The Reactions of Organotin Chlorides with the Cyanodithioimidocarbonate Anion

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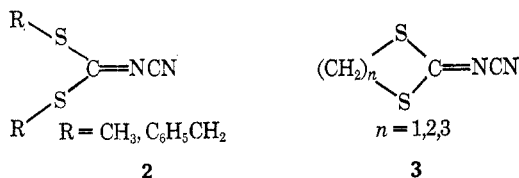
The reactions of dipotassium cyanodithioimidocarbonate (1) with dialkyl(aryl)tin dichlorides lead to high yields (94–96%) of 1,1-dialkyl(aryl)-2,4-dithia-3-cyaniminostannacyclobutanes. However, the reaction of 1 with 2 mol of bistrialkyl(aryl)tin chlorides gives the corresponding bistrialkyl(aryl)tin sulfide and trialkyl(aryl)tin (iso)-thiocyanate. The reaction of 1 with 2 mol of 1-chloro-2,4-dinitrobenzene results in a 65% yield of 2,2′,4,4′-tetra-nitrodiphenyl sulfide. A stepwise mechanism, based on the formation of a resonance stabilized, cyclic, intermediate anion, is suggested to explain the results.

In 1904 Hantzsch and Wolvekamp[1] showed that the reaction of cyanamide, carbon disulfide, and potassium hydroxide leads to the cyanodithioimidocarbonate anion (1). The dimethyl-[1] and dibenzyl cyanodithio-

$$H_2NCN + CS_2 + 2KOH \longrightarrow 2K^+ \underset{-S}{\overset{-S}{\diagdown}} C{=}NCN + 2H_2O$$

1
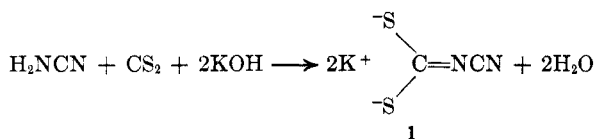
imidocarbonates[2] (2) were prepared by treating 1 with 2 equiv of methyl iodide and benzyl bromide, respectively. More recently, heterocyclic derivatives[3,4] (3) were synthesized from 1 and the app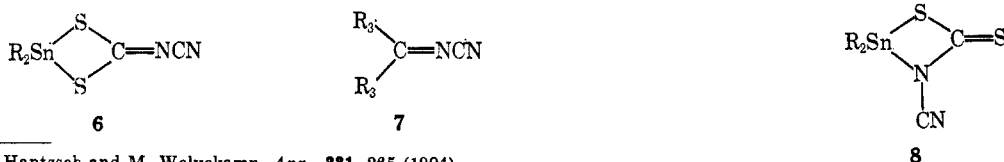ropriate dihalo-alkane. Compounds 2 and 3 are indeed the S,S′ dialkylates rather than the possible S,N dialkylates (4 and 5). The nmr spectrum (CCl₄) of 2, R = CH₃,

R = CH₃, C₆H₅CH₂

2

n = 1,2,3

3

4

5
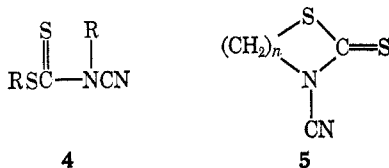
shows a single peak at 2.68 ppm (TMS reference). Hydrolysis of the dibenzyl derivative gave an 86% yield of benzyl mercaptan. The nmr spectrum (chloroform) of 3 (n = 2) showed only a sharp singlet at 3.85 ppm.[3]

In 1875, Fleischer[5] prepared water insoluble salts of 1, and more recently, transition metal complexes of 1 were reported.[6,7]

A recent patent[8] reported the preparation of di-*n*-alkyltin cyanodithioimidocarbonates (6) in 70–75%

6

7

yields and bistrialkyltin cyanodithioimidocarbonates (7) in 85% yields. However, no evidence was presented for the assigned structures. In this paper the results of an investigation, completed prior to the appearance of the patent,[8] of the reactions of 1 with various organotin chlorides are presented.

Results

A. Reactions of 1 and R₂SnCl₂.—The reaction of 1 with a dialkyl(aryl)tin dichloride can lead to a polymer or to novel stannacyclobutanes (6). The planar configuration of 1 and the *gem* arrangement of the two nucleophilic sulfur atoms are factors favoring the latter possibility. Indeed, treating 1 with various R₂SnCl₂ compounds in a tetrahydrofuran (THF)–water medium gave high yields of 1,1,dialkyl(aryl)-2,4-dithia-3-cyan-iminostannacyclobutanes (6). All the stannacyclo-butanes were simply prepared by adding a THF solution of the dialkyl(aryl)tin dichloride to an aqueous solution of 1, stirring the reaction mixture at room temperature for 2–4 hr and then pouring the reaction mixture onto ice. The products precipitated in high yields as white, crystalline solids.

The structure assigned to 6 is based on elemental and molecular weight analyses and the ir spectra. All the compounds shown in Table I show absorption at 2175–

TABLE I

REACTIONS OF 1 AND R₂SnCl₂

1 + R₂SnCl₂ ⟶ 6

R	Yield of 6 (%)
n-Butyl	96
n-Octyl	94
Phenyl	95

2180 cm⁻¹. This region is quite characteristic of the conjugated cyano group in the open chain (2) and hetero-cyclic (3) derivatives of 1.[3] The alternative formulation (8) for the stannacyclobutane is not likely in view
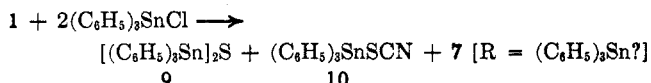

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of the instability of the Sn–N bond to protic solvents.[9] Also, the ir spectrum of structure 8 would be expected to show nitrile absorption at higher wave numbers.[10]

(1) A. Hantzsch and M. Wolvekamp, *Ann.*, **331**, 265 (1904).
(2) E. Fromm and D. Van Gonez, *ibid.*, **355**, 196 (1907).
(3) R. J. Timmons and L. S. Wittenbrook, *J. Org. Chem.*, **32**, 1566 (1967).
(4) J. J. D'Amico and R. H. Campbell, *ibid.*, **32**, 2567 (1967).
(5) A. Fleischer, *Ann.*, **179**, 214 (1875).
(6) J. P. Fackler and D. Coucouvanis, *J. Amer. Chem. Soc.*, **88**, 3913 (1966).
(7) F. A. Cotton and J. A. McCleverty, *Inorg. Chem.*, **6**, 229 (1967).
(8) W. A. Stamm and C. E. Greco, U. S. Patent 3,316,284 (April 25, 1967).
(9) K. Jones and M. F. Lappert, *Proc. Chem. Soc.*, 22 (1964).
(10) A. G. Anastassiou, *J. Amer. Chem. Soc.*, **87**, 5512 (1965).

To our knowledge, compounds of type 6 are the first examples of *heterocyclic* stannacyclobutanes[11] in which *all* bonds to tin in the ring are σ bonded. Previous examples of dithiastannacyclobutanes involved a tin to sulfur coordinate bond resulting in pentacovalent tin.[12]
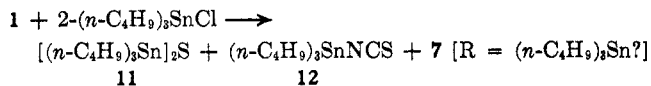
B. Reactions 1 and R₃SnCl.—In view of the behavior of 1 with R₂SnCl₂, it was expected that reactions of 1 with trialkyl(aryl)tin chlorides would lead to high yields of bistrialkyl(aryl)tin cyanodithioimidocarbonates (7). Indeed, ref 8 reports 85% yields of bistri-*n*-butyltin and bistri-*n*-octyltin cyanodithioimidocarbonates. However, in our hands the expected reaction did not occur.

The reaction of 1 with 2 mol of triphenyltin chloride in a THF–water medium at room temperature for 2.5 hr gave a 44% yield of bistriphenyltin sulfide (9) and a 14% yield of triphenyltin thiocyanate (10). Another product (10%) was isolated which, on the basis of the

$1 + 2(C_6H_5)_3SnCl \longrightarrow$

$\quad [(C_6H_5)_3Sn]_2S + (C_6H_5)_3SnSCN + 7 \, [R = (C_6H_5)_3Sn?]$
$\qquad\quad 9 \qquad\qquad\qquad 10$

ir spectrum, may be the desired bistriphenyltin cyanodithioimidocarbonate (7). However, the compound could not be purified, and the structure of this material remains in doubt. Also, the remaining product was a mixture of solids of broad melting range and a viscous oil which we were unable to purify.

The reaction of 1 with 2 mol of tri-*n*-butyltin chloride gave similar results. Using quantitative ir analyses, the yields of bistri-*n*-butyltin sulfide (11) and tri-*n*-butyltin isothiocyanate (12) were found to be 32 and

$1 + 2\text{-}(n\text{-}C_4H_9)_3SnCl \longrightarrow$

$\quad [(n\text{-}C_4H_9)_3Sn]_2S + (n\text{-}C_4H_9)_3SnNCS + 7 \, [R = (n\text{-}C_4H_9)_3Sn?]$
$\qquad\quad 11 \qquad\qquad\qquad 12$

23%, respectively. An attempt to separate the products by distillation was unsuccessful and also led to decomposition (*cf.* Experimental Section). A gas chromatographic analysis showed the presence of 11 and 12, but appreciable decomposition of reference samples on the column excluded a quantitative determination.

The ir spectrum of the crude product, from 1 and tributyltin chloride, showed absorption at 2175 and 2065 cm⁻¹. The former band provides evidence for bistri-*n*-butyltin cyanodithioimidocarbonate (7), while the latter is the exact position of absorption for the isothiocyanate group in tri-*n*-butyltin isothiocyanate (12). A sample of this compound was prepared from tri-*n*-butyltin chloride and potassium thiocyanate following the procedure of Cummins and Dunn.[13]

The far-infrared spectrum of the crude product showed absorption at 370 cm⁻¹ which is characteristic of bistri-*n*-butyltin sulfide (11). This band is absent in tri-*n*-butyltin isothiocyanate and compounds con-
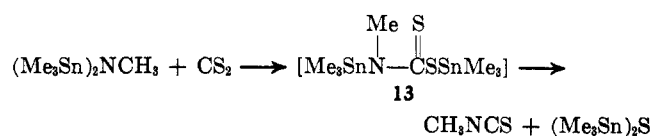
taining the Sn–S–C linkage. Thus, the bands at 2065 and 370 cm⁻¹ were used to determine the yields of 12 and 11, respectively.

Discussion

A number of explanations can be offered for the observed difference in reaction path between R₃SnCl and R₂SnCl₂ with 1.

Kupchik and Calabretta[14] reported the thermal decomposition of various diphenyltin and triphenyltin dithiocarbamates to the corresponding sulfides and oxides. The reported temperatures of decomposition ranged from 80° in benzene to 250° neat. Recently, Bonati and Ugo[15] showed that a refluxing benzene solution of triphenyltin chloride with sodium N-ethyldithiocarbamate led to bistriphenyltin sulfide. These workers suggested the formation and decomposition of an unstable triorganotin N-alkyldithiocarbamate. Therefore, there is a possibility that the products from 1 and R₃SnCl arise from the decomposition of the initially formed bistrialkyl(aryl)tin cyanodithioimidocarbonate (7). However, in all our experiments the temperature never exceeded 30° during the reaction or subsequent work-up. Also, the contrasting behavior of 1 and R₂SnCl₂ remains to be explained.

Recently, a reaction between N-methylhexamethyldistannazane and carbon disulfide was reported to

$$(Me_3Sn)_2NCH_3 + CS_2 \longrightarrow [Me_3Sn\overset{\displaystyle Me}{\overset{|}{N}}\!\!-\!\!\overset{\displaystyle S}{\overset{\|}{C}}SSnMe_3] \longrightarrow$$
$$13$$

$$CH_3NCS + (Me_3Sn)_2S$$

yield methyl isothiocyanate and bistrimethyltin sulfide.[16] These workers postulate an intermediate bistrimethyltin S,N-alkylate (13) which breaks down to give the observed products. Intermediate 13 is analogous to structure 4, arising from the S,N alkylation of 1. However, all previous experience with 1 and various alkylating agents[1–3] shows preferred reaction at the two sulfur atoms. Also, the reactions of 1 with the organotin chlorides were conducted in a THF–water medium. Therefore, an intermediate having an R₃Sn–N bond would be expected to react with the water to give the corresponding bistrialkyl(aryl)tin oxide. There is no evidence to indicate the presence of these compounds.

Reichle[17] found that the reaction of bistriphenyltin oxide with carbon disulfide gave bistriphenyltin sulfide. Thus, it is conceivable that carbon disulfide arises by the following equilibrium, while hydrolysis of triphenyl-

$$1 \rightleftharpoons CS_2 + 2K^+ + NCN^{2-}$$
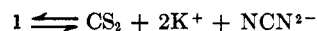
tin chloride leads to the oxide. Thus, the two intermediates required for sulfide formation would be present. However, this possibility was eliminated by reacting 1 with triphenyltin chloride heterogeneously in dry THF. Again, a 40% yield of bistriphenyltin sulfide and a 12% yield of triphenyltin thiocyanate were obtained.

(11) Recently, the all-tin-containing cyclic compounds, octa-*t*-butylstannacyclobutane and octabenzylstannacyclobutane were reported: W. V. Farrar and H. A. Skinner, *J. Organometal. Chem.*, 1, 434 (1964); W. P. Neumann, J. Pedain, and R. Sommer, *Ann.*, 694, 9 (1966).

(12) W. Kuchen, A. Judat, and J. Metten, *Ber.*, 98, 3981 (1965); K. Jones and M. F. Lappert, *Organometal. Chem. Rev.*, 1, 76 (1966).

(13) R. A. Cummins and P. Dunn, *Aust. J. Chem.*, 17, 411 (1964). Based on infrared studies, these workers have assigned the isothiocyanate structure to the product rather than the isomeric thiocyanate formula. The isothiocyanate structure is also a possibility for the triphenyltin derivative discussed earlier, but the problem was not investigated.

(14) E. J. Kupchik and P. J. Calabretta, *Inorg. Chem.*, 4, 973 (1965).

(15) F. Bonati and R. Ugo, *J. Organometal. Chem.*, 10, 257 (1967).

(16) K. Itoh, I. K. Lee, I. Matsuda, S. Sakai, and Y. Ishii, *Tetrahedron Lett.*, 26, 2667 (1967).

(17) W. T. Reichle, *Inorg. Chem.*, 1, 650 (1962).

The difference in behavior between R_3SnCl and R_2SnCl_2 with **1** may be explained in terms of stepwise mechanisms. Thus, initial alkylation of **1** with R_2SnCl_2 would lead to intermediate **14**. Subsequent intramolecular displacement of the second chlorine atom would give the dithiastannacyclobutane (**6**).
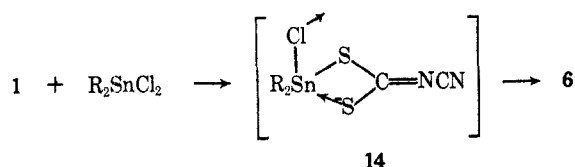

Intermolecular displacement would result in the polymer, but the high yield of the cyclic compound demonstrates the great propensity for intramolecular attack.

Analogously, the initial alkylation of **1** with the first mole of R_3SnCl would lead to intermediate **15**. Again, intramolecular attack might be expected, but, in this case, it is suggested that the result would be a resonance stabilized, intermediate anion (**16**) involving
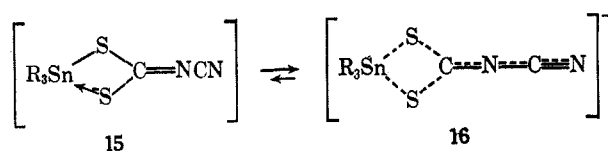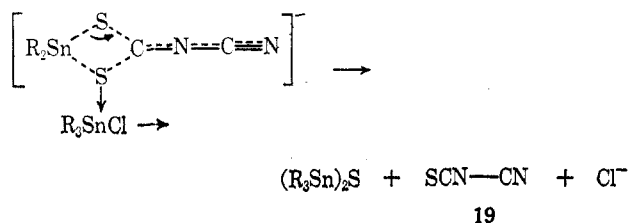

pentacoordinate tin. Cyclic structures (**17** and **18**) involving pentacoordinate tin[12] are well recognized.
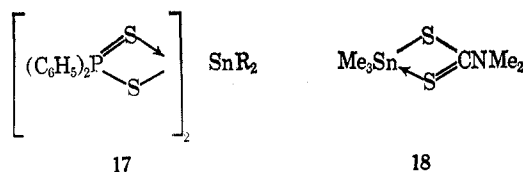
Also, there are numerous examples of similar structures involving other metal atoms.[18]

Subsequent reaction of **16**, *via* a nucleophilic sulfur atom, with the second mole of R_3SnCl would give $(R_3Sn)_2S$ and cyanoisothiocyanate (**19**).[19] The tri-

$$(R_3Sn)_2S + SCN—CN + Cl^-$$
19

alkyl(aryl)tin thiocyanates or isothiocyanates may arise from the reaction of **19** with either unreacted R_3SnCl or $(R_3Sn)_2S$.

The infrared evidence indicated that some **7** may be present in the product. Its formation may be attributed to the reaction of the open chain intermediate (**14**) with the second mole of R_3SnCl. Thus,

there is probably an equilibrium between intermediates **15** and **16** lying in the direction of **16**.

Support for the proposed mechanism is provided by the reaction of **1** with 2 mol of 1-chloro-2,4-dinitrobenzene. Under experimental conditions identical with that of **1** with $2R_3SnCl$, a 65% yield of 2,2′,4,4′-tetranitrodiphenyl sulfide (**20**) was obtained. This
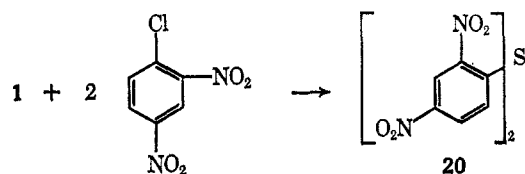

product is analogous to that obtained with **1** and R_3SnCl and suggests a similar mechanistic path.

The generally accepted mechanism for nucleophilic displacement of an activated aryl halide involves the formation of an intermediate anion (**21**). Subsequent loss of chloride ion regenerates the aromatic system
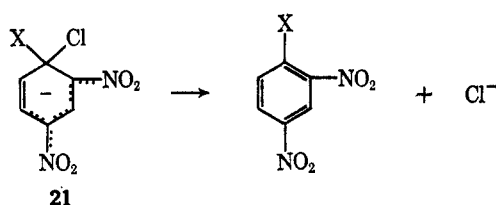
giving the product. A stable complex, analogous to **21**, was isolated in the classic work of Meisenheimer,[20] and more recently, the spiro anion (**22**)[21] was prepared and isolated.
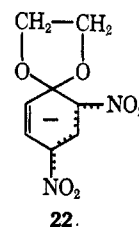
The reaction of **1** with 1 mol of 1-chloro-2,4-dinitrobenzene can give the intermediate **23**. Subsequent *intramolecular* attack would give the intermediate spiro anion (**24**), analogous to **22** and the organotin
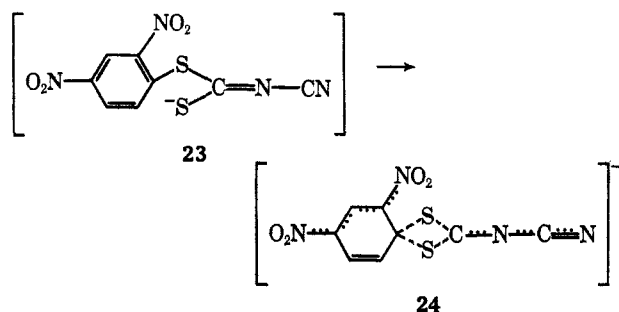
intermediate (**16**). As with **16** and R_3SnCl, intermediate **24** may react with the second mole of 1-chloro-2,4-dinitrobenzene to yield the tetranitrodiphenyl sulfide (**20**).

The similar reactivity of **1** toward R_3SnCl and 1-chloro-2,4-dinitrobenzene may be attributed in both

(18) F. A. Cotton and J. A. McCleverty, *Inorg. Chem.*, **3**, 1398 (1964); J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Nature*, **177**, 1043 (1956).

(19) Hantzsch[1] reported the formation of cyanoisothiocyanate on heating the lead and silver salts of cyanodithioimidocarbonic acid. However, it polymerizes on standing.

(20) J. Meisenheimer, *Ann.*, **323**, 205 (1902).

(21) R. J. Pollit and B. C. Saunders, *J. Chem. Soc.*, 1132 (1964)

cases to the formation of a highly resonance stabilized, cyclic, intermediate anion. It is suggested that it is this species which reacts further to give the sulfides.

Finally, it follows that, if the formation of the cyclic intermediate can be prevented, the reaction will take the normal course. Indeed, reaction of 1 with 1 mol of dimethyl sulfate followed by the addition of 1 mol of triphenyltin chloride gave a 60% yield of S-methyl-S'-triphenyltin cyanodithioimidocarbonate (26). In
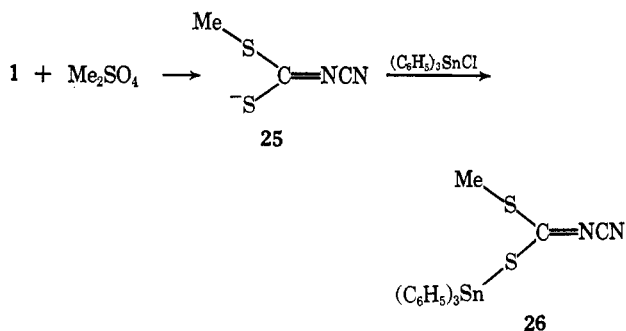
intermediate 25, having an S-methyl group, there is no driving force to form a cyclic intermediate. Thus, reaction of 25 with triphenyltin chloride proceeds in the normal manner.

Experimental Section

The infrared analyses were determined on Beckman IR-4 and IR-8 spectrophotometers. Spectra were determined using the pure liquid or were in Nujol for solids; the quantitative analyses were conducted in carbon tetrachloride. The gas chromatographic analyses were determined on a F & M Model 720 gas chromatograph using a silicone DC 550 column programmed from 80–250° at 15° min⁻¹. The molecular weights of 6 (R = *n*-butyl, phenyl) were determined osmometrically in THF containing 0.8% water. These compounds are insoluble in pure THF and water, but soluble in the aforementioned composition. The efficacy of this solvent composition was checked against standards. The molecular weights of all other compounds were determined in pure THF.

Dipotassium Cyanodithioimidocarbonate (1).[1]—To a solution of 610 g (14.5 mol) of cyanamide (American Cyanamid Co.) in 1650 ml of absolute ethanol was added 1214 g (16.0 mol) of carbon disulfide. The resulting mixture was cooled to 18°, and to it was added, while stirring vigorously, a solution of 1915 g (29.0 mol) of potassium hydroxide (Baker Reagent, 85%) in 6 l. of absolute ethanol over a 1.5-hr period. Solids deposited, and the mixture was stirred for an additional 2 hr. The mixture was filtered, and the residue was washed with THF and then dried in a circulatory oven at 50–55° to yield 2545 g (91%), mp 215°.

Anal. Calcd for $C_2K_2N_2S_2$: N, 14.4; S, 32.9; K, 40.3. Found: N, 14.3; S, 32.9; K, 39.6.

1,1-Di-*n*-butyl-2,4-dithia-3-cyaniminostannacyclobutane (6, R = *n*-Butyl).—To a solution of 19.4 g (0.10 mol) of 1 in 100 ml of water at room temperature was added dropwise a solution of 30.4 g (0.10 mol) of di-*n*-butyltin dichloride (mp 39–41°) in 100 ml of THF over a 30-min period. The temperature rose to 30° during the addition. The reaction mixture was stirred at room temperature for an additional 2.5 hr and then poured onto crushed ice. The resulting white solid was filtered, washed with water, and dried to give 33.5 g (96%) of 6 (R = *n*-butyl): mp 148–151° dec (red melt); ir 2180 cm⁻¹ (C≡N). Recrystallization from methanol gave an analytical sample, mp 150–154° dec (red melt). The ir spectra of this material and the crude product were identical.

Anal. Calcd for $C_{10}H_{18}N_2S_2Sn$: C, 34.45; H, 5.16; N, 8.03; S, 18.35; Sn, 34.01; mol wt, 345. Found: C, 34.72; H, 5.18; N, 7.87; S, 18.10; Sn, 34.45; mol wt, 350.

1,1-Diphenyl-2,4-dithia-3-cyaniminostannacyclobutane (6, R = Phenyl).—Using 19.4 g (0.10 mol) of 1 and 34.4 g (0.10 mol) of diphenyltin dichloride (mp 40–42°) and following the previous

procedure, 39.0 g (100%) of crude 6 (R = phenyl) was obtained: mp 163–165° dec (red melt); ir 2175 cm⁻¹ (C≡N). Purification of the crude product was difficult owing to its insolubility in numerous organic solvents.

A.—The crude product, 10.0 g, was stirred and refluxed in 275 ml of acetonitrile and filtered. The residue, 6 (R = phenyl), amounted to 9.50 g (95%), mp 173–175° dec (red melt). The ir spectrum was identical with that of the crude.

Anal. Calcd for $C_{14}H_{10}N_2S_2Sn$: C, 43.25; H, 2.59; N, 7.20; S, 16.45; Sn, 30.51; mol wt, 389. Found: C, 44.34; H, 2.99; N, 6.85; S, 15.40; Sn, 29.86; mol wt, 410.

B.—A sample of the crude material was dissolved in THF containing 0.8% water and then precipitated by adding more water: mp 173–175° dec (red melt).

Anal. Found: C, 44.07; H, 2.83; N, 6.85; S, 15.90; Sn, 30.21; mol wt, 390.

1,1-Di-*n*-octyl-2,4-dithia-3-cyaniminostannacyclobutane (6, R = *n*-Octyl).—In the usual way, 19.4 g (0.10 mol) of 1 and 41.6 g (0.10 mol) of di-*n*-octyltin dichloride (mp 45–47°) gave 43.0 g (94%) of 6 (R = *n*-octyl): mp 134° dec (red melt); ir 2180 cm⁻¹ (C≡N). Recrystallization from chloroform gave 30.0 g of analytically pure 6 (R = *n*-octyl), mp 135–138° dec (red melt). The ir spectrum was identical with that of the crude material.

Anal. Calcd for $C_{18}H_{34}N_2S_2Sn$: C, 46.90; H, 7.43; N, 6.08; S, 13.89; Sn, 25.70; mol wt, 461. Found: C, 46.91; H, 7.52; N, 6.03; S, 13.86; Sn, 26.00; mol wt, 480.

1 and Triphenyltin Chloride (THF–Water).—To 9.70 g (0.05 mol) of 1 dissolved in 50 ml of water at room temperature was added dropwise over a 30-min period a solution of 38.5 g (0.10 mol) of triphenyltin chloride (mp 105–107°) in 50 ml of THF. The temperature rose to 30° during the addition. After stirring for an additional 2.5 hr at room temperature, the reaction mixture was poured onto ice. The resulting yellow oil was extracted with chloroform. Drying the chloroform extract (Na₂SO₄) and then stripping the solvent at room temperature left 39.0 g of a yellow gum. Trituration with acetonitrile in the cold gave 20.0 g of an off-white solid, mp 139–143° (cloudy).

A.—Recrystallization from ethyl acetate gave 6.61 g of bis-triphenyltin sulfide, mp 142–144°. An additional 9.50 g of bistriphenyltin sulfide, mp 140–143°, was obtained by stripping the mother liquor. Mixture melting points of both fractions with authentic bistriphenyltin sulfide showed no depression (lit.[22] mp 141.5–143°). The ir and far-infrared spectra of both fractions were identical with the spectra of authentic bistriphenyltin sulfide. The total yield of bistriphenyltin sulfide was 16.1 g (44%).

An ethyl acetate insoluble fraction, 4.0 g (ir 2210 and 2164 cm⁻¹), was isolated but not characterized.

B.—The mother liquor from the acetonitrile trituration was stripped at room temperature. The gummy residue was triturated with benzene to give 5.80 g (14%) of an off-white solid, mp 150–163°. The ir spectrum shows absorption at 2080 cm⁻¹ and is identical with the spectrum of an analytical sample of triphenyltin thiocyanate. Recrystallization from chloroform gave 1.10 g of triphenyltin thiocyanate, mp 166–168° (lit.[23] mp 167–167.5°); mixture melting point with an analytical sample showed no depression.

Anal. Calcd for $C_{19}H_{15}NSSn$: C, 55.91; H, 3.71; N, 3.43; Sn, 29.10; mol wt, 407. Found: C, 55.41; H, 3.63; N, 3.81; Sn, 28.40; mol wt, 410.

1 and Triphenyltin Chloride (THF).—To a suspension of 9.70 g (0.05 mol) of 1 in 100 ml of THF was added dropwise a solution of 38.5 g (0.10 mol) of triphenyltin chloride in 100 ml of THF. The temperature rose to 28° during the addition. After stirring for an additional 4 hr at room temperature, the reaction mixture was filtered. The residue amounted to 7.05 g. Washing with water left 0.90 g of solid, mp 53°. The solvent was stripped from the filtrate at room temperature leaving 41.0 g of a yellow gum. Trituration with acetonitrile gave 14.5 g (40%) of bistriphenyltin sulfide, mp 138–145°. Recrystallization from isopropyl alcohol gave 11.5 g of pure material, mp 144–145°; mixture melting point with an analytical sample of bistriphenyltin sulfide showed no depression. The ir spectra of the two samples were identical.

(22) G. Noltes and G. J. M. Van der Kerk, *Chem. Ind.* (London), 294 (1959).

(23) P. L. Bartlett, M.S. Thesis, Massachusetts Institute of Technology, 1955.

The mother liquor from the acetonitrile trituration was stripped leaving 26.0 g of a gum. Trituration with acetonitrile gave 4.50 g of a light yellow solid: mp 205–226°; ir 2210 and 2164 cm⁻¹. Stripping the mother liquor from this trituration and triturating the residue with benzene gave 4.83 g (12%) of triphenyltin thiocyanate, mp 155–166°. Recrystallization from chloroform-hexane gave 1.10 g of pure material, mp 166–168°; mixture melting point with an analytical sample of triphenyltin thiocyanate showed no depression. The ir spectra of the two samples were identical.

Triphenyltin Thiocyanate (10).—A mixture of 95.0 g (0.25 mol) of triphenyltin chloride and 30.0 g (0.31 mol) of potassium thiocyanate (Baker, Reagent) in 1 l. of absolute ethanol was stirred and refluxed for 24 hr. The reaction mixture was filtered, and the filtrate was stripped to dryness. The residue, a white solid, amounted to 97.0 g (96%), mp 150–165°. Recrystallization from benzene gave an analytical sample of triphenyltin thiocyanate, mp 166–168° (lit.²³ mp 167–167.5°).

Anal. Calcd for C₁₉H₁₅NSSn: N, 3.43; S, 7.85; Sn, 29.10. Found: N, 3.57; S, 7.83; Sn, 29.46.

1 and Tri-*n*-butyltin Chloride.—Using 9.70 g (0.05 mol) of 1 and 32.5 g (0.10 mol) of tri-*n*-butyltin chloride and following the procedure for 1 and triphenyltin chloride, 29.0 g of a yellow oil, ir 2175 and 2065 cm⁻¹, was isolated. The former band provides evidence for bistri-*n*-butyltin cyanodithioimidocarbonate (7) while the latter is characteristic for tri-*n*-butyltin isothiocyanate (12). The far-infrared spectrum exhibited absorption at 370 cm⁻¹, showing the presence of bistri-*n*-butyltin sulfide (11).

Gas chromatographic analysis of the crude material showed the presence of 11 and 12, but considerable decomposition of reference samples prevented a quantitative determination.

A vacuum distillation of 15.0 g of the crude gave 7.20 g of distillate, bp 147–168° (0.5 mm). The ir spectrum showed bands at 2065 and 370 cm⁻¹ showing the presence of 12 and 11. The pot residue (7.51 g) was a dark brown gum, indicating decomposition during the distillation.

Using the bands at 2065 and 370 cm⁻¹, standard Beer's law plots were prepared from which it was established that the crude product consisted of 8.13 g (23%) of tri-*n*-butyltin isothiocyanate (12) and 9.75 g (32%) of bistri-*n*-butyltin sulfide (11).

Tri-*n*-butyltin Isothiocyanate (12).¹³—To a solution of 32.5 g (0.10 mol) of tri-*n*-butyltin chloride in 100 ml of ethanol was added a solution of 12.5 g (0.15 mol) of potassium thiocyanate in 25 ml of ethanol and 10 ml of water. The mixture was refluxed for 3 hr. After cooling, the mixture was filtered, and the filtrate was diluted with 400 ml of water. The resulting oil was extracted with ethyl ether. Drying the extract (MgSO₄) and then stripping the ether left 31.8 g (92%) of a colorless liquid. Distillation of 15.0 g of the crude product gave 1.30 g of a forerun, bp 152–153° (0.5 mm), followed by 11.5 g of pure tri-*n*-butyltin isothiocyanate, bp 155–156° (0.5 mm), *n*²⁰D 1.5413 [lit.¹³ bp 146° (0.2 mm), *n*²⁰D 1.5432].

Anal. Calcd for C₁₃H₂₇NSSn: N, 4.03; Sn, 34.10. Found: N, 3.79; Sn, 34.30.

1 and 1-Chloro-2,4-dinitrobenzene.—To a solution of 9.70 g (0.05 mol) of 1 in 50 ml of water was added 20.2 g (0.10 mol) of 1-chloro-2,4-dinitrobenzene dissolved in 50 ml of THF. The mixture was stirred at room temperature for 4 days and then was filtered. The residue, 9.50 g of a yellow solid (A), mp 188–196°, was washed with water and dried.

The filtrate was poured into water, and the mixture was extracted with chloroform. Drying the extract (Na₂SO₄) and then stripping the solvent left an orange solid, mp 185–200°. Adding hexane and then filtering gave 0.54 g of a yellow solid, mp 185–200°. Stripping the hexane from the filtrate left 4.00 g of a yellow solid, mp 47–52°; the mixture melting point range with authentic 1-chloro-2,4-dinitrobenzene was 48–52°. The ir spectra of the two samples were identical.

The ir spectrum of A was identical with the spectrum of an authentic sample of 2,2',4,4'-tetranitrodiphenyl sulfide. Recrystallization of A from a N,N-dimethylformamide–chloroform solution gave 5.02 g of pure 2,2',4,4'-tetranitrodiphenyl sulfide (20), mp 196–198° (lit.²⁴ mp 195°); mixture melting point with an analytical sample showed no depression. Based on recovered 1-chloro-2,4-dinitrobenzene the yield is 65%.

Running the reaction in an all-THF system at reflux for 5.5 hr gave an 82% yield of 2,2',4,4'-tetranitrodiphenyl sulfide.

Potassium S-Methylcyanodithioimidocarbonate (25) and Triphenyltin Chloride.—To a solution of 19.4 g (0.10 mol) of 1 in 100 ml of water was added 12.6 g (0.10 mol) of dimethyl sulfate. The reaction mixture was stirred at room temperature for 2 hr. To the resulting green solution was added 38.5 g (0.10 mol) of triphenyltin chloride dissolved in 100 ml of THF; the temperature rose to 30°. After stirring the reaction mixture for 20 hr at room temperature, it was poured into water and extracted with chloroform. Drying the extract (MgSO₄) followed by stripping the solvent gave 44.0 g of a yellow gum. Trituration with acetonitrile gave 20.0 g (60%) of S-methyl-S'-triphenyltin cyanodithioimidocarbonate (26), mp 150–152°. A recrystallization from acetonitrile gave 13.0 g: mp 153.5–154.5° (red melt); ir 2200 cm⁻¹ (C≡N).

Anal. Calcd for C₂₁H₁₈N₂S₂Sn: C, 52.42; H, 3.77; N, 5.83; S, 13.32; Sn, 24.66. Found: C, 52.01; H, 3.54; N, 6.08; S, 12.67; Sn, 24.90.

The yield of 26 is based on recovered triphenyltin chloride. Gas chromatographic analysis of the mother liquor from the acetonitrile trituration showed the presence of 0.03 mol of triphenyltin chloride and 0.006 mol of dimethylcyanodithioimidocarbonate. The latter product arises from the dialkylation of 1 with dimethyl sulfate.

Registry No.—1, 13145-41-0; 6 (R = *n*-Bu), 15836-03-0; 6 (R = Ph), 17396-52-0; 6 (R = *n*-octyl), 15836-04-1; 26, 17396-54-2.

(24) F. Challenger and A. D. Collins, *J. Chem. Soc.*, 1380 (1924).