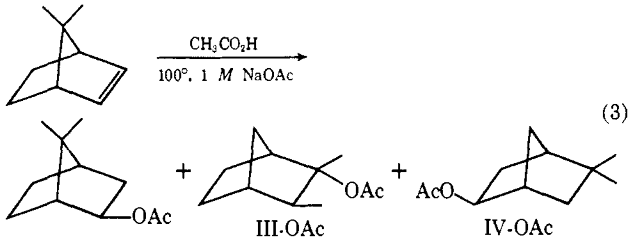
the vinyl position.[10] The present product underwent elimination to give I containing only 3% of the deuterium at the vinyl position. This establishes that the alcohol cannot have a significant amount of deuterium at the *endo*-3 position and might have some 40% of the deuterium at C-5 due to a 6,2-hydride shift.

We therefore conclude that the addition of deuteriotrifluoroacetic acid to I must proceed in a stepwise manner, with the deuteron adding predominantly *exo* to the 3 position to form the carbonium ion, which partially undergoes both hydride and Wagner–Meerwein shifts, and which completes the reaction to give II-TFA-*d* adding trifluoroacetate almost exclusively *exo*.

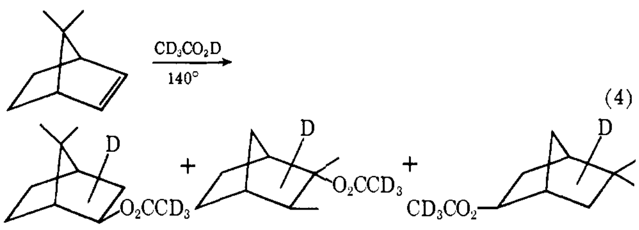
The addition of acetic acid to I proceeded much slower, but revealed the same stereochemistry and stereoselectivity. Treatment of I with acetic acid (1 *M* in sodium acetate[11]) for 4 days at 100° yielded 7% acetates (eq 3).[8] Again, the 7,7-dimethylnorbornyl ester (II-OAc) was obtained in high stereoselectivity, 99.92% *exo* and 0.08% *endo*,[9] similar to that observed in solvolysis of the brosylate, 99.95% *exo*-II-OAc and 0.05% *endo*-II-OAc.[13]



(3)

II-OAc 69% (99.92% *exo*, 0.08% *endo*) III-OAc 7% IV-OAc 24%

The stereochemistry of the protonation was established by adding perdeuterioacetic acid to I at 140°.[14] In 4 days, there was obtained a 49% yield of the deuterated esters, containing 65% of 7,7-dimethyl-*exo*-norbornyl-*d* acetate-d_3, together with isomerized products (eq 4). Chromatography over alumina of the corresponding alcohols yields a mixture containing 90% II-OH-*d* and 10% III-OH-*d*. The pmr spectrum revealed more than 90% deuterium located at the *exo*-3 position of II-OH-*d*.[15] It is reasonable that the remaining 10% of the deuterium is essentially at C-5 as a consequence of a 6,2-hydride shift.



(4)

	II-OAc-d_4	III-OAc-d_4	IV-OAc-d_4
0 NaOAc-d_3	64%	26%	10%
0.1 *M* NaOAc-d_3	67%	24%	9%

Consequently, the addition of acetic acid to 7,7-dimethylnorbornene reveals the same features as the addition of trifluoroacetic acid to the bicyclic olefin. Neither system reveals the presence of any significant amount of *endo* addition, such as might have been anticipated for the oft postulated molecular *cis* addition.[4,5] Both systems reveal only *exo* addition of the proton (within the comparatively large uncertainty of the isotopic analysis) and almost exclusive *exo* addition of the anion (99.92%). These results are consistent with the stereochemistry postulated for two-stage noncyclic additions of moieties of small steric requirements to 7,7-dimethylnorbornene. The extensive rearrangements are consistent with a two-step carbonium ion process, with the lower extent of rearrangement observed in the acetic acid system attributable to the higher nucleophilicity of the acetic acid, resulting in a shorter lifetime for the intermediate.

In conclusion, the present results strongly support a two-stage carbonium ion process for the addition of both acetic acid and trifluoroacetic acid to bicyclic olefins of the norbornene type, and fail to support the oft postulated incursion of a competitive molecular cyclic addition.

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[11] No significant effect of sodium acetate, 0.1 or 1 *M*, on reaction rate or product ratio was observed.[12] The sodium acetate was used to provide a direct comparison with the products formed in acetolysis of the brosylate under the same conditions.

[12] See also S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *J. Org. Chem.*, **31**, 2733 (1966).

[13] Acetolysis of 3,3-dimethyl-*endo*-norbornyl brosylate at 100° in the presence of 1 *M* sodium acetate gives 44% II-OAc, 8% III-OAc, and 48% IV-OAc. See also A. Colter, E. C. Friedrich, N. J. Holness, and S. Winstein, *J. Amer. Chem. Soc.*, **87**, 378 (1965).

[14] The higher temperature was used to realize a faster rate and a larger yield of product required to establish the position of the deuterium atom. Approximately 25% of 7,7-dimethyl-*exo*-norbornyl acetate undergoes solvolysis under these conditions. However, this should not affect the stereochemistry of the deuterium in this derivative.

[15] The pmr spectrum for 1 *M* solutions of II-OH in 95% pyridine–5% deuterium oxide exhibits a doublet of doublet (J = 8 and 3.5 Hz) at δ 4.0 (1 H) and a complex pattern at δ 2.02 (1 H). Both are separated from other signals at 100 MHz.[16] For *exo*-3-*d*-7,7-dimethyl-*exo*-norbornanol, the former is a distinct doublet (J = 8 Hz) and the latter disappears.

[16] We are grateful to Professor L. M. Stock of the University of Chicago for providing the use of the Varian HA-100 spectrometer for this study.

[17] Graduate assistant on a grant (GP 6492 X) provided by the National Science Foundation.

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Stereochemistry of Additions to *anti*-7-Bromobenzonorbornadiene. Evidence in Support of the Recent Interpretation of the Steric Influence with Stepwise Electrophilic Additions to the Norbornene System

Sir:

It has recently been postulated[1] that reactions which proceed in two stages, and which involve reaction intermediates of modest steric requirements, will involve attack at the corners of the ethylene bridge in a norbornane skeleton. Furthermore, it has been suggested that the reagents of this type will exhibit an *exo* selectivity and will not be greatly influenced sterically by groups located at the *syn*-7 position. Thus, for example, camphor (**1**) exhibits largely *exo* monodeuteration, to produce **2**, upon mild base-catalyzed exchange conditions.[2,3]

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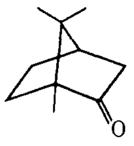
[1] H. C. Brown and J. C. Kawakami, *J. Amer. Chem. Soc.*, **92**, 202 (1970).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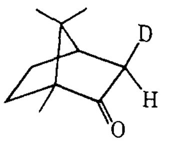

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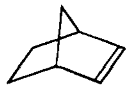
Reactions, however, that proceed through a cyclic transition state are postulated[1] to be influenced by the size of the substituent located at the *syn*-7 position. Norbornene (**3**), for example, forms a very stable complex with silver ion (presumably *exo*)[4] whereas apobornene (**4**) does not.[1]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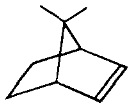
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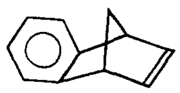
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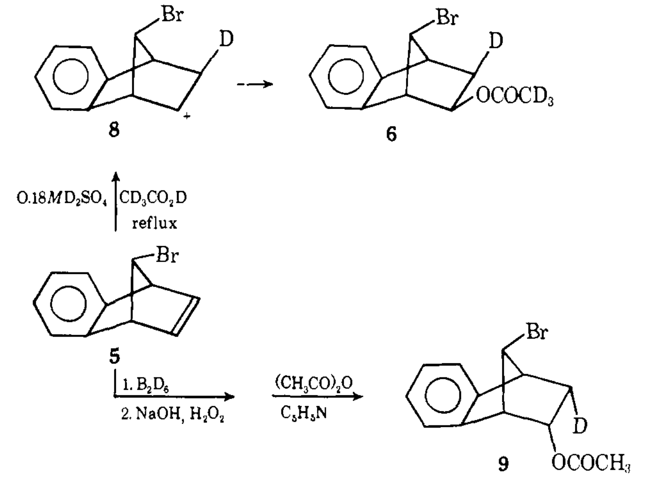
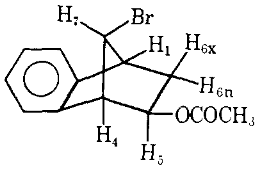
The proposal was postulated to be capable of being tested for addition reactions by utilizing mechanisms which were clearly either single-stage or two-stage additions. The acid-catalyzed addition of acetic acid has been shown previously to occur in a stepwise manner[5,6] and the hydroboration reaction is known to proceed in a concerted fashion to yield the *cis* addition product resulting from attack on the least-hindered side of the olefin.[7] These two reactions seem, therefore, well suited for testing the above hypothesis on a *syn*-7 substituted norbornene system.

The sulfuric acid-d_2 catalyzed addition of acetic acid-d_4 to *anti*-7-bromobenzonorbornadiene (**5**) produced the unrearranged *cis-exo* addition product **6** as the first and only observable (nmr) product. Addition of the same reagent to benzonorbornadiene (**7**) produced extensive rearrangement.[5] The analogous rearrangement is precluded in the addition to **5** by the apparent need to keep the bulky groups, bromine and acetate, as far apart as possible in product formation. The acid-catalyzed addition of acetic acid-d_4 to **5** provides, then, an example of a stepwise *cis-exo* addition where conceivably some factor is accounting for both the preference for *exo* electrophilic attack and for the *exo* nucleophilic attack on the intermediate benzonorbornenyl cation **8**.



Whereas the stepwise electrophilic addition of acetic acid-d_4 is *cis-exo*, the deuterioboration of **5** occurred exclusively *cis-endo* to produce, after acetylation, the acetate **9**. The concerted nature of this reaction, according to the above argument,[1] prevents attack at the corners of **5** and hence interaction with bromine, which is located *syn* to the double bond, is inevitable with *exo* approach. This makes *endo* approach more favorable on steric grounds, as expected.

The configurations of the acetates **6** and **9** were established by comparison (nmr) with the corresponding undeuterated acetates, **10** and **11**.[8-10] In *anti*-7-bromo-*exo*-5-benzonorbornenyl acetate (**10**), the signal for H_5 occurs at δ 4.70 with $J_{5,6n}$ = 7.5 Hz, $J_{5,6x}$ = 3.5 Hz, and $J_{5,7}$ = 1.2 Hz. In the corresponding *cis*-deuterio acetate **6**, this signal collapses to a quartet with $J_{5,6n}$ = 7.5 Hz and $J_{5,7}$ = 1.2 Hz. In *anti*-7-bromo-*endo*-5-benzonorbornenyl acetate (**11**), the signal for H_5 occurs at δ 5.71 with $J_{5,6x}$ = 8.7 Hz, $J_{5,6n}$ = 3.1 Hz, and $J_{5,4}$ = 4.0 Hz. In the corresponding *cis*-deuterio acetate **9** this multiplet collapses to a quartet with $J_{5,6x}$ = 8.7 Hz and $J_{5,4}$ = 4.0 Hz.



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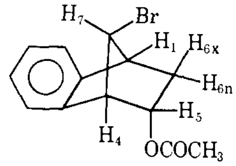

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Acknowledgment. We are indebted to the donors of The Petroleum Research Fund, administered by he American Chemical Society, for partial support of this research.

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(7) G. Zweifel, K. Nagase, and H. C. Brown, *J. Amer. Chem. Soc.*, **84**, 183 (1962).

(8) Correct microanalyses were obtained for the acetates.

(9) Chemical shifts are relative to tetramethylsilane (60 MHz).

(10) S. J. Cristol and G. W. Nachtigall, *J. Org. Chem.*, **32**, 3738 (1967), and references cited therein.

(11) National Science Foundation Undergraduate Research Participant, 1967–1969.

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On the Relative Importance of Through-Space *vs.* Through-Bond Interaction between the Lone Pairs in 1,4-Diazabicyclo[2.2.2]octane[1,2]

Sir:

Some time ago Hoffmann, Imamura, and Hehre[3] discussed the electronic mechanism for the interaction of electron lone pairs in diazabicycloalkanes (I). They showed that the relative sequence of the orbitals $a_1'(n_+)$, $a_2''(n_-)$ associated with the linear combinations $n_+ = N_+(n_1 + n_2)$ (S) and $n_- = N_-(n_1 - n_2)$ (A)

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(1) Part X of "Applications of Photoelectron Spectroscopy."

(2) Part IX: E. Haselbach and E. Heilbronner, *Helv. Chim. Acta*, in press.

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