

Preliminary communication

Organometallic compounds

XXXIII*. Influence of tris(dipivaloylmethanato)europium(III) on the PMR spectra of, and evidence for intramolecular complexation in functionally-substituted organotin compounds

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It has been suggested that nucleophilic assistance, involving coordination prior to the rate-determining step, is necessary in cleavage of an alkyl-tin bond by an electrophile².

We have synthesized some functionally substituted tetraorganotins** in which intramolecular coordination is possible. The kinetic aspects of the halodemethylations of these compounds are now being studied in our laboratory, and we report here some of their spectral properties.

The compound $\text{PhMe}_2\text{SnCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{OH}$ (I), which has been made by the addition of dimethylphenyltin hydride to the corresponding unsaturated alcohol³ shows two diastereotopic methyl groups ($\Delta\delta$ 0.3 Hz at 60 MHz). It is possible to increase this small nonequivalence by the addition of tris(dipivaloylmethanato)europium(III)

TABLE I

INFLUENCE OF THE $\text{Eu}(\text{DPM})_3$ ON THE CHEMICAL SHIFT AND COUPLING CONSTANTS OF THE CH_3Sn PROTONS

$\text{Eu}(\text{DPM})_3$ $\times 10^2$ (M)	δ (Me-Sn) ppm (TMS = 0)	$\Delta\delta$ ppm	$J(^{117/119}\text{Sn}-\text{CH}_3) \equiv J(^{117/115}\text{Sn})$ (Hz)
<i>PhMe₂SnCH₂CH₂CH(CH₃)OH (I) (c 0.32 M)</i>			
0	0.255 0.250	0.005	51.3 / 53.4
14.2	0.767 0.742	0.025	
20	1.082 1.036	0.046	51/53.1 50.8/53.4
<i>BrMe₂SnCH₂CH₂CH(CH₃)OH (V) (c 0.32 M)</i>			
0	0.708	0	60.6 / 63.4
14.2	1.048	0	60.0 / 62.8
20	1.115	0	59.0 / 61.6
26	1.307	0	~59 / ~61

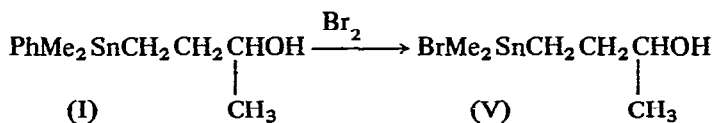
*For part XXXII, see ref. 1.

**All the organotin compounds have been characterized by their mass spectra.

[Eu(DPM)₃] (see Table 1; see also ref. 4). No detectable nonequivalence can be seen for cyclo-C₆H₁₁ Me-*i*-PrSnCH₂CH₂CMe₂OH (II) or for cyclo-C₆H₁₁ Et-*i*-PrSnCH₂CH₂CH₂NMe₂ (III), even with large amounts of Eu(DPM)₃ ([Eu] / [Sn] ~0.8). The γ -methyl groups of (II) do show a broadened peak, but this can not be attributed to a nonequivalence since the analogous methyl groups of Ph₃SnCH₂CH₂CMe₂OH (IV) (m.p.: 78–79°) show the same broadening-effect in the presence of the same amount of Eu(DPM)₃.

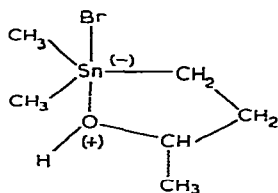
It will be noticed that the *ortho* protons of the phenyl ring of (I) and (IV) are much more influenced by the presence of Eu(DPM)₃ (downfield shift up to 90 Hz) than the *meta* and *para* protons, so that it is possible to determine the coupling constant between the *ortho* protons and tin ($J(^{117/119}\text{Sn}) \sim 54$ Hz). This is also true for Ph₃SnCH₂CH₂CH(CH₃)OH (m.p. 66–67°) and for Ph₃Sn(CH₂)₃OH (m.p. 105–106°).

(I) reacts smoothly with bromine in CCl₄⁵ and yields the corresponding triorganotin bromide (V):



which does not show any detectable nonequivalence^{1,8}, even in the presence of Eu(DPM)₃ (see Table 1). Two observations are noteworthy: (i) a graph of $\delta(\text{Me})$ vs. [Eu] gives straight lines with a slope which is twice as great for (I) than for (V); (ii) the $J(\text{CH}_3\text{Sn})$ coupling constant of (V) is abnormally large in CCl₄ and does not change very much by dilution ($J(^{117/119}\text{Sn})$ 60.6/63.4 for a 0.32 *M* solution and 59.6/62.4 for a 0.04 *M* solution; $\delta(\text{Me})$ decreases also from 42.5 Hz to 40.4 Hz, and $\delta(\text{OH})$ from 220 to 148 Hz). One may compare for instance, the value of J 60.6 Hz for (V) with that of J 49.1 Hz for cyclohexyldimethyltin bromide of J 52.1 Hz for Ph(CH₂)₃-SnMe₂Br (VI) or PhO(CH₂)₄SnMe₂Br⁶. The addition of one equivalent of *sec*-BuOH to the solution of (VI) in CCl₄ causes an increase of the coupling constant ΔJ of only +0.8 Hz (ΔJ of V 0.5 Hz under the same conditions). Even in *sec*-BuOH as solvent, J of (VI) is as small as 55.0 Hz. The addition of one equivalent Me₃SnBr to the solution of (V) in CCl₄ gives a small ΔJ of +0.2 Hz (and a ΔJ for Me₃SnBr equal to +0.7 Hz) whereas the addition of 0.6 equivalent Eu(DPM)₃ causes a decrease of the coupling constant of -1.7 Hz.

These results strongly suggest that (V) has to a large extent a cyclic structure as follows^{*}:



^{*}This might also be the case for (EtO)₂CHCH₂CH₂SnMe₂Br, for which $J(^{117/119}\text{Sn-Me})$ is 58/61 Hz⁷.

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