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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 electrophile[2].

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

The compound $PhMe_2SnCH_2CH_2CH(CH_3)OH$ (I), which has been made by the addition of dimethylphenyltin hydride to the corresponding unsaturated alcohol[3] 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 $Eu(DPM)_3$ ON THE CHEMICAL SHIFT AND COUPLING CONSTANTS OF THE CH_3Sn PROTONS

$Eu(DPM)_3$ $\times 10^2$ (*M*)	δ (Me–Sn) ppm (TMS = 0)	$\Delta\delta$ ppm	$J(^{117/119}Sn\text{–}CH_3) \equiv J(^{117/119}Sn)$ (Hz)
$PhMe_2SnCH_2CH_2CH(CH_3)OH$ (I) (c 0.32 M)			
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
$BrMe_2SnCH_2CH_2CH(CH_3)OH$ (V) (c 0.32 M)			
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

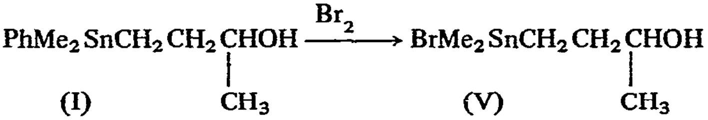
[★] For part XXXII, see ref. 1.

[★★] 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-C_6H_{11}Me-i-PrSn$CH_2CH_2CMe_2OH$ (II) or for cyclo-C_6H_{11}Et-i-Pr$SnCH_2CH_2CH_2NMe_2$ (III), even with large amounts of $Eu(DPM)_3$ ([Eu] / [Sn] $\sim$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 $Ph_3SnCH_2CH_2CMe_2OH$ (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 ($J(^{117/119}Sn)$ $\sim$54 Hz). This is also true for $Ph_3SnCH_2CH_2CH(CH_3)OH$ (m.p. 66-67°) and for $Ph_3Sn(CH_2)_3OH$ (m.p. 105-106°).

(I) reacts smoothly with bromine in CCl_4[5] and yields the corresponding triorganotin bromide (V):

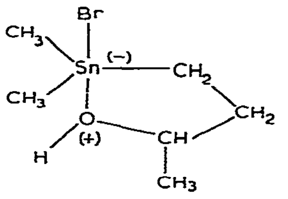


$$PhMe_2SnCH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HOH \xrightarrow{Br_2} BrMe_2SnCH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HOH$$

(I) (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 δ(Me) *vs.*[Eu] gives straight lines with a slope which is twice as great for (I) than for (V); (ii) the $J(CH_3Sn)$ coupling constant of (V) is abnormally large in CCl_4 and does not change very much by dilution ($J(^{117/119}Sn)$ 60.6/63.4 for a 0.32 *M* solution and 59.6/62.4 for a 0.04 *M* solution; δ(Me) decreases also from 42.5 Hz to 40.4 Hz, and δ(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 $Ph(CH_2)_3$-$SnMe_2Br$ (VI) or $PhO(CH_2)_4SnMe_2Br$[6]. The addition of one equivalent of sec-BuOH to the solution of (VI) in CCl_4 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 Me_3SnBr to the solution of (V) in CCl_4 gives a small ΔJ of + 0.2 Hz (and a ΔJ for Me_3SnBr 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 $(EtO)_2CHCH_2CH_2SnMe_2Br$, for which $J(^{117/119}Sn\text{-}Me)$ is 58/61 Hz[7].

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