Additions to Bicyclic Olefins. IX. Electrophilic Addition of Acetic Acid and Perdeuterioacetic Acid to Norbornene and 7,7-Dimethylnorbornene. A Remarkable Stereoselectivity for the Addition Process with Evidence for the Capture of the 2-Norbornyl Cation in an Unsymmetrical (Classical) State[1]

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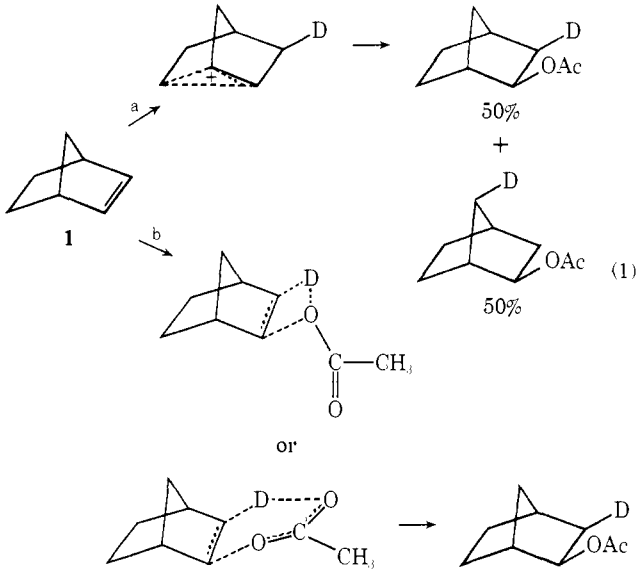
Abstract: Norbornene adds acetic acid slowly at 100° to yield 2-norbornyl acetate with a remarkable stereoselectivity, 99.98% exo. The acetolysis of *exo*-norbornyl tosylate at 100° proceeds with comparable stereoselectivity: 99.95% *exo*-norbornyl acetate. The similarity in the stereoselectivities of the two reactions indicates that they must be proceeding through similar intermediates. Yet this intermediate cannot be the symmetrical σ-bridged (nonclassical) 2-norbornyl cation since the addition of perdeuterioacetic acid to norbornene gives 67% of unrearranged *exo*-3-*d* acetate. Concerted cyclic addition of acetic acid was also excluded because the addition of acetic acid to 7,7-dimethylnorbornene is only slightly slower, $k_{\text{norbornene}}/k_{\text{7,7-dimethylnorbornene}} = 2.8$, and exhibits a solvolytic-like stereoselectivity of 99.92% exo. The addition of perdeuterioacetic acid to 7,7-dimethylnorbornene reveals that the deuterium also adds exo to the double bond. Previous studies demonstrated that cyclic addition reactions to 7,7-dimethylnorbornene are both very slow and prefer endo attack because of the bulky 7,7-dimethyl substituents. Therefore, both the rate and the formation of cis exo product indicate a two-stage addition process. The results are not compatible with an addition process involving the formation of σ-bridged (nonclassical) cations as the sole intermediate. It is proposed that the capture by acetic acid of the rapidly equilibrating unsymmetrical (classical) cations is the most likely pathway to the observed products.

The addition of deuterated acetic acid to norbornene (**1**)[3] and several of its derivatives[4,5] yields products with a distribution of the tag that is not compatible with an addition process proceeding through the formation of a symmetrical nonclassical ion as the sole intermediate. The data can be accommodated by a mechanism involving the capture of rapidly equilibrating classical ions[6] before they have attained full equilibration, as proposed for the addition of hydrogen chloride[7] and trifluoroacetic acid.[8]

However, it has been argued that such results could also be rationalized in terms of competing concurrent mechanisms, such as (a) an ionic addition proceeding through the σ-bridged symmetrical (nonclassical) 2-norbornyl cation and (b) a concerted cyclic molecular addition which places the tag exclusively at the exo-3 position[5,9] (eq 1).



(1)

We have proposed the use of norbornene (**1**) and 7,7-dimethylnorbornene (**2**) as diagnostic tools to test for the importance of such cyclic addition processes.[10,11] Thus, both the rates and the stereochemistry of cyclic addition processes are greatly affected by the presence of the 7,7-dimethyl substituents, whereas the rates and stereochemistry of two stage noncyclic additions are generally influenced to a much lesser degree by these substituents.[11] Consequently, we undertook a detailed study of the addition of acetic acid and perdeuterioacetic acid to norbornene (**1**) and 7,7-dimethylnorbornene (**2**) in order to test the importance of the postulated cyclic process in the mechanism of the addition and to define more precisely the nature of the intermediate involved in this electrophilic addition.

Results

The addition of acetic acid to **1** and **2**, in the presence and absence of sodium acetate, and the acetolysis of *exo*-norbornyl tosylate (**3**) and 3,3-dimethyl-*endo*-norbornyl brosylate (**4**) in the presence of sodium acetate were carried out at 100°. All the products were stable to the reaction conditions. The compositions were determined by GLC analysis using appropriate columns. In 4 days, **1** gave a 20% yield of 2-norbornyl acetate with a remarkably high exo stereoselectivity: 99.99% exo in the absence of sodium acetate and 99.97% exo in the presence of 1 *M* sodium acetate. The acetolysis of **3** in the presence of 0.5–0.6 *M* sodium acetate produced 99.95% *exo*-norbornyl acetate (**5**) and 0.05% *endo*-norbornyl acetate (**6**).[12,13]

The addition of acetic acid to **2** proceeded at a rate somewhat slower than to **1**. A competition reaction indicated that **1** was 2.8 times more reactive than **2**. Treatment of **2** with acetic acid containing 0.1 or 1 *M* of sodium acetate gave a 7% yield of acetates which the GLC analysis indicated to contain 71% of 7,7-dimethyl-, 22% of 5,5-dimethyl-, and 7% of 3,3-dimethyl-2-norbornyl acetate. No significant effect of the sodium acetate on the reaction rate or the

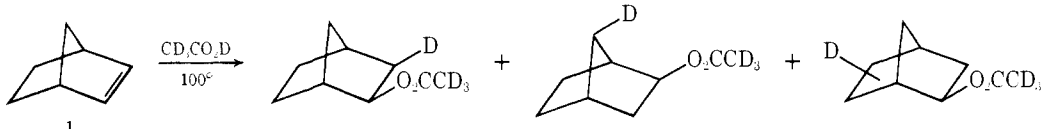
Table I. Comparison of the Products and Stereochemistry in the Addition of Acetic Acid to Norbornene and 7,7-Dimethylnorbornene and in the Acetolysis of the Corresponding Arenesulfonates

Starting material	[NaOAc], *M*	Time	% reaction	Product, % 5	6	7	8	9 + 10
1	0	4 days	20	99.99	0.01			
1	1		20	99.97	0.03			
3	0.6	15 min	100	99.95	0.05			
3	0.5		100	99.96	0.04			
2	0.1	4 days	7			20.1	6.4	73.5% (99.91% 9)
2	1	4 days	7			23.7	7.4	68.9 (99.92% 9)
4	1	9 hr				48.0	8.2	43.8 (99.95% 9)

product ratio was observed. Presumably the exo/endo ratio for 5,5-dimethyl- (**7**) and 3,3-dimethyl-2-norbornyl acetate (**8**) was similar to that for norbornyl acetate. However, the 7,7-dimethyl-2-norbornyl acetate contained 99.92% exo (**9**) and 0.08% endo (**10**) isomers. Acetolysis of **4** in the presence of 1 *M* sodium acetate gave about 48% of **7**, 8% of **8**, and 44% of **9** and **10**. The selectivity was 99.95% exo.[14] The results are summarized in Table I.

The addition of perdeuterioacetic acid (CD_3COOD) to **1** and **2** was slower than the addition of acetic acid, indicating a kinetic isotope effect of approximately 2. At 100°, **1** yielded 10% acetate in 4 days. The products, also consisting of 99.98% exo isomer, were reduced to the corresponding alcohol. ^1H NMR analysis revealed that the resultant *exo*-norbornanol-d_4 had more deuterium at the exo-3 than at the syn-7 position[8,15] (eq 2).

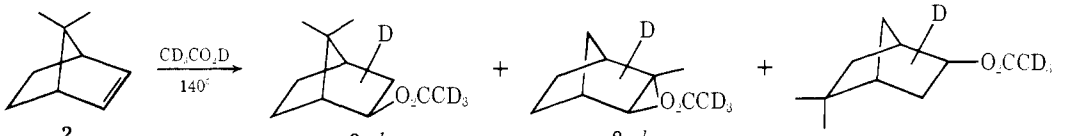
The reaction of **2** with perdeuterioacetic acid was carried out at 140°. The higher temperature was employed merely for the purpose of increasing the yield of product. Although control experiments revealed that approximately 25% of **9** would undergo acetolysis under these conditions, such acetolysis would not affect the observed stereochemistry of deuterium in **9** significantly. In 4 days, there was obtained a 49% yield of the deuterated acetates containing 65% of **9**-d_4, 25% of **8**-d_4, and 10% of **7**-d_4 (eq 3). The very high exo stereoselectivity was also realized. In the 7,7-dimethylnorbornyl derivatives, it was 99.92% exo, 0.08% endo. The stereochemistry of deuteronation, and thus protonation, was established by ^1H NMR of the corresponding alcohol following reduction with lithium aluminum hydride. The alcohols were separated by chromatography over alumina, and a mixture of 90% of 7,7-dimethyl-*exo*-norbornanol-*d* (**11**-*d*) and 10% of 3,3-dimethyl-*exo*-norbornanol-*d* was obtained. The ^1H NMR spectrum of the undeuterated **11** taken with 1 *M* solution in 95% pyridine–5% deuterium oxide exhibited a doublet of doublet at δ 4.0 (J = 8 and 3.5 Hz) for the α-methine proton and a complex pattern at δ 2.02 for the exo-3 proton. Authentic **11**-*d*, prepared from oxymercuration of **2**,[16] showed only a doublet (J = 8 Hz) at δ 4.0 and no absorptions at δ 2.02.[17] The ^1H NMR spectrum of the reaction product revealed more than 90% deuterium located at the exo-3 position in **11**-*d* and, therefore, in **9**-d_4. Referring to the result on the addition of deuteriotrifluoroacetic acid to **2**,[8] in which about 40% of the deuterium is at C-5 due to hydride shift, it is reasonable that, in the present case, the remaining 10% of deuterium is also at C-5 but not at endo-3. The essential absence of 3-endo deuteronation to **2** was further supported by examining the ^1H



1

0 *M* CD_3CO_2Na 69% 19% 12%

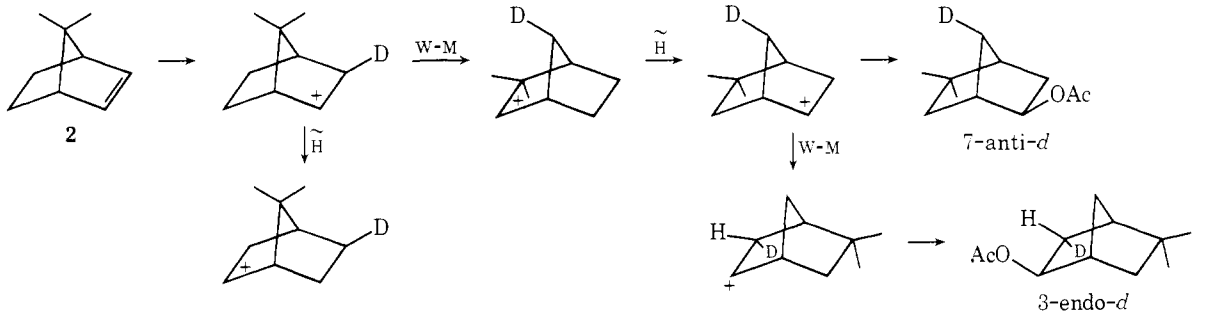
1 *M* CD_3CO_2Na 64% 21% 15%



2 **9**-d_4 **8**-d_4 **7**-d_4

0 *M* CD_3CO_2Na 64% 26% 10%

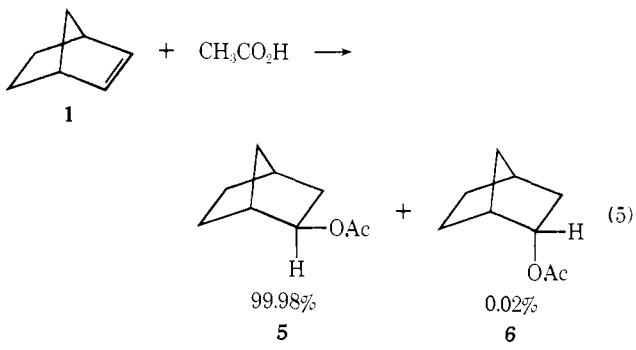
0.1 *M* CD_3CO_2Na 67% 24% 9%



NMR spectrum of 5,5-dimethyl-2-*exo*-norbornanol-*d* obtained by reducing the acetate with lithium aluminum hydride and purification by chromatography over alumina. The α-methine proton exhibited a mixture of a doublet (J = 3.5 Hz) and doublet of doublet, which were consistent with 7-*anti*-*d*- and 3-*endo*-*d*-5,5-dimethyl-2-*exo*-norbornanols, respectively (eq 4).

Discussion

The present results reveal that the addition of acetic acid to norbornene at 100° proceeds to give 2-norbornyl acetate with a remarkable stereoselectivity: 99.99% exo in the absence of sodium acetate and 99.97% exo in its presence (eq 5).



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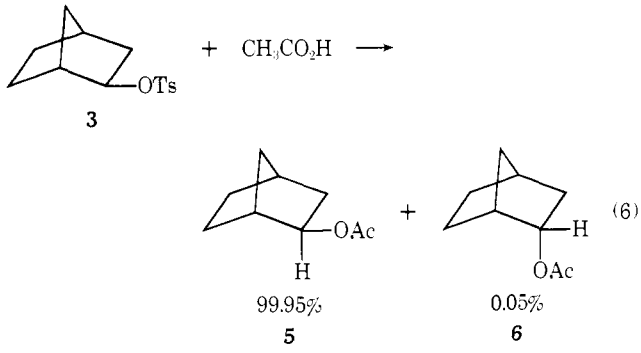
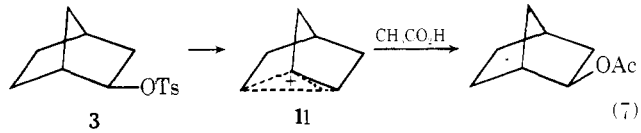
The acetolysis of *exo*-norbornyl tosylate at 100° likewise proceeds to give 2-norbornyl acetate with comparable stereoselectivity: 99.95% exo (eq 6).



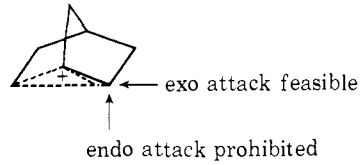
(6)

Such a remarkably high stereoselectivity in the solvolysis has been considered to require the formation of a symmetrical σ-bridged (nonclassical) norbornyl cation (**11**) in the course of the reaction[18,19,20] (eq 7). The high exo stereo-



(7)

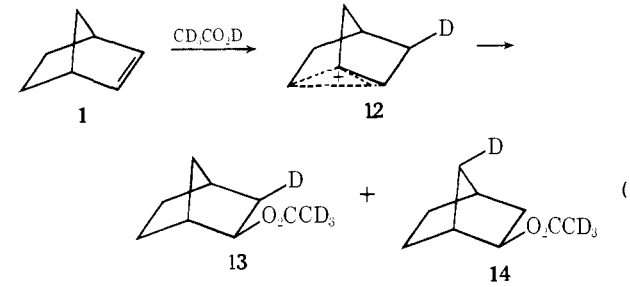
selectivity is postulated to result from a prohibition by the σ bridges to attack by the nucleophile from the endo direction (**11**).



11

The very similar exceptionally high stereoselectivities observed for the addition reaction (5) and in the solvolysis reaction (6) support the conclusion that the reactions must be proceeding through very similar intermediates. It is tempting to adopt the nonclassical ion **11** as this intermediate.

The nonclassical ion **11** possesses a plane of symmetry.[20] Consequently, the addition of perdeuterioacetic acid to norbornene must yield a 50–50 distribution of the exo-3-*d* and syn-7-*d* isomers if the addition proceeds through such a symmetrical intermediate (eq 8). However, experimentally there is obtained 69% **13** and 19% **14,** with 12% of hydride shifted material.



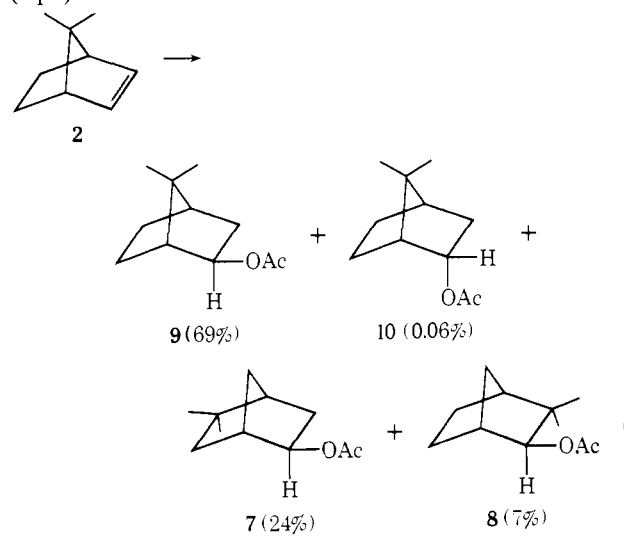
(8)

It has been suggested that a possible way out of this dilemma is to postulate that approximately half of the addition reaction proceeds through the nonclassical carbonium ion and approximately half through a concerted molecular addition[9] (eq 1). This could account for the observed formation of **13** in approximately 50% excess to **14.** However, this proposal creates a new difficulty for the nonclassical ion interpretation.

One of the major arguments for the formation of the nonclassical species **11** in the acetolysis process is the remarkably high stereoselectivity revealed by the 2-norbornyl acetate product, 99.95% exo.[14] It was argued that a stereoselectivity of this magnitude was unexplicable except in terms of the special substitution characteristics of the σ-bridged species **11.** However, the addition of acetic acid to norbornene exhibits a comparable stereoselectivity, 99.98% exo. If only half of the addition process goes through the carbonium ion pathway, then the pathway responsible for the other half of the reaction, the proposed concerted addition process, must involve a stereoselectivity of comparable magnitude. But this then would mean that processes involving intermediates other than the nonclassical ion could achieve stereoselectivities of this magnitude.

In order to provide an experimental test of this proposal of a competing cyclic addition process, the addition of acetic acid and of perdeuterioacetic acid to 7,7-dimethylnorbornene (**2**) was undertaken.

The addition of acetic acid to **2** produces the exo isomer (**9**) predominantly, together with appreciable quantities of Wagner–Meerwein (**8**) and hydride-shifted (**7**) derivatives (eq 9).

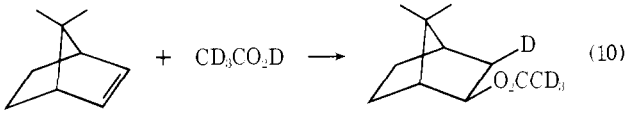


(9)

The unrearranged products, **9** and **10,** are formed with a stereoselectivity slightly smaller than that observed for norbornene itself (eq 5). However, the value, 99.92% exo- (**9**), 0.08% endo- (**10**), is still remarkably high. Clearly, the 7,7-dimethyl substituents do not exert a major influence on the stereochemistry of the addition process, such as is generally observed for cyclic addition processes.[11,21]

Competitive experiments revealed $k_{\text{norbornene}}/k_{\text{7,7-dimethylnorbornene}}$ to be 2.8. The relative rates of exo addition are very much higher, in the range of 480–1820, for representative cyclic additions.[11,22]

The addition of perdeuterioacetic acid to 7,7-dimethylnorbornene proceeds to give the exo acetate containing the deuterium in the exo-3 position (eq 10). Consequently, the 7,7-dimethyl substituents fail to affect stereochemically either the addition of the proton (deuteron) in the first stage or the addition of the acetoxy nucleophile in the second. As was pointed out earlier, this is the characteristic pattern observed for two stage additions of all types involving attack of free radicals, electrophiles or nucleophiles, where the attacking reagent is one of not very large steric requirements.[11]



(10)

Consequently, we have now been able to capture the 2-norbornyl cation in the unsymmetrical classical state in the electrophilic addition to norbornene of hydrogen chloride,[7] of trifluoroacetic acid,[8] and of acetic acid. Indeed, we have recently pointed out that such capture of the norbornyl cation in unsymmetrical form is not as uncommon as one might gather from reviews of the topic.[23] Indeed, we recently listed some 11 different reactions in which the unsymmetrical 2-norbornyl cation has been captured.[8]

Only in solvolysis has the capture of the 2-norbornyl cation in the unsymmetrical state not yet been reported. For example, the acetolysis of optically active *exo*-norbornyl brosylate fails to provide optically active acetate.[24] In past discussions, it has generally been assumed that the rate of collapse of classical secondary carbonium ions to products must be very fast, competitive with the rate of rotation about a single bond.[25] As pointed out earlier,[7] the difficulty may be 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[26] 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. Thus it would be solvolysis that would be singular, not representative of typical carbonium ion reactions of the 2-norbornyl species.

To sum up, the present results do not support the proposal of competitive dual mechanisms for electrophilic additions to norbornene and its derivatives.[4,5,9] The results can be accommodated by a mechanism involving a rapidly equilibrating pair of unsymmetrical (classical) 2-norbornyl cations[19] which are captured before they are fully equilibrated. In terms of this interpretation, the larger amount of Wagner–Meerwein and hydride-shifted products in the acetolysis of 2-norbornyl derivatives than in the addition of acetic acid to the olefin is due to the longer lifetime of the ion-pair intermediate in the solvolysis. Similarly, the larger amount of Wagner–Meerwein and hydride-shifted products in the addition of trifluoroacetic acid to norbornene,[8] as compared with that observed in the addition of acetic acid, is to be attributed to the stronger nucleophilic properties of acetic acid and acetate ion in the latter reaction, providing a shorter lifetime for the cationic intermediate. Moreover, the higher degree of Wagner–Meerwein and hydride shift observed in the acetate fraction from the reaction of deuterium chloride in perdeuteroacetic acid with norbornene,[7] as compared with that realized in the uncatalyzed addition of acetic acid itself, is consistent with the lower nucleophilic properties of acetic acid as compared with those of acetate ion.

Consequently, the simplest, most consistent interpretation of the addition of representative protonic acids, hydrogen chloride,[7,27] hydrobromic acid,[27] trifluoroacetic acid,[8] and acetic acid, to norbornene and related bicyclic olefins is through the formation of rapidly equilibrating unsymmetrical (classical) 2-norbornyl cations, which can be captured prior to full equilibration, and which react with nucleophiles with remarkably high stereoselectivity. It follows that the high stereoselectivity observed in the solvolysis of 2-norbornyl derivatives cannot be used to support the incursion of symmetrical σ-bridged nonclassical cations.

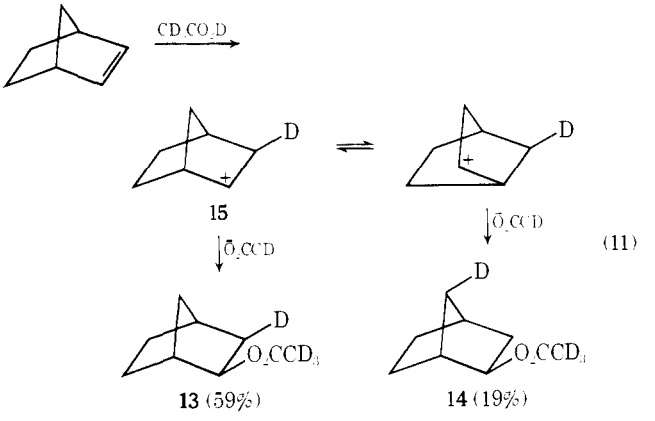
Conclusion

The present publication completes our studies of additions to bicyclic olefins. We established that additions involving essentially concerted cyclic additions, such as hydroboration[28] or epoxidation,[29] proceed with high exo stereoselectivity to norbornene. The presence of 7,7-dimethyl substituents affects strongly both the stereochemistry and the relative rates of such additions.[11]

Two-stage addition processes not involving concerted cyclic additions also proceed predominantly exo-cis in the case of norbornene. This is true both for electrophilic reactions, such as the addition of mercuric acetate[16] and mercuric trifluoroacetate,[30] or free radical additions, such as that of thiophenol.[11] In the case of such addition processes, the presence of 7,7-dimethyl substituents exerts little effect upon either the rates or the stereochemistry of the addition process.[11]

Application of these criteria, rates and stereochemistry, to the addition of representative protonic acids, such as hydrogen chloride,[7] trifluoroacetic acid,[8] and acetic acid, supports the conclusion that these additions must proceed through two-stage processes, not involving cyclic molecular additions. The first stage of the two-stage process must involve the transfer of a proton or deuteron to norbornene with the formation of the 2-norbornyl cation. If this intermediate were the symmetrical σ-bridged nonclassical cation (**12**), completion of the reaction would yield the product with equal distribution of deuterium at the exo-3 and syn-7 position (eq 8).

This is not observed. Therefore the carbonium ion intermediate must be an unsymmetrical cation (**15**) which is captured prior to full equilibration (eq 11).



(11)

As was pointed out earlier,[8] the nonclassical ion problem has gone through three successive phases. In the first phase, emphasis was placed on the high exo:endo rate and product ratios in the solvolysis of 2-norbornyl derivatives as an argument for σ participation presumed to lead to the σ-bridged cation.[24] However, the demonstration that highly stabilized 2-aryl-2-norbornyl derivatives, which yield classical 2-aryl-2-norbornyl cations,[31] exhibit high exo:endo rate and product ratios[32] comparable to those of 2-norbornyl itself eliminated this basis for the proposed nonclassical interpretation.

In the second phase, it was proposed that bridging lags behind ionization[25] 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, the present study, as well as the many studies recently summarized[8] clearly establishing that the 2-norbornyl cation can be readily trapped in the unsymmetrical (classical) form, refutes this position.

In the third phase, it has been argued that the norbornyl cation can be prepared and observed spectroscopically in superacid media.[33,34] However, there are major difficulties with the experimental data and their interpretation.[7,8,35] It is not even clear as to how pertinent are the results and conclusions for studies under stable ion conditions to the behavior of cations under solvolytic conditions. Consequently, it would appear that caution is called for before Olah's conclusion (". . . the long standing controversy as to the nature of the 2-norbornyl cation is unequivocally resolved in favor of the nonclassical carbonium ion"[34]) can be generally adopted.

Over the years, numerous arguments and evidences have been advanced to favor the formation of the symmetrical σ-bridged 2-norbornyl cation.[19] One by one they have crumbled under the impact of further study. We feel that we have given the concept a long, careful, patient examination. We look forward to seeing a serious objective consideration of all of our data and conclusions by those who continue to favor the proposal.

Experimental Section

Materials. Baker Analyzed glacial acetic acid was dried by heating under reflux for several hours over a small amount of acetic anhydride. Sodium acetate was dried at 120° for several hours and then transferred to a vacuum desiccator and dried at 1 mm for 12 hr over phosphorus pentoxide. Norbornene (Aldrich) was distilled under nitrogen, mp 46° (lit.[36] 46.0–46.5°). 7,7-Dimethylnorbornene was prepared as described before.[37] The Pyrex ampoules used for the addition of acetic acid were washed with concentrated ammonium hydroxide, rinsed well with water, and dried in a 120° oven.

GLC Analysis. All the analyses were carried out on a Perkin-Elmer Model 226 gas chromatograph using appropriate columns.

^{1}H NMR Analysis. The analyses were run with a Varian A-60A spectrometer. For quantitative purpose the integrations were repeated for ten times, and the average value was recorded. About a 30-sec delay between each sweep helped to give more reproducible spectra.

Addition of Acetic Acid to Norbornene (1). A 1 *M* solution of **1** in glacial acetic acid was prepared and was transferred to ampoules in 5-ml portions. The ampoules were sealed under nitrogen and were placed in a 100 ± 2° bath for 4 days. Then the contents in each ampoule were added to 50 ml of water and extracted with 25 ml of pentane. The organic layer was washed successively with 50 ml of water, 25 ml of 0.2*N* sodium bicarbonate, 25 ml of water, 2 × 25 ml of 1 *M* aqueous silver nitrate, and finally 25 ml of water. After drying, the pentane was distilled off through a 6-in. Vigreux column with 40–50° water bath, and the residue was analyzed on a 150 ft × 0.01 in. TCEP column at 70°.

Addition of Acetic Acid to 1 in the Presence of 1 *M* Sodium Acetate. To 0.82 g (10 mmol) of dry sodium acetate placed in an ampoule was added 10 ml of a 1.0 *M* solution of **1** in glacial acetic acid. The ampoule was sealed and was allowed to react at 100°. The reaction product was isolated and analyzed as before.

Addition of Perdeuterioacetic Acid to 1. The solution and ampoules were prepared as before. After 4 days at 100°, the ampoule was cooled and opened, and a 0.5-ml sample was placed in a ^{1}H NMR tube. The yield of acetate was determined by comparing the area of the olefin bridgehead proton with the acetate bridgehead protons. In order to recover the perdeuterioacetic acid, the following work-up procedure was employed. About 10 ml of pentane and a magnetic stirring bar was added to the ampoule under nitrogen. With stirring, the mixture was cooled to −15° until solidification occurred. The pentane layer was decanted, and fresh pentane was added and the procedure repeated. Two additional extractions were adequate to extract greater than 90% of the norbornyl acetate-d_4. The pentane solution was worked up as usual.

Addition of Perdeuterioacetic Acid and Sodium Acetate-d_3 to 1. The sodium acetate-d_3 solution was prepared from 0.46 g (20 mmol) of sodium and 20 g of perdeuterioacetic acid. To this solution, 1.88 g (20 mmol) of **1** was added. The reaction was carried out, and the product was analyzed as before.

Lithium Aluminum Hydride Reduction of Norbornyl Acetate-d_4. The acetates were reduced to the alcohols with 100% excess of lithium aluminum hydride in ether. The excess hydride was decomposed with water and 3 *M* sodium hydroxide. The ether solution was dried ($MgSO_4$), and the solvent was removed on a rotary evaporator at 0–5°.

Purification of Alcohols by Column Chromatography. The crude alcohol was chromatographed over Merck chromatographic grade alumina. The unreacted norbornene was eluted first with pentane, and the *exo*-norbornanol was then eluted with ether. Evaporation of ether yielded 61% of the theoretically expected alcohol from the ^{1}H NMR yield data on the original acetate. Sublimation at 1 mm gave pure *exo*-norbornanol, mp 124–126°.

Acetolysis of *exo*-Norbornyl Tosylate (3). The acetic acid solution (10 ml), containing sodium acetate (5 mmol), was heated up to 100° for 30 min under nitrogen. Then finely divided **3** (4 mmol) was added slowly with a spatula over a 10-min period and was stirred at 100° for an additional 15 min. The same work-up procedure used for the addition of acetic acid was employed.

Addition of Acetic Acid to 7,7-Dimethylnorbornene (2). A 1 *M* solution of 7,7-dimethylnorbornene in dried glacial acetic acid was prepared. Sodium acetate was added, and the mixture was allowed to react at 100°. The product was isolated as in the case of **1**. The composition was determined by GLC using DEGS column at 90°.

Acetolysis of 3,3-Dimethyl-*endo*-norbornyl Brosylate (4). Similar to the acetolysis of **3**, the acetolysis of **4** was carried out at 100° for 9 hr. The product was isolated as described before and was analyzed by GLC using DEGS column.

Addition of Perdeuterioacetic Acid to 2 at 140°. The procedure is essentially the same for the addition of perdeuterioacetic acid to **1**. After 4 days at 140 ± 2°, ^{1}H NMR analysis indicated 48% reaction. The reaction mixtures were worked up in the usual way, and analysis on a DEGS column showed the composition.

Stability Test of 9. At 100°, **9** is stable in acetic acid. However, a mixture of 99.2% of **9**, 0.7% of **7**, and 0.1% of **8** changed into 82.7% of **9**, 12.2% of **7**, and 5.1% of **8** in 4 days at 138°. The reaction is about 25% on assuming that acetolysis of **9** would give equal amounts of **7** and **9**.

Chromatography of Alcohols from Dimethylnorbornyl Acetate-d_4 Mixture. The crude acetate-d_4 was reduced with lithium aluminum hydride to give 0.71 g of crude alcohol. It was chromatographed on a column prepared from 94 g of alumina and 6 g of water. The unreacted olefin was eluted with 140 ml of 3% ether in pentane. Then from 120 ml of 5% ether in pentane, **11**-*d* and a small amount of 3,3-dimethyl-*exo*-norbornanol-*d* were isolated. Sublimation yielded 90% pure **11**-*d*, mp 136.5–140° (lit.[28] mp 142–143.5° for undeuterated **11**).

Competition Reaction between 1 and 2. A sample containing 61 mg (0.5 mmol) of **2**, 47 mg (0.5 mmol) of **1**, and 8 mg (0.1 mmol) of sodium acetate in 1 ml of acetic acid was sealed in an ampoule and heated to 100° for 4 days. GLC analysis indicated that **1** was 2.8 times more reactive than **2**.

References and Notes

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Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. XIX. Persistent Cyclohexadienyls and Related Radicals[1]

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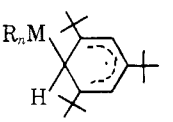
Abstract: A variety of persistent radicals of the cyclohexadienyl type have been generated by the addition of certain carbon, silicon, oxygen, and phosphorus centered radicals (e.g., $\dot{C}F_3$, $Cl_3Si\cdot$, $Me_3CO\cdot$, $(CH_3CH_2O)_2\dot{P}{=}O$) to the following sterically hindered aromatic compounds: 1,3,5-tri-*tert*-butylbenzene, 2,4,6-tri-*tert*-butylpyridine, 2,4,6-tri-*tert*-butyl-λ^3-phosphorin, 1,3-di-*tert*-butylbenzene, and 2,6-di-*tert*-butylpyridine. The structures of the radicals, which have been deduced from their epr spectra, should assist in the identification of more transient cyclohexadienyls. It is shown that persistence is a consequence of steric protection of the reactive sites in these radicals. Kinetics for decay of some of the radicals are reported.

We have recently emphasized the dominant role that steric factors play in determining the persistence (i.e., the lifetime) of carbon-centered free radicals in solution.[1,5,6] Our success in generating persistent secondary and tertiary alkyls,[1,7,8] α-aminoalkyls,[9] phenyls,[10] vinyls,[1,11] and allyls,[1] together with Berndt's preparation of a persistent benzyl[12] and a persistent allyl,[13] led us to extend our experiments to cyclohexadienyls and related radicals. These species are of great interest as they are formed as intermediates in all homolytic aromatic substitutions.[14] Thermodynamically, cyclohexadienyls are strongly stabilized,[15] but simple cyclohexadienyls are nevertheless very transient radicals which normally decay by bimolecular processes at, or near, the diffusion-controlled limit.[17] It was our expectation that addition of a radical, $\cdot MR_n$, to a sterically hindered aromatic such as 1,3,5-tri-*tert*-butylbenzene would produce a persistent, stabilized,[18] cyclohexadienyl (**1**) since there would be no easy route open for this radical to decay, provided the addition of $\cdot MR_n$ was irreversible. Thus, a radical of type **1** should be too hindered to dimerize or disproportionate.



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Unfortunately, tri-*tert*-butylbenzene is so hindered that a persistent radical (**1**) was only obtained with $MR_n = C_6F_5$. Extension of our experiments to 2,4,6-tri-*tert*-butylpyridine yielded only the 1-trichlorosilyl adduct. However, with 2,4,6-tri-*tert*-butyl-λ^3-phosphorin,[19] several persistent radicals of the cyclohexadienyl type were produced by the addition of various $\cdot MR_n$ to the phosphorus. Similar radicals were produced from 2,4,6-triphenyl-λ^3-phosphorin.[19]

Cyclohexadienyl and cyclohexadienyl type radicals were also produced by $\cdot MR_n$ additions to 1,3-di-*tert*-butylbenzene and 2,6-di-*tert*-butylpyridine. (The corresponding phosphorin is not available.) As well as the expected adducts, viz., **2** and **3**, which are relatively short lived, some extremely persistent radicals having structures such as **4**