

NUCLEAR MAGNETIC RESONANCE STUDIES. II. THE ABSENCE OF A SIGNIFICANT INFLUENCE OF TRIS(DIPIVALOMETHANATO)EUROPIUM ON COUPLING CONSTANTS OF NORBORNANOLS AND 7,7-DIMETHYLNCRBORNANOLS¹

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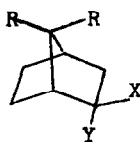
The ability of lanthanide shift reagents to lower the order of the spectrum of a substrate without causing significant peak broadening or peak distortion provides a simple way for the measurement of coupling constants.² In some cases, however, the variation of coupling constants due to the presence of shift reagents has been demonstrated.^{1,3,4} Therefore, it should be cautious of considering the equivalence of coupling constants obtained from the shifted spectra to those of the substrate itself.

The analysis of the pmr spectra of norbornane derivatives is always a difficult task owing to the overlap of peaks and the non-first order couplings.⁵ For compounds with suitable coordination sites, such as hydroxyl group, the problem might be circumvented by the use of a shift reagent. Borneol^{2b} and exo-norbornanol(I)^{2d} have been studied by this means. However, no confirmation of the constancy of the coupling constants was given. In the present study the pmr spectra of some model alcohols, namely, exo-norbornanol, endo-norbornanol(II), 7,7-dimethyl-exo-norbornanol (III) and 7,7-dimethyl-endo-norbornanol(IV), under the influence of

tris(dipivalomethanato)europium, $\text{Eu}(\text{dpm})_3$, have been examined. The constancy of coupling constants was observed.

Compounds I-IV and the partially deuterated derivatives, 3-exo-d-exo-norbornanol(IId),⁶ 2-exo-d-endo-norbornanol(IIId),⁷ and 3-exo-d-7,7-dimethyl-exo-norbornanol(IIIId),⁶ were purified by sublimation before use. The advantage of using deuterated compounds Id-IIIId is to afford a more simplified spectrum, and to make possible the measurement of some couplings in the absence of $\text{Eu}(\text{dpm})_3$. The pmr spectra of I-IV and of Id-IIIId were taken as previously described.¹ The coupling constants were extracted from the first-order spectra or from appropriate spectral analysis of the simplified spectra. The pertinent data are shown in Table I.

Evidently the coupling constants are essentially unchanged in the presence of $\text{Eu}(\text{dpm})_3$. Moreover, the isotope effect is also insignificant. Consequently, the coupling constants of norbornanols and their derivatives could easily be determined from the spectra of alcohol- $\text{Eu}(\text{dpm})_3$ adducts without employing sophisticated or expensive instrumentation. It should also be noted that the presence of 7,7-dimethyl substituents induces a small but substantial variation on the magnitude of $J_{2x,3x}$ and of $J_{2n,3n}$. Probably these substituents cause a certain degree of molecular distortion. The details about the coupling constants of norbornanols and methyl substituted norbornanols will be reported elsewhere.



| | | | |
|-----|-----------------------|---------|--------|
| I | R = H, | X = CH, | Y = H |
| II | R = H, | X = H, | Y = CH |
| III | R = CH ₃ , | X = CH, | Y = H |
| IV | R = CH ₃ , | X = H, | Y = OH |

Table I. Pertinent Coupling Constants of Norbornanols and 7,7-Dimethylnorbornanols^a

| Substrate | n ^b | J _{2x,3x} | J _{2n,3n} | J _{2x,3n} | J _{3x,3n} | J _{3x,4} | J _{7,7} |
|------------|----------------|--------------------|--------------------|--------------------|--------------------|-------------------|------------------|
| I, Id | 0 | - | 6.9 ^c | - | - | - | - |
| | 0.28 | - | 6.8 | - | - | - | 9.8 |
| | 0.41 | - | 6.8 | - | 13.0 | 4.3 | 9.7 |
| II, IIId | 0 | - | - | - | 13.2 | - | - |
| | | | | | 13.3 ^c | - | - |
| III, IIIId | 0.30 | 9.7 | - | 3.4 | 13.1 | - | 9.9 |
| | 0.40 | 9.8 | - | 3.4 | 13.1 | - | 9.7 |
| | 0.52 | - | - | 3.3 | - | 4.3 | 9.8 |
| | 0 | - | 7.8 ^c | - | - | - | - |
| IV | 0.32 | - | 7.8 ^c | - | - | - | - |
| | 0.39 | - | 7.8 | - | 13.5 | - | - |
| | 0.54 | - | 7.7 | - | 13.5 | - | - |
| | 0.34 | 9.1 | - | 3.1 | 13.4 | 4.1 | - |
| | 0.48 | 9.2 | - | 3.1 | 13.3 | 4.2 | - |
| | 0.60 | 9.2 | - | 3.2 | 13.5 | 4.2 | - |

^a Absolute values with accuracy of ± 0.1 Hz. ^b Molar equivalent ratio of Eu(dpm)₃ to substrate. ^c From Id, IIId, or IIIId.

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