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APPLICATION OF PARAMAGNETIC INDUCED SHIFTS IN PMR SPECTRA TO THE DETERMINATION OF THE POSITIONS OF DEUTERIUM SUBSTITUTION IN BORNANES DERIVED FROM α-PINENE USING TRIS(DIPIVALOMETHANATO)EUROPIUM(III)

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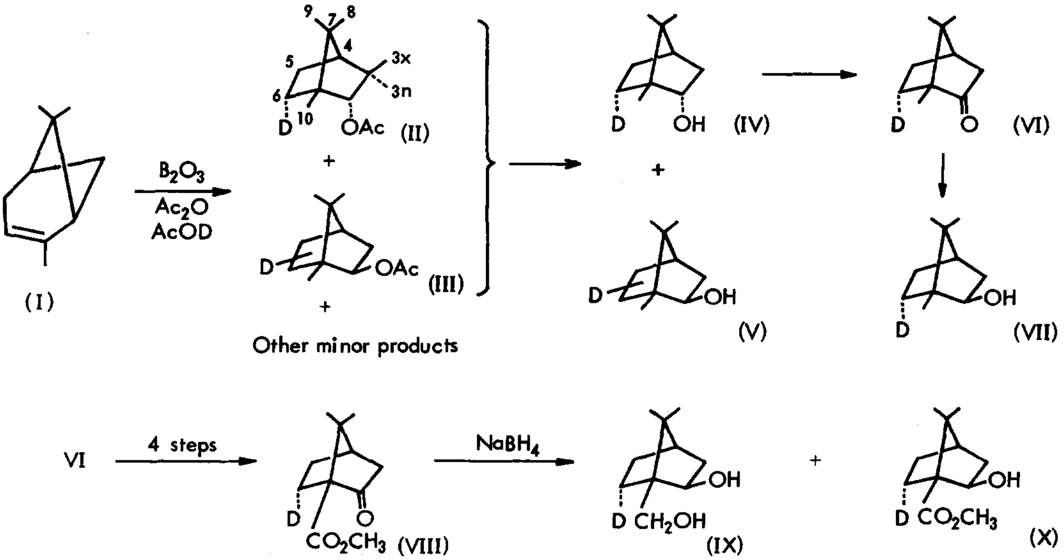
Applications of paramagnetic induced shifts of metal complexes (1) in PMR spectra to structure determinations of organic molecules (2) have recently been highlighted by Hinckley's discovery of tris(dipivalomethanato)bis(pyridino)europium(III) [$Eu(DPM)_3 \cdot Py_2$] as a shift reagent (3); thereafter, the pyridine-free complex, $Eu(DPM)_3$, has been suggested as a better shift reagent (4).

In the course of a reaction mechanism study (5), it became necessary to employ 1-carbomethoxy-*endo*-6-deuterioapoisoborneol (X), which was synthesized from α-pinene (I) as shown in the Chart (6). However, it is not known whether the products, bornyl- and isobornyl acetates [(II) and (III), res-



Chart

pectively], derived from I are solely endo-6-D derivatives or not. In order to confirm the positions of deuterium substitution in several bornane derivatives produced in the synthetic course, we successfully applied paramagnetic induced shifts in their PMR spectra using Eu(DPM)$_3$. A recent publication describing the paramagnetic shifts of Eu(DPM)$_3$ in the PMR spectra of borneol and isoborneol (7), has prompted us to report our results here.

The 100-MHz PMR spectra of borneol, isoborneol, camphor, and 10-hydroxycamphor were examined at various concentrations of Eu(DPM)$_3$ in CDCl$_3$ to find the optimum complex-concentration for each experiment (for example, see FIGs. 1a, 2a and b). Signals were assigned on the bases of the known spin-coupling sequence for the norbornane system (8,9), spin-decoupling experiments, and the fact that the paramagnetic induced shifts of Eu(DPM)$_3$ are dominantly pseudo-contact shifts (1,3,10,11). Thus, the positions substituted by deuteriums were readily revealed by comparing the above spectra with those of

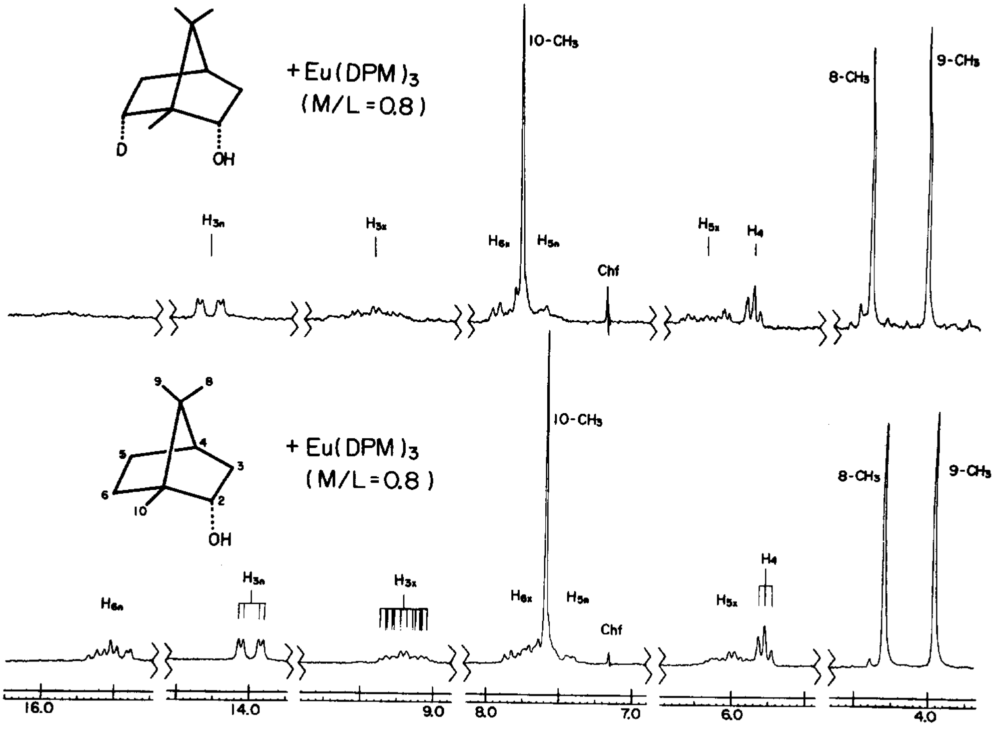


FIG. 1. PMR spectra of borneol (a) and its deuterio derivative (IV) (b) in CDCl$_3$ containing Eu(DPM)$_3$ at 100 MHz.

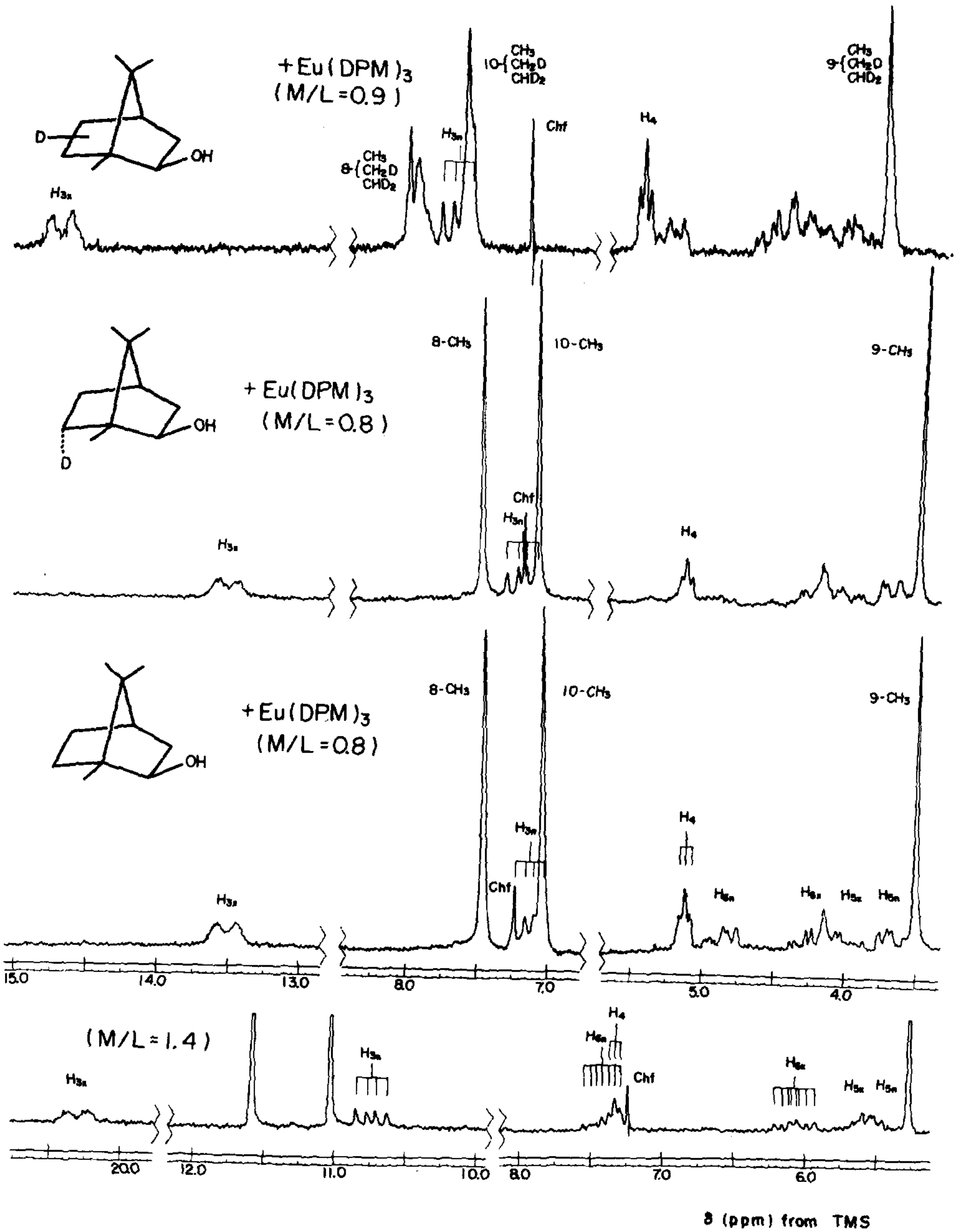


FIG. 2. PMR spectra of isoborneol (a and b) and its deuterio derivatives (VII) (c) and (V) (d) in $CDCl_3$ containing $Eu(DPM)_3$ at 100 MHz.

the corresponding D-containing compounds, IV-VII, and IX, at similar concentrations of $Eu(DPM)_3$. The compounds IV, VI, VII, and IX are solely endo-6-deuterio derivatives, whereas in V, C-8, C-10, C-9, and C-6-endo are partially deuteriated in a ratio of 37 : 29 : 24 : 10 (see FIGs. 1 and 2).

The present PMR results were very similar to those of Demarco and coworkers (7) and confirmed the earlier assignment of the methyl signals of borneol and isoborneol (12). A result identical to Hinckley's was obtained for the assignment of the methyl signals of camphor (11). The structures of other minor products in the first reaction shown in the Chart will be reported elsewhere together with the reaction mechanism. The PMR spectra were recorded on a Varian HA-100 spectrometer operating in the frequency-swept and TMS-locked mode.

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