THE ADDITION OF ORGANOTIN HYDRIDES TO ISOCYANATES AND ISOTHIOCYANATES: SYNTHESIS AND STRUCTURE OF SOME ORGANOTIN-SUBSTITUTED AMIDES[a,b]

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INTRODUCTION

During recent years the chemistry of organotin hydrides has been the subject of considerably study[2]. The reactivity of these compounds towards carbon–carbon unsaturated bonds allowing among other things the synthesis of a variety of functionally substituted organotin compounds[3,4], organotin compounds containing other IVth group metals[5] and linear poly-addition polymers[6], has been firmly established. The scope of this type of reaction recently has been extended by the introduction of suitable catalyst systems[4].

More recently, reactions of organotin hydrides with compounds containing double bonds involving heteroatoms have been studied as well. Ketones and aldehydes upon reaction with organotin hydrides in the absence of catalysts are readily reduced to the corresponding carbinols[7,8,9]. Very recently a note appeared describing the uncatalyzed reduction by triphenyltin hydride of aromatic isocyanates to the corresponding N-arylformamides in 40–50 % yield[10]. Phenyl isothiocyanate yielded a mixture of reduction products upon reaction with the same hydride[10]. However, recent work has shown that addition of trialkyltin hydrides across the carbon–oxygen double bond of aldehydes and ketones may be effected under the influence of UV radiation[11] or suitable catalysts such as azobisisobutyronitrile or zinc chloride[12]. The uncatalyzed reduction by triphenyltin hydride of benzalaniline under rather forced conditions (22 h at 124°) afforded the corresponding amine in 35 % yield[10]. Addition of triethyltin hydride across the carbon–nitrogen double bond of benzal-*p*-toluidine has, however, been realized using suitable catalysts[12].

The communications of Becker *et al.*[10] and Neumann *et al.*[12] cause us to publish some results of our study of reactions of organotin hydrides with isocyanates and isothiocyanates. These compounds had been selected for study because the presence of both a carbon–oxygen (carbon–sulfur) and a carbon–nitrogen double bond gives rise to interesting structural possibilities in case of adduct formation.

RESULTS AND DISCUSSION

In the present study we have found that trialkyltin hydrides readily react with aromatic isocyanates to afford in excellent yields $1:1$ addition products:

(I.a) $R = C_2H_5$; $X = H$
(I.b) $R = C_4H_9$; $X = H$
(I.c) $R = C_2H_5$; $X = Cl$
(I.d) $R = C_2H_5$; $X = NO_2$

$$R_3SnH + X-\langle\rangle-N=C=O \longrightarrow \begin{array}{c} R_3Sn \\ (OCN)-\langle\rangle-X \\ H \\ (I) \end{array}$$
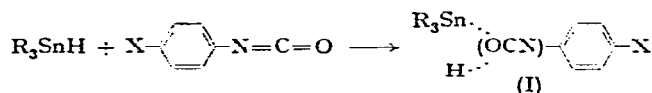
The reaction products are crystalline solids which have been purified by distillation *in vacuo* (I, a, b, c) or by recrystallization (I, d).
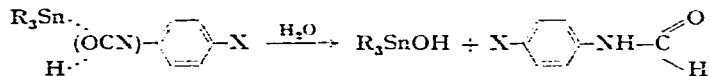
Arguments for the structure of the adducts will be put forward in the following section. The progress of these reactions is easily followed by the disappearance from the IR spectrum of the intense Sn–H stretching absorption at 1810 cm^{-1} and the $N=C=O$ stretching absorption at 2275 cm^{-1}.

The trialkyltin hydride–isocyanate additions proceed in the absence of any added catalyst contrary to the addition reactions involving ketones[11,12] or azomethines[12]. The recently reported addition of phosphine to aromatic isocyanates leading to carbamoylphosphines likewise requires a basic catalyst[13]. The facile uncatalyzed addition of triethyltin hydride to phenyl isocyanate contrasts with the observation that triethylgermanium hydride and phenyl isocyanate had failed to react after 16 h at reflux temperature ($150°C$). Other examples of the decreased mobility of the hydrogen atom in organogermanium hydrides as compared with in organotin hydrides are cited by Rykens[14].

In fact, the isocyanate additions are exothermal to the extent that the use of a diluent is called for, the reactions being carried out in benzene. No attempts have been made to establish minimum reaction times. The occurrence of side reactions involving the chloro or nitro substituent under these conditions has not been observed (compare ref. 8).
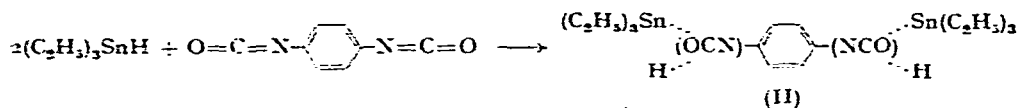
Formation of N-arylformamides, the only product isolated by Becker *et al.*[10] from the reaction of aryl isocyanates with two moles of triphenyltin hydride, did not occur under our conditions, NH absorption being totally absent from the IR spectrum of the crude reaction products. We have obtained proof that reduction of phenyl isocyanate by triphenyltin hydride[10] proceeds via formation of the $1:1$ adduct (I) $(R = C_6H_5; X = H)$[15].

The aryl isocyanate adducts are very susceptible to hydrolysis which leads to the corresponding N-arylformamides:

$$\begin{array}{c} R_3Sn \\ (OCN)-\langle\rangle-X \\ H \end{array} \xrightarrow{H_2O} R_3SnOH + X-\langle\rangle-NH-C\begin{array}{c}O\\ \\ H\end{array}$$
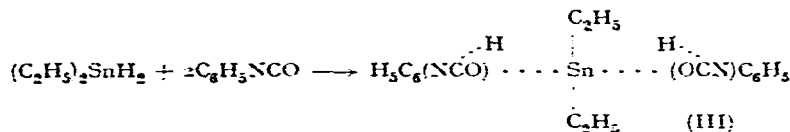
Thus, an alternative reduction method requiring only an equimolar amount of triorganotin hydride is available. A hydrolysis step is, however, necessary (compare ref. 10).
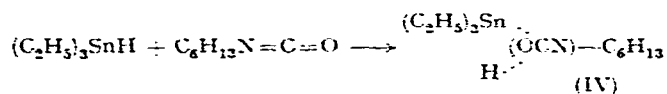
p-Phenylene diisocyanate on reaction with two moles of triethyltin hydride readily affords the expected 1:2 adduct:

$$2(C_2H_5)_3SnH + O=C=N-\langle\ \rangle-N=C=O \longrightarrow \begin{array}{c} (C_2H_5)_3Sn \cdots \\ (OCN)-\langle\ \rangle-(NCO) \\ H \cdots \end{array} \begin{array}{c} \cdots Sn(C_2H_5)_3 \\ \cdots H \end{array}$$

$$(II)$$

The reaction of diethyltin dihydride with two moles of phenylisocyanate under very mild conditions (2 h at 45° in benzene solution) affords the 1:2 adduct in quantitative yield:

$$(C_2H_5)_2SnH_2 + 2C_6H_5NCO \longrightarrow H_5C_6(NCO) \cdots \overset{\overset{\displaystyle C_2H_5}{|}}{\underset{\underset{\displaystyle C_2H_5}{|}}{Sn}} \cdots (OCN)C_6H_5$$
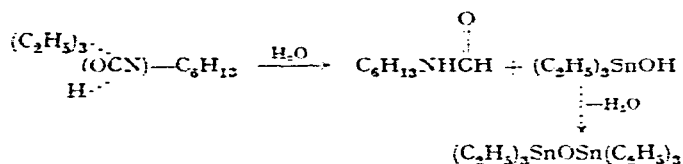
$$(III)$$

Aliphatic isocyanates are somewhat less reactive towards organotin hydrides and the reaction appears to be more complex. Triethyltin hydride and hexyl isocyanate do not react exothermally. Reaction is, however, complete after 1 h at 90°C as evidenced by the disappearance of Sn–H absorption from the IR spectrum. Fractional distillation afforded two fractions of which the higher boiling (54 % yield) analyzed correctly for the 1:1 adduct:

$$(C_2H_5)_3SnH + C_6H_{13}N=C=O \longrightarrow \begin{array}{c} (C_2H_5)_3Sn \cdots \\ (OCN)-C_6H_{13} \\ H \cdots \end{array}$$
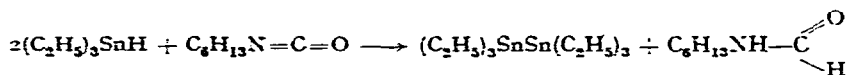
$$(IV)$$

This adduct by gas chromatography appeared to be a single compound. Its structure will be discussed below.

The low boiling fraction gave rise to four peaks in its gas-chromatogram of which one appeared identical with the 1:1 adduct (IV). Two other peaks have been characterized as *N*-hexylformamide and hexaethylditin. Hydrolysis of (IV) gives rise to the formation of *N*-hexylformamide and triethyltin hydroxide:

$$\begin{array}{c} (C_2H_5)_3 \cdots \\ (OCN)-C_6H_{13} \\ H \cdots \end{array} \xrightarrow{H_2O} C_6H_{13}NHCH \overset{\overset{\displaystyle O}{||}}{} + (C_2H_5)_3SnOH$$

$$\Big\downarrow -H_2O$$

$$(C_2H_5)_3SnOSn(C_2H_5)_3$$

Triethyltin hydroxide or triethyltin oxide which has the same retention time as hexaethylditin but is easily detected in very small concentration by its strong unsymmetrical Sn–O–Sn stretching vibration at 765 cm^{-1}, were, however, notably absent, excluding the possibility of hydrolysis. Thus, the two products observed result from the reducing action of triethyltin hydride on hexyl isocyanate:
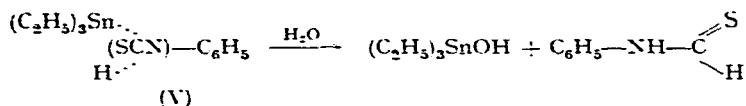
$$2(C_2H_5)_3SnH + C_6H_{13}N=C=O \longrightarrow (C_2H_5)_3SnSn(C_2H_5)_3 + C_6H_{13}NH-C\overset{\displaystyle \nearrow O}{\underset{\displaystyle \searrow H}{}}$$

Triethyltin hydride and phenyl isothiocyanate readily react to give a liquid containing crystals. Whereas Sn–H absorption is completely absent after 1 h at 100°C, slight residual $N=C=S$ absorption (band at 2080 cm^{-1}) is still present. The main product (85 % by fractional distillation) consists of the expected 1:1 adduct, the structure of which will be discussed below:

$$(C_2H_5)_3SnH + C_6H_5—N=C=S \longrightarrow \begin{array}{c}(C_2H_5)_3Sn\cdots\\(SCN)—C_6H_5\\H\cdots\end{array}$$

$$(V)$$
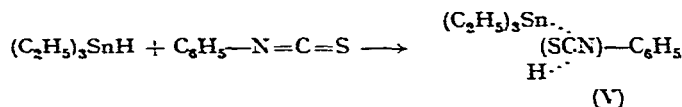
The solid product (2 %) was identified as N-phenylthioformamide. Apparently, some reduction of the isothiocyanate group (presumably the thiocarbonyl portion) by triethyltin hydride has occurred:

$$2(C_2H_5)_3SnH + C_6H_5—N=C=S \longrightarrow (C_2H_5)_3SnSn(C_2H_5)_3 + C_6H_5—NH—C\overset{S}{\underset{H}{\diagdown}}$$
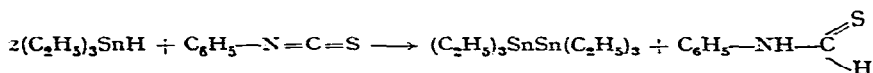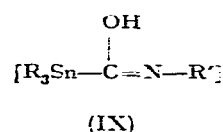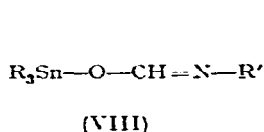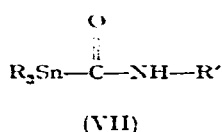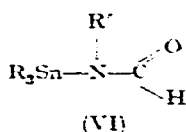
The same compound separates in the form of large needles from the 1:1 adduct (V) when the latter is left in contact with moist air:

$$\begin{array}{c}(C_2H_5)_3Sn\cdots\\(SCN)—C_6H_5\\H\cdots\end{array} \xrightarrow{H_2O} (C_2H_5)_3SnOH + C_6H_5—NH—C\overset{S}{\underset{H}{\diagdown}}$$

$$(V)$$

Surprisingly, the main product resulting from the exothermal reaction of triethyltin hydride and methyl isothiocyanate was triethyltin sulfide. No 1:1 addition product was isolated.

STRUCTURE OF THE ADDUCTS

The following structures must be considered for the 1:1 adduct of an organotin monohydride and an isocyanate:

$$\begin{array}{cccc}
R_3Sn—N—C\overset{O}{\underset{H}{\diagdown}} & R_3Sn—C—NH—R' & R_3Sn—O—CH=N—R' & [R_3Sn—C=N—R']\\
(VI) & (VII) & (VIII) & (IX)
\end{array}$$

Structure (IX) is the lactim tautomer of (VII) and may be disregarded, since there is no reason to believe that in amides in which a triorganotin group is attached to the carbon atom the equilibrium between the tautomeric forms is displaced in favour of (IX). Moreover, absorption in the NH/OH region of the infrared, when observed, occurred at 3300 cm^{-1} which is more characteristic for NH vibrations.

The reaction product of triethyltin hydride and phenyl isocyanate (I, a) does not show any IR absorption in the OH/NH region which excludes structure (VII) (Fig. 1). The UV spectrum which shows a strong band at 239 mμ (log $\varepsilon = 4.08$) and weak

absorption at 280 mμ (log ε about 3) is remarkably alike to that of N-phenylformamide (λ_{max} 240 mμ; log ε = 4.10 and weak absorption around 280 mμ; log ε about 3), but differs appreciably from that of ethyl N-phenylformimidate, $C_6H_5-N=CH-OC_2H_5$, which has an absorption maximum at 248 mμ with log ε = 3.78 (Fig. 2).
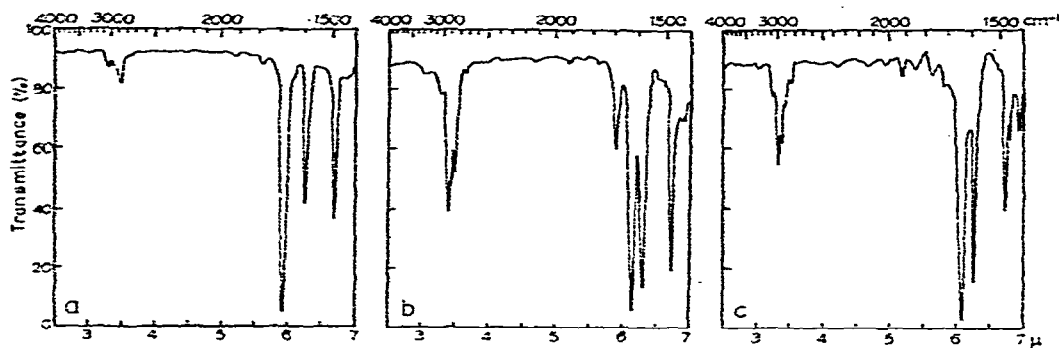

Fig. 1. IR absorption spectra in carbon tetrachloride: a) N-phenyl-N-methylformamide; b) adduct of triethyltin hydride and phenyl isocyanate (I.a: VI, R = C_2H_5; R' = C_6H_5); c) ethyl N-phenylformimidate.

The spectrum of the adduct was taken under conditions which exclude the possibility of hydrolysis which, of course, would lead to the formation of N-phenyl-formamide.
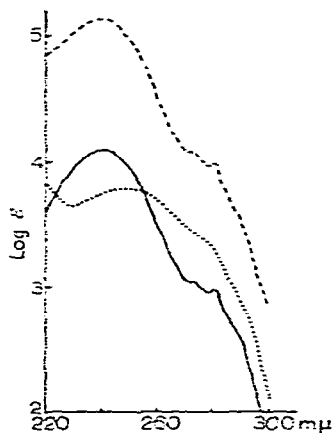

Fig. 2. UV absorption spectra in cyclohexane: —— N-phenylformamide; – – – adduct of triethyltin hydride and phenyl isocyanate (I.a: VI, R = C_2H_5; R' = C_6H_5 (log ε ÷ 1); ··· ethyl N-phenylformimidate.

Thus the UV spectra strongly support structure (VI). IR evidence for this structure is not conclusive since both reference compounds show strong bands in the carbonyl region (Fig. 1). These bands are located at 1690 cm^{-1} for N-phenyl-N-methyl-formamide and at 1640 cm^{-1} for ethyl N-phenylformimidate. The adduct absorbs strongly at 1630 cm^{-1} and shows a weak band at 1695 cm^{-1}. The intensity of the latter band could be reduced to nearly zero when extreme care was taken to exclude traces of moisture, so that this band presumably must be attributed to the presence of

traces of N-phenylformamide due to hydrolysis of the adduct[a]. At first sight the 1630 cm^{-1} band of the adduct would seem to point to structure (VIII), in conflict with the results of UV spectroscopy. Further information was therefore sought from NMR measurements[b]. The signal of the proton at the CH group appeared at 8.40 δ for N-phenyl-N-methylformamide, at 7.60 δ for ethyl N-phenylformimidate and at 8.34 δ for the adduct (I,a) (shifts are in ppm down field from tetramethylsilane), thus plainly favouring structure (VI). The solution of the adduct in carbon tetrachloride after measurement of the NMR spectrum displayed a very low intensity IR band at 1695 cm^{-1}, indicating that hydrolysis had not occurred to any appreciable extent.

The low IR frequency of the carbonyl band in a structure such as (VI) is not completely unexpected. In trialkyltin carboxylates this band is found at the low value of 1650 cm^{-1} (organic esters absorb at 1740 cm^{-1}). In another compound containing the sequence $\geq$Sn–N–C=O, viz. N,N'-bis(triethyltin)-N,N'-dicarbethoxy-hydrazine the carbonyl band is found at 1670 cm^{-1}, whereas the diethyl analogue absorbs at 1715 cm^{-1} (ref. 15). The shift to lower frequency of the carbonyl absorption in the compounds under discussion must be due to the influence of the heavy tin atom (compare ref. 16).

Similarly, the IR spectra of the products of the reactions between triethyltin hydride and p-chlorophenyl isocyanate, p-nitrophenyl isocyanate and p-phenylene diisocyanate do not show NH absorption and the pattern in the carbonyl region is the same. Consequently, in the aromatic series addition occurs across the carbon–nitrogen double bond with the formation of a tin–nitrogen bond.

UV spectroscopy is no longer a useful tool with the adduct of triethyltin hydride and hexyl isocyanate (IV). Its structure follows, however, unambiguously from the IR spectrum. A rather sharp band at 3300 cm^{-1} characteristic of the presence of an NH group is found. Moreover, in the region from 1700–1300 cm^{-1} in which bands characteristic for the amide group are to be found the spectrum of the adduct resembles that of N-hexylformamide (Fig. 3).
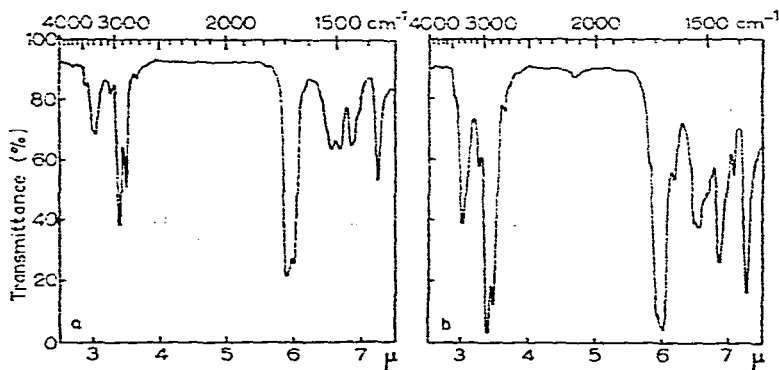

Fig. 3. IR absorption spectra in carbon tetrachloride: a) N-hexylformamide; b) adduct of triethyltin hydride and hexyl isocyanate (IV: VII. R = C$_2$H$_5$; R' = C$_6$H$_{13}$).

Thus, as in the case of phenyl isocyanate, addition across the carbon–nitrogen double bond has occurred, but now the organotin group has become attached to the carbon atom with formation of triethyl(N-hexylcarbamoyl)tin (VII, R = C_2H_5; R' = C_6H_{13}). To our knowledge this is the first example of an organotin compound containing a carbonyl group directly bound to tin.

The addition product of triethyltin hydride and phenyl isothiocyanate (V) did not display NH absorption in the IR spectrum, so that it should have structure (X) or (XI):

$$(C_2H_5)_3Sn—N—C\begin{matrix}C_6H_5\\ \\ \nearrow S \\ \searrow H\end{matrix}$$

(X)

$$(C_2H_5)_3Sn—S—CH=N—C_6H_5$$

(XI)
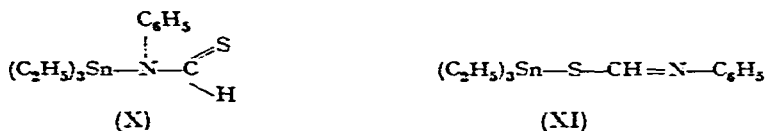
It might be expected that its UV spectrum would resemble the UV spectrum of N-phenylthioformamide if structure (X) were correct. In particular the low intensity n-π^* band between 350 and 450 mμ, common to all thioamides ought to be easily detected. No such band was found, however, and in fact the spectrum shows absorption maxima not incompatible with the partial structure C_6H_5 —N=C< (Fig. 4).

Consequently, in this case addition across the carbon–sulfur double bond has occurred with formation of triethyltin N-phenylthioformimidate (XI). The addition along this course is supported by the isolation of triethyltin sulfide from the reaction of triethyltin hydride and methyl isothiocyanate (compare ref. 10).
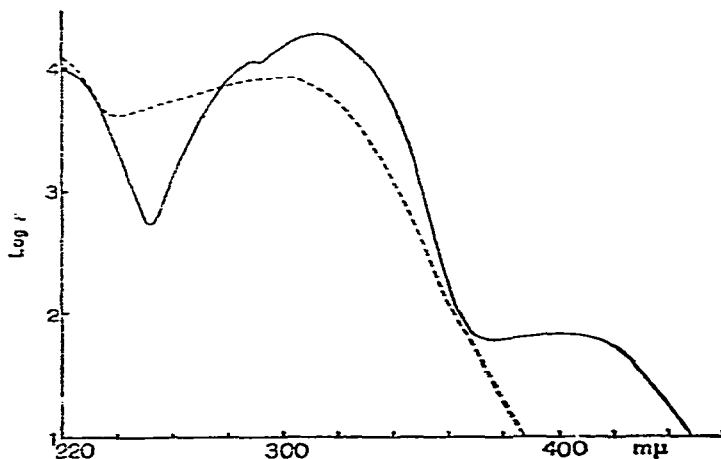

Fig. 4. UV absorption spectra in cyclohexane —— N-phenylthioformamide; — — — adduct of triethyltin hydride and phenyl isothiocyanate (V: XI).

Thus, depending on the unsaturated reactant used each of the possible modes of addition has been observed.

EXPERIMENTAL PART

An atmosphere of dry nitrogen was maintained throughout these experiments.

Gas-chromatographic experiments were carried out with a F & M Model 500 gas chromatograph with silicon gum rubber as the stationary phase. Temperature pro-

gramming (9°/min) was applied. Fractions were collected by cooling and dissolved in appropriate solvents for IR spectroscopy.

Organotin hydrides[17], p-chlorophenyl isocyanate[18], p-nitrophenyl isocyanate[19] and p-phenylene diisocyanate[20] were prepared by published methods. Phenyl isocyanate, phenyl isothiocyanate and methyl isothiocyanate were redistilled commercial preparations (Fluka). N-Phenyl-, N-hexyl- and N-methyl-N-phenylformamide were prepared by formylation of the corresponding amines.

Triethyl(N-phenylformamido)tin (I, a)

An exothermal reaction occurred when triethyltin hydride (4.14 g, 0.02 mole) and phenyl isocyanate (2.38 g, 0.02 mole) were mixed at room temperature. Ice cooling was applied and the reaction mixture gradually solidified. The IR spectrum of the product was devoid of Sn–H and N=C=O absorption (bands at 1810 cm^{-1} and 2275 cm^{-1}). Distillation afforded 5.92 g (90 %) of a colourless liquid with b.p. 171–172° at 13 mm which readily crystallized (m.p. 50–53°). (Found: N, 4.29; Sn, 36.45. C$_{13}$H$_{21}$NOSn calcd.: N, 4.29; Sn, 36.41 %.)

Tributyl(N-phenylformamido)tin (I, b)

Similarly, the exothermal reaction of 2.91 g (0.01 mole) of tributyltin hydride and 1.19 g (0.01 mole) of phenyl isocyanate afforded 3.36 g (82 %) of a colourless crystalline solid (m.p. 64°) with b.p. 170° at 0.1 mm. (Found: N, 3.31; Sn, 29.36. C$_{19}$H$_{33}$NOSn calcd.: N, 3.42; Sn, 29.00 %.)

Triethyl[N-(p-chlorophenyl)formamido]tin (I, c)

A solution of 6.21 g (0.03 mole) of triethyltin hydride and 4.55 g (0.03 mole) of p-chlorophenyl isocyanate in 25 ml of dry benzene was heated under reflux for one hour. The IR spectrum was devoid of Sn–H or N=C=O absorption. Distillation of the reaction product afforded 9.30 g (87 %) of a colourless liquid (b.p. 120–122° at 0.1 mm) which readily crystallized (m.p. 77–79°). (Found: N, 4.04; Sn, 33.10. C$_{13}$H$_{20}$ClNOSn calcd.: N, 3.89; Sn, 32.94 %.)

Triethyl[N-(p-nitrophenyl)formamido]tin (I, d)

A solution of 7.45 g (0.036 mole) of triethyltin hydride and 5.90 g (0.036 mole) of p-nitrophenyl isocyanate in 60 ml of dry benzene was heated under reflux for two hours. The IR spectrum was devoid of Sn–H or N=C=O absorption. A slight precipitate was removed by filtration. The filtrate after partial evaporation (40 ml) upon cooling deposited a yellow crystalline solid with m.p. 116–119°. Yield 10.9 g (82 %). (Found: N, 7.77; Sn, 32.28. C$_{13}$H$_{20}$N$_2$O$_3$Sn calcd.: N, 7.55; Sn, 32.00 %.)

p-Bis[N-(triethyltin)formamido]benzene (II)

To a solution of 2.00 g (0.0125 mole) of p-phenylene diisocyanate in 150 ml of dry benzene 5.20 g (0.0250 mole) of triethyltin hydride was added. Upon heating the clear solution under reflux colourless crystals started to deposit. Refluxing was continued for ninety minutes and then the reaction mixture was cooled. The solid was collected, washed with pentane and dried. Yield 6.40 g (90 % of theory). M.p. 191–195°. (Found: N, 5.10; Sn, 40.96. C$_{20}$H$_{36}$N$_2$O$_2$Sn$_2$ calcd.: N, 4.88; Sn, 41.37 %.)

Bis(N-phenylformamido)diethyltin (III)

A solution of 5.37 g (0.03 mole) of diethyltin dihydride and 7.14 g (0.06 mole) of phenyl isocyanate in 50 ml of benzene was heated at 45° for two hours. Residual Sn–H or $N=C=O$ absorption in the IR spectrum was absent after this period. After evaporation of the solvent *in vacuo* a colourless oil remained which crystallized on standing. Attempted distillation *in vacuo* resulted in decomposition, a mixture of solid and liquid products being obtained. Attempts at recrystallization unvariably led to separation as an oil which solidified on standing. (Found: N, 6.57; Sn, 28.73. $C_{18}H_{22}N_2O_2Sn$ calcd.: N, 6.72; Sn, 28.46 %.)

Triethyl(N-hexylcarbamoyl)tin (IV)

The reaction product obtained after heating a mixture of 8.28 g (0.04 mole) of triethyltin hydride and 5.08 g (0.04 mole) of hexyl isocyanate at 90° for one hour did not contain residual Sn–H absorption in the IR spectrum. Repeated distillation finally resulted in the isolation of two fractions.

The fraction with b.p. 105–106° at 0.1 mm and n_D^{20} 1.4910 by gas chromatography appeared to be a single compound. Yield 7.18 g (54 % of theory). The compound which slowly crystallized (m.p. 28°) analyzed for the 1:1 adduct. (Found: N, 4.31; Sn, 35.70. $C_{13}H_{29}NOSn$ calcd.: N, 4.20; Sn, 35.54 %.)

The fraction with b.p. 93–100° consisted of four components as shown by gas chromatography. The three major components were identified as N-hexylformamide, hexaethylditin and triethyl(N-hexylcarbamoyl)tin by comparison (gas-chromatographic retention time and infrared spectra) with authentic samples.

Triethyltin N-phenylthioformimidate (V)

A solution of 10.6 g (0.05 mole) of triethyltin hydride and 6.9 g (0.05 mole) of phenyl isothiocyanate in 60 ml of dry benzene was refluxed during two hours. The IR spectrum displayed slight residual $N=C=S$ absorption (band at 2080 cm^{-1}) but Sn–H absorption was absent. Upon fractionation *in vacuo* of the reaction product the distillate partly solidified in the condenser. Redistillation of the liquid portion afforded 14.8 g (85 % of theory) of a yellow oil with b.p. 115° at 0.2 mm and n_D^{20} 1.5910. This product which turns dark brown on standing analyzed for the 1:1 adduct. (Found: N, 3.87; Sn, 34.55. $C_{13}H_{21}NSSn$ calcd.: N, 4.09; Sn, 34.70 %.)

The solid product which after recrystallization from 95 % ethanol melted at 138–139° (long pale yellow needles) was identified as N-phenylthioformamide (reported m.p. 137.5° [21]). Yield 140 mg (2 % of theory). (Found: C, 61.08; H, 5.53; N, 10.21. C_7H_7NS calcd.: C, 61.36; H, 5.16; N, 10.22 %.)

Reaction of triethyltin hydride with methyl isothiocyanate

When warming up a mixture of 6.18 g (0.03 mole) of triethyltin hydride and 1.86 g (0.03 mole) of methyl isothiocyanate an exothermal reaction occurred at about 50° causing the reaction mixture to reflux. Fractional distillation revealed the absence of either triethyltin hydride or methyl isothiocyanate. The main product was a pale yellow liquid with b.p. 125–128° at 0.10 mm and n_D^{20} 1.5485, identified by comparison of its IR spectrum with an authentic sample as triethyltin sulfide (reported[2] n_D^{20} 1.5468). A white crystalline solid with m.p. 113–114° the identity of which has not been established was isolated in 1 % yield.

SUMMARY

Organotin hydrides add across the carbon–nitrogen double bond of aryl isocyanates (tin–nitrogen bond formation) and hexyl isocyanate (tin–carbon bond formation) and across the carbon–sulfur double bond of phenyl isothiocyanate (tin–sulfur bond formation) to afford in excellent yield 1:1 adducts. Structures have been assigned on the basis of IR and UV evidence.

Hexyl isocyanate (but not aryl isocyanates) and phenyl isothiocyanate are reduced to a small extent by triethyltin hydride to N-hexylformamide and N-phenyl-thioformamide.

Each of the adducts is readily hydrolyzed to the corresponding N-aryl(alkyl)-formamide or N-phenylthioformamide.

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