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STRUCTURAL ASSIGNMENT OF CHLORO- AND BROMO-VINYL ALDEHYDES BY Yb(DPM)$_3$-ASSISTED PROTON NUCLEAR MAGNETIC RESONANCE

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The addition of rare earth chelates to solutions of organic compounds with a heteroatom lone pair has lead to numerous studies by proton NMR (2). This method was applied to a series of chloro and bromovinyl aldehydes (3), and tris(dipivalomethanato)ytterbium (4) used as shift reagent. Table 1, containing Δ Yb(4) values obtained for 10% CCl_4 solutions at 60 MHz and 38°C, includes the corresponding aldehydes as reference.

All existing reports have stressed the inactivity of halogens in complex formation, therefore results are related to interaction with the carbonyl oxygen. The decreasing shift order observed is $H_{ald} > R_3 > R_2 > R_1$, and even a primary distance-dependence leads to an s-trans conformation for all investigated compounds. A geometrical model for the interaction was therefore attempted by two approaches, both described by a pseudocontact term (5):

$$\Delta Yb = \frac{\Delta H}{H} = K\,\frac{(3\cos^2_i \chi - 1)}{R_i^3} \qquad (I)$$

with K- constant in a molecule for a given temperature
R_i- Yb-i proton distance
χ_i- corresponding O-Yb-proton internuclear angle.

HINCKLEY's approximation (6) was first used and χ considered invariant for all protons. The log ΔYb=f(log R) functions were found for Yb-O distances between 2 and 4 Å and ψ (angle formed by the Yb-O vector and x-axis of the carbonyl bond) varying between +30° and -90° . For the ytterbium ion located as in figure 1, a straight line with a slope of -3 was obtained. In the second approach, the angular variations of equation (I) were respected (7), and a similar straight line was found only when placing Yb^{3+} on the x-axis at 3Å from the carbonyl oxygen (figure 2), with better accuracy when R_3=H.

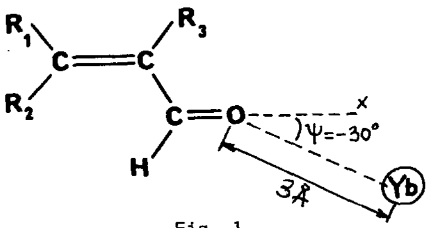

Fig. 1

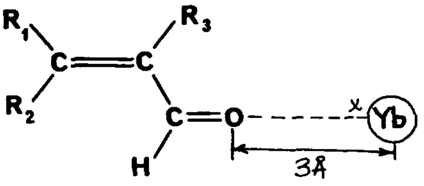

Fig. 2

$\Delta Yb = (\delta - \delta_{CCl_4})$ ppm, extrapolated to equimolar ratio of solute to chelate.

Table 1 (*) o- ortho, m- meta, p- para.

(a) stereochemistry determined previously by solvent effects(3)

Compound and its configuration		R_1		R_2		R_3		H
butene-2-al-1	E(a)	CH_3	12.7	H	25.2	H	45.2	81
chloro-3-butene-2-al-1	Z(a)	CH_3	9.8	Cl	-	H	39	66.4
chloro-3-butene-2-al-1	E(a)	Cl	-	CH_3	16.0	H	37.2	69.8
bromo-3-butene-2-al-1	Z(a)	CH_3	9	Br	-	H	36	56
bromo-3-butene-2-al-1	E(a)	Br	-	CH_3	14.7	H	36	56
methyl-2-butene-2-al-1	E(a)	CH_3	13.5	H	25.2	CH_3	34	80
chloro-3-methyl-2-butene-2-al-1	Z(a)	CH_3	10.8	Cl	-	CH_3	29.8	68
chloro-3-methyl-2-butene-2-al-1	E(a)	Cl	-	CH_3	14.3	CH_3	32	80
bromo-3-methyl-2-butene-2-al-1	Z(a)	CH_3	7.7	Br	-	CH_3	20.7	39.6
bromo-3-methyl-2-butene-2-al-1	E(a)	Br	-	CH_3	10.4	CH_3	24	49.6
phenyl-3-propene-2-al-1	E	$C_6H_5^{(*)}$	o:8.0m,p:3.3	H	19.8	H	34.2	60.4
chloro-3-phenyl-3-propene-2-al-1	Z	C_6H_5	o:7.0m,p:2.9	Cl	-	H	31.5	51.4
bromo-3-phenyl-3-propene-2-al-1	Z	C_6H_5	o;5.1m,p:2.2	Br	-	H	24	41
chloro-2-butene-2-al-1	Z	CH_3	7.7	H	15.2	Cl	-	50.6
bromo-2-butene-2-al-1	Z	CH_3	6.1	H	11.6	Br	-	37.2
chloro-2-phenyl-3-propene-2-al-1	Z	C_6H_5	o:4.4m,p:2.2	H	11.1	Cl	-	31.9
bromo-2-phenyl-3-propene-2-al-1	Z	C_6H_5	o:2.8m,p:1.2	H	7.9	Br	-	22.7

This model, which fits all the compounds investigated, appears more acceptable than the former, or that proposed by SANDERS and WILLIAMS (9), and accounts well for data obtained previously with other carbonyl compounds (4). The 3Å distance is somewhat greater than that observed for Yb-O in ytterbium acetylacetonate trihydrate (7)(10).

Our results lead to successful attribution of conformation, as well as configuration at the ethylenic bond for R_3=Cl,Br previously derived from considerations on magnetic anisotropies (3) for compounds in Table 1. The effect of aromatic substituents, which deprive solvent effects of meaningful conclusions, is also eliminated. However, a closer inspection of Table 1 reveals secondary effects, such as decreasing shifts when going from a chloro to a bromosubstituted aldehyde, which cannot be accounted for at this point, and remain subject to further investigation.

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(8)it should be noted that due to time-and distance-averaged effects,the proposed geometry is, at best,but a practical model. The $(3\cos^2\chi - 1)$ function decreases to zero at $\chi = 54^0$ and gives negative values for larger angles. As yet, no such reverse shifts have been reported despite the variety of investigated geometries.

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