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REACTIONS OF THIOAMIDES WITH BIS(TRIPHENYLSTANNYL)-CARBODIIMIDE AND (TRIPHENYLSTANNYL)CYANAMIDE

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Summary

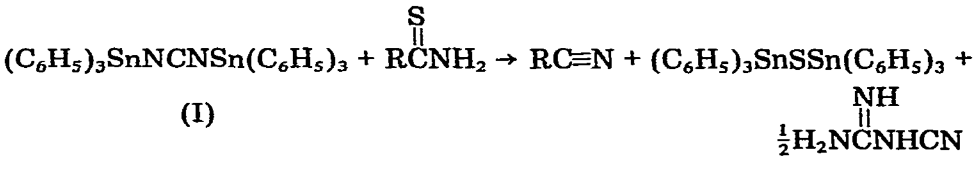
Bis(triphenylstannyl)carbodiimide reacts with thioamides to give organic nitriles and with *N*-substituted thioamides to give *N'*-substituted-*N*-cyanoamidines. The latter compounds may also be prepared by the reaction of (triphenylstannyl)cyanamide with *S*-(triphenylstannyl)isothioamides, which are obtainable from the reaction of triphenyltin iodide with *N*-substituted thioamides in the presence of triethylamine. (Triphenylstannyl)cyanamide reacts with thioamides to give organic nitriles.

Introduction

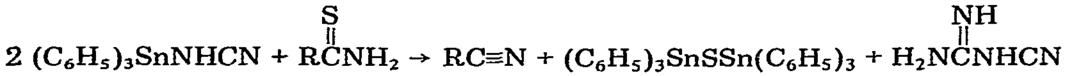
The reaction of bis(triphenylstannyl)carbodiimide (I) with 1,3-disubstituted thioureas to give bis(triphenyltin) sulfide and *N,N'*-disubstituted-N″-cyanoguanidines has been reported [1]. We now wish to report on the reactions of I with thioamides. We wish to describe also the reactions of (triphenylstannyl)cyanamide with thioamides and *S*-(triphenylstannyl)isothioamides.

Results and discussion

Bis(triphenylstannyl)carbodiimide (I) and (triphenylstannyl)cyanamide were found to react separately with thioamides in either diethyl ether or acetonitrile at the reflux temperature to give organic nitriles, bis(triphenyltin) sulfide, and dicyandiamide, eqns. 1 and 2 (R = CH_3 or C_6H_5). The sulfide and



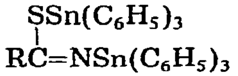
$$\underset{\text{(I)}}{(C_6H_5)_3SnNCNSn(C_6H_5)_3} + R\overset{S}{\overset{\|}{C}}NH_2 \rightarrow RC{\equiv}N + (C_6H_5)_3SnSSn(C_6H_5)_3 + \tfrac{1}{2}H_2N\overset{NH}{\overset{\|}{C}}NHCN \qquad (1)$$



$$2\,(C_6H_5)_3SnNHCN + R\overset{S}{\overset{\|}{C}}NH_2 \rightarrow RC{\equiv}N + (C_6H_5)_3SnSSn(C_6H_5)_3 + H_2N\overset{NH}{\overset{\|}{C}}NHCN$$

(2)

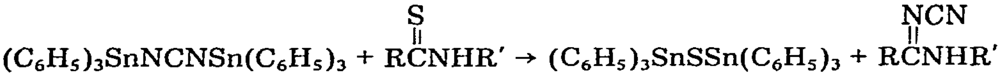
organic nitrile formed in reactions 1 and 2 may arise by decomposition of the common intermediate II. The dicyandiamide very likely results from the dimerization of cyanamide, a reaction which is well-known [2]; the cyanamide very likely accompanies the formation of II.



$$\begin{array}{l} SSn(C_6H_5)_3 \\ \,| \\ RC{=}NSn(C_6H_5)_3 \end{array}$$

(II)

The reaction of bis(triphenylstannyl)carbodiimide (I) with *N*-substituted thioamides in either acetonitrile (63 h) or ethanol (15 h) at the reflux temperature gave bis(triphenyltin) sulfide (78-97%) and the corresponding *N'*-substituted *N*-cyanoamidine (23-67%) (eqn. 3). The amidines were identified by elemental



$$(C_6H_5)_3SnNCNSn(C_6H_5)_3 + R\overset{S}{\overset{\|}{C}}NHR' \rightarrow (C_6H_5)_3SnSSn(C_6H_5)_3 + R\overset{NCN}{\overset{\|}{C}}NHR'$$

(3)

(I)

TABLE 1

N'-SUBSTITUTED-*N*-CYANOAMIDINES $R\overset{NCN}{\overset{\|}{C}}NHR'$

Compound	R	R'	M.p. (°C)[a]	Analysis found (calcd.) (%) C	H	N
I	CH_3	C_6H_5	190-192[b]	67.98 (67.91)	5.72 (5.70)	26.11 (26 40)
II	C_2H_5	C_6H_5	133-135	69.52 (69.34)	6.44 (6.40)	24.50 (24 26)
III	C_6H_5	C_6H_5	230-231	75.95 (76.00)	5.00 (5.01)	19.18 (18.99)
IV	*p*-$CH_3C_6H_4$	C_6H_5	190-191	76.67 (76.90)	5 33 (5.16)	17.66 (17.94)
V	$C_6H_5CH_2$	C_6H_5	173-175	77.05 (76.90)	5 39 (5.16)	17.80 (17.94)
VI	C_6H_5	CH_3	175-178[c]	67.92 (67.91)	5.80 (5.70)	26.57 (26.40)
VII	C_6H_5	C_2H_5	161-163	69.58 (69.34)	6.36 (6.40)	24.31 (24 26)
VIII	C_6H_5	$C_6H_5CH_2$	125-127	76.74 (76.57)	5.59 (5.57)	17.60 (17.86)
IX[d]	C_6H_5	*p*-FC_6H_4	242-243	70.19 (70.28)	4 21 (4.21)	17.37 (17.56)
X	C_6H_5	*p*-$C_2H_5OC_6H_4$	206-208	72.72 (72.43)	6.00 (5.70)	15.63 (15.84)

[a] Refers to the analytical sample; recrystallization solvents were ethanol (I-V), ethyl acetate (VI, VII, IX, X), and acetonitrile (VIII). [b] Lit. [3] m.p. 190-192°C. [c] Lit. [4] m p. 177°C. [d] F, found 8.09, calcd. 7.94%.

TABLE 2

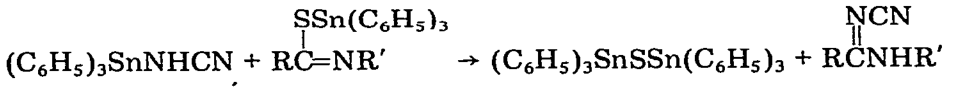
IR SPECTRA OF *N*-CYANO-*N'*-SUBSTITUTED AMIDINES [a]

Compound	NH	C=N [b]	C≡N
I	3311m, 3226w	1538s	2179s
II	3279m, 3215w	1527s	2174s
III	3215m, 3185m	1504s	2179s
IV	3226m, 3185m	1511s	2174s
V	3311m, 3226w	1538s	2179s
VI	3226m	1541s	2183s
VII	3226m	1534s	2174s
VIII	3247s	1538s	2174s
IX	3205m, 3155m	1493s	2174s
X	3247m, 3205m	1504s	2174s

[a] Values are expressed in cm^{-1}. [b] This assignment is somewhat uncertain due to the presence of aromatic C=C bands in this region.

analysis (Table 1) and by their IR spectra (Table 2). Compounds I and VI (Table 1) have been reported previously [3,4]. The fact that the yields of the amidines are considerably lower than that of the bis(triphenyltin) sulfide may be due to the instability of the amidines under the reaction conditions; no attempt was made to optimize the yields of the amidines.

Both (triphenylstannyl)cyanamide and an *S*-(triphenylstannyl)isothioamide may be intermediates in reaction 3, since reaction of these two compounds under conditions no more strenuous than those employed in reaction 3, also gave bis(triphenyltin) sulfide (31-98%) and the corresponding amidine (compounds I-V, IX) (22-77%), eqn. 4. The *S*-(triphenylstannyl)isothioamides required for reac-



$$(C_6H_5)_3SnNHCN + R\overset{\overset{\displaystyle SSn(C_6H_5)_3}{|}}{C}{=}NR' \rightarrow (C_6H_5)_3SnSSn(C_6H_5)_3 + R\overset{\overset{\displaystyle NCN}{\|}}{C}NHR' \qquad (4)$$

TABLE 3

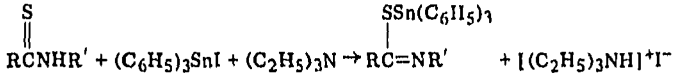
IR SPECTRA OF *S*-(TRIPHENYLSTANNYL)ISOTHIOAMIDES [a]

Compound	C=N [b]	C_6H_5 ring vibration [c]	SnS	SnC_6H_5 [q]	
				ν_{as}	ν_s
XI	1603s	439s	348m	274s	214w [d]
XII	1587s	441s	354m	272s	226s [e]
XIII	1582s	444s	338s	272s	236s [f]
XIV	1558s	443s	352s	268s	236s [g]
XV	1587s	441s [h]	325s	278s	225s [i]
XVI	1565s	446s	348s [j]	272s	234m [k]
XVII	1567s	451s [p]	355s [m,n]	268s [m]	236s [m,o]

[a] Values are expressed in cm^{-1}. [b] This assignment is somewhat uncertain due to the presence of aromatic C=C bands in this region. [c] See ref. 5-7. [d] Also present were bands at 204w and 248s cm^{-1}. [e] A band was present at 256s cm-1. [f] A band was present at 252s cm^{-1}. [g] A band was present at 257s cm^{-1}. [h] A band was present at 451s cm^{-1}. [i] A band was present at 255s cm^{-1}. [j] A band was present at 340s cm^{-1}. [k] A band was present at 252m cm^{-1} [l] A band was present at 435 cm^{-1}. [m] CsI pellet. [n] Bands were also present at 308m and 378m cm^{-1}. [o] A band was present at 265s cm^{-1}. [p] A band was present at 435 cm^{-1}. [q] See ref. 7-11.

TABLE 4

S (TRIPHENYLSTANNYL)ISOTHIOAMIDES [a]



$$RC(=S)NHR' + (C_6H_5)_3SnI + (C_2H_5)_3N \rightarrow RC(SSn(C_6H_5)_3)=NR' + [(C_2H_5)_3NH]^+I^-$$

Compound	R	R	Triethylammonium iodide (%) [b]	Isothioamide (%) [c]	M.p. (°C)	Analysis [g] found (calcd.) (%)				
						C	H	N	S	Sn
XI	CH_3	C_6H_5	79	96 [e]	156-158	62.37	4.68	2.82	6.32	23.75
						(62.43)	(4.63)	(2.80)	(6.41)	(23.73)
XII	C_2H_5	C_6H_5	91	94	139-140	63.33	4.76	2.94	5.97	23.36
						(63.06)	(4.90)	(2.72)	(6.23)	(23.08)
XIII	C_6H_5	C_6H_5	75	88	139-141	66.29	4.22	2.59	5.63	21.53
						(66.22)	(4.48)	(2.49)	(5.70)	(21.11)
XIV	*p* $CH_3C_6H_4$	C_6H_5	87	93	157-158	66.39	4.62	2.63	5.80	20.81
						(66.69)	(4.72)	(2.43)	(5.56)	(20.59)
XV	$C_6H_5CH_2$	C_6H_5	80	84	109-110	66.70	4.87	2.54	5.49	20.50
						(66.69)	(4.72)	(2.43)	(5.56)	(20.59)
XVI [d]	C_6H_5	*p* FC_6H_4	69	72	117-119	64.21	4.20	2.70	5.27	20.38
						(64.16)	(4.17)	(2.41)	(5.53)	(20.45)
XVII	C_6H_5	*p* $C_2H_5OC_6H_4$	35 [f]	21	115-117	65.33	4.82	2.43	5.17	19.66
						(65.31)	(4.83)	(2.31)	(5.30)	(19.61)

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[a] The *N* substituted thioamide, triphenyltin iodide, and triethylamine (1/1/1 + slight excess mole ratio) were allowed to react in refluxing acetonitrile. The reaction times were as follows: (compounds XI, XIII, XV, 2 h); (compounds XII and XIV, 0.25 h); (compound XVI, 15 h); (compound XVII, 63 h). [b] Based on material melting within 5°C of the literature value. [c] Based on material melting within 5°C of the analytical sample [d] F, found 3.33; calcd. 3.27%. [e] In another run in ethanol at 25°C for 0.25 h, 86%, m.p. 150-152°C was isolated. [f] In another run, 2 h in refluxing acetonitrile, 93% was isolated [g] The analytical samples were recrystallized from the following solvents: acetonitrile (compounds XI-XIII, XVI), ethanol (compounds XIV, XV), and n-hexane (compound XVII).

tion 4 were prepared by the reaction of triphenyltin iodide with the appropriate *N*-substituted thioamide in the presence of triethylamine (Table 4); their characteristic IR absorption bands are shown in Table 3.

Experimental

Melting points were determined with a Mel-Temp capillary melting point apparatus and are uncorrected. Several reaction mixtures were subjected to gas-liquid chromatography using a Perkin—Elmer Model 154 Vapor Fractometer. The infrared data (4000-400 cm^{-1}) were obtained using KBr pellets with a Beckman IR 8 infrared spectrophotometer or Perkin—Elmer Infracord and with 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 spectrophotomer (nujol or, where indicated, cesium iodide pellet). Elemental analyses were perfomed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Reaction of bis(triphenylstannyl)carbodiimide with thiobenzamide

A mixture of bis(triphenylstannyl)carbodiimide (7.40 g, 0.01 mol), thiobenzamide (1.37 g, 0.01 mol), and acetonitrile (200 ml) was refluxed for 16 h. A sample of the acetonitrile solution was injected into a gas-chromatograph (carbowax 1500-2 m column), and benzonitrile was shown to be present.

The reaction mixture was cooled to 0°C and filtered to give 6.37 g (87%) of bis(triphenyltin) sulfide, m.p. 141-143°C (lit. [12] m.p. 145.5-147°C).

The acetonitrile was evaporated from the filtrate, the residue was stirred with hot benzene (25 ml), and the mixture was cooled and then filtered to give 0.34 g (81%) of dicyandiamide, m.p. 175-183°C, IR spectrum superimposable on that of an authentic sample.

Evaporation of the benzene from the filtrate followed by stirring of the residue with acetonitrile gave, upon filtration, an additional 0.33 g (5%) of bis(triphenyltin) sulfide, m.p. 142-143°C.

Reaction of bis(triphenylstannyl)carbodiimide with thioacetanilide

A mixture of bis(triphenylstannyl)carbodiimide (14.80 g, 0.02 mol), thioacetanilide (3.03 g, 0.02 mol), and ethanol (100 ml) was refluxed for 15 h. The mixture was cooled to 0°C and filtered to give 14.23 g (97%) of bis(triphenyltin) sulfide, m.p. 141-143°C.

The ethanol was evaporated from the filtrate, and the solid residue was stirred with diethyl ether (75 ml) and filtered to give 1.49 g (43%) of pure *N'*-phenyl-*N*-cyanoacetamidine (I, Table 1), m.p. 195-196°C.

Evaporation of the diethyl ether from the filtrate left 0.88 g (25%) of less pure amidine, m.p. 168-181°C.

Preparation of S-(triphenylstannyl)isothioacetanilide (XI, Table 4)

A mixture of triphenyltin iodide (16.0 g, 0.033 mol), thioacetanilide (5.04 g, 0.033 mol), triethylamine (3.57 g, 0.035 mol), and acetonitrile (200 ml) was refluxed for 2 h. The mixture was cooled to 0°C and filtered to give 16.16 g

(96%) of pure *S*-(triphenylstannyl)isothioacetanilide, m.p. 154-156°C.

Evaporation of the acetonitrile from the filtrate left a semi-solid which was stirred with benzene (150 ml). The mixture was filtered to give 6.08 g (79%) of triethylammonium iodide, m.p. 176-180°C (Lit. [13] m.p. 181°C).

Reaction of (triphenylstannyl)cyanamide with S-(triphenylstannyl)isothioacetanilide

A mixture of (triphenylstannyl)cyanamide (7.80 g, 0.02 mol), *S*-(triphenylstannyl)isothioacetanilide (10.01 g, 0.02 mol), and ethanol (100 ml) was refluxed for 15 h. The mixture was cooled to 0°C and filtered to give 13.45 g (92%) of bis(triphenyltin) sulfide, m.p. 142-144°C.

The ethanol was evaporated from the filtrate, the residue was stirred with diethyl ether, and the mixture was filtered to give 1.57 g (49%) of pure *N'*-phenyl-*N*-cyanoacetamidine (I, Table 1), m.p. 191-195°C. Concentration of the diethyl ether filtrate afforded 0.23 g (7%) of less pure amidine, m.p. 160-163°C.

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