

Investigation of dialkyltin compounds as catalysts for the synthesis of dialkyl carbonates from alkyl carbamates

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Abstract

New syntheses for dibutyldimethoxytin, dibutyldiisocyanatotin and 1,1,3,3-tetrabutyl-1,3-diisocyanatodistannoxane as well as the novel compounds dibutylisocyanatomethoxytin and 1,1,3,3-tetrabutyl-1-methoxy-3-isocyanatodistannoxane are described. These compounds were characterized by elemental analyses as well as ^{119}Sn , ^{13}C , and proton NMR, FTIR, MS and HPLC. They were found to have good catalytic activity for the synthesis of symmetrical dialkyl carbonates from alkyl carbamates and the corresponding alcohols. Extensive NMR and IR data indicate that tin compounds containing both an alkoxy and an isocyanato moiety bounded to tin are reaction intermediates in the synthesis of dialkyl carbonate and their formation is a key step in this catalytic process. The mechanism of carbonate synthesis involves the interconversion of the various tin species present in the reaction mixture to these reaction intermediates. Dibutyldimethoxytin, dibutylisocyanatomethoxytin and 1,1,3,3-tetrabutyl-1-methoxy-3-isocyanatodistannoxane have similar activity and are more active (10–14%) than dibutyloxotin for the synthesis of symmetrical dialkyl carbonates. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Dialkyltin; Dialkyl carbonates; Catalyst

1. Introduction

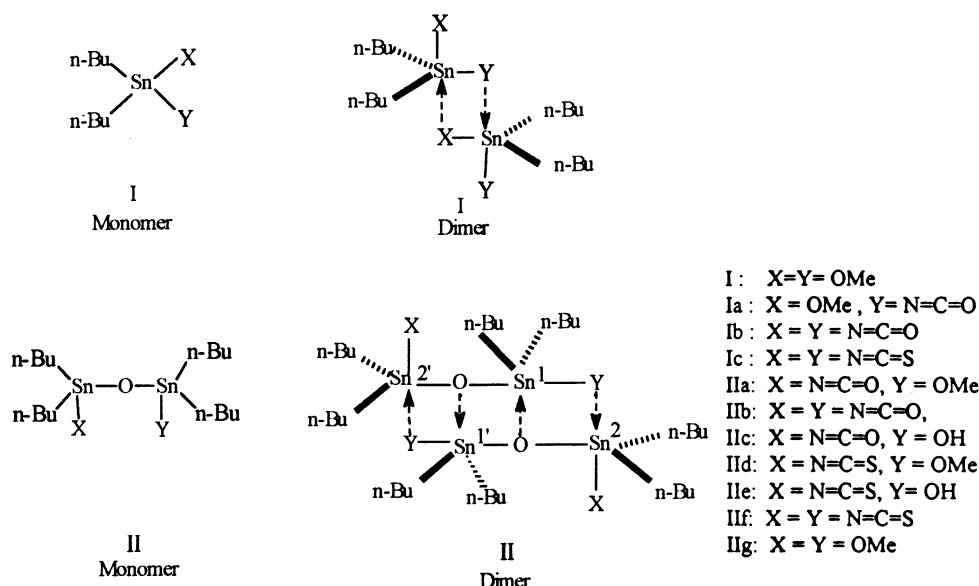
Recent efforts have been directed to the replacement of toxic chemicals such as phosgene and dimethyl sulfate with environmentally friendly reagents such as dimethyl carbonate (DMC). DMC is a versatile chemical reagent that can replace phosgene in the syntheses of pharmaceuticals, agro chemicals, dyes and polymers [1]. It can also function as an alkylating agent [1]. DMC has good solvent power compared to ethyl acetate. It can also be used as a fuel additive for the enhancement of the octane number [2]. The standard method for preparing organic carbonates involves the treatment of alcohols with phosgene. New methods for the manufacture of DMC which do not employ phosgene are based on the oxidative carbonylation of methanol with copper salts [1,3–6] or alkyl nitrates and platinum or palladium salts [7]. Alternatively, dimethyl and higher carbonate homologs can be synthe-

sized in a two step reaction from urea and an alcohol via a carbamate intermediate [Eq. (1)] [8,9]



The most active catalysts reported in the literature for the conversion of a carbamate to a carbonate are organotin derivatives such as dibutyldimethoxytin, (Scheme 1) [8,9]. Dibutyldimethoxytin is more effective as a catalyst for the synthesis of carbonates than dibutyloxotin [8], however, dibutyldimethoxytin is also an order of magnitude more expensive than dibutyloxotin. Hence, an inexpensive synthetic route to the former material was developed based on dibutyloxotin, which would also allow catalyst regeneration to be accomplished in a cost-effective manner should deactivation occur. An effort was also made to synthesize other organotin compounds which, potentially, could have higher catalytic reactivity than those reported in literature.

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Scheme 1. Conversion of carbamate to carbonate using the organotin derivative dibutyldimethoxytin.

The synthesis of dibutyldiisocyanatotin, **Ib**, based on dibutyldichlorotin has been published [10]. Compounds **IId**, **e**, and **f** have also been described earlier [11–13]. However, organotin compounds which combine both the methoxy and isocyanato groups in the same molecule as in dibutylisocyanatomethoxytin, **Ia**, and 1,1,3,3-tetrabutyl-1-methoxy-3-isocyanatodistannoxane, **IIa**, have not been reported in the literature to date. Dibutyloxotin is a convenient starting material for the synthesis of dibutyldiisocyanato-tin, **Ib**, 1,1,3,3-tetrabutyl-1,3-diisocyanatodistannoxane, **IIb** and 1,1,3,3-tetrabutyl-1-methoxy-3-isocyanatodistannoxane, **IIa**.

Stannoxanes and distannoxanes of type **I**, **II** respectively are known to exist as dimers bound via pentacoordinated tin atoms. [11–15]b However, dimers of type **I** exhibit a single peak in ^{119}Sn -NMR corresponding to two equivalent pentacoordinated tin atoms while the distannoxanes dimers, of type **II** exhibit pairs of non-equivalent pentacoordinated tin atoms (Table 1). The two Sn(1) atoms in **II** form an internal four membered ring structure via bridging by the oxygen linkage, whereas both Sn(2) atoms coordinate via Y substituents resulting in external four-membered rings. Thus, the catalytic activity of these compounds may also be a function of the state of aggregation of the catalyst (Scheme 1).

The objective of this study was to evaluate the catalytic properties of various dialkyltin compounds which

can be readily synthesized from dibutyloxotin. Based on the technical literature and our experimental results, the scheme shown in Fig. 1 summarizes the various equilibria which exist when dibutyloxotin is treated with methanol and methylcarbamate.

2. Results and discussion

2.1. Synthesis of dibutyldimethoxytin, **I**

One synthetic route for the preparation of dibutyldimethoxytin involves the reaction of dibutyldichlorotin with sodium methoxide [16]. The crude dibutyldimethoxytin is subsequently purified by vacuum distillation. The cost of dibutyldimethoxytin prepared using the above process is high which prompted our investigation of alternative synthetic routes using relatively inexpensive starting materials. Dibutyltin dialkoxides based on primary alcohols have been synthesized via a two step reaction. The first step involves condensation of dibutyloxotin with a primary alcohol in refluxing benzene or toluene at 80–110°C, to produce a 1,1,3,3-tetrabutyl-1,3-dimethoxydistannoxane with concurrent azeotropic removal of water. In the second step the distannoxane undergoes disproportionation at 180–220°C under reduced pressure to produce dibutyldialkoxytin and dibutyloxotin [17] [Eq. (2)]:

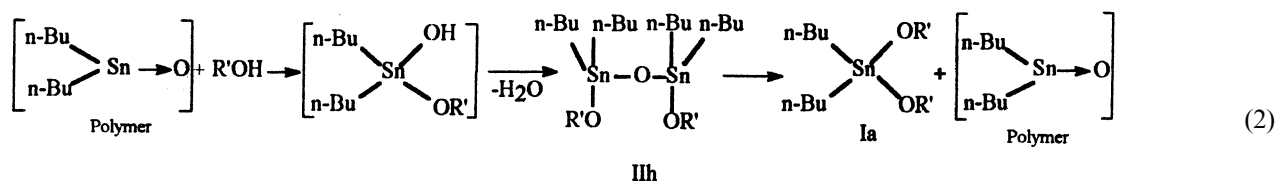
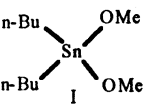
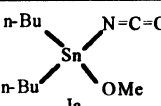
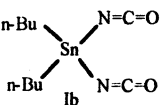
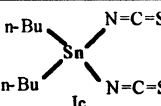
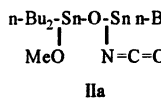
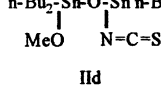
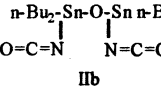
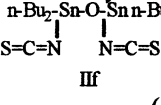
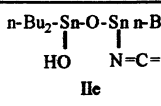
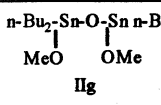


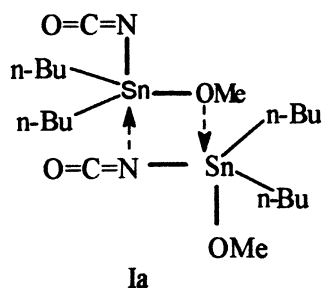
Table 1
Spectra data

COMPOUND	NMR/ppm			IR	
	^{119}Sn	^{13}C			
		N=C=X*	OMe	N=C=X*	OCH ₃
	δ	δ	δ	cm^{-1}	
 (Lit.) (16)	(Lit.) (-160) (24)		51.95	(Lit.) (1069) (1038)	(Lit.) (20)
 Ia	-180	128.10	51.44	2206 2178	1080 1037
 Ib (10)	-71.6	128.30		2209 (2194) 2178 (2173) (21)	
 Ic (25)	-128(br)	128		2064 2010	
	Sn1; Sn2				
 IIa	-166; -206	128.0	50.64	2204	1060 1024
 IIb (13)	(-161; -208) (13)	139.50	50.64	2053	1052 1024
 IIc (10)	-148; -169	130.68		2209 2190	
 IId (12,25)	(-147; -168) (14,15a)	147.83		2021 1959	
 IIe (12)	(-162; -211) (14,15a)			2064	
 IIg (17)	(-173; -185) (26)		51.04		1067 1020

X* = O, S

Owing to the low boiling point of methanol the above procedure is not effective for the synthesis of either dibutyldimethoxytin or the corresponding distannoxane. The reaction of dibutyloxotin with dimethyl carbonate (in the presence of traces of methanol) in refluxing toluene produces 1,1,3,3-tetrabutyl-1,3-

dimethoxydistannoxane, **IIg**, exclusively, as described by Davies [17]. We have discovered that dibutyldimethoxytin can be synthesized by reacting dibutyloxotin with methanol and dimethyl carbonate at elevated temperatures and pressures [18] (Scheme 2). Alternatively, one can use 1,1,3,3-tetrabutyl-1,3-



The Me–O bands at 1080 and 1037 cm^{-1} and two bands for $\text{N}=\text{C}=\text{O}$ at 2206 and 2178 cm^{-1} are indicative of the covalent and coordinate bonds of these groups, each of the lower frequencies corresponds to the respective coordinate bond as described for similar compounds [20,21] (Table 1). The ^{13}C -NMR spectrum displays a single resonance for OMe (δ 51.44) and $\text{N}=\text{C}=\text{O}$ (δ 128.10) indicating an averaged environment. A single resonance at δ –180, ca. 20 ppm upfield of **I**, is also observed using ^{119}Sn -NMR, which indicates pentacoordination of the tin atom [15]b. The facile formation of **Ia** by the reaction of **I** with methyl carbamate in the absence of a solvent (molar ratio 1:1) was monitored by ^{119}Sn - and ^{13}C -NMR. A 30% conversion of **I** to **Ia** was achieved at room temperature (r.t.). The conversion increased to 60% within minutes when heated to 65°C.

2.2.1. Reaction of dibutylisocyanatomethoxytin, **Ia** with methanol (Fig. 1)

The formation of **Ia** is a reversible reaction. With an excess methanol at higher temperature (175°C) the presence of methyl carbamate and dibutyldimethoxytin, **I** was detected.

2.2.2. Reaction of dibutylisocyanatomethoxytin, **Ia** with water

The presence of traces of water in the system results in the formation of distannoxanes [Eq. (3)]. This was evidenced by a decrease in melting point of **Ia** (65–80°C), the loss of the methoxy group (IR and ^{13}C -

NMR), the appearance of Sn–OH band at 3545 cm^{-1} (IR) as well as the appearance of the distannoxane dimer peaks in ^{119}Sn -NMR at δ –171, δ –211 ppm and broadening of the peak at δ –180 ppm. Similar chemistry has been reported for other tin derivatives such as **Ib** [10].

2.2.3. Reaction of dibutylisocyanatomethoxytin, **Ia** with benzyl alcohol

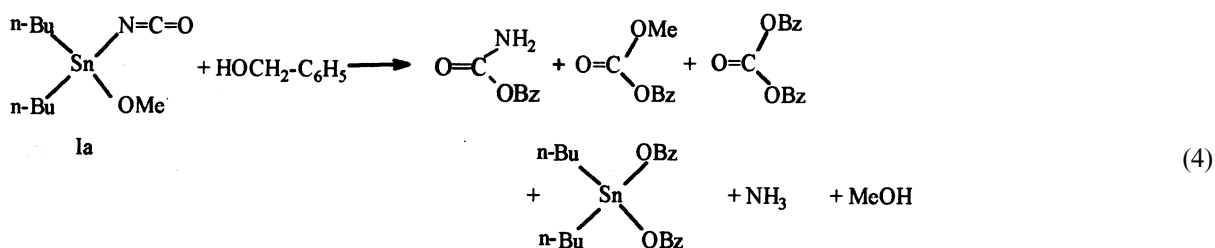
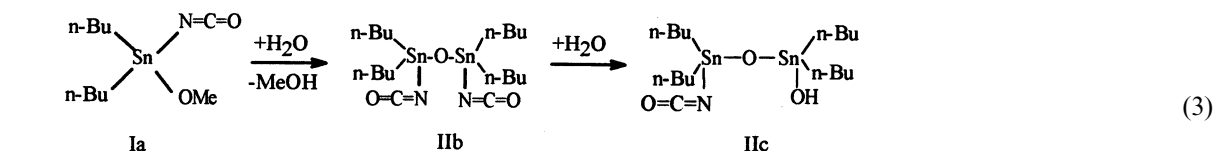
The reaction of **Ia** with benzyl alcohol at 175°C and atmospheric pressure yields benzyl carbamate, methyl benzyl carbonate, dibenzyl carbonate, dibutyldibenzoxytin, ammonia, and methanol [Eq. (4)]. These products were detected by ^{13}C -NMR, IR, GC and MS.

This experiment supports the hypothesis that dibutylisocyanatoalkoxytin compounds are plausible reaction intermediates in the formation of carbonates by the reaction of dibutyldialkoxytin with carbamates and alcohols.

2.3. Synthesis of dibutyldiisocyanatotin, **Ib**

Dibutyldimethoxytin, **I**, and excess methyl carbamate (mole ratio 1:2) in refluxing toluene (110°C) yields a mixture of compounds which include **Ia** and **Ib** as indicated by ^{119}Sn -NMR. However, in the absence of solvent at 175°C and atmospheric pressure, only dibutyldiisocyanatotin, **Ib**, was obtained after removal of MeOH and DMC (Fig. 1). The MS fragmentation via Cl/CH_4 and Cl/NH_3 displayed, among others, the parent peaks $\text{M} + \text{H}$ (317) and $\text{M} + \text{NH}_4$ (336), respectively.

Although compound **Ib** exhibits two bands for $\text{N}=\text{C}=\text{O}$ at 2209 and 2178 cm^{-1} , the observation of only a single peak at a high field frequency ^{119}Sn δ –71.6 (Table 1) indicates that the compound exists as a monomer containing only tetra coordinated tin atoms [15]b. This structure was also favored by Leung and Herber based on Mössbauer studies [21]. It is interesting that the corresponding dibutyldiisothiocyanatotin, **Ic**, exhibits two $\text{N}=\text{C}=\text{S}$ IR bands at 2064 and 2010 cm^{-1} and a broad ^{119}Sn peak at δ –128. This is



indicative of a polymeric structure, comprised of penta-coordinated tin nuclei and is consistent with earlier Mössbauer studies [22]. The fact, that **Ic** exists as a dimer while **Ib** is a monomer, is probably due to electronic differences between the $\text{N}=\text{C}=\text{O}$ and the $\text{N}=\text{C}=\text{S}$ ligands [23]. The ^{119}Sn -NMR data for compounds **Ib** and **Ic** are recorded here for the first time.

2.4. Synthesis of 1,1,3,3-tetrabutyl-1-methoxy-3-isocyanatodistannoxane, **Ila** from **Ilg** and methyl carbamate

1,1,3,3-Tetrabutyl-1,3-dimethoxydistannoxane, **Ilg**, was synthesized according to Davies [17]. The crude product was treated with a stoichiometric amount of methyl carbamate in toluene at 110°C to give 1,1,3,3-tetrabutyl-1-methoxy-3-isocyanatodistannoxane, **Ila**, (Fig. 1). The product **Ila** is a white powder with m.p. $124\text{--}128^\circ\text{C}$. It exhibits spectral data similar to those described for isothiocyanato **IId** [13] (Table 1). Two peaks, characteristic of a distannoxane dimer, appear at ^{119}Sn δ -166 and -206 . Coordination of the monomers occurs via the methoxy oxygen bond, not the $\text{N}=\text{C}=\text{X}$ ($\text{X} = \text{O}, \text{S}$) moiety. This structure is indicated by $\text{O}-\text{Me}$ IR bands at 1060 (covalent) and 1020 cm^{-1} (coordinated) but only a single $\text{N}=\text{C}=\text{O}$ band in the region $2204\text{--}2050\text{ cm}^{-1}$. Again, as for compound **Ia**, only one OMe peak was detected by ^{13}C -NMR which appears at δ 50.64 . The elemental analyses obtained for this compound are consistent with the proposed structure for **Ila**. The ^{119}Sn -NMR spectrum reveals two small peaks at δ -148 and -169 corresponding to the diisocyanato **Iib**. This is paralleled in ^{13}C -NMR by the appearance of two $\text{N}=\text{C}=\text{O}$ peaks at δ 128.80 and 128.0 along with two minor peaks at δ 137.70 and 126.16 .

The reaction of **Ilg**, with excess methyl carbamate at 110°C surprisingly gave the same result, with formation of **Ila** and only a small amount of the diisocyanato **Iib**.

2.4.1. Reaction of **Ila** with benzyl alcohol

Compound **Ila** reacts with benzyl alcohol at r.t. Heating to 175°C for 4 h, results in the nearly complete disappearance of the $\text{N}=\text{C}=\text{O}$ band, and the formation of a mixture of carbamates and carbonates as depicted in Eq. (4). This experiment supports the hypotheses that isocyanato alkoxy tin compounds are plausible reaction intermediates in the formation of carbonates.

2.5. Attempt to synthesize 1,1,3,3-tetrabutyl-1,3-diisocyanatodistannoxane, **Iib** from dibutyloxotin and methyl carbamate

The reaction of dibutyloxotin with methyl carbamate in toluene yields a white powder with m.p. $175\text{--}177^\circ\text{C}$ (Fig. 1). The material consists of a dimer of 1,1,3,3-

tetrabutyl-1,3-diisocyanatodistannoxane, **Iib**, and 1,1,3,3-tetrabutyl-1-hydroxy-3-isocyanatodistannoxane, **Iic**. The structures are supported by ^{119}Sn -NMR with resonances of diisocyanato derivative **Iib** at δ -148 and -169 (broad) and those of the hydroxyisocyanato **Iic**, at δ -162 and -212 , broad. It is interesting that these ^{119}Sn characteristics are similar to those of the analogous isothiocyanato compounds **IIf** and **Ile**. (Table 1). The elemental analysis for the dimer **Iib-Iic** is identical to that reported by Mufti [10]. Mufti interpreted the structure as the dimer **Iic-Iic** by omitting the nitrogen component. We propose that the compound has the **Iib-Iic** structure (Fig. 1) which is supported by the spectral evidence below. The ^{13}C -NMR spectra exhibits $\text{N}=\text{C}=\text{O}$ peaks at δ 130.68 and 129.96 and the IR reveals the two characteristic strong $\text{N}=\text{C}=\text{O}$ bands corresponding to the covalent and bridged bonds at 2209 and 2190 cm^{-1} .

The reaction of dimers **Iib-Iic** with MeOH at 175°C at the autogenic pressure of the system afforded methyl carbamate, urea, and **I**. The formation of these compounds were accompanied by the disappearance of the $\text{N}=\text{C}=\text{O}$ IR bands.

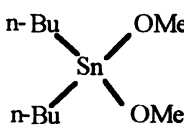
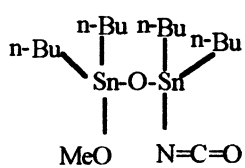
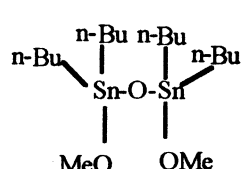
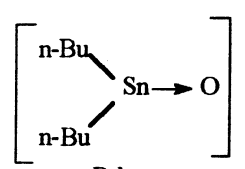
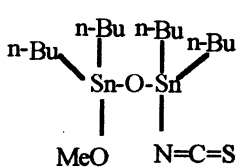
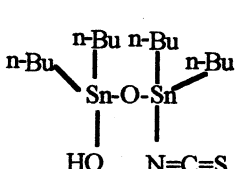
2.5.1. Evaluation of dialkyltin catalysts for the synthesis of bis-(2-ethylhexyl)-carbonate

The dialkyltin compounds described above were evaluated as catalysts for the synthesis of bis-(2-ethylhexyl)-carbonate from methyl carbamate and 2-ethyl-1-hexyl alcohol [Eq. (1)]. This reaction was selected because activity data for dibutyldimethoxytin and dibutyloxotin as catalysts have been published [8]. The use of a higher molecular weight alcohol than methanol allows evaluation of catalytic activity at elevated temperatures and ambient pressure. The first step of the reaction as indicated in Eq. (1) consists of the transesterification of methyl carbamate with 2-ethyl-1-hexyl alcohol to give the corresponding 2-ethyl-1-hexyl carbamate accompanied by the formation of methanol which is removed by distillation. Transesterification occurs during the heating period (20 min) required to raise the reaction temperature from r.t. to 190°C . The formation of the carbonate by alcoholysis of the amide group was monitored at 190°C by the evolution of ammonia as well as by an analysis of the reaction mixture using GC and ^{13}C -NMR. The data are summarized in Table 2.

The isothiocyanatotin compounds **IId** and **Ile**, which are transesterification catalysts [12,13] performed poorly because of decomposition at 190°C . Although the difference in activity between the other catalysts was not large, conversion of 92% for **I**, and **Ila** vs. 80%, for **Ilg**, and $n\text{-Bu}_2\text{SnO}$, these differences are real and they are based on a number of replicate runs. Dibutyldimethoxytin, **I**, has higher activity than dibutyloxotin, which agrees with previous literature data [8].

Table 2

Catalyst activity for the conversion of methyl carbamate to bis-(2-ethylhexyl)-carbonate

Catalyst	% Conversion*
 I	92
 IIa	92
 IIg	81
 Polymer	80
 IIId13	78
 IIe12	65

* % Conversion calculated based on ammonia released, selectivity in all cases was 100%.

Reaction Conditions	mmole	mole%
Methyl carbamate	240	24.60
2-Ethyl-1-hexyl alcohol	730	74.80
Catalyst	5meq	0.560
Temperature 190–195°C; Time 12 hr.		

2.6. Catalytic activity of **I** versus **IIg**

In order to determine the difference in activity between **I** and **IIg** the reaction was repeated at a higher catalyst concentration ($25 \times$) which enabled us to monitor the tin catalyst species by ^{119}Sn -, ^{13}C -NMR and FTIR. The key observations follow.

2.6.1. Increasing catalyst levels has a relatively small effect on reaction rate

The initial rates (0–1.5 h) for **I** and **IIg** at high level catalyst (0.5 mole catalyst/mole methyl carbamate) are about four times higher than those at low level catalyst (0.02 mole catalyst/mole methyl carbamate) (Fig. 2). Thus a twenty-five fold increase in catalyst concentration produced a four-fold increase in rate. At both catalyst levels **I** is more active than **IIg**.

At low catalyst concentration conversions of 80–90% were achieved in 12 h for **IIg** and **I** respectively, while at high catalyst concentration the same conversion (87%) was achieved in 6 h for both catalysts (Tables 2 and 3).

2.6.2. Spectroscopic data indicate that the $\text{Sn}-\text{OR}$ band of **I** undergoes a rapid conversion to $\text{Sn}-\text{N}=\text{C}=\text{O}$ with methyl carbamate at r.t. while **IIg** does not

Samples of the reaction mixture were taken after methyl carbamate had dissolved (65°C). The NMR spectra of these samples exhibit a broadening of the ^{119}Sn peaks corresponding to **I** and **IIg** indicative of the exchange between $\text{Sn}-\text{OMe}$ and $\text{C}_8\text{H}_{17}\text{OH}$ to give $\text{Sn}-\text{OC}_8\text{H}_{17}$ and methanol. The most significant difference between **I** and **IIg** is that **I** undergoes a rapid exchange of the $\text{Sn}-\text{OR}$ with methyl carbamate to form $\text{Sn}-\text{N}=\text{C}=\text{O}$ at low reaction temperature (65°C) while **IIg** requires a longer time and, or a higher reaction temperature. This exchange reaction was confirmed by the appearance of an isocyanato band (FTIR) at 2211 cm^{-1} . The experiment containing the isocyanato tin species, $n\text{-Bu}_2\text{Sn}(\text{N}=\text{C}=\text{O})(\text{OC}_8\text{H}_{17})$, produced 8% conversion to carbonate during the heating time to 190°C . The experiment utilizing catalyst **IIg** gave 0% conversion during the same heating time (Fig. 2, Table 3). Hence the isocyanatotin has a higher catalytic activity than **IIg**. The relative rate of conversion of distannoxane **IIg** to **IIa** is slow versus the relative rate of formation of **Ia** from **I**. (Fig. 1). The slower conversion of **IIg** to an active $\text{Sn}-\text{N}=\text{C}=\text{O}$ species is probably due to steric effects. It is interesting that distannoxane **IIa** which contains both methoxy and isocyanato moieties exhibits the same catalytic activity as **I** (Table 2), which supports the hypothesis that an isocyanatotin compound is an important intermediate in this synthetic route to carbonates. The relative rate of conversion of **IIa** to **Ia** is also slow, however **IIa** already contains the isocyanato moiety in the molecule and hence has high catalytic activity.

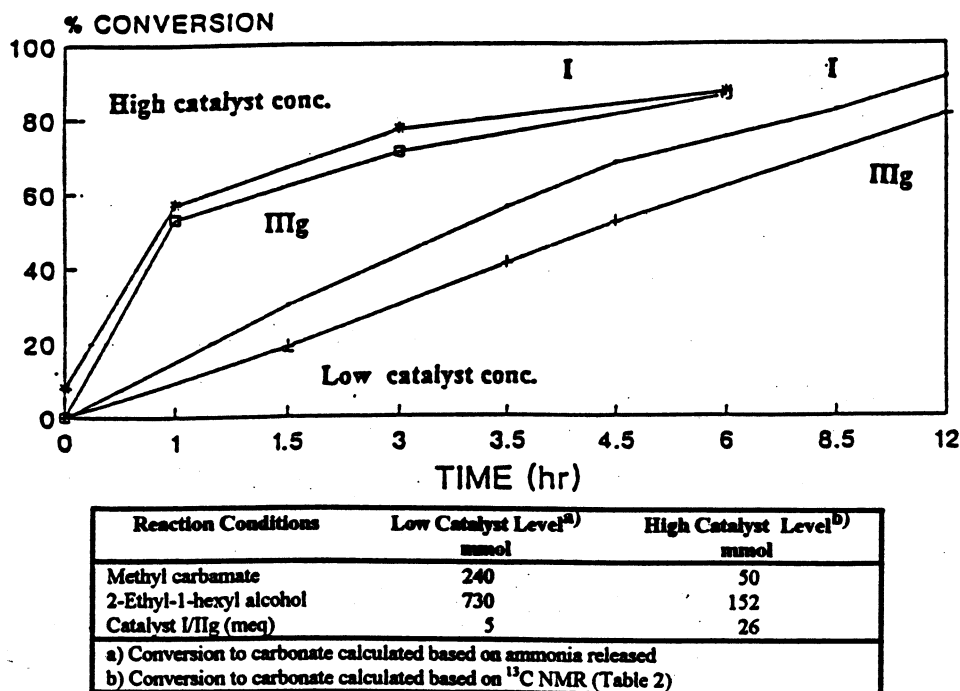


Fig. 2. High levels of catalyst have a small effect on rate at 190°C.

2.6.3. Reaction of I or IIg with methyl carbamate proceed through a common intermediate

2.6.3.1. Distribution of tin species. At 190°C, both experiments exhibited identical ¹¹⁹Sn-NMR spectra indicating that the heating period (20 min) provides sufficient time for the initially dissimilar reaction mixtures to equilibrate. The tin compounds detected were Bu₂Sn (OC₈H₁₇)₂, δ – 80 as a monomer, main peak (67%), Bu₂Sn (OC₈H₁₇)(N=C=O) δ – 180, (~16%) as well as unidentified species at δ – 50 (~16%) (Scheme 3). Speculations about the identity of the unknown compounds are discussed below.

2.6.3.2. The concentrations of *n*-Bu₂Sn (OC₈H₁₇)(N=C=O) and the unknown species are the same and depend on the concentration of methyl carbamate in the reaction mixture. At the start of the reaction when the concentration of carbamate was high (GC analysis) the ratio *n*-Bu₂Sn(OC₈H₁₇)₂:*n*-Bu₂Sn(OC₈H₁₇)(N=C=O) was 4:1 as was the ratio of *n*-Bu₂Sn(OC₈H₁₇)₂:unknowns (δ – 50). After 3 h, both ratios were 10:1, corresponding to a decrease in the concentration of carbamate due to its conversion to carbonate (> 70%; Fig. 2, Table 3). These data suggest that the unidentified tin species are very likely in equilibrium with the dialkoxytin compound and the alkoxy isocyanato tin species.

2.6.3.3. Analysis of the reaction mixture by ¹³C-NMR and correlation with ¹¹⁹Sn-NMR data. Samples taken at different reaction times from the reaction mixture were analyzed also by ¹³C-NMR. The transesterification reaction was monitored by the disappearance of the peak at δ 157.5 (NH₂COOMe), and the peak at δ 50.34 (NH₂COOMe) as well as the appearance of the peak at δ 157.4 (NH₂COOC8H17) and of the peak at δ 65.58 (NH₂COOC8H17). The reaction of the tin species with the carbamate to give the isocyanato tin moiety Sn–N=C=O was evidenced by the peak at δ 127. The formation of bis-(2-ethylhexyl)-carbonate, O=C(OC₈H₁₇)₂ was followed by the intensity of the carbonyl resonance at δ 154.4, and the alkoxy group at δ 68.48 (see carbonyl data in Table 3).

Parallel analyses by ¹³C- and ¹¹⁹Sn-NMR show that the concentration of Sn–N=C=O and the unidentified tin species decreases with decreasing concentration of methyl carbamate.

2.6.3.4. Additional support for the formation of *n*-Bu₂Sn (OC₈H₁₇)(N=C=O) species obtained from FTIR data. The reaction was also monitored by FTIR. Strong bands appear at 2210 cm^{–1} corresponding to Sn–N=C=O as well as the bands at 1710, 1746 and 3358 cm^{–1} corresponding to the carbonyl in carbamate, carbonate and the hydroxyl of the alcohol respectively. The decrease in Sn–N=C=O and alcohol concentration parallels the conversion of carbamate to carbonate as evidenced by IR.

Table 3

¹³C NMR^a data for the conversion of methyl carbamate^b to 2-ethylhexyl carbonate at a high level of catalyst

Catalyst type	Temp (°C)	Time (h)	NH ₂ COOMe δ 157.5 peak area	NH ₂ COOC ₈ H ₁₇ δ 157.4 peak area	O=C(OC ₈ H ₁₇) ₂ δ 154.4 peak area	Conversion of NH ₂ COOC ₈ H ₁₇ %
I	65	—	5.8	0	0	0
IIg	—	—	3.7	0	0	0
I	190	0	0	4.7	0.4	8
IIg	—	—	0	4.1	0	0
I	190	1	0	2.2	2.9	57
IIg	—	—	0	1.8	2.0	53
I	190	3	0	1.1	3.4	77
IIg	—	—	0	1.0	2.4	71
I	190	6	0	0.5	3.5	87
IIg	—	—	0	0.4	2.5	86

^a External reference Me₄Sn 0.0 ppm.^b Conversion calculated based on fraction of total peak area NH₂COOC₈H₁₇/O=C(OOC₈H₁₇)₂.

2.6.3.5. *Spectroscopic data are consistent with the structure of tin carbamate species of type $n\text{-Bu}_2\text{Sn}(\text{NHCOOC}_8\text{H}_{17})(\text{OC}_8\text{H}_{17})$.* A carbamate species is the most likely precursor of an isocyanato compound since isocyanic acid is not present in the reaction mixture. The tin atom in dibutylcarbamatoalkoxytin is hindered by the 2-ethyl-hexyl group which inhibits dimerization. The resonance signal for the monomeric tin species is expected to appear at higher field frequency ($\delta > -100$) [24]. The peaks which appear in ¹¹⁹Sn-NMR at $\delta -50$ are consistent with this assumption. Although a dibutylalkoxy-carbamato tin of this type has not been reported in literature alkoxy *N*-substituted carbamatotins have been reported [19] $n\text{-Bu}_3\text{Sn-NHCOOBu}$ was claimed by Gerega [25] resulting from the reaction of the corresponding isocyanate and butanol at 135°C in a sealed tube. He and his coworkers reported that the compound readily dissociates into starting materials when distillation is attempted. The evidence which supports the presence of a carbamate compound as a reaction product are the IR bands observed at 3330 and 1615 cm⁻¹ for NH, and the band at 1720 cm⁻¹ which corresponds to the carbonyl frequency. However the infrared spectrum is also consistent with a mixture of Bu₃SnOBu and NH₂COOBu which are compounds likely to have been formed at the reaction conditions reported by Gerega. Our attempt to synthesize the tin carbamate compound $n\text{-Bu}_2\text{Sn}(\text{NHCOOC}_8\text{H}_{17})(\text{OC}_8\text{H}_{17})$, from NH₂COOC₈H₁₇ and $n\text{-Bu}_2\text{Sn}(\text{OC}_8\text{H}_{17})_2$ failed to produce compelling evidence for the formation of this compound.

3. Proposed reaction mechanism

The evidence presented indicates that the difference in reactivity between various tin catalysts may be ex-

plained by the relative rate of their conversion to tin compounds containing both alkoxy and carbamate or isocyanato moieties. Evidence for the formation of Sn–N=C=O species was provided by ¹¹⁹Sn-NMR ($\delta -180$), ¹³C-NMR (δ 127), and IR (2207–2210 cm⁻¹). These characteristics are in agreement with those obtained for compound **1a** which was independently synthesized (Table 1).

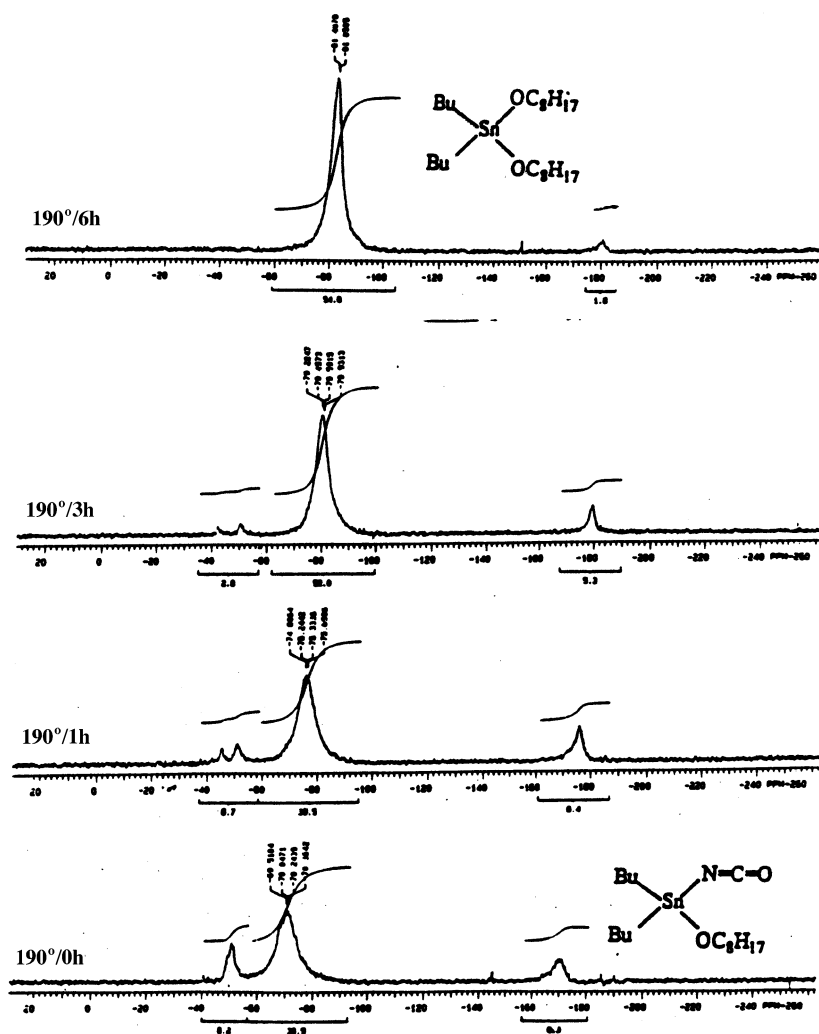
The formation of a dialkyl carbonate from an alkyl carbamate is postulated to include the following steps: Step 1, the reaction of dibutyl dimethoxytin, **I**, with alkyl carbamate yielding dibutylalkoxycarbamatotin, **1**, in equilibrium with dibutylalkoxyisocyanatotin, **1a**. Step 2, an intramolecular or intermolecular nucleophilic attack of the alcohol on the carbonyl carbon of the carbamatotin species, resulting in elimination of the carbonate and formation of an aminotin intermediate **2**. Finally step 3, which involves the reaction of the carbamate with **2**, to regenerate **1** with concomitant elimination of ammonia (Scheme 4).

Support for an intramolecular transfer of an alkoxy group from the tin atom to the carbonyl carbon with concomitant formation of a dialkyl carbonate can be obtained from the work of Shizuyoshi [26] who showed that carbonates can also be synthesized by insertion of a carbon oxysulfide into a tin alkoxy bond followed by an intramolecular rearrangement [Eq. (5)].

However, the formation of carbonates in our system could also occur by the intermolecular attack of an alcohol molecule present in the reaction medium with the postulated tin carbamate species.

4. Conclusions

Tin catalysts which have the highest activity for the synthesis of dialkyl carbonates by the reaction of alkyl



^{119}Sn NMR Spectra
- All spectra recorded at Room Temperature

Scheme 3. ^{119}Sn -NMR spectra of compounds **I** and **IIg** at 190°C.

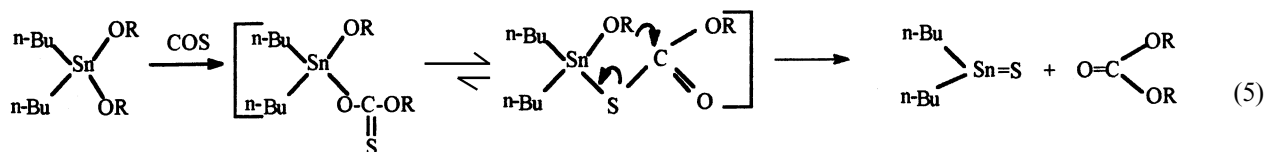
carbamates with alcohols are stannoxane and distannoxane which contain both methoxy and isocyanato groups bound to tin.

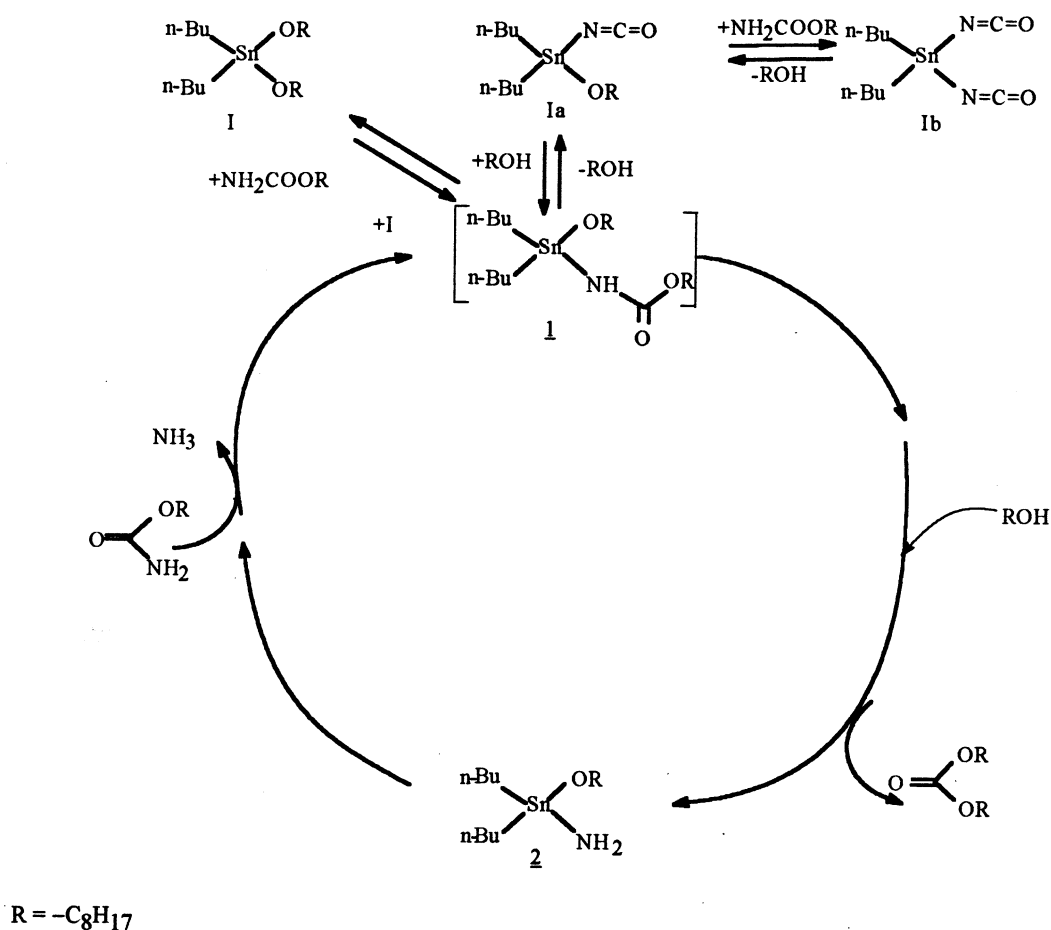
Observed differences in the catalytic activity of alkoxy stannoxanes and distannoxanes are correlated with the relative rates of their conversion to the above derivatives at reaction conditions.

The alkoxy isocyanato stannoxanes and distannoxanes can be readily synthesized from alcohol, alkyl carbamate, and dibutyltin.

5. Experimental details

The NMR spectra were recorded on a Varian XL-300 and Jeol-400. GC analyses were performed on HP-5880 FID instrument using a capillary column megabore DB5 ($L = 30$ m, Film thickness = 5 μm , $D = 0.53$ mm). HPLC analyses were performed on a HP-1040, high performance, liquid chromatograph, using a Supelco LC-18 column $D = 25$ cm/2.1 mm, with mobile phase methanol (isocratic), Flow: 0.200 ml min $^{-1}$. pro-





Scheme 4. Proposed reaction mechanism for the formation of a dialkyl carbonate from an alkyl carbamate.

vided with Diode Array detector: 240 nm, BW 4 nm, Ref 450 nm, BW 80 nm, peak width 0.054 min. Column temperature = 40°C. A Mattson Polaris was employed for IR studies. Melting points were determined on an Electrothermal melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith (Sycamore, Knoxville). Mass spectra were performed on Finnigan 4500 or TSQB quadrupole instruments using direct insertion probe chemical ionization mass spectrometric analyses with either ammonia or *i*-butane as CI reagent gas for tin compounds or GC/MS on b.p. columns for regular organic mixtures analyzed by EI or CI techniques.

5.1. Synthesis of dibutyldimethoxytin, **I**

Crude 1,1,3,3-tetrabutyl-1,3-dimethoxydistannoxane, **Ilg**, (36.2 g, 66.5 mmol) was synthesized as described by Davies [17], and charged to a 300 ml Hastelloy® C autoclave. After evaporation of solvent, methanol (101.9 g, 3184 mmol) and dimethyl carbonate (42.0 g, 466 mmol) were charged to the reactor and sparged

with nitrogen. The reactor was heated at 179°C at a pressure of ~3890 kPa for 4 h while sparging with nitrogen at a flow rate of 200 ml min⁻¹. The reactor was cooled and depressurized. The product (170 g) collected under nitrogen as a clear colorless solution was stripped of excess methanol and dimethyl carbonate. Analysis: ¹¹⁹Sn δ -160 (external ref Me₄Sn at 0.00 ppm) ¹³C δ 13.80 (CH₃), δ 19.29 (CH₂-Sn), δ 27.25 (CH₂-CH₂-CH₂-Sn), δ 27.81 (CH₂-CH₂-Sn), δ 51.91 (OMe). (ref at 0.1 ppm TMS) HPLC/retention time 3.14 min.

5.2. Synthesis of dibutyldimethoxytin, **I** from dibutyloxotin

Dibutyloxotin (50.5 g, 203 mmol), methanol (100.1 g 3130 mmol) and dimethyl carbonate (39.40 g, 438 mmol) were charged to a 300 ml Hastelloy® C autoclave and sparged with nitrogen. The reactor pressure was set at ~3500 kPa by means of a back pressure regulator. The nitrogen which exited the reactor was passed through a trap containing drierite and then through a trap containing a weighed amount of ascarite. The gas exiting the

ascarite trap was sent to a bubbler containing mineral oil for visual evidence of gas flow. The reactor was heated at 177°C. After 2 h the vessel containing ascarite became hot to the touch as a result of carbon dioxide absorption. After 1 h the ascarite trap began to cool. The reactor was maintained at 177°C for an additional 1.5 h and then cooled and depressurized. Analysis: ^{119}Sn - and ^{13}C -NMR as assigned for **I**. The ascarite trap showed a gain of 8.87 g (200 mmol CO_2).

5.3. Synthesis of dibutylisocyanatomethoxytin, **Ia** in Refluxing Toluene

To a solution of dibutyldimethoxytin (7.40 g, 25.10 mmol), in toluene (100 ml), methyl carbamate (1.90 g, 25.30 mmol) was added and the solution was refluxed under nitrogen to remove methanol, ca. 1 h. The solution was concentrated in vacuum to dryness to give 7 g, 91.00% yield of a pale yellow oily material which crystallized on standing.

Analysis: ^{119}Sn (C_6D_6): δ –180 (external ref Me_4Sn at 0.00 ppm). ^{13}C , solv CDCl_3 : δ 13.86 (CH_3) δ 22.50 ($\text{CH}_2\text{--Sn}$), δ 26.93 ($\text{CH}_2\text{--CH}_2\text{--CH}_2\text{--Sn}$), δ 27.59 ($\text{CH}_2\text{--CH}_2\text{--Sn}$) δ 51.44 (OMe), δ 128.10 (N=C=O), (ref at 77.0 ppm, CDCl_3). ^1H : δ 0.8 (CH_3), δ 1.1 ($\text{CH}_2\text{--Sn}$), δ 1.2 ($\text{CH}_2\text{--CH}_2\text{--CH}_2\text{--Sn}$), δ 1.5 ($\text{CH}_2\text{--CH}_2\text{--Sn}$), δ 3.2 (OCH_3); $\text{CH}_3/\text{OCH}_3 = 2/1$ (ref at 77.2 ppm, CDCl_3). IR (nujol): 2206 cm^{-1} , 2178 cm^{-1} (vs), (N=C=O), 1036 cm^{-1} (s) (OCH_3), 683 cm^{-1} (m) (CH_2Sn), 619 cm^{-1} (m) (Sn--O) and 503 cm^{-1} (m) (Sn--C).

Recrystallization from hexane gave a white solid with m.p. 103–105°C. Elemental analysis: MW = 306. Anal. Calc. for $\text{C}_{10}\text{H}_{21}\text{N}_1\text{O}_2\text{Sn}_1$: C, 39.26, H 6.92, N 4.58, O 10.46, Sn 38.79%. Found: C 38.55, H 6.58, N 4.31, Sn 38.99%. MS: DIP/IC4. Mass/ R_{int} : 308 (5) M + H; 276 (100), 291 (40), 276 (80), 235 (5), 119 (100).

5.4. Preparation of dibutylisocyanatomethoxytin, **Ia** at ambient temperature

A reaction mixture of dibutyldimethoxytin, **I**, (2.95 g, 10 mmol), and methyl carbamate (0.75 g, 10 mmol) was analyzed immediately following mixing by ^{119}Sn -NMR. (ext. ref $\text{Sn}(\text{Me})_4$ at 0.0 ppm). At r.t. the solution exhibited two peaks corresponding to **I** and **Ia** at δ –160 and δ –180 respectively. The yield of **Ia** varied with temperature as follows: at 25°C, 30%, at 65°C, 60%. The carbonyl group of Sn--N=C=O resonated at ^{13}C δ 128.0.

5.4.1. Reaction of dibutylisocyanatomethoxytin, **Ia** with methanol

A solution prepared from **Ia** (0.280 g, 90 mmol) in MeOH (1.40 g, 43.75 mmol) was heated in a 10 ml Swagelok® autoclave [27] at 175°C for 1 h. The solution, analyzed by ^{13}C -NMR, exhibited the following spec-

trum: δ 159.58 ($\text{NH}_2\text{--COOMe}$), 51.59 (OMe) and δ 13.35, δ 20.35, δ 27.22, δ 27.66, as assigned for **I** (Bu_2Sn) (ref at 128 ppm, benzene).

5.4.2. Reaction of dibutylisocyanatomethoxytin, **Ia** with water

Compound **Ia**, when exposed to air, underwent a decrease in the melting point from 103°C to 65–80°C and a decrease in the intensity of the OMe IR band. Analysis: ^{119}Sn -NMR: δ –180 (br), δ –171, δ –211, (ext ref Me_4Sn at 0.00 ppm), ^{13}C -NMR: δ 128.0 (N=C=O) no peak at δ 50.44 for OMe. (ref at 77.00 ppm chloroform) and IR (nujol): 3540 cm^{-1} (Sn--OH), 3425 cm^{-1} (bonded OH), 2207, 2178 cm^{-1} (N=C=O).

5.4.3. Reaction of dibutylisocyanatomethoxytin, **Ia** with benzyl alcohol

A solution of dibutylisocyanatomethoxytin **Ia** (42 g, 1.37 mmol) in benzyl alcohol (2.00 g, 18.50 mmol) was heated under nitrogen at 175°C for 6 h in a Swagelok® autoclave [27]. Analysis: ^{13}C -NMR: δ 157.18 ($\text{NH}_2\text{--COOBz}$), δ 156.30 O=C (OMe) (OBz), δ 154.58 O=C (OBz)₂. (ref 77.20 ppm chloroform). IR: 1711 cm^{-1} (C=O). GC/MS: EI: methyl benzyl carbonate (166), benzyl carbamate (151), dibenzyl carbonate (242).

5.5. Synthesis of dibutyldiisocyanatotin, **Ib**

A solution of methyl carbamate (6.10 g, 81.33 mmol) in xylene (62 g), was refluxed in a 200 cc flask equipped with a Dean Stark apparatus, and condenser, at 145°C to remove traces of water. After half of the xylene was removed, the condenser was connected to a H_2SO_4 (1N) trap for ammonia detection. Neat dibutyldimethoxytin, **I**, (11.70 g, 39.66 mmol), was added, and the solution was heated (silicon bath) at 175°C for 0.5 h. After cooling to r.t. the volatiles MeOH, dimethyl carbonate, xylene, and small amounts of methyl carbamate collected in the Dean Stark apparatus were analyzed by GC.

No ammonia was detected in the acid trap. After concentration of the reaction mixture, and drying at r.t., $P = 0.1$ mm, 15 g of a semi solid white ppt were obtained. The major component of the mixture was **Ib**. Analysis: ^{119}Sn -NMR (CDCl_3): δ –71.50 (external ref Me_4Sn at 0.0 ppm), ^{13}C -NMR: δ 13.49 (CH_3) δ 22.56 ($\text{CH}_2\text{--Sn}$), δ 26.39 ($\text{CH}_2\text{--CH}_2\text{--CH}_2\text{--Sn}$), δ 26.72 ($\text{CH}_2\text{CH}_2\text{--Sn}$) δ 128.30 (N=C=O), (ref at 77.13 ppm, CDCl_3). IR (nujol): 2209 cm^{-1} , 2178 cm^{-1} , N=C=O , 691 cm^{-1} (m) (CH_2Sn), 619 cm^{-1} (m) (SnC). MS DIP/IC4: Mass/ R_{int} %: 317 (20) M + H, 291(40), 276 (100), 249 (5), 233(5), 177(5), 119(100). MS +/CI- $\text{NH}_3/\text{Q1}$: 336(100) M + NH_4 , 308(50), 293(70), 266(5), 252(10), 235(5).

5.6. Synthesis of 1,1,3,3-tetrabutyl-1-methoxy-3-isocyanatodistannoxane, **IIa**

1,1,3,3 - Tetrabutyl - 1,3 - dimethoxydistannoxane **IIg** was synthesized from dibutyloxotin (50 g, 200 mmol), dimethyl carbonate (18.25 g, 203 mmol), methanol (0.63 g, 19 mmol) and toluene (240 ml), as described by Davies [17]. The reaction was performed in a 500 ml flask, equipped with a magnetic stirrer, temperature control and a condenser which was connected through a cold trap to a wet test meter. At reflux dibutyloxotin dissolved within 1 h. The evolution of CO₂ was monitored via the wet test meter; reflux was continued until gas evolution ceased, (100 mmol CO₂ were generated), total reaction time approx 3 h. Analyses: ¹¹⁹Sn-NMR, solvent toluene: δ -171, δ -183, solvent CDCl₃: δ -169, δ -176 (ext. ref Me₄Sn at 0.00 ppm) IR (neat): 1067, 1020, (OMe), HPLC: one peak retention time 5.26 min. After replacing the condenser with a Dewar column length 18 cm provided with a distillation head, which was connected to a 250 ml flask, a hot solution of methyl carbamate (7.50 g, 100 mmol) in toluene (20 ml) was added dropwise over a period of 0.5 h under reflux. During this time a mixture of methanol, dimethyl carbonate, and toluene was collected in the receiving flask until the temperature at the distillation head reached 110°C. The clear solution in the reaction pot was concentrated at 50–60°C, ~39 kPa, followed by evaporation at 1 mmHg. 50 g of **IIa** were obtained (91% yield) as a semisolid white material. The same material was obtained in a separate experiment, when an excess of methyl carbamate (200 mmol) was used as the reagent. The excess of methyl carbamate was separated by filtration from the toluene solution, followed by vacuum drying.

The product, crystallized on standing (m.p. 124–128°C), Analysis: ¹¹⁹Sn-NMR, solvent toluene: δ -166, δ -206, (ratio 1:1) minor peaks at δ -148 and δ -165 (external ref. Me₄Sn at 0.0 ppm). ¹³C-NMR, solv CDCl₃: δ 13.53 (-CH₃), δ 22.21, 22.56 (CH₂Sn), δ 26.75 27.01, (CH₂CH₂CH₂-Sn), δ 27.17 δ 27.35, (CH₂-CH₂-Sn), δ 50.65 (OMe), δ 128.0 (N=C=O), small peaks, at δ 126.15 and δ 137.70. IR neat: 2204 cm⁻¹ (N=C=O), 1060 and 1024 cm⁻¹ (vs) (OMe), 695 cm⁻¹ (CH₂Sn), 613–580 cm⁻¹ (SnO and SnC). Analysis: MW = 1110. Anal. Calc. for C₃₆ H₇₈ N₂ O₆ Sn₄: C: 38.90, H: 7.03, N: 2.52, Sn: 42.90%. Found C:39.08, 38.94 H:7.30, 7.02 N: 2.17, 2.67 O:7.61, 7.22 Sn:44.46,40.75%. HPLC: retention time 5.28 min.

5.6.1. Reaction of **IIa** with benzyl alcohol

A solution of **IIa** (1.10 g, 1 mmol) in benzyl alcohol (1.57 g, 14.5 mmol) was heated for 4 h at 175°C. Evolution of ammonia, concomitant with a decrease in the N=C=O band at 2210 cm⁻¹ was paralleled by an increase of a band at 1715 cm⁻¹, corresponding to the

carbonyl groups of the carbamates and carbonates. Analysis: ¹³C-NMR: δ 157.18 (NH₂COOBz), δ 156.30 (O=C(OMe) (OBz), δ 154.58 O=C(OBz)₂. The peak corresponding to -OMe at δ 50.74 nearly disappeared (ref 77.00 ppm chloroform). IR: 2206 cm⁻¹ (N=C=O), 1711 cm⁻¹ (C=O), MS.

5.7. Attempt to synthesize 1,1,3,3-tetrabutyl-1,3-diisocyanatodistannoxane **IIb** from dibutyloxotin and methyl carbamate

A solution of dibutyloxotin (7.46 g, 30 mmol) and methyl carbamate (2.25 g, 30 mmol) in toluene (100 ml) was refluxed for 5 h. under nitrogen. After concentration in vacuum to dryness, a semisolid white precipitate (7.50 g, 89% yield) was obtained. A portion of the material, dried on a porous plate under nitrogen and washed with hexane, exhibited m.p. 175–177°C. Analysis: ¹¹⁹Sn-NMR, solv. C₆D₆: δ -147, δ -169, (**IIb**), δ -162, δ -212, (**IIc**) (external ref Me₄Sn at 0.0 ppm). ¹³C-NMR, solv C₆D₆: δ 129.00 and 130.68 (N=C=O), IR (nujol): 3529 cm⁻¹ (w) (OH), 2209, 2190 cm⁻¹ (N=C=O covalent and bridged), 677 cm⁻¹ (m) (CH₂-Sn), 616, 562 cm⁻¹ (SnO and Sn-C). The material analysis for a dimer consisting of **IIb** and **IIc** 1/1, MW = 1107. Anal. Calc. for C₃₅ H₇₃ N₃ O₆ Sn₄: C: 37.99, H: 6.59, N: 3.79, O: 8.67, Sn: 42.99%. Found: C: 38.22, H: 6.70, N: 3.57, O: 6.83, Sn: 44.90%.

6. Evaluation of dialkyltin catalysts—synthesis of bis-(2-ethylhexyl)-carbonate

A mixture of 2-ethyl-1-hexanol (95 g, 73 mol), methylcarbamate (18.20 g, 0.24 mol) and catalyst (5 meq) was heated to 190°C within 30–45 min. with stirring under nitrogen. in a 250 ml flask provided with magnetic stirring and temperature control. During this period the methanol resulting from the transesterification reaction was collected in a Dean Stark trap. The vapors containing ammonia were passed through a condenser to a sulfuric acid (1.6 N) trap. Following collection of methanol, the Dean Stark trap was disconnected, and the reaction flask was connected directly to the condenser; the temperature was maintained at 190–195°C for 12 h. Samples were removed periodically from the sulfuric acid trap and analyzed by potentiometric titration with a solution of NaOH (1N). Analysis of the reaction mixture was performed by GC and ¹³C-NMR. Selectivity for the carbonate in all cases was 100%. The conversion of methyl carbamate and 2-ethyl-1-hexanol to dicarbonate for different catalysts is presented in Table 2. In the case of the isothiocyanatotin catalysts decomposition with deposit of a black sulfide was observed at 190°C.

6.1. Evaluation of dialkyltin catalysts-effect of catalyst concentration

In parallel experiments compound **I** (7.67 g, 26 mmol), and compound **IIg** (7.65 g, 14.06 mmol/28 meq Sn) were treated with 2-ethyl-1-hexanol (19.76 g, 152 mmol) and methyl carbamate (3.75 g 50 mmol) and heated to 190°C (20–30 min) with stirring under nitrogen in a 250 ml flask equipped with a magnetic stirrer and temperature control device. The methanol which was formed as a reaction product was collected in a Dean Stark apparatus. Following the collection of methanol, the Dean Stark apparatus was disconnected and the reaction mixture was heated for an additional 6 h. Samples were collected periodically and analyzed. Analytical data for the initial sample obtained from the reaction with **I**: ^{119}Sn -NMR: δ – 159 (br), (external ref Me_4Sn at 0.0 ppm). ^{13}C -NMR: NH_2COOMe δ 157.50, δ 50.34, $\text{NH}_2\text{COOC}_8\text{H}_{17}$ δ 65.74, $\text{C}_8\text{H}_{17}\text{OH}$ δ 63.17, Sn–OMe moiety δ 49.0; IR 2206 cm^{-1} . Analytical data for the initial sample obtained with **IIg**: ^{119}Sn -NMR: δ – 175.6, δ – 185.5 br (External Ref Me_4Sn 0.0 ppm). ^{13}C -NMR: NH_2COOMe δ 157.65, δ 50.31, $\text{C}_8\text{H}_{17}\text{OH}$ δ 63.19. Sn–OMe moiety δ 49.0. All data recorded at r.t. The data are presented in Fig. 2 and Table 3. Conversion was calculated based on integrated NMR peak areas for the carbamate and the carbonate.

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