of 6.5 Hz. With the exception of the chemical shifts of the H_6 *exo* protons, the spectra of 2-methyl- and 2-ethylnorbornane are very similar to that reported by Farnum and Mehta[9] for the 2-phenylnorbornyl cation generated in neat FSO_3H. Chemical shifts of the H_6 *exo* protons of the 2-methyl-, 2-ethyl-, and 2-phenylnorbornyl cations are observed at δ 3.28, 3.46, and 2.81, respectively. It has been shown conclusively[9] that the doublet observed for H_1 (J = 6.5 Hz) is a result of coupling of H_6 *exo* and H_1 in the 2-phenylnorbornyl cation. Irradiation of the signals at δ 3.28 and δ 3.46 in the pmr spectra of 2-CH_3 and 2-C_2H_5, respectively, leads to a collapse of the doublets assigned to H_1 to yield broad singlets. Thus, although in all three cases the H_6 *exo* proton is deshielded and shown by decoupling and isotopic labeling to be coupled to the proton at the one-bridgehead position, its chemical shift is at substantially higher field for the 2-phenyl- than the 2-methyl- and 2-ethylnorbornyl cations. Another interesting feature observed in the 2-methylnorbornyl cation is the long-range coupling of the methylene protons to the methyl group of 3 Hz. Similar long-range coupling occurs with the methylene proton of the ethyl group in the 2-ethylnorbornyl cation.



(X = F, Cl, Br, OH) R = CH_3, C_2H_5, C_6H_5

^{13}C Nuclear Magnetic Resonance Spectroscopic Study. The ^{13}C satellites in the proton spectrum of the 2-methylnorbornyl cation due to the two-bond coupling of the methyl group with C_2 ($J \sim$ 6 Hz) and those due to the direct coupling to C_1 (J = 168 Hz) were located, and the ^{13}C shifts of these carbons were obtained by the indor method. The shift of C_1 in the methylcyclopentyl cation was obtained in an analogous fashion.

For the 2-phenylnorbornyl cation, the long-range coupling from the *ortho* proton resonances to $^{13}C_2$ was used to obtain the C_2 chemical shift and the same procedure was adopted for the phenylcyclopentyl cation. In the latter case the indor spectrum was very broad and an error of ±2 ppm in the shift was estimated. In the

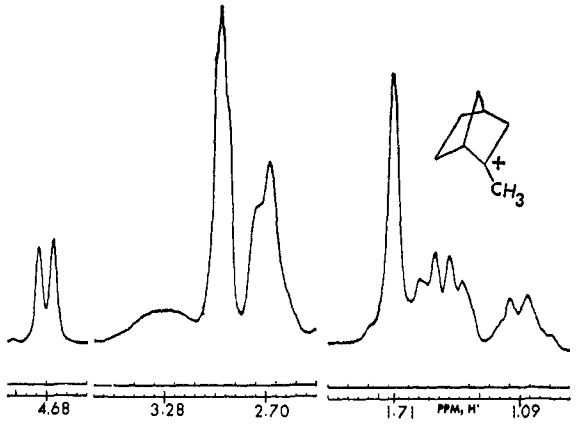
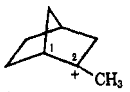
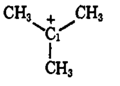
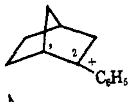
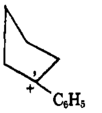
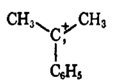


Figure 6. Pmr spectra (100 MHz) of the 2-methylnorbornyl cation generated in SbF_5-SO_2 solution from 2-*exo*-chloro-2-methylnorbornane and recorded at −95°.

Table IV. ^{13}C Chemical Shifts of the Carbonium Carbon Atoms in the 2-Methyl- and 2-Phenylnorbornyl Cations and Model Carbonium Ions[a]

Ion	Solvent	δ ^{13}C
	$FSO_3H-SbF_5-SO_2$ −80°	C_1 +118.0 (J = 168 Hz) C_2 −76.1
	SbF_5-SO_2 −60°	C_1 −142.2
 $(CH_3)_2\overset{+}{C_1}CH_3$	SbF_5-SO_2ClF −60°	C_1 −135.4
	FSO_3H −35°	C_1 +130.8 ± 2 (J = 152 ± 5 Hz) C_2 −65.8
	FSO_3H −20°	C_1 −70 ± 2
 $(CH_3)_2\overset{+}{C_1}C_6H_5$	$FSO_3H-SbF_5-SO_2$ −60°	C_1 −61.1

[a] In parts per million from $^{13}CS_2$.

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

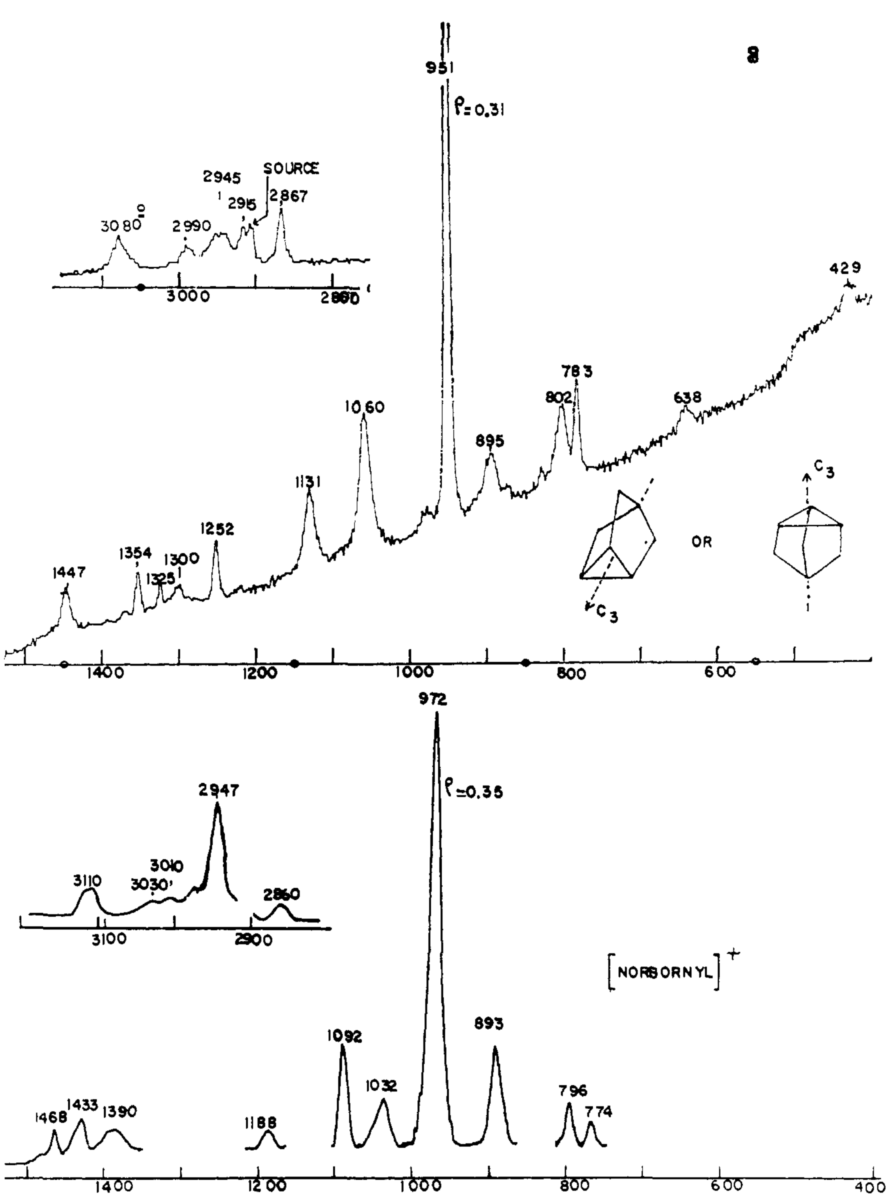

Figure 7. (A) Raman spectrum of nortricyclene. (B) Raman spectrum of ion in SbF_5-FSO_3H-SbF_5-SO_2 at −80° (solvent and gegenion have been deleted).

other quoted shifts the error is believed to be ±0.2 ppm. The ^{13}C shifts in the ions are summarized in Table IV.

Because of the complexity of the proton spectra of the 2-methyl-, 2-ethyl-, and 2-phenylnorbornyl cations, main peak enhancement and a systematic search for coupling constants must be used to obtain and assign the complete ^{13}C indor spectra of these ions. We are presently involved in a concerted effort toward this end. Of particular importance are the ^{13}C chemical shifts of the C_6 carbon atoms in these ions since it would clearly show (with data reported herein for C_1 and C_2) the distribution of charge over C_1, C_2, and C_6 in these molecular systems.

C. Laser Raman Spectroscopic Studies. The main Raman spectral data of the norbornyl and 2-methyl- and 2-ethylnorbornyl cations are summarized in Table V. Included also are the vibrational data observed for a series of structural models. Raman spectra were recorded on a Cary Model 81 spectrophotometer with a He–Ne laser source for ~20% (mol) cation solutions in FSO_3H-SbF_5-SO_2. The temperature of the samples was maintained between −70 and −80° by means of the low-temperature cell described previously.[10] Only the strong bands in the C–H (3100–2700 cm^{-1}) and C–C skeletal frequency region (1000–250 cm^{-1}) are shown in Table V for each species.

The ionizations of the precursor 2-chloronorbornane, 2-chloro-2-methylnorbornane and 2-chloro-2-ethylnorbornane were monitored by Raman and ^{19}F and ^{1}H nmr spectra. The observation of the strong Raman line at ~390 cm^{-1} for $Sb_2F_{10}Cl^-$ anion as the only intense line in the 300–500 cm^{-1} region and the characteristic resonance absorptions of the anion observed in the ^{19}F nmr spectra clearly indicate the ionization of the halide precursors.[10] The ^{1}H nmr spectra of the solutions showed the presence of only the cations both be-

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[10] A. Commeyras and G. A. Olah, *J. Amer Chem. Soc.*, **91**, 2929 (1969).

Table V. Main Raman Spectral Lines (cm^{-1}) of the Norbornyl and 2-Methyl- and 2-Ethylnorbornyl Cations and Vibrational Data of Nortricyclene and Norbornane[a]

	C–H region (3100–2700 cm^{-1})					C–C region (1000–250 cm^{-1})			
Norbornyl cation	3110	3030	3010	2947	2860		972 (vs, p)	796 (w)	390
3-Br-Nortricyclene	3087	3006	2975	2955	2875		959 (vs, p)	732 (m)	300
Nortricyclene	3080	2990	2945	2915	2867		951 (vs, p)	783 (w)	
2-Me-Norbornyl cation			2984	2960	2855	911 (s)	880 (s, p)	770 (m)	350 (m, p)
2-Et-Norbornyl cation			2980	2965	2873	920 (s)	884 (s, p)	765 (m)	350 (m, p)
Norcamphor			2964	2920	2882	938 (s)	880 (m)	786 (m)	
Norbornane			2964	2936	2873	920 (s, p)	871 (s, p)	753 (m)	
2-Cl-Norbornane			2976	2933	2878	925 (s, p)	879 (s, p)	764 (m)	345
2-Br-Norbornane			2978	2933	2878	925 (s)	878 (s)	762 (m)	294
1-Me-Nortricyclene	3069	2994	2967	2930	2871	905 (s, wp)	857 (vs, wp)	794 (m)	
2-Me-Norbornane[b]			2952	Source	2869	923 (s)	873 (m)	719 (m)	
2-Et-Norbornane[b]			2947	Source	2869	923 (m)	878 (m)	696 (m)	

[a] s = strong; m = medium; w = weak; p = polarized; vs = very strong. [b] V. T. Alexsanyan and Kh. E. Sterin, *Fiz. Sb. L'vov. Gos. Univ.*, **1**, 59 (1957); *cf. Chem. Abstr.*, **53**, 21158*a* (1959).

fore and after recording Raman spectra with no unionized precursors present.

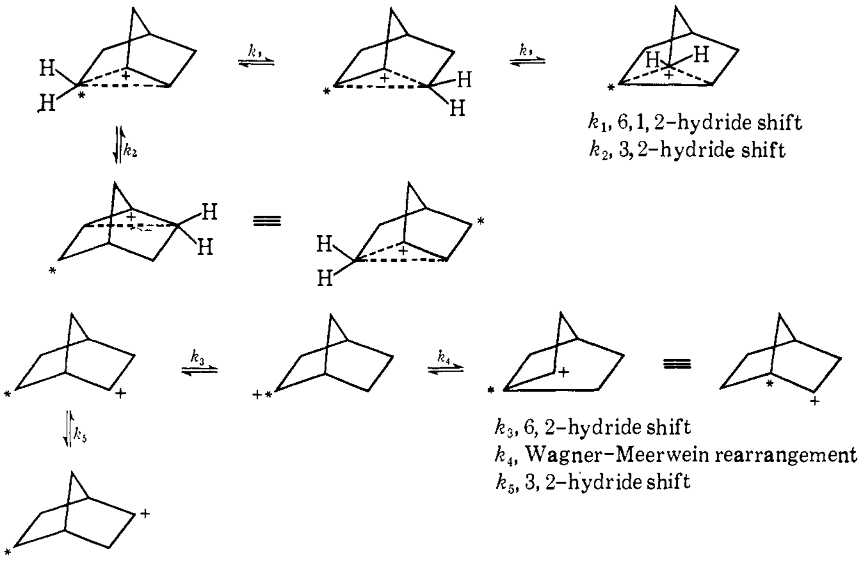
The 1000–250 cm^{-1} regions of nortricyclene and 1-bromonortricyclene show only one very strong polarized Raman line at 950 cm^{-1}. In contrast, norbornane and its derivatives display consistently two intense lines at ~920, ~875 and one moderately intense around 750 cm^{-1}. In the C–H stretching frequency region, norbornane and its derivatives show only three lines at frequencies below 3000 cm^{-1}. On the other hand, nortricyclene, 3-bromonortricyclene, and 3-methylnortricyclene display a minimum of five lines in this region with the line at 3080 cm^{-1} being characteristic of the cyclopropane ring.

Raman spectra obtained for the norbornyl cation and nortricyclene are shown in Figure 7. Identical nmr and Raman spectra are obtained from the ionization of *exo*-chloronorbornane and the protonation of nortricyclene in FSO_3H–SbF_5–SO_2 media. Close correlation between the Raman spectrum of the norbornyl cation and that of nortricyclene reflects the close skeletal similarity of these two species. The presence of only one very intense line at 972 cm^{-1} (ρ = 0.35) and observation of bands characteristic of cyclopropane type C–H stretch indicate the nortricyclene related structure of the norbornyl cation.

A similarity between the Raman spectrum of the 2-methylnorbornyl cation and that of norbornane, 2-methyl- and 2-ethylnorbornane, and other substituted norbornanes can be seen from the data of Table V. However, a similarity between the Raman spectral lines in the 1000–700 cm^{-1} region of norbornane derivatives and 1-methylnortricyclene is also observed. The latter in all probability indicates that a methyl group attached to the cyclopropane ring causes observable distortion in the skeletal vibration of the rigid tricyclic molecule. No such distortion is observed if all substitutents on the cyclopropane ring are hydrogen, as in the case of ion **1**, or if bulkier substituents are located on the methylene groups.

Discussion

Distinction between the Classical and Nonclassical Norbornyl Cations. The degenerate rate processes needed to account for the spectroscopic behavior of the 2-norbornyl cation are summarized below for the ion in both the classical and nonclassical representations (an asterisk denotes a ^{13}C label).



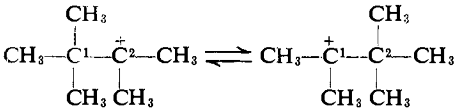
k_1, 6,1,2-hydride shift
k_2, 3,2-hydride shift

k_3, 6, 2-hydride shift
k_4, Wagner–Meerwein rearrangement
k_5, 3, 2-hydride shift

It can readily be seen that if all these degenerate rearrangements are fast with respect to the nmr time scale in both the classical and nonclassical descriptions, then all protons and all carbons become indistinguishable. This is the situation in nmr spectra recorded at ambient temperatures. If k_2 (or k_5) is decreased below the relaxation time of the proton (or carbon) in the nmr experiment four "cyclopropane" protons, the six methylene protons, and the single bridgehead proton become distinguishable (as do $C_{1(2)(6)}$, $C_{3(5)(7)}$, and C_4), as is observed in the temperature range −50 to −130°. Finally the ^{1}H (and ^{13}C) spectra below −130° require that k_1 (or k_3) be now slow enough to permit distinction of the separate proton (and carbon) resonances.

Considering the proton spectrum alone, one feature in particular casts doubt on the possibility of an equilibrating classical structure and this is the chemical shift of the protons in the −150° spectrum of the ion. Since at this temperature only k_4 need be considered, in case of equilibrating classical ions, a peak of area two should be present in the proton spectrum at a position which is the average of the shift of a proton at a secondary carbonium ion center and that at the bridgehead position, adjacent to the positive charge. Taking the isopropyl cation as a model for the former shift (δ 13 ppm)[6c] and using the low temperature ^{13}C evidence to assign the peak at δ 6.6 ppm to the averaged proton shift would lead to a shift of δ 0.2 ppm for the bridgehead proton—a value which is completely unacceptable. In norbornane the bridgehead proton shift is δ 2.18 ppm. No such problem arises in rationalizing the observed shifts in terms of the nonclassical ion.

The ^{13}C spectrum provides confirmation that the norbornyl cation cannot be classical. In the −150° spectrum, the two-carbon resonance at 70 ppm could only be assigned, in the classical ion formulation, to an average of a secondary carbonium ion center and a bridgehead carbon. Taking the former shift again as that in the isopropyl cation (−125 ppm) and the latter as the bridgehead carbon shift in norbornane (158 ppm) leads to an average shift of $(158 - 125)/2 = 16.5$ ppm; 158 ppm is a high estimate for the bridgehead carbon atom in the ion since it is now adjacent to a positive charge. A more accurate estimate for the average shift would be therefore 6.5 rather than 16.5 ppm. This approach, in ions known to be classical, leads to estimates of the averaged carbon shifts to within 5 ppm of the observed values[6c] as, for example, in the case of the pentamethylethyl cation (dimethyl-*t*-butylcarbonium ion). The difference of 54 ppm between the observed and estimated values in the case of the norbornyl therefore precludes the classical ion interpretation of the spectrum.



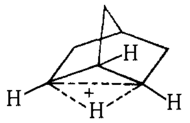
$$\mathrm{CH_3{-}\overset{CH_3}{\underset{CH_3}{C^1}}{-}\overset{+}{\underset{CH_3}{C^2}}{-}CH_3 \rightleftharpoons CH_3{-}\overset{+}{\underset{CH_3}{C^1}}{-}\overset{CH_3}{\underset{CH_3}{C^2}}{-}CH_3}$$

$\delta_{C^{1,2}}\mathrm{av} = -11.5$ ppm

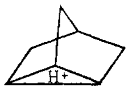
A similar approach, with the same conclusions, can be invoked for the −70° ^{13}C spectrum of the ion. The cyclopentyl cation (+95.4 ppm) can be used as a model for the classical ion. Rapid hydride shifts in the "classical" cyclopentyl cation lead to the observed ^{13}C shift being the average of a carbon bearing a positive charge, two carbons one bond removed, and two carbons two bonds removed from the charge.[6c] By comparison the 101.8-ppm shift observed in the spectrum of the norbornyl cation would, if the ion were classical, have to be the average of one carbon bearing the positive charge, one carbon one-bond removed, and one carbon two-bonds removed. The isopropyl cation shift (−125 ppm) with 150 ppm each for the remaining four carbons gives excellent agreement with the observed shift in the cyclopentyl cation. These values, when used to calculate the shift for the classical norbornyl cation, give 59 ppm, a value which is incompatible with the observed shift (101.8 ppm). To arrive at this latter shift, for the norbornyl model, either the chemical shift of the charged carbon atom has to be increased to −6 ppm or the shifts of the adjacent carbon atoms both increased to 215 ppm. Both of these possibilities (or any other combination of values) are quite unreasonable and therefore some drastic change in structure and charge distribution (as is the case with the nonclassical ion) is required.

No definitive conclusions can be reached from the 53.3 Hz J_{CH} average coupling constant observed for the 101.8 ppm ^{13}C resonance at −70° since averaging of estimated coupling constants in either the classical or nonclassical structures would give rise to a coupling constant of this order of magnitude.[6c] It was not possible to obtain fine structure and coupling values in the "frozen out" ion at −150° using the natural abundance "main peak" indor method. We are, however, pursuing this problem by synthesizing high ^{13}C enriched norbornyl precursors to be able to effect these studies.

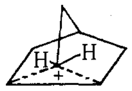
Some comments are in order at this point on the chemical shifts and coupling constants in relation to the nonclassical ion. First, regarding the ion as protonated nortricyclene and hence as a molecule containing a protonated cyclopropane ring, the possibility of the edge-protonated structure being the predominant species under our conditions has to be considered. Theoretical calculations[11] on the norbornyl cation, while showing that face-protonated nortricyclene (the nortricyclonium ion) and the classical ion had a substantially higher energy than either the corner- or edge-protonated species, showed the latter differed in energy by only 3 kcal compared to an estimated error in the calculations of ±10 kcal. Furthermore the calculations apply, of course, to the gas phase and thus take no account of solvation energies. The edge-protonated species can however be ruled out since this species would not give the observed −150° proton nmr spectrum. For this species, a low-field resonance of area 1 due to the edge proton and two peaks at higher field in the ratio 2:1 due to the cyclopropane ring protons would be expected. The face-protonated nortricyclene ion is also inconsistent with the observed spectrum for similar reasons, leaving the corner-protonated species (the nonclassical norbornyl cation) as the only compatible structure. Several conformations of the bridging methylene protons can be envisaged. Since they appear to be equivalent in the low-temperature



"edge" protonated



"face" protonated



"corner" protonated

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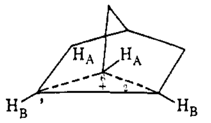
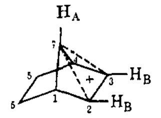
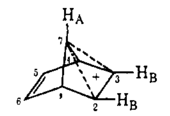
(11) G. Klopman, *J. Amer. Chem. Soc.*, **91**, 89 (1969).

spectrum of the ion, the conformation in which these protons eclipse two of the bridging methylene protons would appear to be preferred. The nature of the bonding could thus be best described as a three-center molecular orbital comprising a vacant lobe of the sp^3-hybridized bridging carbon and two orbitals from the remaining two carbons in the three-membered ring (Figure 8). The bonding would thus be analogous to the description of the bonding of the bridging methyl groups in alkyl organometallics such as the dimers of trimethylaluminum, dimethylberylium, and dimethylmagnesium[12] and also to the bonding in the stable nonclassical 7-norbornenyl and 7-norbornadienyl cations observed by Story and Saunders,[13a] Winstein,[13b,c] and Richey.[13d] Winstein[13e] has pointed out recently the similarities of the proton nmr shifts in these ions and this comparison can also be extended to the ^{13}C nmr shifts. The ^{13}C nmr data obtained are presented in Table VI.

Table VI. Proton and Carbon-13 Nmr Data[a] for the 2-Norbornyl, 7-Norbornenyl, and 7-Norbornadienyl Cations

		
H_A 3.05	H_A 3.25[c]	H_A 3.24[c]
H_B 6.59	H_B 7.04[c]	H_B 7.48[c]
C_A 173 ppm	C_A 162.2 ppm[c]	C_A 152.7 ppm[c]
C_B 70 ppm	C_B 68.7 ppm	C_B 75.8 ppm
$J_{CH_A} + J_{CH_B} = 320$ Hz[b]	$J_{CH_B} = 194$ Hz[d]	$J_{CH_A} = 220 \pm 5$ Hz $J_{CH_B} = 200 \pm 5$ Hz

[a] Proton shifts are in parts per million from internal tetramethylsilane. Carbon-13 shifts are in parts per million from carbon disulfide. [b] From −70° 100-MHz proton spectrum in SbF_5–SO_2 solution; other values at −150° in SbF_5–SO_2ClF–SO_2F_2 solution. [c] From spectra obtained at −60° in 4:1 *M* FSO_3H–SbF_5 solution (diluted 1:1 by volume with SO_2). [d] J_{CH_A} could not be determined due to overlapping peaks in the proton spectrum. Other shifts: 7-norbornenyl, C_1 138.0 ppm (J = 160 Hz); $C_{5,6}$ 171.5 ppm (J = 130 Hz); 7-norbornadienyl C_1 132.6 ppm (J = 176 Hz), $C_{5,6}$ 68.9 ppm (J = 180 Hz).

A corner-protonated cyclopropane ring can be seen to be common to all three ions. This common structural feature and the resultant similar charge distribution are reflected in the correspondence between the carbon and proton chemical shifts associated with the cyclopropane ring in the three ions. This similarity allows us to estimate the magnitude of J_{CH_A} in the norbornyl cation. We would expect that J_{CH_B} in the three ions would be of similar magnitude as a result of a similar charge distribution and hybridization associated with the CH_B bonds. Therefore taking a value of 195 Hz for J_{CH_B} in the norbornyl cation, and knowing that the sum of J_{CH_A} and J_{CH_B} is 320 Hz, leads to a value of 125 Hz for J_{CH_A}. This is considerably lower than the 220 Hz observed for J_{CH_A} in the 7-norbornadienyl cation. This difference can be rationalized since there is an obvious dissimilarity between the orientation of the CH_A bonds in the two ions. This would be expected to result in a higher s character for this bond in the 7-norbornadienyl ion and hence a larger carbon–hydrogen coupling constant. In fact the coupling constant of 125 Hz estimated for J_{CH_A} in the 2-norbornyl cation is that expected for sp^3 hybridization and is in agreement with our conclusions originally put forth[6b] on the basis of studies of the trimethylaluminum dimer.

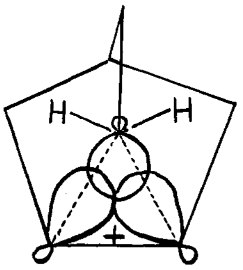
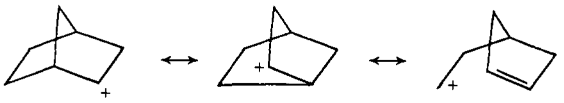


Figure 8. Molecular orbital picture of the nonclassical three-center bond in the norbornyl cation.

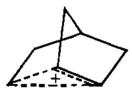
We conclude from these studies that there is a close relationship between the charge distribution in the nonclassical 2-norbornyl, 7-norbornenyl, and 7-norbornadienyl cations. Further in all these cations the positive charge resides mainly at the cyclopropane-type carbon atoms rather than at the bridging carbon. In valence-bond terms this work thus provides evidence that in the 2-norbornyl cation the major contributing resonance structures[14] are thus **2** and not **3**. The



2 **3**

unimportance of canonical form **3** to the mesomeric structure means that **1b** is a better representation of the 2-norbornyl cation than the usual formulation **1a** using three dashed lines.

1b



1a

The proton and carbon shifts of the methylene and bridgehead positions are also of interest in terms of the nonclassical formulation of the ion. Comparison of these shifts with those in nortricyclene shows the carbon shifts of the methylenes to be virtually identical while the bridgehead shift is deshielded by 9 ppm in the norbornyl cation. This can suggest a cage effect on the methine group sitting, as it does, directly above the charged cyclopropane ring. This effect is also evident in comparisons of the proton spectra.

In the discussion of the nmr spectra of the 2-norbornyl cation we have described the nonclassical ion as protonated nortricyclene. Additional evidence which

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(12) For a discussion see, R. G. Vranka and E. L. Amma, *J. Amer. Chem. Soc.*, **89**, 3121 (1967).

(13) (a) P. R. Story and M. Saunders, *ibid.*, **84**, 4876 (1962); P. R. Story, *et al.*, **85**, 3630 (1963); (b) R. K. Lustgarten, M. Brookhart, and S. Winstein, *ibid.*, **89**, 6350, 6352, 6354 (1967); (c) M. Brookhart, A. Diaz, and S. Winstein, *ibid.*, **88**, 3135 (1966); (d) H. G. Richey, Jr., and R. K. Lustgarten, *ibid.*, **88**, 3136 (1966); (e) S. Winstein, 21st National Organic Chemistry Symposium of the American Chemical Society, Salt Lake City, Utah, June 1969.

(14) It should be emphasized that these resonance structures are *not* equivalent to the structures of the classical ion. In the latter a C_2–C_6 bond distance of 2.5 Å is expected while in the contributing resonance structures of the nonclassical ion, 1.54 Å is a more realistic figure. This point has caused some confusion in the past.[11]

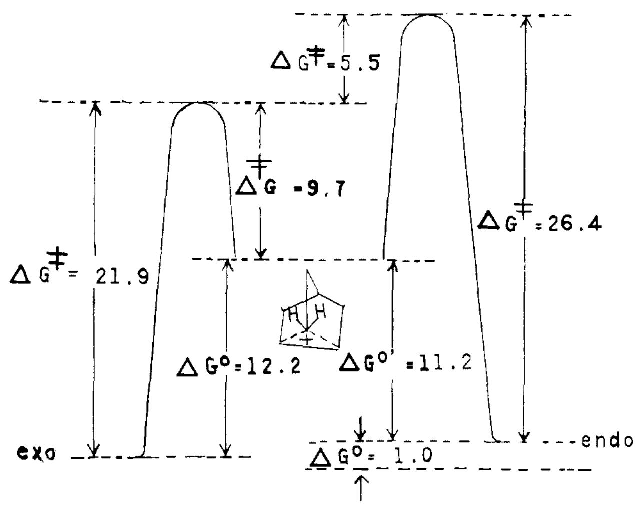

Figure 9. Goering–Schewene diagram for the acid-catalyzed acetolysis of 2-*exo*- and 2-*endo*-norbornyl acetates at 75°. (All numbers are in kcal/mol^{-1}.)

supports this suggestion comes from the laser Raman spectrum of the ion.

Since the lifetime of vibrational transitions is of the order of 10^{-12} sec it can be assumed that they are faster than any chemical equilibrations. Vibrational spectroscopy thus permits the differentiation between rapidly equilibrating and static bridged species provided the vibrational spectra of these two limiting cases can be distinguished.

The complexity of the structure and the size of the norbornyl cation do not permit analysis of the Raman spectrum by normal coordinate analysis. The approach adopted was therefore to compare the spectrum with that of limiting model compounds whose structure would be expected to show skeletal similarity to those of the nonclassical and classical ions. The models chosen were tricyclo[2.2.1.0^{2,6}]heptane (nortricyclene) and bicyclo[2.2.1]heptane and their derivatives, respectively.

The norbornyl derivatives display Raman spectra which differ markedly from that of the norbornyl cation (see Table V and Figure 7) suggesting that the ion does *not* have a bicyclo[2.2.1]heptyl-type carbon skeleton. On the other hand, similarities between Raman spectra of nortricyclene, 3-bromonortricyclene, and the norbornyl cation indicate that the norbornyl cation is structurally related to a tricyclo[2.2.1.0^{2,6}]-heptane or nortricyclene skeleton and therefore is best described as a protonated nortricyclene. This does not however imply the presence of an equitriangular cyclopropane ring with identical C_1–C_2, C_1–C_6, and C_2–C_6 bond lengths. As a matter of fact the C_1–C_2 and C_1–C_6 bonds involved in three-center bond formation should be lengthened compared with the C_2–C_6 bond. The sensitivity of the Raman skeletal modes and hence the observed Raman spectral patterns to changes in the C–C bond lengths is not exactly known. We can, however, estimate that increase in the C–C bond distances of greater than 20% should be reflected in the Raman spectra of the cation. We would expect that any significant increase in the C_2–C_6 bond distance going from a nortricyclene to a norbornyl type system would be evidenced by loss of cyclopropane character and the corresponding disappearance of the signal at 3110 cm^{-1}. Since the gradual lengthening and subsequent opening of a C_2–C_6 bond would be accompanied by *gradual* changes in the Raman spectra (*i.e.*, character changing slowly from that expected for a nortricyclene compound to that expected for the bicyclo[2.2.1]heptane) we can suggest, based on the Raman spectra, only overall skeletal similarities within the limits mentioned.

The Raman spectroscopic approach of using model compounds for comparison has clearly the drawback that we can gain knowledge only of the structural similarity of the carbon skeleton. Locating the protons in the ion or even specific carbon–carbon bond frequencies and therefore distinguishing between edge- and corner-protonated nortricyclene would require a complete analysis of the Raman spectrum or the availability of good model compounds for these two possibilities. Neither of these approaches is at present feasible and we have to rely on the low-temperature nmr spectra of the ion to answer this question.

Rates of the 3,2- and 6,1,2-Hydride Shifts. Data on the competition between solvent capture and the rate of the 6,1,2-hydride shift under solvolytic conditions are available from both ^{14}C and ^{3}H scrambling experiments.[15a,b] From the tritium scrambling experiments in acetic acid, the ratio of the rate of solvent capture to the rate of the 6,1,2-hydride shift is 2.88 at 45° and 1.76 at 25°. Solvent capture thus has the higher free energy of activation ($\Delta G^{\ddagger}$) by 3.9 kcal/mol^{-1}.[16] The free energy of activation for the 6,1,2-hydride shift in SbF_5–SO_2ClF–SO_2F_2 solution is calculated from rate data to be 5.8 kcal/mol^{-1}. Making the assumption that the rate of 6,2-hydride shift in acetic acid is the same as that in SbF_5–SO_2ClF–SO_2F_2, one obtains a free energy of activation for pseudounimolecular solvent capture of $5.8 + 3.9 = 9.7$ kcal/mol^{-1}. To a first approximation the stability of the norbornyl cation relative to the 2-*exo*-norbornyl acetate can be estimated as $21.9 - 9.7 = 12.2$ kcal/mol^{-1} and can be incorporated into the Goering–Schewene diagram[17] for the acid-catalyzed acetolysis of *exo*- and *endo*-norbornyl acetates as shown in Figure 9.

The rate of the 3,2-hydride shift is abnormally slow compared with other 1,2-hydride shifts in secondary carbonium ions. In the cyclopentyl cation a maximum activation energy of 5 kcal (corresponding to a rate constant of 10^4 sec^{-1} at −150°) can be estimated from the fact that no change in the spectrum of the ion in SbF_5–SO_2ClF–SO_2F_2 is observed down to this temperature. The 3,2-hydride shift barrier in the norbornyl cation is thus at least 5.8 kcal higher than that in the cyclopentyl cation corresponding to a rate ratio of 10^{11} at −150° or 10^4 at 25°. Comparisons of models of the two ions show that torsional and steric effects[18] could not account for this difference. An attractive explanation for this marked difference in behavior is that the difference in activation energies represents loss of σ-delocalization energy in the nonclassical

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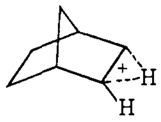
(15) (a) J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, **76**, 4501 (1954); (b) C. C. Lee and L. K. M. Lam, *ibid.*, **88**, 2831 (1966); **88**, 5355 (1966).

(16) J. A. Berson, R. G. Bergman, J. H. Hammons, and A. W. McRowe, *ibid.*, **89**, 2581 (1967).

(17) (a) H. J. Goering and C. B. Schewene, *ibid.*, **87**, 3516 (1965); (b) H. C. Brown and M-H. Rei, *ibid.*, **90**, 6216 (1968).

(18) P. von R. Schleyer, *ibid.*, **89**, 699, 701 (1967).

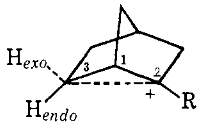
norbornyl cation upon reaching the transition state for the 3,2-hydride shift. The 3,2-hydride shift is known to be *exo–exo* and the transition state could be represented[18,19] by



It is known that an electron donor at C_2 in the norbornyl cation (*e.g.*, CH_3 or C_6H_5) drastically reduces the degree of σ participation[20] and since the 3,2-hydride shift transition state must involve delocalization of the positive charge from C_2 to C_3 (and *exo* H_3) a substantial decrease in σ delocalization is expected. We would thus conclude that σ delocalization contributes at least 5.8 kcal to the stability of the norbornyl cation. In terms of the Goering–Schewene diagram for solvolysis this would imply at least 3 kcal of delocalization in the transition state for *exo* solvolysis although it should be emphasized that this figure is the result of a number of assumptions and would not therefore be expected to be very reliable. It is, however, close to the value of 3.5 kcal suggested by Goering and Schewene, and Brown.[17]

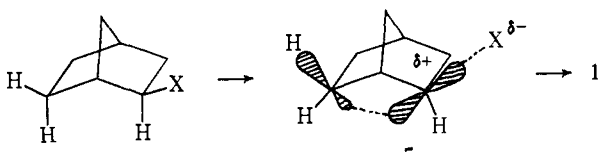
There is an indication which could be taken to show that the rates of hydride shifts are not medium independent as is assumed in the above arguments. This is significant because it could be argued that although the nonclassical nature of the norbornyl cation in SbF_5–SO_2 (SO_2ClF, SO_2F_2) solutions has been demonstrated, it would be an unwarranted extrapolation to say that the ion has the same structure under solvolytic conditions. The discrepancy referred to lies in the relative rates of the 3,2- and 6,1,2-hydride shifts. The data for the stable ion extrapolated to 25° gives rates of 2.5×10^4 and 1×10^6 sec^{-1} for the 3,2- and 6,1,2-hydride shifts, respectively, or a rate ratio of 4×10^3 (at 100° this ratio is 6×10^2). This is inconsistent with the fact that 7–10% of the 3,2-hydride shift has been reported to occur in the acetolysis of 2-norbornyl *p*-bromobenzenesulfonate at 25–45° on the basis of tritium labeling experiments.[15b] There appears to be some question however as to whether this shift occurs under kinetically controlled conditions since the product, 2-norbornyl acetate, underwent some scrambling under the same conditions. Other results[16] are much more consistent with our data. (−)-*endo*-7-Methyl-2-norbornyl acetate underwent no racemization on acetolysis (acetic acid at 100°). Berson concluded from this result that the rate of the secondary–secondary hydride shift was at least 122 times faster than the rate of solvent capture. If this latter rate is assumed to be the same as that in the unsubstituted ion, this means that the 6,1,2-hydride shift in the norbornyl cation is faster than that of the 3,2-hydride shift in the *endo*-7-methyl derivative by at least 10^3, a value which is quite compatible with the rate ratio of 6×10^2 in the norbornyl cation under stable ion conditions. Clearly further work is required to settle the question of the relative rates of the hydride shifts in the norbornyl cation under solvolytic and stable ion conditions. Extending the solvolytic studies to intermediate and strong acid systems (like CF_3COOH,CF_3SO_3H, HF, and FSO_3H) probably in a common solvent like SO_2 or SO_2ClF will help to bridge what we think is no longer a formidable gap between solvolysis studies and stable ion chemistry. Our studies in this regard are in progress (with G. Liang).

Comparison between the 2-Norbornyl Cation and the 2-Methyl-, 2-Ethyl-, and 2-Phenylnorbornyl Cations. The most significant observation in the proton nmr spectra of 2-alkyl(aryl)norbornyl cations is the extensive deshielding of the H_6 *exo* proton in the 2-methyl- and 2-ethylnorbornyl cations.[20] The H_6 *exo* proton of 2-phenylnorbornyl cation is shifted upfield approximately 0.5 ppm relative to the 2-alkyl substituted derivatives. This is consistent with a competitive dissipation of the positive charge at C_2 in the 2-phenylnorbornyl cation by first, σ delocalization and second, delocalization into the adjacent phenyl group. Apparently π participation of the phenyl group predominates over σ delocalization in this case. On the other hand, the significant deshielding of the H_6 *exo* proton in the proton nmr spectra of the 2-methyl- and 2-ethylnorbornyl cations indicates a selective withdrawal of electron density from the σ C_6–H_6 *exo* bond. This selectivity can be accounted for by considering interaction of the backside of the C_6–H_6 *exo* sp^3 orbital with the empty p orbital at C_2. Thus the observed large differences in the chemical shifts of the H_6 *exo* and H_6 *endo* protons of the 2-methyl- and 2-ethyl- *vs.* the 2-phenylnorbornyl cations are due primarily to this interaction in the 2-alkyl ions as shown below.



It is interesting to consider the 2-alkylnorbornyl cations as models for the unsubstituted classical norbornyl cation. As ionization must, at least to some degree, precede participation, the process of ionization of *exo*-2-substituted norbornane **4** can be envisaged to involve a transition state such as **5**. The developing p orbital at C_2 is well oriented for interaction with the back lobe of the C_6–H *exo* orbital but not with the C_1–C_6 bond.

When the ion is more fully formed, C_2–C_6 bond formation with delocalization of the C_1–C_6 bond can take place through what obviously is a low barrier to a 1,2-Wagner–Meerwein shift in a secondary–secondary system. The related barrier to 1,2-Wagner–Meerwein shift in 2-alkylnorbornyl cations is much higher, since they represent tertiary–secondary carbonium ion systems.



4 **5**

The long-range coupling (J = 3 Hz) of the methyl group at C_2 is similar to that observed for an sp^2-hybridized carbonium ion center (for example, in the

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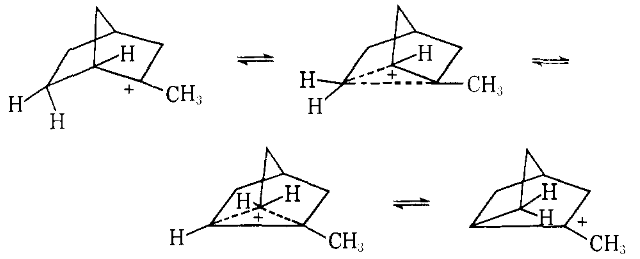
(19) J. A. Berson in "Molecular Rearrangements," Part 1, P. deMayo, Ed., Wiley-Interscience, New York, N. Y., 1963, pp 111–231.

(20) G. A. Olah, J. R. DeMember, C. Y. Lui, and A. M. White, *J. Amer. Chem. Soc.*, **91**, 3958 (1969).

1-methylcyclopentyl cation)[21] and can be interpreted as an indication that the C_2 carbon in the 2-methylnorbornyl cation is very nearly sp^2 hybridized.

The proton spectra of the 2-methyl-, 2-ethyl-, and 2-phenylnorbornyl cations at −60° in superacid solutions show these ions to be static, with the H_6 *exo* and *endo* protons as well as the bridgehead protons giving separate nmr signals. This argues against a symmetrically delocalized nonclassical structure for these ions since if the ions had a structure closely related to the 2-norbornyl cation itself (*vide supra*) a rapid equilibration of these protons would be expected to occur leading to a much more simplified pmr spectrum. In fact changes of the spectrum of the 2-methylnorbornyl cation do occur, but at much higher temperature. In the temperature range −20 to +20°, the peaks due to H_6 (*exo* and *endo* protons) broaden, and although decomposition prevents the spectra being studied above +20°, the spectrum tends toward that expected for the 6,1,2-hydride shift occurring fast with respect to the nmr time scale. An estimate of the barrier for this shift is 15 kcal, or 9 kcal higher than that in the norbornyl cation. This would indicate that the 2-methylnorbornyl ion is substantially more "classical" than the 2-norbornyl cation with the 6,1,2-hydride shift proceeding through a transition state which, however, obviously cannot be symmetrical. The nmr spectra of the 2-phenylnorbornyl cation show no evidence of a 6,1,2-hydride shift even at 35°[9] thus indicating the barrier to this shift is even higher than that in the 2-methylnorbornyl cation. This can be taken again to indicate partial nonclassical character to the 2-methylnorbornyl cation which is substantially lessened (or absent) in the 2-phenylnorbornyl cation.



The similarity in the 1000–700 cm^{-1} region of the Raman spectra of the 2-methyl- and 2-ethylnorbornyl cations to norbornyl derivatives but also 1-methylnortricyclene prevents any conclusive comparison of the Raman data of these cations and model compounds in this spectral region. However, the absence of cyclopropane-type C–H stretching in the Raman spectra of these cations (demonstrated by the absence of lines above 3000 cm^{-1}) indicates a closer similarity to the norbornane-type skeleton. While the distance between the C_2 and C_6 carbon atoms in the 2-methyl- and 2-ethylnorbornyl cation has to be close to that in norbornane, a relatively small decrease in the distance between the C_2 and C_6 carbon atoms due to a degree of C–H_6 *exo* to C_2 σ delocalization would not be expected to alter significantly the Raman spectra of the C–H stretching frequency region (2700–3100 cm^{-1}) of a bicyclo[2.2.1]heptane system. Furthermore the polarized lines at ~350 cm^{-1} (ρ = 0.20) in the Raman spectra of the 2-methyl- and 2-ethylnorbornyl cation are very similar to those observed for several tertiary alkylcarbonium ions (342 cm^{-1}; ρ = 0.25). This correlation and the fact that these signals are apparently due to symmetrical out-of-plane bending about the sp^2 hybridized carbon atom for the planar alkylcarbonium ions lead us to believe that there is substantial positive charge in the 2-alkylnorbornyl cations localized at the C_2 carbon atom. In addition, this correlation tends to indicate that there can be little deviation in the planarity of the C_1, C_2, C_3, and C-methyl skeletal part of the molecule.

Of particular significance is the ^{13}C chemical shift of C_2. A model for this classical ion is the 1-methylcyclopentyl cation in which a C_1 shift of −142.2 ppm was found (see Table IV). This value is quite compatible with that in the *t*-butyl cation (−135.4 ppm) but is 66.1 ppm to low field in the case of the C_2 shift of the 2-methylnorbornyl cation. This very substantial difference can only be accounted for by invoking σ delocalization. An estimate of what the shift would be in the completely nonclassical ion (*i.e.*, protonated methylnortricyclene) can be made from the C_1 and C_2 shift in the norbornyl cation (+70 ppm), although obviously the methyl substituent would cause the ion to be unsymmetrical. Replacing hydrogen by methyl in both alkanes and in carbonium ions typically results in a downfield shift of up to 10 ppm.[4c] Thus 60 ppm would be a good estimate of the $^{13}C_2$ shift or 136.1 ppm to high field of the observed shift. Consequently the 2-methylnorbornyl cation presents a case intermediate between limiting classical and nonclassical ions.[22]

The buildup of charge at C_2 appears to involve electron withdrawal from the C_6–H (*exo*) bond as evidenced by the fact that H_6 (*exo*) is deshielded from H_6 (*endo*) by 2.2 ppm. This is not an unexpected behavior due to the orientation of the C_6–H (*exo*) bonding orbital with respect to the vacant 2p orbital at C_2 (*vide infra*).

The ^{13}C chemical shift of C_1 in the 2-methylnorbornyl cation is +118 ppm ($J_{^{13}C-^1H}$ = 168 Hz). The ^{13}C shift of the same carbon atom in the 2-phenylnorbornyl cation is +130.8 ppm ($J_{^{13}C-^1H}$ = 152 ± 5 Hz) and that obtained for C_1 in norcamphor is +142.9 ppm ($\delta^{13}C_2$) = −21.3 ppm). Assuming that norcamphor and the 2-phenylnorbornyl cation are models for the classical nondelocalized 2-methylnorbornyl cation, interpolation of the C_1 and C_2 chemical shifts of these models with the shift of C_2 in the 2-methylnorbornyl cation (−76.1 ppm) yields a predicted shift of +128 ppm for C_1 in the 2-methylnorbornyl cation. This is 10 ppm to higher field of the observed shift for C_1 in this ion. This small deshielding of the C_1 carbon in the 2-methylnorbornyl cation does not account for the substantial shielding of C_2 in this ion relative to the shift of the

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(21) G. A. Olah, J. M. Bollinger, C. A. Cupas, and J. Lukas, *J. Amer. Chem. Soc.*, **89**, 2692 (1967).

(22) It is here that one runs into difficulties of nomenclature since the term "nonclassical," as it has been used in the past, is indiscriminate regarding the degree and type of σ delocalization present. Now that we are able to probe the extent and direction of this delocalization in the stable ions we propose that to overcome this problem, the ^{13}C shift be assumed to be a linear measure of the extent of σ delocalization and that, in this example, the two model ions considered (cyclopentyl and norbornyl) be taken to represent 0 and 100% delocalization, respectively. On this scale, 31% of σ delocalization is present in the 2-methylnorbornyl cation. An alternative explanation of the observed ^{13}C shift would be to consider a fast equilibrating mixture of approximately one-third of the completely delocalized ion and two-thirds of its classical counterpart. It would, however, be difficult to rationalize the proton nmr and Raman spectral results if this were the case and we thus favor a static formulation of the ion.

carbonium carbon in the 1-methlcyclopentyl cation ($\Delta\delta = +66$ ppm; *vide supra*). Together with the unusually large proton deshielding of H_6 *exo* in the 2-methylnorbornyl cation, therefore, these ^{13}C nmr results strongly support a structure of the ion in which selective interaction with the C_6–H *exo* orbital is the major contributing factor to charge delocalization.

The C_2 shift in the 2-phenylnorbornyl ion was found to be -65.8 ppm and compares to a shift of -70 ± 2 ppm in the 1-phenylcyclopentyl cation and -61.1 ppm in the phenyldimethylcarbonium ion. This close similarity in shifts between the 2-phenylnorbornyl cation and its classical models suggests that σ delocalization is very small or absent in the 2-phenylnorbornyl ion. The ^{13}C data are somewhat inconclusive in this case since a nonclassical model is not available.[23] There seems to be no doubt, however, that the 2-phenylnorbornyl cation under stable ion conditions is predominantly classical both from present data and from Farnum's study of the proton spectrum of the ion.[9]

Conclusions

All evidence clearly demonstrates that the 2-norbornyl cation, under stable ion conditions, is nonclassical and furthermore its structure corresponds to corner-protonated nortricyclene. The charge distribution in the ion, as indicated by the ^{13}C and ^1H nmr shift data, shows little positive charge to be localized on the bridging methylene group. There appears to be a close relationship (as far as the carbon and proton nmr chemical shift data are concerned) between the charge distribution in the 2-norbornyl cation and that in the 7-norbornenyl and 7-norbornadienyl cations, all of which contain a pentacoordinated bridging carbon atom. The norbornyl cation also represents an example of a directly observable protonated cyclopropane, *e.g.*, corner-protonated cyclopropane. If, as is probable, the edge-protonated form is an intermediate during the 6,1,2-hydride shift then the 5.9-kcal activation energy for this process represents a maximum energy difference between the two forms.

Quenching the stable ion gives either nortricyclene and/or an *exo*-2-norbornyl derivative depending on conditions and the nucleophile.[24] Complete deprotonation to nortricyclene takes place in tertiary base quenchings (pyridine) with no other nucleophile being present. When quenched with pyridine and methanol, nortricyclene and methyl norbornyl ether are both formed in varying amounts depending on conditions. Hydrolysis or methanolysis under conditions where the solutions are not neutralized, on the other hand, give a practically quantitative yield of 2-*exo*-norbornyl quenching products, showing the great ease of the acid-catalyzed opening of the cyclopropane ring under solvolytic conditions.

A minimum of 5.8 kcal of σ-delocalization energy is estimated to be present in the norbornyl cation, a minimum of 3 kcal of which is estimated to be present in the transition state for acetolysis of *exo*-2-norbornyl acetate. σ delocalization is substantially reduced in the 2-methylnorbornyl cation and is absent in the 2-phenylnorbornyl cation. We regard the 2-methylnorbornyl cation as being an ion in which there is partial overlap of the vacant p orbital at C_2 and the C_6–H (*exo*) bonding orbital at C_6 with limited decrease in the C_2–C_6 bond distance from that in norbornane.

We have also indicated that this type of σ delocalization may be involved generally in the formation of norbornyl cations generated from *exo*-2-substituted norbornane precursors.

We feel that data presented in this work prove unequivocally the symmetrical bridged structure of the stable long-lived norbornyl cation and its identity with corner-protonated nortricyclene. Whether symmetrical bridging is reached under solvolytic conditions, where solvent capture may compete with σ delocalization of the C–C_6 bond, is a question which cannot be fully answered at the present time.

Experimental Section

Preparation of Solutions of the Norbornyl Cations. As discussed in the Results, the 2-norbornyl cation can be generated from a variety of precursors in a variety of acid systems. Typical of the experimental procedures used is that for the ion in SbF_5–SO_2 solution. A saturated solution of freshly distilled SbF_5 in SO_2 is prepared and cooled to $-78°$ in a Dry Ice–acetone bath. To this solution is added, with continuous vigorous stirring using a vortex-type stirrer, *exo*-2-chloronorbornane to give an approximately 10% solution. The solution, which is colorless or faintly yellow, is then transferred to an nmr tube. Solutions prepared in this way and kept at $-80°$ are stable indefinitely. Solutions in neat SbF_5 can be kept at room temperature without appreciable decomposition for about a week.

For the very low temperature nmr spectra described, solutions of the ion were prepared in SbF_5–SO_2ClF solution (approximately 10% SbF_5) at $-78°$ and, after transfer to an nmr tube, were diluted with an equal volume of SO_2F_2. These latter solutions sometimes deposit a white precipitate. The nature of this precipitate has not been determined but is presumably a complex of SbF_5 with the diluents (SO_2 and SO_2ClF) since its formation can be avoided by having only a slight excess of SbF_5 present in the solution.[25]

Solutions of the 2-methyl-, 2-ethyl-, 2-phenylnorbornyl cations were prepared in a similar manner.

Quenching of Solutions of Norbornyl and 2-Alkyl(aryl)norbornyl Cations. Quenching of the cation solutions was generally carried out by addition of a 10% solution of the cation to an excess of base (pyridine), or a mixture of methanol and pyridine or a slurry of $NaHCO_3$ or sodium methylate in methanol at $-78°$. The resulting solutions were slowly allowed to warm to $-20°$, poured into ice extracted with ether, then washed with dilute HCl, dilute $NaHCO_3$, and again with water. The ether extracts were dried and the products identified by glc and nmr spectroscopy.

Proton Nuclear Magnetic Resonance Spectra. Spectra were recorded at both 60 and 100 MHz using Varian Associates Model A56-60A and HA100 spectrometers. TMS contained in a concentric capillary was used as a reference signal, the shift of external TMS being 0.21 ppm to high field of internal TMS. Spectra at temperatures down to $-154°$ were obtained on the Varian HA100 spectrometer using a modified V4333 variable temperature probe and a V6040 temperature controller. Temperature measurement was accomplished with a low-temperature thermometer calibrated from $+20$ to $-150°$ which is constructed to fit inside a 5 mm nmr

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[23] The effect of replacing hydrogen by a phenyl group on the ^{13}C shift in alkanes is small (~ -10 ppm) while in carbonium ions it is large ($+64$ ppm, comparing the cumyl cation with the isopropyl cation). The effect of phenyl at C_2 in the norbornyl cation (in the absence of any change in σ delocalization) might be expected to be somewhere intermediate between those extremes leading to an estimate of *ca.* 100 ppm for the nonclassical model (*i.e.*, protonated phenylnortriyclene).

[24] Acetolysis of *exo*-2-norbornyl brosylate produces, in addition to *exo*-norbornyl acetate, about 4% nortricyclene: S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *J. Amer. Chem. Soc.*, 87, 376 (1965). For a discussion, see also C. J. Collins, "Carbonium Ions," G. A. Olah and P. von R. Schleyer, Ed., Vol. I, Wiley-Interscience, New York, N. Y., 1968, p 331.

[25] Gillespie's studies [J. Bacon, P. A. W. Dean, and R. J. Gillespie, *Can. J. Chem.*, 47, 1655 (1969)] and our own investigations[10] have shown that with both alkyl fluorides and chlorides in SbF_5–SO_2 solution, the anion is $Sb_2F_{11}^-$

tube (Scientific Glass Apparatus, Bloomfield, N.J.). Temperature is believed to be accurate to within ±0.5°. Analysis of rate processes was achieved by line-shape fitting with computed spectra (Fortran IV coded program based on the Gutowsky-Holm equation).[26] In the case of the 6,1,2-hydride shift, a Fortran IV coded program based on the Gutowsky-Holm equations was used in conjunction with a Univac 1108 computer and a CalComp plotter. Spectra for determination of the 3,2-hydride shift rates were computed using Saunders multisite program as described previously.[4b]

Carbon-13 Nuclear Magnetic Resonance Spectra. ^{13}C spectra were obtained by irradiation of the 100-MHz proton spectrum with a swept 25.1-MHz frequency source (indor method). The detailed techniques employed have been described previously.[6] Modified instrumentation using a Monsanto 3300A digital frequency synthesizer as the 25.1 MHz frequency source were used for some of the most recent measurements. ^{13}C shifts were computed with respect to TMS as a reference and converted to the carbon disulfide standard by adding 194.6 ppm. Negative shifts thus correspond to resonances which are to low field of $^{13}CS_2$.

Acknowledgments. Support of the work by grants of the National Science Foundation, the Petroleum Research Fund administered by the American Chemical Society, and the C. F. Mabery Fund of Case Western Reserve University is gratefully acknowledged.

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(26) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, 25, 1228 (1956).

Carbenoid Species from Methyl and Methylene Halides

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Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received September 10, 1969*

Abstract: Carbenoid species were generated by dehydrohalogenation of methyl halides with phenylsodium and dehalogenation of methylene halides with organolithium reagents. The reactive species *via* both modes of formation undergoes stereospecific addition to carbon–carbon double bonds. Relative rates of cyclopropane formation obtained *via* competition reactions and the absence of carbon–hydrogen insertion products indicate that a carbene complex is involved. Methylenation of olefins *via* methylene halides and organolithium reagents provides a simple route to cyclopropanes in moderate yield. Organolithium reagents, activated by tertiary amine chelating agents, were found to be excellent nucleophiles toward methyl chloride, and give the methylation products in high yield.

Depending on the precursor, mode of formation, and environment, methylene[2] exhibits a wide range of properties and reactivities.[3] In addition to the question of spin multiplicity there is the added problem of whether *free* carbenes or complexed carbenes (carbenoids) are the reactive intermediates. Free carbenes are undoubtedly produced by photolysis or thermolysis of diazo compounds (and ketenes). Carbenoids are the intermediates in most organometallic systems and metal (or metal ion) catalyzed decomposition of diazo compounds. The nature of the intermediate in *trans* methylenation (photolysis of oxiranes, thermolysis of methanocyclodecapentaene, etc.) is yet to be resolved. Carbenoids in general are much less reactive (more selective) than (corresponding) carbenes and they usually do not insert into the C–H bond.

In addition to the more preparatively useful methylenation (*e.g.*, $CH_2/h\nu$, Δ, Cu^0, Cu^+; CH_2I_2/Zn, etc.) techniques,[3a] methylenation of cyclohexene with methyl chloride and phenylsodium was also shown to occur.[1a] It was of interest to extend this earlier work in light of the subtleties that have developed since, by reacting other methyl halides with phenylsodium and to attempt to characterize the nature of the intermediate *via* olefin competition studies.

Results and Discussion

1. Reactions of Methyl Halides with Phenylsodium.

Products obtained from reaction of methyl halides with phenylsodium in the presence of cyclohexene are listed in Table I. Methyl iodide was not investigated, since extrapolation of the results indicated that α-elimination processes would at best be negligible. Cumene and *n*-propylbenzene reported as products earlier[1a] could not be detected.

Toluene is presumably formed *via* nucleophilic displacement of halide by phenylsodium, while methylene generated by dehydrohalogenation is trapped by cyclohexene to give norcarane (Scheme I). Conceivably, methylene could also insert into phenylsodium to give benzylsodium which would then react to give mainly ethylbenzene.[4] However, the data sup-

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[1] (a) A portion of this work has appeared in preliminary form: L. Friedman and J. G. Berger, *J. Amer. Chem. Soc.*, 82, 5758 (1960); (b) support in part by The National Science Foundation (Grant No. GP-3976) is gratefully acknowledged; (c) Allied Chemical Fellow, 1964–1966; (d) taken in part from the Ph.D. Thesis of R. J. H., Case Western Reserve University, 1970, and the Masters Dissertation of J. G. B., New York University, 1961.

[2] A definition of the term methylene is in order. By the term *methylene* or *carbene* we infer *any* formally divalent carbon species capable of transferring the $:CH_2$ group. The designation *carbenoid* refers specifically to complexed carbenes, α-halocarbanions, metal-complexed carbenes, etc.

[3] (a) For recent summaries of the structure and chemistry of carbenes and carbenoids, see W. Kirmse, "Carbenes, Carbenoids, and Carbene Analogs," Verlag Chemie GmbH., Weinheim/Bergstr., Germany, 1969; G. L. Closs in "Topics in Stereochemistry," Vol. 3, E. L. Eliel and N. L. Allinger, Ed., Interscience Publishers, New York, N. Y., 1968; W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964; J. Hine, "Divalent Carbon," The Ronald Press Co., New York, N. Y., 1964; (b) W. R. Moser, *J. Amer. Chem. Soc.*, 91, 1135, 1141 (1969); (c) J. M. Mallan and R. L. Rebb, *Chem. Rev.*, 69, 693 (1969); (d) R. A. Finnegan, *Ann. N. Y. Acad. Sci.*, 159, 242 (1969).

[4] (a) It was suggested by a referee that ethylbenzene might be a result of methylene insertion on toluene.[5] Since no other carbon-insertion products (*e.g.*, with cyclohexane) were observed in the system, it is highly unlikely, although it cannot be completely excluded; (b)