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PROTON MAGNETIC RESONANCE STUDY OF 2-ENDO-HYDROXYMETHYL-5-NORBORNENE. THE EFFECT OF TRIS(DIPIVALOMETHANATO)EUROPIUM ON COUPLING CONSTANTS

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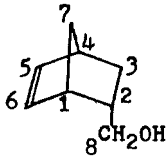
Following Hinckley's discovery of the potential of the dipyridine adduct of tris(dipivalomethanato)europium, $Eu(dpm)_3 \cdot 2Py$, in the application to nmr spectroscopy,[1] lanthanide shift reagents (LSR) have been widely employed as a valuable aid for the analysis of nmr spectra of complex organic molecules bearing Lewis-basic functional groups.[2] A complex spectrum of a substrate can be simplified to a first-order one, provided sufficient LSR is used. Since it has been shown that coupling constants are essentially unaffected in the presence of LSR,[3] coupling constants which are difficult to determine otherwise, can be measured easily. The recent interest in the effect of LSR on coupling constants[4] prompt the author to report the results with 2-*endo*-hydroxymethyl-5-norbornene(I).[5] Changes in coupling were observed only with the protons on C-8, the carbon *alpha* to the coordinating site.

Proton magnetic resonance chemical shift data of I has been reported, but a definite assignment of olefinic protons or of bridgehead protons were not made.[6] In the present study different amount of Tris(dipivalomethanato)-europium,[7] $Eu(dpm)_3$, was added to 0.2-0.3 *M* solutions of I in carbon tetrachloride. 60 MHz spectra[8] were taken at nine different $Eu(dpm)_3$ to substrate mole ratios. Proton assignments were based on observed splitting patterns and decoupling experiments. Plot of the induced shift,$\Delta\delta$,[9] versus the mole ratio, n, gave excellent linear relationships, from which the normalized shift value, $\Delta Eu(dpm)_3$, for each protons could be obtained by measuring the slope[10,11](Table I).

The coupling constants are reported in Table II. It is clear that only the coupling constants concerning C-8 protons are changed by the addition of $Eu(dpm)_3$. The variations were small but significant. Moreover, in constrast to the finding by Shapiro and coworkers,[4] they were essentially unchanged as the concentration of $Eu(dpm)_3$ was increased up to the amount indicated. Further increase of the concentration of LSR caused considerable peak broadening leading to some uncertainty in the measurement.

The increase in absolute magnitude of geminal coupling, $J_{8,8}$, is consistent with the electronic effect of coordination on the substituent. Like carbonyl oxygen,[4,12] coordination of hydroxyl oxygen with $Eu(dpm)_3$ would be expected to cause an increase in $|J_{8,8}|$ as was observed. On the other hand, the vicinal coupling, $J_{2,8}$, for the coordinated substrate is larger than that for the uncoordinated one. This is inconsistent with the usual electronegativity mechanism.[13] Other effects should be involved.[14] Further study is in progress.



(I)

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Table I. Chemical Shifts and Paramagnetic Shifts of Different Protons of I[a]

Proton	δ	$\Delta_{Eu(dpm)_3}$[b]	Proton	δ	$\Delta_{Eu(dpm)_3}$
1	2.92	10.6	5	6.08	3.9
2	2.23	15.5	6	5.92	7.1
exo-3	1.75	6.6	syn-7	1.24	4.5
endo-3	0.46	8.7	anti-7	1.45	3.6
4	2.76	3.6	8	3.28; 3.10	25.3; 24.0

[a] In ppm downfield of TMS. [b] $\Delta_{Eu(dpm)_3} = \delta^{n=1}_{Eu(dpm)_3} - \delta^{n=0}$

Table II. Pertinent Coupling Constants of I at Various Mole Ratio of $Eu(dpm)_3$ to I[a]

n	$J_{2,3x}$	$J_{2,3n}$	$J_{3,3}$	$J_{4,5}$	$J_{5,6}$	$J_{1,6}$	$J_{3n,7a}$	$J_{7,7}$	$J_{8,8}$	$J_{2,8}$
0		4.4	11.4				2.2	8.2	10.2	6.5; 8.3
0.24			11.3	2.6	5.6	2.6		b	10.6	6.6; 8.7
0.42			b	2.7	5.7	2.7		8.3	10.7	6.6; 8.8
0.66	9.2	4.3	11.4	2.7	5.6	2.7	2.2	8.2	10.7	6.6; 8.8

[a] Absolute values with accuracy of ± 0.1 Hz. [b] Not determined due to the fortuitous equivalence of the protons.

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