

# Formation of dimeric 1-alkoxy-3-acyloxytetrabutyl-distannoxanes by reaction of dibutyltin oxide with esters

## I. Characterization in solution by multinuclear NMR spectroscopy and application to polymer crosslinking

Josyane Bonetti, Christian Gondard \*, Roger Petiaud \*\*, Marie-France Llauro and Alain Michel

Laboratoire des Matériaux Organiques à Propriétés Spécifiques, CNRS, BP 24, 69390 Vernaison (France)

(Received October 22, 1993)

### Abstract

The product of the reaction of both ethylene–vinyl acetate copolymers (EVA) and ethylene–methyl acrylate copolymers (EMA) with dibutyltin oxide at 200°C, which leads to the crosslinking of the polymer matrix, is shown to be a dimeric 1-alkoxy-3-acyloxy-distannoxane. The reaction mechanism was studied with model esters (n-octyl acetate, n-octadecyl acetate and methyl nonanoate) in absence of solvent at 200°C. The formation of the main reaction product,  $(R-CO-O-(C_4H_9)_2Sn-O-(C_4H_9)_2Sn-OR')_2$ , is complete after heating for 25 min. This non-crystalline compound with an inorganic skeleton and an organic exterior was characterized in solution by  $^1H$ ,  $^{13}C$  and  $^{119}Sn$  NMR spectroscopy.

**Key words:** Tin; Polymerization; Stannanes; NMR; Crosslinking; Polymer

### 1. Introduction

Dibutyltin oxide was shown to be an excellent crosslinking agent for individual copolymers of vinyl acetate or alkyl acrylate (e.g. with vinyl chloride or ethylene) and an excellent catalyst for transesterification when mixed with them [1,2]. The crosslinking produced at 200°C has been followed by rheological measurements [3,4].

In order to elucidate the polymer crosslinking mechanism, reactions of model esters with dibutyltin oxide were carried under conditions as close as possible to those in the molten state of the polymers in the absence of solvent at 200°C.

Since their discovery in 1914 by Pfeiffer and Brach [5], organotin compounds of stoichiometry  $R_4Sn_2X_2O$

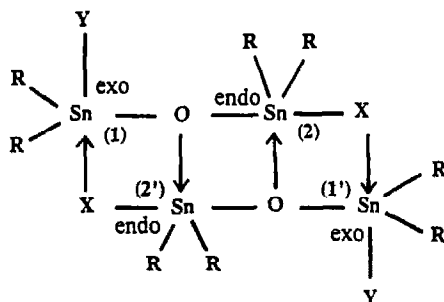
and more generally  $R_4Sn_2XYO$  (tetraorganodistannoxanes) have been the subject of much study. Their dimeric structure, with two types of non-equivalent pentacoordinate tin, was proposed by Okawara and Wada [6] on the basis of the X-ray analysis on some crystalline compounds. Harrison *et al.* [7] demonstrated the two-dimensional centrosymmetric dimeric structure with an essentially planar  $(-R_2\overset{\cdot}{\underset{\cdot}{O}}Sn-O-Sn\overset{\cdot}{\underset{\cdot}{O}}R_2-)$  central ring and a global “staircase” structure in some cases or “ladder-like” (entirely planar) structure in others. The four tin atoms are pentacoordinate in two different ways (*endo* or *exo* in Scheme 1). X-Ray techniques discriminate them, whereas Mössbauer spectroscopy does not [7].

Some pure, crystallizable tetraorganodistannoxanes have already been studied by means of  $^{119}Sn$  NMR spectroscopy in solution, and their dimeric structures have been established both in solution and in the solid state [8–11]. Since some tetraorganodistannoxanes are not crystalline, an X-ray analysis is not always possible. Multinuclear NMR techniques in solution are a powerful method for elucidating their structure.

Correspondence to: Dr. A. Michel.

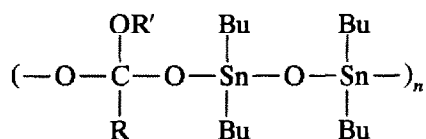
\* Present address: LVM, Industriepark Schoonhees West, Stationstraat, B-3980 Tessenderlo, Belgium.

\*\* Permanent address: Service Central d'Analyse CNRS, BP 22, 69390 Vernaison, France.



Scheme 1.

Many types of crystallizable dimeric distannoxanes have been synthesized [12–14] but no dimeric 1-alkoxy-3-acyloxydistannoxanes have yet been obtained directly from the corresponding ester. A polymeric organotin compound having the structure was claimed in a pat-



ent in 1955 [15] to be the product of the reaction of an ester  $\text{R-CO-OR}'$  with dibutyltin oxide. Since then, no paper concerning the action of organotin oxides on esters has been published.

This paper provides analytical evidence for the formation of an asymmetric, dimeric 1-alkoxy-3-acyloxy-tetrabutyl-distannoxane by means of  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR spectroscopy. This non-crystalline product cannot be studied by X-ray techniques. The formation of this dimeric distannoxane accounts for the crosslinking of ethylene-alkyl acrylate copolymers and ethylene-vinyl acetate copolymers in the presence of dibutyltin oxide. A reaction mechanism is proposed.

## 2. Experimental details

### 2.1. Reagents

Dibutyltin oxide, n-octyl acetate, n-octadecyl acetate and methyl nonanoate were commercial products (Aldrich); ethylene-vinyl acetate (EVA) and ethylene-methyl acrylate (EMA) copolymers were kindly supplied by Atochem. The molar composition of the acetate and acrylate units are 10.6 and 10.8%, respectively.

### 2.2. Reaction of dibutyltin oxide with model esters (typical procedure)

Equimolar amounts (0.032 mol) of dibutyltin oxide and ester (methyl nonanoate or octyl acetate) were mixed in a reactor equipped with a magnetic stirrer and a reflux condenser. The mixture was heated at 200°C. After a few minutes the mixture became clear.

After cooling, an oily, colourless, translucent liquid which is not crystallizable was obtained.

### 2.3. Reaction of dibutyltin oxide with molten copolymer

Molten EVA or EMA was mixed with 5% of dibutyltin oxide in a mixer (Haake Rheocord mixer) equipped with a cam-type rotor. The mixer chamber temperature was set at 200°C and the stirring speed was set at 50 rpm after the introduction of the polymer mixture. The stirring of the polymeric medium was continued until a steady torque was reached.

### 2.4. Preparation of diacetoxytetrabutyl-distannoxane (model compound)

Two methods are available [13], reaction of acetic acid with dibutyltin oxide and partial hydrolysis of dibutyltin diacetate, and the latter was used here. A white, crystalline distannoxane was obtained.  $\text{C}_{20}\text{H}_{42}\text{O}_5\text{Sn}_2$  (599.4) requires C, 40.04; H, 7.01; Sn, 39.60; found: C, 40.05; H, 7.09; Sn, 42.40%.

### 2.5. NMR spectroscopy

High-resolution liquid NMR spectroscopy was carried out with a Bruker AC250 instrument working at 250 MHz for  $^1\text{H}$  and 62.9 MHz for  $^{13}\text{C}$ , and with a Bruker AC200 instrument working at 74.6 MHz for  $^{119}\text{Sn}$ . Tetrachloroethylene (TCE)/deuterated benzene ( $\text{C}_6\text{D}_6$ ) mixtures (2:1 by volume) were used as solvents. Chemical shifts values ( $\delta$ ) are in ppm with reference to internal tetramethylsilane ( $\text{TM}_4\text{Si}$ ) for  $^1\text{H}$  and  $^{13}\text{C}$ , and to external tetramethyltin for  $^{119}\text{Sn}$ .

The Bruker COSYX.AU microprogram was used for the  $^{119}\text{Sn}$ - $^{119}\text{Sn}$  COSY spectrum; 128 experiments were used to create the  $F_1$  domain, with 288 scans for each; 512 data points were used for acquisition with no zero-filling in the  $F_2$  dimension. A fixed delay of 3.448 ms was added to the variable delay between the two 90° pulses. A squared sine-bell filter was used in both dimensions.

#### 2.5.1. $^{119}\text{Sn}$ Mössbauer data

For the tin compound synthesized from octyl acetate the values obtained were  $\delta = 1.10$  and  $\Delta = 2.57$  whereas diacetoxytetrabutyl-distannoxane gave values of  $\delta = 1.30$  and  $\Delta = 3.24$  ( $\delta =$  quadrupole splitting;  $\Delta =$  isomer shift,  $\text{mm s}^{-1}$ ). In both cases a single quadrupole split resonance was observed. However, the resonance lines are broad and indicate an envelope of overlapping peaks. In the well known diacetoxytetrabutyl-distannoxane, the non-equivalence of the two tin atoms has been shown previously by  $^{119}\text{Sn}$  NMR spectroscopy, whereas Mössbauer data only indicate a coordination number greater than four. Values of  $\delta = 1.08$  and  $\Delta = 2.06$  were obtained for dibutyltin oxide.

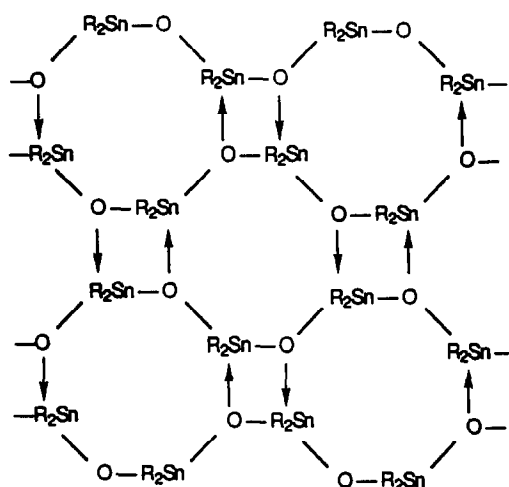
### 3. Results and discussion

The composition of the ethylene–vinyl acetate copolymers (EVA) used in this study is 10 mol% of vinyl acetate units. The ester with the closest hydrocarbon chain length per ester group should be octadecyl acetate. Nevertheless octyl acetate,  $\text{CH}_3\text{-CO-O-(CH}_2\text{)}_7\text{-CH}_3$ , and methyl nonanoate,  $\text{CH}_3\text{-O-CO-(CH}_2\text{)}_7\text{-CH}_3$ , were chosen as models for EVA and EMA in order to reduce the intense resonance of methylene protons in the  $^1\text{H}$  NMR spectra which increases the detection threshold of the other resonances.

#### 3.1. Preliminary observations

The opacity of the suspension of dibutyltin oxide in octyl acetate disappears completely in 10 min at  $200^\circ\text{C}$  when the initial amount of dibutyltin oxide is less than 2 mole equivalents of ester. This is a first indication of a fast reaction. In fact, it is well known that dibutyltin oxide is amorphous, insoluble in most organic solvents and that it decomposes above  $200^\circ\text{C}$  to  $\text{SnO}_2$  and alkenes. Dibutyltin oxide is polymeric [16] with about 20 tin atoms in a chain. The crosslinking of this organometallic polymer is supposed to occur through dative bonds between oxygen and tin atoms. Mössbauer studies show a pentacoordinate tin in dibutyltin oxide. This crosslinked polymeric structure responsible for the insolubility is commonly represented as in Scheme 2.

The loss of opacity, without being a real proof of reaction, at least proves that the crosslinks are disrupted. All attempts to crystallize the reaction products failed.



Scheme 2.

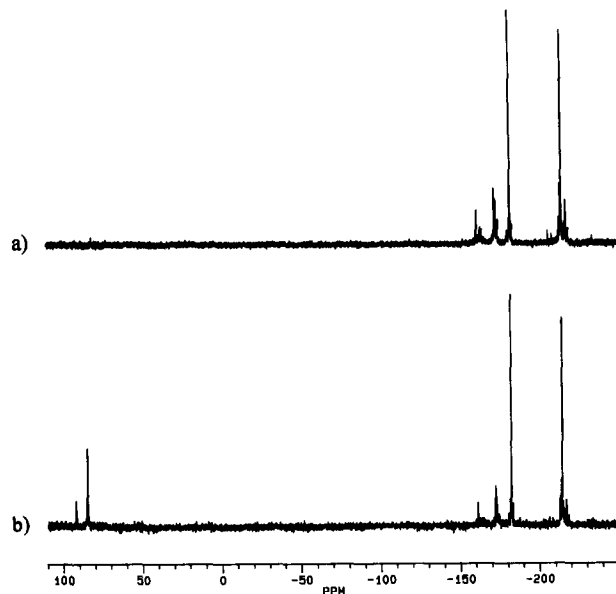


Fig. 1.  $^{119}\text{Sn}$  NMR spectra of the reaction products of dibutyltin oxide with n-octyl acetate (initial oxide/ester molar ratio  $R = 2:1$ ) at  $200^\circ\text{C}$  after (a) 15 and (b) 180 min.

The  $^{119}\text{Sn}$  NMR spectra (Fig. 1(a)) reveal two major tin resonances of equal intensity at  $\delta = -182.5$  and  $-215$  ppm. They are the first evidence of reaction, because the single resonance of dibutyltin oxide is at  $\delta = -172.2$  ppm (dibutyltin oxide is slightly soluble at  $90^\circ\text{C}$  in the solvents used).

As shown in Fig. 1(b), for an initial ratio  $R$  of  $\text{Bu}_2\text{SnO/ester}$  of 2, some by-products (resonances at  $\delta = 84.4$  and  $91.5$  ppm) appear when the reaction temperature is maintained at  $200^\circ\text{C}$  for a long time. Figure 2 shows that an increase in the initial ratio leads to new tin compounds with resonances in the same chemical shift region as those of the main product. A more complete analysis of  $^{119}\text{Sn}$  spectra will be discussed below, in the light of the  $^1\text{H}$  NMR spectra.

#### 3.2. $^1\text{H}$ NMR analysis

The  $^1\text{H}$  NMR spectra indicate one acyloxy, one alkoxy and four butyl groups attached to tin whatever the ester. A series of mixtures with different oxide/ester ratios and different reaction times at  $200^\circ\text{C}$  (0.25–6.0 h) were studied.

Figure 3 shows a typical  $^1\text{H}$  NMR spectrum obtained with an initial molar ratio of 2. The low-field region ( $S'_1$ ) corresponds to a triplet of the residual acetate, whereas  $S''_1$  is a badly resolved multiplet at  $\delta = 3.525$  corresponding to  $-\text{Sn-O-CH}_2-$ . Resonance due to free octyl alcohol (expected at  $\delta = 3.435$ ) cannot be excluded.

Similarly, in the resonance  $S_2$  region, the singlet at  $\delta = 1.850$  corresponds to residual acetate whereas that at  $\delta = 1.865$  is assigned to the methyl protons of  $-\text{Sn}-$

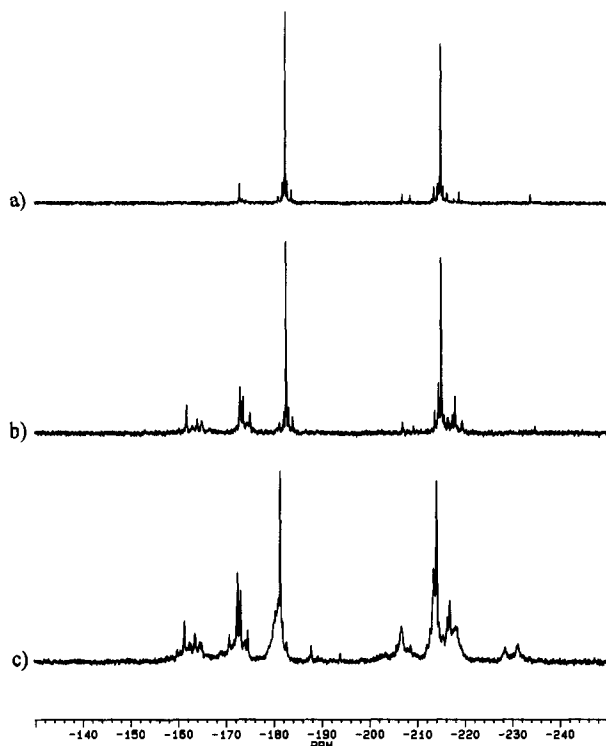


Fig. 2.  $^{119}\text{Sn}$  NMR spectra of the reaction products of dibutyltin oxide with n-octyl acetate at  $200^\circ\text{C}$  after 15 min. Initial oxide/ester molar ratio  $R =$ : (a) 1, (b) 2 and (c) 3.

$\text{O}-\text{CO}-\text{CH}_3$ . Sometimes a singlet appears at  $\delta = 1.935$ , due to tributyltin acetate, a by-product, unambiguously identified by  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{119}\text{Sn}$  NMR spectroscopy. The  $S_2$  region can also be used for quantitative determination.

The  $S_3$  resonance region corresponds to central

methylene protons of the alkyl part of the ester (residual and attached to the tin atom) and to alkyl groups of all organotin compound(s) soluble in the solvent mixture.

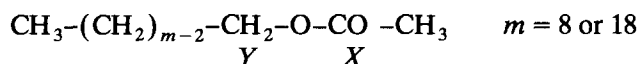
The  $S_4$  region corresponds to methyl protons of alkyl groups, the alkoxy resonances ( $\delta = 0.885$ ), and two triplets of equal intensity ( $\delta = 0.940$  and  $0.965$ ) to two non-equivalent butyl groups.

The molar fraction  $\rho$  of reacted ester is easily determined from the relative intensities in the  $S_1$  region:

$$\rho = S_1''/S_1' + S_1''$$

This assumes that hydrolysis of  $\text{Sn}-\text{O}-\text{R}$  to give the corresponding alcohol is negligible. The triplet due to  $\text{C}7-\text{CH}_2-\text{OH}$  is in the  $S_1$  region ( $\delta = 3.345$ ). Both alcohol and ester remain in the reaction mixture because of their high boiling points.

The number of pairs of butyl groups on organotin compounds soluble in the solvent mixture per mole of ester,  $N$ , was determined from  $^1\text{H}$  NMR as follows. If  $S_1$  is the intensity of the  $\text{O}$ -methylene resonance of the alkyl part of the alkyl acetate,  $Y$ , and  $S_2$  is the corresponding intensity of the methyl resonances of the acyl part,  $X$ , then  $Y = S_1/2$  and  $X = S_2/3$ .



Arithmetic considerations show that  $S_4 = 6NY + 3Y$  and  $S_3 = 2(m-2)Y + 12NY$ . Eliminating  $Y$  from these two expressions using  $S_1 = 2Y$  gives two equations for the number of pairs of butyl groups  $N$ :

$$N = (S_4/3S_1) - 1/2$$

$$N = (S_3/6S_1) - (m-2)/6$$

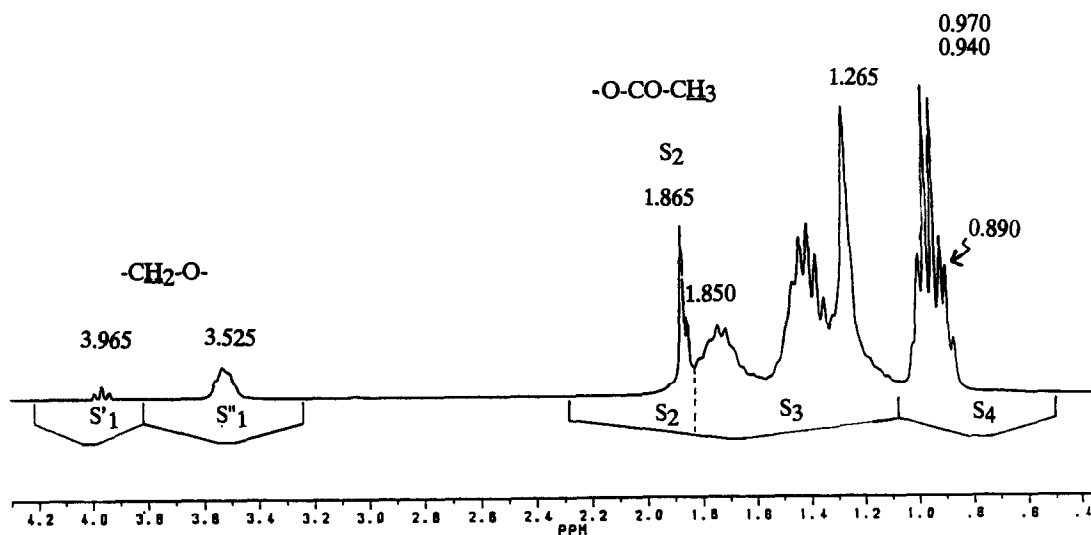


Fig. 3.  $^1\text{H}$  NMR spectrum of the reaction products of dibutyltin oxide with n-octyl acetate at  $200^\circ\text{C}$  after 15 min. (initial oxide/ester molar ratio  $R = 2$ ).

TABLE 1. Experimental  $\rho$  and  $N$  values (see text) under different reaction conditions

$I$	$m$	$t$ (h)	$\rho$	$N$
0.5	18	1	0.32	0.47
0.5	18	5	0.27	0.44
1	8	0.25	0.54	1.00
1.5	8	3	0.70	1.43
1.5	18	3	0.63	1.54
2.	8	0.25	0.86	2.00
2	8	3	0.84	1.89
3	8	0.25	0.92	1.93
6	18	3	0.90	1.89

Average empirical values are given in Table 1. In this determination, all soluble organotin compounds are assumed to be dibutyltin compounds. However, tributyltin acetate was also detected, for instance in the experiments with an oxide/ester ratio greater than 2.

The variation of  $\rho$  with this ratio (Fig. 4) and the corresponding calculated  $N$  values (Table 1) are strong arguments for a reaction with a single main product with a stoichiometry of one ester to two dibutyltin oxides. When  $R < 2$ , the experimental values of  $\rho$  are almost equal to  $R/2$ . Maximum  $\rho$  values are reached for  $R > 2$ , but complete consumption of the ester never occurs.

The  $N$  values show that in an excess of  $\text{Bu}_2\text{SnO}$  ( $R > 2$ ) there are nearly 2 mol of soluble dibutyltin compound per mole of ester, and with a deficiency of dibutyltin oxide the soluble dibutyltin compound corresponds to nearly all the oxide introduced ( $N \sim R$ ). This stoichiometry is consistent with previous observations [15].

### 3.3. $^{13}\text{C}$ NMR analysis

Complementary results are obtained by  $^{13}\text{C}$  NMR analysis. The methylene carbons of the alkoxytin groups

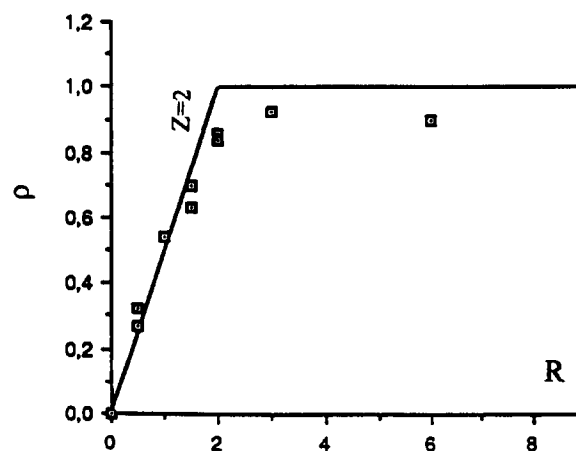


Fig. 4. Molar fraction of reacted ester  $\rho$  versus the initial oxide/ester molar ratio  $R$ .

$\text{Sn-OR}'$   $\alpha$  or  $\beta$  to the oxygen atom resonate at different frequencies to those of the corresponding carbons in  $\text{R-CO-OR}'$ . Methyl carbons from an acyloxy organotin compound ( $\text{Sn-O-CO-CH}_3$ ) and unreacted ester ( $\text{R}'\text{O-CO-CH}_3$ ) can also be differentiated. Two non-equivalent butyl groups are detectable. The methylene carbons of butyl groups  $\alpha$  to tin (C4) have typical  $^1J_{\text{Sn-C}}$  coupling constants and chemical shifts. The spectra obtained are confused by the presence of some residual ester, but all resonances can be assigned. In order to assign the carbon resonances (C1 to C4) of the butyl groups, a model compound was investigated first; the well known and easily crystallizable [13] 1,3-diacetoxytetrabutyl-distannoxane is dimeric in solution ( $^{119}\text{Sn}$  NMR spectroscopy) and in the solid state (X-ray techniques).

#### 3.3.1. Carbons of alkoxy and acyloxy groups

Figure 5 shows a typical  $^{13}\text{C}$  NMR spectrum obtained after reaction of octyl acetate with dibutyltin oxide. The resonance at  $\delta = 176$  ppm is assigned to the carbonyl attached to the tin atom ( $\text{Sn-O-CO-CH}_3$ ), whereas the carbonyl of octyl acetate is at  $\delta = 169.30$  ( $\Delta\delta = 6.70$ ). The methyl carbon resonance of the tin acetate is at  $\delta = 23.30$  compared with  $\delta = 20.55$  for the corresponding carbon in octyl acetate ( $\Delta\delta = 2.75$ ). The resonances of methylenes  $\alpha$  to oxygen of the alkoxy group are not well separated ( $\delta = 64.25$  and  $64.15$ ), whereas the methylene in the  $\beta$  position is much more deshielded in the product  $-\text{Sn-O-CH}_2-\text{CH}_2-$  ( $\delta = 35.15$  and  $29.10$ ,  $\Delta\delta = 6.05$ ) than in the ester.

Figure 6 shows a typical spectrum of the reaction mixture obtained with the methyl nonanoate. Chemical shift differences between a given carbon in the tin product and in the initial corresponding ester are nearly the same for the carbonyl groups ( $\Delta\delta = 6.15$ ) compared with 6.70 for octyl acetate. This is also true of the carbons  $\alpha$  to oxygen of alkoxy groups ( $\Delta\delta = 0.10$  for both). For the carbons  $\alpha$  to the carbonyl, chemical shift differences are nearly the same ( $\Delta\delta = 2.20$  and  $2.75$ , respectively). The resonance of the methylene  $\beta$  to the carbonyl,  $\delta = 26.40$  in the case of the organotin compound, is slightly more deshielded than in the ester ( $\delta = 25.25$ ,  $\Delta\delta = 1.15$ ).

#### 3.3.2. Resonance assignments of carbons of the butyl groups

The model compound 1,3-diacetoxytetrabutyl-distannoxane (S) has a simple  $^{13}\text{C}$  NMR spectrum (Fig. 7). Whereas only one resonance is observed at  $\delta = 13.85$  for methyl carbons (C1) of the butyl groups, six peaks are observed for the three methylene carbons C2, C3 and C4, in  $\gamma$ ,  $\beta$  and  $\alpha$  position to the tin atom. This

also applies to the organotin compounds obtained from octyl acetate (B) and methyl nonanoate (D) (circled resonances in Figs. 5 and 6). Table 2 summarizes the  $^{13}\text{C}$  NMR data obtained for S, B and D.

The C4 chemical shifts are typical of dibutyltin compounds. The assignments for resonances of the C3 and C2 carbons were made considering the coupling constants,  $^2J_{\text{Sn-C-C}}$  for C3 and  $^3J_{\text{Sn-C-C-C}}$  for C2, where available. The chemical shifts of C3 and C2 (four resonances) in the organotin compounds from those of octyl acetate and methyl nonanoate are close. Nevertheless, differences are observed (for one C2 and C3) from diacetyldistannoxane, and therefore tentatively assigned to a butyl group associated with an alkoxytin group.

Mitchell [17] and Holecek [18] observed that the values of  $^1J_{\text{Sn-C}}$  and  $^3J_{\text{Sn-C}}$  in the dibutyltin compounds are related to the coordination number of the tin atom. In this work all  $^1J$  values correspond to limiting values for five coordination.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR analyses are consistent in the following points: the main product of the reaction has a stoichiometry of one ester for two dibutyltin oxide with only one type of Sn-OR and Sn-O-CO-R. It is a pentacoordinate tin compound with two non-equivalent butyl groups. A dimeric distannoxane structure is therefore highly probable.

### 3.4. $^{119}\text{Sn}$ NMR analysis

As observed in previous  $^{119}\text{Sn}$  NMR studies of other distannoxanes in solution [8,9,18], the resonances of distannoxane compounds are most shielded in the pentacoordinate dibutyltin family.

All the  $^{119}\text{Sn}$  spectra obtained from reaction products of dibutyltin oxide with alkyl acetates, whatever the alkyl chain length, show the same chemical shift for the main tin resonances, except for small differences observed in the case of methyl nonanoate. Table 3 summarizes chemical shifts and coupling constants. A typical  $^{119}\text{Sn}$  NMR spectrum is shown in Fig. 8(a). The

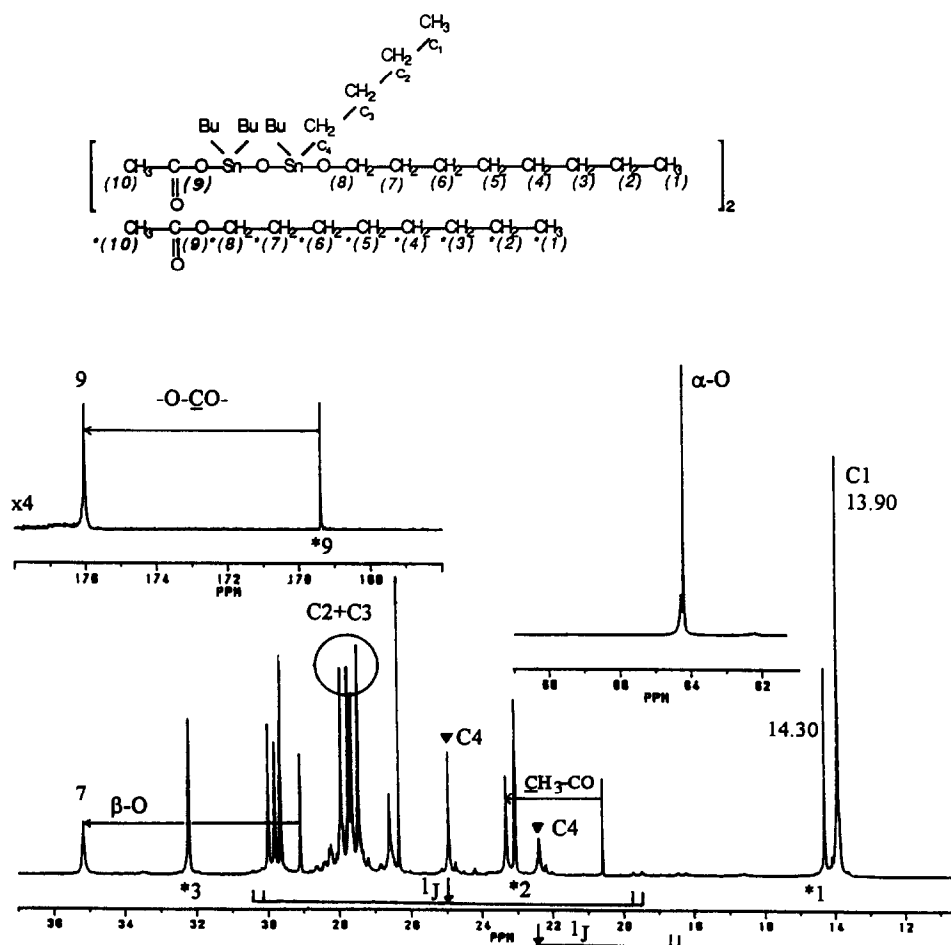


Fig. 5.  $^{13}\text{C}$  NMR spectrum of the reaction products of dibutyltin oxide with n-octyl acetate at 200°C after 15 min (initial oxide/ester molar ratio  $R = 1$ ).

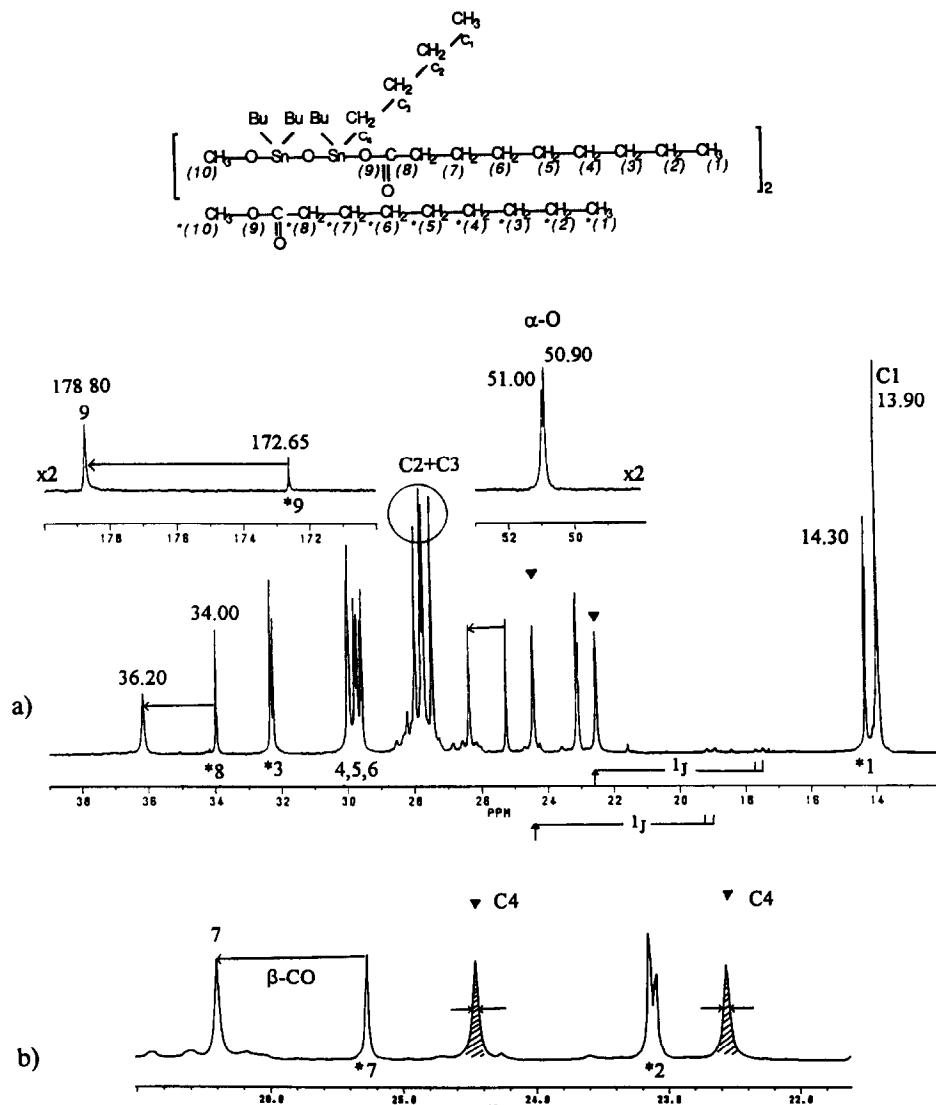


Fig. 6.  $^{13}\text{C}$  NMR spectrum of the reaction products of dibutyltin oxide with methyl nonanoate at  $200^\circ\text{C}$  after 15 min (initial oxide/ester molar ratio  $R = 1$ ). (a) Carbonyl, methoxy and other carbon resonances, (b) enlargement of 27–22 ppm region: C4 resonances of butyl groups.

main resonances always consist of two groups of peaks corresponding to equal populations. A homonuclear COSY Sn–Sn correlation spectrum (Fig. 9) shows that the tin atoms are coupled to each other. Each tin

resonance (Fig. 8(b)) has two doublet satellite peaks (1–5), (2–4), (6–10) and (7–9) with different coupling constants. Each tin atom is coupled through oxygen to two other tin atoms. This is in complete agreement

TABLE 2.  $^{13}\text{C}$  chemical shifts ( $\delta$  in ppm) of methylene carbons C2, C3 and C4 and  $^1J_{\text{Sn-C4}}$  (Hz) values for the two distinct butyl groups in dibutyltin compounds obtained by reaction of dibutyltin oxide with esters: comparison with a distannoxane model compound

Sample <sup>a</sup>	C3	C2	C3	C2	C4 ( $^1J_{\text{Sn-C}}$ ) <sup>c</sup>	
S	27.90	27.25	27.60	27.10	29.40 (770–732)	27.55 (726–692)
B	27.90	27.65 <sup>b</sup>	27.75 <sup>b</sup>	27.45	24.95 (688–657)	22.35 (520–488)
D	28.00	27.75 <sup>b</sup>	27.80 <sup>b</sup>	27.50	24.45 (693–662)	22.55 (736–608)

<sup>a</sup> S = 1,3-diacetyltetrabutyltinnoxane; B = tin compound of reaction of dibutyltin oxide with n-octyl acetate; D = tin compound of reaction of dibutyltin oxide with methyl nonanoate.

<sup>b</sup> An inversion of assignments between C2 and C3 is possible.

<sup>c</sup>  $^1J_{119\text{Sn-C}} - ^1J_{117\text{Sn-C}}$ ; values in parentheses.

with a dimeric distannoxane structure (Scheme 1) with an exocyclic Sn(1) coupled (i) to an endocyclic Sn(2) through a covalent link and (ii) to the endocyclic Sn(2') through a coordinate bond [7,8].

Four dimeric distannoxane structures P, P1, P2 and P3 (Scheme 3) can describe the organotin species having the required overall stoichiometry. Only the P structure is considered, because it is the only structure which allows the two coordinations of the exocyclic tins with the carbonyl oxygen, which is the strongest donor. It is the only structure fully consistent with all the NMR observations. We infer a dimeric distannoxane, of a single monomeric species of stoichiometry  $R'O-Sn-O-Sn-O-CO-R$ . Assignment of exocyclic and endocyclic tin resonances is reported in Table 3.

In the 1,3-diacetyldistannoxane (S) the donor group is the oxygen of the carbonyl of  $O-CO-CH_3$ . We

assign  $\delta_{Sn(endo)}$  and  $\delta_{Sn(exo)}$  for this compound because the tin chemical shift of pure dibutyltin oxide (slightly soluble at 80°C in the same solvent,  $\delta = -172.2$ ) is more deshielded than both tin chemical shifts of (S) (Table 3). The substitution of oxygen by  $O-CO-CH_3$  induces a high field shift. The following orders would be expected:  $\delta_{Bu_2SnO_3} > \delta_{Bu_2SnO_2(O-CO-CH_3)} > \delta_{Bu_2SnO(O-CO-CH_3)_2}$ . The endocyclic tin atom will be more deshielded than the exocyclic atom, consistent with  $\delta_{Sn(1)} = -229.8$  and  $\delta_{Sn(2)} = -219.4$ . These arguments support the tentative assignment proposed by Otera *et al.* [9].

In alkoxyacyloxydistannoxane the donor group is also  $O-CO-CH_3$ , owing to the higher donor power of the carbonyl oxygen compared with the alkoxy oxygen. Consequently, the exocyclic tins (1 and 1') bear an alkoxy group in the distannoxane from octyl acetate

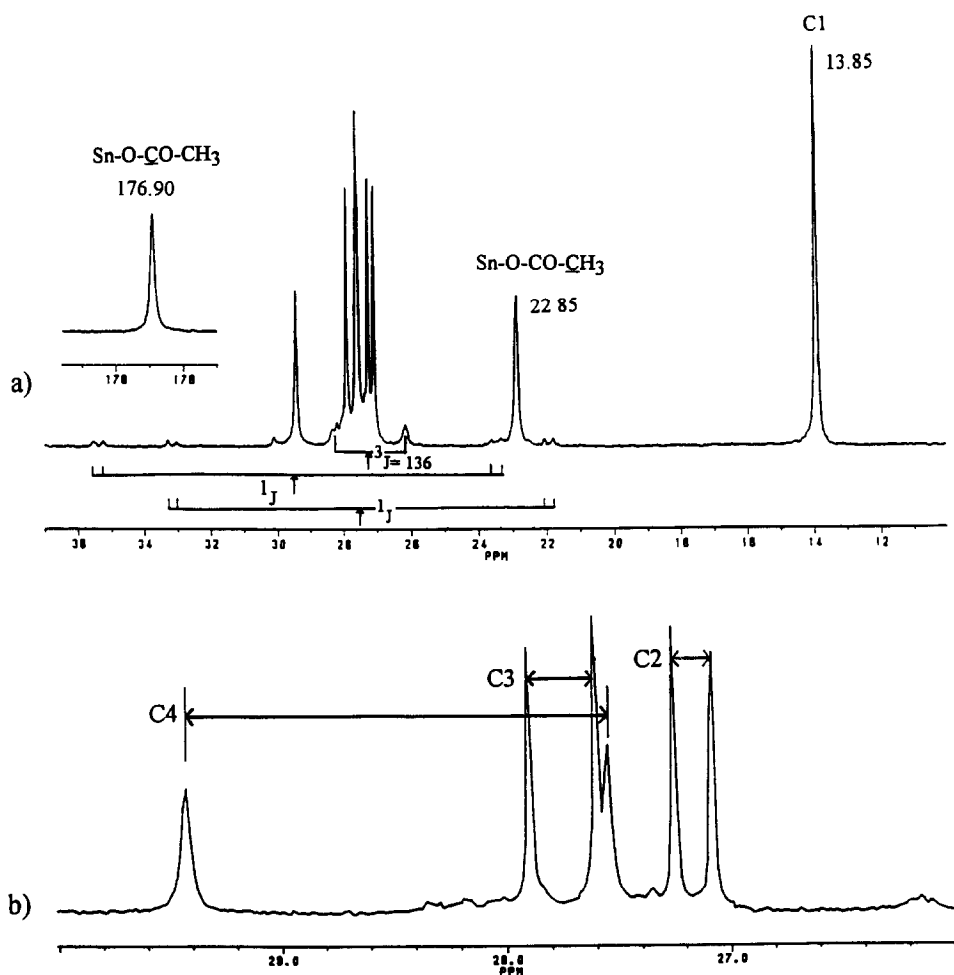


Fig. 7.  $^{13}C$  NMR spectrum of 1,3-diacetyltetrabutylstannoxane: (a) methyl and methylene carbon resonances and carbonyl resonance region; (b) enlargement of C2, C3 and C4 resonances of butyl tin groups.



TABLE 3. Tin chemical shifts and coupling constant for compounds S, B, C and D

Distannoxane compounds <sup>a</sup>		$\delta$ (ppm) <sup>b,c</sup>	$^2J_{\text{Sn-Sn}}$ (Hz) <sup>d</sup>	$^2J_{\text{Sn-H}}$ (Hz) <sup>d</sup>
S	O-CO-CH <sub>3</sub> O-CO-CH <sub>3</sub>	-219.4(2)	122	90
		-229.8(1)		
B	X O-CO-CH <sub>3</sub> Y O-C <sub>8</sub>	-182.5(1)	72;205	70
		-214.5(2)		
C	O-CO-CH <sub>3</sub> O-C <sub>18</sub>	-182 (1)	70;204	
		-214.5(2)		
D	O-CO-C <sub>8</sub> O-CH <sub>3</sub>	-181.4(1)	72.5;217 (208) <sup>e</sup>	
		-218.2(2)		

<sup>a</sup> X:O-CO-R part of the ester (donor group in the distannoxane structure). Y:OR part of the ester (free group in the distannoxane structure).

<sup>b</sup> Tin sites (1) and (2) are exocyclic and endocyclic tin sites of the dimeric distannoxane structure, respectively.

<sup>c</sup>  $\pm 0.1$  ppm.

<sup>d</sup>  $\pm 3$  Hz.

<sup>e</sup>  $^2J_{\text{Sn-119Sn}}$  ( $^2J_{\text{119Sn-117Sn}}$  in parentheses).

(B), the distannoxane from octadecyl acetate (C) and the distannoxane from methyl nonanoate (D), but not in (S):

$$\delta\text{Sn}(1)(\text{S}) = -229.8 \neq \delta\text{Sn}(1)(\text{B}) \approx \delta\text{Sn}(1)(\text{C}) \approx \delta\text{Sn}(1)(\text{D})$$

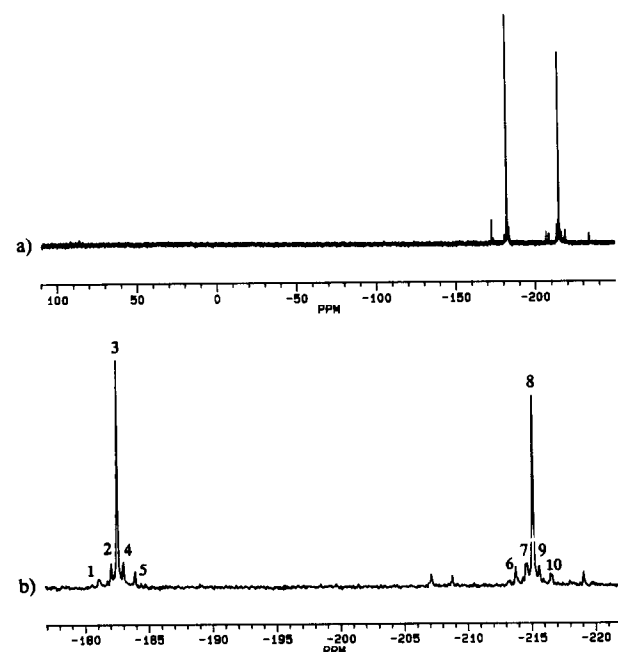


Fig. 8. <sup>119</sup>Sn NMR spectrum of the reaction products of Bu<sub>2</sub>SnO with n-octyl acetate at 200°C after 15 min.

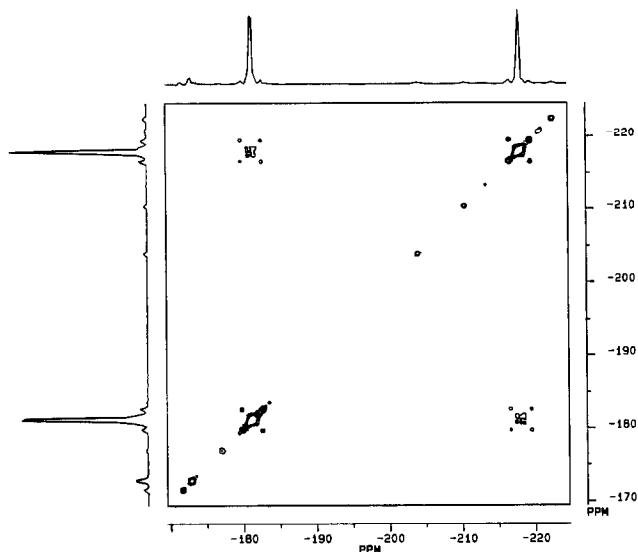
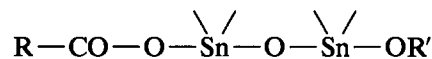


Fig. 9. Contour plot of the 2D Sn-Sn COSY spectrum of the reaction products of Bu<sub>2</sub>SnO with methyl nonanoate at 200°C after 15 min. Homonuclear chemical shift correlation.

The endocyclic tin atoms, Sn(2), bear an OCOCH<sub>3</sub> group, as in 1,3-diacetoxystannoxane:

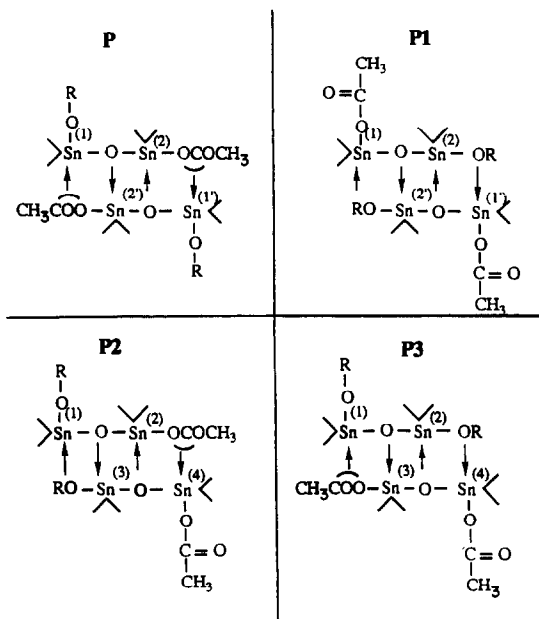
$$\delta\text{Sn}(2)(\text{B}) = \delta\text{Sn}(2)(\text{C}) \approx \delta\text{Sn}(2)(\text{D}) \approx \delta\text{Sn}(2)(\text{S}) = -219.4$$

The fact that the reaction of an ester R-CO-OR' with dibutyltin oxide leads to a single asymmetric monomeric entity



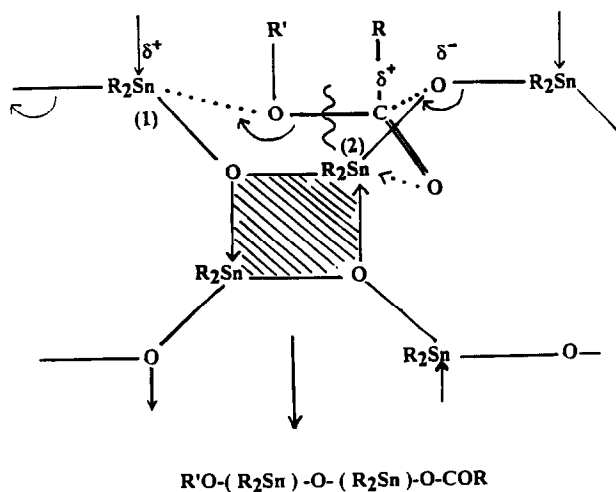
suggests a mechanism (Scheme 4) in which the attack of the ester is at the central (R<sub>2</sub>Sn-O-R<sub>2</sub>Sn-O) square part of the two-dimensional centrosymmetric structure of polystannoxane chain of dibutyltin oxide. The first reaction step would consist of a nucleophilic attack of the carbonyl group on the endocyclic tin atom while the both exocyclic oxygen and tin atoms of the same polystannoxane chain would attack the ester group at the carbon of the carbonyl and the oxygen of the alkoxy group. This first step would lead to a six, six-membered double ring. Alkoxy ester cleavage and two Sn-O cleavages in the polystannoxane chain would occur with the formation of R-CO-O-Sn-O-Sn-OR'.

The proposed six, six-membered double ring (boat and chair) accounts for the exclusive formation of distannoxanes, excluding polystannoxanes. No tristanoxanes were detected. These should result from a highly and regularly crosslinked polystannoxane polymer containing octahedral rings, through the same mechanism. This suggests that such a regular diorgan-



Scheme 3.

otin oxide structure proposed by Omae [16] is excluded. Dibutyltin oxide may be the result from the irregular condensation of dimeric distannoxane entities which were previously present during the hydrolysis (a pentacoordinate tin structure) rather than from a highly regularly crosslinked polystannoxane polymer. Moreover, monomeric distannoxane entities were never observed by NMR spectroscopy. Either dimerization occurs immediately and stabilizes the species or the coordinate bonds of the central square part (crosslink knot) are maintained during the attack. It appears that the central square part ( $R_2Sn-O-SnR_2-O$ ) is the skele-



Scheme 4.

ton of both oxide and dimeric alkoxyacyloxydistannoxane. Solubilization should result from the breaking up of this distannoxane structure and return to the initial "monomeric" structure (distannoxane structure) without change of the central crosslinked part of the initial insoluble dibutyltin oxide structure.

As for the experimental observation that there is one single dimeric form, it is probably related to well known fact that the acyl group has a much higher donor ability than an alkoxy group.

#### 4. Conclusion

The crosslinking of both EVA (ethylene-vinyl acetate copolymer) and EMA (ethylene-methylacrylate copolymer) by dibutyltin oxide at 200°C is explained by the formation of intermolecular dimeric species. They result from the reaction of two pendant ester groups of EVA (or EMA) with pre-existing  $-R_2Sn-O-SnR_2-O-$  distannoxane structures of the dibutyltin oxide structure. Although indirect preparation of (methoxy)(acetoxy)distannoxane has already been mentioned [11] and in spite of the fact that mild conditions have to be tested in order to minimize the side-reactions, this is the first direct production of alkoxyacyloxydistannoxanes from the corresponding ester.

Moreover, as both dibutyltin oxide and distannoxanes compounds are catalysts in many reactions, some of them including esters [1-3,11,12,16,19-21], this direct reaction leads us to re-examine the exact nature of the catalytic entities in the reactions of polymers containing esters in presence of dibutyltin oxide. Work in this area is in progress [22,23].

#### Acknowledgement

The authors are indebted to SOTRA Industries (LVM Group) for financial support.

#### References

- 1 C. Gondard and A. Michel, SOTRA Industries and CNRS, *US Patent* 5 244 982, 1993.
- 2 C. Gondard, *Thesis*, Université Claude Bernard Lyon I, Lyon, 1990.
- 3 P. Cassagnau, M. Bert, V. Verney and A. Michel, *Polymer*, **34** (1993) 124.
- 4 P. Cassagnau, M. Bert, V. Verney and A. Michel, *Polym. Eng. Sci.*, **32** (1992) 998.
- 5 P. Pfeiffer and O. Brach, *Z. Anorg. Chem.*, **87** (1914) 229.
- 6 R. Okawara and M. Wada, *J. Organomet. Chem.*, **1** (1963) 81.
- 7 P.G. Harrison, M.J. Begley and K.C. Molloy, *J. Organomet. Chem.*, **186** (1980) 213.
- 8 T. Yano, K. Nakashima, J. Otera and R. Okawara, *Organometallics*, **4** (1985) 1501.
- 9 J. Otera, T. Yano, K. Nakashima and R. Okawara, *Chem. Lett.*, (1984) 2109.

- 10 J.F. Vollano, R.O. Day and R.R. Holmes, *Organometallics*, **3** (1984) 745.
- 11 D.C. Gross, *Inorg. Chem.*, **28** (1989) 2355.
- 12 J. Otera, N. Dan-oh and H. Nozaki, *J. Org. Chem.*, **56** (1991) 5307.
- 13 Y. Maeda and R. Okawara, *J. Organomet. Chem.*, **10** (1967) 247.
- 14 M. Wada, M. Nishino and R. Okawara, *J. Organomet. Chem.*, **3** (1965) 70.
- 15 Metal and Thermit Corporation, British Patent 737033, 1955.
- 16 I. Omae, *Organotin Chemistry*, (*J. Organomet. Chem. Library* Vol. 21), Elsevier, Amsterdam, 1989.
- 17 T.N. Mitchell, *J. Organomet. Chem.*, **59** (1973) 189.
- 18 J. Holecek, M. Nadvornik and K. Handlir, *J. Organomet. Chem.*, **315** (1986) 299.
- 19 J. Otera, *Chem. Rev.*, **93** (1993) 1449.
- 20 Y. Hori, M. Suzuki, A. Yamaguchi and T. Nishishita, *Macromolecules*, **26** (1993) 5533.
- 21 J. Bonetti, *Thesis*, Université Claude Bernard Lyon I, Lyon, 1992.
- 22 I. Espinasse, R. Pétiard, M.F. Llauro and A. Michel, *Int. J. Polym. Mater.*, in press.
- 23 O. Primel and O. Bacati, personal communication.