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PREPARATION OF SOME TRIETHYLAMMONIUM (ORGANOCYANOAMINO)CHLOROTRIPHENYLSTANNATES

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Summary

Seven new anionic triphenyltin complexes, triethylammonium (organocyanoamino)chlorotriphenylstannates, were prepared by the reaction of (triphenylstannyl) cyanamide with acid chlorides, alkyl chlorocarbonates, or benzenesulfonyl chloride in the presence of triethylamine. One of these complexes, triethylammonium (acetylcyanoamino)chlorotriphenylstannate, was also prepared by the reaction of triethylamine hydrochloride with *N*-(triphenylstannyl)-*N*-acetylcyanamide, which was obtained by allowing acetyl chloride to react with bis(triphenylstannyl)carbodiimide. The PMR and IR (4000—140 cm^{-1}) spectrum of each complex was measured. The Mössbauer parameters of two of the complexes were obtained, the quadrupole splittings being consistent with trigonal bipyramidal structures. *p*-Nitrobenzoyl chloride and terephthalyl chloride failed to give complexes on reaction with (triphenylstannyl)cyanamide and triethylamine, but instead gave the triethylammonium salt of the corresponding acylcyanamide. The new anionic complex, triethylammonium dichlorotriphenylstannate, was prepared by the reaction of triphenyltin chloride with triethylamine hydrochloride.

Introduction

We recently described the reactions of (triphenylstannyl)cyanamide with bis(triphenyltin) oxide [1], isothiocyanates [2], isocyanates [2, 3] and carbon disulfide [4]. Its disproportionation to bis(triphenylstannyl)carbodiimide and dicyandiamide upon heating was also described [1]. We now wish to report on the reactions of (triphenylstannyl)cyanamide with acid chlorides, alkyl chlorocarbonates, and benzenesulfonyl chloride in the presence of triethylamine.

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TABLE 1

TRIETHYLAMMONIUM (ORGANOCYANOAMINO)CHLOROTRIPHENYLSTANNATES[a]

$(C_6H_5)_3SnNHCN + RCl + (C_2H_5)_3N \rightarrow [R(CN)NSn(C_6H_5)_3Cl]^-[(C_2H_5)_3NH]^+$

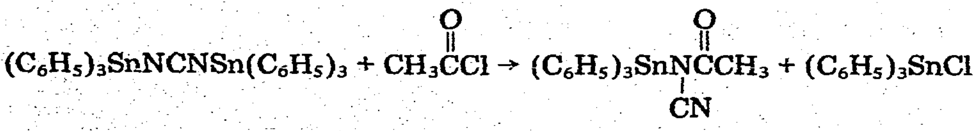
No.	R	M.p. (°C)[b]	Analysis, found (calcd.) (%)				
			C	H	N	Sn	Cl
I	$CH_3\overset{\overset{O}{\|}}{C}$	86—88	56.39 (56.82)	6.07 (6.00)	7.44 (7.36)	20.63 (20.80)	6.26 (6.21)
II	$C_2H_5\overset{\overset{O}{\|}}{C}$	81—83	57.40 (57.51)	6.49 (6.21)	7.34 (7.19)	19.83 (20.30)	5.68 (6.06)
III	$C_6H_5\overset{\overset{O}{\|}}{C}$	97—99	60.84 (60.74)	5.97 (5.73)	6.48 (6.64)	18.78 (18.76)	5.90 (5.60)
IV	$CH_3O\overset{\overset{O}{\|}}{C}$	97—100	55.08 (55.27)	5.81 (5.84)	6.92 (7.16)	20.03 (20.23)	6.38 (6.04)
V	$C_2H_5O\overset{\overset{O}{\|}}{C}$	95—98	56.15 (55.98)	6.19 (6.04)	6.91 (6.99)	19.72 (19.76)	6.00 (5.90)
VI	$C_6H_5CH_2O\overset{\overset{O}{\|}}{C}$	89—92	60.05 (59.80)	5.92 (5.78)	6.27 (6.34)	17.86 (17.91)	5.10 (5.35)
VII[c]	$C_6H_5SO_2$	80—83	55.22 (55.67)	5.46 (5.42)	6.05 (6.28)	18.04 (17.75)	5.31 (5.30)

[a] $(C_6H_5)_3SnNHCN$, RCl, and $(C_2H_5)_3N$ (1/1/2 mole ratio) were allowed to react in tetrahydrofuran at —78° for 3h and then at 26° for 2h; the yields, based on material melting within 5° of the analytical sample, were 91—98%. [b] Refers to the analytical sample; except for VII, which was recrystallized from n-butyraldehyde, the recrystallization solvent was ethyl acetate. [c] S, found 4.65, calcd. 4.79%.

Results and discussion

(Triphenylstannyl)cyanamide was found to react with acid chlorides, alkyl chlorocarbonates or benzenesulfonyl chloride, in the presence of an excess of triethylamine, to give a high yield of the corresponding triethylammonium (organocyanoamino)chlorotriphenylstannates (I-VII, Table 1). In addition to their identification by elemental analysis, the compounds in Table 1 were further identified by their IR (Table 2) and PMR (Table 3) spectra.

It is possible that triethylamine hydrochloride and the corresponding *N*-(triphenylstannyl)-*N*-acetylcyanamide are intermediates in the formation of compounds I-VII. This hypothesis is supported by the fact that compound I was formed in 73% yield when triethylamine hydrochloride was allowed to react with *N*-(triphenylstannyl)-*N*-acetylcyanamide (1/1 mole ratio) in tetrahydrofuran at 26°. The *N*-(triphenylstannyl)-*N*-acetylcyanamide required for this reaction was conveniently prepared in 61% yield by allowing bis(triphenylstannyl)carbodiimide to react with acetyl chloride (eqn. 1).



$$(C_6H_5)_3SnNCNSn(C_6H_5)_3 + CH_3\overset{\overset{O}{\|}}{C}Cl \rightarrow (C_6H_5)_3Sn\underset{\underset{CN}{|}}{N}\overset{\overset{O}{\|}}{C}CH_3 + (C_6H_5)_3SnCl \qquad (1)$$

TABLE 2

IR SPECTRA OF TRIETHYLAMMONIUM (ORGANOCYANOAMINO)CHLOROTRIPHENYLSTANNATES[a]

No.	C≡N	C=O[b]	C_6H_5 ring vibration (refs. 7—9)	SnC_6H_5 (refs. 9, 10—13)	
				ν_{as}	ν_s
I	2165s	1600s	452s	272s	228s[c]
II	2146s	1567s	452s	278s	236m[d]
III	2151s	1555s	448s	278s	231s[e]
IV	2183s	1675s	450s	272s	236s[f]
V	2183s	1675s	455s	268s	236s[g]
VI	2174s	1675s	448s	272s	239s[h]
VII	2174s	[i]	452s	273s	238s[j]

[a] Values are expressed in cm^{-1}. None of the compounds exhibited a strong band near 344 cm^{-1} due to the SnCl bond, as observed in the case of triphenyltin chloride [13]. [b] A weak band due to C=C occurs in this region in the case of triphenyltin chloride and (triphenylstannyl)cyanamide; triethylamine hydrochloride does not have bands in this region. [c] Also present were bands at 203 m and 252 m cm^{-1}. [d] Also present were bands at 218 m, 227 m and 253 m cm^{-1}. [e] A band was also present at 249 m cm^{-1}. [f] Also present were bands at 210 w and 249 m cm^{-1}. [g] Also present were bands at 210 w and 250 m cm^{-1}. [h] Also present were bands at 211 w and 252 m cm^{-1}. [i] Two bands which may be due to SO_2[14] were present at 1253 s and 1138 s cm^{-1}. [j] A band was also present at 204 m cm^{-1}.

TABLE 3

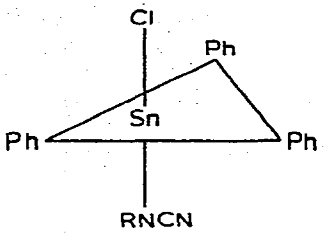
PMR SPECTRA OF TRIETHYLAMMONIUM (ORGANOCYANOAMINO)CHLOROTRIPHENYLSTANNATES[a]

No.	$(C_2H_5)_3N$	NH[b]	$R\overset{O}{\overset{\|}{C}}$	$(C_6H_5)_3Sn$[c]
I	1.13 (t, 9H, CH_3) 3.03 (q, 6H, CH_2)	6.15 (s, 1H)	1.77 (s, 3H, CH_3)	7.45 (m, 10H, $2C_6H_5$) 8.05 (m, 5H, $1C_6H_5$)
II	[d] 3.03 (q, 6H, CH_2)	6.07 (s, 1H)	[d] 2.07 (m, 4H[e], CH_2)	7.43 (m, 10H, $2C_6H_5$) 8.13 (m, 5H, $1C_6H_5$)
III	1.13 (t, 9H, CH_3) 3.02 (q, 6H, CH_2)	6.12 (s, 1H)	[f] [g]	[f] [g]
IV	1.13 (t, 9H, CH_3) 3.03 (q, 6H, CH_2)	6.03 (s, 1H)	3.58 (s, 3H, CH_3)	7.50 (m, 10H, $2C_6H_5$) 8.08 (m, 5H, $1C_6H_5$)
V	[h] 3.03 (q, 6H, CH_2)	6.03 (s, 1H)	[h] 4.00 (q, 2H, CH_2)	7.50 (m, 10H, $2C_6H_5$) 8.12 (m, 5H, $1C_6H_5$)
VI	1.10 (t, 9H, CH_3) 2.98 (q, 6H, CH_2)	5.92 (s, 1H)	5.07 (s, 2H, CH_2) [i]	[i] 8.10 (m, 5H, $1C_6H_5$)
VII	1.20 (t, 9H, CH_3) 3.13 (q, 6H, CH_2)	[j]	[j]	[j] [k]

[a] Chemical shift values are expressed in δ(ppm) units relative to tetramethylsilane and were obtained using 25% solutions in acetone-d_6. [b] Determined by addition of methanol-d_4. [c] Values are given for the approximate center of the multiplet. [d] 1.10 (two overlapping t, 12H, CH_3 of $(C_2H_5)_3N$ and CH_3 of C_2H_5CO). [e] Integration is incorrect due to the presence of some undeuterated acetone. [f] 7.43 (m, 13H, $2C_6H_5$ of $(C_6H_5)_3Sn$ and 3 non *ortho* H of C_6H_5CO). [g] 8.13 (m, 7H, 1 C_6H_5 of $(C_6H_5)_3Sn$ and 2 *ortho* H of C_6H_5CO. [h] 1.13 (two superimposed t, 12H, 1 CH_3 of C_2H_5OCO and 3 CH_3 of $(C_2H_5)_3N$). [i] 7.42 (m, 15H, $2C_6H_5$ of $(C_6H_5)_3Sn$ and 1 C_6H_5 of $C_6H_5CH_2OCO$). [j] 7.97 (m, 8H, 1NH, 2 *ortho* H of $C_6H_5SO_2$ and 1 C_6H_5 of $(C_6H_5)_3Sn$). [k] 7.45 (m, 13H, 3 non *ortho* H of $C_6H_5SO_2$ and 2 C_6H_5 of $(C_6H_5)_3Sn$).

p-Nitrobenzoyl chloride and terephthalyl chloride failed to give complexes on reaction with (triphenylstannyl)cyanamide and triethylamine, but instead gave triethylammonium *p*-nitrobenzoylcyanamide and bis(triethylammonium) terephthalylcyanamide, respectively. The presence of an electron-withdrawing group in the *para* position in these cases probably favors decomposition of the complex, since such a group can enhance the stability of the resulting salt by a resonance effect.

The quadrupole splitting values for compounds I and IV (3.12 mm sec^{-1} in each case) are consistent with a trigonal bipyramidal structure in which the phenyl groups occupy the equatorial positions [5, 6]. Compounds I-VII, therefore, probably have structure A.



(A)

The new anionic complex triethylammonium dichlorotriphenylstannate, was convenietly prepared in 79% yield by allowing triphenyltin chloride to react with triethylamine hydrochloride (1/1 mole ratio) in refluxing n-propanol.

Experimental

Melting points were determined with a Mel-Temp capillary melting point apparatus and are uncorrected. The infrared data (4000—400 cm^{-1}) were obtained using KBr pellets with a Beckman IR 8 infrared spectrophotometer and a Perkin Elmer Model 21 double beam infrared spectrophotometer which was fitted with a cesium bromide prism and purged with nitrogen. The far infrared data (400—140 cm^{-1}) were obtained with a Perkin Elmer Model FIS-3 far infrared spectrophotometer (CsI pellets). The proton magnetic resonance data were obtained with a Varian Model A-60A NMR spectrometer using tetramethylsilane as the internal standard. The Mössbauer spectral data were obtained at 77 K relative to $BaSnO_3$ by Austin Science Associates, Inc., Austin, Texas. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Preparation of triethylammonium (acetylcyanoamino)chlorotriphenylstannate (I)

Triethylamine (4.05 g, 0.04 mol) was added to a solution of 7.80 g (0.02 mol) of (triphenylstannyl)cyanamide [1] in tetrahydrofuran (150 ml), and the mixture was cooled to —78°. A solution of acetyl chloride (1.57 g, 0.02 mol) in tetrahydrofuran (100 ml) was added over 1 h, and the mixture was stirred at —78° for 2 h. The mixture was slowly allowed to come to 26° and then was stirred for 2 h at 26°. The solvent was evaporated, and the residue was stirred with ethyl ether (50 ml) for 1 h. Filtration of the mixture afforded 11.24 g

(98%) of I, m.p. 82—88°. Recrystallization from ethyl acetate (50 ml) gave 10.13 g (89%) of I, m.p. 85—87°. A second recrystallization from ethyl acetate gave the analytical sample, m.p. 86—88°.

The yield of I was 75% when the reaction was carried out at 26°. Mössbauer parameters (77 K relative to $BaSnO_3$): isomer shift, +1.34 mm sec^{-1}, quadrupole splitting, 3.12 mm sec^{-1}.

Preparation of triethylammonium (methoxycarbonylcyanoamino)chlorotriphenylstannate (IV)

The procedure was identical to that described above for I. From triethylamine (4.05 g, 0.04 mol), (triphenylstannyl)cyanamide (7.80 g, 0.02 mol), and methyl chlorocarbonate (1.89 g, 0.02 mol) there was obtained 11.15 g (95%) of IV, m.p. 85—96°. Recrystallization from ethyl acetate (50 ml) gave 10.18 g (87%) of IV, m.p. 95—99°. A second recrystallization from ethyl acetate gave 9.45 g (81%) of IV, m.p. 97—100°.

Mössbauer parameters (77 K relative to $BaSnO_3$): isomer shift, +1.34 mm sec^{-1}, quadrupole splitting, 3.12 mm sec^{-1}.

Preparation of triethylammonium dichlorotriphenylstannate

To a hot solution of triphenyltin chloride (3.85 g, 0.01 mol) in n-propanol (25 ml) was added a hot solution of triethylamine hydrochloride (1.38 g, 0.01 mol) in n-propanol (25 ml). The mixture was refluxed for 2 h and then was cooled at —10° for 16 h. The resulting crystals were collected on a filter and washed with two 50 ml portions of n-propanol and two 50 ml portions of n-pentane to give 4.11 g (79%) of product, m.p. 131—133°. (Found: C, 54.91; H, 5.90; N, 2.90; Cl, 13.65; Sn, 22.27. $C_{24}H_{31}NCl_2Sn$ calcd.: C, 55.11; H, 5.97; N, 2.68; Cl, 13.55; Sn, 22.69%) IR: 455s (C_6H_5 ring vibration), 276s [$\nu_{as}(SnC_6H_5)$], 236w (SnCl) [13] or [$\nu_s(SnC_6H_5)$] cm^{-1}. PMR ($CDCl_3$): δ 1.13 (t, 9H, CH_3), 2.82 (q, 6H, CH_2), 7.48 (m, 10 H, $2C_6H_5$), and 8.02 (m, 5H, $1C_6H_5$) ppm.

Preparation of N-(triphenylstannyl)-N-acetylcyanamide

To a solution of 14.80 g (0.02 mol) of bis(triphenylstannyl)carbodiimide [1] in tetrahydrofuran (100 ml) was added a solution of 1.57 g (0.02 mol) of acetyl chloride in tetrahydrofuran (100 ml) over 1 h. The mixture was stirred at 26° for 2 h, the solvent was evaporated, and the residue (thick oil) was stirred with ethyl ether (50 ml) for 12 h. The resulting solid was collected on a filter to give 5.29 g (61%) of product, m.p. 152—175° (dec.). The product was recrystallized from chloroform/n-hexane three times to give the analytical sample, m.p. 179—183° (dec.). (Found: C, 58.15; H, 4.30; N, 6.69; Sn, 27.51. $C_{21}H_{18}N_2OSn$ calcd.: C, 58.24; H, 4.19; N, 6.47; Sn, 27.41%.) IR: 2193s (CN), 1513s (C=O), 452s (C_6H_5 ring vibration), 278s [$\nu_{as}(SnC_6H_5)$], and 233s [$\nu_s(SnC_6H_5)$] cm^{-1}. PMR ($CDCl_3/CD_3OD$): δ 1.85 (s, 3H, CH_3) and 7.57 (m, 15H, C_6H_5) ppm.

Evaporation of the ethyl ether from the filtrate followed by recrystallization of the residue from n-hexane gave 4.02 g (52%) of triphenyltin chloride, m.p. 103—106°, no depression on admixture with an authentic sample, IR spectrum superimposable on that of an authentic sample.

Reaction of N-(triphenylstannyl)-N-acetylcyanamide with triethylamine hydrochloride

A mixture of *N*-(triphenylstannyl)-*N*-acetylcyanamide (0.433 g, 0.001 mol), triethylamine hydrochloride (0.138 g, 0.001 mol), and tetrahydrofuran (10 ml) was stirred at 26° for 16 h. The solvent was evaporated, and the residue was recrystallized from ethyl acetate to give 0.414 g (73%) of compound I (Table 1), m.p. 85—87°, no depression on admixture with an authentic sample, IR and PMR spectra superimposable on that of an authentic sample.

Reaction of (triphenylstannyl)cyanamide with p-nitrobenzoyl chloride

Triethylamine (4.05 g, 0.04 mol), (triphenylstannyl)cyanamide (7.80 g, 0.02 mol), and *p*-nitrobenzoyl chloride (3.39 g, 0.02 mol) were allowed to react as described above for the preparation of compounds I and IV. The solvent was evaporated, and the residue was refluxed in ethyl acetate (400 ml). The mixture was cooled and filtered to give 2.4 g (41%) of triethylammonium *p*-nitrobenzoylcyanamide (light yellow), m.p. 125—133°. A second run carried out at 26° gave, on direct filtration of the reaction mixture, an 81% yield of this compound, m.p. 126—133°. Recrystallization from ethanol/ethyl acetate gave the analytical sample, m.p. 133—135°. (Found: C, 56.92; H, 6.95; N, 18.72. $C_{14}H_{20}N_4O_3$ calcd.: C, 57.52; H, 6.90; N, 19.16%.) IR: 2174m, 2141s (CN), 1553s (C=O), 461s (C_6H_5 ring vibration). PMR (DMSO-d_6): δ 1.27 (t, 9H, CH_3), 3.27 (q, 6H, CH_2), and 8.27 (s, 4H, C_6H_4) ppm.

Evaporation of the tetrahydrofuran from the filtrate of the second run left a white solid which afforded, after recrystallization from n-hexane, 6.38 g (83%) of triphenyltin chloride, m.p. 102—105°, no depression on admixture with an authentic sample, IR spectrum superimposable on that of an authentic sample.

Reaction of (triphenylstannyl)cyanamide with terephthalyl chloride

Triethylamine (4.05 g, 0.04 mol), (triphenylstannyl)cyanamide (7.80 g, 0.02 mol), and terephthalyl chloride (2.03 g, 0.01 mole) were allowed to react as described above for the preparations of compound I and IV. There was obtained after evaporation of the solvent, stirring of the residue with ethyl ether, and filtration 3.04 g (73%) of bis(triethylammonium) terephthalylcyanamide, m.p. 151—177° (dec.). Three recrystallizations from ethanol/ethyl acetate gave 2.36 g (57%) of product, m.p. 164—177° (dec.) (Found: C, 63.48; H, 8.70; N, 19.91. $C_{22}H_{36}N_6O_2$ calcd.: C, 63.43; H, 8.71; N, 20.17%) IR: 2193m, 2155s (CN), 1580s, 1543s (C=O), 464s (C_6H_5 ring vibration). PMR (DMSO-d_6): δ 1.22 (t, 18H, CH_3), 3.17 (q, 12H, CH_2), and 7.93 (s, 4H, C_6H_4) ppm.

Evaporation of the ethyl ether from the filtrate gave, after recrystallization of the residue from n-hexane, 6.29 g (82%) of triphenyltin chloride, m.p. 103—106°, identified by mixed melting point determination and IR comparison with an authentic sample.

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