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TRIS (DIPIVALOMETHANATO) YTTERBIUM - INDUCED SHIFTS IN PMR KETONES AND ALDEHYDES

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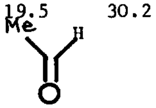
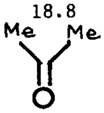
It appears to be well established that tris(dipivalomethanato) chelates of certain lanthanides are capable of inducing remarkable paramagnetic shifts in PMR spectra of organic molecules with lone pairs on oxygen and nitrogen (1)(2). We wish to report results obtained on ketones and aldehydes with tris(dipivalomethanato)ytterbium (2)(3) and present this method as a valuable complement for the investigation of the stereochemistry of carbonyl compounds.

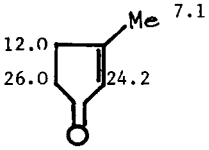
Some of our data for ketones and aldehydes are listed in Table 1. The Yb(DPM)$_3$-induced shifts were obtained at 60 MHz for 10% CCl$_4$ solutions, after extrapolation to an equimolar ratio of Yb(DPM)$_3$ to solute, ΔYb=($\delta - \delta_{CCl_4}$)ppm.

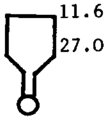
A preliminary analysis reveals the effect of the proximity of the carbonyl oxygen atom on the induced shifts which decrease steadily with distance. As an example in a series of rigid molecules, isophorone trimer (V), $C_{27}H_{38}O$ (4), a pentacyclic ketone with X-ray determined geometry and an analyzed 220 Mc spectrum, is a case where induced shifts could be of great value in structure determination. In conformationally mobile compounds, such as α,β unsaturated ketones and aldehydes it seems that, at least in the complexed form, phorone (VII) and mesityl oxide (VIII) retain an s-cis conformation, since shifts similar to pulegone (VI) are observed. An s-trans conformation can be attributed to other α and β substituted acroleins such as α methyl acrolein (IX), β,β dimethyl acrolein (X), methyl isopropenyl ketone (XI) and α methyl pentenone (XII). For 3,5-heptadienone-2 (XIII) an s-trans-trans conformation is the only acceptable geometry. It has been noted that ketones complex some 35-40% less strongly than alcohols (5) and this is approximately so, from comparison between values for 4-tert-butylcyclohexanols (6) and 4-tert-butylcyclohexanone (IV), considering that as a shift reagent Yb(DPM)$_3$ is two times stronger than the europium analog (2).

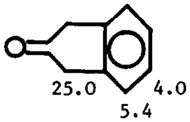
From values obtained with rigid molecules, such as indanones (I,II), fluorenone (III) and 4-tert-butylcyclohexanone (IV) we deduce, at first approximation, a relation between ΔYb and distance to carbonyl oxygen for all protons concerned: Fig. 1 represents logΔYb against log R (measured in Å on molecular models). Although distance dependence is quite apparent, the obtained variations are not linear. In fact, ΔYb may be explained by a model of the complexed organic molecule based on pseudocontact interaction with predominant distance factor (7): such a satisfying geometry was found for amines (2).



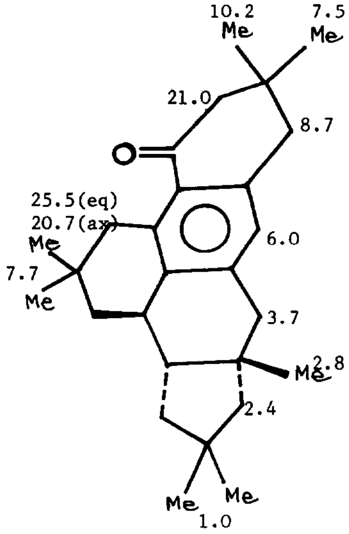








(I)



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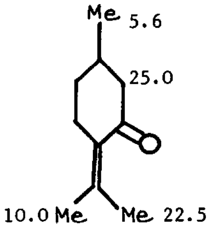

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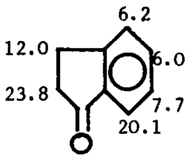

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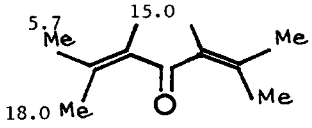

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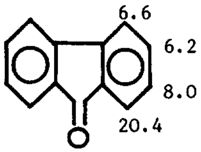

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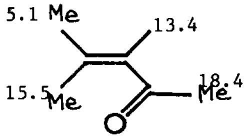
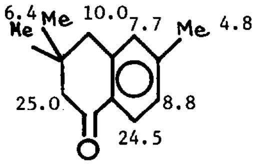
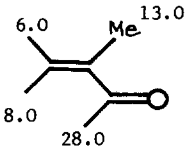


(VIII)

Table 1. ΔYb (Yb(DPM)$_3$-induced shifts)ppm





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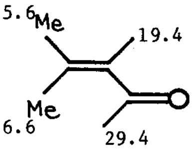
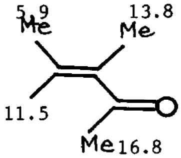
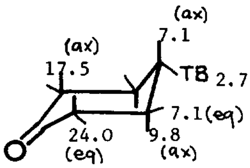


(X)



(XII)



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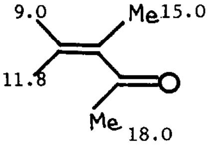
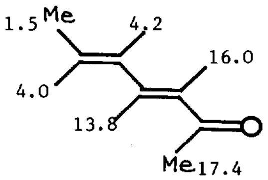


(XI)



(XIII)

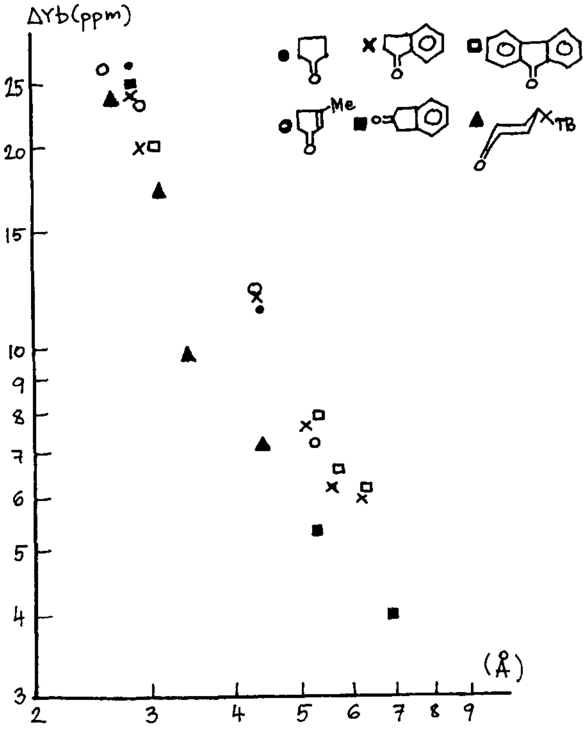


Fig.1

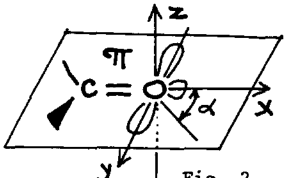


Fig. 2

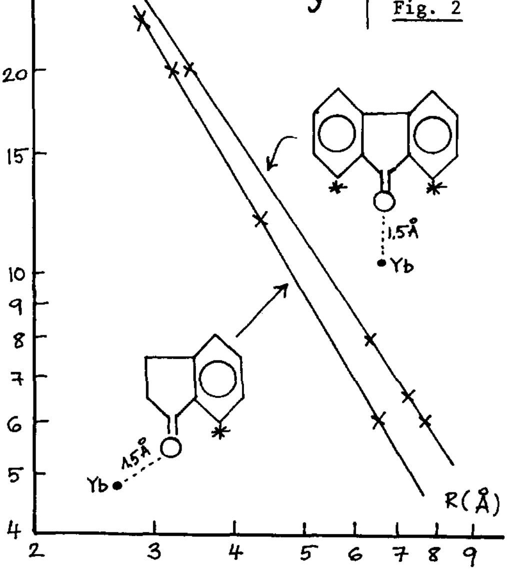


Fig. 3

In the ground state of the carbonyl group (Fig. 2),the oxygen atom carries two lone pairs (8), one formed from $2p_y$ orbitals and directed perpendicularly to the π system, along the y-axis, and another sp hybrid in the x-axis. Although the former lone pair, a p orbital, may well be responsible for interaction with $Yb(DPM)_3$, the latter may also play some part in the association. Different directions of approach in the xy plane were therefore supposed for the lanthanide atom and chelate in a 1:1 complex, along the x or y axis, or in an intermediate direction, at an angle α 60° and 80° to the C=O bond. For two symmetrical molecules, indanone-2 (I) and 4-tert-butylcyclohexanone (IV), distances between Yb and equivalent protons (R_1, R_2) were measured on molecular models for oxygen-ytterbium radii from 1 to 4 Å. The measured ytterbium to proton distances were recalculated considering a simultaneous paramagnetic pseudocontact effect on equivalent but unequally distant protons and thus obtained effective distances ($R = R_1R_2/\sqrt[3]{R_1^3 + R_2^3}$) were related to ΔYb. improvement in linear consistency was observed over Fig. 1 . However, for indanone-1 (II) and fluorenone (III) distances were measured directly from similar models, and linear agreement was found for Yb located at $\alpha = 60°$ in the direction opposed to the benzene ring for indanone-1, and on the x axis for fluorenone, both for an oxygen-ytterbium distance of 1.5±0.2Å (Fig. 3). It is possible that such a model becomes acceptable since approach to oxygen is sterically hindered by aromatic protons (✱) respectively on one or both sides of the carbonyl group.

Although further work remains necessary for the elaboration of an Yb(DPM)$_3$-ketone model, we wish to note the superiority of the described PMR technique over existing benzene and pyridine shift methods for carbonyl compounds, its consistency with results obtained by ASIS (9) and the important possibilities it offers for stereochemical assignment and structure elucidation in organic chemistry.

REFERENCES

(1) L. Ernst, Nachr. Chem. Techn., 18 Nr.23, 459 (1970) and references therein
(2) C.Beauté, Z.W. Wolkowski and N.Thoai, Tetrahedron Letters, in print
(3) K.J. Eisentraut and R.E. Sievers, J. Amer. Chem. Soc. 87, 5254 (1970)
(4) E. Cyrot, N. Thoai and J. Wiemann, Tetrahedron Letters, 83 (1970)
Thanks are due to Dr. E. Cyrot, now with VARIAN S.A., France, for a sample of isophorone trimer
(5) J.K.M. Sanders and D.H. Williams, Chem. Commun, 422 (1970)
(6) P.V. Demarco, T.K. Elzey, R.B. Lewis and E. Wenkert, J. Amer. Chem. Soc. 92, 5734 (1970)
(7) R.R. Fraser and Y.Y. Wigfield, Chem. Commun. 1471 (1970)
(8) H. Suzuki, "Electronic absorption spectra and geometry of organic molecules", Academic Press, 1967
(9) J. Ronayne and D.H. Williams, "Annual review of NMR spectroscopy", vol. 2, Academic Press, 1969