ORGANOTIN CARBOXYLATES
III*. MÖSSBAUER STUDY OF TETRA- AND PENTACOORDINATION IN BRANCHED-CHAIN TRIPHENYLTIN CARBOXYLATES

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SUMMARY

Branched-chain triphenyltin carboxylates can exist in the solid state either as monomeric species similar in structure to organic esters or as polymeric species with pentacoordinate tin atoms and bridging carboxyl groups. The length and position of the branch are important factors in determining the structural type. A $C=C$ bond to the α-carbon atom does not preclude polymerization through $O-Sn-O$ linkages provided the carboxylate group is not bulky. On the other hand, if the group is bulky, the compound is monomeric and conjugation between the $C=C$ and the $C=O$ bonds occurs. No interaction between such vinyl groups and the tin atom is observed.

INTRODUCTION

In general, compounds having the formula $R_3SnOCOR'$ are linear polymers in the solid state[1,2]. The tin atom is pentacoordinate with bridging carboxyl groups which have C_{2v} symmetry. In dilute solutions in non-polar solvents they are monomeric with the tin atom being tetracoordinate. If the R group is bulky, *e.g.* R = iso-propyl[1] or cyclohexyl[3], the compounds are also monomeric. Conclusions concerning the structures have been based mainly upon infrared data for the solids and solutions in the carbonyl/carboxyl region (1700–1300 cm^{-1}) of the spectrum.

Recently, Mössbauer spectroscopy has proved very useful for studying coordination and bonding in organotin compounds. The most informative parameters for this purpose are the isomer shift, δ, and the quadrupole splitting, Δ. The former is primarily sensitive to changes in s-electron density at the tin nucleus and the latter to the stereochemistry about the tin atom. Herber *et al.*[4] have determined Mössbauer parameters for Me$_3$SnOCOMe, ($\delta = 1.34$, $\Delta = 3.47$) and Neo$_3$SnOCOMe** ($\delta = 1.35$, $\Delta = 2.45$). The large difference in quadrupole splittings is due to the fact that the tin atom is in a trigonal bipyramidal environment in the trimethyl compound while in the trineophyl compound the tin atom is tetracoordinate because of the bulky neophyl group.

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* For Part II see ref. 11.
** Neo = neophyl = PhCMe$_2$CH$_2$.

$$
\begin{array}{c}
\text{Me} \\
| \\
\text{Me}-\text{C}-\text{CH}_2- \\
| \\
\text{Ph}
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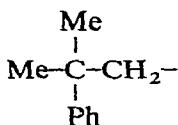
A change from sp^3 to sp^3d hybridization of the Sn bonding orbitals is not expected to effect appreciably the s-electron density at the Sn nucleus.

We have recently reported Mössbauer and infrared data for a number of triphenyltin carboxylates having chain lengths varying from one to eighteen carbon atoms[5]. It had been suggested[1] that lengthening the carboxylate chain might prevent polymerization, however this was not observed[5]. The carbonyl/carboxyl stretching frequencies indicated that the OCO groups were bridging and the large quadrupole splittings ($\Delta \sim 3.4$ mm·sec^{-1}) indicated the presence of pentacoordinate tin atoms.

However, $Ph_3SnOCOCMe_3$, $Ph_3SnOCOCMe=CH_2$ and $Ph_3SnOCOCH$-EtBu were found to be tetracoordinate monomers, and it appeared that branching at the α-carbon atom sterically hindered polymer formation. It was clearly of interest to investigate a number of methyl-branched triphenyltin carboxylates to determine if branching at other positions along the carboxylate chain would also prevent polymerization.

EXPERIMENTAL

All the methyl-branched triphenyltin carboxylates were prepared by mixing triphenyltin chloride with a slight excess of the potassium salt of the appropriate acid in methanol. Evaporation of the solvent left a white product which was purified by washing with water and/or recrystallizing from carbon tetrachloride. Triphenyltin acrylate was prepared by mixing stoichiometric quantities of triphenyltin hydroxide and acrylic acid in carbon tetrachloride. After the solvent was evaporated the product was washed with water. Microanalyses were performed by P. Borda of this Department, and analytical results and melting points are given in Table 1.

TABLE 1

ANALYTICAL DATA AND MELTING POINTS OF TRIPHENYLTIN CARBOXYLATES, $Ph_3SnOCOR$

No.	R	C (%)		H (%)		M.p. (°C)
		Calcd.	Found	Calcd.	Found	
(I)	$(CH_2)_3CHMe_2$	62.63	62.32	5.85	5.76	93–96
(II)	$(CH_2)_2CHMe_2$	62.06	62.08	5.60	5.89	102–105
(III)	$CH_2CHMeEt$	62.06	62.33	5.60	5.76	110–112
(IV)	CH_2CHMe_2	61.19	61.27	5.32	5.52	103–105
(V)	$CHMePr$	62.06	61.01	5.60	6.10	110–112
(VI)	$CHMe_2$	60.41	60.35	5.03	5.28	123–125
(VII)	$CH=CH_2$	59.86	59.72	4.28	4.36	150–151
(VIII)	$CMe=CH_2$[a]					88–89
(IX)	$CHEtBu$[a]					68–69
(X)	CMe_3	61.19	60.94	5.32	5.27	103–105

[a] M.&T. Chemicals Inc.

The Mössbauer spectra were recorded with the compounds at $80° \pm 1°K$, and isomer shifts are reported relative to SnO_2 at this temperature. A narrow-line Ba-$^{119m}SnO_3$ was employed. Infrared spectra of the solids were recorded on a Perkin–Elmer 457 instrument with the solids dispersed in nujol between KBr plates. Solution spectra were run in carbon tetrachloride, using matched NaCl cells.

DISCUSSION

Mössbauer and infrared results are given in Table 2. The quadrupole splittings for compounds (I)–(VII) are essentially constant and lie in the range 3.37 ± 0.05 mm · sec^{-1}. Since the straight-chain triphenyltin carboxylates give nearly identical splittings $(3.39 \pm 0.07$ mm · sec$^{-1})^5$, it is clear that compounds (I)–(VII) are polymeric, with penta-

TABLE 2

MÖSSBAUER PARAMETERS AND OCO STRETCHING FREQUENCIES FOR BRANCHED-CHAIN $Ph_3SnOCOR$ COMPOUNDS

No.	R	$\delta^{a,b}$ (mm·sec^{-1})	Δ^a (mm·sec^{-1})	OCO frequencies (cm^{-1})			
				Mull		Solution	
(I)	$(CH_2)_3CHMe_2$	1.25	3.36	1529	1416	1631	1387
(II)	$(CH_2)_2CHMe_2$	1.26	3.38	1533	1404	1629	1388
(III)	$CH_2CHMeEt$	1.29	3.39	1524	1407	1628	1382
(IV)	CH_2CHMe_2	1.27	3.39	1523	1408	1643	1380
(V)	$CHMePr$	1.26	3.34	1536	1416	1638	1379
(VI)	$CHMe_2$	1.28	3.32	1533	1422	1632	1391
(VII)	$CH=CH_2$	1.28	3.41	1528	1423	1619	1335
(VIII)	$CMe=CH_2$	1.21	2.26	1595	1345	1610	1360
		1.15^c	2.10^c				
(IX)	$CHEtBu$	1.21	2.26	1630	1336	1625	1340
(X)	CMe_3	1.21	2.40	1622	1330	1624	1332

^{a} ± 0.03 mm·sec^{-1}. ^{b} relative to SnO_2 at 80° K. ^{c} Ref. 10.

coordinate tin atoms, while compounds (VIII)–(X) are tetracoordinate monomers.
The infrared data support this interpretation. The carbonyl/carboxyl stretching frequencies for the solids indicate that the carboxyl groups are symmetrical in compounds (I)–(VII). In dilute solution these two bands move out towards the stretching frequencies for organic esters. This is clearly evidence for polymeric species with bridging OCO groups in the solid state, becoming tetracoordinate monomers in solution[1]. On the other hand, the carbonyl/carboxyl bands for compounds (VIII)–(X) are closely similar in the solid state and in solution, indicating monomeric species in both cases.
The melting points for the pentacoordinate compounds range from 93–151° and for the tetracoordinate compounds from 68–106°. There is a 30° decrease in melting point from triphenyltin isobutyrate to triphenyltin 5-methylhexanoate. Since both compounds have polymeric structures it might be expected that the higher molecular weight compound would have the higher melting point. Janssen et al.[1] suggest that a longer alkyl chain may destablize the polymeric structure by steric

interaction and this would explain the lower melting point for triphenyltin 5-methyl-hexanoate. This trend is also evident for the straight-chain carboxylates[5] where the melting point for triphenyltin formate (201–202°) is very much larger than that for triphenyltin stearate (71–73°) and even suggests an optimal stability for triphenyltin carboxylates. The large melting point for triphenyltin acrylate can therefore be explained by a combination of reduced steric interaction and stronger bonding due to the double bond. The tetracoordinate compounds also follow the same melting point trends with the exception that in general, the melting points are lower because there is little or no bonding interaction between monomer units. This explains the surprising decrease of 60° in melting point of triphenyltin methacrylate from that of triphenyltin acrylate, a difference which is certainly larger than one might expect from the simple replacement of a methyl group by a hydrogen.

The isomer shifts for compounds (I)–(VII) are constant within the limits of experimental error and have a mean value of 1.27 ± 0.02 mm · sec^{-1}. This same isomer shift value was also observed for the straight-chain triphenyltin carboxylates previously reported[5]. These results are not unexpected since a change in the length of the carboxylate chain or in the position of the methyl branch should not alter the electron density at the tin nucleus unless there were an accompanying change in the coordination of the tin atom. For example, the tetracoordinate compounds (VIII)–(X) have isomer shifts of 1.21 mm sec^{-1}.

The fact that the isomer shift for the pentacoordinate compounds is slightly larger than that for the tetracoordinate compounds is interesting, since on the basis of the number of electronegative groups bonded to tin one might have expected a difference in the opposite direction. These results can be explained as follows. In the tetracoordinate compounds, let the z-axis lie along the O–Sn bond, and in the polymeric compounds along the O–Sn–O direction. For those compounds with sp^3 hybridization, the p_z-orbital will be primarily involved in the Sn–O bond, while the p_x- and p_y-orbitals will be mainly used for bonding to the phenyl groups. (It is this imbalance in the p-electron distribution which is presumably responsible for the quadrupole splitting[9].) In the pentacoordinate compounds, the p_x and p_y orbitals will again be used principally in the tin–phenyl bonds, and the $(p_z + d_{z^2})$ orbitals in the two Sn–O bonds. There is apparently an increase in p-electron withdrawal along the z-axis, and a resultant increase in s-electron density at the tin nucleus. At the same time, the increased asymmetry of the p-electron distribution leads to a marked increase in the splitting.

It was somewhat surprising that all the branched-chain compounds (I)–(VI) were polymeric. Apparently, a bulkier branching group than methyl is required before there is steric interaction with the phenyl groups. For example, triphenyltin 2-ethyl-hexanoate is tetracoordinate. If the ethyl branch were far enough along the carboxylate chain it is quite likely that steric interaction could be avoided.

An interesting and important experimental result is that triphenyltin acrylate is polymeric while triphenyltin methacrylate is monomeric. The existence of different structures for these compounds is evident from their Mössbauer spectra shown in Fig. 1. These two compounds can be polymerized to form vinyl polymers[6] which have different chemical and thermal properties. The compounds that we are discussing are "monomers" in the sense that there are no carbon to carbon connecting links which are formed via vinyl groups[7]. Considering the size of the groups bonded to the α-car-
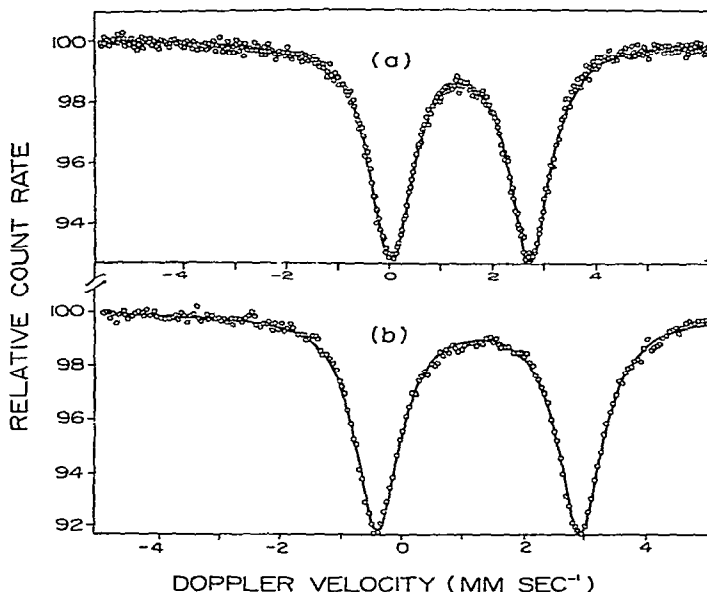
Fig. 1. Mössbauer spectra of (a) $Ph_3SnOCOCMe_3$ in which the Sn atom is tetracoordinate and, (b) $Ph_3Sn-OCOCHMe_2$ in which the Sn atom is pentacoordinate. Absorbers were at 80° K. Isomer shifts are reported relative to SnO_2 at 80° K.

bon atom one might have expected triphenyltin methacrylate, like the isobutyrate compound to be polymeric since the methylene group is about as bulky as a methyl group (Van der Waals radii for both ∼2.0 Å). However in the methacrylate the α-carbon forms sp^2-hybridized orbitals for bonding and therefore the three atoms bonded to it will be closer to a trigonal planar arrangement as opposed to the isobutyrate in which the α-carbon atom is in a tetrahedral environment. The methacrylate group is now restricted in its orientation capabilities and consequently steric interaction prevents polymer formation. In triphenyltin acrylate, all the atoms in the COO and $CH=CH_2$ fragments will again be nearly coplanar because of the sp^2-hybridized carbon atom. However, the replacement of the methyl group in methacrylate by a hydrogen atom makes the carboxylate moiety less bulky and consequently triphenyltin acrylate is polymeric. This difference in steric hindrance due to H and CH_3 is quite dramatic.

The carbonyl/carboxyl stretching frequencies for solid triphenyltin methacrylate are slightly different from those of compounds (XI) and (X), which are also tetra-coordinate monomers. This is probably due to conjugation between the C=C and the C=O bonds[8]. Despite these differences in stretching frequencies for the methacrylate, its Mössbauer parameters are the same as those of the 2-ethylhexanoate compound. Also, the acrylate has about the same parameters as the other polymers. This indicates that any π-interaction between the C=C bond and the COO group does not affect either the electron density or the electron distribution about the tin nucleus.

The fact that triphenyltin isobutyrate is pentacoordinate while the methacrylate and trimethylacetate compounds are tetracoordinate suggests that isobutyrate is almost bulky enough to prevent polymerization. More subtle changes in the α-

carbon substituents, for example CX_3 (X=F, Cl, Br, I) might be helpful in finding a "critical size".

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