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PREPARATION OF SOME *N*-SUBSTITUTED *N*-(TRIPHENYLSTANNYL)-CYANAMIDES

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Summary

Nine *N*-substituted *N*-(triphenylstannyl)cyanamides were prepared by allowing bis(triphenylstannyl)carbodiimide to react separately with acid chlorides, trifluoroacetic anhydride, alkyl chlorocarbonates, and benzenesulfonyl chloride. The tin in these compounds was shown to have a coordination number greater than four be means of IR and Mössbauer spectroscopy.

Introduction

We recently reported that bis(triphenylstannyl)carbodiimide reacts with acetyl chloride to give *N*-acetyl-*N*-(triphenylstannyl)cyanamide and triphenyltin chloride [1]. We now wish to report on the reactions of bis(triphenylstannyl)-carbodiimide with other acid chlorides, as well as with alkyl chlorocarbonates and benzenesulfonyl chloride.

Results and discussion

Bis(triphenylstannyl)carbodiimide was found to react with acid chlorides, alkyl chlorocarbonates, or benzenesulfonyl chloride in tetrahydrofuran at 26°C to give high yields of triphenyltin chloride and the corresponding *N*-acyl *N*-(triphenylstannyl)cyanamides, *N*-alkoxylcarbonyl *N*-(triphenylstannyl)cyanamides, or *N*-benzenesulfonyl-*N*-(triphenylstannyl)cyanamide (I-V, VII-IX, Table 1). *N*-Trifluoroacetyl-*N*-(triphenylstannyl)cyanamide (VI, Table 1) was prepared by allowing bis(triphenylstannyl)carbodiimide to react with trifluoroacetic anhydride. It was found that the previously reported [1] compound, *N*-acetyl-*N*-(triphenylstannyl)cyanamide, could also be prepared (70% yield) from bis(triphenylstannyl)carbodiimide and acetic anhydride.

In addition to their identification by elemental analysis, the compounds in Table 1 were further identified by their IR (Table 2) and PMR spectra.

TABLE 1

N-SUBSTITUTED *N*-(TRIPHENYLSTANNYL)CYANAMIDES[a]

$$(C_6H_5)_3SnNCNSn(C_6H_5)_3 + RCl \rightarrow \underset{(A)}{R(CN)NSn(C_6H_5)_3} + \underset{(B)}{(C_6H_5)_3SnCl}$$

No.	R	M.p. (°C)[b]	Analysis, found (calcd.) (%)				Mol. wt.[c] found (calcd.)	Yield A[d] (%)	Yield B[e] (%)
			C	H	N	Sn			
I	$C_2H_5C(O)$	168-185 (179-185)	58.81 (59.10)	4.43 (4.51)	6.51 (6.27)	26.29 (26.55)	457 (447.11)	91 (73)[g]	78
II	$C_6H_5C(O)$	180-195 (195-198)	63.35 (63.07)	4.25 (4.07)	5.44 (5.66)	23.10 (23.97)	[f] (495.15)	91 (68)[h]	74
III	$C_6H_5CH_2C(O)$	175-185 (184-187)	63.38 (63.69)	4.36 (4.36)	5.71 (5.50)	23.49 (23.31)	486 (509.18)	94 (59)[g]	78
IV	*p*-$NO_2C_6H_4C(O)$	155-176 (166-177)	58.13 (57.82)	3.86 (3.55)	7.55 (7.78)	21.63 (21.97)	617 (540.15)	95 (69)[i]	71
V	*p*-$C(O)C_6H_4C(O)$	233-250 (245-248)	60.80 (60.57)	3.82 (3.76)	5.98 (6.14)	25.53 (26.02)	[f] (912.19)	94 (93)[j]	81
VI[k]	$CF_3C(O)$	144-155 (149-156)	51.66 (51.97)	3.12 (3.10)	5.63 (5.75)	24.52 (24.37)	541 (487.05)	81 (56)[l]	88 (63)[m]
VII	$CH_3OC(O)$	195-204[n] (204-206)[n]	56.13 (56.17)	3.80 (4.04)	6.19 (6.24)	26.61 (26.43)	438 (449.08)	94 (63)[h]	80
VIII	$C_2H_5OC(O)$	190-203[n] (202-205)[n]	56.99 (57.06)	4.28 (4.35)	6.14 (6.05)	25.85 (25.63)	470 (463.11)	90 (64)[h]	83
IX[o]	$C_6H_5SO_2$	169-187 (180-185)	56.71 (56.53)	3.83 (3.80)	5.10 (5.27)	22.60 (22.34)	534 (531.20)	89 (69)[p]	80

[a] $(C_6H_5)_3SnNCNSn(C_6H_5)_3$ and RCl (1/1 mole ratio) were allowed to react in tetrahydrofuran at 26°C for 3 h, except for VI, in which trifluoroacetic anhydride was used instead of the acid chloride, and IX, which was allowed to react for 18 h. [b] Sealed tube, air (sealed tube, N_2 at 8 Torr). All samples melted with decomposition; only II, VI and IX showed slight decomposition sealed in air and no decomposition sealed in N_2 at 8 Torr. [c] Molecular weights were determined by vapor pressure osmometry in acetone at 37°C. [d] Crude (analytical). [e] After one recrystallization from n-propanol. [f] Insoluble in acetone. [g] Recrystallized from 1/3 tetrahydrofuran/heptane. [h] Recrystallized from tetrahydrofuran. [i] Recrystallized from 1/4 tetrahydrofuran/diethyl ether. [j] Insoluble in the most common solvents; washed with 100 ml each: diethyl ether, benzene, chloroform, carbon tetrachloride, acetone, methanol, ethyl acetate, hexane, and tetrahydrofuran. [k] F found (11.76), calcd. (11.70)%. [l] Recrystallized from diethyl ether. [m] Triphenyltin trifluoroacetate crude (after three recrystallizations from benzene/heptane). [n] Decomposed with rapid evolution of a gas and no charring. [o] S found (5.98), calcd. (6.04)%. [p] Washed overnight with hot diethyl ether, as a suitable recrystallization solvent could not be found; it preferred to oil out rather than recrystallize.

Their molecular weights, as determined by vapor pressure osmometry in acetone at 37°C, indicate that these compounds are monomeric in solution.

With the exception of compound VI, the carbonyl stretching frequency of each of the compounds is considerably lower (by about 130 cm^{-1}) than that observed for an *N,N*-disubstituted amide (1680-1630 cm^{-1}) [2]. The presence of the strongly electron-withdrawing CN group on the nitrogen would be expected to reduce the tendency for the carbonyl oxygen to draw electrons from the nitrogen and thus raise the carbonyl stretching frequency. The observed shift to a lower carbonyl stretching frequency may be due to coordination between the tin of the triphenylstannyl group and the carbonyl oxygen. Coordination between tin and the carbonyl oxygen in compound VI is probably weaker than in the other compounds, since the carbonyl stretching frequency of compound VI

TABLE 2

IR SPECTRA OF *N*-SUBSTITUTED *N*-(TRIPHENYLSTANNYL)CYANAMIDES[a]

No.	C≡N	C=O[b]	C_6H_5 ring vibration [11-13]	SnC_6H_5 [13,14-17]	
				ν_{asym}	ν_{sym}
I	2188 s	1508 s	451 s	278 s	233 s[c]
II	2184 s	1515 s	449 s	271 s	234 s[d]
III	2183 s	1520 s	451 s	268 s	214 s[e]
IV	2174 s	1534 s	448 s	272 s	231 s[f]
V	2183 s	1524 s	448 s	272 s	225 s[g]
VI	2198 s	1650 s	442 s	272 s	232 s[h]
VII	2188 s	1546 s	455 s	277 s	223 s[i]
VIII	2188 s	1531 s	454 s	274 s	220 s[j]
IX	2183 s	[k]	446 s[l]	277 s	224 s[m]

[a] Values are expressed in cm^{-1}. [b] A weak band due to C=C occurs in this region in the case of triphenyltin chloride and bis(triphenylstannyl)carbodiimide. [c] Also present were bands at 218 s and 284 s (the band at approximately 284 cm^{-1} when present always appeared as a strong band in KBr, but in CsI appeared as a shoulder in most instances). [d] Also present were bands at 220 s and 286 s. [e] Also present was a band at 262 s. [f] Also present were bands at 220 m(sh) and 285 s. [g] Also present was a band at 283 s. [h] Also present was a band at 284 s. [i] Also present were bands at 214 s, 236 m(sh), and 284 s. [j] Also present were bands at 205 s, 234 m(sh), and 284 s. [h] Two bands which may be due to SO_2 were present at 1284 s and 1152 s. [l] Also present was a band at 441 s. [m] Also present was a band at 208 s.

is only 42 cm^{-1} lower than that observed for *N*,*N*-di-n-butyltrifluoroacetamide (1692 cm^{-1}) [3]. The weaker tin—carbonyl-oxygen coordination in VI is probably due to the strong electron-withdrawing power of the trifluoromethyl group.

The Mössbauer parameters for four *N*-substituted *N*-(triphenylstannyl)-cyanamides are given in Table 3. It was pointed out earlier that a ratio of quadrupole splitting to isomer shift of greater than 2.1 is associated with a tin coordination number of greater than four [4,5]. This conclusion was later questioned [6]. More recently, it has been suggested that a quadrupole splitting value of greater than 2.5 mm sec^{-1} is unlikely to be observed unless tin has a coordination number greater than four [7]. Poller and Ruddick [8] have concluded that large quadrupole interactions of ≈4.0-2.6 mm sec^{-1} for triphenyltin compounds are associated with trigonal bipyramidal structures. Ensling et al. [9] have calculated that triphenyltin compounds in which the three phenyl groups occupy the equatorial positions of a trigonal bipyramid should exhibit a quadrupole splitting value of 3.12 mm sec^{-1}. Thus, the data in Table 3 in-

TABLE 3

MÖSSBAUER PARAMETERS OF *N*-SUBSTITUTED *N*-(TRIPHENYLSTANNYL)CYANAMIDES[a]

No.	Compound	δ	ΔE	$\Delta E/\delta$
VI	$CF_3C(O)(CN)NSn(C_6H_5)_3$	1.07	4.54	4.24
VII	$CH_3OC(O)(CN)NSn(C_6H_5)_3$	1.55	4.23	2.73
IX	$C_6H_5SO_2(CN)NSn(C_6H_5)_3$	1.07	4.54	4.24
X[b]	$CH_3C(O)(CN)NSn(C_6H_5)_3$	1.55	4.23	2.73

[a] Units of δ (isomer shift) and ΔE (quadrupole splitting) are mm sec^{-1}; isomer shifts refer to $BaSnO_3$.
[b] Ref. 1.

dicate that the tin has a coordination number greater than four. It should be noted that compounds VII and X have a lower $\Delta E/\delta$ value than compounds VI and IX. It is possible that the higher ΔE values for compounds VI and IX are due to an enhanced electric field gradient in the σ skeleton around tin in these compounds due to the strongly electron-withdrawing CF_3 and $C_6H_5SO_2$ groups [10].

Experimental

Melting points were determined with a Mel-Temp capillary melting point apparatus and are uncorrected. The infrared data (4000-265 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 N-propionyl-N-(triphenylstannyl)cyanamide (I)

To a solution of 37.00 g (0.05 mol) of bis(triphenylstannyl)carbodiimide in tetrahydrofuran (150 ml) was added a solution of 4.63 g (0.05 mol) of propionyl chloride in tetrahydrofuran (100 ml) over 1 h. The mixture was stirred at 26°C for 2 h, the solvent was evaporated, and the residue (thick oil) was stirred with ethyl ether (100 ml) for 12 h. The resulting solid was collected on a filter to give 20.38 g (91%) of *N*-propionyl-*N*-(triphenylstannyl)cyanamide (I), m.p. 149-175°C (dec.). The product was recrystallized three times from tetrahydrofuran/heptane to give 16.34 g (73%) of the analytical sample, m.p. 168-185°C (dec.) in air; 179-185°C in N_2 at 8 Torr.

Evaporation of the ethyl ether from the filtrate followed by recrystallization of the residue from n-propanol gave 15.07 g (78%) of triphenyltin chloride, m.p. 97-101°C, no depression on admixture with an authentic sample, IR spectrum superimposable on that of an authentic sample.

Preparation of N-trifluoroacetyl-N-(triphenylstannyl)cyanamide (VI)

To a solution of 37.00 g (0.05 mol) of bis(triphenylstannyl)carbodiimide in tetrahydrofuran (150 ml) was added a solution of 10.50 g (0.05 mol) of trifluoroacetic anhydride in tetrahydrofuran (100 ml) over 1 h. The mixture was stirred at 26°C for 2 h, the solvent was evaporated, and the residue (thick oil) was stirred with ethyl ether (100 ml) for 12 h. The resulting solid was collected on a filter to give 19.72 g (81%) of *N*-trifluoroacetyl-*N*-(triphenylstannyl)cyanamide (VI), m.p. 122-144°C (dec.). The product was recrystallized three times from ethyl ether to give 13.57 g (56%) of the analytical sample, m.p. 144-155°C (partial dec.) in air; 149-156°C in N_2 at 8 Torr.

Evaporation of the ethyl ether from the filtrate gave 20.46 g (88%) of triphenyltin trifluoroacetate, m.p. 90-99°C. Three recrystallizations of this product from benzene/heptane gave 14.52 g (63%) of triphenyltin trifluoroacetate, m.p. 117-121°C (lit. [18] m.p. 119-121°C).

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