Additions to Bicyclic Olefins. VII. Electrophilic Addition of Hydrogen Chloride and Deuterium Chloride to Norbornene, 2-Methylenenorbornane, and Related Bicyclic Olefins. Evidence for a Carbonium Ion Process and the Capture of Unsymmetrical (Classical) 2-Norbornyl Cations[1]

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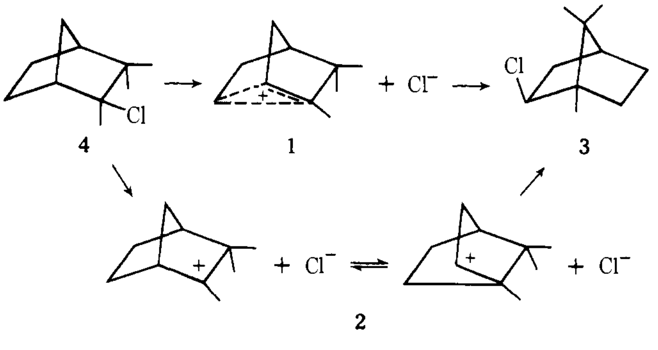
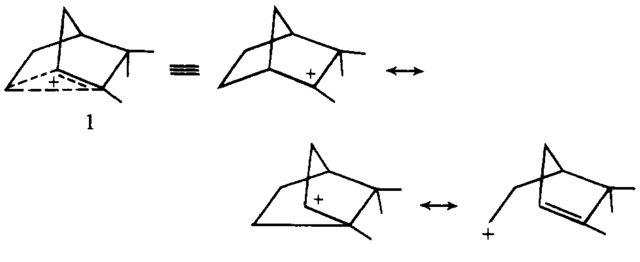
Abstract: The addition of hydrogen chloride to norbornene, 1-methylnorbornene, 2-methylnorbornene, 7,7-dimethylnorbornene, bornylene (1,7,7-trimethylnorbornene), 2-methylenenorbornane, camphene (3,3-dimethyl-2-methylenenorbornane), and α-fenchene (7,7-dimethyl-2-methylenenorbornane) and the addition of deuterium chloride to norbornene, 7,7-dimethylnorbornene, and 1-methyl-2-methylene-d_2-norbornane have been studied in order to ascertain whether in this reaction it is possible to achieve the capture of the classical norbornyl cations before full equilibration. All additions proceed exo-cis, even in the olefins with bulky 7,7-dimethyl substituents. The carbonium ion character of the reaction is established by the formation of both the Markovnikov addition product and the Wagner-Meerwein rearranged product. The essential absence of a cyclic addition process is revealed both by the absence of endo isomer and the low rate ratio, only 2.2, for $k_{\text{norbornene}}/k_{7,7\text{-dimethylnorbornene}}$. The hydrochlorination of norbornene in acetic acid solution gives product containing an approximately constant chloride/acetate ratio under different reaction conditions, indicating that a carbonium ion pair is probably involved which collapses to product in a constant ratio. The hydrochlorination of 1-methyl-d_3-2-methylenenorbornane and the deuteriochlorination of 1-methyl-2-methylene-d_2-norbornane under controlled conditions give the tertiary chloride with incomplete scrambling of the tag, establishing that the reaction cannot be proceeding solely through a symmetrical nonclassical 1,2-dimethylnorbornyl cation. Deuteriochlorination of norbornene yields *exo*-norbornyl-*d* chloride consisting of 57% *exo*-3-*d*- and 41% *syn*-7-*d*-, instead of an equal amount of *exo*-3-*d*- and *syn*-7-*d*-*exo*-norbornyl chloride required by the formation of a symmetrical nonclassical 2-norbornyl cation. Protonation of the double bond in 1-methylnorbornene and bornylene occurs nearly equally at the C2 and C3 positions, failing to show the large directive influence of the 1-methyl substituent anticipated for a reaction proceeding through a σ-bridged intermediate. It is concluded that these hydrochlorination reactions achieve the successful trapping of the classical norbornyl cations prior to full equilibration.

The proposal of a nonclassical (σ-bridged) carbonium ion was first advanced in 1939 by C. L. Wilson and his coworkers.[3] These workers suggested that in the camphene hydrochloride-isobornyl chloride rearrangement the intermediate cation might be considered as a mesomeric species (**1**) instead of the rapidly equilibrating pair of ions (or ion pairs) (**2**) proposed by Meerwein and van Emster.[4]



This idea was further developed by Winstein and Trifan[5] and by Ingold and coworkers[6] based on certain stereochemical and kinetic evidence. The solvolyses of *exo*- and *endo*-norbornyl brosylates,[5] of isobornyl chloride (**3**), and camphene hydrochloride (**4**) were proposed to proceed with participation of the C1-C6 bonding pair to produce cationic intermediates possessing the σ-bridged resonance-stabilized structures **5** and **1**, respectively.[7]

The observation that 2-arylnorbornyl derivatives, which solvolyze to produce classical 2-arylnorbornyl cations, exhibit comparable high exo:endo rate and product ratios demolished the original basis for the proposed σ-bridged structure for the 2-norbornyl cation.[8] Nevertheless, there has been exhibited a major reluctance to surrender this intriguing proposal, and there have been numerous attempts to uncover a new basis to support the existence of σ-bridged 2-norbornyl cations.[7,8]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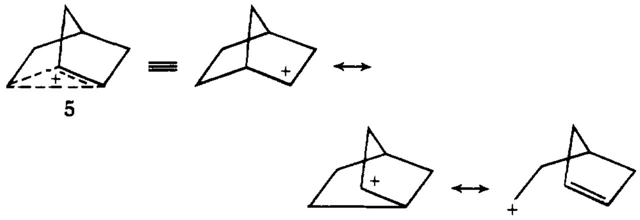
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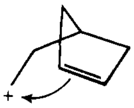
Calculations by Klopman indicated the nonclassical structure to be favored over the classical structure by some 40 kcal mol^{-1}.[9] On the other hand, on the basis of a more refined *ab initio* calculation, Goetz and Allen concluded that the classical structure was more favored by some 5 kcal mol^{-1}.[10]

At one time, empirical calculations based on the Foote-Schleyer correlation appeared to support the σ-bridged formulation.[11] However, this correlation proved incapable of handling steric hindrance to ionization in certain norbornyl derivatives, and it was concluded that the correlation could not resolve the problem.[12]

Then it was argued that the observed degree of racemization in the solvolysis of 2-norbornyl derivatives would require a rate of equilibration of 10^{12} sec^{-1}. It was considered that such a rate was not compatible with formulation as an equilibrating pair of classical cations.[13] However, Fong has recently applied relaxation theory to the problem and has concluded that a rate of equilibration of 10^{12} sec^{-1} is precisely what should be anticipated for a pair of equilibrating classical 2-norbornyl cations.[14]

The introduction of representative substituents in appropriate positions have failed to detect the proposed charge delocalization to the 1 and 6 positions.[8] However, it has been argued that it is a characteristic of nonclassical delocalization that it cannot be detected by such methods.[15]

Meanwhile, the "nonclassical structures" for the 2-norbornyl cation continue to grow. For example, Dewar has suggested a structure (**6**) based on his π-complex concept.[16]



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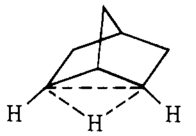
Klopman's calculation favored the edge-protonated structure (**7**) over the face-protonated (**8**) species.[9] Olah, however, has favored a formulation as a corner-protonated nortricyclene (**9**), deleting the dashed double bond of Winstein (**5**).[17a] More recently he has preferred another formulation (**10**).[17b] On the other hand, Traylor has supported a formulation of the 2-norbornyl cation as involving vertical stabilization by the C1–C6 bonding pair but without σ-bridging or movement of the atoms.[18] In other words, the structure would be that of the classical ion **11** but stabilized by an electronic contribution that does not alter the geometry. It should be pointed out that this particular formulation lacks the plane of symmetry possessed by the other proposed structures, **5**, **6**, **7**, **8**, **9**, and **10**. Consequently, there is no lack of formulations for the 2-norbornyl cation. There are lacking only experimental results which require one of these nonclassical formulations over the simple classical one.



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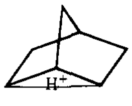

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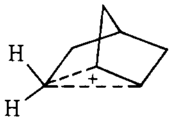

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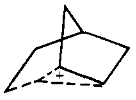

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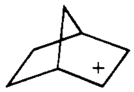

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One might have hoped that the application of various physical methods to the 2-norbornyl cation under stable ion conditions might have solved the problem of the structure of the cation under those conditions. There would then remain only the question as to whether the results could be extrapolated to the structure of the cation under solvolytic conditions. Indeed, Olah and his coworkers have applied pmr,[17a,19] cmr,[17a] Raman,[20] and ESCA[21] to the 2-norbornyl cation and have concluded that it possesses structure **10**. They have further proposed that the cation formed in the solvolysis of 2-norbornyl derivatives proceeds to give the same species but have not as yet discussed the many experiments which have failed to reveal any experimental evidence for the oft postulated charge delocalization from the 2 to the 1 and 6 positions.[8] Nor have they considered Traylor's proposal.[18] Finally, they have ignored Allen's unfavorable calculation, although they make frequent reference to Klopman's "remarkable"[22] calculation.[9]

Major reliance has been placed on the ESCA spectrum in the conclusion that the norbornyl cation is σ bridged under the experimental conditions. The ESCA technique, as applied to carbonium ions in superacid media, is fraught with experimental difficulties.[23] Even more serious is the discovery that such solutions of carbonium ions can involve several equilibria.[24] Consequently, there is no certainty as to the precise solid phase that separates on freezing the solution, the solid phase which is then subjected to ESCA examination.

It has been noted that the original ESCA spectrum[21a] corresponds to a 6:1 distribution of carbon atoms, rather than the 5:2 reported by the authors and required by the σ-bridged formulation.[25] The later ESCA spectrum appears to be that of a mixture.[25]

In spite of these difficulties and uncertainties, not discussed in the publications,[21] the authors have not hesitated to extrapolate their ESCA results in superacid media to the solvolytic field to conclude, ". . . the long standing controversy as to the nature of the norbornyl cation is unequivocally resolved in favor of the nonclassical carbonium ion."[21b,26]

In view of the many conflicting conclusions from the various theoretical and experimental approaches here considered, we decided to undertake a direct experimental probe of the question as to whether the norbornyl cation is a symmetrical (nonclassical) or an unsymmetrical (classical) species. After all, many workers in the field found Goering's solvolysis of optically active 1,2-dimethyl-*exo*-2-norbornyl *p*-nitrobenzoate in 90% aqueous acetone to give alcohols with 9% retention[27a] and the methanolysis of optically active 1,2-dimethyl-*exo*-2-norbornyl chloride to give the methyl ether with 14% retention[27b] more convincing as proof of the classical nature of the 1,2-dimethyl-2-norbornyl cation than our earlier, less direct arguments based on kinetic observations of the effect of the 1-methyl substituent on the rates of solvolysis.[28]

It is clear that the acetolysis of optically active *exo*-norbornyl brosylate fails to provide optically active acetate.[5] It has often been assumed that the rate of collapse of classical secondary ions to products must be very fast, competitive with the rate of rotation about a single bond.[13] Perhaps the difficulty has been that the solvolyses of 2-norbornyl derivatives do not proceed to the formation of the free carbonium ions which can collapse at the postulated fast rate but proceed instead to tight ion pairs[29] with relatively long lives before collapse occurs. In that event, the intermediate could undergo many Wagner–Meerwein interconversions before it is finally captured by solvent.

Indeed, Olah has recently calculated that ΔG^* for the capture of the intermediate by solvent is 9.7 kcal mol^{-1}.[17a] This compares with a value of $\Delta G^* \leq 4$ kcal mol^{-1} estimated for the Wagner–Meerwein interconversion.

We decided to explore processes which involve the formation of carbonium ions but which might not proceed through tight ion pairs of such stability. In fact, the deamination of *exo*- and *endo*-norbornylamine appears to be such a reaction.[30] It proceeds to form *exo*-norbornanol with considerable retention of activity. It was concluded that the reaction does proceed through the formation of the classical

2-norbornyl cation, but it was argued that the exothermic nature of the deamination step made the reaction exceptional so that the result should not be extrapolated to other carbonium ion reactions of the norbornyl system.

The addition of various acids to olefins appears to be a characteristic carbonium ion process.[31] Accordingly, we decided to study the addition of typical acids to norbornene and representative norbornene derivatives. In the present publication, we present our results for the addition of hydrogen chloride to these olefins. The hydrochlorination technique developed in this laboratory[32] provides a simple means for achieving the hydrochlorination of an olefin with minimum exposure of the product to the further action of hydrogen chloride. Consequently, a systematic study of the hydrochlorination of norbornene, methylenenorbornane, and representative methyl-substituted derivatives was undertaken to test the possibility that this reaction might achieve the desired trapping of norbornyl-type cations in an unsymmetrical (classical) form. Attention is called to a study with related objectives, involving the addition of selected acids and other species to 2,3-dideuterionorbornene, which nicely complements this study and lends support to the results and conclusions.[33]

Results

Hydrochlorination and Deuteriochlorination of 2-Methylenenorbornane (12) and Derivatives. 2-Methylenenorbornane (**12**), 1-methyl-2-methylenenorbornane (**13**), camphene (**14**), and α-fenchene (**15**) add hydrogen chloride rapidly at 0 and −78°, the addition being complete in 1.5 to 8 min. In each case, the initial product is the Markovnikov adduct with the chlorine possessing the exo orientation, as indicated by the pmr spectrum. The structure of 2,7,7-trimethyl-*exo*-2-norbornyl chloride (**18**), mp 19-20° (lit.[34] mp 18-20°), was confirmed by its fast rate of ethanolysis and the previous borohydride trapping experiments.[35] Further exposure of these products to hydrogen chloride results in isomerization. Thus, 2-methyl-*exo*-norbornyl chloride (**16**) rearranged to 1-methyl-*exo*-norbornyl chloride (**19**), 1,2-dimethyl-*exo*-norbornyl chloride (**17**) isomerized to the endo isomer **20**,[36] **4** converted into **3**, and **18** rearranged to 2,7,7-trimethyl-*endo*-norbornyl chloride (**21**) and *exo*-fenchyl chloride (**22**) (eq 1-4).

The isomeric chlorides formed in these reactions were identified by their characteristic pmr absorptions (Table I).

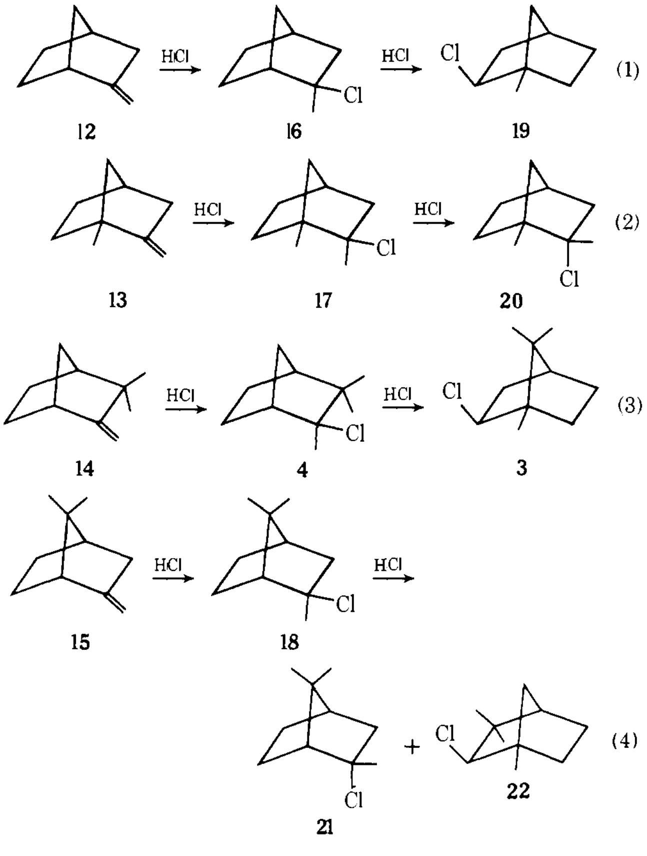
The automatic hydrochlorination technique proved to be very useful to obtain the kinetically controlled chloride *via* hydrochlorination. For example, in diethyl ether solution at −78°, **14** gave **4** in 1.5 min. Following addition of hydrogen chloride, a rapid isomerization took place. In 10 min, the product was almost entirely **3**. Both the addition and the isomerization proceeded less readily in methylene chloride than in ether and still less readily in *n*-pentane.

Like **13**, 1-methyl-d_3-2-methylenenorbornane (**23**) was prepared from 1-methyl-d_3-2-norbornanone using the Wittig reagent produced from methyltriphenylphosphonium bromide and *n*-butyllithium. The isotopic purity of the ketone, 80.7% d_3, 16.7% d_2, and 2.6% d_0, was retained in **23**. However, as a consequence of the incursion of the trans-ylidation equilibrium,[37] the reaction between 1-methylnorbornanone and the reagent from methyl-d_3-triphenylphosphonium iodide and *n*-butyllithium yielded 1-methyl-2-methylene-d_2-norbornane (**24**) containing only 48% of the dideuterio-, 40% of the monodeuterio- and 12% of the undeuterated olefin.

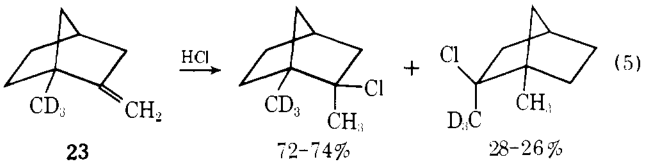
Table I. Pertinent Pmr Chemical Shifts for Norbornyl Chlorides

	δ[a](CH$_3$)						δ[a](α-H)	
Chloride	C-1	C-2	C-3-exo	C-3-endo	C-7-syn	C-7-anti	C-2	C-3
16		1.63						
17	1.23	1.57						
20	1.11	1.50						
4		1.56	1.17	0.97				
18		1.64			1.41	1.05		
21		1.67			1.00	0.97		
26							3.82	
37							4.18	
19	1.24						3.75	
34	1.17							3.88
30			1.12	1.08			3.50	
29					1.31	1.00	3.86	
35[b]					1.06	1.06	4.48	
22	1.15		1.08	1.05			3.40	
3	1.00				1.10	0.87	3.85	
36	0.92				0.92	0.88	4.08	
33	0.88				1.16	0.86		3.83

[a] In carbon tetrachloride solution with tetramethylsilane as internal reference. [b] F. C. Haupt, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1967. The authors thank Professor P. D. Bartlett for this information.



Hydrochlorination of **23** was carried out under different conditions. The per cent scrambling of the tag was calculated from the measured peak height ratio with a correction for the original isotopic impurity in the 1-methyl-d_3 group.[38] When the addition was carried out in ether or methylene chloride solution at 0° for 2 min, the reaction was complete, and the initial product was predominantly 1-methyl-d_3-2-methyl-*exo*-norbornyl chloride, with the distribution of the methyl-d_3 tag corresponding to only 52-56% scrambling (eq 5). Addition of hydrogen chloride to



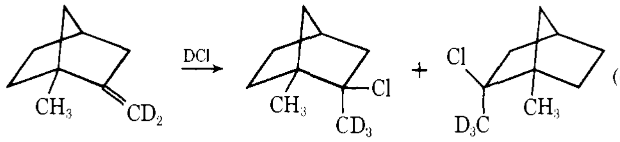
23

72-74%

28-26%

the neat olefin gave chloride which was even less scrambled, 35%. Exposure of the product to hydrogen chloride for a longer period at 0 or $-78°$ results in more or less complete scrambling. The results are summarized in Table II.

Deuteriochlorination of neat **24** at 0° for 2 min gave the corresponding exo chloride, after proper correction of isotopic purity,[38] with 41% scrambling (eq 6).

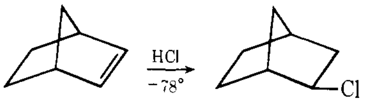


(6)

24 79% 21%

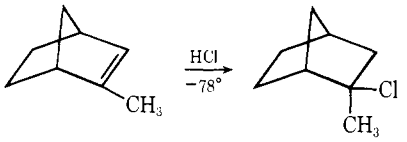
Hydrochlorination of optically active (−)-**13** in pentane at $-78°$ has recently been utilized to produce optically active (−)-**17**.[27] The methanolysis of the resulting chloride proceeds to produce optically active 1,2-dimethyl-*exo*-norbornyl methyl ether, with 14% retention, establishing that the 1,2-dimethylnorbornyl cation can be trapped in its unsymmetrical (*i.e.*, classical) form.[27]

Hydrochlorination and Deuteriochlorination of Norbornene and Derivatives. The rate of hydrochlorination of endo olefins, such as norbornene **25**, was less than that of exocyclic olefins, such as **12**. Nevertheless, the addition proceeded to completion in minutes at $-78°$.[39] Norbornene yielded at least 99.5% *exo*-norbornyl chloride (**26**) in diethyl ether, methylene chloride, or *n*-pentane.[40] Similarly, 2-methylnorbornene (**27**) gave **16**, and 7,7-dimethylnorbornene (**28**) produced 90% of 7,7-dimethyl-*exo*-norbornyl chloride (apoisobornyl chloride **29**) and 10% of 3,3-dimethyl-*exo*-norbornyl chloride (**30**) as revealed by pmr spectra (Table I) (eq 7-9).



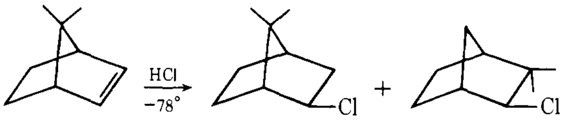
(7)

25 **26**, ≥99.5%



(8)

27 **16**



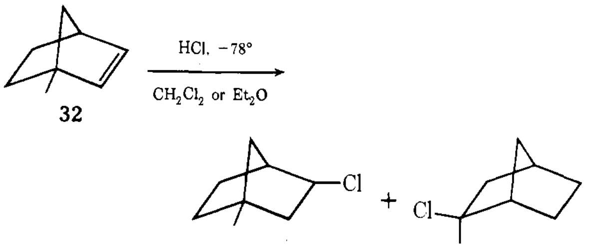
(9)

28 **29**, 90% **30**, 10%

Table II. Per Cent Scrambling in the Hydrochlorination of 1-Methyl-d_3-2-methylenenorbornane

Solvent	Temp, °C	Time, min	Scrambling, %
Ether	0	1	53
Ether	0	2	56
Ether	0	20	73
Ether	0	40	82
Ether	0	60	97
Ether	0	120	100
CH_2Cl_2	0	2	52
CH_2Cl_2	0	20	65
CH_2Cl_2	−20	2	55
CH_2Cl_2	−78	2	84
CH_2Cl_2	−78	10	100
Neat	0	1	35
Neat	0	2	42

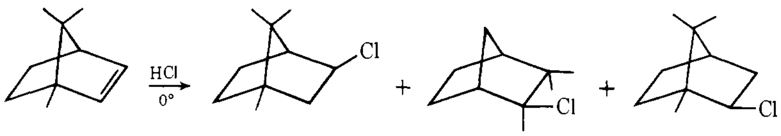
The results of the hydrochlorination of bornylene (**31**) and of 1-methylnorbornene (**32**) are especially interesting. The addition product from **31** contained 45% of epiisobornyl chloride (**33**) and 55% of a mixture of **3** and **4**. Longer reaction times or higher concentrations of hydrogen chloride[41] result in an increase in **3** at the expense of **4**, but there is no change in the yield of **33**[38] (eq 10). Hydrochlorination of **32** under the same conditions also yielded a mixture of about 45% of 4-methyl-*exo*-norbornyl chloride (**34**) and 55% of **16** as indicated by pmr analysis[38] (eq 11). In this case, the tertiary product **16** is less readily converted into the secondary than is the case for **4**. Consequently, essentially pure tertiary **16** can be obtained.



32

(11)

34, 45% **16**, 55%



(10)

31		33	4	3
CH_2Cl_2	4.5 min	44%	48%	8%
	10.0 min	45%	20%	35%
Et_2O	2.5 min	46%	24%	30%

No significant amount of endo product, such as 7,7-dimethyl-*endo*-norbornyl chloride (**35**) or bornyl chloride (**36**), has been detected by pmr, based on the absence of lower field absorption by the exo-α-methine proton.[42]

It was known that **4** would isomerize to **3** and **16** would isomerize to **19** on exposure to hydrogen chloride (eq 1 and 3), but **3** and **19** are stable to the reaction conditions. Consequently, the tertiary chlorides **4** and **16** must be the initially produced products, with some rearrangement of **4** to **3** occurring subsequently.

The addition of deuterium chloride to **28** in diethyl ether or in methylene chloride at $-78°$ was complete in 2-3 min. The product was also 90% of **29**-d_1 and 10% of the Wagner-Meerwein rearranged product **30**-d_1. The structure of **29**-d_1 was assigned as *exo-3-d*-**29** from the distinct doublet (J = 8.5 Hz) at δ 3.86, which is consistent with H_{endo}–H_{endo} coupling.[43-45]

Deuterium chloride added to norbornene (**25**) at $-78°$ to produce *exo*-norbornyl-d_1 chloride (**26**-d_1, 97-99% isotopically pure by mass spectrum), in which the distribution of deuterium could be estimated from quantitative pmr analysis both on the chloride and on the olefin produced by E2 elimination of the chloride. In 30% benzene solution (v/v), **26** or **26**-d_1 exhibited a fairly well-resolved pmr spectrum. Our preliminary analysis based on 60-MHz spectral analy-

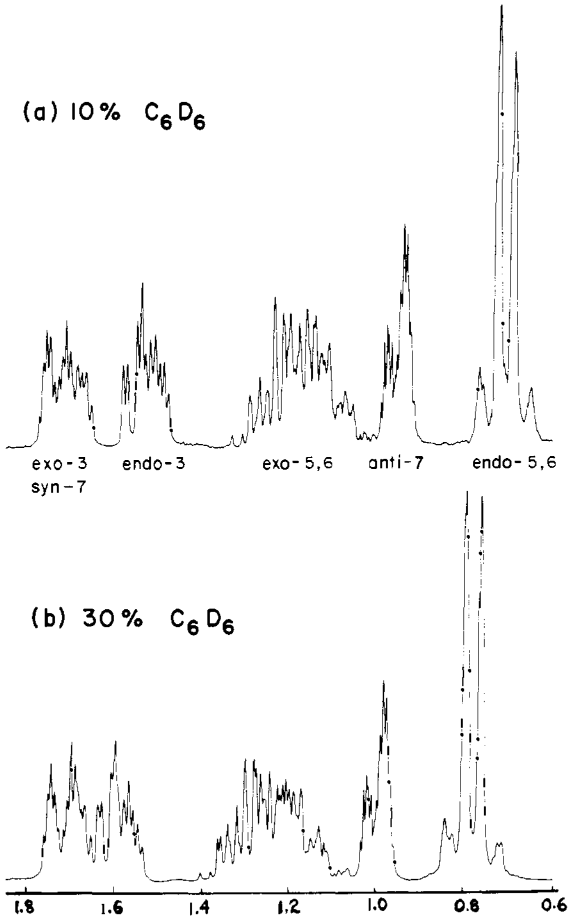


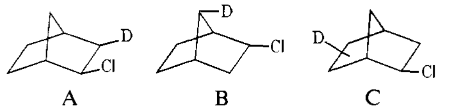
Figure 1. Partial 220-MHz pmr spectra of *exo*-norbornyl-*d* chloride.

sis showed that the adduct consisted of 60% of *exo-3-d-* **26**, 34% of Wagner–Meerwein rearranged product *syn-7-d-* **26**, and 6% of the hydride-shifted product. Although a precise estimation may be hampered by peak overlappings, excellent agreement was realized between the analysis on chloride and on olefin.

Reinvestigation has been undertaken by employing pmr analysis at higher field. At 100 MHz or even at 220 MHz, the spectrum is still not completely resolved. The 220-MHz spectrum of **26** taken for a 10% (v/v) benzene solution[46] shows a complete separation of the endo-3 protons and the syn-7 (Figure 1a). However, the spectrum taken for a 30% (v/v) benzene solution has the advantage that the lower one-half of the signal of the syn-7 proton is almost completely separated (Figure 1b). The assignment of the apparent quintet between δ 1.73 and 1.80 to the lower one-half of the syn-7 proton is confirmed by its identical splitting pattern with that of the anti-7 proton at δ 0.99. From careful measurement of integration curves above appropriate areas in both spectra compared with those of the undeuterated chloride,[38,47] we may conclude that the deuterium distribution is 57% at exo-3, 41% at syn-7, and 2% at exo-5,6. The results obtained from various analyses are summarized in Table III. Similar results have also been observed in other laboratories.[48] Consequently, it appears to be solidly established that the addition of deuterium chloride produces not the 50:50 distribution required by the nonclassical ion **5** but considerably more of the exo-3-*d* than of the syn-7-*d* isomer.

Hydrochlorination of norbornene (**25**) in acetic acid gave both *exo*-norbornyl chloride (**26**) and *exo*-norbornyl acetate (**38**). The chloride was stable, and the ratio of **26**/**38** was essentially constant under various conditions (Table IV). Deuteriochlorination of norbornene (**25**) in acetic acid-d_4 at 25° also yielded 91% of exo chloride and 9% of exo acetate. More strikingly, the deuterium distribution in **26**-d_1 was 57% exo-3, 41% syn-7, and 2% exo-5,6, essentially the same as the distribution observed in methylene chloride at −78°. The tetradeuterioacetate, after glpc isolation, was reduced to *exo*-norbornanol-d_1 with lithium aluminum hydride. Pmr analysis indicated the deuterium distribution was 56% exo-3, 40% syn-7, and 4% exo-5,6.[38,50] Consequently, even the acid-catalyzed addition of acetic-d_4 acid at 25° (under conditions where acetic acid itself exhibits no measurable rate of addition) yields product with excess retained structure.

Table III. Analyses of the Deuterium Distribution in *exo*-Norbornyl-*d* Chloride Produced by the Addition of Deuterium Chloride to Norbornene



Method of analysis	*exo*-3-*d*-**26** (A)	*syn*-7-*d*-**26** (B)	*exo*-5,6-*d*-**26** (C)
220-MHz spectrum of **26**-d_1	57	41	2
100-MHz spectrum of **26**-d_1	58	38	4
60-MHz spectrum of **26**-d_1	61	32	7
60-MHz spectrum of olefin from **26**-d_1	59	36	5

Table IV. Hydrochlorination of Norbornene in Acetic Acid

Concn of **25**, *M*	Temp, °C	**26**/**38**[a]
0.5	25	91.0/9.0
1	25	91.3/8.7
2	35	90.6/9.4
2	10	91.1/8.9

Competitive Hydrochlorination of 25 and 28. Addition of hydrogen chloride to a mixture of **25** and **28** was carried out in methylene chloride at 0° for 5 min. Only 10% or less of the olefins was converted. The products, **26**, **29**, and **30**, were hydrolyzed in the presence of silver nitrate at room temperature. The hydrolysis product from **26** was *exo*-norbornanol. The product from 90% **29** and 10% **30** was a mixture of 63.4% of 7,7-dimethyl-, 24.8% 5,5-dimethyl-, 9.1% of 3,3-dimethyl-, and 2.7% of 6,6-dimethyl-*exo*-norbornanols, similar to the product obtained from hydrolysis of the corresponding brosylates.[51]

The ratio of *exo*-norbornanol to dimethyl-*exo*-norbornanols was found as 1.83 by glpc technique. After being corrected by a factor of 1.2 derived from hydrolysis of standard mixtures, the relative rate of hydrochlorination of **25**:**28** was calculated as 2.2. The data are summarized in Table V.

Discussion

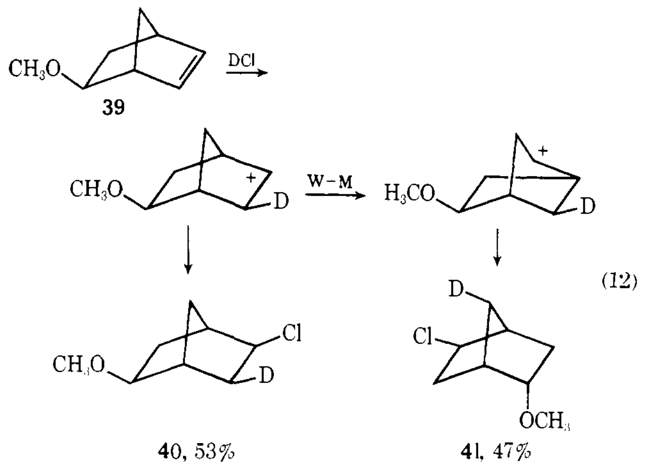
The electrophilic addition of hydrogen chloride to olefins has long been considered to involve intermediates with carbonium ion character.[31] Recent studies have proposed different interpretations of the precise nature of the reaction mechanism. (However, it should be recognized that in some cases the proposed interpretation has been introduced primarily to salvage the nonclassical 2-norbornyl cation as an intermediate.) Thus, it has been proposed that the addition may involve a classical carbonium ion,[33,52-55] or a nonclassical carbonium ion,[56,57] or a π complex,[58,59] or a concerted molecular addition,[56,57,60,61] or a trimolecular addition process (AdE_3),[61-63] or a dual mechanism involving both a nonclassical carbonium ion and a concerted molecular addition,[56,57] or a classical carbonium ion and a termolecular addition process.[63] Moreover, there is evidence that

Table V. Competitive Hydrochlorination of Norbornene and 7,7-Dimethylnorbornene

Starting olefins, mmol		Final product ratio, *exo*-norbornanol/ dimethyl-*exo*-norbornanol
25	**28**	
0.139	0.269	0.972
0.262	0.234	1.99
0.863	0.616	2.48
0.230	0.541	0.806

the structure of the olefin plays a role in the reaction mechanism.[54,62,63]

The difficulties introduced into the interpretation of data by preconceived rigid positions on the nonclassical ion question is nicely illustrated by a recent study of the addition of deuterium chloride to *exo*-5-methoxynorbornene[64] (**39**). The author reports that the addition proceeds to produce 53% of *exo*-2-methoxy-*exo*-5-chloro-*exo*-6-deuterionorbornane (**40**) and 47% of the isomeric *endo*-2-methoxy-*exo*-5-chloro-*anti*-7-deuterionorbornane (**41**). He interprets the reaction as proceeding through a nonclassical intermediate even though this would favor formation of the two isomers in equal amounts. On the other hand, the favored formation of the unrearranged isomer is in accord with the capture of the cation before it has become fully equilibrated (eq 12).



(12)

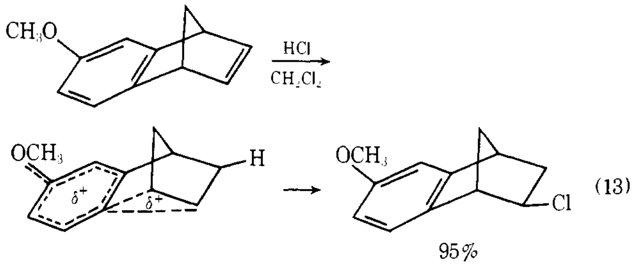
The preferred addition of the proton or deuterion to the 3 position is readily understood in terms of the inductive effect of the methoxy substituent in favoring formation of the charge at the more remote 2 position. Were a nonclassical ion to be formed, with delocalization of charge to the 4 and 5 positions, favored protonation at the 2 position would have been anticipated. (However, see ref 15.)

Recent studies of the addition of hydrogen chloride in acetic acid to phenylallene and its derivatives[65] and to 1-phenylbutadienes and their derivatives[66] indicate how simple the process can be when the nonclassical ion problem is not involved. These authors conclude that the reactions proceed through well-defined carbonium ions. The reactions follow the $\rho\sigma^+$ relationship and reveal ρ values of -4.20[65] and -2.98,[66] respectively. Clearly these reactions have all of the characteristics of simple carbonium ion processes.

An objective examination of the characteristics of the addition of hydrogen chloride to norbornene and related strained olefins[67] supports the conclusion that these reactions must proceed through the formation of carbonium ion intermediates.

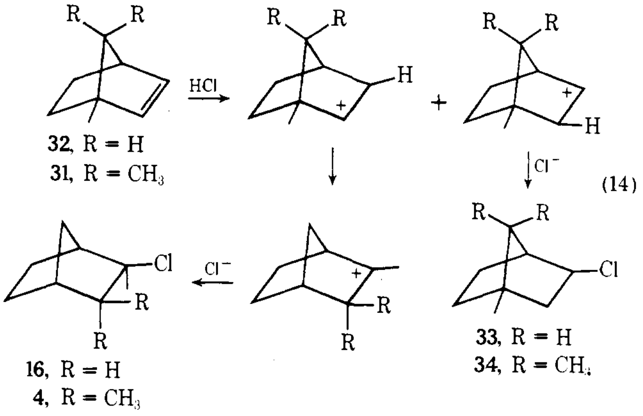
(1) In the addition of hydrogen chloride to olefins with unsymmetrical carbon-carbon double bonds, such as **12**, **13**, **14**, **15**, and **27**, the overwhelming formation of Markovnikov adducts supports the carbonium ion character of such reactions. At the very least, the powerful directive influence indicates that a significant positive charge must be developed at the tertiary carbon atom in the intermediate.[31,68]

(2) The presence of π participation in the 6-methoxybenzonorbornen-2-yl system has been well established.[69,70] The hydrochlorination of 6-methoxybenzonorbornadiene in methylene chloride at 0° yields 95% of 6-methoxy-*exo*-benzonorbornenyl and 5% of 7-methoxy-*exo*-benzonorbornenyl chloride as the kinetically controlled product.[70b] This considerable directive influence on the addition of hydrogen chloride indicates that a carbonium ion intermediate is involved in the reaction (eq 13). (This large directive effect should be compared with the insignificant influence of the 1-methyl substituent in **32**.)



(13)

(3) A concerted molecular addition of hydrogen chloride to **31** or **32** should give two isomeric secondary chlorides **3** and **33** or **19** and **34**, respectively, since these secondary chlorides are stable to the reaction conditions. However, the secondary chloride at C3 and the tertiary chloride at C2 were obtained as the kinetic controlled products (eq 10 and 11) in approximately equal amounts. This result is in line with the formation in approximately equal amounts of each of the pair of secondary carbonium ions, followed by a rapid rearrangement to the tertiary carbonium ion where that can be achieved by a simple Wagner-Meerwein shift (eq 14). (The direct formation of the tertiary cation is not postulated since that should result in the predominant formation of that isomer, as observed in the hydrochlorination of 6-methoxybenzonorbornadiene.)



(14)

(4) Cyclic addition of molecular hydrogen chloride to norbornene has been postulated in several recent publications[56,57,60,61] as a means of accounting for the unequal formation of the two isomers, such as *exo*-3-*d*-**26** and *syn*-7-*d*-**26** (Table III), while retaining the postulated formation of the symmetrical nonclassical intermediate **5**. However, the data available appear to refute this argument. Typical cyclic additions, such as epoxidation and hydroboration, proceed readily with norbornene (**25**) to give products with

exo-cis orientation. However, such cyclic additions to 7,7-dimethylnorbornene (**28**) proceed with great difficulty, giving predominantly the endo isomers.[50] The relative rates of exo addition, $k_{exo\text{-norbornyl}}/k_{7,7\text{-dimethyl-}exo\text{-norbornyl}}$, are quite high, in the range of 480–1820, for such cyclic additions.[71]

On the other hand, the 7,7-dimethyl substituents influence both the rates and the stereochemistry of two-stage noncyclic additions relatively little. Consequently, such additions would be expected to proceed with 7,7-dimethylnorbornene with both stereochemistry and rates that are very similar to those observed for norbornene itself (except for reagents with exceptionally large steric requirements).

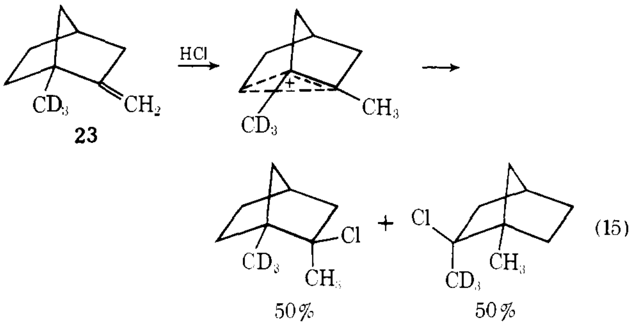
The present results establish that hydrogen chloride adds exo-cis to both norbornene and 7,7-dimethylnorbornene. Moreover, the rate of exo addition to 7,7-dimethylnorbornene is reduced by a small factor of only 2.2. Consequently, we conclude that the addition of hydrogen chloride to these bicyclic olefins does not involve a cyclic addition of molecular hydrogen chloride.

(5) Fahey and McPherson[54] studied the hydrochlorination of styrene in acetic acid. They established that the chloride/acetate ratio varied little with temperature or with concentration of hydrogen chloride. The reaction was considered to proceed with a rate-limiting protonation of the olefin by hydrogen chloride leading to the formation of a carbonium-chloride ion pair. The data in Table IV reveal very similar phenomena. Thus the hydrochlorination of norbornene in acetic acid gives some 91% of the exo chloride **26** and 9% of the exo acetate **38** over a range of conditions. Therefore, it is highly probable that a carbonium ion pair is also involved here.

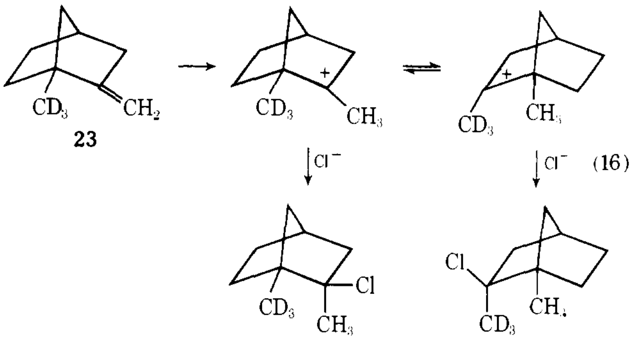
(6) Finally, both the addition of acetic acid and of phenol[33] to norbornene under the influence of acids gives unequal distribution of isomers but cannot possibly involve any reasonable molecular addition process.

In addition to these experimental facts, the molecular orbital symmetry rules also are unfavorable for a one-step molecular addition of hydrogen chloride to olefins.[72] A trimolecular trans addition is also unfavorable in view of the experimental fact that the exo-cis adduct is formed. Consequently, we may conclude with confidence that the addition of hydrogen chloride to norbornene and 2-methylenenorbornane and their methyl derivatives must proceed through a carbonium ion mechanism, with other reaction paths under the conditions studied being insignificant. Accordingly, we now turn our attention to a consideration of the data to see whether it can assist us in deciding whether these carbonium ion intermediates are classical or nonclassical (*i.e.*, σ bridged).

Consider the possibility that the 1,2-dimethylnorbornyl cation possesses a symmetrical nonclassical structure. Then the hydrochlorination of a tagged 1-methyl-2-methylenenorbornane would be expected to proceed through this symmetrical intermediate to produce a product with complete scrambling of the tag. For example, **23** would give an equal amount of two chlorides (eq 15). However, the product obtained possessed a distribution of the methyl-d_3 tag far from 100% scrambling (eq 5, Table II). Similarly, deuteriochlorination of **24** yielded predominantly 1-methyl-2-methyl-d_3-*exo*-norbornyl chloride (eq 6). Therefore, the incomplete scrambling is not the result of an isotope effect. These results are confirmed by the successful synthesis of optically active 1,2-dimethyl-*exo*-norbornyl chloride by hydrochlorination of the olefin.[27b] The above results cannot be rationalized in terms of the formation of a symmetrical nonclassical intermediate, but they are consistent with the proposal of a rapidly equilibrating pair of classical ions[73] with the addition of chloride ion being somewhat faster than the equilibration (eq 16). This position has also been confirmed by Goering and his coworkers in the solvolysis of optically active 1,2-dimethyl-*exo*-norbornyl *p*-nitrobenzoate[27a] and chloride.[27b]

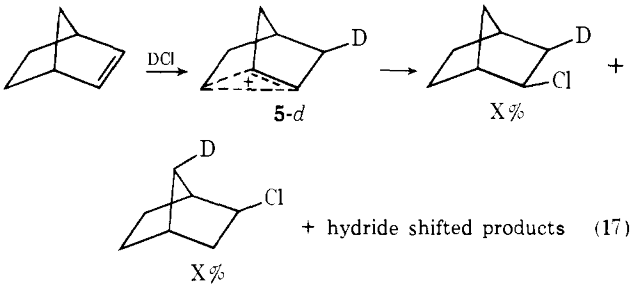


(15)



(16)

At the present time, numerous variations have been proposed for the nonclassical "structure" of the 2-norbornyl cation: **5**, **7**, **8**, **9**, and **10**. All of these possess a plane of symmetry. Consequently, any of these structures produced in the hydrochlorination reaction should produce equal amounts of the two isomers (eq 17.)[74]



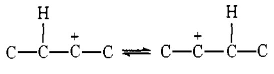
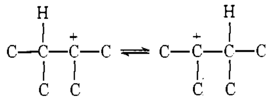
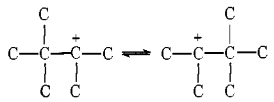
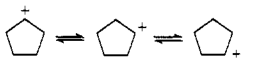
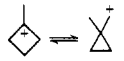
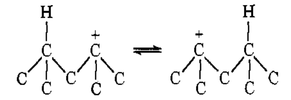
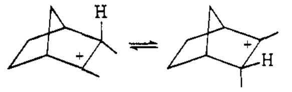
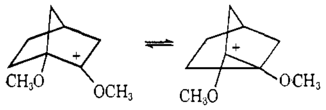
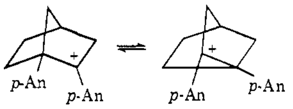
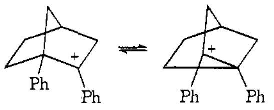
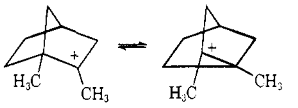
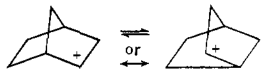
(17)

It is evident that such a distribution was not realized in the experiments here described. Under very different conditions, methylene chloride solution at −78° or acetic acid solution at room temperature, the deuteriochlorination products revealed an unequal distribution of deuterium at the 3 and 7 positions. Obviously, these results are incompatible with the position that the nonclassical norbornyl cation, whatever its structure, **5**, **6**, **7**, **8**, **9**, or **10**, is the intermediate involved.

On the other hand, the results can be accommodated by a mechanism involving a rapidly equilibrating pair of classical carbonium ions which are captured before they have become fully equilibrated. The same conclusion was reached by Stille and Hughes as a result of their related study.[33]

It is, of course, possible to account for the present results by postulating the concurrent formation as intermediates of both the nonclassical and the classical ion in comparable quantities. However, nothing is gained by introducing this additional complexity into the mechanism in the absence of any unambiguous experimental evidence requiring the presence of a nonclassical intermediate.

Table VI. Representative Equilibrating Classical Cations under Stable Cation Conditions

Cation	Structure	Assignment	Ref
2-Butyl		Equil class	Brouwer[75] Olah[76] Saunders[77]
2,3-Dimethyl-2-butyl		Equil class	Brouwer[75] Olah[76] Saunders[77]
2,3,3-Trimethyl-2-butyl		Equil class	Brouwer[75] Olah[76] Saunders[77]
Cyclopentyl		Equil class	Brouwer[75] Olah[76]
1-Methylcyclobutyl		Equil class	Saunders[a]
2,4-Dimethyl-2-pentyl		Equil class	Brouwer[75] Saunders[77]
2,3-Dimethyl-2-norbornyl		Equil class	Olah[b] Sorensen[c]
1,2-Dimethoxy-2-norbornyl		Equil class	Nickon[d]
1,2-Di-*p*-anisyl-2-norbornyl		Equil class	Schleyer[e]
1,2-Diphenyl-2-norbornyl		Equil class	Olah[f]
1,2-Dimethyl-2-norbornyl		Equil class	Olah[g]
2-Norbornyl		Nonclassical	Olah[17,20,21]

[a] M. Saunders and J. Rosenfield, *J. Amer. Chem. Soc.*, **92**, 2548 (1970). [b] G. A. Olah and G. Liang, *ibid.*, **96**, 189 (1974). [c] A. J. Jones, E. Huang, R. Haseltine, and T. S. Sorensen, *ibid.*, in press. [d] A. Nickon and Y. Lin, *ibid.*, **91**, 6861 (1969). [e] P. v. R. Schleyer, D. C. Kleinfelter, and H. G. Richey, Jr., *ibid.*, **85**, 479 (1963). [f] G. A. Olah and G. Liang, *ibid.*, **96**, 195 (1974). [g] G. A. Olah, J. R. DeMember, C. Y. Lui, and R. D. Porter, *ibid.*, **93**, 1442 (1971).

The fact is that the present results cannot be acccounted for in terms of the sole formation of a nonclassical intermediate. They are readily accounted for in terms of the formation of a rapidly equilibrating pair of classical ions.[14,27,33]

Equilibrating Cations under Stable Cation Conditions

Recent advances in the preparation and study of cations in super acids have greatly advanced our knowledge of rapidly equilibrating cations.[75-77] Indeed, many cations, such as 2,3,3-trimethyl-2-butyl, which can be generated and captured in a solvolytic process without equilibration[78] are revealed to be rapidly equilibrating classical cations under stable ion conditions.

A representative series of such ions are listed in Table VI.

It was an unexpected development that so many cations which can be formed and captured without significant equilibration in solvolytic processes are observed under stable ion conditions to exist as rapidly equilibrating pairs or sets of ions even at very low temperatures. It appears that the new theoretical analysis made by Fong[14] may provide a reasonable explanation for this phenomenon.

In any event, Table VI may place things in proper perspective. If one accepts Olah's evidence and arguments,[17a,b,20,21] the norbornyl species appears to be perhaps the last of the symmetrical nonclassical ions, whatever its structure, **5**, **6**, **7**, **8**, **9**, or **10**. However, those who continue to favor this structure cannot be permitted to continue to ignore the evidence that the deamination of *exo*-norbornylamine[30] and the hydrochlorination of norbornene, as presented in this study and others,[33] must proceed through a species which cannot be the symmetrical nonclassical cation, **5**, **6**, **7**, **8**, **9**, or **10**.

Experimental Section

Material. Reagent grade chemicals were used without purification unless otherwise mentioned. Norbornene and camphene were commerical products purified by sublimation. 7,7-Dimethylnorbornene and α-fenchene were prepared as described previously.[79] The preparation of other olefins will be discussed later.

Gas Chromatography. For analytical purpose, a Perkin-Elmer Model 226 instrument fitted with 150 ft × 0.01 in. Golay column or a Varian Aerograph Model 1200 instrument fitted with 6 ft × ⅛ in. column packed with appropriate liquid phases was employed. The *exo*- and *endo*-norbornyl chlorides were analyzed using a 20 ft × 0.25 in. 5% Zonyl E-7 column with Hewlett-Packard Model 5750 instrument. For preparative purpose, an Aerograph Model A90C instrument was used.

Pmr Analysis. The 60-MHz spectra were taken with a Varian A-60 or A-60A spectrometer. The 100-MHz spectra were run on a Varian HA-100 spectrometer. We are grateful to Professor L. M. Stock of the University of Chicago for providing this instrument for our study. The 220-MHz spectra were taken by Mr. L. W. Cary of Varian Associates.

Preparation of 1-Methyl-2-methylenenorbornane (13). A 300-ml three-necked flask fitted with a mechanical stirrer, a reflux condenser with drying tube, and a pressure-equalizing dropping funnel with nitrogen inlet tube, was flame-dried under nitrogen. To this, 23 g (65.0 mmol) of methyltriphenylphosphonium bromide and 80 ml of tetrahydrofuran were added. Then, 42 ml of 15% *n*-butyllithium solution in hexane was slowly added with a syringe. This reaction was slightly exothermic, and the triphenylphosphinemethylene formed almost instantaneously, as indicated by the formation of a brown solution. The solution was warmed in a 70° bath, and a solution of 6.2 g (50 mmol) of 1-methylnorbornanone in 10 ml of tetrahydrofuran was added dropwise. Then the resultant mixture was allowed to heat under reflux for 6 hr. During this period, solid material was precipitating from the solution. After that, the excess ylide (as shown by the reddish brown color of the solution) was destroyed by adding water. The mixture was then cooled in an ice bath, and the precipitate was filtered through filter-aid. The solution was distilled until most of the solvent was removed. More solid material precipitated, and the mixture was cooled in an ice bath. Twenty milliliters of chilled hexane was added, and the precipitate was filtered through Filter-aid. Again the solvent was removed by distillation. Then 5 ml of hexane was added, and the precipitate was separated as before. Next, 5 ml of *n*-dodecane (bp 214°) was added, and the mixture was cooled in an ice-bath. All the inorganic substances were separated after this treatment. 1-Methyl-2-methylenenorbornane was isolated by fractional distillation through a 10-cm Vigreux column at atmospheric pressure in 70% yield: bp 135–137°; n^{20}D 1.4680; ir (film) 6.01 ($C{=}C$ stretching), 11.48 μ ($C{-}H$ out-of-plane deformation of $C{=}CH_2$); pmr δ 1.21 (singlet, CH_3), 4.55 ($C{=}CH_2$). This sample was 98–99% pure and could be purified by glpc on a 4 ft × ⅛ in. column of 20% tricresyl phosphate on Celite at 80°.

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.50; H, 11.55.

Preparation of 1-Methyl-*d*$_3$-2-methylenenorbornane (24). Following the same procedure as described before, 1-methyl-d_3-norbornanone yielded 70% of 1-methyl-d_3-2-methylenenorbornane: bp 135–138°; n^{20}D 1.4682. Mass spectral analysis at 9.02 eV indicated it contained 16.7% 1-methyl-d_2- and 2.4% 1-methyl-d_1-2-methylenenorbornane.

Preparation of 2-Methylenenorbornane (12). Application of the Wittig reaction to norbornanone produced 2-methylenenorbornane, bp 121–123° [lit.[80] bp 123° (760 mm)], in 74% yield.

Preparation of Bornylene (31). α-Pinene, 34 g (0.25 mol), in 15 ml of methylene chloride was hydrochlorinated at 0° for 3 hr. The crude bornyl chloride, 47 g, was isolated after the usual work-up and was then eliminated with sodium 2-cyclohexylcyclohexoxide in 2-cyclohexylcyclohexanol at 100° overnight. Then bornylene, contaminated with some camphene, was distilled at 148° (748 mm). Further purification by glpc using a tricresyl phosphate column at 95° yielded pure **31**, mp 111–112° (lit.[81] mp 112–112.5°).

Preparation of 2-Methylnorbornene (27). A 2-g sample of 2-methyl-*endo*-norbornanol was dissolved in 20 ml of ice-cold dry pyridine and treated with 5 ml of phosphoryl chloride. After standing overnight at 0°, the mixture was poured into ice, and the product was extracted into petroleum ether (35–37°). Then the pyridine was washed out by water. Glpc showed two olefins in a ratio of about 7:3. The minor component was isolated by the use of tricresyl phosphate column at 65°, n^{20}D 1.4620 (lit.[82] n^{20}D 1.4621). The pmr spectrum showed only one olefin proton at δ 5.45.

Preparation of 1-Methylnorbornene (32). 2-*exo*-Methyl-*endo*-norbornanol, 10 g, was treated with hydrogen chloride and stannic chloride at 0° overnight. This mixture was washed with water, and the organic product was isolated as usual. Pmr spectrum indicated the composition was about 10% of **16** and 90% of **19**. The chloride mixture was then solvolyzed in aqueous tetrahydrofuran at room temperature for 2 hr. The solvolysis product was isolated and was treated with sodium 2-cyclohexylcyclohexoxide in 2-cyclohexylcyclohexanol at 120°. 1-Methylnorbornene was separated by extraction with silver nitrate. Pure **32** was obtained by distillation, bp 103–105°; n^{20}D 1.4520 (lit.[83] bp 104°, n^{22}D 1.4519); pmr δ 1.32 (singlet, CH_3), 5.69 and 5.92 (1 H each, olefinic protons).

Preparation of Methyl-*d*$_3$-triphenylphosphonium Iodide. A chilled solution of 55 g (210 mmol) of triphenylphosphine in 400 ml of ether was added dropwise to a solution of 30 g of methyl-d_3 iodide (207 mmol) in 100 ml of ether at ice-bath temperature during 1 hr. Then it was kept at room temperature for 4 days. The resultant solid was isolated and was carefully dried at boiling toluene temperature (1 mm). The dry product, melting at 185–186° (lit.[84] mp 184–186°), was obtained in 94% yield (79 g).

Preparation of 1-Methyl-2-methylene-*d*$_2$-norbornane (24). Using the same method as that for the synthesis of 1-methyl-2-methylenenorbornane, 1-methylnorbornanone reacted with triphenylphosphinemethylene-d_2 to give 1-methyl-2-methylene-d_2-norbornane. Mass spectral analysis at 9.02 eV showed it was actually a mixture containing 48% of 1-methyl-2-methylene-d_2-, 40% of 1-methyl-2-methylene-d_1-, and 12% of 1-methyl-2-methylene-d_0-norbornane.

Hydrochlorination Procedure. The standard hydrochlorination technique[32] was followed with some modifications. For controlled experiments, the apparatus was flame-dried under nitrogen and then was flushed with hydrogen chloride. Both the reaction flask and the olefin, either neat or in solution, were cooled to the desired temperature for 10–20 min before mixing. After the estimated amount of hydrogen chloride had been absorbed, the reaction was stopped, and the reaction flask was immediately attached to a vacuum line at about 0.5 mm to remove the excess hydrogen chloride and solvent. The reaction flask was always kept at the same temperature as during the hydrochlorination. For hydrochlorination in acetic acid, the product was poured into chilled sodium carbonate solution, and the organic product was extracted with pentane.

Deuteriochlorination. A method similar to that for hydrochlorination was utilized. Deuterium chloride was generated from addition of deuterium oxide (99.5%) to phosphorus trichloride cooled in an ice bath. Two Dry Ice-acetone traps were inserted between the gas-generating flask and the reaction flask for deuteriochlorination to trap the phosphorus trichloride. The generation of deuterium chloride was not fast enough to compensate for the pressure drop due to the absorption by olefin. Therefore, excess deuterium oxide was added to phosphorus trichloride to provide a continuous supply of deuterium chloride. The reaction was stopped at the time which was required for the completion of hydrochlorination under the same conditions, and the product was isolated, as described before.

Structure of the Chlorides. The hydrochlorination products were confirmed to have the assigned structure from their pmr spectra (Table I), melting points, and rates of ethanolysis.

The rates were measured as usual at 25.00 ± 0.02°. The products were titrated by 0.02695 *N* potassium hydroxide using methyl red–bromocresol green as indicator. A plot of log $(a - x)$ against time gave a slope equal to $k_1/2.303$. For α-fenchene hydrochloride, owing to the fast reaction rate of ethanolysis at 25°, it was very difficult and also very unsuitable to titrate aliquots. Thus, the reaction flask was used as the titrating flask and potassium hydroxide in absolute ethanol was used as titrant (*ca.* 0.02 *N*). In a water bath maintained at 25.00 ± 0.02° was placed a 250-ml erlenmeyer flask containing approximately 150 ml of absolute ethanol and a few drops of mixed indicator (bromocresol green and methyl red). Then approximately 0.2 mmol of mixed chloride was added with stirring. At certain time intervals, a small excess of potassium hydroxide solution (also kept at about 25°) was added, and the time required to reach the end point was recorded.

Hydrochlorination of 2-methylenenorbornane gave 2-methyl-*exo*-norbornyl chloride, mp 22-24° (lit.[85] mp 25°), $k_1{}^{25} = 2.97 \times 10^{-5}$ sec^{-1} (lit.[86] 3.0×10^{-5} sec^{-1}). The purity by titration was over 99%.

Treatment of **13** with dry hydrogen chloride yielded 1,2-dimethyl-*exo*-norbornyl chloride, mp 120-122° (lit.[87] 123-124°). The purity by titration was 99%.

The rate of ethanolysis of the hydrochlorination product from α-fenchene, mp 19-20°, was constant over more than 80% reaction, $k_1{}^{25} = 8.5 \times 10^{-4}$ sec^{-1} (lit.[88] $k_1{}^{25} = 7.9 \times 10^{-4}$ sec^{-1}).

Addition of hydrogen chloride to **28** at −78° yielded a solid melting at 55-56° (lit.[89] mp 53-54° for pure 7,7-dimethyl-*exo*-norbornyl chloride, mp 56-57° for an impure one). Pmr spectrum showed it contained 90% of **29** and 10% of **30.**

Deuteriochlorination of 25. The same procedure described before was followed. The *exo*-norbornyl-d_1 chloride was further purified by glpc on a 20% tricresyl phosphate column at 85°, n^{20}D 1.4845 (lit.[39] n^{20}D 1.4849 for *exo*-norbornyl chloride), before being subjected to pmr analysis or elimination. Mass spectral analysis at 10 eV indicated an isotopic purity of 97-99%.

Elimination of Chloride with Sodium 2-Cyclohexylcyclohexoxide in 2-Cyclohexylcyclohexanol. For the preparation of 1 *M* base solution, 20 ml of 2-cyclohexylcyclohexanol was placed in a flame-dried 100-ml round-bottomed flask fitted with a magnetic stirrer and a Vigreux column protected with a drying tube. The flask had a sampling port with a serum cap, from which nitrogen flow was introduced for 10 min. To this, 0.6 g (25 mmol) of oil-free sodium hydride was added. The mixture was heated to a certain temperature with stirring until all the sodium hydride had reacted. Then, still under nitrogen atmosphere, the drying tube at the top of the Vigreux column was replaced by a distillation head which was connected with a trap guarded by a drying tube. The trap was then immersed in a Dry Ice-acetone bath contained in a dewar flask. The nitrogen inlet was disconnected, and a 5-ml solution of chloride in warm 2-cyclohexylcyclohexanol was added with a syringe through the sampling port. After a certain period, a suitable vacuum was applied, and the elimination product could be collected in the trap without being contaminated with any high-boiling material.

Competitive Hydrochlorination of 25 and 28. The reaction was carried out at 0° in methylene chloride for 5 min. Neither the addition to **25** nor the addition to **28** was complete under this condition. After the solvent and the excess hydrogen chloride had been stripped off at 0°, the remaining chlorides were dissolved in a small amount of acetone and were then added to aqueous silver nitrate at room temperature with stirring. After being stirred overnight, solid sodium chloride was added to saturate the aqueous layer, and pentane was added to extract the resultant norbornanols. Glps analysis disclosed the composition of the mixture.

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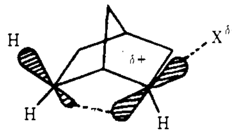

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Solvolysis of *p*-2-Norbornyl-*tert*-cumyl Chlorides. σ^+ Constants for *p*-*exo*- and -*endo*-Norbornyl and the Question of an Unusual Polarizability of the σ-Bonds in the 2-Norbornyl Group[1]

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Abstract: *p*-*exo*-Norbornyl- and *p*-*endo*-norbornyl-*tert*-cumyl chlorides were synthesized and their rates of solvolysis in 90% aqueous acetone determined in order to establish whether there is in this system a significant difference in the ability of the 2-norbornyl group to stablize an electron deficiency from the exo and endo directions. The relative rates and σ^+ constants are as follows: *p*-hydrogen, 1.00, 0.00; *p*-isopropyl, 18.8, −0.280; *p*-*exo*-norbornyl, 25.2, −0.309; *p*-*endo*-norbornyl, 21.8, −0.295; *p*-cyclopentyl, 23.7, −0.302; *p*-cyclohexyl, 19.6, −0.285; *p*-cyclopropyl, 125, −0.462. It is concluded that this probe, although capable of revealing the modest hyperconjugative contributions of a *p*-methyl substituent and the much larger contributions of a *p*-cyclopropyl substituent in stabilizing an electron deficiency, fails to reveal an appreciable difference in the relative abilities of *p*-*exo*-norbornyl and *p*-*endo*-norbornyl to achieve such stabilization. It is pointed out that the 2-aryl-2-norbornyl system provides far greater electron demand. Yet even this probe fails to reveal a directed electron supply in the exo position varying with electron demand.

The physical basis for the high exo:endo rate ratio in the solvolysis of 2-norbornyl derivatives[3] has fascinated chemists for nearly a quarter of a century. The effect was originally attributed to σ-participation in the transition state for the exo isomer.[3]

It was then discovered that equally high exo:endo rate ratios can be observed in tertiary 2-norbornyl derivatives where such σ-participation cannot be a factor.[4] It was proposed that steric hindrance to ionization[5] must be responsible for the high exo:endo rate ratios observed in such stabilized tertiary derivatives.

The problem remaining is that of extrapolating the results realized in the tertiary 2-norbornyl derivatives back to the secondary parent derivatives. Is the large exo:endo rate ratio in 2-norbornyl the result of comparable steric forces, or is there a large electronic component not present in the stabilized tertiary derivatives?

It has been suggested that the exo:endo rate ratios in 2-norbornyl may be the result neither of σ-participation[3] nor of steric effects,[4] but of a hyperconjugative contribution by the strained σ-bonds of the norbornyl structure.[6-8]

Traylor and his coworkers have pointed out that strained or polarized σ-bonds can afford large stabilization of neighboring cations.[11,12] They have suggested that such stabilization takes place through a vertical electronic effect involving σ–π conjugation, with such conjugation not requiring