

The role of μ -hydroxy and μ -alkoxy binuclear complexes in tin(IV)-catalysed urethane formation

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Abstract

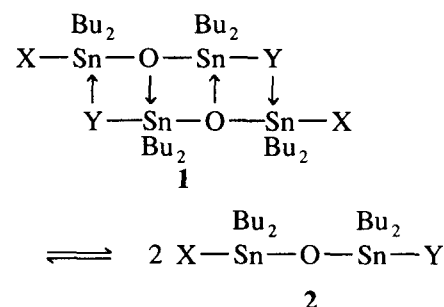
It is proposed that at the catalyst concentrations normally used the distannoxane-catalysed formation of urethanes from isocyanates and alcohols involves the monomeric form of the distannoxane rather than the dimeric form as previously suggested, and that the catalytic species of the reaction is a μ -hydroxy binuclear complex that is formed from the alcohol and the distannoxane. Similar oxygen-bridged binuclear species are believed to be involved when other types of tin(IV) compounds are used as catalysts for urethane formation.

Keywords: Tin; Distannoxane; Urethane formation; Oxygen-bridged; Binuclear

1. Introduction

In 1967 Yokoo et al. reported that the distannoxanes **1a** and **1f** were very effective catalysts for the formation of a urethane from butanol and phenyl isocyanate [1]. Later, Otera et al. reported a more detailed examination of the catalytic activity of a number of distannoxanes and rationalised their activity in terms of their dimeric structure [2]. This dimeric structure has been established by X-ray crystallography for a substantial number of distannoxanes [3], but this is, of course, for the solid state. While early molecular weight measurements [4,5] and vapour-phase osmometry studies [6] suggested that in benzene and with concentrations in the range 0.01–0.1 mol dm⁻³ the distannoxanes **1a** and **1e** maintain their dimeric structure, cryoscopic measurements [7] and ¹¹⁹Sn NMR studies [8] on the diacetate **1a** have shown that in benzene and in chloroform substantial dissociation into the two monomeric units **2** occurs at concentrations below 0.02 mol dm⁻³. A reversible dissociation of their dimeric structures into the individual monomers also accounts for the equilibria that are established in solutions of two different distannoxanes [9]. It may be concluded that while the structures of the distannoxanes in solution “are basically the same as those in the solid

state” [10], dissociation into the monomeric form does occur to some extent, particularly at low concentrations.



- a: X = Y = O · CO · Me;
- b: X = Y = O · CO · CF₃
- c: X = Y = O · CO · (CH₂)₁₀ · Me
- d: X = Y = O · CO · Ph
- e: X = Y = Cl
- f: X = Cl, Y = OH
- g: X = Cl, Y = O · CO · Me
- h: X = Cl, Y = O · CO · CF₃
- i: X = Cl, Y = O · CO · (CH₂)₁₀ · Me
- j: X = Cl, Y = O · CO · Ph

For the reasons given in this paper, we believe that at the concentrations normally used to catalyse urethane formation it is the monomeric form of the distannoxanes which is largely responsible for their catalytic activity, and that binuclear species structurally-related to this monomeric form are also the catalytically-active species

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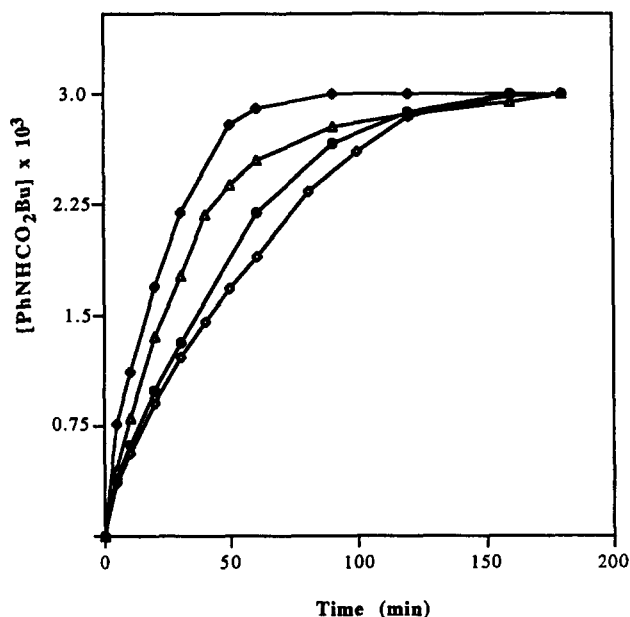


Fig. 1. Concentration of urethane (mol dm^{-3}) as a function of time in the reaction between PhNCO ($3 \times 10^{-3} \text{ mol dm}^{-3}$) and BuOH (0.45 mol dm^{-3}) in the presence of a tin(IV) catalyst ($[\text{Sn}] = 4 \times 10^{-5} \text{ mol dm}^{-3}$): (◇) **1b**; (●) **1a**; (△) **1c**; (◆) **1d**.

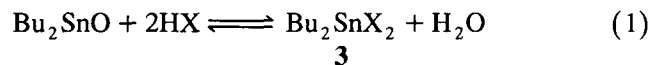
when other tin(IV) compounds are used to catalyse urethane formation.

2. Results and discussion

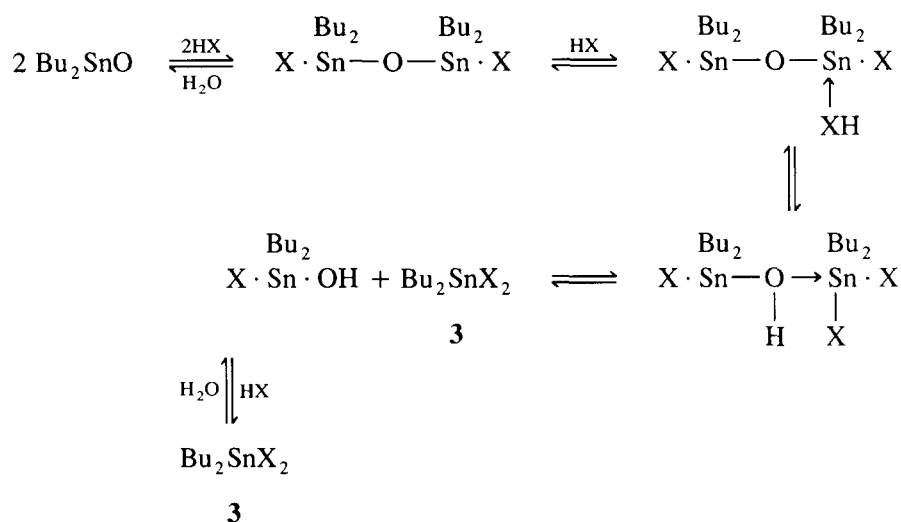
Two distinct steps are involved in the mechanism proposed by Otera et al. [2] for the catalysis of the reaction between alcohols and isocyanates by the distannoxanes **1**, the first of which is the replacement of the ligand *Y* by the alkoxy group of the alcohol. The viability of this step was convincingly demonstrated by these workers [11] for several hydroxy distannoxanes **1**, *Y* = OH (but not for the diacetate **1a**), which were found to be rapidly converted into the corresponding alkoxy compounds when treated in chloroform with ten molecular equivalents of an alcohol. This conversion was readily observed by means of ^{119}Sn NMR. We have prepared the 1,3-dilaurate **1c** and found that in urethane formation this diester has approximately the same level of catalytic activity as the diacetate **1a** (see Fig. 1). When butanol is added to a solution of the dilaurate in chloroform, however, the only changes which occur in the ^{119}Sn NMR spectrum are those which result from the decrease in the concentration of the distannoxane, i.e. the signal ($\delta = 150$) due to the monomeric species **2c** increases in intensity at the expense of the two signals ($\delta = 204$ and -217) which are due [8] to the dimer. By analogy with the dibutyltin diesters [12], some alcoholysis of the dilaurate would be expected, but obviously the extent to which this occurred is not

sufficient to be detected by ^{119}Sn NMR spectroscopy. This indicates that the distannoxane **1c** is not required to undergo alcoholysis to the substantial extent exhibited by the hydroxy distannoxanes in order for it to function as a urethane-forming catalyst. The same observation also applies to the 1,3-dichloro compound **1e**. When this compound is refluxed in methanol for 2 h, replacement of Cl by OMe occurs only to the extent of about 5% [2], and yet the dichloro compound is still quite an effective catalyst for urethane formation at room temperature, albeit not as effective as the hydroxy chloride **1f** [1,2].

The second step in the mechanism proposed by Otera et al. involves one end of each of the two monomeric units which are present in the distannoxane dimer [2]. In this connection we note that, on the basis of the data reported by Okawara and coworkers [7,8], at the low concentration of $2.5 \times 10^{-5} \text{ mol dm}^{-3}$ used by Yokoo et al. [1] to effect urethane formation the diacetate **1a** probably exists almost entirely in the form of the monomer **2a**. It seems highly likely, therefore, that it is this monomer rather than the parent dimer which is catalytically active. If this is so, it follows that one of many factors which determine the catalytic activity of a specific distannoxane could be the extent to which it dissociates in solution. This could be the main reason why the dichloro compound **1e**, with its strong intramolecular Sn–Cl bonds, is less effective as a urethane-forming catalyst than the diacetate **1a**.



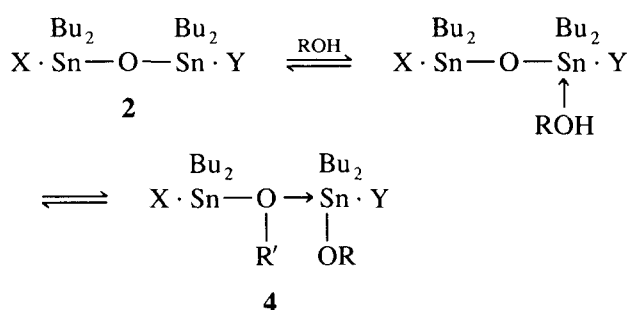
In order to explain the manner in which the monomeric form of a distannoxane might function as a catalytic species it is convenient to refer to a number of reactions which are used for preparing a variety of diorganotin(IV) compounds of the general type **3**, and which collectively are summarised by Eq. (1). These reactions include the treatment of dibutyltin oxide (or an analogous dialkyltin oxide) with a hydrogen halide [13], a thiol [14], a carboxylic acid [15], and nitric acid [5b], i.e. *X* = halogen, SR, O · CO · R, and O · NO₂ respectively. All of these reactions, and the reverse hydrolyses to form the dialkyltin oxide, are known to proceed via the corresponding distannoxane, $\text{X} \cdot \text{Sn}(\text{Bu})_2 \cdot \text{O} \cdot \text{Sn}(\text{Bu})_2 \cdot \text{X}$, which can often be isolated (in the dimeric form) by controlling the reaction conditions. For example, whereas a 1:2 ratio of dibutyltin oxide and a carboxylic acid affords the dibutyltin dicarboxylate, a 1:1 ratio affords the 1,3-dicarboxylato distannoxane [16]. With phenols, the reaction with dibutyltin oxide in refluxing toluene stops at the distannoxane stage even when an excess of the phenol is used [17], and azeotropic distillation in boiling decalin is necessary to obtain the dibutyltin diphenoxide [18]. Conversely, while the complete hydrolyses of dibutyltin dihalides and dicarboxyl-



Scheme 1.

ates afford dibutyltin oxide [14b], partial hydrolysis affords the corresponding 1,3-dihalo and 1,3-dicarboxylato distannoxanes respectively [4,7].

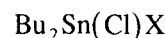
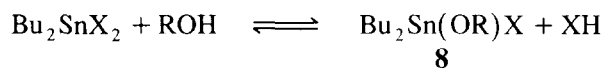
When HX is a weak acid, the most likely process by which the distannoxane that is an intermediate in reaction (1) undergoes cleavage to yield two molecular equivalents of the mononuclear product **3** is shown in Scheme 1. This process, which is based on standard tin(IV) chemistry, proceeds via a binuclear μ -hydroxy species which is formed by coordination of the reagent XH with one of the tin atoms in the distannoxane followed by proton transfer to the bridging oxygen atom. When HX is a strong acid, such as a hydrogen halide or nitric acid, the same species is almost certainly involved, but in this case protonation of the bridging oxygen of the distannoxane is more likely to be the initial step.¹



The plausibility of Scheme 1 suggests that in the presence of an alcohol the monomeric form **2** of a distannoxane **1** exists in equilibrium with the μ -hydroxy binuclear alkoxide **4**, $\text{R}' = \text{H}$, and that the species **4**, $\text{R}' = \text{H}$, $\text{X} = \text{Y} = \text{OR}$, is one of the intermediates involved when dibutyltin oxide reacts with alcohols to

give the corresponding dibutyltin dialkoxide. Although examples of this reaction have been reported in the patent literature [19], it is not a viable route to dialkyltin dialkoxides because the reaction (as with phenols) normally stops at the distannoxane stage [14c], and its use is largely restricted to the preparation of 1,3,2-dioxastannolanes and 1,3,2-dioxastannins from dibutyltin oxide and 1,2- and 1,3-diols respectively [20].

We believe that it is a binuclear alkoxide of the type **4**, $\text{R}' = \text{H}$, which is the actual catalytic species involved when distannoxanes **1** are used to catalyse urethane formation, and that it functions as shown in Scheme 2. Coordination of the isocyanate with one of the tin atoms in the species **4a** affords the adduct **5a** in which the isocyanate is activated towards nucleophilic attack because of electron-withdrawal by the tin. The presence of the μ -hydroxy group allows the nucleophilic alkoxy group on the other tin atom to be transferred onto the activated isocyanate via a six-membered ring transition state. Although the resultant *N*-stannylurethane **6a** could undergo intermolecular alcoholysis to form the parent urethane **7**, an alternative possibility is the one shown in the scheme. Coordination of the alcohol with the second tin atom, followed by proton transfer (again via a six-membered ring transition state), gives the urethane and also regenerates the catalytic species **4a**.

**10****a:** $\text{X} = \text{O} \cdot \text{CO} \cdot \text{R}'$ **b:** $\text{X} = \text{SR}'$ **c:** $\text{X} = \text{O} \cdot \text{CO} \cdot \text{Me}$ **d:** $\text{X} = \text{O} \cdot \text{CO} \cdot \text{CF}_3$

¹ We are grateful to a referee for pointing this out.

- e: $X = O \cdot CO \cdot (CH_2)_6 \cdot Me$
 f: $X = O \cdot CO \cdot Ph$
 g: $X = O \cdot CO \cdot (4-MeO \cdot C_6H_4)$
 h: $X = O \cdot CO \cdot (2-MeO \cdot C_6H_4)$
 i: $X = O \cdot CO \cdot CH_2 \cdot O \cdot (CH_2)_2OMe$
 j: $X = O \cdot CO \cdot CH_2SMe$

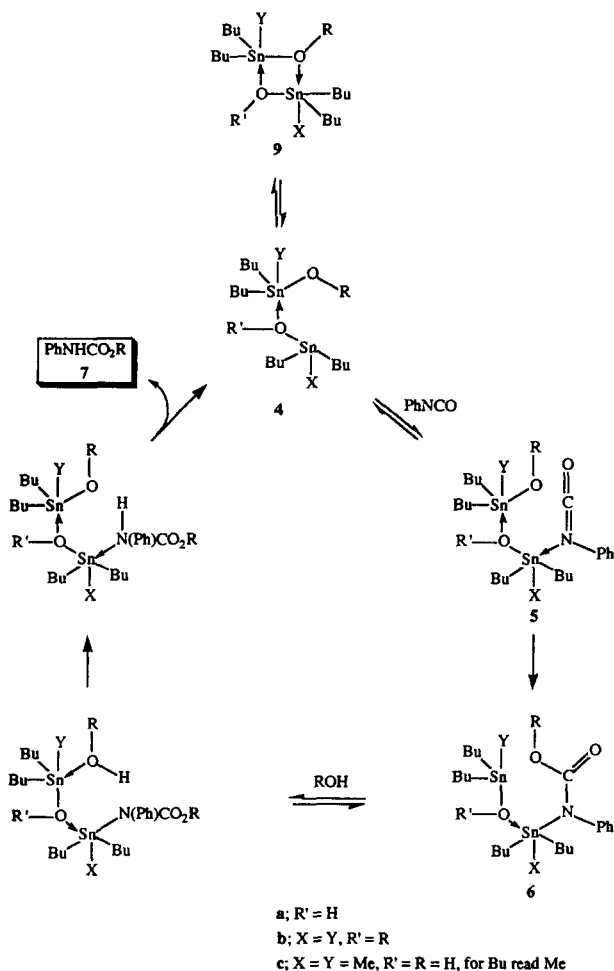
One attractive feature of this mechanism for urethane formation is that not only does its intramolecularity explain the very high catalytic activity of the distannoxanes, which we have found to be exhibited even at concentrations as low as 10^{-6} mol dm $^{-3}$, but that it can be extended to account for the high catalytic activity of a number of tin(IV) compounds, e.g. the dibutyltin diesters **3a** and dithiolates **3b** [12,21]. Evidence that these compounds function as urethane-forming catalysts by initially undergoing partial alcoholysis to give the corresponding mixed alkoxide **8** was presented in a previous paper [12], and was accompanied by the observation that alkoxides of this type are almost certainly oligomeric in nature. By analogy with other tin(IV) alkoxides [22], the most likely oligomer of an alkoxide of type **8** is the cyclic dimer **9b** (see Scheme 2). With

phenyl isocyanate this would be expected to generate the adduct **5b**, which could then participate in the catalytic cycle as described above.

A similar explanation can also be used to account for the catalytic activity [2] of trimethyltin hydroxide, which in solution exists as the cyclic dimer **9c** [23]. In complete contrast to the hydroxy distannoxanes, no substitution of OH by OMe occurs when trimethyltin hydroxide is refluxed in methanol [2], indicating that the equilibrium between the cyclic dimer and the open-chain form **4c** heavily favours the former species. However, in the presence of the strong σ -donor, phenyl isocyanate, ring-opening to give the complex **5c** would be expected to occur to some extent. The transference of OH onto the coordinated isocyanate followed by alcoholysis of the resultant **6c** would afford the carbamic acid, **7**, $R = H$, together with the corresponding tin species **4** in which the group R is now the alkyl group of the alcohol. Subsequent catalytic cycles would therefore afford the urethane.

The catalytic cycle shown in Scheme 2 requires that the dimeric structures involved should be stable towards dissociation into their individual monomeric units at catalytic concentrations, and that they are therefore more stable towards dissociation than the distannoxanes **1**. We believe that this is the case, and that this higher stability is due to the oxygen atoms in tin hydroxides and alkoxides having a much higher Lewis acidity towards tin(IV) than the bridging oxygen atom of a distannoxane. This view is supported by the failure of trimethyltin hydroxide to undergo methanolysis (see above), and the fact that in chloroform and at a concentration of 0.02 mol dm $^{-3}$ the tin dialkoxide, 2,2-dibutyl-1,3,2-dioxastannolane, exists exclusively as oligomers with no detectable amount of the monomer present [22a]. These are the conditions under which the distannoxanes **1** are extensively dissociated [7].

The formation of the μ -hydroxy binuclear alkoxide **4**, $R' = H$, from the distannoxane **2** is a basic part of the mechanism proposed above for distannoxane-catalysed urethane formation, and involves proton transfer to the bridging oxygen atom. In transition metal chemistry, the formation of a μ -hydroxy bridging ligand by protonation of a bridging oxygen atom in a binuclear complex is a frequently encountered process [24], and in recent years it has become of particular importance in connection with the chemistry of those oxygen-bridged di-iron systems which are present at the active site of a number of non-haem enzymes such as methane mono-oxygenase, ribonucleotide reductase, and the purple acid phosphatases [25]. Many oxo-, hydroxy-, and alkoxy-bridged di-iron(III) complexes, i.e. complexes directly analogous to **2**, **4a**, and **4b** respectively, have been synthesised to provide models for these active sites [26], and on the basis of the mechanism proposed in Scheme 2 it was predicted that several of these complexes would



Scheme 2.

exhibit a high level of catalytic activity in urethane-formation. This prediction has, in fact, now been confirmed [27], thus providing strong supporting evidence for the mechanism shown in the scheme.

Returning to the high catalytic activity of the distannoxanes, it was claimed by Yokoo et al. [1] that the diacetate **1a** is a more effective catalyst for urethane formation than dibutyltin dilaurate **3e**. In fact, no evidence was provided to support this claim, and the data reported by these workers concern the relative ability of **1a** and **3e** to catalyse the reaction of phenyl isocyanate with water, not with an alcohol. In order to allow direct comparisons to be made, we have compared the ability of a number of tin(IV) compounds to catalyse the reaction between phenyl isocyanate and butanol in chloroform at room temperature and found that when both types of compound are used at the same tin concentration (4×10^{-5} mol dm⁻³), the tetrabutylstannoxanes are less active as catalysts than the corresponding dibutyltin species. Thus, the distannoxane diesters, **1a**,

1c, and **1d**, are less active than the corresponding diesters **3c**, **3e**, and **3f** (see, for example, Fig. 2 for the two diacetates **1a** and **3c**), and the distannoxane chloride esters **1g**, **1i**, and **1j**, are less active than the corresponding chloride esters **10c**, **10e**, and **10f**, (see Fig. 2 for the chloride acetates **1g** and **10c**).

With the distannoxane diesters the catalytic activity increased in the order: trifluoroacetate < acetate < laurate < benzoate (see Fig. 1). The order: acetate < laurate < benzoate was also observed with the dibutyltin diesters, but with the distannoxane chloride esters and the dibutyltin chloride esters the order was laurate < acetate < benzoate. Relatively little difference was observed between the catalytic activities of the two aromatic dibutyltin diesters, **3f** and **3g**.

The dibutyltin chloride esters showed the highest activity of all the tin(IV) compounds examined. This is not unexpected, for on the basis of the Lewis acidity of Ph₃SnCl being higher than that of Ph₃Sn · O · CO · Me [28], greater activation of the isocyanate would be ex-

Table 1

Melting point, analysis, FTIR and ¹H NMR data for 1-chloro-3-carboxylato tetrabutylstannoxanes, 1,3-dicarboxylato tetrabutylstannoxanes, dibutyltin chloride carboxylates and dibutyltin dicarboxylates

Compound	M.p. (°C)	Analyses (%) found (calc.)		$\nu(\text{CO})$ (cm ⁻¹)	¹ H NMR data (δ)
		C	H		
1b	142–144	34.15 (33.94)	5.15 (5.13)	1661	0.92 (m); 1.40 (m); 1.66–1.86 (m) [Bu];
1c	— ^a	54.65 (54.57)	9.38 (9.39)	1563	0.86–1.14 (m), 1.22–1.52 (m); 1.52–1.81 (br); 2.20 (m) [Bu] and ligand protons
1d	59–62	49.51 (49.76)	6.42 (6.40)	1549	0.59–1.00 (m), 1.14–1.46 (m); 1.48–1.94 (m) [Bu]; 7.46 (t, 4-H); 7.56 (t, 3-H); 8.00 (d, 2-H)
1g	47–50	37.47 (37.57)	6.78 (6.82)	1567	0.9 (m); 1.36–1.62 (m) [Bu]; 1.96 (s, OAc)
1h	46–48	34.68 (34.30)	5.70 (5.76)	1662	0.9 (m); 1.40–1.44 (m); 1.49–1.96 (m) [Bu]
1i	— ^a	46.76 (46.93)	8.26 (8.29)	1562	0.9 (m); 1.18–1.46 (m); 1.52–1.81 (m, O ₂ C(CH ₂) ₁₀) [Bu] and ligand protons
1j	— ^a	43.46 (43.27)	6.54 (6.47)	1596	0.6–1.0 (m); 1.32 (m); 1.50–1.94 (m) [Bu]; 7.46 (t, 4-H); 7.56 (t, 3-H) 7.92 (d, 2-H)
3g	154–156	53.92 (53.86)	5.80 (6.03)	1576	0.93 (t); 1.42 (m); 1.80 (m) [Bu]; 3.90 (s, OMe); 6.94 (d, ³ J 7.2, 3, 5-H); 8.06 (d, ³ J 7.2, 2, 6-H)
10e	28–30	51.58 (51.36)	8.68 (8.84)	1587	0.94 (m); 1.16–1.47 (m); 1.52–1.84 (m); 2.38 (t) [Bu] and ligand protons
10g	26–27	45.98 (45.81)	6.04 (6.01)	1578	0.94 (m); 1.38 (m); 1.75 (m) [Bu]; 3.86 (s, OMe); 6.92 (d, ³ J 7.2, 2, 6-H); 8.06 (d, ³ J 7.2, 3, 5-H)
10h	40–45	45.52 (45.81)	5.83 (6.01)	1599	0.9 (m); 1.40 (m); 1.75 (m) [Bu]; 3.86 and 3.95 (2 × s, chelated and non-chelated OMe); 6.92 (d, ³ J 7.2, 2-H); 8.06 (d, ³ J 7.2, 3-H)
10i	52–56	38.73 (38.89)	6.56 (6.78)	1585	0.90 (t); 1.42 (m); 1.74 (m) [Bu]; 3.38 (s, OMe); 3.58 (t, MeOCH ₂ CH ₂); 3.71 (t, MeOCH ₂ CH ₂); 4.22 (s, OCH ₂ CO ₂)
10j	42–45	35.14 (35.37)	5.87 (6.21)	1559	0.96 (t); 1.40 (m); 1.76 (m) [Bu]; 2.25 (s, SMe); 3.30 (s, MeSCH ₂ CO ₂)

^a Colourless liquid at room temperature.

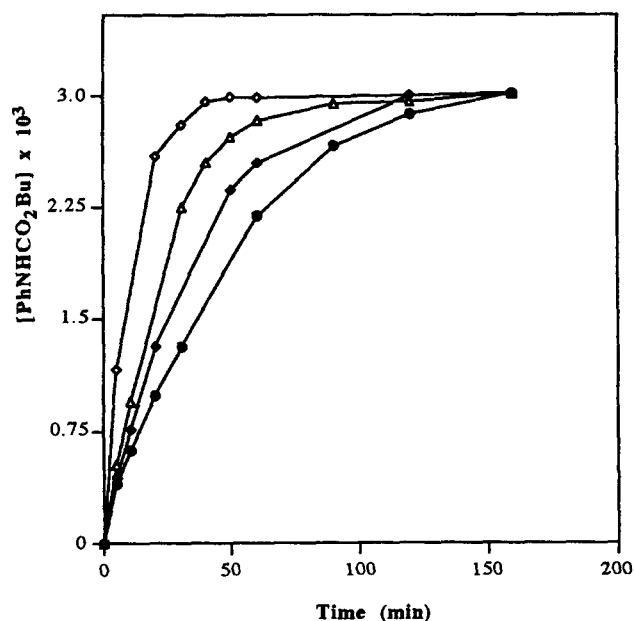


Fig. 2. Concentration of urethane (mol dm^{-3}) as a function of time in the reaction between PhNCO ($3 \times 10^{-3} \text{ mol dm}^{-3}$) and BuOH (0.45 mol dm^{-3}) in the presence of a tin(IV) catalyst ($[\text{Sn}] = 4 \times 10^{-5} \text{ mol dm}^{-3}$): (●) **1a**; (◆) **3c**; (△) **1g**; (◇) **10c**.

pected from coordination with the tin in the species **5** when $X = \text{Cl}$ than when $X = \text{O} \cdot \text{CO} \cdot \text{R}'$.

Physical data for those compounds described in this

paper, but whose preparations have not been reported previously, are given in Tables 1 and 2.

3. Experimental details

The general procedures used were those described in a previous paper [12]. Dibutyltin dicarboxylates and dibutyltin chloride carboxylates were prepared from dibutyltin oxide using the general methods described in Refs. [15] and [29] respectively, while 1-chloro-3-carboxylato- and 1,3-dicarboxylato-1,1,3,3-tetrabutyl-distannoxanes were prepared by the following representative methods.

3.1. Preparation of 1-chloro-3-trifluoroacetoxy-1,1,3,3-tetrabutyl-distannoxane (**1h**) and 1,3-bis(trifluoroacetoxy)-1,1,3,3-tetrabutyl-distannoxane (**1b**)

A mixture of 1,3-dichloro-1,1,3,3-tetrabutyl-distannoxane **1e** [4] (1.5 g, 2.7 mmol), silver trifluoroacetate [30] (0.6 g, 2.7 mmol) and dry toluene (20 ml) was stirred at room temperature in the dark for 22 h, and then the silver chloride was removed by filtration and washed with dry toluene (15 ml). The filtrate and washings were combined, and the solvent was removed under reduced pressure to leave a quantitative yield of

Table 2

^{13}C NMR data for 1-chloro-3-carboxylato tetrabutyl-distannoxanes, 1,3-dicarboxylato-tetrabutyl-distannoxanes, dibutyltin chloride carboxylates and dibutyltin dicarboxylates

Compound	Bu–Sn carbons	^{13}C NMR data	
		Carbonyl	Ligand R carbons
1b	13.45, 26.64 ($^1J(^{119}\text{Sn}-^{13}\text{C})$ 504 Hz), 26.77, 26.95, 27.12, 27.33, 28.17, 26.69	179.84 ($^2J(^{19}\text{F}-^{13}\text{C})$ 39 Hz)	115.49 ($^1J(^{19}\text{F}-^{13}\text{C})$ 288 Hz)
1c	13.71, 26.78 ($^1J(^{119}\text{Sn}-^{13}\text{C})$ 504 Hz), 26.91, 27.05	179.84	14.15, 22.76, 25.90, 27.42, 27.69, 29.42, 29.52, 29.59, 29.72, 32.00, 36.48
1d	13.59, 13.68, 26.87, ($^1J(^{119}\text{Sn}-^{13}\text{C})$ 468 Hz), 27.42, 27.59, 27.91, 28.50, 30.03	172.84	128.20, 129.93, 132.08, 133.51
1h	13.55, 26.63 ($^1J(^{119}\text{Sn}-^{13}\text{C})$ 504 Hz), 26.95, 27.12, 27.23, 27.38, 29.85, 29.93	161.40 ($^2J(^{19}\text{F}-^{13}\text{C})$ 39 Hz)	115.36 ($^1J(^{19}\text{F}-^{13}\text{C})$ 288 Hz)
1i	13.68, 26.84 ($^1J(^{119}\text{Sn}-^{13}\text{C})$ 504 Hz), 27.29, 27.38	180.00	14.14, 22.74, 25.81, 26.70, 27.43, 27.53, 29.39, 29.52, 29.63, 29.69, 31.98
1j	13.59, 13.68, 26.87, 27.42, 27.59, 28.50, 30.03	172.84	128.20, 129.93, 132.08, 133.51
3g^a	13.09, 25.63, 26.51, 26.69	169.16	54.87, 112.98, 122.52, 131.32, 162.70
10e	13.58, 26.69 ($^1J(^{119}\text{Sn}-^{13}\text{C})$ 468 Hz), 26.79, 27.03	184.25	14.17, 22.75, 25.43, 25.90, 26.38, 29.30, 29.40, 29.54, 29.67, 31.98, 33.79
10h	13.51, 26.28 ($^1J(^{119}\text{Sn}-^{13}\text{C})$ 504 Hz), 26.60, 26.69	175.00	56.16, 111.96, 117.93, 120.48, 133.48, 134.72, 159.70
10i	13.47, 26.67, ($^1J(^{119}\text{Sn}-^{13}\text{C})$ 504 Hz), 26.87, 27.04	178.69	58.97, 68.46, 70.52, 71.67
10j	13.41, 26.13, ($^1J(^{119}\text{Sn}-^{13}\text{C})$ 504 Hz), 26.27, 26.71	180.45	16.47, 35.30

^a Spectrum recorded in $\text{DMSO}-d_6$.

analytically pure **1h** as a white solid, m.p. 46–48°C. When the experiment was repeated using 1.2 g (5.4 mmol) of silver trifluoroacetate, a quantitative yield of the analytically pure distannoxane **1b**, m.p. 142–144°C, was obtained.

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