

REACTION OF NORTRICYCLENE WITH DEUTERIOTRIFLUOROACETIC ACID. EVIDENCE FOR THE  
FORMATION OF EDGE-PROTONATED CYCLOPROPANE INTERMEDIATE

Kwang-Ting Liu

Department of Chemistry, National Taiwan University

Taipei, Republic of China

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Protonated cyclopropane intermediates have been considered to play important roles in a variety of cationic reactions.<sup>1</sup> Olah and coworkers have suggested the identity of corner-protonated nortricyclene with norbornyl cation based on the spectroscopic and quenching studies of the ion generated from the ionization of 2-norbornyl halides and from the protonation of nortricyclene (I) in super acid media at low temperature.<sup>2,3</sup> The same conclusion was stated to be applicable to the ion formed in solvolysis.<sup>2</sup> However, no comparative studies on the behavior of such an ion under solvolytic conditions has yet been made. It would be desirable to examine both the electrophilic ring opening of I and the solvolysis of norbornyl derivatives under the same conditions. In this note the author wishes to report the reaction of deuteriotrifluoroacetic acid with I and the deuterium distribution in the resultant exo-norbornyl-d trifluoroacetate(II), which indicates the formation of an edge-protonated cyclopropane intermediate.

Nortricyclene (I) readily undergoes ring opening upon treatment with trifluoroacetic acid. The reaction was complete as soon as I was dissolved in the acid at 0°C to give exo-norbornyl trifluoroacetate.<sup>4</sup> With deuterated acid the product was II.<sup>6</sup> At -20°C the reaction was incomplete in the same period of time. The monodeuterated trifluoroacetate II was converted into the corresponding exo-norbornanol-d,<sup>5</sup> and the 90-MHz<sup>7</sup> and 270-MHz<sup>8</sup> Eu(dpm)<sub>3</sub>-shifted NMR spectra of the latter were measured. At Eu(dpm)<sub>3</sub>/substrate mole ratio of 0.9 the signals of all protons except endo-5 and exo-6 were well-resolved in the 270-MHz spectrum

(Fig.I). Integrations above appropriate areas revealed the distribution of deuterium in II.<sup>9</sup> There is essentially no difference between the products formed via ring opening at -20°C and at 0°C. The results are shown in Table I.

**Table I.** Deuterium Distribution in Exo-norbornyl-d Trifluoroacetate from Nortricyclene and Deuteriotrifluoroacetic Acid

	% D			
	endo-2	1	endo-6	exo-6 and endo-5
Reaction at 0°C	16	21	29	39
Reaction at -20°C	13	20	28	41

Contrary to the controlled addition of deuterium chloride<sup>10</sup> or acetic acid-d<sup>11</sup> to I the incorporation of deuterium took place not only at C6 but also at C1 and C2.<sup>12</sup> Direct ring opening of I to form classical norbornyl cation(III) can be ruled out since there is more deuterium at C1 than at C2 (Scheme I). The presence of deuterium at these positions is therefore difficult to explain without invoking the interconverting protonated nortricyclenes IV or V, which undergo rapid ring rupture with no appreciable exchange with solvent (Scheme II). Symmetrical corner-protonated species or bridged ions (IV) cannot be the sole intermediate because the amount of deuterium at exo-6 and endo-6 is not equal. These results could be accounted for by the initial formation of edge-protonated intermediates (V) followed by ring opening to give classical norbornyl cations (VI). Similar to the addition of trifluoroacetic acid to norbornene<sup>5</sup> the unsymmetrical cations were captured by the nucleophile prior to completely equalibration. The direct conversion of V to II is also possible but seems to be less likely.<sup>13</sup> Although the stereochemistry of electrophilic attack to I and the preference of bond cleavage in V are not yet clear and need additional studies, it is clear that the intermediate leading to the product in the reaction of I with trifluoroacetic acid at 0°C or at -20°C is different from that with super acid at -70°C or lower temperature. Consequently, the applicability of results obtained under stable ion conditions to ordinary conditions is doubtful.

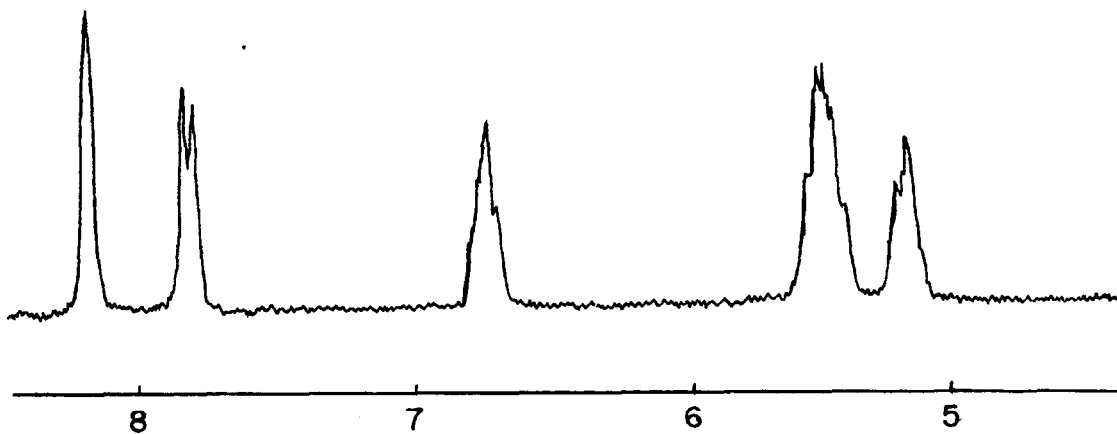
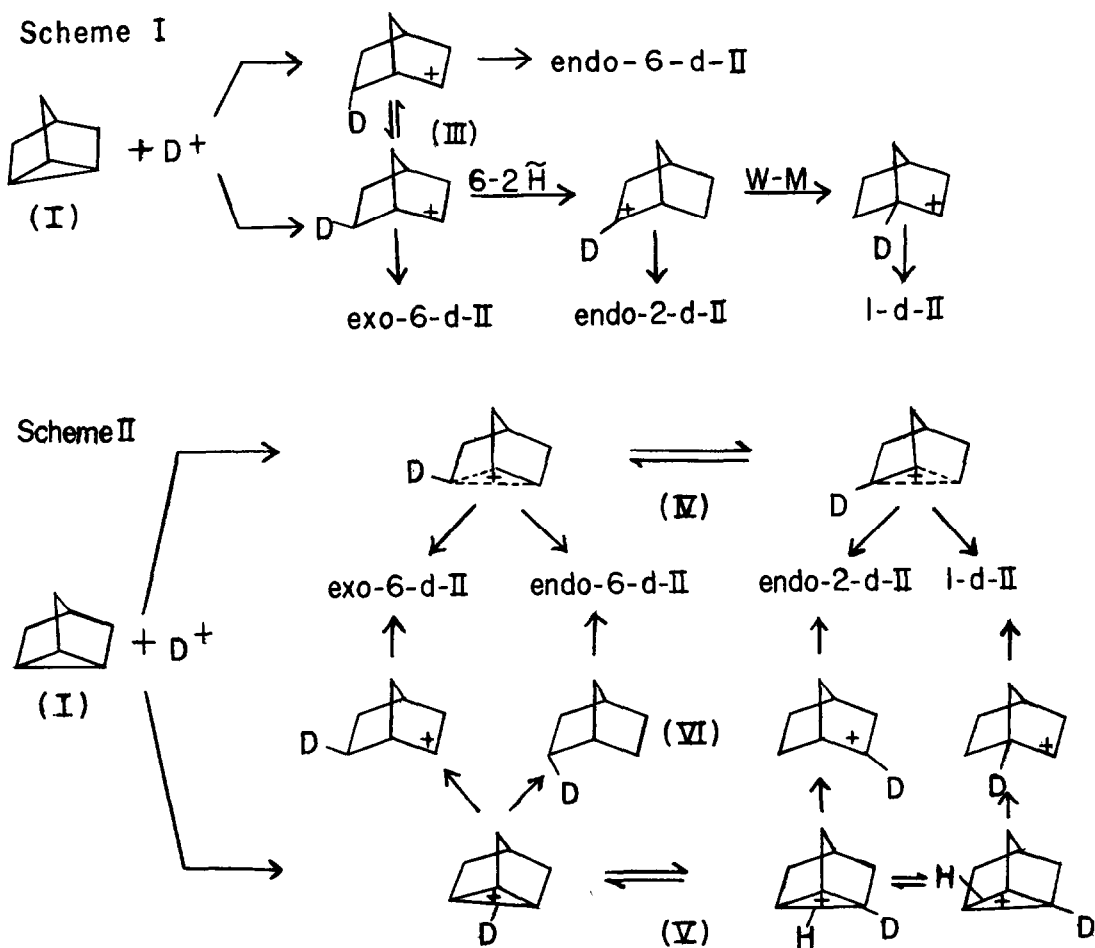


Fig.1. Partial 270 MHz Proton NMR Spectrum of Exo-norbornyl Trifluoroacetate



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### References and Notes

1. For reviews see (a) C. J. Collins, Chem. Rev., 69, 543 (1969); (b) C. C. Lee, Prog. Phys. Org. Chem., 7, 129 (1970); (c) M. L. Saunders, et al., Accounts Chem. Res., 6, 53 (1973); (d) C. H. DePuy, Top. Curr. Chem., 40, 73 (1973); (e) G. M. Kramer, Int. J. Mass Spec. and Ion Phys., 19, 139 (1976).
2. G. A. Olah, Accounts Chem. Res., 9, 41 (1976) and references cited therein.
3. This proposition has been challenged. See for examples: (a) G. M. Kramer, Adv. Phys. Org. Chem., 11, 177 (1975); (b) Ref. 1e; (c) H. C. Brown, "The Nonclassical Ion Problem," Plenum Press, 1977, Chapter 13.
4. GC analysis showed the exo stereoselectivity was greater than 99.5%.<sup>5</sup>
5. H. C. Brown and K.-T. Liu, J. Am. Chem. Soc., 97, 2469 (1975).
6. Mass and NMR spectral analysis indicated only one deuterium atom (1.00+0.05) was incorporated.
7. Obtained on a Perkin-Elmer R32 spectrometer at Purdue University.
8. Obtained on a Bruker 270 MHz spectrometer at the University of Chicago.
9. K.-T. Liu, Tetrahedron Lett., 1207 (1977).
10. J. M. Brown and M. C. McIvor, Chem. Commun., 238 (1969).
11. A. Nickon and J. H. Hammons, J. Am. Chem. Soc., 86, 3322 (1964).
12. Nickon and Hammons<sup>11</sup> pointed out the possibility of deuterium distribution at C1 and C2 but were unable to confirm it by infrared technique.
13. Recently DePuy and coworkers reported that the formation of edge-protonated cyclopropane was rate determining but not product determining in the reaction of proton with cis- and trans-1,2,3-trimethylcyclopropane (J. Am. Chem. Soc., 99, 6297 (1977)).