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THE PREPARATION AND PROPERTIES OF SOME ALLYLTIN CARBOXYLATES: $R_3SnOOCR'$ ($R'=CH_3$, CH_2Cl), $R_2Sn(OOCR')_2$ ($R'=CH_2Cl$, $CHCl_2$) AND $[R_2Sn(OOCR')]_2O$ ($R'=CH_2Cl$, $CHCl_2$, CCl_3)

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SUMMARY

Triallyl- and diallyltin carboxylates [$(CH_2{=}CH{-}CH_2)_3SnOOCR'$ with $R'=CH_3$ and CH_2Cl, $(CH_2{=}CH{-}CH_2)_2Sn(OOCR')_2$ with $R'=CH_2Cl$ and $CHCl_2$)] and tetraallyl-1,3-diacyloxydistannoxanes $\{[(CH_2{=}CH{-}CH_2)_2SnOOCR']_2O$ with $R'=CH_2Cl, CHCl_2$ and $CCl_3\}$, have been prepared from the reaction of tetraallyltin with carboxylic acids in methanol.

These compounds have been characterized, and some of their properties have been established by IR spectra and molecular weight determinations.

INTRODUCTION

There have been few reports on mono- and di-substituted allyltin derivatives[1] and no allyltin carboxylates have been described.

As a part of our studies of organotin carboxylates[2-4], we have investigated the preparation and the properties of organotin compounds of the type: R_3SnX (I), R_2SnX_2 (II) and $(R_2SnX)_2O$ (III), where R is an allyl group and X denotes a carboxylate group. We have succeeded in preparing some compounds of the type (I), ($X=OOCCH_3$ and $OOCCH_2Cl$), (II) ($X=OOCCH_2Cl$ and $OOCCHCl_2$), and (III) ($X=OOCCH_2Cl$, $OOCCHCl_2$ and $OOCCCl_3$) by treating tetraallyltin with carboxylic acids in methanol at room temperature.

EXPERIMENTAL

Tetraallyltin, purchased from Alfa Inorganics Inc. (USA), was used without further purification. Carboxylic acids and all the solvents employed were from C. Erba (Milan).

IR spectra were recorded on a Perkin–Elmer Model 457 spectrophotometer equipped with KBr or CsI optics, using Nujol mulls, KBr pellets or chloroform and carbon tetrachloride solutions.

Melting points (uncorrected) were taken with a Gallenkamp apparatus (England) using open capillaries. Molecular weights were determined in chloroform or carbon tetrachloride with a Mechrolab Model 302B Vapour Phase Osmometer.

TABLE 1

PREPARATION OF ALLYLTIN COMPOUNDS: EXPERIMENTAL CONDITIONS, AND ANALYTICAL AND PHYSICAL DATA

No.	*Prepared compound (R=allyl)*	*$[R_4Sn]/[R'COOH]$*	*Yield[a] (g)*	*M.p. (°C)*	*Analysis found (calcd.) (%)*			
					C	*H*	*Cl*	*Sn*
I	$R_3SnOOCCH_3$[b]	1/0.2	0.8	78	43.51 (43.90)	5.91 (6.03)		39.40 (39.44)
II	$R_3SnOOCCH_2Cl$[b]	1	1.2	73	39.05 (39.39)	5.01 (5.11)	10.41 (10.57)	35.30 (35.39)
III	$R_2Sn(OOCCH_2Cl)_2$	0.5	2.3	105	30.50 (30.97)	3.60 (3.64)	18.29 (18.28)	29.87 (30.60)
IV	$[R_2SnOOCCHCl_2]_2O$	1	2.4	100	28.20 (28.53)	3.32 (3.29)	21.14 (21.05)	35.15 (35.24)
V	$R_2Sn(OOCCHCl_2)_2$	0.5	1.2	120	26.71 (26.30)	2.56 (2.65)	30.94 (31.05)	25.92 (26.00)
VI	$[R_2SnOOCCCl_3]_2O$	1	3.1	132	25.49 (25.88)	2.72 (2.71)	28.17 (28.65)	31.54 (31.97)

[a] The figures represent the quantities (g) of the purified product. [b] These compounds are stable at −20°.

Preparation of allyltin carboxylates

The preparations of triallyl-, diallyltin carboxylates, and tetraallyl-1,3-diacyloxydistannoxanes were carried out as follows. In a 200 ml three necked flask equipped with a magnetic stirring bar, a dropping funnel and a nitrogen inlet tube, were placed 75 ml of methanol containing 2 ml of tetraallyltin (8.8 mmole, 2.48 g). A quantity of carboxylic acid sufficient to give a ratio $R_4Sn/R'COOH$ of 1 or 0.5, dissolved in 10 ml of methanol, was added. The mixture was set aside, with stirring under nitrogen, for about 24 h at room temperature, and then evaporated to dryness. The residue was dissolved in a chloroform/n-hexane mixture, and the solution kept at −20°, to give white needles.

The compounds obtained by the above procedure are listed in Table 1: analytical and physical data are shown, along with the ratio $R_4Sn/R'COOH$ used.

Hydrolysis of $R_3SnOOCR'$ in moist methanol. Preparation of $[(CH_2{=}CH{-}CH_2)_2SnOOCCH_2Cl]_2O$

A solution of triallyltin monochloroacetate (2.9 mmole, 1 g) in 50 ml of moist methanol (few drops of water) was stirred under nitrogen for 12 h at room temperature. Propylene was evolved during the reaction. Solvent was removed under reduced pressure to leave a residue, which was crystallized from chloroform/n-hexane to give tetraallyl-1,3-monochloroacetoxydistannoxane (0.6 g), m.p. 84°. (Found: C, 31.76; H, 3.99; Cl, 12.03; Sn, 39.15. $C_{16}H_{24}O_5Cl_2Sn_2$ calcd.: C, 31.78; H, 4.00; Cl, 11.72; Sn, 39.26%.)

Triallyltin acetate treated in moist methanol, was not converted into the corresponding distannoxane by the above procedure. Several attempts to obtain well defined products failed: in all cases products having very low carbon contents (10–15%) were isolated.

Reaction of $R_3SnOOCR'$ *and* $R'COOH$ *in methanol. Preparation of* $(CH_2{=}CH{-}CH_2)_2$-$Sn(OOCCH_2Cl)_2$

Triallyltin monochloroacetate (3.4 mmole, 1.15 g) in 100 ml of methanol was treated with an equimolecular amount of monochloroacetic acid, and the mixture was set aside for 24 h at room temperature. The solvent was then pumped off, and the solid residue crystallized from chloroform/n-hexane mixture to give diallyltin bis-

TABLE 2

MOLECULAR WEIGHTS OF ALLYLTIN CARBOXYLATES (37°)

Compound (*Mol. wt. formal*)	*Chloroform solution*			*Carbon tetrachloride solution*		
	Concn. (*mg/ml*)	*Mol. wt. found*	i[a]	*Concn.* (*mg/ml*)	*Mol. wt. found*	i[a]
$R_3SnOOCCH_3$	23.60	358	1.19	10.70	357	1.18
(300.95)	11.80	358	1.19	5.35	328	1.09
	5.90	339	1.13	2.67	325	1.08
	2.95	313	1.04	1.34	313	1.04
		321[b]	1.06		313[b]	1.04
$R_3SnOOCCH_2Cl$	10.00	559	1.66	5.95	802	2.40
(335.39)	5.00	462	1.38	2.97	642	1.91
	2.50	366	1.09	1.49	494	1.46
	1.25	354	1.05	0.74	412	1.22
		344[b]	1.02		415[b]	1.23
$R_2Sn(OOCCH_2Cl)_2$	36.24	517	1.33	7.15	1186	3.04
(387.81)	18.12	527	1.35	3.57	1060	2.73
	9.06	493	1.27	1.73	864	2.22
	4.53	454	1.18	0.86	678	1.74
		471[b]	1.21		710[b]	1.83
$R_2Sn(OOCCHCl_2)_2$	35.12	588	1.29	7.62	892	1.95
(456.69)	17.56	557	1.22	3.81	758	1.66
	8.78	518	1.13	1.90	628	1.37
	4.39	466	1.02	0.95	548	1.20
		476[b]	1.04		550[b]	1.20
$[R_2SnOOCCH_2Cl]_2O$	66.35	989	1.63	7.65	917	1.52
(604.65)	33.17	881	1.45	3.82	807	1.33
	16.58	869	1.43	1.91	767	1.27
	8.29	800	1.32	0.95	749	1.24
		833[b]	1.37		728[b]	1.20
$[R_2SnOOCCHCl_2]_2O$	48.68	1077	1.68	36.95	1250	1.85
(637.52)	24.34	1077	1.68	18.47	1172	1.74
	12.17	1077	1.68	9.23	1051	1.56
	6.08	1077	1.68	9.61	937	1.40
		1077[b]	1.68		956[b]	1.42
$[R_2SnOOCCCl_3]_2O$	104.50	1268	1.71	52.30	1369	1.84
(742.41)	52.25	1268	1.71	26.15	1367	1.84
	26.12	1260	1.70	13.07	1388	1.87
	13.06	1206	1.62	6.54	1276	1.72
		1225[b]	1.65		1320[b]	1.65

[a] i=Mol. wt. found/Mol. wt. formular. [b] Extrapolated value (concn. → 0).

(chloroacetate) (0.8 g), m.p. 104–105°, which has the same analytical and physical characteristics as compound (III) (*cf.* Table 1) obtained from the reaction of tetraallyltin and monochloroacetic acid in 1/2 ratio.

Triallyltin acetate remained unchanged when treated with an equimolecular amount or an excess of acetic acid. The difficulty of producing the diacetate was confirmed by treating tetraallyltin with acetic acid in the ratios of $R_4Sn/R'COOH$ varying between 1 and 0.2 (*cf.* Table 1).

Molecular weights in chloroform and carbon tetrachloride

All the compounds prepared are fairly soluble in chloroform and less soluble in carbon tetrachloride. Molecular weights were determined in such solvents, and are shown in Table 2. From the given values of the ratio *i* (*cf.* Table 2), it appears that the monocarboxylates are not associated in the solvents used, while some association occurs in the case of dicarboxylates. The results with the distannoxanes indicate the existence of dimeric and monomeric forms in solution.

Infrared spectra

The spectra of all the allyltin carboxylates show the characteristic vibration absorption bands of the allylic group at values near those found for the tetraallyltin[5,6]: the (C=C) stretch occurs at 1628 cm^{-1}, the $\nu(=CH_2)$ at 3080 cm^{-1}, the $(=CH_2)$ o.o.p. bending mode at 880 cm^{-1}, the (–CH=) o.o.p. bending mode at 990 cm^{-1}.

Assignments of the COO asymmetric and symmetric stretching vibrations and the Sn–C bond vibrations (*cf.* Table 3) were made by reference to the spectra of the sodium carboxylates, tetraallyltin (one absorption band is found at 485 cm^{-1} in the Sn–C region), and trimethylallyltin and triethylallyltin, for which Sn–C stretching frequencies have been noted[7] (480 and 478 cm^{-1}, respectively).

The following points are noteworthy: (*i*) for the monocarboxylates there is more separation between the COO asymmetric and the symmetric vibration bands in solution than in the solid state. Such behaviour is fairly similar to that of analogous organotin compounds such as trialkyl-[3,8–11] and trivinyltin carboxylates[4]; (*ii*) the spectra of the dicarboxylates in solution show a COO stretching band in the 1720–1730 cm^{-1} range; (*iii*) the spectra of the distannoxanes show two sets of COO absorptions at values which undergo practically no change on going from the solid state to solution.

For the absorptions of the Sn–O–Sn linkage in the distannoxanes, we tentatively suggest the following assignments: ν_{as}(Sn–O–Sn) at 625, 610, 615 cm^{-1} (strong bands) and ν_s(Sn–O–Sn) at 505, 515, 510 cm^{-1} (medium bands) for $R' = CH_2Cl$, $CHCl_2$ and CCl_3 respectively. These assignments seem reasonable since bands of these frequencies and intensities are absent in the spectra of the mono- and di-allyltin derivatives. On the other hand, the Sn–O stretching vibrations for some tetraalkyl-1,3-diacetoxydistannoxanes[12] were assigned to frequencies of 650–610 cm^{-1} and 510–470 cm^{-1} for the ν(Sn–O) and the Sn–O ring vibrations respectively.

DISCUSSION

Some comments on the preparation of the allyltin derivatives

The high reactivity of the tin–allyl bond[13] in tetraallyltin generally prevents controlled stepwise cleavage of one, two, or more allylic groups[14]. Several attempts to

TABLE 3

IR DATA OF THE PREPARED ALLYLTIN COMPOUNDS (WAVE NUMBERS, cm^{-1}).

Compound	*Carboxylic region*					*Sn–C region*		
	Nujol mull $\nu_a(COO)$	$CHCl_3$[a]		CCl_4		*Nujol mull*	$CHCl_3$	CCl_4
		$\nu_a(COO)$	$\nu_s(COO)$	$\nu_a(COO)$	$\nu_s(COO)$			
$R_3SnOOCCH_3$	1550 s (br)	1620 s, br	1305 s	1640 (sh)	1305 s	490 m (br)	490 s	495 m
$R_3SnOOCCH_2Cl$	1605 s (br)		1340 m	1650 (sh)	1340 s	490 s (br)	485 m (br)	485 m (br)
$R_2Sn(OOCCH_2Cl)_2$	1605 s			1730 m 1650 (sh)	1350 s (br) 1410 s (br)	490 m		
$R_2Sn(OOCCHCl_2)_2$	1615 s			1720 (sh) 1660 (sh)	1350 s 1400 s	490 m (br)		
$[R_2SnOOCCH_2Cl]_2O$	1665 s 1585 s	1585 s	1335 s	1650 (sh)	1335 s 1410 s	485 m	485 s	485 s (br)
$[R_2SnOOCCHCl_2]_2O$	1670 s 1635 s	1660 (sh) 1615 s	1330 m (br)	1670 (sh) 1645 (sh)	1330 s 1400 s	470 s	485 m	485 m
$[R_2SnOOCCCl_3]_2O$	1685 s 1650 s			1680 s (br) 1645 s	1300 s 1380 s	485 s	480 s (br)	480 s (br)

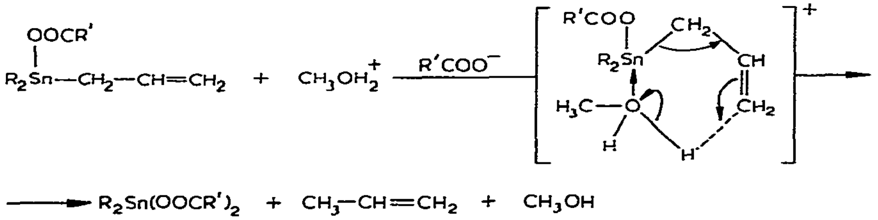
[a] Spectra in $CHCl_3$ show very broad bands.

prepare triallyltin carboxylates by the procedures previously employed for trimethyl- and trivinyltin derivatives proved unsuccessful.

Cleavage of the tin–allylic group bond by carboxylic acids in methanol appears to offer a useful way of preparing allyltin carboxylates, although different products can be formed from different acids even under fixed conditions. The products arise by the following sequence of reactions, all the steps of which have been verified in the case of $R'=CH_2Cl$:

$$\begin{tikzcd}
R_3Sn{-}CH_2{-}CH{=}CH_2 \arrow[r, "R'COOH", "(a)"'] & R_3SnOOCR' \arrow[r, "R'COOH", "(b)"'] \arrow[d, "H_2O", "(c)"'] & R_2Sn(OOCR')_2 \\
& \frac{1}{2}[R_2SnOOCR']_2O &
\end{tikzcd}$$

We suggest that a protonolysis is responsible for the cleavage of the tin–carbon bond in the steps (a) and (b), thus the following mechanism would apply to step (b):

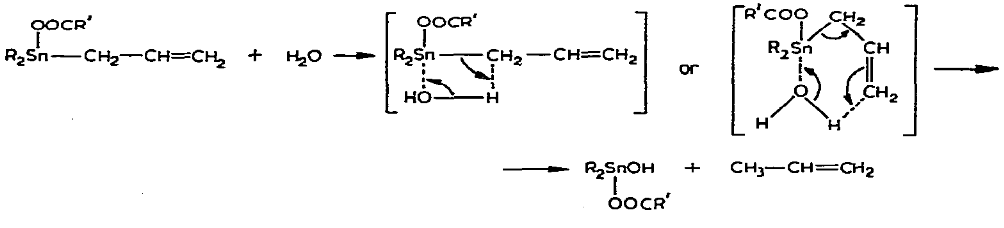


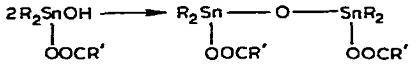
The transition state, which is similar to that proposed for the cleavage of the tin–allylic group bond by HCl or $HClO_4$ in methanol/water[15], involves nucleophilic attack at the tin centre. This is consistent with the observation that carboxylate moieties in which the R′ groups have increased electron-withdrawing power promote the tin–carbon cleavage: triallyltin acetate does not react with an excess of acetic acid, whereas treatment of tetraallyltin with trichloroacetic acid in 1/2 ratio causes cleavage of more than two allyl–tin bonds.

The distannoxanes are usually made by hydrolysis of the disubstituted organotin compounds[12,14,16,17], as the following scheme:

$$R_2SnX_2 \rightarrow R_2Sn(X)OH \rightarrow R_2Sn(X)OSnR_2(X)$$

This does not apply in the case of the dicarboxylates studied; under hydrolytic conditions they undergo Sn–C cleavage with formation of a mixture of ill-defined products. On the other hand, triallyltin monochloroacetate reacts with moist methanol to give the corresponding distannoxane (step c). It follows that distannoxane production also involves allyl–tin cleavage, to give a diallyltin hydroxide carboxylate, which then condenses to the distannoxane, as represented in the following scheme:





$$2R_2Sn(OOCR')OH \longrightarrow R_2Sn(OOCR')-O-SnR_2(OOCR')$$

In this case carboxylate groups involving R′ groups of enhanced electron-withdrawing power render the tin centre more susceptible to nucleophilic attack by the water. Consequently the distannoxane formation in the reaction between tetraallyltin and di- or tri-chloroacetic acid in a 1/1 $R_4Sn/R'COOH$ ratio can be explained by the increased rate of step (c) it being remembered that some water is probably present in the reaction medium*.

Configuration of the allyltin carboxylates

The IR and molecular weights data of the triallyltin acetate and monochloroacetate show a pattern analogous to that found for trialkyltin carboxylates[3,8–11]. Thus we consider that the triallyltin compounds are polymeric in the solid state, with five-coordinated tin atoms in a trigonal bipyramidal structure involving bridging carboxylate groups. Depolymerization occurs when the compounds are dissolved, and they are both monomeric in solution.

Molecular weights measurements on the diallyltin dicarboxylates reveal the presence in solution of dimeric forms. IR spectra recorded in chloroform and carbon tetrachloride solutions show COO vibrational bands in the regions 1730–1650 cm^{-1} and 1350–1400 cm^{-1} (*cf.* Table 3): the presence of the band at 1700 cm^{-1} indicates that these compounds contain ester-like carboxylate groups in solution, which is unusual, since dialkyltin diacetates have been found to be monomeric in solution. In addition the spectra show only COO vibrational bands in the regions 1600–1610 cm^{-1} and 1370–1380 cm^{-1} indicating a chelated configuration of the COO group[12].

Two COO asymmetric and symmetric vibrations bands, which remain at the same value on passing from the solid to solution, are found with the distannoxanes prepared (*cf.* Table 3). They could be ascribed to two different configurations of the COO groups, as proposed for tetrabutyl-1,3-diacetoxydistannoxane[18]. For the latter, the carbonyl absorptions at 1560 and 1418 cm^{-1} were attributed to bridging carboxylate groups, and the bands centered at 1630 and 1362 cm^{-1} to non-bridging groups.

A dimeric structure for the distannoxanes which would be consistent with our IR data is one involving a chelated configuration for the COO groups. The observed COO splitting could be ascribed to carboxylate groups around tin atoms having coordination numbers of five and of six. This necessarily implies that monomeric entities are held together to form dimeric species only by Sn–O linkages. Such a hypothesis, is based however, only on the IR spectra, and requires confirmation by other physical chemical investigations.

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* It is likely that water is present in the commercial methanol and carboxylic acid used.

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