The Application of
tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)Europium(III)
in Elucidation of Structures of Bicyclic Ethers

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The complexation of organic solutes containing a heteroatom lone pair with rare earth chelates produces spectacular chemical shift dispersions in the nmr spectra of the organic bases. The promise of this phenomenon as an extremely useful methodology for structure determination was first pointed out by Hinckley (1). The emergence of these shift reagents offered us an opportunity to re-examine two 2-oxabicyclo[4.2.0]octane derivatives obtained in previous studies (2,3). By using a europium chelate as a probe of structural conformation in these mono-functional systems, we hoped to remove the uncertainty of the structural assignments previously reported for one of these compounds (2).

Since both compounds were soluble in carbon tetrachloride, the shift reagent Eu(fod)$_3$ (4) was utilized in this investigation because of its superior solubility properties in carbon tetrachloride (5). The shift reagent was added in increments of 5 milligrams to a solution containing 1×10^{-4} moles of ether in 0.5 milliliters of carbon tetrachloride. The spectra were obtained on a Varian HA-60-IL spectrometer. Also, because the shift reagent reportedly operates *via* a pseudo-contact interaction, molecular models were constructured of each ether studied in order to correlate the observed shifts with the internuclear distances between the hydrogens and the europium atom in the adduct.

The stereochemical assignments on the bicyclooctanes were made on the premise than when J *cis* and J *trans* for the four-membered ring have significantly different values, J *cis* > J *trans* (6,7). In this connection, it is noted that the value of a single coupling constant is insufficient evidence to establish the *cis* or *trans* alignment of the coupled protons. However, from the several vicinal coupling constants obtained from each spectrum, from confirmatory decoupling experiments on the shifted spectra and from fore knowledge of the photochemistry involved,

there are no exceptions to the J *cis* > J *trans* rule in these systems. It is also assumed that the low concentrations of Eu(fod)$_3$ used have no effect on the size of the coupling constants (8).

The first compound analyzed was 7,8-*cis-endo*-diphenyl-2-oxabicyclo[4.2.0]octane(II), which was the product of the catalytic hydrogenation of 7,8-diphenyl-2-oxabicyclo[4.2.0]oct-7-ene, (I) (9), over potassium oxide. It was also one of the cycloaddition products of the photochemical reaction of stilbene with 2,3-dihydropyran (2). Hydrogenation over platinum is known to yield a *cis*-addition product with no double bond migration (10), thus one would expect II to be a *cis*-diphenyl compound. The untreated nmr spectrum of II, Figure 1, which was quite complex, was simplified by the stepwise addition of up to 15 mg. of Eu(fod)$_3$. Three hydrogens appeared to be closer to the europium atom than the rest as evidenced by the extent of their shift upon the addition of Eu(fod)$_3$. Of special note was the appearance of a triplet J = 8 Hz (H$_1$) which came out of a multiplet in the untreated spectrum. In other reported six-four ring systems, H$_6$ appeared in the region of 2.5-3.0 ppm (7). Double irradiation of H$_6$ on the shifted spectrum collapsed the triplet (H$_1$) to a doublet J = 8 Hz. Double irradiation of H$_8$ collapsed H$_7$ to a doublet J = 10 Hz. The J$_{1,6}$ = 8 Hz confirmed that the *cis* relationship of H$_1$ and H$_6$ in II had been retained. J$_{1,8}$ = 8 Hz suggested a *cis* arrangement of H$_1$ and H$_8$ (7). The *cis* addition of hydrogen over a platinum catalyst and the size of the coupling constant J$_{7,8}$ = 10 Hz established the all *cis* orientations of H$_1$, H$_6$, H$_7$, and H$_8$. Confirmatory proof as to the *cis* arrangement of H$_7$ and H$_8$ was found by treating II with potassium *t*-butoxide in *t*-butanol. Two new products, as shown by gas liquid partition chromatography, were formed while II disappeared.

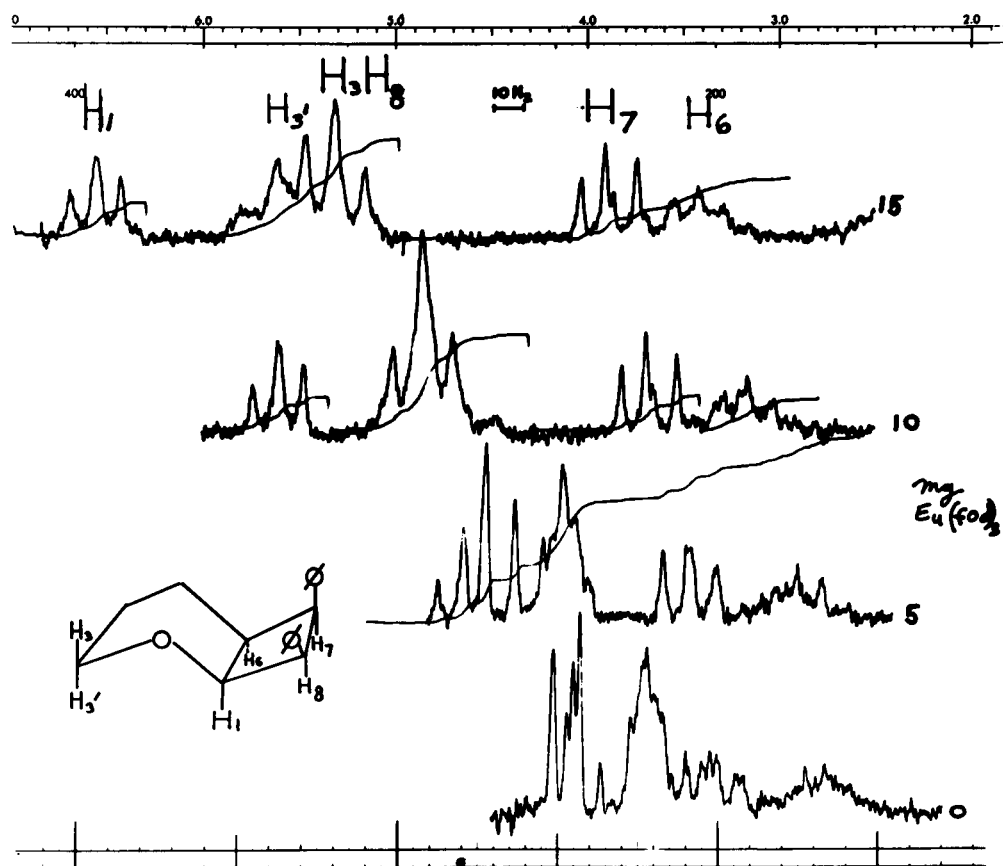The photocycloaddition of 1,1-diphenylethylene to

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Figure 1. Effect of Adding Eu(fod)₃ to a Hydrogenation Product of 7,8-diphenyl-2-oxabicyclo[4.2.0]oct-7-ene.

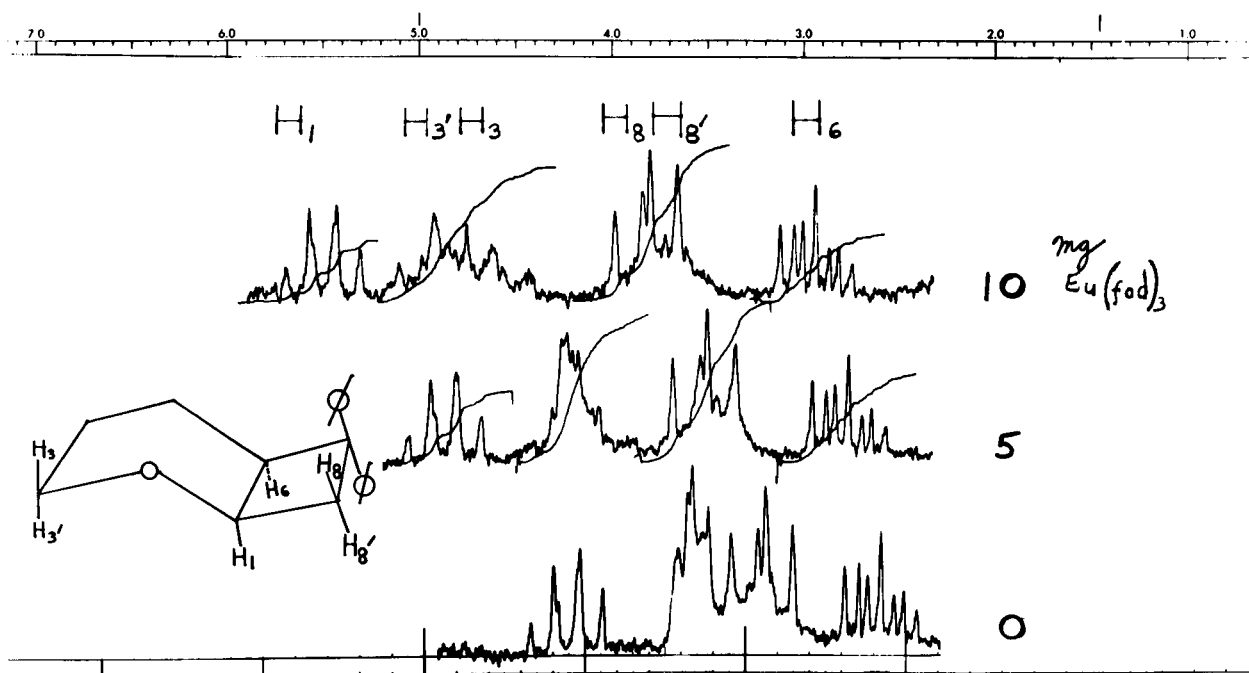
Figure 2. Effect of Adding Eu(fod)₃ to a Photocycloaddition Product of 1,1-diphenylethylene and 2,3-dihydropyran.

2,3-dihydropyran yielded the *gem*-diphenyl product, 7,7-diphenyl-2-oxabicyclo[4.2.0]octane(III) (3). The structure of this related octane was again deciphered by repeated treatments with $Eu(fod)_3$, Figure 2. The structure could be inferred from the one spectrum treated with 10 mg. of the shift reagent. This spectrum consisted essentially of 4 multiplets with an intensity ratio of 1,2,2,1. Strictly from the relative shifting order, the multiplets were tentatively assigned to protons 1,3 and 3', 8 and 8' and 6. This assignment was based on the distances of these hydrogens from the assumed position of the europium (between the equatorial and axial electron lobes of the oxygen) in the adduct. Spin decoupling experiments confirmed the assignment.

Thus, the systematic application of $Eu(fod)_3$ not only produced significant spectral clarification but also uncovered several spectral clues which eventually led to the elucidation of both structures. For example, in the case of compound II, treatment with the shift reagent pulled one of the coincidental H_3 absorptions downfield at approximately the same rate as the H_1 resonance. These shifts indicated a preferred direction of the Eu-oxygen bond and pinpointed the position of the europium in the adduct. As a result of this additional information, proton assignments based on their proximity to the lanthanide ion could be made with much greater confidence. In fact, no other spectral technique would have been sufficiently discriminating to differentiate the structural subtleties between this particular compound and the 7,8-*cis-exo* isomer.

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