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RAPID SOLUTION OF STEREOCHEMICAL PROBLEMS WITH EUROPIUM-TRIS(TETRAMETHYLHEPTANEDIONE), $Eu(thd)_3$

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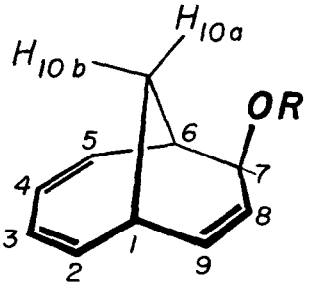
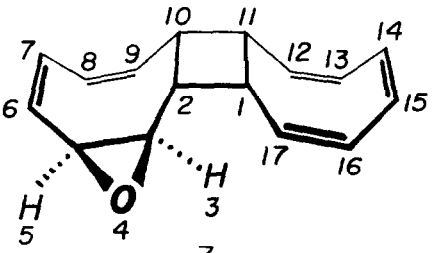
The important discovery by C. C. Hinckley [1] that proton nuclear magnetic resonance signals are dramatically shifted in a predictable manner in compounds which form a complex with $Eu(thd)_3$ has opened a new field of study [2].

We have isolated compounds 1 [3a] and 2 [4] in the course of our studies of bridged bis-homotropylium ions [3]. Photolysis of compound 3, prepared by epoxidation [5] of the cyclooctatetraene dimer which melts at 53° [6] forms oxa [17]annulene [5]; thus, 3 is of considerable interest to us [7].



1: R = CH_3 2: R = H



3

The following stereochemical questions arise:

- are the methoxyl and hydroxyl groups in 1 and 2 exo or endo (relative to the butadiene bridge)?
- is the epoxide ring of 3 syn or anti to the proton at carbon atom 2 ?

Even though homonuclear double resonance experiments do not provide unequivocal results for answering these questions, the changes of the proton chemical shifts in the presence of $Eu(thd)_3$ does permit an unambiguous assignment of the stereochemistry of each of these three molecules.

Syntheses of 1, 2 and 3

1 The preparation of 1 is reported in ref. [3]. 1 can also be synthesized via the procedure outlined for 2 but substituting methanol for water.

2 Bicyclo[4. 2. 2]decatetraene reacts with HBr in CH_2Cl_2 at -75° to form liquid 7-bromobicyclo[4. 3. 1]deca-2, 4, 8-triene (90%), which is purified by fractional vacuum distillation [8]. The NMR, UV and IR spectra are in agreement with the structure. The bromide is rapidly hydrolized in water-acetone-$NaHCO_3$ to 7-hydroxybicyclo[4. 3. 1]deca-2, 4, 8-triene (2) [8] (yield 90%; mp 67° (from pentane-ether)). The spectroscopic data are identical to those reported by Vogel, Roth and Fus [9].

3 Dimeric cyclooctatetraene, mp 53° [6], is epoxidized with 40% peraceticacid in $CHCl_3$ at 25°C; 3 (mp 43 - 44°) was isolated from the reaction mixture in 40% yield by column chromatography (silica; pentane) [8]. UV spectrum (ether): 232 nm (sh, 6500).

NMR spectra in presence of $Eu(thd)_3$

The three NMR spectra of 1 reproduced on figure 1 show the effect of adding $Eu(thd)_3$ to the sample [10]. We observe that the magnitude of the resonance shifts is a function of $Eu(thd)_3$

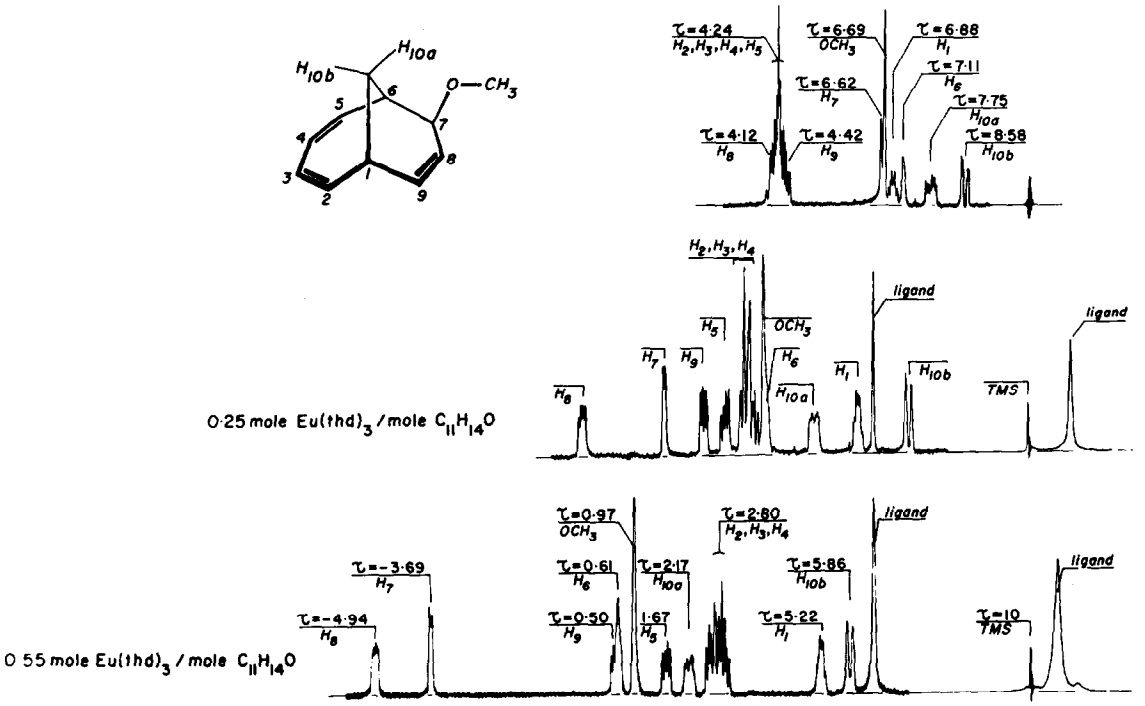


Figure 1: ^{1}H-NMR spectra of 7-methoxybicyclo[4. 3. 1] decatriene in CCl_4 in absence and in presence of $Eu(thd)_3$ (100 MHz - +25°C).

concentration and, for each proton, a function of its distance from europium [1, 2]. When the O...H_i distance r_i taken from a Dreiding model is used as an approximation to the Eu...H_i distance d_i then we expect the correct structure to be that in which the shifts ($\Delta\nu_i$ in Hz) of the proton signals are proportional to r_i^{-a} where the exponent a = 2 to 3 [1, 2c].

In the case of 7-methoxybicyclo[4. 3. 1]decatriene this condition ($\Delta\nu_i \propto r_i^{-2.2}$) is satisfied only by an exo methoxy group. Even so we can still discuss two conformations for the six-membered ring, the half-chair and the half-boat. A distinction between the two conformations is possible from the analysis of the shifts $\Delta\nu_i$ observed for the protons of the six-membered ring, but is more convincingly shown by the small coupling $J_{6,7} \leq 0.5$ Hz observed in the spectra of 1 in presence of Eu(thd)$_3$ (cf. Fig. 1). The dihedral angle H_6-C_6-C_7-H_7 is either ca. 70° (half-chair) or ca. 170° (half-boat); the small observed coupling is associated with the 70° conformation. Therefore the half-chair conformation is favoured even though it contains an axial methoxy group.

In the case of 7-hydroxybicyclo[4. 3. 1]decatriene the different protons show, in presence of Eu(thd)$_3$, paramagnetic shifts similar to those observed for 1 [10]. From these observed shifts it could be deduced that the C_7-hydroxy group is in the exo position, 2. Here again the relationship $\Delta\nu_i \propto r_i^{-2.2}$ is found to hold; however, at equal mole ratios of Eu(thd)$_3$ to substrate the paramagnetic shifts are greater for 2 than for 1. First-order fine structure of signals of proton 6 or 7 as observed in spectra of 2 in presence of Eu(thd)$_3$ also indicates that the half-chair conformation for the cyclohexene ring is again preferred.

The three NMR-spectra of the tetracyclic epoxide 3 (Fig. 2) show the effect of adding Eu(thd)$_3$ to the sample [10]. The upper spectrum, without Eu(thd)$_3$, exhibits a complex pattern between τ = 3.8 to 4.7 for the ten olefinic protons. The signals of the aliphatic protons at τ = 6.56(m) and 7.78(m), in the intensity ratio 5 : 1, demonstrate that the epoxide ring is unsymmetrically placed on the COT dimer. In presence of Eu(thd)$_3$ the two epoxide protons 3 and 5 are more strongly shifted towards lower field than any other ; the remaining protons undergoing a paramagnetic shift are, in the order of decreasing shift : 2, 6, 1, 10, 7, 17, 9, 8, 11, 12, 13 and 14. The individual shifts $\Delta\nu_i$ of all these protons correlate with the O...H_i distances r_i obtained from a Dreiding model of the syn isomer, 3 ($\Delta\nu_i \propto r_i^{-2.22}$); the same shifts can not be correlated with the O...H_i distances r_i in the anti compound. The protons 15 and 16 exhibit diamagnetic shifts; this observation is readily explained by the controlling features of the equation for the pseudocontact shift [2d] $\Delta\nu_i \propto (3\cos^2\chi_i - 1)d_i^{-3}$ where d_i is the distance between Europium and proton i and χ_i is the angle O...Eu...H_i. The angles χ_i for protons 15 and 16 are respectively 58° and 55°; they are thus greater than 54.7° (i. e. $3\cos^2\chi_i - 1 < 0$) and the shift are diamagnetic.

Acknowledgment

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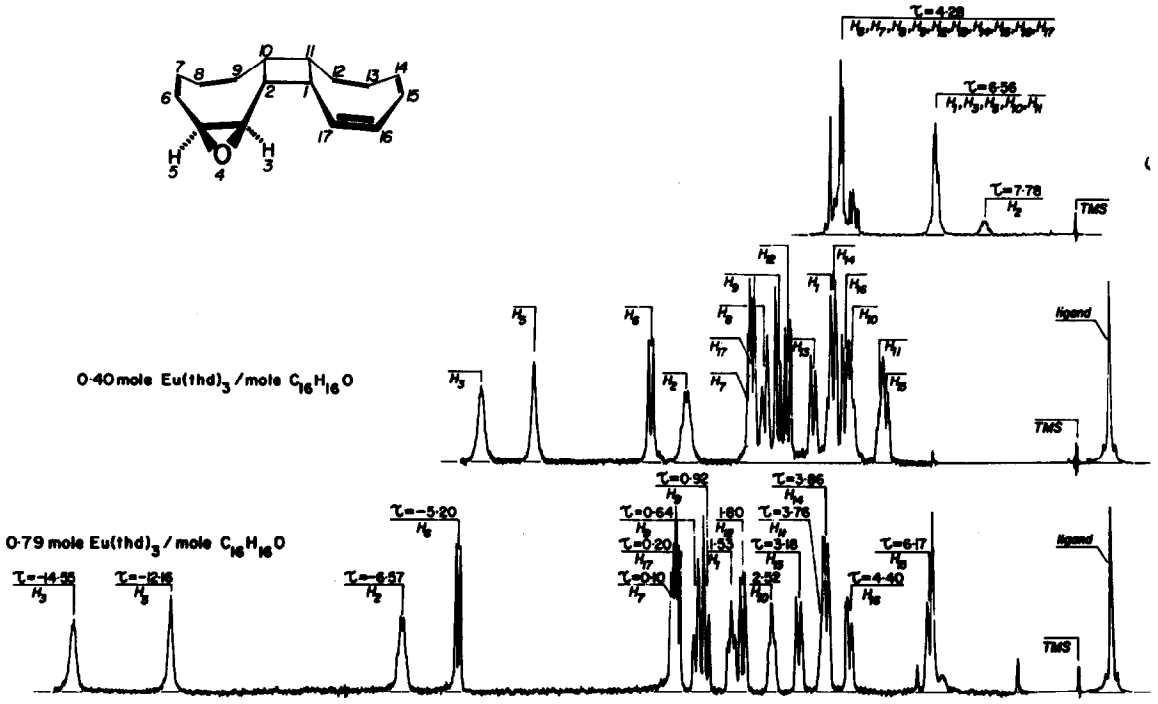

Figure 2: ^{1}H-NMR spectra of epoxide 3 in CCl_4 in absence and in presence of Eu(thd)$_3$ (100 MHz - +25°C).

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[8] Satisfactory C, H analyses were obtained.

[9] 2 had been synthesized previously by another method. E. Vogel, W. R. Roth and M. Fus; Dissertation, University of Köln 1968 of M. Fus.

[10] Spectra were obtained for ten different mole ratios (0.1 to 1.0) Eu(thd)3/substrate. The shift effect $\Delta\nu_i$ for a particular proton is defined as the slope of the straight line which is obtained from a graph of the position of the resonance signal ν_i versus the mole ratio Eu(thd)3/substrate.