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Preparation of Polymeric Organotin Carboxylates and Organostannoxanes. Mössbauer and Infrared Characterization

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New polymeric organotin carboxylates and organostannoxanes have been prepared by reacting $R_2(CH_2{=}CH{-}CH_2)_2Sn$ *compounds* ($R = CH_3$, $CH_2{=}CH$, C_6H_5) *with lactic, glycollic and 2-hydroxybutyric acid in water–acetone medium The polymeric nature of these highly insoluble compounds has been inferred from infrared and Mossbauer data*

Introduction

Previous works showed that the reaction between $R_2(CH_2{=}CH{-}CH_2)_2Sn$ compounds and carboxylic acids in equimolar amount and in water–acetone or moist methanol medium leads to distannoxanes type compounds [1–4] The initial protolytic step in the reaction sequence [5],

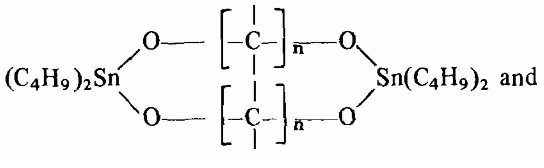
$$R_2(CH_2{=}CH{-}CH_2)_2Sn + R'COOH \rightarrow R_2(CH_2{=}CH{-}CH_2)SnOOCR' + CH_2{=}CH{-}CH_3 \quad (1)$$

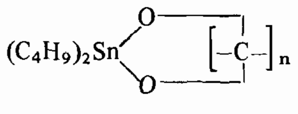
has been proposed to be followed by a solvolytic cleavage of the second allylic group [1]

$$R_2(CH_2{=}CH{-}CH_2)SnOCOR' + H_2O \rightarrow R_2Sn(OH)OCOR' + CH_2{=}CH{-}CH_3 \quad (2)$$

$$2R_2Sn(OH)OCOR' \rightarrow [R_2SnOCOR']_2O + H_2O \quad (3)$$

In the present work we have studied the products formed when hydroxy carboxylic acids such as lactic, glycollic and 2-hydroxybutyric were employed Cyclic organotin alkoxides





have been prepared by reacting dibutyltin oxide [6] or methoxide [7] with diols These compounds are remarkable for their resistance to hydrolysis in contrast to the hydrolytic lability generally observed in organotin alkoxides and phenoxides [6]

Our aim has been to find out whether the OH group in α or β position might compete for the cleavage of the second allylic group (reaction 2) and/or in the water elimination (reaction 3) leading eventually to different compounds

Experimental

Dimethyl- (b p 114 °C at 20 torr) [8], divinyl- [3] and diphenyldiallyltin [9] were prepared from the corresponding dichloride and allyl magnesium bromide in anhydrous diethyl ether as previously described [10]

Analytical grade reagents were used throughout IR spectra of Nujol and hexachlorobutadiene mulls or KBr pellets were recorded on a Perkin–Elmer Model 457 spectrophotometer

The Mossbauer spectra were obtained with a conventional electromagnetic instrument working at constant acceleration The source used, a 4 mCi $Ca^{119m}SnO_3$ (The Radiochemical Centre, Amersham, England), was at room temperature, the absorbers at 80 °K Velocity calibration was against four inner lines of enriched iron foil absorber All centre shift values are relative to SnO_2 absorber at room temperature

To give truly random samples, the absorbers were powders mixed with a finely ground inert matrix of perspex and compressed between mylar foils All spectra were run using a Hofman dewar (HLDT-1), conveniently adapted and equipped with a selffeeding liquid nitrogen device. The temperature was measured with a constantan–iron thermocouple.

The contents of the multichannel analyzer were taken by a teleprinter equipped with tape punch and X–Y recorder. All experimental spectra were fitted without constraints to Lorentzian line shapes using a program [11] adapted by us for the CDC 7600 computer.

Reaction of $R_2(CH_2{=}CH{-}CH_2)_2Sn$ with Lactic Acid

Dimethyldiallyltin (1.16 g, 5 mmol) was mixed with the equimolar amount of lactic acid in 30 ml of acetone–water mixture (50/50, v/v) and kept under magnetic stirring at room temperature. A white suspended solid began to form after a few hours giving a separating solid mass after three days. This was removed after six days, washed with the same solvent, then with chloroform, and dried, yielding 1.1 g of pure product (I). *Anal.* Found: C, 21.80; H, 4.22; Sn, 58.81; $C_7H_{16}O_4Sn_2$ requires: C, 20.92; H, 4.01; Sn, 59.12%.

When the dimethyldiallyltin to lactic acid molar ratio was 2/1, 1.1 g of the same product was still recovered, while with an excess of acid (ratio 1/10) a different product with elemental analysis and IR spectrum not consistent with the above compound was obtained (II). *Anal.* Found: C, 25.32; H, 4.43; Sn, 49.77; $C_5H_{10}O_3Sn$ requires: C, 25.35; H, 4.25; Sn, 50.11 %.

In the same way divinyldiallyltin (1.0 g; 3.9 mmol) and lactic acid were mixed in 1:1 molar ratio. A white solid (0.31 g) was recovered after four days (III). *Anal.* Found: C, 29.42; H, 3.64; Sn, 51.03; $C_{11}H_{16}O_4Sn_2$ requires C, 29.38; H, 3.59; Sn, 52.79 %. Evaporation to dryness under reduced pressure of the filtrate left a product as a solid (0.35 g) (IV). *Anal.* Found: C, 32.73; H, 3.62; Sn, 44.20; $C_7H_{10}O_3Sn$ requires C, 32.23; H, 3.86; Sn, 45.50 %.

Similarly diphenyldiallyltin (0.96 g, 2.42 mmol) and lactic acid in molar ratio 1:1 gave after seven days 0.7 g of a white solid product (V). *Anal.* Found: C, 49.67; H, 3.80; Sn, 37.02; $C_{27}H_{24}O_4Sn_2$ requires C, 49.90; H, 3.72; Sn 36.53 %.

Reaction of Dimethyldiallyltin with 2-Hydroxybutyric Acid

Following the same procedure, from dimethyldiallyltin (1.16 g, 5 mmol) and 2-hydroxybutyric acid, in 1:1 as well as 2:1 molar ratio, 1.1 g of a white solid was recovered as a precipitate after six days (VI). *Anal.* Found: C, 22.94; H, 4.40; Sn 56,40; $C_8H_{18}O_4Sn_2$ requires C, 23.11; H, 4.36; Sn, 57.11 %.

Reaction of Diphenyldiallyltin with Glycollic Acid

From diphenyldiallyltin (0.75 g, 2 mmol) and the equimolar amount of glycollic acid, 0.66 g of a white solid was recovered following the usual method (VII). *Anal.* Found: C, 48.57; H, 3.44; Sn, 33.11; $C_{14}H_{12}O_3Sn$ requires C, 48.47; H, 3.44; Sn, 34.21 %. All the compounds are insoluble in the organic solvents and do not melt below 260 °C but (IV) begins to decompose turning brown at 240 °C. Therefore it was problematic to purify the compounds and to separate the components when mixtures had formed. Thus some products were not undoubtedly identified and are not reported here.

Results and Discussion

Elemental analysis data allow to distinguish between two series of compounds: (II), (IV) and (VII) contain one organic ligand per $R_2Sn{=}$group, while (I), (III), (V) and (VI) contain one organic ligand per $[R_2Sn{-}]_2O$ group. The Sn–O–Sn linkage has been frequently observed in the reaction products between $R_2(CH_2{=}CH{-}CH_2)_2Sn$ and carboxylic acids in 1:1 molar ratio [1–4].

Both lactic and 2-hydroxybutyric acids gave this type of compounds; moreover (I) and (VI) were obtained in the same yield when $(CH_3)_2(CH_2{=}CH{-}CH_2)_2Sn$ to lactic or 2-hydroxybutyric acid molar ratios of 1:1 as well as 2:1 were employed. Compounds of the first series were obtained only with the lactic and glycollic acids.

All the compounds have been characterized by infrared spectra in solid state and Mössbauer spectra.

TABLE I. Relevant Infrared Absorption Frequencies (cm^{-1}) of COO, C–O–Sn, Sn–O–Sn Stretching Vibrations.

No.	Compound	ν_a(COO)	ν_s(COO)	ν_{as}(C–O–Sn)	ν(Sn–O–Sn)
(I)	$C_7H_{16}O_4Sn_2$	1575 vs, br	1415 m	1045 s	630 s
(II)	$C_5H_{10}O_3Sn$	1580 vs, br	1410 m	1050 s	–
(III)	$C_{11}H_{16}O_4Sn_2$	1565 vs, br	1410 m	1045 m	635 s
(IV)	$C_7H_{10}O_3Sn$	1565 s, br	1415 m	1045 m	–
(V)	$C_{27}H_{24}O_4Sn_2$	1580 s 1560 s	1405 m	1045 m	605 s
(VI)	$C_8H_{18}O_4Sn_2$	1550 vs, br	1410 m	1065 m	615 s
(VII)	$C_{14}H_{12}O_3Sn$	1585 s 1560 s	1405 m	1065 m	–

Infrared Spectra

The spectra of the compounds did not exhibit the absorption band assignable to the O–H stretching, which suggests that an alkoxidic bond together with the carboxylic one should have formed. On the other hand the strong absorption near 1050 cm^{-1} (Table I) not observed in analogous organotin carboxylates or diacyloxy diorganotin-distannoxanes, may be attributed to the Sn–O–C stretching vibration as in alkyltinalkoxides [7, 12].

The two COO vibration absorption values fall in the range 1550–1585 and 1405–1415 cm^{-1} respectively and may be reasonably assigned to the asymmetric and symmetric stretching of a bridging coordinating carboxylate group [13]. It is remarkable that only bridging type carboxylate groups seem to be present, as in 1-acyloxy-3-hydroxy distannoxane compounds [2, 3, 11], whereas 1,3-diacyloxy distannoxanes present bridging as well as non-bridging carboxylate groups [2, 3, 14, 15].

Compounds (I), (III), (V), (VI) show the Sn–O–Sn stretching vibration between 605 and 630 cm^{-1}, as generally reported for diorganotin distannoxanes [15, 16]. On the other hand this absorption does not appear in the other compounds.

Mössbauer Spectra

The Mössbauer spectra of all the compounds (Table II) display doublets with an average Γ_{av}, computed full width at half maximum (fwhm), of 1.58 mm/sec at 80 °K and an average area ratio for random polycrystalline sample of 1.44, suggesting the presence of only one kind of tin environment from a Mössbauer point of view. A Mössbauer effect at room temperature is detectable in all cases (Fig. 1, Mössbauer spectra of compound(II) at 80 °K and 295 °K), being quantitatively evident for the compounds (II), (III), (VI) but not enough well defined for an accurate determination for the others. The room temperature Mössbauer effect can be considered as an evidence of polymeric lattices, even though it must be emphasized that an intermolecular association is not ruled out by its absence [17, 18]. Moreover the asymmetry of the intensities of doublet components, with a probable presence of a Goldanskii–Karyagin effect, also supports the polymeric nature of our compounds [19].

TABLE II. Mössbauer Parameters.

No.	Temperature (°K)	CS^{a,b} (mm/sec)	QS^{b} (mm/sec)	Γav^{c} (mm/sec)	$\frac{QS}{CS}$
(I)	80	1.17	2.86	1.58	2.44
(II)	80	1.40	3.78	1.42	2.70
	295	1.33	3.59		
(III)	80	1.13	3.52	1.47	3.11
	295	1.11	3.49		
(IV)	80	1.10	2.73	1.76	2.47
(V)	80	1.12	2.76	1.98	2.46
(VI)	80	1.03	2.73	1.27	2.65
	295	0.93	2.64		
(VII)	80	1.05	2.82	1.49	2.68

^{a}Relative to SnO$_2$ at room temperature. ^{b}±0.02 at 80 °K; at 295 °K < 0.10 for compounds (II), (III), (VI); ⩾0.10 for the others. ^{c}Computed average fwhm.

The quadrupole splitting (QS) to the centre shift (CS) ratio values are all much greater than 2.10 (Table II). This situation strongly indicates a higher than four-coordination at tin, following Herber's

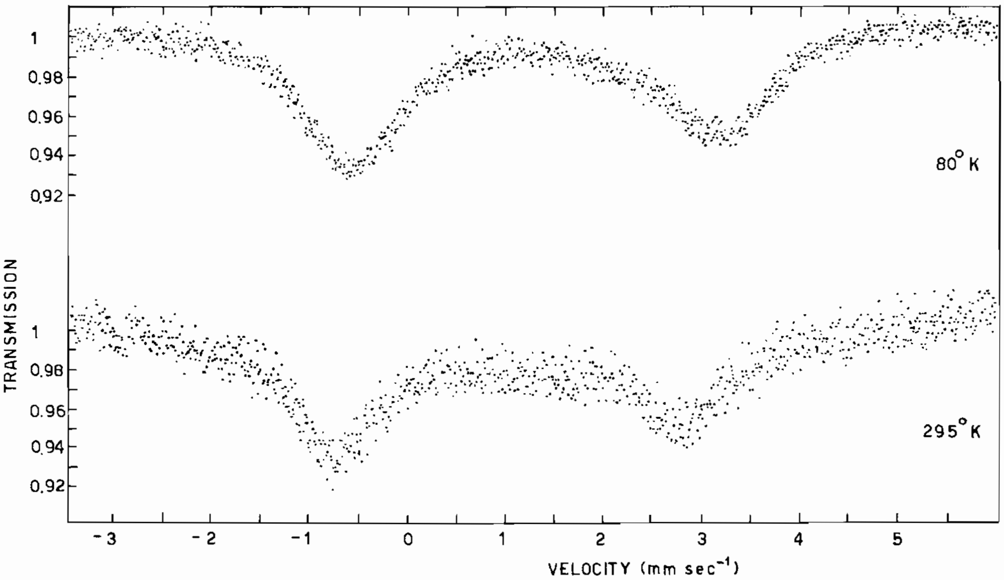


Figure 1. Mössbauer spectra of compound (II), $C_5H_{10}O_3Sn$, at 80° and 295 °K (1 cm = 0.51 mm/sec).

criterion which has become the one generally considered in this respect [20–23]. Besides the QS values are consistent with a trigonal bipyramidal configuration [24].

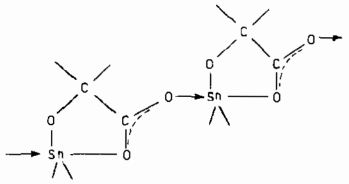
Conclusion

The reactions performed confirm the easy cleavage under mild conditions of both allylic groups in $R_2(CH_2{=}CH{-}CH_2)_2Sn$ compounds.

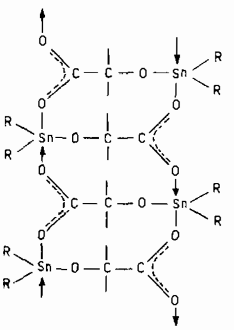
The formation of both tetraorganotin-1,3-diacyloxy-distannoxanes and tetraorganotin-1-acyloxy-3-hydroxy-distannoxanes in the reactions with carboxylic acids has been reported [1–4]. The reaction sequence becomes potentially complicated in the case of the hydroxycarboxylic acids and appears not absolutely clear.

It seems that formally the alcoholic group might at least take part in the cleavage of the second allylic group, but even perhaps in the cleavage of the first one when a substrate to acid ratio of 2:1 was employed, followed in this case by reaction (2) and formation of the distannoxane-like compounds of the second series; but probably the final product is determined, in a complex equilibrium system taking place, by its insolubility in the medium.

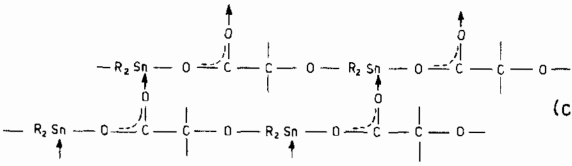
Several formulas may be proposed for the obtained compounds taking into account the spectroscopic results which indicate penta-coordination in a trigonal bipyramidal structure at the tin atom and essentially C_{2v} local symmetry of the COO group. Looking at the compounds of the first series stannaoxacycloalkanes should form if the alcoholic OH group cleaves intramolecularly the allylic group (a), whereas intermolecular cleavage would lead to cyclic dimers as (b) or linear polymeric chains as (c).



(a)

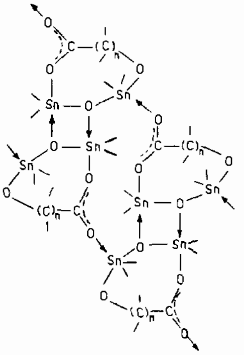


(b)

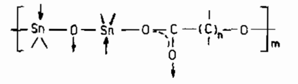


(c)

On the other hand, only an intermolecular reaction of the OH group can be admitted in case of the second series. Cyclic distannoxanes in the dimeric form characteristic of this type of compounds (d) or polymeric distannoxanes (e) may be suggested.



(d)



(e)

Carboxylic bridging groups give a polymeric nature to the cyclic forms (a), (b) and (d) as generally attributed to $R_3SnOOCr'$ carboxylates, which also present Mössbauer effect at room temperature [25]. Moreover trimethyltinformate and acetate are insoluble compounds as obtained from the reaction of the corresponding hydroxide with formic or acetic acid, but they can be converted in a soluble form [26] on heating in a sealed tube with cyclohexane at 90 °C for 24 h. Following the same treatment our compounds do not become soluble. In our opinion the polymeric forms (c) and (e) with carboxylic cross-linking groups better fit both the spectroscopic and physical characteristics of the prepared compounds.

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