

APPLICATION OF YTTERBIUM SHIFT REAGENT TO TRIFLUOROACETATE ESTERS. DETERMINATION OF DEUTERIUM DISTRIBUTIONS IN EXO-NORBORNYL-D TRIFLUOROACETATE¹

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Electrophilic addition of trifluoroacetic acid to norbornene and related olefins has been found to exhibit all of the characteristics of a carbonium ion process.² The intermediate is most likely to be a classical 2-norbornyl cation, since deuterio-trifluoroacetoxylation of norbornene was found to give 99.98% of exo-norbornyl-d trifluoroacetate consisted of 37% of exo-3-d, 26% of syn-7-d, and 37% of the hydride-shifted products on the basis of the ¹H-NMR analysis of the corresponding exo-norbornanol-d and the E2 elimination product of the tosylate.² To confirm that no rearrangement of the label was involved during these transformations, direct examination of the labeled trifluoroacetate by using the widely employed lanthanide-induced shift technique would be the most unambiguous approach. However, trifluoroacetates showed negligible signal shifts with Eu(dpm)₃.^{3,4} A number of more powerful shift reagents have been studied. Tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)ytterbium(III), Yb(fod)₃, was found to give the first example that induced downfield signal shifts for nearly all protons in exo-norbornyl trifluoroacetate, whereas Eu(fod)₃ and Eu(tfn)₃⁵ brought about only a small signal shift for the endo-2 proton.

The shift reagent was added to a carbon tetrachloride solution of exo-norbornyl or exo-norbornyl-d trifluoroacetate as usual. Separation of signals was realized had the molar ratio of Yb(fod)₃ to substrate was greater than 0.3. Although the overlap of signals with residual peaks of Yb(fod)₃ is inevitable, individual signals or a group of signals could be integrated⁶ by appropriate choice of the concentration of Yb(fod)₃ added. The exo-norbornyl-d trifluoroacetate (I) obtained from the reaction of norbornene with deuteriotrifluoroacetic acid was analyzed accordingly. The results are shown in Table I.

The distribution of deuterium is essentially the same as has been observed (vide supra). In addition, the amount of deuterium at the anti-7 position can also be determined. The trifluoroacetate I was reduced to the corresponding alcohol II, and the Eu(dpm)₃-shifted spectrum of the latter was then measured. At the Eu(dpm)₃ to substrate ratio of 0.7 the deuterium distribution was found to be 35% at exo-3, 2% at

Table I Deuterium Distribution in Exo-norbornyl-d Trifluoroacetate (I)

Molar ratio ^a	Chemical shift, δ (% D)							
	endo-2	1	exo-3	endo-3	syn-7	4	anti-7	5,6
0.38	7.14 (0)	3.52 (0)	(2.07-2.87 (64%)) ^b	(0.87-1.98 (35%)) ^b
0.42	8.19 (0)	4.04	3.37 (35%)	(2.50-3.00 (28%)) ^b	(0.90-2.00 (35%)
0.61	12.92 (0)	6.10			4.27	3.28	2.37 (0)	(0.97-2.10) ^b (12%) (24%)

^a Yb(fod)₃/substrate. ^b Overlapped signals.

endo-3, 26% at syn-7, 15% at anti-7, and 22% at exo-6, and exo- and endo-5.⁶ The analyses for I and II are consistent with each other, and are in excellent agreement with that has been established.²

In conclusion, the present study based on the analysis of Yb(fod)₃-shifted spectra of trifluoroacetate I confirms the results previously obtained from the analyses of the alcoholic and olefinic derivatives, and the formation of a classical 2-norbornyl cation as an intermediate in the addition of trifluoroacetic acid to norbornene seems to be out of question.

References and Notes

1. Part V of "Nuclear Magnetic Resonance Studies." For Part IV, see K.-T. Liu, J. Chinese Chem. Soc., **23**, 1 (1976).
2. H. C. Brown and K.-T. Liu, J. Am. Chem. Soc., **97**, 2469 (1975).
3. D. B. Crump, J. K. M. Sanders and D. H. Williams, Tetrahedron Lett., 4949 (1970).
4. A. Ius, G. Vecchie and G. Carrea, ibid., 1543 (1972).
5. Tris(1,1,1,2,2,3,3,7,7,8,8,9,9-tetradecafluoro-4,6-nonanedionato)europium(III), purchased from Kary Laboratories, Anderson, South Carolina, U. S. A.
6. The spectra were recorded on a Varian T-60 spectrometer as was described.¹ Twenty integrations have been taken for measuring the relative area of peaks. These results were checked by using a Perkin-Elmer R20B instrument at National Defense Medical Center. The author is indebted to Mr. C.-B. Wang for his assistance in this concern.