*Journal of Organometallic Chemistry*, 56 (1973) 167–173

# REACTION OF (TRIORGANOSTANNYL)CYANAMIDES WITH CARBON DISULFIDE

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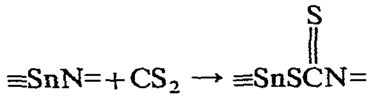
(Received November 15th, 1972)

## SUMMARY

(Triorganostannyl)cyanamides were found to react with carbon disulfide to give dicyandiamide, the corresponding bis(triorganotin) sulfide, and the corresponding *N,N'*-dicyano-*N'*-(triorganostannyl)-*S*-(triorganostannyl)isothiourea. (Trimethylstannyl)cyanamide, (tri-n-butylstannyl)cyanamide, and (tribenzylstannyl)cyanamide were prepared for the first time by the reaction of cyanamide with trimethyltin hydroxide, bis(tri-n-butyltin) oxide, and tribenzyltin hydroxide, respectively. The IR spectrum of (trimethylstannyl)cyanamide in the solid state indicates that the trimethyltin group is planar. Bis(trimethylstannyl)carbodiimide and bis(tri-n-butylstannyl)carbodiimide were prepared by the disproportionation of the corresponding (triorganostannyl)cyanamide.

## INTRODUCTION

The tin–nitrogen bond of (dimethylamino)trimethylstannane[1,2] and *N*-(tributylstannyl)diphenylmethyleneamine[3] is known to add across the multiple bond of carbon disulfide:



$$\equiv \mathrm{SnN}{=} + \mathrm{CS_2} \rightarrow \equiv \mathrm{SnS}\overset{\overset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{N}{=}$$

The reaction of *N*-phenylaminotrimethylstannane with carbon disulfide, on the other hand, affords bis(trimethyltin) sulfide and *sym*-diphenylthiourea[19]. We now report the behavior of (triphenylstannyl)cyanamide[4,5] and some new (triorganostannyl)-cyanamides towards carbon disulfide.

## RESULTS AND DISCUSSION

(Triorganostannyl)cyanamides were found to react with carbon disulfide at the reflux temperature to give dicyandiamide (64–98%), the corresponding bis-

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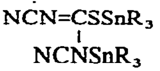
$$4R_3SnNHCN + CS_2 \rightarrow H_2N\underset{\underset{NH}{\|}}{C}NHCN + R_3SnSSnR_3 + NCN{=}\underset{\underset{NCNSnR_3}{|}}{C}SSnR_3 \qquad (1)$$

(I), $R = CH_3$
(II), $R = C_6H_5$
(III), $R = C_6H_5CH_2$

(triorganotin)sulfide (78–99 %), and the corresponding *N*,*N'*-dicyano-*N'*-(triorganostannyl)-*S*-(triorganostannyl)isothiourea (I–III) (69–97 %), eqn. (1). The dicyandiamide and sulfides were identified by their IR spectra and by comparison of their melting or boiling points with the literature values. The isothioureas were identified by elemental analysis (Table 1) and by their IR spectra (Table 2). A bis(triorganotin) cyanodithioimidocarbonate (IV) could be an intermediate in reaction (1). (IV) could subsequently decompose to give bis(triorganotin) sulfide and cyanoisothiocyanate (V). (V) could react with (triorganostannyl)cyanamide to give the iso-

TABLE 1

*N*,*N'*-DICYANO-*N'*-(TRIORGANOSTANNYL)-*S*-(TRIORGANOSTANNYL)ISOTHIOUREAS



$$NCN{=}\underset{\underset{NCNSnR_3}{|}}{C}SSnR_3$$

| *No.* | *R* | *M.p.* (°C) | *Analysis, found (calcd.) (%)* | | | | | *Mol. wt.*[a] *found (calcd.)* |
|---|---|---|---|---|---|---|---|---|
| | | | *C* | *H* | *N* | *S* | *Sn* | |
| (I) | $CH_3$ | [b] | 24.09<br>(23.93) | 4.09<br>(4.02) | 12.01<br>(12.40) | 7.11<br>(7.10) | 52.80<br>(52.55) | 1203[c]<br>(451.71) |
| (II) | $C_6H_5$ | 233–235[d] | 57.13<br>(56.84) | 3.91<br>(3.67) | 6.96<br>(6.80) | 3.86<br>(3.89) | 29.05<br>(28.80) | 825[c]<br>(824.14) |
| (III) | $C_6H_5CH_2$ | 118–127[e] | 59.31<br>(59.51) | 4.84<br>(4.66) | 6.32<br>(6.17) | 3.72<br>(3.53) | 25.98<br>(26.13) | 950[f]<br>(908.31) |

[a] Vapor pressure osmometry at 37°. [b] Recrystallized from tetrahydrofuran/n-pentane; no melting was observed up to 300°. [c] Solvent was chloroform. [d] Washed with diethyl ether; decomposition of the melt occurred at 236°. [e] Recrystallized from acetone; melting occurred with decomposition. [f] Solvent was *p*-dioxane.

TABLE 2

IR SPECTRA OF *N*,*N'*-DICYANO-*N'*-(TRIORGANOSTANNYL)-*S*-(TRIORGANOSTANNYL)-ISOTHIOUREAS[a]

| *No.* | *C≡N* | *SnS*[b] | $\nu_{as}(SnC)$ | $\nu_s(SnC)$ |
|---|---|---|---|---|
| (I) | 2174 s | 327 w | 550 s | 508 m[c] |
| (II) | 2169 s | 328 w | 265 s[b,d] | 224 m[b,d] |
| (III)[e] | 2174 s | 330 w | [f] | |

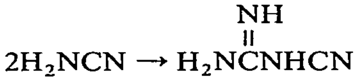
[a] Values are expressed in $cm^{-1}$; each compound had characteristic bands at 1453–1462 s, 1362–1366 s, 1139–1147 m, 1095–1101 m, and 1049–1053 m $cm^{-1}$. [b] Nujol. [c] A band at 535 s $cm^{-1}$ was present. [d] Ref. 16. [e] A band at 1595 m $cm^{-1}$ was present. [f] Bands were present at 556 m (sh), 546 m, 450 s, 427 s, and 415 s $cm^{-1}$; the band at 450 s may be due to a phenyl ring vibration[7,15,17].

thiourea, eqns. (2)–(5). Addition of eqns. (2)–(5) gives eqn. (1). The fact that the reaction

$$2R_3SnNHCN + CS_2 \rightarrow \underset{(IV)}{(R_3SnS)_2CNCN} + H_2NCN \quad (2)$$

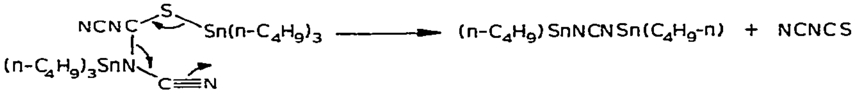
$$(IV) \rightarrow R_3SnSSnR_3 + \underset{(V)}{SCNCN} \quad (3)$$

$$(V) + 2R_3SnNHCN \rightarrow (I), (II), \text{or } (III) + H_2NCN \quad (4)$$

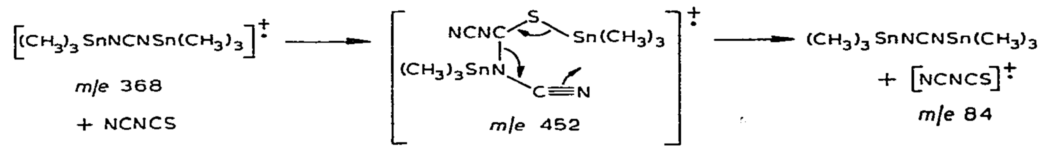


$$2H_2NCN \rightarrow H_2N\overset{\overset{NH}{\|}}{C}NHCN \quad (5)$$

of dipotassium cyanodithioimidocarbonate with triorganotin chlorides affords the corresponding bis(triorganotin)sulfide and probably (V), instead of (IV), lends support to the above reaction scheme[6]. Only dicyandiamide (89–99%) could be isolated from the reaction of (tri-n-butylstannyl)cyanamide with carbon disulfide. The IR spectrum of the liquid remaining after removal of the dicyandiamide and carbon disulfide indicated the presence of the expected *N,N'*-dicyano-*N'*-(tri-n-butylstannyl)-*S*-(tri-n-butylstannyl)isothiourea. However, attempts to isolate this material by distillation gave bis(tri-n-butylstannyl)carbodiimide, which was identified by comparison of its boiling point and IR spectrum with that of an authentic sample. The decomposition of the isothiourea to the carbodiimide may have occurred by a cyclic mechanism (eqn. 6). The mass spectrum of (I) indicated the presence of carbodiimide and NCNCS also. The expected parent ion (*m/e* 452) was not present. A peak at *m/e* 437 is probably due to loss of $CH_3\cdot$ from the parent ion. The peaks at *m/e* 368 and 84 (base peak) may be due to rearrangement of the parent ion to give bis(trimethylstannyl)carbodiimide and NCNCS:



(6)



In contrast to the thermal and hydrolytic instability of *N*-phenyl-*N'*-cyano-*N'*-(triphenylstannyl)-*S*-(triphenylstannyl)isothiourea[5], compound (II) (Table 1) was found to be remarkably stable to both heat and water. For example, 86% of (II) was recovered unchanged after being refluxed in benzene for 24 h, and 79% of (II) was recovered unchanged after being refluxed in tetrahydrofuran/water (50/50) for 24 h. The hydrolytic stability of the tin–nitrogen bond in (II) may be due to inter- or intramolecular pentacoordination around the tin due to the CN group. The formation of pentacoordinate tin by the intermolecular coordinating action of a nitrogen atom also probably accounts for the unusual hydrolytic stability exhibited by certain other organotin–nitrogen compounds[4].

The (triphenylstannyl)cyanamide required for reaction (1) was prepared by the reaction of bis(triphenyltin)oxide with cyanamide as previously described[4]. The other (triorganostannyl)cyanamides used in reaction (1) are new compounds (Table 3). (Tri-n-butylstannyl)cyanamide (VII) was prepared in 96% yield by the reaction of bis-(tri-n-butyltin) oxide with cyanamide (1/2 mole ratio) in refluxing diethyl ether. (Trimethylstannyl)cyanamide (VI) and (tribenzylstannyl)cyanamide (VIII) were prepared in 100% and 86% yield, respectively, by the reaction of the corresponding triorganotin hydroxide with cyanamide (1/1 mole ratio) in refluxing diethyl ether. The IR spectra of the new (triorganostannyl)cyanamides are summarized in Table 4. The absence of a $\nu_s$(SnC) band for (trimethylstannyl)cyanamide (VI) in the solid state suggests that the $(CH_3)_3Sn$ group is planar[8]. (VI), therefore, may have a polymeric structure in the solid state, with the tin atom being pentacoordinate. The IR spectrum of (VI) in *p*-dioxane, on the other hand, contains a band at 461 cm$^{-1}$ which may be due to the $\nu_s$-(SnC) band; *p*-dioxane does not have a band in this region. In *p*-dioxane, therefore, the trimethyltin group of (VI) is probably non-planar. A molecular weight determination showed (VI) to be monomeric in *p*-dioxane (Table 3). A molecular weight determination showed (tri-n-butylstannyl)cyanamide (VII) to be associated in benzene (Table 3).

TABLE 3

(TRIORGANOSTANNYL)CYANAMIDES $R_3SnNHCN$

| *No.* | *R* | *M.p. (°C)* | *Analyses, found (calcd.) (%)* | | | | *Mol. wt.*[a] *found (calcd.)* |
|---|---|---|---|---|---|---|---|
| | | | *C* | *H* | *N* | *Sn* | |
| (VI) | $CH_3$ | 106–108[b,c] | 23.51 | 4.89 | 13.91 | 58.21 | 205[d] |
| | | | (23.45) | (4.92) | (13.67) | (57.95) | (204.83) |
| (VII) | n-$C_4H_9$ | [e] | 47.23 | 8.47 | 8.20 | 35.47 | 503[f] |
| | | | (47.16) | (8.52) | (8.46) | (35.85) | (331.07) |
| (VIII) | $C_6H_5CH_2$ | 129–132[b,g] | 61.28 | 5.25 | 6.61 | 27.12 | 439[h] |
| | | | (61.01) | (5.12) | (6.48) | (27.40) | (433.12) |

[a] Values are expressed in cm$^{-1}$. [b] 541 s in *p*-dioxane (10% solution). [c] Absent in solid; 461 w in *p*-dioxane hydrofuran/n-pentane. [d] Solvent was *p*-dioxane. [e] Viscous oil. [f] Solvent was benzene. [g] Recrystallized from tetrahydrofuran/n-hexane. [h] Solvent was chloroform.

TABLE 4

IR SPECTRA OF (TRIORGANOSTANNYL)CYANAMIDES[a]

| *No.* | *NH* | *C≡N* | $\nu_{as}$*(SnC)* | $\nu_s$*(SnC)* |
|---|---|---|---|---|
| (VI) | 3247 m | 2183 s, 2146 s | 538 s[b] | [c] |
| (VII)[d] | 3425 m | 2174 s | 610 s[e] | 515 m |
| (VIII) | 3333 m | 2174 s | [f] | |

[a] Values are expressed in cm$^{-1}$. [b] 541 s in *p*-dioxane (10% solution). [c] Absent in solid; 461 w in *p*-dioxane (10% solution). [d] Liquid film. [e] A band at 565 m was present. [f] Bands were present at 552 m, 541 m, and 448 s cm$^{-1}$; the band at 448 s may be due to a phenyl ring vibration[7,15,17].

Like (triphenylstannyl)cyanamide[4], compounds (VI) and (VII) (Table 3) disproportionated in refluxing benzene to give high yields of dicyandiamide and the corresponding bis(triorganostannyl)carbodiimide. This reaction represents a new method for preparing bis(trimethylstannyl)carbodiimide[9,18] and bis(tri-n-butylstannyl)carbodiimide[10,11]. Compound (VIII) (Table 3), on the other hand, was considerably more stable in refluxing benzene, affording only a 20% yield of dicyandiamide. The IR spectrum of the reaction mixture showed a weak carbodiimide band and a strong nitrile band. In refluxing toluene, (VIII) afforded a 40% yield of dicyandiamide.

The IR spectrum of bis(trimethylstannyl)carbodiimide in the solid state lacked a $\nu_s$(SnC) band which suggests that the $(CH_3)_3Sn$ group is planar. This result is in agreement with an X-ray study of this compound[9].

## EXPERIMENTAL

Melting points were determined with a Mel-Temp capillary melting point apparatus and are uncorrected. 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 unless otherwise specified) 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). Elemental analyses and molecular weight determinations were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

### *Reaction of (triorganostannyl)cyanamides with carbon disulfide*

(1). *Reaction of (triphenylstannyl)cyanamide with carbon disulfide.* A mixture of 19.50 g (0.05 mol) of (triphenylstannyl)cyanamide[4] and carbon disulfide (300 ml) was refluxed for 5 h. After being allowed to cool to 25°, the mixture was filtered. The solid which was obtained was recrystallized from water to give 0.605 g of dicyandiamide, m.p. 206–208°, no depression on admixture with an authentic sample, IR spectrum superimposable on that of an authentic sample. Concentration of the mother liquor afforded an additional 0.203 g of dicyandiamide, m.p. 204–207°, bringing the total yield of dicyandiamide to 77%.

Evaporation of the carbon disulfide from the original filtrate left an oil which solidified upon being stirred with hot acetonitrile (100 ml). The solid was collected on a filter and washed with hot acetonitrile to give 9.68 g of *N*,*N'*-dicyano-*N'*-(triphenylstannyl)-*S*-(triphenylstannyl)isothiourea (II), m.p. 230–233°.

The filtrate was allowed to cool, and the crystals which separated were collected on a filter to give 6.20 g of bis(triphenyltin) sulfide, m.p. 146.5–148°, no depression on admixture with an authentic sample, IR spectrum superimposable upon that of an authentic sample.

Concentration of the filtrate afforded an additional 0.764 g of bis(triphenyltin) sulfide, m.p. 140–144°, (90% total yield) and an additional 0.13 g of (II), m.p. 229–233°, (95% total yield).

(2). *Reaction of (trimethylstannyl)cyanamide with carbon disulfide.* A mixture of 10.2 g (0.05 mol) of (trimethylstannyl)cyanamide and carbon disulfide (300 ml) was refluxed for 8 h. The mixture was filtered, and the solid which was obtained was recrystallized from water to give 1.01 g (96%) of dicyandiamide, m.p. 201–203° (dec.).

Evaporation of the carbon disulfide from the filtrate left an oil which solidified upon being stirred with hot acetonitrile. The solid was collected on a filter to give 3.05 g of *N,N'*-dicyano-*N'*-(trimethylstannyl)-*S*-(trimethylstannyl)isothiourea (I), m.p.: no melting up to 300°.

The acetonitrile was evaporated from the filtrate, and the residue was stirred with n-hexane. The mixture was filtered to give an additional 4.61 g of (I) (84% total yield).

Evaporation of the n-hexane from the filtrate left an oil which afforded, after distillation, 3.46 g (77%) of bis(trimethyltin) sulfide, b.p. 60–61° (0.1 mmHg) [lit.[12] b.p. 63–66° (3 mmHg)], $n_D^{22}$ 1.5589 (lit.[13] $n_D^{20}$ 1.5600). IR: 529 [$\nu_{as}$ Sn(CH$_3$)$_3$], 505 [$\nu_s$ Sn(CH$_3$)$_3$], 364 ($\nu_{as}$ Sn$_2$S), and 316 ($\nu_s$ Sn$_2$S) cm$^{-1}$.

(3). *Reaction of (tribenzylstannyl)cyanamide with carbon disulfide.* A mixture of 21.65 g (0.05 mol) of (tribenzylstannyl)cyanamide and carbon disulfide (300 ml) was refluxed for 4 h and filtered to give 1.03 g (98%) of dicyandiamide, m.p. 203–206° (dec.).

The carbon disulfide was evaporated from the filtrate, the resulting oil was dissolved in hot acetone (25 ml), and the solution was cooled to 4°. The solid which separated was collected on a filter to give 10.69 g (97%) of *N,N'*-dicyano-*N'*-(tribenzylstannyl)-*S*-(tribenzylstannyl)isothiourea (III), m.p. 118–127° (dec.).

To the filtrate was added acetonitrile (50 ml), and the solution was heated to boiling and allowed to cool. The resulting solid was collected on a filter to give 10.17 g (100%) of bis(tribenzyltin)sulfide, m.p. 81–86° (lit.[14] m.p. 85°).

(4). *Reaction of (tri-n-butylstannyl)cyanamide with carbon disulfide.* A mixture of 59.62 g (0.10 mol) of bis(tri-n-butyltin) oxide, 8.41 g (0.20 mol) of cyanamide, and diethyl ether (300 ml) was refluxed for 1 h, the diethyl ether was evaporated, and the residue was refluxed with carbon disulfide (300 ml) for 4 h. The resulting solid was collected on a filter to give 4.16 g (99%) of dicyandiamide, m.p. 198–204° (dec.).

The carbon disulfide was evaporated, and the resulting oil was distilled to give 25.29 g (83%) of bis(tri-n-butylstannyl)carbodiimide, b.p. 180–186° (0.05 mmHg), IR spectrum superimposable upon that of an authentic sample.

### *Preparation of (triorganostannyl)cyanamides*

(1). *(Trimethylstannyl)cyanamide.* A mixture of trimethyltin hydroxide (12.88 g, 0.071 mol), cyanamide (3.28 g, 0.078 mol), and diethyl ether (500 ml) was refluxed for 18 h. The resulting solid was collected on a filter to give 10.2 g (70%) of (trimethylstannyl)cyanamide, m.p. 105–109° (dec.). Evaporation of the diethyl ether from the filtrate followed by recrystallization of the residue from tetrahydrofuran/n-pentane gave an additional 2.96 g of product, m.p. 106–108° (dec.) (91% total yield).

(2). *(Tri-n-butylstannyl)cyanamide.* A mixture of bis(tri-n-butyltin) oxide (5.962 g, 0.010 mol), cyanamide (0.841 g, 0.02 mol), and diethyl ether (50 ml) was refluxed for 0.5 h and filtered. Evaporation of the diethyl ether from the filtrate gave 6.37 g (96%) of (tri-n-butylstannyl)cyanamide (oil).

(3). *(Tribenzylstannyl)cyanamide.* A mixture of tribenzyltin hydroxide (20.45 g, 0.05 mol), cyanamide (2.21 g, 0.053 mol), and diethyl ether (300 ml) was refluxed for 18 h. The resulting solid was collected on a filter to give 17.73 g (82%) of (tribenzylstannyl)cyanamide, m.p. 121–126°. Three recrystallizations from tetrahydrofuran/n-hexane gave the analytical sample, m.p. 129–132° (dec.).

*Disproportionation of (triorganostannyl)cyanamides*

(1). *Preparation of bis(trimethylstannyl)carbodiimide.* A mixture of (trimethylstannyl)cyanamide (1.025 g, 0.005 mol) and benzene (50 ml) was refluxed for 24 h. The mixture was filtered to give 0.0957 g (91%) of dicyandiamide, m.p. 205–207°.

The benzene was evaporated from the filtrate, and the resulting oil was stirred with hexane. The solid which formed was collected on a filter to give 0.714 g (77%) of bis(trimethylstannyl)carbodiimide, m.p. 98–102°. Recrystallization from n-hexane gave the analytical sample, m.p. 102°. (Found: C, 23.07; H, 5.14; N, 7.90; Sn, 64.54: mol. wt. by vapor pressure osmometry at 37° in benzene, 352. $C_7H_{18}N_2Sn_2$ calcd.: C, 22.87; H, 4.94; N, 7.62; Sn, 64.57%; mol. wt., 367.61.) IR: 2000 (NCN), and 549, 538 [$\nu_{as}$ $Sn(CH_3)_3$]$cm^{-1}$.

(2). *Preparation of bis(tri-n-butylstannyl)carbodiimide.* A solution of (tri-n-butylstannyl)cyanamide (47.9 g, 0.145 mol) in benzene (300 ml) was refluxed for 18 h. The mixture was filtered to give 3.00 g (99 %) of dicyandiamide, IR superimposable on that of an authentic sample.

Evaporation of the benzene from the filtrate left 44.6 g of an oil. Distillation gave 20.1 g (45%) of bis(tri-n-butylstannyl)carbodiimide, b.p. 190° (0.05 mmHg) [lit.[10] b.p. 201–203° (2 mmHg)], $n_D^{25}$ 1.5110 (lit.[10] $n_D^{20}$ 1.5160). (Found: C, 48.65; H, 8.92; N, 4 68; Sn, 38.58; mol. wt. by vapor pressure osmometry at 37° in benzene, 603. $C_{25}H_{54}N_2Sn_2$ calcd.: C, 48.42; H, 8.78; N, 4.52; Sn, 38.28 %; mol. wt. 620.10.) IR: 2083 (NCN), 666, 599 (SnC), 506 (SnC), and 474 $cm^{-1}$.

## ACKNOWLEDGEMENT

The authors wish to thank Professor Harold A. Horan for the infrared spectral data.

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