addition reaction, the α carbon of the iminosulfenes appears to be of nucleophilic character.[9,10]

(9) For commentary on the various canonical structures as well as valence tautomers available to sulfenes and 1,2 *vs.* 1,3 addition reactions, the reader is referred to the review cited in ref 2.

(10) For other "abnormal" additions to sulfenes see J. F. King, K. Piers, D. J. H. Smith, C. L. McIntosh, and P. deMayo, *Chem. Commun.*, 31 (1969).

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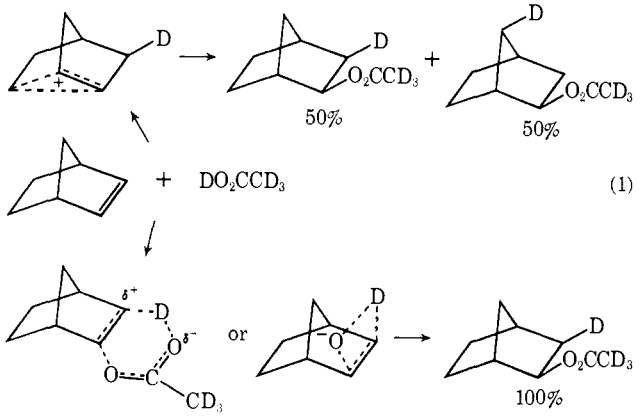
exo-cis Addition of Trifluoroacetic Acid and Acetic Acid to 7,7-Dimethylnorbornene. Evidence for the Essential Absence of Molecular Cyclic Addition Processes

Sir:

The addition of deuteriotrifluoroacetic acid and of perdeuterioacetic acid to 7,7-dimethylnorbornene gives *exo*-3-*d*-7,7-dimethylnorbornyl *exo*-trifluoroacetate and the corresponding *exo*-acetate-d_3, respectively, with remarkably high *exo* stereoselectivity. According to the recently proposed generalization,[1,2] the essential absence of *endo*-substituted product indicates that molecular cyclic addition processes cannot be significant in these additions.

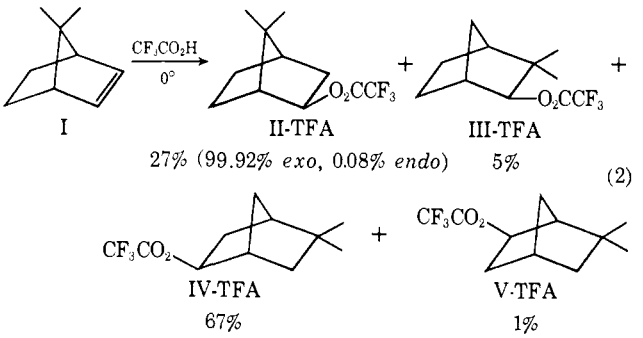
The additions of deuterated acetic acid to norbornene[3] and a number of its derivatives[4] yield products with a distribution of the deuterium tag that is not consistent with the formation of a symmetrical nonclassical ion as sole intermediate. Such distributions are consistent with the trapping of classical ions before they have attained full equilibration. However, it has been argued that the results can also be accommodated by postulating a dual mechanistic pathway, an ionic addition resulting in distribution of the tag to the *exo*-3 and *syn*-7 positions, and a concerted *cis* addition[4,5] which places the tag exclusively at the *exo*-3 position (eq 1).



(1)

It was recently proposed that additions to 7,7-dimethylnorbornene provide an experimental test for the presence of cyclic additions. All additions examined, additions which are generally considered to proceed through cyclic transition states or intermediates, are markedly influenced by the presence of the 7,7-dimethyl substituents. Such reactions take a predominantly *exo* course for norbornene, but either take a preferential *endo* course or are so badly hindered that they fail to proceed with 7,7-dimethylnorbornene.[1,2] Accordingly, it appeared desirable to examine the importance of the postulated concerted molecular processes by examining the addition of acetic acid and trifluoroacetic acid (and the deuterium tagged acids) to 7,7-dimethylnorbornene.

The addition of trifluoroacetic acid to olefins has been demonstrated to possess typical carbonium ion characteristics.[6] We observed that the reaction of trifluoroacetic acid with 7,7-dimethylnorbornene (I) was quite fast, the addition being complete in 6–8 min at 0°. The product contained 27% 7,7-dimethylnorbornyl trifluoroacetate (II-TFA), consisting of 99.92% *exo* and 0.08% *endo*, and a great deal of Wagner–Meerwein and hydride shifted products (III-TFA–V-TFA), as indicated by glpc analysis (eq 2).[7–9] The



(2)

formation of such large amounts of typical carbonium ion rearranged products, III-TFA–V-TFA, confirms the conclusion that the reaction must involve a major carbonium ion pathway. The insignificant amount of the *endo* isomer formed argues against the presence of any significant amount of cyclic addition, in accordance with the proposed generalization.[1,2]

It was of interest to establish the stereochemistry for the addition of the proton in this reaction. Under the same conditions the addition of deuteriotrifluoroacetic acid to I yielded the same mixture of monodeuterated trifluoroacetates (II-TFA-*d*–V-TFA-*d*). A mixture of II-TFA-*d* and IV-TFA-*d* was separated from the others by preparative glpc over a tricresyl phosphate column. After conversion to the alcohols, 7,7-dimethyl-*exo*-norbornanol-*d* was isolated by chromatography over alumina.

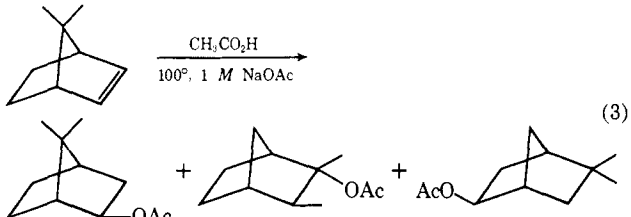
E2 elimination of a synthetic sample of *exo*-3-*d* tosylate proceeds with predominant loss of the *exo*-3 deuterium atom.[10] Indeed, I obtained in the elimination retains only 5% of the original deuterium at

(1) H. C. Brown and J. H. Kawakami, *J. Amer. Chem. Soc.*, **92**, 201 (1970).
(2) H. C. Brown and K.-T. Liu, *ibid.*, **92**, 3502 (1970).
(3) E. Vogelfanger, Ph.D. Thesis, University of California, Los Angeles, Calif., 1963.
(4) S. J. Cristol, *et al.*, *J. Org. Chem.*, **31**, 2719, 2726, 2741 (1966); *ibid.*, **33**,106 (1968).
(5) R. C. Fahey, *Top. Stereochem.*, **3**, 253 (1969).
(6) P. E. Peterson, *et al.*, *J. Amer. Chem. Soc.*, **89**, 5902 (1967), and previous papers in this series.
(7) The mixture of the trifluoroacetates was reduced with lithium aluminum hydride to the corresponding alcohol mixture, which was analyzed by glpc with a 150 ft × 0.01 in. UCON 50 LB 550X column on the Perkin-Elmer Model 226 chromatograph. The composition of the alcohol mixture was shown to be the same as the trifluoroacetates.
(8) All of the esters are stable to the reaction conditions.
(9) III-TFA–V-TFA are presumably the *exo* isomer predominantly, but no attempt was made to analyze the *exo*:*endo* ratio for other than II-TFA.
(10) H. C. Brown and K.-T. Liu, *J. Amer. Chem. Soc.*, **92**, 200 (1970).

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

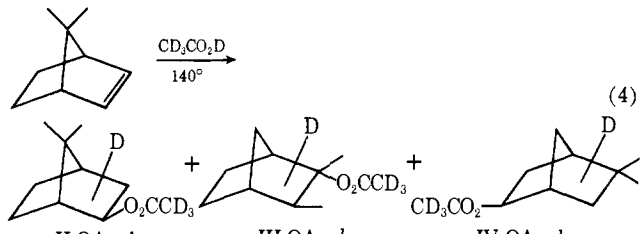


(3)

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

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]

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.

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]

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