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SYNTHESIS AND SOME REACTIONS OF BIS(TRIPHENYLSTANNYL)-CARBODIIMIDE, *N*-(TRIPHENYLSTANNYL)-*N'*-TRITYLCARBODIIMIDE, AND (TRIPHENYLSTANNYL)CYANAMIDE

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SUMMARY

Some methods for preparing bis(triphenylstannyl)carbodiimide (I), *N*-(triphenylstannyl)-*N'*-tritylcarbodiimide (II), and (triphenylstannyl)cyanamide are described. (I) was found to react with 1,3-disubstituted thioureas in refluxing acetonitrile or toluene to give bis(triphenyltin) sulfide and the corresponding *N*,*N'*-disubstituted-*N''*-cyanoguanidine. Some evidence for a diorganocarbodiimide intermediate in this reaction was found. The reaction of (I) with thiourea in refluxing acetonitrile was found to give bis(triphenyltin) sulfide, (triphenylstannyl)cyanamide and unchanged thiourea. The reaction of (I) with cyanamide gave (triphenylstannyl)cyanamide. (Triphenylstannyl)cyanamide was found to react with bis(triphenyltin) oxide in refluxing acetonitrile to give (I). (Triphenylstannyl)cyanamide was found to disproportionate in refluxing benzene to give (I) and dicyandiamide. (II) was found to be more hydrolytically stable than (I). The SnN bonds in both (I) and (II) were found to be readily cleaved by acetic acid. It was found that triphenyltin iodide and triphenyltin chloride can be conveniently prepared in good yield by the reaction of bis(triphenyltin) oxide with either calcium iodide or calcium chloride in refluxing acetonitrile.

INTRODUCTION

Very little information on the synthesis and reactions of organotin carbodiimides has appeared in the literature. It was reported in a review article[1] that bis(triphenylstannyl)carbodiimide can be prepared by the reaction of triphenyltin chloride with sodium cyanamide. In a subsequent review[2], a melting point of 99–100.5° was given for this compound. Gerega *et al.*[3] reported that this compound, prepared by the reaction of triphenyltin hydroxide with cyanamide in ethyl ether, has a melting point of 53–55°. We have reported[4] that this compound, prepared by the reaction of bis(triphenyltin) oxide with cyanamide in refluxing acetonitrile, has a melting point of 95–97°. The only other organotin carbodiimides reported in the literature are bis(triethylstannyl)carbodiimide[3,5] and bis(trimethylstannyl)carbodiimide[5a]. The sparsity of data in this area and the possibility that organotin carbodiimides may have synthetic utility prompted the present investigation.

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RESULTS AND DISCUSSION

We previously reported[4] that bis(triphenylstannyl)carbodiimide (I) can be prepared by the reaction of bis(triphenyltin) oxide with cyanamide in refluxing acetonitrile:

$$(C_6H_5)_3SnOSn(C_6H_5)_3+H_2NCN \rightarrow \underset{\text{(I)}}{(C_6H_5)_3SnNCNSn(C_6H_5)_3}+H_2O \qquad (1)$$

Since the tin–nitrogen bond in many organotin–nitrogen compounds is hydrolytically unstable[2,6–8], the reaction represented by eqn. (1) was carried out in the presence of anhydrous magnesium sulfate to ensure that the water formed in the reaction did not hydrolyze (I). We have since found this precaution to be unnecessary; (I) is completely stable to the water that is formed. In view of the crystal structure of bis(trimethylstannyl)carbodiimide[5a], the hydrolytic stability of (I) may be due to the formation of pentacoordinate tin by the intermolecular coordinating action of a nitrogen atom. This explanation also probably accounts for the hydrolytic stability exhibited by certain other organotin–nitrogen compounds[9–17].

In addition to the method represented by eqn. (1), it has been found that compound (I) can be prepared in good yield by the reactions represented by eqns. (2)–(6).

$$2(C_6H_5)_3SnOSn(C_6H_5)_3+H_2NC(S)NH_2 \rightarrow \text{(I)}+(C_6H_5)_3SnSSn(C_6H_5)_3+2\,H_2O \qquad (2)$$

$$2(C_6H_5)_3SnI+H_2NCN+2(C_2H_5)_3N \rightarrow \text{(I)}+2(C_2H_5)_3N\cdot HI \qquad (3)$$

$$2(C_6H_5)_3SnI+Na_2NCN \rightarrow \text{(I)}+2\,NaI \qquad (4)$$

$$(C_6H_5)_3SnOSn(C_6H_5)_3+2(C_6H_5)_3SnNHCN \rightarrow 2\text{(I)}+H_2O \qquad (5)$$

$$4(C_6H_5)_3SnNHCN \rightarrow 2\text{(I)}+H_2NC(=NH)NHCN \qquad (6)$$

The (triphenylstannyl)cyanamide was identified by elemental analysis and by its infra-prepared in 76% yield by allowing bis(triphenyltin) oxide to react with an excess of cyanamide in refluxing ethyl ether:

$$(C_6H_5)_3SnOSn(C_6H_5)_3+2NH_2CN \rightarrow 2(C_6H_5)_3SnNHCN+H_2O \qquad (7)$$

The (triphenylstannyl)cyanamide was identified by elemental analysis and by its infrared spectrum, which shows an NH band[18] at 3.00 μ, a strong band at 4.60 μ, due to the CN linkage[19], and strong bands at 13.75 μ and 14.40 μ, due to monosubstituted phenyl groups[18]. Reaction (5) is of some significance since substitution of other organometallic oxides or hydroxides for bis(triphenyltin) oxide should give carbodiimides containing tin and another metal. We intend to explore this possibility.

Substitution of tritylthiourea for thiourea in reaction (2) gave *N*-(triphenylstannyl)-*N'*-tritylcarbodiimide (II) in 73% yield, eqn. (8). (II) was also prepared in good yield by the reaction of bis(triphenyltin) oxide with tritylcyanamide in refluxing acetonitrile, eqn. (9), and by the reaction of triphenyltin iodide with tritylcyanamide and triethylamine in refluxing benzene, eqn. (10). Like (I), (II) is stable to the water that is formed along with it.

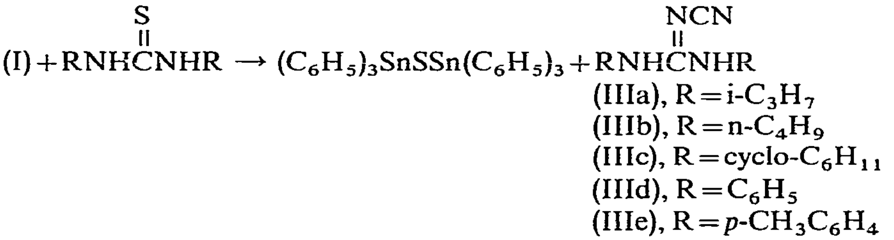
$$3\,(C_6H_5)_3SnOSn(C_6H_5)_3+2\,(C_6H_5)_3CNHC(S)NH_2 \rightarrow$$
$$\rightarrow 2\,\underset{\text{(II)}}{(C_6H_5)_3SnNCNC(C_6H_5)_3}+2\,(C_6H_5)_3SnSSn(C_6H_5)_3+3\,H_2O \quad (8)$$

$$(C_6H_5)_3SnOSn(C_6H_5)_3+2\,(C_6H_5)_3CNHCN \rightarrow 2\,(II)+H_2O \quad (9)$$

$$(C_6H_5)_3SnI+(C_6H_5)_3CNHCN+(C_2H_5)_3N \rightarrow (II)+(C_2H_5)_3N\cdot HI \quad (10)$$

The infrared spectrum of (II) shows a stong carbodiimide band[21] at 4.80 μ and strong monosubstituted phenyl bands[18] at 13.25 μ, 13.70 μ, and 14.40 μ. In tritylcyanamide and ditritylcarbodiimide the strong monosubstituted phenyl bands occur at 13.25 μ and 14.35 μ. The band at 13.25 μ in (II), therefore, must be due to the phenyl groups attached to carbon.

Bis(triphenylstannyl)carbodiimide (I) was found to react with 1,3-disubstituted thioureas to give bis(triphenyltin) sulfide (82–90%) and the corresponding *N,N'*-disubstituted-*N''*-cyanoguanidine (III) (45–74%), eqn. (11). The yields given for (III)



$$(I)+RNH\overset{\overset{\displaystyle S}{\|}}{C}NHR \rightarrow (C_6H_5)_3SnSSn(C_6H_5)_3+RNH\overset{\overset{\displaystyle NCN}{\|}}{C}NHR \quad (11)$$

(IIIa), $R = i\text{-}C_3H_7$
(IIIb), $R = n\text{-}C_4H_9$
(IIIc), $R = cyclo\text{-}C_6H_{11}$
(IIId), $R = C_6H_5$
(IIIe), $R = p\text{-}CH_3C_6H_4$

are based on material that melts within five degrees of the melting point of the analytical sample; the crude yields were much higher. For R = aryl the reaction was carried out in refluxing acetonitrile. For R = alkyl the reaction was carried out in refluxing toluene, since for $R = n\text{-}C_4H_9$ no reaction was observed in refluxing acetonitrile. Compounds (IIIa)–(IIIe) were identified by their elemental analyses, by their spectral properties, and, with the exception of (IIIe), which is a new compound, by comparison of their melting points with the literature values. Compounds (IIIa)–(IIId) have been prepared previously by different methods[22–28].

A carbodiimide, RNCNR, and cyanamide may be intermediates in reaction (11), since the reaction of dicyclohexylcarbodiimide with cyanamide and bis(triphenyltin) sulfide (1/1/1 mole ratio) in refluxing toluene afforded (IIIc) in 53% yield. The yield was 50% in refluxing acetonitrile. The bis(triphenyltin) sulfide probably catalyzes the addition of the cyanamide to the carbodiimide since the yield of (IIIc) (in toluene) was only 14% in the absence of the sulfide. In the absence of sulfide, dicyandiamide (48%) was also isolated. Organotin compounds have previously been found to catalyze the addition of water and of alcohols to carbodiimides[29]. A carbodiimide has previously been shown to be an intermediate in the reaction of 1,3-disubstituted thioureas with bis(tri-n-butyltin) oxide[30] and bis(triphenyltin) oxide[4]. No reaction was observed between (I) and ethylenethiourea (2-imidazolidinethione) in refluxing toluene. In this case carbodiimide formation is not possible because of ring strain.

The reaction of (I) with thiourea (1/1 mole ratio) in refluxing acetonitrile gave bis(triphenyltin) sulfide in 46% yield. The sulfide crystallized directly from the acetonitrile solution on cooling and was collected by suction filtration. Evaporation of the acetonitrile from the filtrate left a solid whose IR spectrum contained a strong band at 4.6 μ which is probably due to the CN linkage. No band at 4.8 μ due to the carbodiimide linkage was present, indicating complete consumption of (I). Thin-layer chromatographic analysis of the solid showed it to contain thiourea and (triphenylstannyl)cyanamide. (Triphenylstannyl)cyanamide was prepared independently in 69% yield by the reaction of (I) with cyanamide (1/1 mole ratio) in refluxing ethyl ether. The (triphenylstannyl)cyanamide from (I) and thiourea, therefore, may have arisen from the reaction of (I) with cyanamide, which may be formed as an intermediate. The fact that the yield of bis(triphenyltin) sulfide is not quantitative and that some of the thiourea remains unreacted, while all of (I) is consumed, means that (I) is more reactive towards the cyanamide produced in the reaction than towards thiourea. In summary, the reactions represented by eqns. (12) and (13) occur when an acetonitrile solution of (I) and thiourea is refluxed.

$$\text{(I)} + H_2NC(S)NH_2 \rightarrow (C_6H_5)_3SnSSn(C_6H_5)_3 + 2\ H_2NCN \qquad (12)$$

$$\text{(I)} + H_2NCN \rightarrow 2\,(C_6H_5)_3SnNHCN \qquad (13)$$

N-(Triphenylstannyl)-*N'*-tritylcarbodiimide (II) was found to be more hydrolytically stable than bis(triphenylstannyl)carbodiimide (I). Both (I) and (II) were found to readily dissolve in refluxing 95% ethanol. After 20 h, (I) gave bis(triphenyltin) oxide (87%) and dicyandiamide (27%), whereas (II) was recovered unchanged in 81% yield. In the crude reaction mixture from (I) no band at 4.8 μ due to the carbodiimide linkage was present, indicating complete reaction with water. In the crude reaction mixture from (II) a carbodiimide band at 4.8 μ was present, while no band at 12.9 μ due to the SnOSn linkage was present.

As expected, the SnN bonds in both (I) and (II) were found to be readily cleaved by acetic acid. The reaction of (I) with acetic acid (1/2 mole ratio) in refluxing acetonitrile gave triphenyltin acetate (88%) and dicyandiamide. The reaction of (II) with acetic acid (1/1 mole ratio) in refluxing acetonitrile gave triphenyltin acetate (65%) and tritylcyanamide (39%).

The triphenyltin iodide used in this research was conveniently prepared in high yield by the reaction of bis(triphenyltin) oxide with calcium iodide hydrate in refluxing acetonitrile. The triphenyltin iodide crystallized in pure form directly from the acetonitrile solution on cooling. This method is more convenient than the usual procedure, which involves the reaction of tetraphenyltin with iodine in carbon tetrachloride[31]. Similarly, triphenyltin chloride can be prepared using anhydrous calcium chloride.

EXPERIMENTAL

Melting points were determined with a Mel-Temp capillary melting point apparatus and are uncorrected. All reactions were followed by thin-layer chromatography using silica gel plates; spots were detected using either ultraviolet light or a sodium nitroprusside-potassium ferricyanide spray for the detection of cyanamide and its derivatives[32]. The infrared data were obtained using KBr pellets with a Perkin–Elmer Infracord. The far infrared data were obtained with a Perkin–Elmer Model FIS-3 far infrared spectrophotometer (polyethylene pellets) and with a Perkin–

Elmer Model 21 double beam infrared spectrophotometer which was fitted with a cesium bromide prism and purged with nitrogen (KBr pellets). The NMR spectra were determined with a Varian Model A-60 NMR spectrometer using tetramethylsilane as the internal standard. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Preparation of bis(triphenylstannyl)carbodiimide (I)

(1). *Reaction of bis(triphenyltin) oxide with cyanamide.* A mixture of bis(triphenyltin) oxide (28.64 g, 0.04 mole), cyanamide (1.85 g, 0.044 mole), and acetonitrile (300 ml) was refluxed for 5 h. The solvent was evaporated, and the residue was recrystallized from ethanol to give 25.91 g (88 %) of (I), m.p. 96–99°, no depression on admixture with an analytical sample[4]. Two recrystallizations from ethanol raised the m.p. to 98–100°. IR: 4.80 (NCN), 13.72 and 14.35 (C_6H_5) μ; far IR: 21.30 (SnN)[3], 22.80 (C_6H_5)[33], 36.90 and 43.67 (SnC_6H_5)[33] μ; NMR (CCl_4): τ 2.4–2.8 (multiplet, C_6H_5).

(2). *Reaction of bis(triphenyltin) oxide with thiourea.* A mixture of bis(triphenyltin) oxide (14.32 g, 0.02 mole), thiourea (0.76 g, 0.01 mole), and acetonitrile (100 ml) was refluxed for 5 h. The solution was allowed to cool to room temperature, and the colorless needles which separated were collected on a filter to give 6.97 g of solid, m.p. 138–142°. Recrystallization from acetonitrile gave 6.03 g (82 %) of bis(triphenyltin) sulfide, m.p. 143–146° (lit.[34] m.p. 145.5–147°). Evaporation of the original filtrate gave a pale-yellow, viscous gum which afforded solid (6.96 g, m.p. 90–95°) upon addition of 20 ml of ethanol. Recrystallization from ethanol gave 5.67 g (77 %) of (I), m.p. 94–97°.

(3). *Reaction of triphenyltin iodide with cyanamide and triethylamine.* A mixture of triphenyltin iodide (4.77 g, 0.01 mole), cyanamide (0.21 g, 0.005 mole), triethylamine (2.02 g, 0.02 mole) and ethyl ether (100 ml) was refluxed for 2½ h. The solid which separated was collected on a filter to give 1.67 g (73 %) of triethylamine hydroiodide, m.p. 175–179° (lit.[35] m.p. 181°). The solid which remained after evaporation of the filtrate was recrystallized from ethanol to give 3.22 g (87 %) of (I), m.p. 85–93°. A second recrystallization from ethanol gave 2.13 g (58 %) of (I), m.p. 96–97°.

(4). *Reaction of triphenyltin iodide with sodium cyanamide.* A mixture of triphenyltin iodide (2.38 g, 0.005 mole), sodium cyanamide (0.43 g, 0.005 mole), and benzene (50 ml) was refluxed for 23 h. The mixture was filtered, and the filtrate was evaporated to give a solid (1.84 g, m.p. 80–89°) which afforded, after recrystallization from ethanol, 1.25 g (68 %) of (I), m.p. 96–99°.

(5). *Reaction of bis(triphenyltin) oxide with (triphenylstannyl)cyanamide.* A mixture of bis(triphenyltin) oxide (0.716 g, 0.001 mole), (triphenylstannyl)cyanamide (0.782 g, 0.002 mole), and acetonitrile (10 ml) was refluxed for 19 h. Evaporation of the solvent gave 1.38 g (93 %) of (I), m.p. 94–97°. Recrystallization from ethanol gave 1.06 g (72 %) of (I), m.p. 96–98°.

(6). *Disproportionation of (triphenylstannyl)cyanamide.* A mixture of triphenylstannylcyanamide (0.469 g, 0.0012 mole) and anhydrous benzene (10 ml) was refluxed for 19 h. Filtration afforded 0.014 g (56 %) of dicyandiamide, m.p. 201–208° (lit.[36] m.p. 207–209°). Evaporation of the filtrate gave 0.45 g (100 %) of (I), m.p. 95–98°.

Preparation of N-(triphenylstannyl)-N'-tritylcarbodiimide (II)

(1). *Reaction of bis(triphenyltin) oxide with tritylcyanamide.* A mixture of bis-(triphenyltin) oxide (0.716 g, 0.001 mole), tritylcyanamide[37] (0.569 g, 0.002 mole), and acetonitrile (10 ml) was refluxed for 22 h. The solvent was evaporated to a volume of about 3 ml, and the colorless crystals which separated were collected on a filter to give 0.99 g (78 %) of (II), m.p. 107–109°. Repeated recrystallizations from acetonitrile did not change the m.p. (Found: C, 72.21; H, 4.92; N, 4.49; Sn, 18.52. $C_{38}H_{30}N_2Sn$ calcd.: C, 72.06; H, 4.77; N, 4.42; Sn, 18.74 %.) IR: 4.78 (NCN), 13.25 (CH of CC_6H_5), 13.70 (CH of SnC_6H_5), and 14.40 (CH of CC_6H_5 and SnC_6H_5) μ; far IR: 36.90 and 44.44 (SnC_6H_5)[33] μ; NMR (CCl_4): τ 2.68 [singlet, 15 H, $Sn(C_6H_5)_3$] and 2.90 [singlet, 15 H, $C(C_6H_5)_3$]; NMR of $(C_6H_5)_3CNCNC(C_6H_5)_3$ ($DCCl_3$): τ 2.68–3.17 (multiplet, C_6H_5).

(2). *Reaction of bis(triphenyltin) oxide with tritylthiourea.* A mixture of bis-(triphenyltin) oxide (7.16 g, 0.01 mole), tritylthiourea[37] (2.12 g, 0.0067 mole), and acetonitrile (70 ml) was refluxed for 19 h. The solution was allowed to cool to room temperature, and the colorless crystals which separated were collected on a filter to give 5.09 g of solid, m.p. 138–141°. Recrystallization from acetonitrile gave 4.20 g (86 %) of bis(triphenyltin) sulfide, m.p. 143–145°. Evaporation of the original filtrate gave a viscous gum which afforded solid (4.00 g, m.p. 102–106°) upon addition of pentane (70 ml). Recrystallization from acetonitrile gave 3.06 g (73 %) of (II), m.p. 105–108°.

(3). *Reaction of triphenyltin iodide with tritylcyanamide and triethylamine.* A mixture of triphenyltin iodide (0.94 g, 0.002 mole), tritylcyanamide (0.569 g, 0.002 mole), triethylamine (0.243 g, 0.0024 mole), and benzene (30 ml) was refluxed for 23 h. Triethylamine hydroiodide (0.32 g, 70 %) was filtered off, and the filtrate was evaporated to give a viscous gum which afforded solid (0.89 g, m.p. 95–100°) after stirring with pentane. Recrystallization from acetonitrile gave 0.42 g (33 %) of (II), m.p. 107–109°.

Preparation of (triphenylstannyl)cyanamide

(1). *Reaction of (I) with cyanamide.* A mixture of (I) (0.740 g, 0.001 mole), cyanamide (0.042 g, 0.001 mole), and ethyl ether (10 ml) was refluxed for 18 h. The solid which was present was collected on a filter and washed with ethyl ether to give 0.54 g (69 %) of (triphenylstannyl)cyanamide, m.p. 138–141°. (Found: C, 58.08; H, 4.18; N, 7.30; Sn, 30.10. $C_{19}H_{16}N_2Sn$ calcd.: C, 58.36; H, 4.12; N, 7.16; Sn, 30.35 %.) IR: 3.00 (NH), 4.60 (CN), 13.75 and 14.38 (C_6H_5) μ; far IR: 36.63 and 45.04 (SnC_6H_5)[33] μ; NMR (acetone-d_6): τ 2.30–2.62 (multiplet, C_6H_5).

(2). *Reaction of bis(triphenyltin) oxide with cyanamide.* A mixture of bis(triphenyltin) oxide (2.86 g, 0.004 mole), cyanamide (0.673 g, 0.016 mole), and ethyl ether (60 ml) was refluxed for 22 h. The solid which was present was collected on a filter and washed with ethyl ether to give 2.37 g (76 %) of (triphenylstannyl)cyanamide, m.p. 137–140°.

Reaction of (I) with 1,3-di-p-tolylthiourea

A mixture of (I) (3.70 g, 0.005 mole), 1,3-di-*p*-tolylthiourea (1.28 g, 0.005 mole), and acetonitrile (50 ml) was refluxed for 20 h. The bis(triphenyltin) sulfide which separated on cooling was collected on a filter to give 3.19 g (87 %), m.p. 141–144°, Evaporation of the filtrate gave 1.62 g of solid, m.p. 169–185°, which was recrystallized from ethanol to give 0.75 g (57%) of *N,N'*-di-*p*-tolyl-*N''*-cyanoguanidine (IIIe), m.p. 190–193°. Extraction of this material with carbon tetrachloride (8 ml) left 0.59 g (45%) of (IIIe), m.p. 195–197°. Recrystallization from ethanol gave the analytical sample, m.p. 200–201°. (Found: C, 72.67; H, 6.20; N, 21.48. $C_{16}H_{16}N_4$ calcd.: C, 72.70; H, 6.10; N, 21.20%.) IR: 3.03 (NH), 4.58 (C≡N), 6.32 (C=N), and 12.20 (*p*-phenylene) μ; NMR (DMSO-d_6): τ 7.76 (singlet, 6 H, CH_3), 2.84 (singlet, 8 H, C_6H_4), and 0.84 (singlet, 2 H, NH).

Reaction of (I) with 1,3-dicyclohexylthiourea

A mixture of (I) (3.70 g, 0.005 mole), 1,3-dicyclohexylthiourea (1.20 g, 0.005 mole), and toluene (40 ml) was refluxed for 24 h. The mixture was cooled to 4° overnight and filtered to give 1.02 g (82%) of colorless crystals, m.p. 180–190°. Extraction of this material with carbon tetrachloride (7 ml) left 0.92 g (74%) of *N,N'*-dicyclohexyl-*N''*-cyanoguanidine (IIIc), m.p. 185–190° (lit.[24] m.p. 189–192°). Two recrystallizations from 95% ethanol gave the analytical sample, m.p. 192–194°. (Found: C, 67.78; H, 9.75; N, 22.80. $C_{14}H_{24}N_4$ calcd.: C, 67.70; H, 9.74; N, 22.56%.) IR: 3.10 (NH), 4.60 (C≡N), and 6.31 (C=N) μ.

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