Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

COMPARATIVE PMR STUDY OF METHYL-, ETHYL- AND HALOGENOMETHYLTIN HALIDES

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(Received August 10th, 1967)

INTRODUCTION

The proton magnetic resonance spectra of methyl- and ethyl-tin halides were reported earlier[1-3] and empirical relations were derived concerning the chemical shift and coupling constant data with respect to molecular parameters such as the inductive effect of substituents, the magnetic anisotropy of bonds and spin-orbital interactions.

More experimental information however is needed on this subject. This paper reports on the PMR spectra of halogenomethyltin halides and compares the data with those for other organotin compounds.

EXPERIMENTAL

Synthesis of halogenomethyltin halides

The compounds, $(ClCH_2)_nSnCl_{4-n}$ and $(BrCH_2)_nSnBr_{4-n}$ were prepared by treating $SnCl_4$ and $SnBr_4$, respectively, with diazomethane, CH_2N_2, as described by Yakubovich *et al.*[4]. The dry benzene solution of CH_2N_2 required in this reaction was prepared by the destruction of *N*-nitrosomethylurea with KOH as outlined by Arndt[5]. The dark-yellow benzene solution is dried over KOH pellets and, with vigorous stirring and cooling to 2°, is then added to a solution of $SnCl_4$ or $SnBr_4$ in benzene. Excess stannic halide and benzene are removed by fractional distillation at 16 mm Hg pressure, after filtration of the reaction mixture. Fractional distillation of the liquid yields the various compounds, the physical properties of which are given below.

$ClCH_2SnCl_3$ (b.p. 72–73°, 5 mm Hg) viscous colourless liquid, fuming in air and darkening on standing.

$(ClCH_2)_2SnCl_2$ (m.p. 89.5–90°) colourless needles from benzene.

$(ClCH_2)_3SnCl$ (b.p. 138–140°, 5 mm Hg) viscous liquid.

$(BrCH_2)_2SnBr_2$ (m.p. 87°, recrystallized from benzene).

$(BrCH_2)_3SnBr$ (b.p. 165°, 5 mm Hg).

Spectra

The spectra were recorded with a V-4300-B Varian dual purpose spectrometer, at a fixed frequency of 56.44 Mc. The coupling constants were measured on the spectra of concentrated solutions in benzene. The chemical shift data were obtained from spectra of dilute solutions in either $CHCl_3$ or CCl_4. The τ-values listed in Table 1 have been corrected for susceptibility difference to standard conditions in $CHCl_3$ by the

TABLE 1

PMR SPECTRAL PARAMETERS FOR HALOGENOMETHYLTIN HALIDES

Compound	τ	$J(^{117,119}Sn\text{-}C\text{-}H)$	$J(^{13}C\text{-}H)$
$(ClCH_2)_3SnCl$	6.31	18.3	155
$(ClCH_2)_2SnCl_2$	6.17	18.7	158
$ClCH_2SnCl_3$	5.92	19.4	162
$(BrCH_2)_3SnBr$	6.67	16.4	154
$(BrCH_2)_2SnBr_2$	6.47	16.4	157.5

formula proposed by Lussan[6]. All the compounds studied yield sharp signals but the tin satellites for ^{117}Sn and ^{119}Sn coupling could not be observed separately. The results are given in Table 1.

RESULTS AND DISCUSSION

Chemical shift data of compounds $(CH_2X)_nSnX_{4-n}$ $(X = Cl, Br)$

From the chemical shift data of methyl-[1] ethyl-[2,3] and benzyl-tin[7] halides as a function of the nature of the halide, it has already been concluded that both the electronic inductive effect and the neighbour anisotropy effect determine the shielding of the α-protons in an organotin molecule. In the halogenomethyltin halides, besides the magnetic anisotropy of the tin–halogen bond (which was responsible for the deshielding in the compounds previously studied) there is also the carbon–halogen bond, which is able to exert a paramagnetic effect on the methylenic protons. This effect should be stronger for a C–Br than for a C–Cl bond and actually enhances the effect of the Sn–Br, or Sn–Cl bond. The τ-values for $(CH_2Br)_nSnBr_{4-n}$ compounds, however, are higher than those for the $(CH_2Cl)_nSnCl_{4-n}$ molecules, which would be expected if only the electronic inductive effect were important. It is therefore concluded that the magnetic anisotropy of the carbon–halogen bonds is of little or no importance. The comparison of two molecular species containing, respectively, a Sn–Cl or a Sn–Br bond does not invalidate this argument as the effect of halogen substitution directly on tin is known sufficiently from previous studies[1,2,3,7].

On the other hand, the τ-values of Table 1 show only very slight dependence on the number of halogen substituents on tin. This can be ascribed without doubt to the very small electronegativity difference between the CH_2X-group and the X-atom so that the electronic inductive effect over two bonds changes only slightly as *n* increases. Furthermore, it can be seen that the decrease of τ-values with progressive halogenation is more important for bromides than for chlorides. This is probably due to the greater importance of the Sn–X neighbour anisotropy effect in bromides than in chlorides, which itself is independent of *n*, but becomes relatively more important as the increase of the electronic inductive effect diminishes.

Comparison of chemical shifts for methyl-, ethyl- and halogeno-methyltin halides

All these compounds can be considered as methyltin compounds where a proton has been replaced by CH_3, Cl or Br. A comparison of the τ-values (see refs. 1 and 2) yields the sequence

$$\tau(CH_3)_nSnX_{4-n} > \tau_\alpha(C_2H_5)_nSnX_{4-n} > \tau(BrCH_2)_nSnBr_{4-n} > \tau(ClCH_2)_nSnCl_{4-n}$$

It has already been seen that these τ-values result from the joint deshielding action of both the electronic inductive effect and the neighbour anisotropy effect and that the contributions of the latter originating from the C–X bond in the halogenomethyltin compounds are negligibly small. In all these compounds, the anisotropy effect of the Sn–X bond for the same substituent, X, bonded to tin will be approximately the same. The electronic inductive effect exerted by the group or atom bonded to CH_2 is, however, proportional to its electronegativity. The chemical shift sequence given above reflects, therefore, the electronegativities of the substituents bonded to CH_2:

$$E_H < E_{CH_3} < E_{Br} < E_{Cl}$$

This sequence parallels values obtained by other methods and so confirms our views on the origin of the chemical shifts.

Coupling constants of $(XCH_2)_nSnX_{4-n}$ *compounds* ($X = Cl, Br$)

The tin-proton coupling constants over two bonds, listed in Table 1, show only very slight changes with progressive halogen substitution on tin because the electronegativity difference between the halogenomethyl group and the corresponding halogen is rather small, so that changes in the electronic structure around tin are relatively unimportant. The values of the carbon-13 proton couplings can be calculated using Malinovski's[1,9] additivity rule and thus deserve no special comment.

Comparison of tin–proton coupling constants for methyl-, ethyl- and halogeno-methyltin halides

PMR spectral parameters for some important species of this group of compounds are listed in Table 2, and other data are to be found in the reports already cited[1–3].

TABLE 2

COMPARATIVE TABLE OF PMR SPECTRAL DATA FOR TRIORGANOTIN HALIDES

	$J(^{117/119}Sn-H_\alpha)$	τ_α
$(CH_3)_3SnCl$	56.0	9.34
$(CH_3CH_2)_3SnCl$	38.7	8.64
$(ClCH_2)_3SnCl$	18.3	6.31
$(CH_3)_3SnBr$	56.0	9.20
$(CH_3CH_2)_3SnBr$	37.5	8.61
$(BrCH_2)_3SnBr$	16.4	6.67

First, for molecules with the same halogen bonded to tin

$$J(\text{Sn–H})[(CH_3)_nSnX_{4-n}] > J(\text{Sn–H}_\alpha)[(C_2H_5)_nSnX_{4-n}] > J(\text{Sn–H})[(XCH_2)_nSnX_{4-n}]$$

According to Juan and Gutowsky[10], an electronegative substituent bonded to carbon might enhance the electronegativity of the carbon in an halogenomethyl group by 0.1–0.2 units. As a result, the electronegativity difference, $E_{Sn} - E_C$, increases and so does the polarity of the tin–carbon bond. This increase will, however, be rather small, and by no means explains the drastic decrease of J on substitution of H in CH_4 by CH_3, Cl or Br. On page 488 we have already drawn attention to a parallel sequence for τ_x-values and concluded that these values were mainly determined by the inductive effect, and hence reflected the changes of electron density around the protons. It seems, therefore, that the decrease of the J(Sn–C–H), values as stated above, is also caused principally by the decrease of electron density.

The empirical relation for $J(\text{Sn–H}_x)$ values suggested for the ethyltin compounds[3]

$$J(\text{Sn–H}_x) \simeq \Phi^2_{\text{Sn}}(0) \cdot \frac{1}{\lambda(\text{Sn–C})}$$

should thus be completed for $(\text{XCH}_2)_n\text{SnX}_{4-n}$ compounds to give

$$J(\text{Sn–H}_x) \simeq \Phi^2_{\text{Sn}}(0) \cdot \Phi^2_{\text{H}}(0) \cdot \frac{1}{\lambda(\text{Sn–C})}$$

where $\Phi^2_{\text{H}}(0)$ is the electron density around the coupling proton. This empirical relation means also that $J(\text{Sn–H}_x)$ coupling constants are mainly determined by the Fermi contact interaction term.

With these conclusions in mind we now can reconsider the J(Sn–C–H) values for the benzyltin compounds[7]. Isovalent rehybridization around tin has already been postulated. There is however another possibility. If the π-electron system of the phenyl group is slightly delocalized towards the tin nucleus, then the electron density around the protons of the methylene group should increase and therefore $J(\text{Sn–H}_x)(\text{CH}_3)$ values will be smaller than $J(\text{Sn–H}_x)$(benzyl) values, although the phenyl substituent is more electronegative than hydrogen.

SUMMARY

The PMR spectra of $(\text{CH}_2\text{X})_n\text{SnX}_{4-n}$ (X = Cl, Br) compounds are reported. Examination of τ-values and tin–proton coupling constants as a function of n and of the nature of X, and comparisons with other similar data of triorganotin halides, show that the tin–proton coupling constants are a function of the electron density around both the tin and the hydrogen nucleus and of the Sn–C bond polarity. Fermi contact interaction is therefore the dominating mechanism.

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