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Preliminary communication

THE EFFECT OF TRIS(DIPIVALOMETHANE)EUROPIUM CHELATE ON THE ^{1}H NMR SPECTRA OF TERTIARY SILANOLS

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Summary

The europium chelate of tris(dipivalomethane) (Eu(DPM)$_3$) has a marked effect on the proton chemical shifts in the ^{1}H NMR spectra of tertiary silanols of the type $(C_6H_5)_x(CH_3)_nSiOH$ ($x = 3—n$, $n = 0 — 2$). The largest changes were found for the protons of CH$_3$ groups while those for protons of phenyl groups were smaller. The ^{1}H NMR spectra of polymethylpolysiloxanes were not affected by addition of Eu(DPM)$_3$.

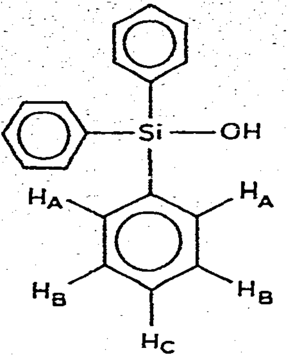
The europium chelate of tris(dipivalomethane) and similar chelates of some lanthanides (known as lanthanide shift reagents) are useful in high resolution nuclear magnetic resonance studies of organic compounds containing hydroxyl groups, e.g. alcohols, phenols, oximes, steroids [1,2,3]. In the field of organosilicon chemistry Eu(DPM)$_3$ was used in the stereochemical assignment of (1-*exo*-hydroxy-1-*endo*-methyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene)(cyclopentadienyl)cobalt. This suggested to us that lanthanide shift reagents might be useful for studying other silanols and the preliminary study described below confirms this.

We summarize in Table 1 the effects of stepwise additions of Eu(DPM)$_3$ to the CCl$_4$ and CDCl$_3$ solutions of triphenylsilanol (I), methyldiphenylsilanol (II) and dimethylphenylsilanol (III) on the proton chemical shifts at 25° C.

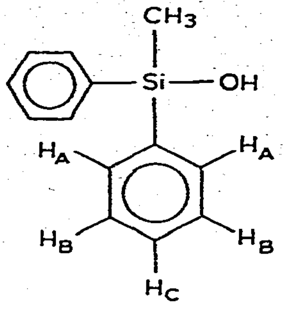
The values of the "bound" shifts ("the bound" chemical shifts for each proton of the molecule form the basis for geometry determination) are used to illustrate the effect under study. These were determined graphically as the slopes of plots of $\Delta\delta$ versus [Eu(DPM)$_3$] [substrate], according to eq. 1 [5].

$$\delta(\text{Eu}) - \delta(\text{S}) = \frac{[\text{Eu(DPM)}_3]}{[\text{Substrate}]} \qquad [1]$$

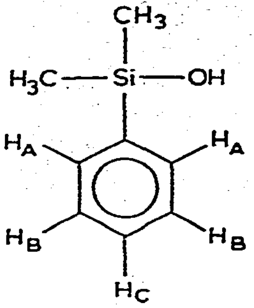
where δ(S) is the chemical shift of proton signals in the NMR spectra of substrates, and δ(Eu) is the chemical shift of proton signals in the NMR spectra of substrates after addition of the Eu(DPM)$_3$.



(I)



(II)



(III)

The relative values of "bound" shifts ρ° (the ratio of ρ for each proton to that of proton H_A) were used for comparison. When the concentrations of $Eu(DPM)_3$ are constant, the values of "bound" shift depend on the initial concentrations of the substrates, [6] so this method of assessing the effect under study is satisfactory.

TABLE 1

THE VALUES OF "BOUND" SHIFTS ρ AND RELATIVE "BOUND" SHIFTS (ρ° DETERMINED ACCORDING TO EQ. 1) FOR ADDITION OF $Eu(DPM)_3$ [a] ON ^1H NMR SPECTRA OF CCl_4 AND $CDCl_3$ SOLUTIONS OF TERTIARY SILANOLS (I—III) AT 25°C

Compound	Solvent	Concentration of substrate (mol/l)	H_A		$H_{B,C}$		CH_3	
			ρ	ρ°	ρ	ρ°	ρ	ρ°
I	CCl_4	0.074	7.5	1.0	1.0	0.133	—	—
I	$CDCl_3$	0.074	3.6	1.0	0.4	0.111	—	—
II	CCl_4	0.100	9.6	1.0	1.9	0.198	10.7	1.115
II	$CDCl_3$	0.063	4.3	1.0	0.7	0.163	4.8	1.116
III	CCl_4	0.125	9.8	1.0	2.5	0.255	11.1	1.133
III	$CDCl_3$	0.156	7.9	1.0	1.5	0.190	8.7	1.101

[a] The six stepwise additions of $Eu(DPM)_3$ covered the $[Eu(DPM)_3]$ [substrate] ratios of 0.1—0.6.

It is clear from Table 1 that the differences in "bound" shifts of protons are considerable. The largest values of paramagnetic shifts of signals are observed for $SiCH_3$ groups. The differences in the paramagnetic shifts of phenyl group proton signals measured as a percentage of the shift for $SiCH_3$ are lower for H_A protons (90.0%) and lowest for $H_{B,C}$ protons of phenyl groups (20.0%).

The multiplet structure of $H_{B,C}$ proton signals were not resolved. When $Eu(DPM)_3$ was used the paramagnetic shifts of $SiCH_3$ proton signals were unusually accompanied by considerable broadening and this phenomenon is under investigation in this laboratory. The differences observed for values of ρ° for protons of $SiCH_3$ groups and H_A in $CDCl_3$ were equal to those in CCl_4. The values of ρ for compound I (which was measured at the same concentration in both solvents) in $CDCl_3$ were only ca. 50% of those in CCl_4. It is evident that the nature of the solvent plays an important role.

Furthermore we observed that $Eu(DPM)_3$ does not change the ^1H NMR spectra of 1,1,1,3,3,3-hexaalkylsiloxanes-1,3 or polysiloxanes terminated by trimethylsilyl groups. We utilized this phenomenon for quantitative determination of silanols in polysiloxanes [7]. Replacing $Eu(DPM)_3$ by $Pr(DPM)_3$ in solutions of organosilicon compounds had similar effects to those in solutions of organic compounds; $Eu(DPM)_3$ induces downfield shifts and the praseodymium analogue upfield shifts. For this reason $Eu(DPM)_3$ is the better reagent for phenylsilanols while $Pr(DPM)_3$ is advantageous for alkylsilanols.

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