Additions to Bicyclic Olefins. VIII. Electrophilic Addition of Trifluoroacetic Acid and Deuteriotrifluoroacetic Acid to Norbornene and Related Bicyclic Olefins. Evidence for the Capture of the Unsymmetrical (Classical) 2-Norbornyl Cation[1]

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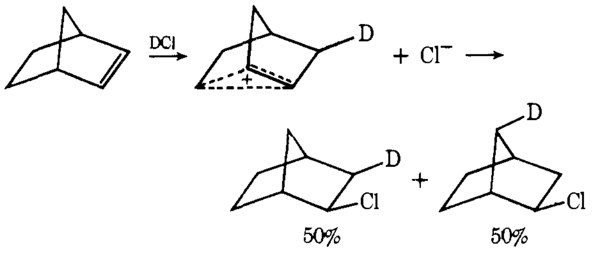
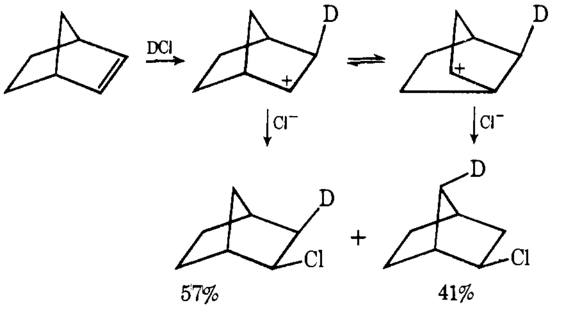
Abstract: A detailed study of the addition of trifluoroacetic acid to norbornene, 2-methylenenorbornane, 1-methylnorbornene, 5,5-dimethylnorbornene and 7,7-dimethylnorbornene was undertaken in order to establish the mechanism of the reaction and the factors influencing both the direction and stereochemistry of the addition process. A study of the addition of deuteriotrifluoroacetic acid to 7,7-dimethylnorbornene and to norbornene was also made in order to establish the stereochemistry of the addition of the proton (deuteron) and to explore in this system the possibility of capturing the 2-norbornyl cation in its unsymmetrical (classical) form before full equilibration. All additions proceed to give the *exo*-trifluoroacetate, even in 7,7-dimethylnorbornene. 2-Methylenenorbornene gives only the Markovnikov adduct, 2-methyl-*exo*-norbornyl trifluoroacetate, with a minor amount of the Wagner–Meerwein secondary isomer, consistent with a reaction proceeding through carbonium ion intermediates. The remarkably fast addition of trifluoroacetic acid at 0° to norbornene and its methyl derivatives is accompanied by the formation of considerable quantities of Wagner–Meerwein rearranged products, as well as of hydride-shifted products, consistent both with the proposed reaction path involving the formation of carbonium ion intermediates and the relatively low nucleophilicity of trifluoroacetic acid. Protonation of 1-methylnorbornene occurs 42% at C2 and 58% at C3, while protonation of 6,6-dimethylnorbornene occurs 51% at C2 and 49% at C3. It is suggested that the low directive influence of methyl substituents on the direction of the addition is not compatible with the formation of a σ-bridged intermediate. The additions of deuteriotrifluoroacetic acid to norbornene and 7,7-dimethylnorbornene proceed rapidly and yield exo–cis products, ruling out mechanisms involving a concerted molecular addition. The *exo*-norbornyl-*d* trifluoroacetate product consisted of 37% of exo-3-*d*, 26% of syn-7-*d*, with the remainder representing hydride-shifted products. The excess of exo-3-*d* product is not compatible with a process proceeding solely through the formation of a symmetrical σ-bridged (nonclassical) 2-norbornyl cation. It is compatible with a process involving rapidly equilibrating unsymmetrical (classical) cations which are captured prior to full equilibration. The presence of cesium chloride in the reaction mixture appears to intercept the cationic intermediate. The product is largely *exo*-norbornyl chloride revealing both decreased amounts of hydride-shifted material and increased yields of the unscrambled exo-3-*d* isomer. The results support the conclusion that the 2-norbornyl cation can be captured in the unsymmetrical (classical) form. The implications of the results for the nonclassical-ion problem are discussed.

The addition of hydrogen chloride to 2,3-dideuterionorbornene[3] and of deuterium chloride to norbornene[4] proceeds to give *exo*-norbornyl chloride containing more of the adding proton (deuteron) in the exo-3 than in the syn-7 position. Clearly the addition cannot be proceeding through a path involving formation of the symmetrical σ-bridged (nonclassical) 2-norbornyl cation[5] as sole intermediate (eq 1). The results are compatible with the proposed formation of unsymmetrical rapidly equilibrating (classical) 2-norbornyl cations[6] (eq 2).



(1)

(predicted values for the nonclassical ion intermediate)



(2)

It appeared desirable to explore the generality of this phenomenon. Is the capture of the 2-norbornyl cation in the unsymmetrical form restricted to the addition of hydrogen chloride, or can it be observed in the addition of other acids to norbornene?

Trifluoroacetic acid appeared to provide an especially severe test case. It possesses exceptionally weak nucleophilic characteristics and has been utilized extensively as a medium for the solvolysis of organic tosylates where it is desirable to minimize such nucleophilic contributions.[7,8] Moreover, the addition of trifluoroacetic acid to olefins has been shown to possess typical carbonium ion characteristics.[9] Indeed, the data reveal that the addition of trifluoroacetic acid to representative olefins exhibits inductive effects similar to those observed in the trifluoroacetolysis of the related tosylates.[10]

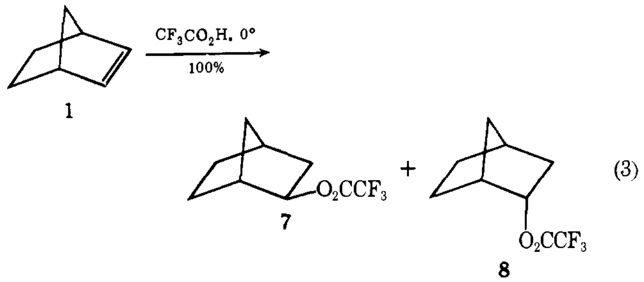
Accordingly, we undertook to examine the addition of trifluoroacetic acid and deuteriotrifluoroacetic acid to norbornene and representative related norbornene derivatives.

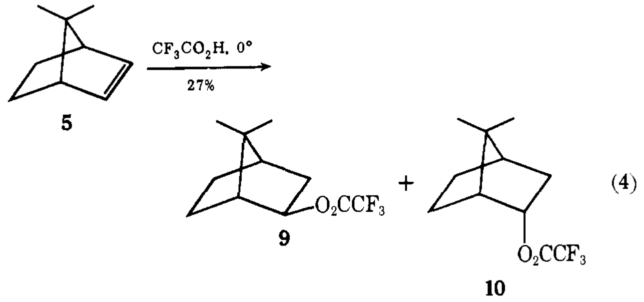
Results

Addition of Trifluoroacetic Acid. The addition of trifluoroacetic acid to these olefins was an exceedingly fast reaction, even at 0°. Thus the addition to 2-methylenenorbornane (**2**) was complete in approximately 15 sec, to norbornene (**1**), 1-methylnorbornene (**3**), and 5,5-dimethylnorbornene (camphenilene, **4**) in approximately 1–2 min, while 7,7-dimethylnorbornene (apobornylene, **5**) required approximately 6–8 min.

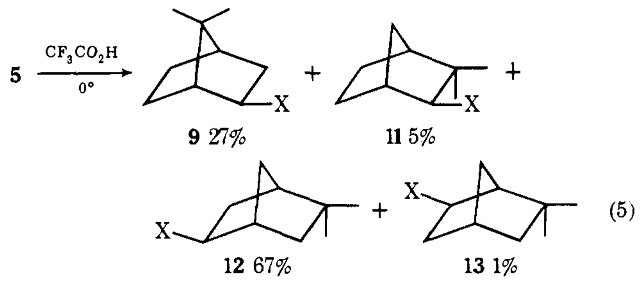
The completion of the reaction and the composition of the products were examined by GLC using appropriate columns. Because of the observed instability under the analytical conditions of 2-methyl-*exo*-norbornyl trifluoroacetate (**6**) and certain of the other trifluoroacetates produced from the methylnorbornenes, the products from **2** to **5** were first reduced to the alcohols by treatment with lithium aluminum hydride. It was established that the composition of the alcohols realized in this treatment corresponds accurately to the composition of typical synthetic mixtures of such trifluoroacetates.

The addition is highly stereoselective. For example, norbornene (**1**) gave 99.98% of *exo*- (**7**) and 0.02% of *endo*-norbornyl trifluoroacetate (**8**) (eq 3). Even 7,7-dimethylnorbornene (**5**) exhibited a remarkably high stereoselectivity, with 99.92% exo (**9**) and 0.08% endo (**10**) (eq 4).

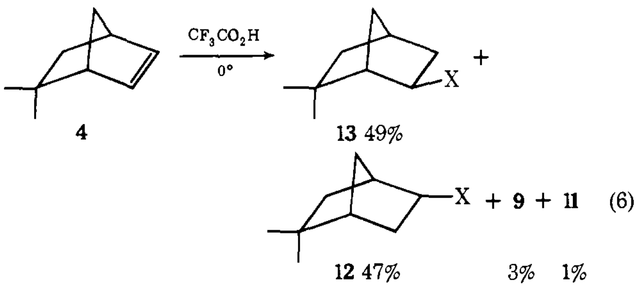




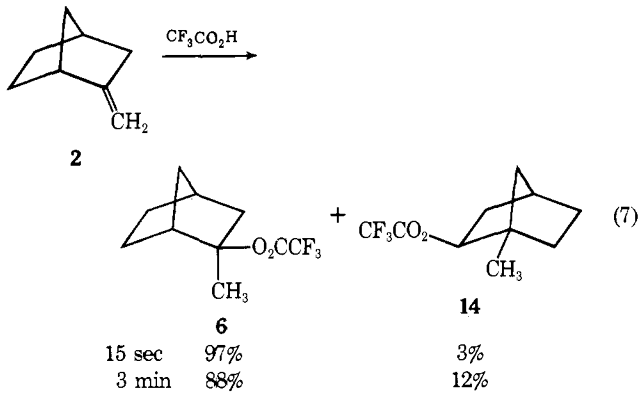
In the latter reaction, the major product is **12**, attributable to a 6:2 hydride shift in the carbonium ion corresponding to **11** (eq 5, X = CF_3CO_2–).



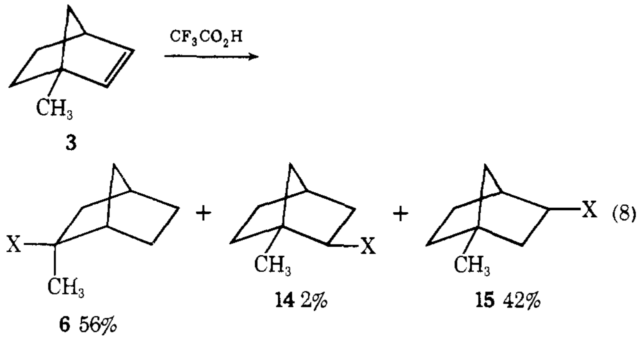
The addition of trifluoroacetic acid to 5,5-dimethylnorbornene (**4**) proceeds with almost no selectivity between the two positions of the double bond (eq 6). All of these secondary trifluoroacetates were established to be stable to the reaction conditions.



On the other hand, the addition of trifluoroacetic acid to **2** gave predominantly the tertiary ester **6**, but this was unstable to the reaction conditions and was slowly transformed into the isomeric secondary isomer **14** (eq 7). Extrapolation of the results to zero time indicates that the initial product must be essentially pure tertiary ester **6**.



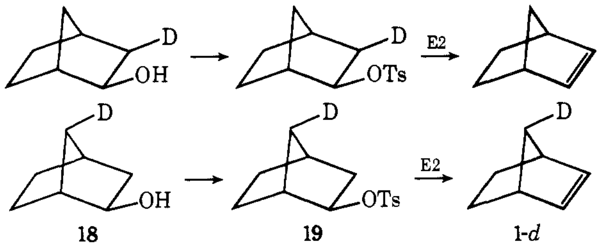
Addition of trifluoroacetic acid to 1-methylnorbornene (**3**) proceeded to give predominantly the secondary trifluoroacetate **15** and the tertiary derivative **6**. In 15 sec, the product was 56:2:42 (eq 8). Here also the minor amount of the secondary isomer **14** is attributed to an isomerization of the initially formed tertiary product **6**.



Addition of Deuteriotrifluoroacetic Acid. The addition of deuteriotrifluoroacetic acid to **1** and **5** gave the same composition of products which revealed the same remarkably high stereoselectivity for the trifluoroacetate group as the addition of trifluoroacetic acid mentioned earlier (eq 3, 4).

In order to establish the stereochemistry of the addition of the deuteron to **5**, a mixture of the monodeuterated trifluoroacetates, **9**-*d* and **12**-*d*, was separated from the other products by preparative GLC over tricresyl phosphate. The esters were converted into the alcohols with lithium aluminum hydride. Then 7,7-dimethyl-*exo*-norbornanol-*d* (**16**) was isolated by liquid-phase chromatography over alumina and converted into the tosylate **17**. Treatment of the tosylate with sodium 2-cyclohexylcyclohexoxide in triglyme[11] yielded the olefin **5** with only 3% of the deuterium in the vinyl position. Under identical conditions, a synthetic sample of *exo*-3-*d*-7,7-dimethyl-*exo*-norbornyl tosylate was converted into **5** containing 5% of the original deuterium in the vinyl position.[11] Consequently, the present result established that the alcohol **16** could not have had a significant amount of endo-3-*d*, but could have some 40% of the original deuterium at C5 as a result of a 6:2 hydride shift.

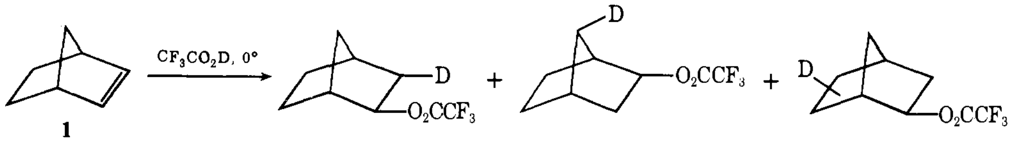
The position of the deuterium atom in the *exo*-norbornyl-*d* trifluoroacetate (**7**-*d*) produced in the addition of deuteriotrifluoroacetic acid to norbornene **1** was determined both by ^{1}H NMR analysis of the corresponding *exo*-norbornanol-*d* (**18**) and the E2 elimination product of the corresponding tosylate[11] **19** (eq 9).



(9)

18 19 1-*d*

The 60-MHz and 100-MHz spectra of 1 *M* solutions of **18** in 95% pyridine-5% deuterium oxide exhibited the most satisfactory separation of signals of the bridgehead protons and the syn-7 proton among all of the spectra taken at a variety of concentrations in different solvents. By analyzing the shape of the α-methine proton at δ 3.89 and by measuring the relative intensity of the syn-7 proton at δ 1.88, the deuterium distribution could be determined[12] (eq 10).



(10)

1

^{1}H NMR of alcohol **18**:	37	26	37
^{1}H NMR of olefin 1-*d*:	36	25	39

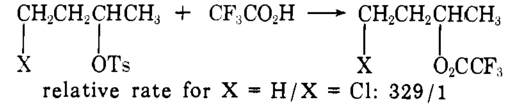
The analysis based on the ^{1}H NMR examination of the alcohol was confirmed by a 60-MHz ^{1}H NMR analysis (eq 10) of the olefin derived from **18** through the E2 elimination of the tosylate **19** (eq 9). The amount of deuterium at the exo-3 position was also confirmed by mass spectral analysis of the olefin **1**-*d*.

Reaction of Norbornene with Deuteriotrifluoroacetic Acid in the Presence of Dissolved Cesium Chloride. Cesium chloride proved to be quite soluble in trifluoroacetic acid. When norbornene (**1**) was added to trifluoroacetic acid at 0° containing dissolved cesium chloride, there was a rapid reaction. The major product, however, was not the trifluoroacetate **7**, but *exo*-norbornyl chloride (**20**). An increase in the amount of dissolved cesium chloride resulted in a reduction in the amount of the trifluoroacetate and an increase in the yield of the chloride.

The reaction of norbornene with deuteriotrifluoroacetic acid and cesium chloride proceeded similarly. From the mixture of **20**-*d* and **7**-*d* thus produced, the former could be readily isolated by GLC. The distribution of deuterium in **20**-*d* was estimated both by 60-MHz ^{1}H NMR analyses of the chloride itself and of the olefin produced by E2 elimination of **20**-*d*.[4] The results are summarized in Table I.

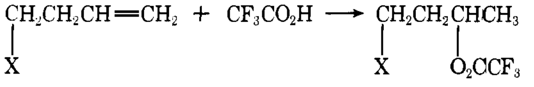
Discussion

Addition of Trifluoroacetic Acid as a Carbonium Ion Process. The remarkably fast reaction of a variety of olefins with trifluoroacetic acid exhibits all of the characteristics of a carbonium ion process.[9] The addition proceeds to give the Markovnikov products cleanly, indicative of the development of considerable positive charge at the carbonium ion center.[9] Indeed, it was observed that a 4-chloro substituent exerted essentially the same rate-retarding effect in the trifluoroacetolysis of 2-butyl tosylate (eq 11) as in the addition of trifluoroacetic acid to the corresponding olefins[10] (eq 12).



$$\underset{X}{CH_2}CH_2\underset{OTs}{CH}CH_3 + CF_3CO_2H \longrightarrow \underset{X}{CH_2}CH_2\underset{O_2CCF_3}{CH}CH_3 \qquad (11)$$

relative rate for X = H/X = Cl: 329/1



$$\underset{X}{CH_2}CH_2CH{=}CH_2 + CF_3CO_2H \longrightarrow \underset{X}{CH_2}CH_2\underset{O_2CCF_3}{CH}CH_3 \qquad (12)$$

relative rate for X = H/X = Cl: 421/1

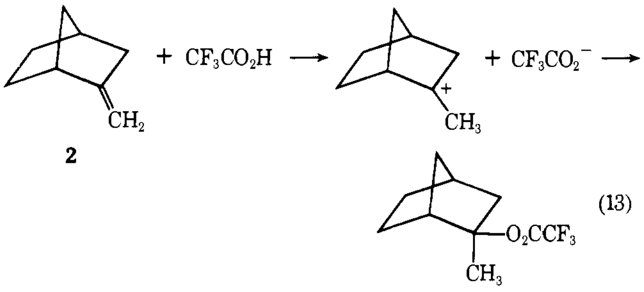
Table I. Product Analyses for the Reaction of Norbornene with Deuteriotrifluoroacetic Acid at 0° in the Presence of Dissolved Cesium Chloride

CF_3-CO_2D, ml	**1**, mmol	CsCl, mmol	**7**-*d*, %	**20**-*d*,[a] %	Deuterium distribution exo-3-*d*:syn-7-*d*:other
15	5	5	9	91	48:36:16
15	5	20	3	97	61:34:5

[a] It was established that **20**-*d* was stable to the reaction conditions.

It has been suggested that the mechanism for additions to strained olefins might be different from those involving unstrained olefins.[13] Consequently, it may be desirable to exercise caution in extrapolating Peterson's results and conclusions based on the study of relatively simple unstrained olefins to highly strained bicyclic olefins of the norbornene type.[14]

However, the present results clearly support a carbonium ion process for the additions examined in this study. Thus the addition of trifluoroacetic acid to 2-methylenenorbornane requires only 15 sec at 0°. The product (extrapolated to zero time) is essentially pure tertiary trifluoroacetate (eq 7). Such a powerful directive effect, in accordance with Markovnikov orientation, is normally considered to involve a carbonium ion intermediate.[15] The reaction must proceed via an initial transfer of a proton to the primary carbon atom, forming the tertiary carbonium ion which adds trifluoroacetate with the usual preference for exo stereochemistry exhibited by the norbornyl system[16] (eq 13).



2 **6**

(13)

The addition of trifluoroacetic acid to norbornene yields 99.98% *exo-* and 0.02% *endo*-norbornyl acetate. This remarkably high stereoselectivity is essentially identical with that realized in the acetolysis of *exo*-norbornyl tosylate.[17] This similarity in the stereoselectivity supports the conclusion that both reactions must be proceeding through the same intermediate, the 2-norbornyl cation.

The carbonium ion character of the addition reaction is further supported by the large amounts of Wagner-Meerwein rearranged and hydride-shifted products observed in these additions. For example, the predominant product in the addition of trifluoroacetic acid to 7,7-dimethylnorbornene (**5**) is **12** (eq 5), which must involve a 6:2 hydride shift.

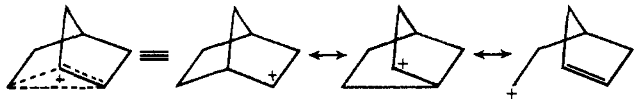
Question of a Molecular Addition. It is possible to account for the production of unsymmetrically tagged norbornyl derivatives, such as were realized in our earlier hydrochlorination studies[4] and in the reaction summarized in eq 10, by postulating two concurrent addition processes, one involving the usual symmetrical σ-bridged cation and the other involving a cyclic molecular addition.[18,19] We believe that the present results clearly rule out the incursion of a cyclic molecular addition in amounts sufficient to disturb the present results.

First, a molecular addition of trifluoroacetic acid to 1-methylnorbornene (**3**) would be expected to yield approximately equal amounts of the two secondary trifluoroacetates **14** and **15**. These are stable to the reaction conditions. However, the observed products are the secondary derivative **8** and the tertiary derivative **6** (eq 8). Clearly, the proposed molecular addition cannot be significant.

We have proposed 7,7-dimethylnorbornene (**5**) as a diagnostic tool to test for such cyclic molecular additions. Typical cyclic additions, such as epoxidation and hydroboration, proceed readily with norbornene (**1**) to give products with exo-cis orientation but proceed with great difficulty with 7,7-dimethylnorbornene (**5**) to give the endo isomers predominantly.[20]

The present results reveal exo-cis addition of deuteriotrifluoroacetic acid to **5**. Moreover, the exo isomer **9** constitutes 99.92% of the unrearranged product, with only 0.08% of the endo isomer **10** (eq 4). Although we did not attempt to establish the relative rates of addition of trifluoroacetic acid to **5** and **1**, the reaction times for complete reaction at 0°, 6-8 min for **5** and 1-2 min for **1**, reveal the absence of any major difference in reactivity always observed for cyclic addition processes.[20]

Directive Effects in the Addition Reaction. The nonclassical formulation of the 2-norbornyl cation was originally represented as a resonance hybrid of three canonical structures[5] (**21**). This interpretation suggests that the introduction of methyl groups at position 6 should stabilize the canonical structure **21c** and thereby stabilize the resonance hybrid **21**.

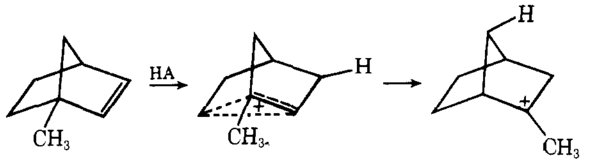

21 **21a** **21b** **21c**

However, the addition of acetic acid to 6,6-dimethylnorbornene **4** failed to reveal any significant preference for protonation at positions 2 or 3.[21] Similarly, 6,6-dimethyl-*exo*-norbornyl tosylate failed to exhibit an enhanced rate of solvolysis.[22]

The nucleophilic properties of trifluoroacetic acid are far lower than those of acetic acid. For example, the trifluoroacetolysis of even so open a structure as 2-propyl tosylate is believed to be limiting or nearly so.[23] Consequently, σ participation, if it can occur in the 2-norbornyl cation, would be anticipated to be especially favored in this medium. Yet the addition of trifluoroacetic acid to **4** gives essentially equal quantities of the two isomeric secondary products: 47% of **12** and 49% of **13** (eq 6).

Consequently, the present results confirm the conclusion that canonical form **21c** does not contribute to the resonance hybrid.[22] We are left with the problem as to whether **21a** and **21b** are canonical contributors to a symmetrical σ-bridged cation,[24] **21**, or whether they represent a rapidly equilibrating pair of unsymmetrical (classical) cations.[6]

1-Methylnorbornene (**3**) is an interesting system. Irrespective of the question as to whether σ participation is important in symmetrical 2-norbornyl derivatives, it would be anticipated that protonation would be favored at position 3 as the system passes over a stabilized transition state (**22**) leading to the tertiary carbonium ion **23** (eq 14).

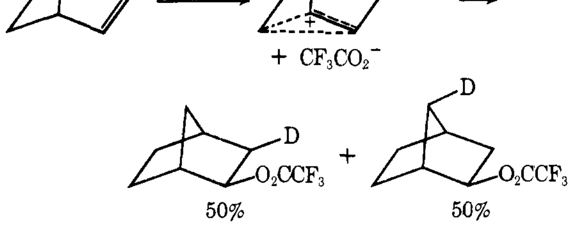


3 **22** **23**

(14)

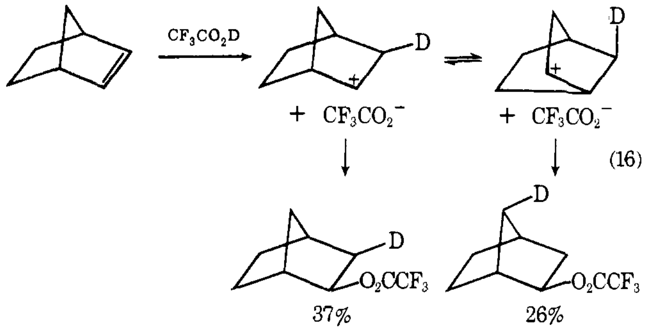
However, it was previously observed that there is little discrimination between protonation at C2 and C3 in the addition of formic acid[25] and of hydrogen chloride.[4] The use of trifluoroacetic acid does not alter the situation significantly (eq 8). Clearly, σ participation cannot be very significant in the transition states produced by the transfer of a proton from the acid to C2 or C3.

Capture of an Unsymmetrical 2-Norbornyl Cation. Transfer of a deuteron from deuteriotrifluoroacetic acid to C2 or C3 of norbornene takes place from the exo direction to give the 2-norbornyl cation with a deuterium tag. If this ion possesses the symmetrical σ-bridged (nonclassical) structure, it must react with the anion to give *exo*-norbornyl trifluoroacetate with an equal distribution of deuterium between the exo-3 and syn-7 positions (eq 15). However, an equal distribution was not realized. The product contained more of the deuterium at the exo-3 than at the syn-7 position (eq 10). The observed distribution is compatible with the formation of a rapidly equilibrating pair of cations which is captured prior to full equilibration (eq 16).



(15)

(predicted distribution)

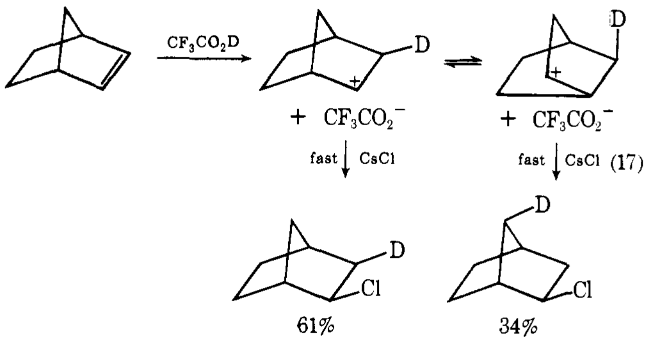


(16)

A considerable quantity of hydride-shifted isomers is produced (37%). This was not a problem in the hydrochlorination experiments reported earlier.[4] Presumably, in those experiments, the presence of a more favorable nucleophile, chloride ion, made possible a faster capture of the first formed cation, exo-3-*d*, before it was as fully converted to the syn-7-*d* isomer and simultaneously avoided diversion of the intermediates into the hydride-shifted path.

These considerations suggested adding an external, more favorable nucleophile to the trifluoroacetic acid. Many of the materials we attempted to use were insoluble in the acid. Fortunately, cesium chloride is quite soluble in this acid. Moreover, hydrogen chloride is a stronger acid than trifluoroacetic acid.[26] Consequently, the chloride ion should largely exist as such.[27]

Indeed, the system behaved as predicted for the existence of the intermediate as a rapidly equilibrating pair. The reaction proceeded very rapidly, just as rapidly as the original addition of trifluoroacetic acid. However, the product was diverted to the formation of the chloride. With deuteriotrifluoroacetic acid containing 1.33 *M* CsCl, the product was only 3% *exo*-norbornyl-*d* trifluoroacetate and 97% *exo*-norbornyl-*d* chloride. The ratio of exo-3-*d* to syn-7 was 61:34. Thus, in contrast to eq 16, chloride ion appears to capture the first intermediate at a considerably enhanced rate (eq 17). Moreover, the amount of hydride-shifted isomers was reduced to 5% (Table I).



Implications for the Nonclassical-Ion Problem. In 1946, it was proposed that rates of solvolysis of highly branched tertiary derivatives can be facilitated by relief of steric strain.[28] A number of systems were investigated, and the results strongly supported the proposal.[29] The concept was adopted and utilized to correlate data for many systems.[30]

However, in the early 1950's, a new concept, stabilization through σ bridging, was advanced as an alternative explanation.[5] This concept was utilized to account for the fast rates of solvolysis of such derivatives as camphene hydrochloride,[31] tri-*tert*-butylcarbinyl *p*-nitrobenzoate[32] and cyclodecyl tosylate.[33]

It appeared that 2-norbornyl provided the most favorable example of this new phenomenon. It had long been recognized that the rearrangements of carbonium ions in bicyclic terpenes are unusually facile.[34] Consquently, the transformation had to involve a relatively stable σ-bridged transition state (Figure 1). In essence, the proposal was that this relatively stable σ-bridged species was not a transition state but was instead a relatively stable symmetrical intermediate so stable that there was no longer any need to consider the original equilibrating unsymmetrical cations[35] (Figure 1). Accordingly, we undertook a research program to test this proposal of σ bridging as a major factor in facilitating solvolysis by making an intensive study of the 2-norbornyl system.[36]

In essence, the proposal in its original form was that both *exo*- and *endo*-norbornyl derivatives undergo solvolysis to produce a symmetrical, stabilized σ-bridged norbornyl cation[5] (**21**). This σ-bridged species was considered to be partially formed in the transition state for the exo isomer, but not in the case of the endo isomer, thereby accounting for the observed exo:endo rate ratio of approximately 300 (1100 to 1600 if one allows for internal return).[5]

The formulation of the proposed σ-bridged structure as **21** requires the delocalization of charge from the 2 to the 1 and 6 positions. However, a variety of tests for such charge delocalization by the introduction of appropriate substituents failed to confirm the phenomenon.[16,36]

^1H NMR studies of the 2-phenyl- and 2-*p*-anisyl-2-norbornyl cations revealed these cations are classical, with no evidence for σ bridging.[37] Yet the solvolysis of 2-*p*-anisyl-2-norbornyl *p*-nitrobenzoates revealed an exo:endo rate ratio (284)[39] comparable to that observed in the acetolysis of 2-norbornyl tosylates (280).[22]

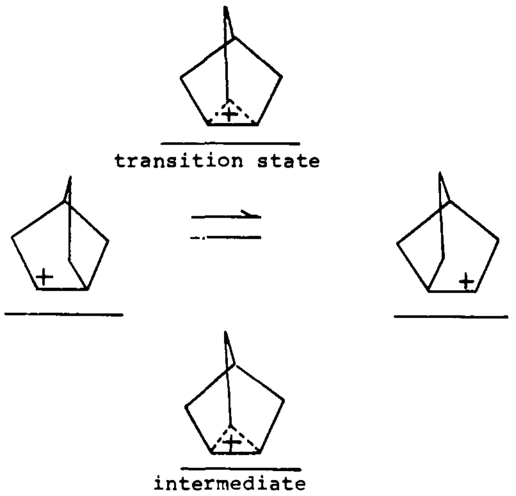
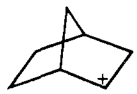


Figure 1. Proposed transformation of the relatively stable transition state responsible for the rapid equilibration of 2-norbornyl cations into a stabilized symmetrical intermediate sufficiently stable so as to make unnecessary further consideration of the unsymmetrical 2-norbornyl cations as intermediate.

These results led to the suggestion that, in the solvolysis of 2-norbornyl derivatives, bridging may lag behind ionization.[39] This proposal could account for the failure to detect any delocalization from the 2 to the 1 and 6 positions in the solvolysis of 2-norbornyl derivatives.[36,40]

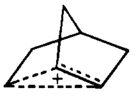
This proposal made it desirable to shift the emphasis of our study from the factor or factors responsible for the high exo:endo rate ratio to the nature of the carbonium ion intermediate produced in the 2-norbornyl system.

The isolation of inactive *exo*-norbornyl acetate in the acetolysis of active *exo*-norbornyl brosylate[5] establishes that the intermediate cannot be the classical 2-norbornyl cation **24**. This cation does not possess a plane of symmetry.

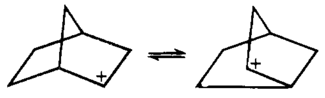


24

The nonclassical ion **21** does possess a plane of symmetry. However, a rapidly equilibrating pair of unsymmetrical classical cations (**25**) can behave as though it possesses a plane of symmetry provided the rate of equilibration is rapid compared with the rate of reaction of the intermediate with solvent.



21



25

Originally the solvolysis of such derivatives was interpreted as going through the formation of the free ions.[5] It was considered inconceivable that the rate of equilibration could exceed the rate of reaction of secondary cations with solvent.[39]

There have been three significant developments which require a reconsideration of this position. First, there is now considerable evidence that the solvolysis of such secondary tosylates leads to the formation of tight ion pairs.[41] Such ion pairs may have a relatively long life, permitting many equilibrations before solvent finally penetrates the ion pair and converts it to product.[42] Second, a large number of cations under stable-ion conditions have been characterized as rapidly equilibrating classical cations.[43] Many of these systems equilibrate so rapidly that the equilibration is not frozen out even at temperatures in the range of −150°. Finally, Fong has applied relaxation theory to such equilibrating systems and has concluded that rates of equilibration as high as 10^{12} sec^{-1} are entirely feasible for 2-norbornyl and related equilibrating cations.[44]

It is quite clear that there is one distinct difference between the symmetrical σ-bridged (nonclassical) 2-norbornyl cation (**21**) and the pair of unsymmetrical rapidly equilibrating (classical) cations. A probe which is sufficiently fast should achieve the capture of the latter in the unsymmetrical form. On the other hand, such a probe, no matter how fast, cannot achieve the capture of the symmetrical species in the unsymmetrical form.

The 2-norbornyl cation has not been captured in unsymmetrical form in some 11 different reactions.

1. Deamination of optically active *exo*-norbornylamine to give *exo*-norbornanol with approximately 10% of residual activity.[45]

2. Addition of hydrogen chloride to 2,3-dideuterionorbornene.[3]

3. Reaction of 2,3-dideuterionorbornene with deuteriobromic acid.[3]

4. Acid-catalyzed O-alkylation of phenol with 2,3-dideuterionorbornene.[3]

5. Addition of deuterium chloride to norbornene.[4]

6. Addition of deuteriotrifluoroacetic acid to norbornene.[46]

7. Chloride ion capture of the 2-norbornyl cation in trifluoroacetic acid.[46]

8. Addition of deuterioacetic acid to norbornene.[47,48]

9. Acid-induced addition of deuterioacetic acid to norbornene.[4]

10. Capture of the hydride-shifted tagged 2-norbornyl cation in the acetolysis of 2-(Δ^3-cyclopentenyl)ethyl-*2*-^{14}C tosylate.[49,50]

11. Capture of the hydride-shifted tagged 2-norbornyl cation in the acetolysis of *exo*-norbornyl-*4*-^{13}C brosylate.[51]

Consequently, the accumulating evidence supports the original position[6] that a σ bridge may not be involved in the high exo:endo rate and product ratios observed in the solvolysis of 2-norbornyl derivatives. The intermediate produced is evidently not the symmetrical σ-bridged (nonclassical) species, but a rapidly equilibrating pair of unsymmetrical (classical) cations.

2-Norbornyl Cation in Superacids. The problem of the proposed σ-bridged structure for the 2-norbornyl cation is now entering a third phase, its nature in superacids.

In the first phase, emphasis was placed on the high exo:endo rate and product ratios as an argument for the σ participation presumed to lead to the σ-bridged cation.[5] However, the demonstration that highly stabilized 2-aryl-2-norbornyl derivatives, which yield classical 2-aryl-2-norbornyl cations,[37] exhibit high exo:endo rate and product ratios[38] comparable to those of 2-norbornyl itself eliminated this basis for the proposed nonclassical interpretation.

The discussion then entered a new, second phase. It was proposed that bridging lags behind ionization[39] so that kinetic studies which provide information on the transition state could not disprove the proposed formation of a symmetrical σ-bridged species as the intermediate. However, as discussed in the last section, the many reactions which have now trapped the norbornyl cation in the unsymmetrical form appear to refute this position.

The norbornyl cation can be prepared and observed spectroscopically in superacid media.[52] Olah has been the most active worker in this area and has applied ^1H NMR,[52] ^{13}C NMR,[53] Raman,[54] and ESCA[55] to the problem. He has concluded "... the long standing controversy as to the nature of the 2-norbornyl cation is unequivocally resolved in favor of the nonclassical carbonium ion."[55]

Unfortunately, there are major difficulties with the results and conclusions.[56] For example, Kramer points out that the ^{13}C shifts in the 2-propyl cation fail to provide a reasonable calculated value[56] for the ^{13}C shift[57] observed in the rapidly equilibrating pair of 2-butyl cations.[58]

If one cannot extrapolate the 2-propyl data to calculate the observed shifts for an equilibrating pair of classical 2-butyl cations, what reliance can be placed on the existence of a similar discrepancy between the calculated and observed values for the ^{13}C shifts in 2-norbornyl based on a much greater extrapolation to provide the basis for the conclusion that the 2-norbornyl cation must be present as the σ-bridged species? There is certainly no agreement between the observed shifts and those calculated for the nonclassical ion (no one has suggested a means of calculating shifts for such a species).[59]

Major problems, both practical and theoretical, with the ESCA technique and results have been discussed earlier[4,56] and need not be repeated here.

Finally, the point needs to be emphasized that it has not yet been established as to how pertinent are the results and conclusions for studies under stable-ion conditions to the behavior of cations under solvolytic conditions. For example, the 2,3,3-trimethyl-2-butyl cation exists in superacid as a rapidly equilibrating system in which the methyl migration cannot be frozen out even at −150°.[60]

However, methanolysis of the tagged *p*-nitrobenzoate at 100° yields the methyl ether without detectable scrambling of the tag.[61] Clearly caution is in order before we extrapolate results and conclusions from the superacid systems to solvolytic systems.

Conclusion

With the passage of the years, all of the original cases where σ bridging was proposed to account for fast rates of solvolysis[31-33] have been reconsidered.[16] The 2-norbornyl cation may now be considered to be the last of the classical nonclassical structures still under active study.

The fact is that the σ-bridged symmetrical structure of the 2-norbornyl cation was originally proposed to account for certain solvolytic behavior of 2-norbornyl derivatives. Detailed study of these phenomena have failed to support the original proposal. The present results, as well as related studies, clearly establish that the 2-norbornyl cation can be captured in its unsymmetrical (classical) form. Before additional effort is devoted to the proposal for the existence of a symmetrical σ-bridged (nonclassical) intermediate, there is a real need for careful consideration and analysis of the huge mass of data now available and a clear statement as to why these data are not convincing to those who continue to favor the symmetrical σ-bridged species.

Experimental Section

Material. Reagent grade chemicals were used without purification. Trifluoroacetic acid was distilled and stored under nitrogen. Olefins were prepared as previously described.[4] 6,6-Dimethylnorbornene, bp 131–133°, was kindly supplied by Dr. S. Ikegami of this laboratory.

Gas Chromatography. All the GLC analyses were accomplished on a Perkin-Elmer Model 226 instrument equipped with a 150 ft × 0.01 in. or a 50 ft × 0.02 in. Golay column. For preparative purpose, an Aerograph Model A90C instrument was employed.

^1H NMR Analyses. The 60-MHz spectra were taken with a Varian A-60A spectrometer using tetramethylsilane as internal reference. 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.

Preparation of *exo*-Norbornyl Trifluoroacetate (7). Peterson's procedure[7a] was followed. Three mililiters of trifluoroacetic anhydride was added to 1.12 g of *exo*-norbornanol (0.01 mol) in 10 ml of pyridine at 0°. After being stirred for 1 min, the mixture was poured into a mixture of 50 ml of ice-water and 15 ml of ether. The ether layer was separated, and the aqueous layer was extracted with 10 ml of ether. The combined ether solution was washed with two 30-ml portions of chilled 1 *N* hydrochloric acid and subsequently with water, two 20-ml portions of 5% sodium carbonate, and again water. Then it was dried and decolorized, and the ether was stripped off on a rotary evaporator. There was obtained 1.89 g (91%) of the product with about 98% purity. Further purification by GLC on a 4 ft × ⅛ in. column of 20% TCP on 60-80 Celite at 85° gave the pure trifluoroacetate: n^{20}D 1.4019; ir (film) 5.58 μ (CF$_3$CO); ^{1}H NMR (CCl$_4$) δ 4.78 (α-methine H, doublet with $J \sim 7$, which is further split into a doublet, $J \sim 0.5$, of doublet, $J \sim 3$ Hz).

Anal. Calcd for C$_9$H$_{11}$O$_2$F$_3$: C, 51.91; H, 5.32. Found: C, 52.15; H, 5.27.

Preparation of 7,7-Dimethyl-*exo*-norbornyl Trifluoroacetate (9). Using the same procedure, 0.01 mol of 7,7-dimethyl-*exo*-norbornanol (1.40 g) yielded 2.09 g (89%) of about 98% pure trifluoroacetate. GLC purification with 20% TCP column at 100° gave the pure product: n^{20}D 1.4145; ir (film) 5.57 μ (CF$_3$CO); ^{1}H NMR (CCl$_4$) δ 1.03 (singlet, CH$_3$), 1.16 (singlet, CH$_3$), 4.82 [doublet ($J \sim 4$) of doublet ($J \sim 7$ Hz), α-methine H].

Anal. Calcd for C$_{11}$H$_{15}$O$_2$F$_3$: C, 55.93; H, 6.40. Found: C, 56.03; H, 6.48.

Preparation of *endo*-Norbornyl Trifluoroacetate (8). Twenty millimoles of *endo*-norbornanol in 20 ml of pyridine was allowed to react with 6 ml of trifluoroacetic anhydride at 0°. The esterification was not complete in 1 min. After work-up in the usual procedure and solvent removal, the *endo*-norbornyl trifluoroacetate was isolated by distillation in vacuo: bp 62° (17 mm); n^{20}D 1.4022; ir (film) 5.58 μ (CF$_3$CO); ^{1}H NMR (CCl$_4$) δ 5.14 [doublet ($J \sim 4$) of doublet ($J \sim 10$ Hz), α-methine H].

Addition of Trifluoroacetic Acid to Norbornene (1). Ten millimoles of norbornene (0.94 g) was added to 10 ml of trifluoroacetic acid (ca. 130 mmol) chilled in an ice bath. The solid olefin was completely dissolved in 1–2 min with vigorous stirring. Then the product was poured into 150 ml of ice-cooled 5% aqueous sodium carbonate. After the generation of carbon dioxide ceased, 15 ml of ether was added, and the organic layer was separated. The aqueous layer was extracted with two 10-ml portions of ether. The combined ether solution was washed with water, dried, and decolorized. GLC analysis using a 150 ft × 0.01 in. Apiezon L column indicated the absence of **1** or *exo*-norbornanol. With a 50 ft × 0.02 in. tricresyl phosphate column at 100°, the product was shown to contain 99.98% **7** and 0.02% **8**.

Addition of Trifluoroacetic Acid to 7,7-Dimethylnorbornene (5). The reaction was carried out under the same condition as for norbornene and was complete in 6–8 min. GLC analysis using a 50 ft × 0.02 in. TCP column at 100° and a nitrogen flow of 20 psi showed four components with retention time of 26, 27, 29, and 34.6 min. They were identified as 6,6-dimethyl- (**13**), 3,3-dimethyl- (**11**), 5,5-dimethyl- (**12**), and 7,7-dimethyl-*exo*-norbornyl trifluoroacetate (**9**), respectively. The two main components, **9** and **12**, were isolated by GLC on a 4 ft × ⅛ in. column of 20% TCP on 60–80 Celite at 100°, one of which was identical with **9**. The other one, n^{20}D 1.4091, was identified as 5,5-dimethyl-*exo*-norbornyl trifluoroacetate (**12**) by reduction with lithium aluminum hydride to 5,5-dimethyl-*exo*-norbornanol, mp 59–60° (lit.[62] mp 60–61°). The infrared spectrum (film) of **12** shows the characteristic carbonyl absorption at 5.56 μ (CF$_3$CO), and the ^{1}H NMR spectrum (CCl$_4$) exhibited δ 0.99 (singlet, CH$_3$), 1.02 (singlet, CH$_3$), and 4.77 [doublet ($J \sim 3$) of doublet ($J \sim 7$ Hz), α-methine H].

Anal. Calcd for C$_{11}$H$_{15}$O$_2$F$_3$: C, 55.93; H, 6.40. Found: C, 55.91; H, 6.50.

Lithium Aluminum Hydride Reduction of the Mixture of Dimethylnorbornyl Trifluoroacetate. To a mixture of 10 mmol of lithium aluminum hydride (95% pure, 0.4 g) in 10 ml of anhydrous ether, a solution of the dimethylnorbornyl trifluoroacetate mixture (ca. 8 mmol) was added dropwise at ice-bath temperature. After being stirred at 0–2° for 2 hr, the product was isolated by the following procedure.[63]

Ten mililiters of chilled water, 10 ml of chilled 15% sodium hydroxide, and 30 ml of chilled water were added to the reaction mixture in succession. After a vigorous stirring for another 20 min, the mixture was filtered with suction, and the white granular precipitate was washed thoroughly with ether. The combined ether solution was washed with ice-water and then dried over anhydrous magnesium sulfate. The composition of the resultant alcohol mixture was then examined by GLC using a 150 ft × 0.01 in. UCON polar column at 100°. The results were shown in eq 5 and 6. The ratio of **9**/**10** was estimated from the ratio of 7,7-dimethyl-*exo*-norbornanol/7,7-dimethyl-*endo*-norbornanol, 99.92:0.08. The composition of this alcohol mixture has been proved to be the same as that of the original trifluoroacetates.

Addition of Trifluoroacetic Acid to 6,6-Dimethylnorbornene (4). The reaction was complete in 2 min at 0°. The trifluoroacetate mixture was reduced to the corresponding alcohol mixture which was analyzed by GLC (eq 2).

Preparation of 1-Methyl-*exo*-norbornyl Trifluoroacetate (14). From 1-methyl-*exo*-norbornanol and trifluoroacetic anhydride, **14** was obtained. Pure **14**, after GLC purification, showed $n^{19.5}$D 1.4030, $\nu_{\mathrm{C=O}}$ (film) 5.60 μ.

Anal. Calcd for C$_{10}$H$_{13}$O$_2$F$_3$: C, 54.05; H, 5.90. Found: C, 54.00; H, 6.17.

Addition of Trifluoroacetic Acid to 2-Methylenenorbornane (2). The reaction was complete in 15 sec, and it was also allowed to react for 3 min. The product was reduced with lithium aluminum hydride, and the resulting alcohols were analyzed by GLC (eq 7).

Addition of Trifluoroacetic Acid to 1-Methylnorbornene (3). By employing the general procedure, **3** was allowed to react with trifluoroacetic acid for 15 sec. The product was reduced to the alcohols which were then analyzed by GLC.

Preparation of Deuteriotrifluoroacetic Acid. A 200-ml round-bottomed flask, equipped with a drying tube-protected Dry Ice condenser, a magnetic stirrer, and a side arm with serum cap, was flame dried under nitrogen flow. It was cooled to 0°, and 105 g of trifluoroacetic anhydride (0.5 mol) was introduced with a syringe through the side arm. Then 10 g (0.5 mol) of deuterium oxide (99.5% pure) was slowly injected with stirring. The resultant deuteriotrifluoroacetic acid was stored under nitrogen. ^{1}H NMR analysis using chloroform as internal standard showed an isotopic purity of 98%.

Addition of Deuteriotrifluoroacetic Acid to Norbornene. The same procedure as described for the addition of trifluoroacetic acid was followed, except the deuteriotrifluoroacetic acid was cooled under dry nitrogen. The product was isolated, and the ratio of *exo*- to *endo*-trifluoroacetate was also found to be 99.98 to 0.02 by VPC.

Reduction of *exo*-Norbornyl-*d* Trifluoroacetate. The *exo*-norbornyl-*d* trifluoroacetate (99.98% pure) was reduced with lithium aluminum hydride in ether at 0° to give 90% yield of *exo*-norbornanol-*d* (**18**). ^{1}H NMR analysis was performed with a 1 *M* solution in 95% pyridine–5% deuterium oxide.

Elimination of *exo*-Norbornyl-*d* Tosylate (19). The alcohol **17** was converted into tosylate which was treated with tenfold excess of sodium 2-cyclohexylcyclohexoxide in triglyme at 80°. The product was purified by GLC on a 5% silver nitrate column to remove the trace amount of nortricyclene (ca. 0.5%). ^{1}H NMR analysis was taken with a 10% chloroform solution. The amount of deuterium (exo-3-*d*) eliminated was confirmed by mass spectral analysis of the norbornene (63% d_1 and 37% d_0) at 5.5 eV.

Addition of Deuteriotrifluoroacetic Acid to 7,7-Dimethylnorbornene (5). A similar procedure to that of addition of trifluoroacetic acid to **5** was used. The product was isolated, and a mixture of **9**-*d* and **12**-*d* was separated from others by GLC using a tricresyl phosphate column at 100°. This mixture was reduced to the corresponding alcohols which were separated by chromatography on deactivated alumina (94% neutral alumina and 6% water). The alcohol **16** was eluted with petroleum ether (35–37°), and the 5,5-dimethyl-*exo*-norbornanol-*d* was eluted with ether–petroleum ether (35–37°) mixture. Then **16** was converted into the tosylate **17** which was eliminated by tenfold excess of sodium 2-cyclohexylcyclohexoxide in triglyme at 80°.

Reaction of Norbornene with Cesium Chloride and Deuteriotrifluoroacetic Acid. Cesium chloride (99.9%, Fisher Scientific Co.) was dried and placed in a flame-dried flask equipped with a sampling port and protected by a drying tube. Under nitrogen flow, the flask was cooled in an ice bath for 10 min. The deuteriotrifluoroacetic acid was introduced with a syringe. The mixture was stirred with a magnetic stirrer until all the solid was dissolved. Norbornene was then added all at once. After being stirred vigorously for 2 min, the product was isolated by the same procedure used for the addition of trifluoroacetic acid. The resulting mixture of chloride and trifluoroacetate was analyzed by GLC and by ^{1}H NMR. The chloride was separated by GLC on a 4 ft × ⅛ in. 20% tricresyl phosphate column at 85°.

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