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Journal of Organometallic Chemistry 518 (1996) 21–27

Journal of Organometallic Chemistry

Mechanism of tin(IV)-catalysed urethane formation

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Received 20 October 1995

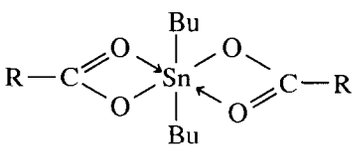
Abstract

It has been found that dibutyltin dilaurate and dibutyltin dibutanethiolate are almost equally effective as catalysts in the formation of a urethane from phenyl isocyanate and butanol, and that the catalytic activity of both compounds is inhibited by thiols. These results are consistent with a mechanism which involves the N-coordination of the isocyanate with a tin alkoxide that is formed by alcoholysis of the starting tin compound.

Keywords: Tin carboxylates; Tin thiolates; Urethane formation

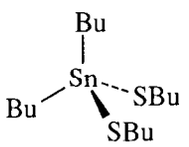
1. Introduction

The reaction between organic isocyanates and alcohols to give urethanes is strongly catalysed by amines and by a wide variety of Lewis acids [1]. Of the latter, remarkably high catalytic activity is exhibited by a range of tin compounds [2] including several which can be represented by the general formula Bu_2SnX_2 (**1**), e.g. dibutyltin dilaurate (DBTDL, **2a**), the corresponding di(2-ethylhexanoate) ester **2b**, and dibutyltin dibutanethiolate (DBTDB, **3**). The two esters **2a** and **2b** are used extensively in the industrial production of polyurethanes from diisocyanates and polyols.



2a; $R = (CH_2)_{10} \cdot Me$

2b; $R = CH(Et) \cdot Bu$



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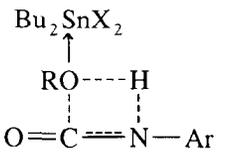
While the mechanism of the amine-catalysed reaction is now well understood [3], that of the tin-catalysed reaction is still uncertain in spite of the numerous investigations (largely kinetic) which have been carried out over a substantial period of time. An inspection of the literature shows that while a number of mechanisms have been proposed for the tin system, they differ from each other mainly on the basis of whether it is the alcohol, the isocyanate, or both of these reactants that is activated by interaction with the tin catalyst.

The earliest mechanism appears to be that by Entelis et al. [4], who suggested that the alcohol is activated by coordinating with the tin to give a complex, shown as **4** in Scheme 1. This coordination increases the normal polarization of the O–H bond, thus enabling the alcohol to react with the isocyanate via a four-membered ring transition state (see **5**) at an enhanced rate. In the case of the dialkyltin diesters **1**, the suggestion that the alcohol coordinates with the tin is consistent with the known ability of the diesters to function as Lewis acids for a wide range of oxygen-donor ligands [5].



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Following an earlier suggestion by Bruenner and Oberth [6] which related to the catalysis of urethane formation by inorganic compounds other than those of tin, some workers [7,8] have suggested a modification of the Entelis mechanism in which the isocyanate reacts with a tin alkoxide, generated from the alcohol and the tin catalyst, rather than with a tin–alcohol complex.

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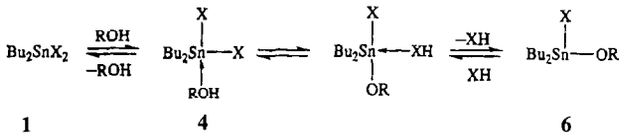
PII S0022-328X(96)06223-7

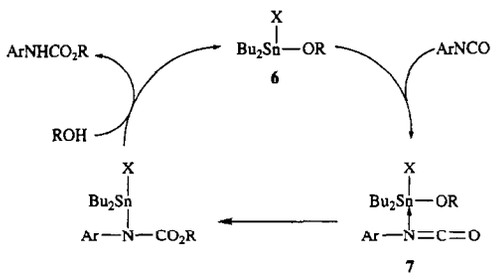


Scheme 1.

This suggestion was supported by the observation that trialkyltin alkoxides add to isocyanates to give N-stannylurethanes which, with alcohols, give the parent urethane plus the expected tin(IV) alkoxide, thus providing the basis for a catalytic cycle [7]. However, two very recent and detailed investigations by Tondeur et al. [9] provided kinetic data that were interpreted in terms of the original Entelis mechanism.

Other workers have suggested that the isocyanate can also be activated by coordination with the tin, either via the oxygen [10] or the nitrogen atom [10b,11]. In both cases it is postulated that this coordination increases the polarization within the N=C=O group, and thereby activates the carbonyl carbon atom towards attack by either the adjacent coordinated alcohol or, in the case of a tin alkoxide, the alkoxide anion. As all these possibilities require attack on the isocyanate to occur intramolecularly, they all predict that the $-\Delta S^{\ddagger}$ value will be lower for the catalysed reaction than for the uncatalysed one as, in fact, is the case [10a,4,12].

In order to obtain further information about the tin-catalysed system, we have studied the reaction between phenyl isocyanate and butanol in chloroform at room temperature using a number of tin(IV) compounds as catalysts [13]. In this paper we present evidence which strongly suggests that, for the two catalysts DBTDL and DBTDB, the catalytic cycle for urethane formation is that shown in Scheme 2. The cycle involves N-coordination of the isocyanate with the tin alkoxide **6**, formed by alcoholysis of the starting tin compound **1** as shown in Scheme 1, to give the complex **7**. Transfer of the alkoxide anion onto the coordinated isocyanate affords an N-stannylurethane which then undergoes alcoholysis to give the urethane and the original tin alkoxide **6** as observed by Bloodworth and Davies for the trialkyltin system [7].



Scheme 2.

2. Results and discussion

The tin-catalysed reaction between phenyl isocyanate and butanol in chloroform was conveniently followed using FTIR by observing the disappearance of the isocyanate ν_{NCO} band at 2261 cm^{-1} and the increase in intensity of the urethane ν_{CO} band at 1731 cm^{-1}. With both reactants at a concentration of 0.2 mol dm^{-3}, DBTDB and DBTDL were found to be almost equally effective as catalysts. For example, with catalyst concentrations of 4×10^{-4} and 4×10^{-6} mol dm^{-3}, both catalysts required approximately 6 and 55 min respectively to convert half the isocyanate into urethane ($t_{1/2}$) (see Fig. 1 for a catalyst concentration of 4×10^{-4} mol dm^{-3}).

The similar catalytic activity of a dialkyltin diester and a dialkyltin dithiolate was also found by earlier workers for dibutyltin diacetate and dibutyltin di(dodecanethiolate) [2,8c], and appears to rule out conclusively the possibility that tin-catalysed urethane formation involves attack by the isocyanate on a species of type **4** in which the alcohol is σ-bonded with the tin. In contrast to that in the diesters, the tin atom in the dialkyltin dithiolates is almost coordinatively saturated [14]. One result of this is that not only will the affinity of DBTDB for alcohols be considerably less than that of DBTDL but, even if complex formation takes place to a small extent, the lower electronic requirements of the tin will ensure that the polarizing effect on the coordinated alcohol will not be nearly as great as in the corresponding DBTDL complex. If the reaction of the isocyanate with an alcohol complex were a key step, the

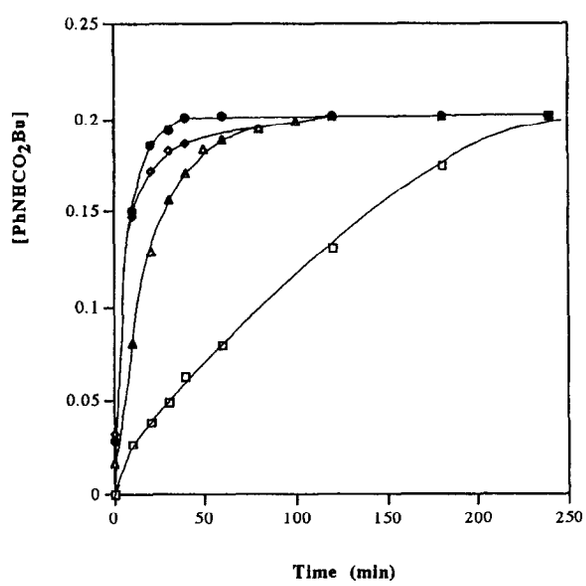


Fig. 1. Concentration of urethane (mol dm^{-3}) as a function of time in the reaction between PhNCO and BuOH (both at 0.2 mol dm^{-3}) in the presence of a tin(IV) catalyst (4×10^{-4} mol dm^{-3}): ●, DBTDL; ◇, DBTDB; △, DBTDB + BuSH (4×10^{-3} mol dm^{-3}); □, DBTDL + BuSH (0.02 mol dm^{-3}).

catalytic activity of DBTDB would be considerably less than that of DBTDL.

With both DBTDL and DBTDB it was observed also that their catalytic activities were strongly inhibited by the presence of butanethiol. For example, at a catalyst concentration of 4×10^{-4} mol dm^{-3} the $t_{1/2}$ value of 6 min for DBTDB was increased to 20 min by a thiol concentration of 4×10^{-3} mol dm^{-3}, and that of DBTDL was increased to 80 min by a thiol concentration of 2×10^{-2} mol dm^{-3} (see Fig. 1). No inhibition at all was observed with either DBTDL or DBTDB when tetrahydrothiophen was present, even at a concentration of 2×10^{-2} mol dm^{-3}.

This effect of thiols appears initially to be consistent with the involvement of the alcohol complex **4**, for if the thiol were able to coordinate with the tin, this would inhibit the alcohol from doing so. This explanation for the inhibition is unlikely to be the correct one, however, for neutral sulfur ligands have less affinity for tin(IV) than the corresponding oxygen ones [5b]. From the viewpoint of coordinating with the tin, therefore, a thiol would not be expected to compete successfully against an alcohol which, in the urethane-forming mixtures described here, was present at much higher concentrations. In fact, because of its very low Lewis acidity it is unlikely that DBTDB will coordinate to an appreciable extent with either alcohols or thiols, both of which are relatively weak donor ligands. In agreement with this, we have found that the addition of butanethiol causes no change in the ^{119}Sn NMR spectrum of a deuterochloroform solution of DBTDB.

A more likely explanation for the lowering of the catalytic activity of DBTDB by butanethiol is that in urethane formation with this catalyst it is the mixed alkoxide (**6**; X = SBu) formed by alcoholysis of the DBTDB that reacts with the isocyanate, and the thiol decreases the concentration of this species by repressing the alcoholysis (c.f. Scheme 1). With DBTDL the role of the thiol would be to compete with the alcohol in an analogous type of ligand-exchange process and form a dibutyltin thiolate at the expense of the catalytically active dibutyltin alkoxide (**6**; X = laurate). It should be noted that when DBTDL or the corresponding diacetate is used as the catalyst, the catalytic activity is decreased by the addition of carboxylic acids [8a,15] but increased by the addition of amines [16]. Both these effects can be rationalized in terms of a change in the concentration of the catalytically active alkoxide (**6**; X = O · CO · R′) as a result of a displacement of the equilibria shown in Scheme 1.

The idea that a tin alkoxide formed by alcoholysis of the starting tin compound is the active catalyst has already been advanced by a number of workers (see above), including Robins et al. [8b] who established that the catalytic activity of a series of tin compounds of type **1** decreases in the order $X^- = MeO^- > C_{11}H_{23}CO_2^- > C_3F_7CO_2^- > C_6H_5SO_3^- > Cl^-$. This order is consistent with the equilibria involved in the formation of the tin alkoxide being displaced towards the alkoxide as the acidity of HX decreases. This correlation only applies, of course, if the ligands X^- are of a closely related type, for there are a number of factors which ensure that the relative affinities of a pair of anions for a 'hard' proton do not always correspond to their relative affinities for the 'soft' dibutyltin(IV) cation (compare the 'soft' butanethiolate and 'hard' laurate anions below).

$$\underset{\mathbf{1}}{Bu_2SnX_2} \underset{X\text{–}H}{\overset{Y\text{–}H}{\rightleftharpoons}} \underset{\mathbf{8}}{Bu_2Sn(X)Y} \underset{X\text{–}H}{\overset{Y\text{–}H}{\rightleftharpoons}} Bu_2SnY_2$$

Scheme 3.

2.1. Ligand-exchange reactions

On the basis that the relative concentration of a tin alkoxide formed by the alcoholysis of the starting tin 'catalyst' would be an important factor in determining the activity of that 'catalyst', information was sought about the equilibrium position of several of these alcoholyses and related ligand-exchange reactions (see Scheme 3), many of which have been used for preparative purposes [17].

With the alcoholysis of thiolates, the reversibility of the reaction has been established by Mehrotra and coworkers [18], who found that while the formation of the expected dithiolate from a 1 : 2 mixture of dibutyltin diethoxide and a number of thiols proceeded very rapidly, the alcoholysis of the dithiolates required prolonged refluxing, even when a large excess of the alcohol was used and the thiol formed was continuously removed from the system. This indicates that the equilibria involved in the alcoholyses strongly favour the dithiolate.

Although Robins et al. [8b] observed the appearance of the infrared carbonyl absorption band due to acetic acid when a ten-fold molar excess of the chelating diol, 1,2-dihydroxyethane, was added to a solution of dibutyltin diacetate in THF, we detected no change in the FTIR spectrum of a 0.2 mol dm^{-3} solution of DBTDL in chloroform when butanol (final concentration 0.4 mol dm^{-3}) was added. Similarly, using ^{1}H NMR no butanethiol was detected in a solution (0.01 mol dm^{-3}) of DBTDB in $^2H_4$–methanol, even though the work by Mehrotra and coworkers [18] would suggest that it was present, albeit at very low concentration. Clearly, both the butanethiolate and the laurate anion have considerably higher affinity for tin(IV) than the butoxide anion.

The addition of butanethiol (final concentration 0.4 mol dm^{-3}) to a chloroform solution of DBTDL (0.2 mol dm^{-3}) resulted in an immediate change in the FTIR spectrum that corresponded to the formation of a significant proportion of lauric acid (ν_{max} 1708, 2300–3300 cm^{-1}). This thiolysis was also detected by the use of ^{119}Sn NMR when the addition of butanethiol (final concentration 0.5 mol dm^{-3}) to a solution of DBTDL (0.5 mol dm^{-3}, δ_{Sn} − 150) in deuterochloroform resulted in the appearance of the signal characteristic of DBTDB (δ_{Sn} + 126). A third signal which would have indicated the presence of the mixed species (**8**; X = laurate, Y = SBu) was not observed, indicating that if this species was formed initially in the thiolysis it disproportionated into DBTDL and DBTDB. The presence of the two signals characteristic of DBTDL and DBTDB in the spectrum shows that with these two compounds there is an absence of the rapid ligand-exchange process which occurs with mixtures of dialkyltin compounds of the types R_2SnCl_2 and $R_2Sn(OCOR')_2$, and which results in the observed chemical shifts and coupling constants being the average of those of the two individual compounds [19]. Presumably, this difference between the two systems is because halogens are very effective at acting as bridging ligands, and thereby facilitate the ligand exchange process.

Using the information obtained from the ^{119}Sn NMR spectrum and by comparing the absolute intensities of the two carbonyl absorption bands due to lauric acid (ν_{max} 1708 cm^{-1}) and DBTDL (ν_{max} 1597 cm^{-1}) in the infrared experiment, the equilibrium constant for the following reaction was calculated to be approximately one:

$$\text{DBTDL} + 2\text{BuSH} \rightleftharpoons \text{DBTDB} + 2 \text{ lauric acid}$$

The fact that the (monodentate) butanethiolate anion has roughly the same affinity for the tin as the (bidentate) laurate anion explains the similarity of the catalytic activity of DBTDL and DBTDB in urethane formation for, under identical conditions, both compounds would be expected to undergo alcoholysis to form a catalytically active alkoxide to about the same extent.

Although a mixed species could not be detected in the thiolysis of DBDTL, evidence for the formation of the species (**6**; X = SBu and R = Bu) for DBTDB and butanol was obtained as follows. Firstly, it should be noted that no reaction occurred when a solution of the isocyanate and butanethiol (both 0.2 mol dm^{-3}) in chloroform was kept at room temperature for 30 h. This is consistent with the general observation that, under neutral conditions and compared with alcohols, thiols are relatively unreactive towards isocyanates [20]. Also, no reaction occurred and no indication of complex formation was obtained, when a solution of DBTDB and phenyl isocyanate (both 0.2 mol dm^{-3}) in chloroform was kept for 30 h. However, directly butanol (final concentration 0.2 mol dm^{-3}) was added to the last solution a reaction occurred immediately and was complete (within 3 min) by the time the infrared spectrum could be recorded. This spectrum revealed that in addition to the expected urethane the solution contained a small proportion of the corresponding thiocarbamate, Ph · NH · CO · SBu, whose presence was confirmed by a thin-layer chromatogram of the reaction mixture. The thiocarbamate was also detected by ^1H NMR, and when phenyl isocyanate (initial concentration 0.01 mol dm^{-3}) was added to a solution of DBTDB (0.01 mol dm^{-3}) in $^2H_4$–methanol, a comparison of the signal integrals due to $CO–S–CH_2–$ (δ 2.98) in the thiocarbamate and the aromatic protons in the mixture of urethane and thiocarbamate indicated that the ratio of urethane to thiocarbamate was about 20 : 1.

The infrared features which indicated the presence of the thiocarbamate in the reaction mixture were a shoulder at approximately 1685 cm^{-1} on the side of the urethane carbonyl absorption band (ν_{max} 1731 cm^{-1}) and a sharp absorption band of low intensity at 876 cm^{-1}. Both these features were also present in the spectra of the DBTDL-catalysed mixtures when butanethiol was added to inhibit the activity of the catalyst.

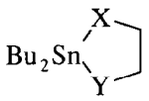
As the thiocarbamate that was formed in the reactions described above clearly did not come from the interaction of the isocyanate with either the DBTDB or the butanethiol formed by alcoholysis of the DBTDB, the only viable explanation which is consistent with the rapidity of the reactions is that it was formed by interaction of the isocyanate with the other product formed by the alcoholysis, i.e. the mixed species (**6**; X = SBu, R = Bu). This interaction would give the corresponding species **7**, in which the subsequent transfer of an anionic ligand from the tin onto the coordinated isocyanate would largely involve the alkoxide, rather than the thiolate anion, because of the higher affinity of the tin for the sulphur.

The mixed species (**6**; X = SBu, R = Bu) formed by alcoholysis of DBTDB is probably relatively short-lived and, like that generated in the thiolysis of DBTDL described above, rapidly disproportionates. In this connection it should be noted that while there is one example in the literature of a tin complex which contains an alkoxide and a thiophenolate ligand [21], there appears to be no examples of complexes of the type **6** in which the ligand X is the anion of a simple thiol. In an attempt to prepare such a complex, Mehrotra and coworkers [18] treated dibutyltin diethoxide with butanethiol on a 1 : 1 basis, but subsequent distillation afforded only a mixture of the starting diethoxide and the dibutanethiolate.

Two points should be noted concerning the formation of the thiocarbamate in the stoichiometric experiments

described above. The first is that when the DBTDB was replaced by DBTDL, immediate and complete formation of the urethane still occurred. The infrared spectrum of the reaction mixture, however, indicated the absence of the mixed anhydride, Ph · NH · CO · O · CO · $(CH_2)_{10}$ · Me [22], which would have been formed if transfer of one of the laurate ligands onto the isocyanate had occurred. Presumably, this is the result of the laurate ligand being bidentate; the transfer would therefore require the simultaneous breaking of two bonds to the tin rather than one as in the transfer of the butanethiolate.

The second point is that while DBTDB does not react with phenyl isocyanate under the conditions indicated above, the mixed species (**6**; X = SBu, R = Bu) apparently does. The most obvious explanation for this is that with the former compound the very low Lewis acidity of the tin inhibits the initial coordination of the isocyanate which is essential for reaction to occur. Replacement of one of the sulphur-bonded ligands by an oxygen-bonded one, however, increases the Lewis acidity of the tin and permits the coordination.



9a: X = S, Y = S
9b: X = S, Y = O
9c: X = O, Y = O

This effect of increasing the Lewis acidity of tin(IV) by replacing a sulphur-bonded ligand by an oxygen one has often been observed. For example, in solution the dithiastannolanes **9a** [23], and also DBTDB [5a], exist as monomeric species with the tin having the quasi-tetrahedral stereochemistry illustrated in structure **3**. The oxathiastannolanes **9b**, however, are dimeric with the tin having a coordination number of five as the result of intermolecular Sn–O bonds [24]. The still higher Lewis acidity of the dioxastannolanes **9c** results in these compounds existing not only as dimers, but also as oligomeric species which contain six-coordinate tin [25].

2.2. The coordination of the isocyanate

The contrast between the ability of the mixed species (**6**; X = SBu, R = Bu) to react with phenyl isocyanate and the failure of DBTDB to do so was rationalised above in terms of the relative ability of the isocyanate to coordinate with the tin in these two compounds. This coordination, as illustrated by structure **7** in Scheme 2, is considered to involve the nitrogen atom of the ambidentate isocyanate group, rather than the oxygen atom, on the basis that tin(IV) alkoxides add to isocyanates to give N–Sn-bonded products [7]. With this addition it is thought unlikely that O–Sn products are formed initially, and these then rearrange to give the N-bonded products that are isolated. While the complexes formed by phenyl isocyanate and the very strong Lewis acids $SnBr_4$ and $SnCl_4$ – and also $AlCl_3$ [26] – are bonded through the oxygen [27], it should be noted that the ambidentate ligand, urea, bonds to the first of these tin(IV) compounds through its oxygen atom, but to the latter through its nitrogen [28].

Possibly related to this N-coordination of the isocyanate is the observation that when dibutyltin dicarboxylates are used to catalyse the reaction between aryl isocyanates and methanol, the ρ value for the reaction is significantly lower (0.9) than for the uncatalysed one (3.3) [10a,29]. This reduction has been interpreted as an indication that the electrophilic character of the carbonyl carbon of the isocyanate is of lesser importance in the catalysed reactions. One possible reason for this is that the nitrogen lone pair which is involved in coordinating the isocyanate with the tin is in an sp^2 hybridised orbital, and is not part of the π-system which links the carbonyl group of the isocyanate with the aromatic ring. Substituents in the aromatic ring will, therefore, have a smaller effect on the N-donor strength of the isocyanate, and hence on the concentration of the key species **7**, than they do on the electrophilicity of the carbonyl carbon atom.

2.3. The nature of the tin alkoxide

Evidence has been presented above to show that when DBTDL and DBTDB are used as catalysts the tin species which reacts with the isocyanate is the mixed alkoxide **6**. In view of the tendency for tin complexes with mixed ligands to disproportionate, it is possible that urethane-formation could also involve, at least in part, the corresponding dialkoxide, whose catalytic activity would probably be different from that of the monoalkoxide. This species would also be present as the result of further alcoholysis (cf. Scheme 3). Regardless of the route by which it is formed, however, the dialkoxide would be favoured by high alcohol : tin ratios. One would expect that at extremely high alcohol : tin ratios most of the tin would be present as the dialkoxide, and that a further increase in the ratio would cause little change in the catalytic activity of the system. Such a situation has been observed, but not interpreted in terms of the formation of tin alkoxides [9].

A further point is that for convenience the alkoxide **6** is shown as being monomeric in nature. In solution, however, dialkyltin alkoxides usually exist as mixtures of oligomers (particularly those derived from primary alcohols), with the alkoxide group acting as a bridging ligand [5a,24,25,30] and with the higher oligomers being favoured by high alkoxide concentrations [25,31]. This would almost certainly be true of the alkoxide **6**. We believe that the various oligomers of this alkoxide exhibit different levels of catalytic activity, and that it is one of the dimeric forms which is the most active (see the following paper). The higher oligomers exhibit much

lower levels of activity, and it is these alkoxides that constitute the 'non-productive aggregates' which Tondeur et al. [9] have proposed to account for the complex manner in which catalytic activity depends on tin concentration, and the fact that the activity reaches a plateau at high tin concentrations.

On the basis of these considerations it may be concluded that in any tin-catalysed urethane-forming reaction there are several types of tin alkoxide present, each having its own level of activity and whose concentration is dependent upon a number of factors which include the alcohol and tin concentrations. This situation will result in extremely complex kinetics, and this is probably the main reason why the numerous kinetic studies which have been carried out over a period of about 30 years, and which have often involved different solvents and widely different alcohol and tin concentrations, have failed to produce a generally accepted mechanism.

3. Experimental

Phenyl isocyanate, dibutyltin dilaurate, and butanol (HPLC grade; water < 0.03%) were obtained from Aldrich Chemical Co. and were used as received. ^{1}H and ^{119}Sn NMR spectra were recorded on a Bruker WM 360 spectrometer for solutions in $CDCl_3$ (internal reference $SiMe_4$ and $SnMe_4$ respectively) at 360 MHz for ^{1}H and 134.3 MHz for ^{119}Sn. Infrared absorption spectra were recorded on a Perkin-Elmer 1600 FTIR spectrophotometer for solutions in spectrophotometric grade chloroform (Aldrich) which was stored over type 4Å molecular sieves.

Dibutyltin dibutanethiolate [dibutylbis(butylthio)stannane] was prepared from dibutyltin oxide and butanethiol as described in the literature [18] and had b.p. 157–160°C (0.7 mm), lit. b.p. 160°C (0.6 mm). Anal. Found: C, 46.65; H, 8.80. $C_{16}H_{36}S_2Sn$ Calc.: C, 46.72; H, 8.82%.

Butyl N-phenylthiocarbamate was obtained in 96% yield by refluxing a solution of phenyl isocyanate (4.11 g, 35 mmol), butanethiol (3.2 g, 36 mmol) and triethylamine (0.2 cm) in toluene (70 cm^3) for 48 h. After crystallisation from hexane/ethanol (15 : 1) the compound had m.p. 67–68°C, lit. [20c] m.p. 69°C.

Acknowledgements

We thank Dr. M.J.E. Hewlins for recording the ^{119}Sn NMR spectra.

References and notes

[1] A. Farkas and G.A. Mills, *Adv. Catal.*, *13* (1962) 393.
[2] F. Hostettler and E.F Cox, *Ind. Eng. Chem.*, *52* (1960) 609.
[3] K. Schwetlick, R. Noack and F. Stebner, *J. Chem. Soc., Perkin Trans. 2* (1994) 599.
[4] S.G. Entelis, O.V. Nesterov and V.B. Zabrodin, *Kinet. i Katal.*, *7* (1966) 627; Chem. Abstr., 65 (1966) 18478.
[5] (a) J. Holecek, M. Nadvornik and K. Handlir, *J. Organomet. Chem.*, *315* (1986) 299. (b) N. Samsodin, S.W. Ng and V.G. Kumar Das, *Chemistry and Technology of Silicon and Tin*, Oxford University Press, 1992, p. 599. (c) A.S. Mufti and R.C. Poller, *J. Chem. Soc., C*, (1967) 1362. (d) S.W. Ng, Z.A. Chen Wei, V.G. Kumar Das, W.H. Yip, R.-J. Wang and T.C.W. Mak, *J. Cryst. Spectrosc. Res.*, *21* (1991) 39.
[6] (a) R.S. Bruenner and A.E. Oberth, *J. Org. Chem.*, *31* (1966) 887. (b) A.E. Oberth and R.S. Bruenner, *Ind. Eng. Chem. Fundam.*, *8* (1969) 383.
[7] A.J. Bloodworth and A.G. Davies, *J. Chem. Soc., C*, (1966) 5238.
[8] (a) F.W. Van Der Weij, *J. Polym. Sci., Polym. Chem.*, *19* (1981) 381. (b) J. Robins, B.H. Edwards and S.K. Tokach, *Adv. Urethane Sci. Technol.*, *9* (1984) 65. (c) E.P. Squiller and J.W. Rosthauser, *Modern Paints and Coatings*, June (1987) 28.
[9] (a) J.-J. Tondeur, G. Vandendunghen and M. Watelet, *J. Chem. Res. (M)*, (1992) 3039; (b) 2024.
[10] (a) R. Bacaloglu, L. Cotarca, N. Marcu and St. Tölgyi, *J. Prac. Chem.*, *330* (1988) 541. (b) J. Robins, *J. Appl. Polym. Sci.*, *9* (1965) 821. (c) J.W. Britain and P.G. Gemeinhardt, *J. App. Polym. Sci.*, *4* (1960) 207.
[11] K. Wongkamolsesh and J.E. Kresta, *Urethane Chemistry and Applications*, ACS Symp. Ser. Vol. 270, 1985, p. 111.
[12] S.G. Entelis and O.V. Nesterov, *Kinet. i Katal.*, *7* (1966) 464; *Chem. Abstr.*, *65* (1966) 10462.
[13] A.W. Mulvaney, *Ph.D. Thesis*, University of Wales, 1995.
[14] J.D. Kennedy and W.J. McFarlane, *Chem. Soc., Perkin Trans. 2*, (1974) 146.
[15] A similar retarding effect of carboxylic acids has been noted in the catalysis of the polymerization of lactide by tin(II) diesters. This reaction also is thought to involve the formation of a catalytically active tin alkoxide as the result of alcoholysis of the starting tin diester; X. Zhang, D.A. Macdonald, M.F.A. Goosen and K.B. McAuley, *J. Polym. Sci., Polym. Chem.*, *32* (1994) 2965.
[16] *Kirk Othner Encyclopedia of Chemical Technology*, Vol. 23, Wiley, New York, 3rd edn., 1983, p. 589.
[17] R.K. Ingham, S.D. Rosenberg and H. Gilman, *Chem. Rev.*, *60* (1960) 459.
[18] D. Sukhani, V.D. Gupta and R.C. Mehrotra, *J. Organomet. Chem.*, *7* (1967) 85.
[19] (a) W.D. Honnick and J.J. Zuckerman, *J. Organomet. Chem.*, *178* (1979) 133. (b) T.N. Mitchell, *J. Organomet. Chem.*, *59* (1973) 189.
[20] (a) Y. Iwakura and H. Okada, *Can. J. Chem.*, *38* (1960) 2418. (b) J.F. Smith and E.C. Friedrich, *J. Org. Chem.*, *81* (1959) 161. (c) E. Dyer and J.F. Glenn, *J. Am. Chem. Soc.*, *79* (1959) 366.
[21] A. Pushpa Rupani, A. Singh and R.C. Mehrotra, *J. Organomet. Chem.*, *185* (1980) 209.
[22] (a) C. Naegeli and Y. Tyabji, *Helv. Chim. Acta.*, *17* (1934) 931; (b) 18 (1935) 142.
[23] (a) M.A. Delmas, J.C. Maire, W. McFarlane and Y. Richard, *J. Organomet. Chem.*, *87* (1975) 285. (b) J.D. Kennedy, W. McFarlane and G.S. Pyne, *Bull. Soc. Chim. Belg.*, *84* (1975) 289. (c) A.G. Davies, S.D. Slater, D.C. Povey and G.W. Smith, *J. Organomet. Chem.*, *352* (1988) 283.
[24] P.A. Bates, M.B. Hursthouse, A.G. Davies and S.D. Slater, *J. Organomet. Chem.*, *325* (1987) 129.
[25] T.B. Grindley and R. Thangarasa, *J. Am. Chem. Soc.*, *112* (1990) 1364.
[26] J.R. Horder and M.F. Lappert, *J. Chem. Soc., A*, (1968) 2004.

[27] C. Owens, J.M. Woods, K. Filo, L.L. Pytlewski, D.E. Chasan and N.M. Karayannis, *Inorg. Chim. Acta, 37* (1979) 89.
[28] D.S. Bystrov, T.N. Sumarokava and V.N. Filiminov, *Optic. Spectrosc., 9* (1960) 239.
[29] S.G. Entelis, O.V. Nesterov and R.P. Tiger, *DAN UUSSR, 178* (1968) 661.
[30] P.J. Smith and A.P. Tupiauskas, *Ann. Rep. NMR Spectrosc., 8* (1978) 291.
[31] (a) S. Roelens and M. Taddei, *J. Chem. Soc., Perkin Trans. 2*, (1985) 799. (b) P.J. Smith, R.F.M. White and L. Smith, *J. Organomet. Chem., 40* (1972) 341. (c) A.C. Chapman, A.G. Davies, P.G. Harrison and W. McFarlane, *J. Chem. Soc., C*, (1970) 821.