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PMR SHIFT TO HIGH FIELD INDUCED BY TRIS(DIPIVALOMETHANATO)EUROPIUM

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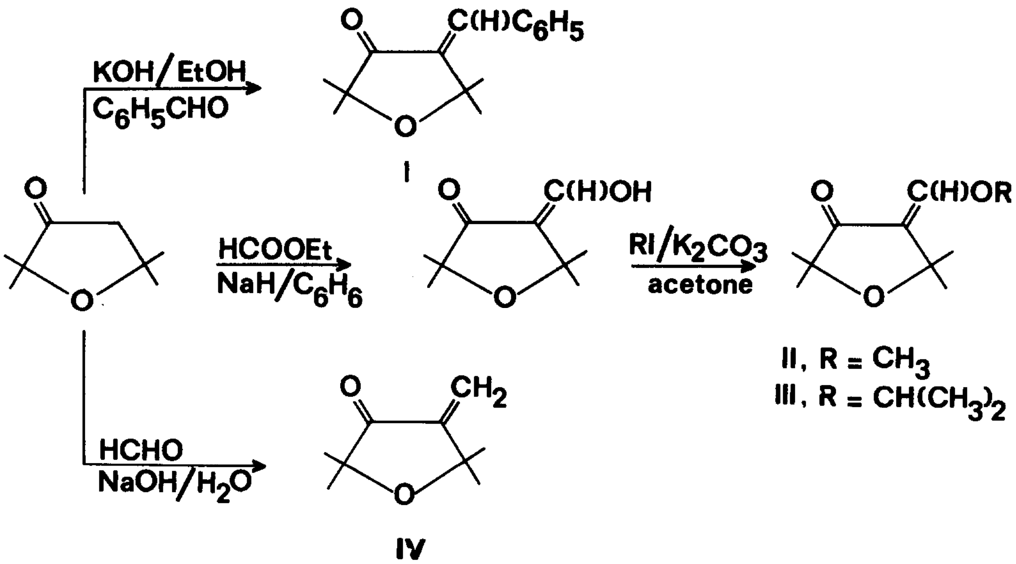
Recently Siddall[1)], Willcott *et al.* [2)], and Mazzocchi *et al.*[3)] reported upfield shifts induced by tris(dipivalomethanato)europium[Eu(DPM)$_3$]; the shifts were ascribed to a pseudo-contact mechanism. The pseudo-contact shift, $\Delta\nu_i$, is given by the equation[4)]

$$\Delta\nu_i = K(3\cos^2\theta_i - 1)/r_i^3$$

and will be upfield when $(3\cos^2\theta_i - 1) < 0$, i.e. when $\theta_i > 54.7^\circ$.

In the course of an investigation into the configuration of the alkylidenefuranones I-III through use of Eu(DPM)$_3$, we observed an upfield shift for the protons of the alkoxy groups in compounds II and III. The benzylidene derivative I, the methyl and isopropyl ethers II and III, and the methylene derivative IV were prepared from 2,2,5,5-tetramethyl-3(4*H*)-furanone as indicated in the Scheme. Compounds I-III were shown by pmr spectrometry to occur exclusively in one of the two possible configurations, but on the basis of this spectral data alone (see Table) it is not possible to decide whether the olefinic proton is *cis* or *trans* with respect to the carbonyl group.

The shifts which are observed in the pmr spectra of compounds I-IV when Eu(DPM)$_3$ is added to the solutions (exemplified in the Figure for compound II) provide valuable insight into the molecular configuration. The magnitude of the shifts depends upon the spatial orientation of the respective protons with respect to the Eu atom[5,6)]. However, the magnitude of the shifts also depends upon the molar ratio of Eu(DPM)$_3$ to the solute, and to permit meaningful comparison between the various protons in each compound we determined the Δ_{Eu} defined by Demarco *et al.*[6)]: the Δ_{Eu} for each proton is derived from the slope of the straight line obtained by plotting the magnitude of the shift induced at various values of the molar ratio Eu(DPM)$_3$ to solute.

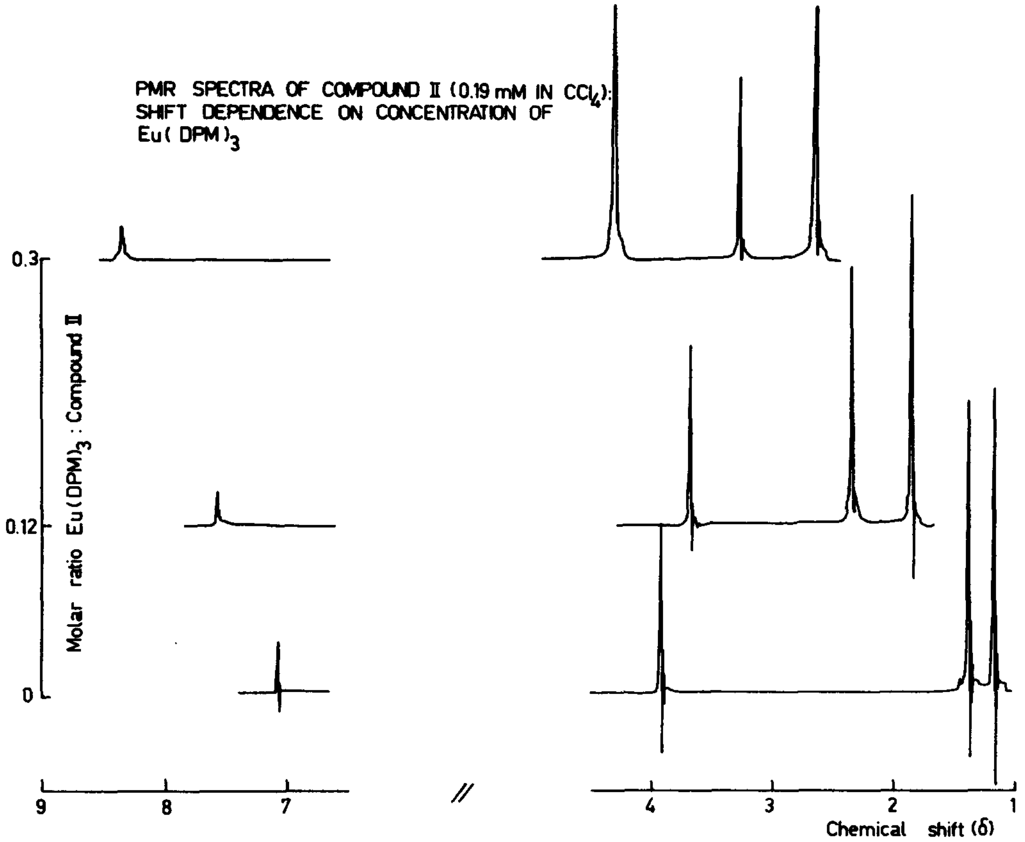


Chemical shifts (δ, ppm) and Δ_{Eu} values (ppm) for compounds I-IV in CCl_4. Solute concentration 1.90×10^{-4}M: internal standard TMS (1%).

		$>\overset{2}{C}(CH_3)_2$	$>\overset{5}{C}(CH_3)_2$	$=C<^{H}$	$—OCH_3$	$—OCH(CH_3)_2$
I	δ	1.23(s)	1.45(s)	7.36[a](m)		
	Δ_{Eu}	-7.8	-3.5	-8.8		
II	δ	1.10(s)	1.31(s)	7.06(s)	3.89(s)	
	Δ_{Eu}	-10.0	-4.3	-4.2	+1.8	
III	δ	1.15(s)	1.36(s)	7.22(s)		4.23[a](m) 1.31 (d)
	Δ_{Eu}	-10.7	-3.8	-3.8		+3.3 +1.1
IV	δ	1.20(s)	1.38(s)	5.99(*cis*) (d) 5.26(*trans*) (d)		
	Δ_{Eu}	-8.3	-4.2	-8.8 (*cis*) -3.9 (*trans*)		

[a] Centre of multiplet

From the Δ_{Eu} values reported in the Table it is clear that the europium atom is preferentially coordinated by the carbonyl oxygen in the furanones I and IV. We may thus conclude that in compound I the olefinic proton is *cis* with respect to the carbonyl group, but *trans* in compounds II and III. The positive Δ_{Eu} values observed for the protons of the alkoxy groups in compounds II and III indicate a shift to high field. In view of the *syn* configuration of the methylene groupings with regard to the carbonyl group, and the *cis* orientation of the alkoxy groups with respect to the latter, compounds II and III can conceivably function as bidentate ligands.



Although the explanation provided by Siddall, Willcott *et al.*, and Mazzocchi *et al.* could also hold for the compounds we studied, in our case it seems more likely that the observed upfield shifts are due to the fact that both contact and pseudo-contact mechanisms are operating, and that the respective shifts are of unequal magnitude and opposite sign(7).

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