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BENZYL COMPOUNDS

VI*. THE NMR (^{1}H, ^{119}Sn) SPECTRA OF BENZYLTIN DERIVATIVES

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SUMMARY

The NMR spectra of $(YC_6H_4CH_2)_nSnCl_{4-n}$ (Y=H, F, Cl and n=2, 3, 4) compounds have been studied from which evidence has been obtained for the existence of a predominant conformation. The ^{119}Sn chemical shift may be related to inductive and neighbour anisotropy effects and to p_π–d_π interaction.

INTRODUCTION

As a continuation of a PMR study of tin bonding in benzyltin derivatives[1] we have now examined the PMR, as well as the ^{119}Sn INDOR, spectra of $(C_6H_5CH_2)_n$-$SnCl_{4-n}$ (n=2, 3, 4) and $(YC_6H_4CH_2)_nSnCl_{4-n}$ (Y=F, Cl and n=2, 3) compounds. Attention has also been paid to the *para*-substituent effect on different NMR parameters in the series $YC_6H_5CH_2Z$(Y=H, F, Cl; Z=$(YC_6H_5CH_2)_2SnCl$, $YC_6H_5CH_2$-$SnCl_2$).

EXPERIMENTAL

The synthesis of tetrabenzyltin has been described in a previous paper[1]. The various benzyltin halides were prepared by direct synthesis from tin metal and the organic halides following the procedure elaborated by Sisido *et al.*[2].

The NMR spectra were recorded using a frequency-sweep mode with a 90 MHz Bruker-Physik HFX4 instrument. The ^{119}Sn resonance frequencies were measured by recording the ^{119}Sn INDOR spectra; the ^{119}Sn frequency was 33.54 MHz.

Benzylic proton shifts were measured using the lowest measurable concentrations in CH_2Cl_2. The coupling constants and the ^{119}Sn shifts however were taken from the spectra of the saturated solutions in CH_2Cl_2. For the dichlorides, due to their low solubility, a Fabri-Tek Series 1070 signal averaging system was to be used in estimating the coupling constants.

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* For part V see ref. 12.

TABLE 1

NMR DATA FOR THE SERIES $(YC_6H_4CH_2)_nSnCl_{4-n}$

Compound	$\delta_H(CH_2)^a$ *(ppm)*	$\delta(^{119}Sn)^b$ *(ppm)*	*J(Sn–C–H) (Hz)* ^{117}Sn	^{119}Sn	$J(^{13}C\text{–}H)^c$ *(Hz)*
$(C_6H_5CH_2)_4Sn$	3.13	+36	56.5	58.5	132
$(C_6H_5CH_2)_3SnCl$	2.67	−53	62.5	65	135
$(C_6H_5CH_2)SnCl_2$	2.14	−35	74	77	138
$(FC_6H_4CH_2)_3SnCl$	2.67	−53	60.5	63	134
$(FC_6H_4CH_2)_2SnCl_2$	2.14		75	78	139
$(ClC_6H_4CH_2)_3SnCl$	2.67	−50	61	63.5	134.5
$(ClC_6H_4CH_2)_2SnCl_2$	2.14		76	79	138

[a] $\delta_H(CH_2Cl_2)$, 0. [b] $\delta(^{119}Sn)[(CH_3)_4Sn]$, 0. [c] Of the CH_2 group.

TABLE 2

^{119}Sn CHEMICAL SHIFTS AND TAFT σ^* CONSTANTS FOR R_4Sn COMPOUNDS

Compound	σ^*	$\delta(^{119}Sn)$ *ppm*
$(CH_2{=}CH)_4Sn^a$	+0.360	+165.1
$(C_6H_5CH_2)_4Sn$	+0.215	+ 36
$(CH_3)_4Sn^a$	0.000	0
$(CH_3CH_2)_4Sn^a$	−0.100	+ 6.7
$(CH_3CH_2CH_2)_4Sn^a$	−0.115	+ 16.8
$\{(CH_3)_2CH\}_4Sn^a$	−0.190	+ 43.9

[a] See ref. 10.

The results are summarised in Tables 1 and 2. The ^{119}Sn data are represented graphically in Fig. 2.

RESULTS AND DISCUSSION

Chemical shift of the benzylic protons

Fraser *et al.*[3] have shown that in 11 series of *para*-substituted toluenes, each having different α substituents, a correlation exists between the effect of these substituents on the chemical shift and their Hammett σ values. These authors have concluded that there appears to be a reasonably consistent relationship between the degree of correlation, ρ (which is defined as the slope of the τ_A versus σ_p plot), and the size of Z, with ρ decreasing as Z increases. This was interpreted as an indication that ρ depends to a large extent on the conformation of the methylene group with respect to the benzene ring. Fraser *et al.* also concluded that when Z is large the conformation shown in Fig. 1 would predominate, and that this always occurs at small ρ values.

Comparison of the chemical shifts in the series of compounds $YC_6H_4CH_2Z$ (Y=H, F, Cl and Z= $(YC_6H_4CH_2)_2SnCl$, $YC_6H_4CH_2SnCl_2$) investigated in this work (Table 1) appears to indicate that the *para*-substituent effect on the benzylic protons

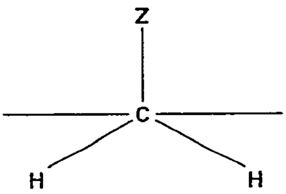

Fig. 1.

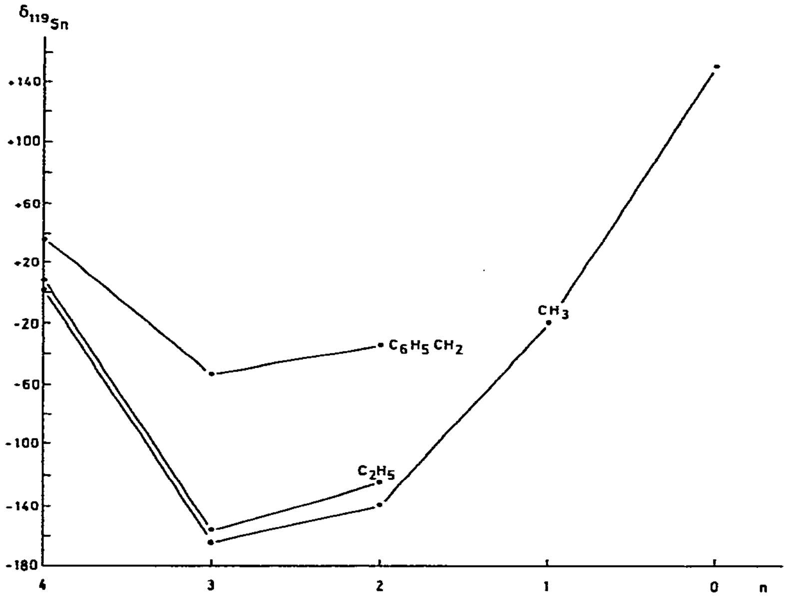

Fig. 2. ^{119}Sn chemical shifts in the series R_nSnCl_{4-n}.

is absent in the benzyltin compounds, the degree of correlation, ρ, in this instance being zero. It follows, therefore, that in benzyltin compounds (where $Z=SnR_3$ is very large) the predominant conformation is as shown in Fig. 1. However some reservation must be expressed concerning the angle between the plane of the phenyl ring and the CCZ plane, since Raman depolarisation measurements show no symmetry in the benzyl molecules thus indicating that this angle should differ from 90°.

^{119}Sn chemical shift

It is generally accepted that for heavy atoms the screening of the nucleus is dominated by the paramagnetic term[4,5]. In a series of similar compounds, such as SnR_4, in which p_π–d_π bonding is supposed to be negligible and for which the mean excitation energy, ΔE, and the hybridisation of the tin atom can be assumed constant, the ^{119}Sn chemical shift should be primarily determined by the inductive effect of the R groups.

For the SnR_4 compounds listed in Table 2, therefore, some correlation should exist between the ^{119}Sn chemical shifts and the Taft σ^* induction constants[6] for the R group. For $R=CH_3$, C_2H_5, n-C_3H_7, and i-C_3H_7 a rough correlation of this type is found with the ^{119}Sn chemical shift increasing with decreasing values of σ^*.

The benzyl group ($\sigma^*=0.215$, $\delta=+36$) and to an even larger extent the vinyl group, shows anomalous high-field shifts ($\sigma^*=+0.360$, $\delta=+165.1$). The tin tetrahalides also have their ^{119}Sn resonance shifted to very high field values. For these compounds the shift is explained by the concomitant action of $(p_x$–$d_{Sn})\pi$-bonding and neighbour anisotropy effects. Egorochkin *et al.*[7] have shown by means of a PMR study that the CH_2 group disrupts the p_π–d_π interaction between the sp^2 carbon and the metal in allyl derivatives of the type $(CH_3)_3MCH_2CH{=}CH_2$ (M=Si, Ge and Sn).

Nagy and Réffy[8] concluded from a comparison of dipole moment data of $(CH_3)_3MR$ compounds (M = Si, Ge, Sn and R = vinyl, alkyl, phenyl, benzyl) that the methylene group in alkyl and benzyl derivatives greatly hinders p_π–d_π interaction. Griffiths and Derwish[9], from UV spectral data, also concluded that the π-electron cloud of the phenyl ring of the benzyl moiety is screened from the 5*d* orbitals of tin by the methylene group. The relative paramagnetic shifts observed in this work should therefore be ascribed primarily to magnetic effects induced by electron circulation in the molecule. This argument is supported by the strong high field shifts observed by Davies *et al.*[5] for Ph_3SnMe and for $Ph_3SnOSiPh_3$ in comparison to $(Bu_3Sn)_2O$.

The general trend of ^{119}Sn chemical shift with progressive halogen substitution in the series R_nSnCl_{4-n} ($R = CH_3, C_2H_5, C_6H_5CH_2$) is also very similar (Fig. 2); the first chlorine atom produces a deshielding effect, but all subsequent chlorine atoms up to $SnCl_4$ are shielding. The latter effect may be due to p_π–d_π bonding between chlorine and tin[5,10,11], the tin *d*-orbitals acting as unhybridized acceptors for the chlorine p_π-electrons. In addition, the efficiency of π-overlap with a *p*-orbital can be improved by hybridising *d*-orbitals to give the resultant orbital a small amount of *p*-character. As the extent of d_π–p_π overlap increases with increasing effective nuclear charge on the tin atom, the observed ^{119}Sn shift sequence can be explained in terms of p_π–d_π bonding.

The deshielding effect of the first chlorine atom still remains to be explained however. This deshielding is obviously related to the inductive effect of the chlorine atom which exceeds the shielding action of the p_π–d_π interaction and of the diamagnetic anisotropy contribution of the Sn–Cl bond. For $R = C_6H_5CH_2$ however, the low-field ^{119}Sn shift is about half that observed for R_3SnCl compounds where $R = CH_3, C_2H_5$ (Fig. 2), and for this reason it must be assumed that a considerable part of this upfield shift is due to the ring current effect of the benzyl group. Secondly, substitution of Cl for $C_6H_5CH_2$ causes less change in the electronic polarization around the tin atom than the corresponding substitution of Cl for CH_3, since the benzyl group itself is more electronegative than the methyl group.

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