THE PROTON MAGNETIC RESONANCE SPECTRA OF BENZYLTIN DERIVATIVES

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Received October 28th, 1965

INTRODUCTION

Recent observations in the PMR spectra of the ethyltin chlorides[1], namely on the coupling constants between ^{119}Sn and ^{117}Sn and the protons of the ethyl group removed respectively 2 and 3 bonds away from the tin atom, have shown that the concept of the linear relationship between these coupling constants and the per cent s character of the tin orbitals directed towards the aikyl radical[2] should be revised[3].

In order to gain a deeper insight into this problem a group of benzyltin compounds has been examined. The benzyltin halides can in fact be considered as derivatives of the corresponding methyltin compounds by substituting a hydrogen atom by a phenyl group. Since the group electronegativity $E(C_6H_5CH_2)$ is higher than $E(CH_3)$ one would expect that $J(^{117,119}Sn–C–H)$ would be smaller for the benzyl than for the methyl compounds, according to the isovalent rehybridization theory of Bent[4].

Special attention is also paid to the substituent shifts of the phenyl group signals and to the position of the CH_2 signals as a function of the inductive effect and the neighbour anisotropy effect of the Sn–X and the phenyl group.

EXPERIMENTAL

Preparation of compounds

Tetrabenzyltin. For the synthesis of this compound the procedure elaborated by Pfeiffer and Schnurmann[5], modified by Luijten and Van der Kerk[6] for tetraphenyltin, was followed. The yield was found to depend highly on the excess amount of benzylmagnesium bromide brought into reaction. It is advisable to use twice the required amount of the Grignard reagent solution or even more. Following the addition of ice-water and of a 10 % hydrochloric acid solution the ether layer is separated from the water layer and dried over calcium chloride. The ether is distilled off and a viscous oily material is obtained. This oil is distilled under low pressure and the distillation is stopped when the vapour temperature reaches 140° at 8 mm. The residue left in the flask is then recrystallized from light petroleum ether (b.p. ± 40°). On cooling to 0° beautiful transparent crystals are obtained. The melting point of the pure tetrabenzyltin is 42–43°.

Tribenzyltin chloride. This product was synthesized by the method of Sisido[7]; the yield was 80 %.

Tribenzyltin hydride. The hydride was prepared by the normal procedure: *i.e.* the reduction of tribenzyltin chloride with $LiAlH_4$[8]. Because of the poor solubility of

the chloride in ether a somewhat different procedure was used. Lithium aluminium hydride is brought into suspension in dry ether; the suspension is stirred vigorously and the chloride is added in small portions. When all the chloride has been added the reaction mixture is refluxed for 3 h. In contrast to the observations of Noltes and Van der Kerk, on removing the solvent ether by distillation, we obtained a white solid instead of an oily liquid. The recrystallization of this solid from 96 % alcohol offered no difficulties and transparent bright crystals were obtained with a melting point of 52–53°.

Tribenzyltin acetate. This compound was the commercial Fluka product.

Dibenzyltin dichloride, dibromide, diiodide and diacetate. These compounds were obtained by treatment of dibenzyltin oxide (Fluka product) with respectively: concd. hydrochloric acid, concd. hydrobromic acid, concd. hydroiodic acid and glacial acetic acid. The products were recrystallized from 96 % alcohol.

Apparatus and procedures

The spectra were recorded with a Varian V 4300-B dual purpose NMR spectrometer at 56.44 Mc; the operating techniques and various accessories were the same as those described previously[9].

The spectra of tribenzyltin hydride, of tetrabenzyltin and of tribenzyltin chloride were taken on the pure liquid at respectively 70, 70 and 150°. For tetrabenzyltin and tribenzyltin chloride spectra were also measured on solutions in chloroform with a concentration of less than 10 mole per cent. All the other compounds were studied in chloroform solutions under similar conditions. In order to gain the best information on the phenyl proton resonances solutions of less than 5 mole per cent in CCl_4 were also investigated.

A capillary containing a solution of 10 vol.% of TMS in $CHCl_3$ served as an external reference.

RESULTS AND ANALYSES OF THE SPECTRA

Tribenzyltin hydride shows the most complex spectrum in this series of compounds. With increasing magnetic field, starting from the chloroform resonance we first observe the phenyl group multiplet, then the hydride proton resonance and finally the CH_2 resonance. Centered on the sharp hydride peak are the tin satellites with separations $J(^{117/119}Sn\text{–}H)$ (1692, 1770 cps). On both sides of the CH_2 signal we observe the satellites due to $J(^{117/119}Sn\text{–}C\text{–}H)$ couplings and to $J(^{13}C\text{–}H)$.

TABLE 1

PMR SPECTRA OF THE NEAT LIQUIDS

Compound	$\tau(CH_2)$	$J(^{117}Sn\text{–}C\text{–}H)$	$J(^{119}Sn\text{–}C\text{–}H)$	$J(^{13}C\text{–}H)$
$(C_6H_5CH_2)_4Sn$	8.069	55.9	58	133
$(C_6H_5CH_2)_3SnCl$	7.385	62.0	64.8	133
$(C_6H_5CH_2)_3SnH$[a]	8.158	59.8	62	131

[a] τ(H) 4.488; $J(^{117}Sn\text{–}H)$ 1.692; $J(^{119}Sn\text{–}H)$ 1.770.

The spectra of all the other benzyltin derivatives show the same pattern, except for the hydride signal and its satellites. In the case of the acetates a single sharp peak is also observed for the CH_3 protons of the acetoxy group.

In every case a simple first order treatment allowed the assignment of the various peaks and the calculation of the spectral parameters which are listed in Tables 1 and 2. The assignment for the *ortho*, respectively the *meta–para* proton resonances is based on the integrated respective intensities (2:3) of the groups and on earlier measurements on the phenyltin chlorides[10] and on other monosubstituted phenyl compounds.

TABLE 2

PMR SPECTRA OF CHLOROFORM SOLUTIONS

Compound	$\tau(CH_2)$	$\tau(CH_3)$	$J(^{117}Sn-C-H)$	$J(^{119}Sn-C-H)$	$J(^{13}C-H)$	δ_o[a]	$\delta_{m,p}$[a]
$(C_6H_5CH_2)_4Sn$	7.784		56.8	59	133.5	33.5	15.75
$(C_6H_5CH_2)_3SnCl$	7.340		64.3	66.9	134	26.5	11.75
$(C_6H_5CH_2)_3SnOAc$	7.358	7.979	67.1	69.8		29.75	13.75
$(C_6H_5CH_2)_2SnCl_2$	6.800		76.3	79.3	136	15.5	5.75
$(C_6H_5CH_2)_2SnBr_2$	6.684		70.5	73.4		14.5	5.5
$(C_6H_5CH_2)_2SnI_2$	6.543		62.2	64.9		15.5	5.0
$(C_6H_5CH_2)_2Sn(OAc)_2$	6.943	8.023	86.1	90.1		10.5	10.5
$C_6H_5CH_2$	7.66[b]					14.5	14.5

[a] The chemical shift values δ_o and $\delta_{m,p}$ for the *o*-, respectively the *m*- and *p*-proton resonance are expressed in cps upfield of the chloroform signal. [b] $\tau(CH_3)$.

DISCUSSION

Ring protons of the benzyl group – chemical shift

At first glance it would be expected that the protons of the phenyl ring would be rather weakly influenced by the $SnX_{(4-n)}$ group which is separated by two bonds from the ring and by at least four bonds from these protons. The experimental results (Table 2, columns 7 and 8), however, show that this influence is not negligible. A comparison of the results for R_3SnCl and R_2SnCl_2 ($R = C_6H_5$ and $C_6H_5CH_2$ respectively)[10] shows that even the relative importance of the downfield shift with progressive chlorine substitution is the same for the phenyltin compounds as for the benzyltin compounds.

The benzyltin compounds can be considered as derivatives of toluene wherein a hydrogen atom has been replaced by the group SnX_3. The $(C_6H_5CH_2)_3Sn$ group will be more electropositive than H although the difference will not be large. The electron inductive effect would thus shift the phenyl group signals of tetrabenzyltin to higher field than those of toluene, but this shift should be small. From the data of Table 2 it is seen that for *m,p*- and for *o*-protons the shift is in the right sense. For the *o*-protons however, this shift is much too large to be attributed to the rather small change in the inductive effect. The best explanation then would be through orbital interaction between the tin atom and the π-electron system of the ring. The relative shifts of the ring proton signals with the number and the nature of the substituents, should only be a function of long range effects. Indeed, as already mentioned, there is only substitution

on the tin atom which itself is removed four bonds away from the nearest ring protons. Contributions to the shifts from the inductive effect parameter and from the neighbour anisotropy effect term will be negligible and could possibly only explain a small proportion of the *o*-proton shifts. Thus only effects resulting from the changes in the π-electron density of the phenyl ring could be considered as a cause of the relatively large shifts. Such changes in the π-electron density then should act equally over the ring and the internal chemical shifts between the *o*, and the *m,p* proton signals should be nearly constant. The results given in Table 2 agree in a rather striking fashion with this theory.

Methylene protons of the benzyl group – chemical shift

The position of the methylene proton signal will be determined by three factors: the electronic inductive effect, the neighbour anisotropy effect of the Sn–X bond, the ring current effect of the phenyl group. For any of the benzyltin compounds studied, the downfield shift *versus* the shift for tetramethyltin ($\tau = 9.86$), is higher than 2.1 ppm. This paramagnetic shift is too large to be attributed to the weak *I*-effect of the phenyl group and clearly results from the ring current effect.

The remaining relatively small shift range, from $\tau = 7.784$ to $\tau = 6.543$ remains to be explained by the *I*-effect and the neighbour anisotropy contributions. Both act in the same sense and therefore a complete analysis of the data will be impossible. The shift observed in going from $(C_6H_5CH_2)_3SnCl$ ($\tau = 7.340$) to $(C_6H_5CH_2)_2SnCl_2$ will be mainly determined by the *I*-effect. The smaller shifts observed in the series of $(C_6H_5CH_2)_2SnX_2$ compounds (X = Cl, Br, I) are still towards lower field, thus showing that the decrease of the inductive effect term [$E(Cl) = 3 > E(Br) = 2.8 > E(I) = 2.5$] is overcompensated by the increase of the neighbour anisotropy term in the sequence Sn–Cl < Sn–Br < Sn–I[2,3].

The statements made above were substantiated by the τ-values for the acetates, where the neighbour anisotropy term will be of negligible importance, but the inductive effect will be rather strong.

Hydride proton and direct tin–proton coupling constant

The hydride proton resonance yields a very low τ-value as compared to the value for $(CH_3)_3SnH$[9]. This is clearly due to the far reaching ring current effect.

The $J(^{117,119}Sn–H)$ values are slightly higher than for trimethyltin hydride as a result of higher group electronegativity for benzyl than for methyl[4]. A comparison of the $J(Sn–H)$ values for trimethyl-, tribenzyl-, and triphenyltin hydride yields the following sequence for the group electronegativites of the organic radicals.

$$E(CH_3) > E(C_6H_5CH_2) > E(C_6H_5).$$

Substitution of H by C_6H_5 in the methyl group thus has increased the group electronegativity. This conclusion is also in agreement with the increase in the $J(^{13}C–H)$ values.

The arguments presented above implicate that the per cent *s* character of the tin orbitals directed towards the carbon atom in the benzyl compounds is smaller than in the methyl compounds. According to the theory advanced by Holmes and Kaesz[2], that there should be a linear relationship between the indirect tin–proton

coupling constants J(Sn–C–H) and the per cent s character of the tin orbitals directed towards carbon, we ought to obtain J(Sn–C–H) (benzyltin) $<$ J(Sn–C–H) (methyltin). A comparison of the previously published data for methyl compounds[2] and the corresponding data for benzyl compounds in Tables 1 and 2 shows that there is no agreement upon this theoretical base.

These results and the results obtained with the ethyltin chlorides[1] thus demonstrate that other factors must be taken into consideration in these problems and more research will be necessary, part of which is under way in this laboratory.

ACKNOWLEDGMENT

The authors have pleasure in expressing their gratitude to Prof. dr. Z. EECKHAUT for his interest in this work and for discussion of the paper.

SUMMARY

The PMR spectra of a series of benzyltin compounds $(C_6H_5CH_2)_nSnX_{4-n}$ ($1 \leqslant n \leqslant 4$, X = H, Cl, Br, I, $OCOCH_3$) have been studied. Evidence is presented that substituents X equally influence all the ring protons chemical shifts and this is ascribed to changes in the π-electron system of the ring. The methylene group shifts are the result of ring current, inductive effect and diamagnetic anisotropy contributions. The coupling constants J(Sn–C–H) cannot be interpreted by changes in s electron density around the tin atom only.

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