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Abstract

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STUDY OF ORGANOTIN DERIVATIVES OF BARENES BY MÖSSBAUER SPECTROSCOPY

In recent years much attention has been devoted to the study of the properties of a new class of organoboron compounds—barenes (carboranes-10) (1-5). The unusual valence state of carbon in barenes, and the strong electron-acceptor properties of the barene system in combination with its exceptional stability, make especially interesting the investigation of organometallic derivatives of barenes containing a direct σ bond between the metal and barene carbon. Such compounds, formed with the participation of heavy metals (tin, mercury, etc.), differ substantially in a number of chemical properties from ordinary organometallic compounds (6).

Since by now considerable experience has been accumulated in the use of Mössbauer spectroscopy for the study of the chemical structure and reactivity of organotin compounds (7), it seemed of interest to study the resonance absorption spectra of γ quanta for a series of barenyl derivatives of tin and thereby to compare the influence of the barenyl group on the electronic environment of the tin nucleus with the influence of a large number of ordinary organic substituents.

For this purpose we studied the Mössbauer spectra of various barene-organic compounds of tetravalent tin. The resonance absorption spectra were measured on instruments with variable and constant velocity, using scintillation and resonance counters as radiation detectors (8). All the samples studied were cooled to a temperature of 77° K; the source of γ quanta, SnO_2, was at room temperature. The results of the measurements are presented in Table 1, which gives the values of the quadrupole-splitting constants Δ and the magnitudes of the isomer shifts δ. As a rule, quadrupole splitting in compounds of tetravalent tin appears only when the substituents differ appreciably from one another in their electronegativity and when at least one of the bonds formed by tin differs noticeably from the other three in the degree of ionicity (7, 9). With a few exceptions (10, 11), apparently due to the formation of a fifth—coordination—bond of tin with oxygen or to an inductive effect, the spectra of compounds in which the tin atom is bonded to four carbon atoms consist of a singlet line. Meanwhile, as is evident from the data given in Table 1, all barenyl compounds with four Sn—C bonds give quadrupole splitting of the Mössbauer lines in the range $\Delta = 0.7$-1.7 mm/sec. Hence it follows with certainty that the barenyl system, unlike most ordinary organic substituents, exerts a strong electron-acceptor action with respect to the tin atom. It is characteristic that the quadrupole splitting in the spectra of tri-(phenylbarenide)-tin chloride (No. 5) and di-(phenylbarenyl)-tin dichloride (No. 6) is substantially smaller than in the spectra of triphenyltin chloride ($\Delta = 2.4$ mm/sec). This means that in the two named barenyl derivatives of tin the ionicities of the Sn—Cl and Sn-barenyl bonds are close, and therefore the symmetry of the electric ⋯

fields at the |Sn| nucleus are considerably higher than in the analogous phenyl derivatives, owing to the strong electron-acceptor influence of the barenyl substituents.

From comparison of the spectra of phenylbarenyltriphenyltin (No. 1) and pentafluorophenyltriphenyltin (12), it follows that the phenylbarenyl group exerts

Table 1

Compound	Δ, mm/sec	δ, mm/sec
1. $C_6H_5C—C—Sn(C_6H_5)_3$ (barenyl fragment $B_{10}H_{10}$)	1.20 ± 0.06	1.30 ± 0.07
2. $(C_3H_7)_3Sn—C—CH$ (barenyl fragment $B_{10}H_{10}$)	1.65 ± 0.08	1.45 ± 0.07
3. $(C_3H_7)_3Sn—C—C—Sn(C_3H_7)_3$ (barenyl fragment $B_{10}H_{10}$)	1.50 ± 0.05	1.45 ± 0.05
4. $(C_4H_9)_2$Sn-bis(barenyl fragment $B_{10}H_{10}$)-$Sn(C_4H_9)_2$	1.60 ± 0.04	1.20 ± 0.03
5. $(C_6H_5C—C)_3SnCl$ (barenyl fragment $B_{10}H_{10}$)	0.40 ± 0.04	1.20 ± 0.05
6. $(C_6H_5C—C)_2SnCl_2$ (barenyl fragment $B_{10}H_{10}$)	0.90 ± 0.05	1.25 ± 0.06

Compound	Δ, mm/sec	δ, mm/sec
7. $(C_6H_5C{-}C)_2SnBr_2$ (barenyl fragment $B_{10}H_{10}$)	0.80 ± 0.04	0.90 ± 0.05
8. $HC{-}C{-}Sn(C_6H_5)_3$ (barenyl fragment $B_{10}H_{10}$)	0.95 ± 0.05	1.05 ± 0.05
9. $(C_6H_5C{-}C)_2Sn(C_4H_9)_2$ (barenyl fragment $B_{10}H_{10}$)	1.70 ± 0.08	1.20 ± 0.06
10. $(C_6H_5)_3Sn{-}C{-}C{-}Sn(C_6H_5)_3$ (barenyl fragment $B_{10}H_{10}$)	0.70 ± 0.04	0.95 ± 0.05
11. $C_6H_5C{-}C{-}Sn(C_3H_7)_3$ (barenyl fragment $B_{10}H_{10}$)	1.50 ± 0.07	1.35 ± 0.05

on the electronic environment of the tin nucleus the same effect as the pentafluorophenyl group. This conclusion may be compared with the NMR frequencies of Cl^{35} in pentafluorochlorobenzene (39.42 MHz), trifluorochloromethane (38.089 MHz) (13), and trinitrochloromethane (42.948 MHz) (14), which makes it possible to estimate approximately the electron-acceptor ability of the phenylbarenyl group. Specifically, the phenylbarenyl group as an acceptor is stronger than the trifluoromethyl group, approximately equal to the pentafluorophenyl group, and markedly inferior to the trinitromethyl group.

It is interesting to note the substantial difference in the spectra of phenylbarenyltriphenyltin (No. 1) and barenyltriphenyltin (No. 8). The very fact that a substituent located in the β-position to the tin atom affects the Mössbauer spectroscopy of organotin compounds is observed for the first time*. However, the increase in the chemical (isomer) shift and quadrupole splitting when the second Hc atom is replaced by phenyl cannot be explained from the standpoint of the usual concepts of inductive influence. It is difficult to assume that the increase in the acceptor ability of the phenylbarenyl residue in comparison with the barenyl residue occurs because of the electron-acceptor influence of the phenyl group, which cannot be so significant. Possibly, the reason for this difference lies in some specific interaction of the electronic systems of the barene and phenyl nuclei.

In those cases where two tin atoms are bonded to the barene nucleus (No. 10),

Fig. 1

Figure 1: Fig. 1

there is a regular decrease in its influence on each of the Sn atoms (Δ falls to 0.7 mm/sec); in the ring system formed by two Sn atoms and two barenylene groups (No. 4), this influence again becomes significant. Until now Mössbauer spectra of organotin compounds formed by divalent tin have not been studied. Tin dialkyls R_2Sn, which formally contain divalent tin, are in reality polymers $[(R_2Sn)_x]$ and contain tetravalent tin (16). It is characteristic that freshly prepared diphenyltin, unlike its aliphatic analogues, is monomeric (17), which apparently is connected with the delocalization of two S-electrons of divalent tin over the phenyl rings. Taking into account the strong electron-acceptor character of phenylbarenyl groups, one could expect that di-(phenylbarenyl)-tin would prove no less stable.

Fig. 1

The Mössbauer spectra of compounds of divalent and tetravalent tin differ sharply (7). The chemical shift of the lines of organic and inorganic derivatives of tetravalent tin relative to α-Sn (gray tin with wholly covalent four hybrid sp^3 bonds) is negative, whereas derivatives of divalent tin possess positive chemical shifts relative to α-Sn, i.e. $\delta \geq 2.1$ mm/sec relative to SnO_2. It was natural to expect that an analogous difference would also appear in organotin compounds. Indeed, from the magnitude of the chemical shift, di-(phenylbarenyl)-tin, obtained by the action of phenylbarenyllithium on anhydrous tin dichloride in ether, can be reliably assigned to derivatives of divalent tin (Fig. 1a).

* If one disregards tin trialkylacetonates, where, however, the appearance of quadrupole splitting is due not simply to the introduction of oxygen into the β-position to the tin atom, but to the formation of a coordination bond of this oxygen with tin (15).

When an ether solution of di-(phenylbarenyl)tin was allowed to stand, a precipitate gradually began to form, and the spectrum of the suspension took the form shown in Fig. 1*b*. The shape of the spectrum differs sharply from the Lorentzian one. This change in the spectrum is evidently due to partial oxidation of the divalent compound. To verify this assumption, 7 days after the start of the experiment the spectra of the solution and of the precipitate were recorded separately (Fig. 1*b*, *c*). It turned out that the precipitate contains tetravalent tin ($\delta = 1.35$ mm/sec, $\Delta = 1.30$ mm/sec), whereas divalent tin is still present in the solution ($\delta = 2.95$ mm/sec, $\Delta = 1.90$ mm/sec). The spectrum of the solution separated from the precipitate remained unchanged for two weeks.

Thus, di-(phenylbarenyl)tin did indeed prove to be a very stable compound, the oxidation of which proceeds relatively slowly. Data on the chemical properties of di-(phenylbarenyl)tin and on the kinetics of its oxidation will be published separately.

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