Organotin Chemistry. 16.[1] Reactions of Stannane with Organic Functional Groups

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Received March 8, 1993

The reactions of stannane with a variety of organic substrates have been studied. Benzaldehyde, acetone, nitrobenzene, and 2-nitropropane are reduced to benzyl alcohol, isopropyl alcohol, aniline, and isopropylamine, respectively. With boron trifluoride etherate and benzyl chloride, stannane undergoes halogen-hydrogen exchange, while with isopropylamine and acetic acid, it is decomposed catalytically into its elements. Tetrakis(2-cyanoethyl)tin is formed by the addition of stannane to acrylonitrile. Stannane did not react with the following: (a) ethyl acetate, (b) methyl acrylate, (c) aniline, (d) triethylamine, (e) dimethylacetamide, and (f) *N*-ethylacetamide. The results obtained with stannane are for the most part analogous to those reported for the corresponding organotin hydrides.

Introduction

Until the publication of the preliminary communication[1] of this work, very little had been reported on the chemistry of tin tetrahydride (stannane). The chemistry of this hydride has been most recently reviewed by Gmelin.[3] Although a few reactions of stannane with inorganic substrates were known, no reactions with organic compounds had ever been reported. This lack of activity in stannane chemistry is due, in part at least, to experimental difficulties. Stannane is toxic. It is a gas at room temperature with bp -52.5 °C. While relatively stable, stannane does decompose slowly at room temperature. To minimize decomposition, we worked under an atmosphere of 0.1% O_2 diluted with nitrogen.[4] We prepared stannane by the $LiAlH_4$ reduction of $SnCl_4$, the method of Emeléus and Kettle.[4]

Reactions of the more stable organotin hydrides with organofunctional groups have been studied in detail.[5a-c] In this paper the reactions of stannane with some representative organofunctional groups are reported and discussed. Wherever possible, a comparison of the relative reactivities between stannane and organotin hydrides toward a common substrate is made.

Results and Discussion

The reduction of ketones and aldehydes by organotin hydrides to the corresponding alcohols has been first reported by Kuivila and Beumel.[6] In this reaction, run at temperatures from room temperature up to about 140 °C, no hydrolysis step is necessary and the alcohols are formed directly, generally in good yields. We found that stannane is capable of reducing aldehydes and ketones in an analogous fashion at 0 °C. For example, benzaldehyde and acetone were reduced to the corresponding alcohols in high yields. In the former case, the yield of benzyl alcohol was quantitative and all four hydrogens of stannane were utilized. With acetone, the yield of isopropy alcohol was lower (71%). This lower yield paralleled the experience of Kuivila and Beumel[6] who showed that the reduction of benzaldehyde with several different organotin hydrides occurred in high yields, while reductions of acetone were not straightforward. These authors reported that while dibutyltin dihydride was able to reduce the ketone, no reduction occurred with diphenyltin dihydride. Only decomposition of the latter was observed.

It has been reported that strongly basic amines accelerate the decomposition of organotin hydrides.[6,7] Isopropylamine strongly catalyzed the decomposition of stannane to metallic tin and hydrogen. On the other hand, triethylamine and aniline did not cause decomposition under similar conditions. In the latter two experiments, good recoveries of the reactants were realized. The lack of catalysis by triethylamine may simply be due to our inability to carry out this reaction at a sufficiently high temperature. It has been reported that the ease of decomposition of organotin hydrides is in the order[8] 3° < 2° < 1°.

The lack of catalysis by aniline, a much weaker base than the aliphatic amines, is not unexpected since it will not cause the decomposition of triphenyltin hydride[8] under conditions whereby aliphatic amines act as decomposition catalysts.

Stannane does not react with simple amides, such as *N,N*-dimethylacetamide and *N*-ethylacetamide, or esters, such as ethyl acetate and methyl acrylate. This is not surprising in view of the known lack of reactivity of organotin hydrides toward amide[9] and ester[10] functional groups.

The reduction of nitrobenzene by stannane yields aniline. No intermediate reduction products could be detected and the yield of aniline, based on reacted stannane, was 94%. A similar reduction with triphenyltin hydride is known.[10]

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0276-7333/93/2312-3015$04.00/0

The reaction of stannane with aliphatic nitro compounds, e.g., 2-nitropropane, is complex. As was found with nitrobenzene, the corresponding amine (isopropylamine) is the only reduction product, but the yield, based on reacted stannane, was only 29%. However, the product, isopropylamine, has been shown to catalyze the decomposition of stannane (*vide supra*). As soon as some amine is formed, it will enter into competition with 2-nitropropane for stannane. On the basis of the low yield of amine, it appears that the decomposition of stannane is more rapid than the reduction of the nitro compound.

Stannane will add to the double bond of acrylonitrile forming tetrakis(2-cyanoethyl)tin. Depending on reaction conditions, yields of 5–35% were obtained in a number of runs and no reduction of the nitrile group was observed. van der Kerk et al.[10] have successfully added organotin hydrides to acrylonitrile, forming (2-cyanoethyl)tin compounds and have never observed any subsequent reaction between the nitrile group and the tin–hydrogen bond. The low yields for our reaction stand in marked contrast with the high yields generally obtained when organotin hydrides are used. The instability of stannane limits the maximum reaction temperature to about room temperature. Usually, temperatures of 70–100 °C[11] are required for the addition of organotin hydrides to acrylonitrile in the absence of catalysts, and thus it is quite possible that the yield of tetrakis(2-cyanoethyl)tin would be improved if we were able to use higher reaction temperatures.

Although organotin hydrides add readily to the carbon–carbon double bond in methyl acrylate,[11] we were unable to observe stannane addition to this substrate under conditions in which a partial reaction occurs with acrylonitrile. Here also it is possible that a reaction would take place if more drastic conditions (higher temperatures) were possible.

Organotin hydrides are known to undergo halogen–hydrogen exchange with inorganic and organic halides.[5,11,12] Similarly, we have found that stannane can also undergo such exchange reactions. For example, stannane reacts readily with boron trifluoride etherate, forming SnF_4 quantitatively (based on reacted hydride). To obtain a good tin balance, the reaction was carried out in the presence of a quantity of 1-octene sufficient to trap any gaseous diborane as the nonvolatile trioctylborane.[13] Tri-*n*-propyltin hydride previously has been shown to undergo a similar hydrogen–fluorine exchange with boron trifluoride etherate forming tri-*n*-propyltin fluoride.[11]

The reaction of stannane with benzyl chloride is very complex. In a number of runs, the initially colorless chloride turned deep red as the reaction temperature was raised. This was accompanied by the vigorous evolution of gases (some SnH_4 and HCl) that persisted even after the reaction mixture was allowed to rise to ambient temperature. In all cases, toluene, tin tetrachloride, and hydrogen chloride were formed as products. Toluene and tin tetrachloride most probably arose from a simple chlorine–hydrogen exchange (eq 1). However, the quantities of HCl formed were greater than expected if all of the hydrogens in stannane were utilized. In addition, virtually no benzyl chloride remained at the end of the reaction, even though a large excess (based on eq 1) was used. Vapor phase chromatographic analysis of the reaction mass showed that the major products were high boiling compounds. We tentatively propose the following as an explanation for the observed facts. One of the initial products (eq 1), tin tetrachloride, is known to be a mild Friedel–Crafts catalyst.[14] As such it could cause secondary reactions such as the self-condensation of benzyl chloride and/or the condensation of benzyl chloride with toluene to form substituted diarylmethanes. In turn, these products could condense further with benzyl chloride forming polyarylmethanes. In support of this proposal, we mixed benzyl chloride with a small amount of tin tetrachloride. In a short time, the mixture became very warm, viscous, and deep red in color. Although no quantitative data on the products were obtained, we are confident that our proposed explanation is essentially correct.

$$4C_6H_5CH_2Cl + SnH_4 = SnCl_4 + 4C_6H_5CH_3 \qquad (1)$$

On the other hand, organotin hydrides reduce benzyl chloride to toluene with no apparent formation of side products.[15] The organotin chloride formed as a coproduct is a much weaker Lewis acid than $SnCl_4$ and does not promote secondary reactions.

Carboxylic acids react with organotin hydrides forming organotin carboxylates.[11,16] When stannane is passed into glacial acetic acid, tin metal is obtained as the main product in *ca.* 90% yield based on reacted stannane. In addition, a small quantity of tin (*ca.* 4%) in the tetravalent state is found dissolved in the acetic acid. The tin-containing product most likely is present in the acetic acid as the acetate $Sn(OOCCH_3)_4$. The tin metal probably is formed *via* an unstable intermediate I which would be expected to decompose as shown (eq 2).

$$2SnH_4 + 2HOAc = 2\underset{\textbf{I}}{[SnH_3OAc]} + H_2 \qquad (2)$$

$$2[SnH_3OAc] = Sn^0 + H_2 + HOAc$$

Table I summarizes the results obtained for reactions of stannane with organic substrates. This study has shown that stannane is capable of reacting with some but not all organic functional groups in a manner similar to that observed with organotin hydrides.

Because of the experimental complications posed by the low boiling point of stannane and its instability, we made a material balance in each case to ensure that we were not missing important side reactions.

Experimental Section

Vapor phase chromatography was performed on a Model 720 F&M gas chromatograph. Infrared spectra were obtained with a Beckman IR-8 infrared spectrophotometer. X-ray diffraction data were obtained with a XR-D5 diffraction unit from the General Electric Co.

Preparation[4] and Characterization of SnH_4. $LiAlH_4$ (4.75 g, 0.125 mol) and dry diethyl ether (50 mL) were added to the reaction flask (500 mL) connected to a series of five traps. The reaction flask and the last four traps were immersed in liquid nitrogen (−195 °C), and the first trap was immersed in an ice–methanol bath (−23 °C). The entire system was purged with

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Table I. Reactions of Stannane with Organic Substrates

organic reactants	reaction products	yield[a] (%)	conversion to products (%)	material[b] balance (%)
PhCHO	$PhCH_2OH + Sn$	100	52	97
$(CH_3)_2C{=}O$	$(CH_3)_2CHOH + Sn$	71	56	94
$(CH_3)_2CHNH_2$	$Sn + H_2$	95	95	95
$PhNO_2$	$PhNH_2 + H_2O + Sn$	94	25	93
$(CH_3)_2CHNO_2$	$(CH_3)_2CHNH_2 + Sn + H_2 + H_2O$	29[c]	89	89
$CH_2{=}CHCN$	$(NCCH_2CH_2)_4Sn$	5–35[d]		
$BF_3(C_2H_5)_2O$	$SnF_4 + B_2H_6$	100	56	99
$PhCH_2Cl$	$PhCH_3 + SnCl_4 + HCl$	*e*		92
CH_3COOH	$Sn + H_2 + Sn(OOCCH_3)_4$[f]	100	96	97

[a] Based on reacted stannane. [b] Based on tin. [c] Based on tin metal isolated. [d] Based on stannane charged. [e] Other products postulated are polyarylmethanes. [f] Minor product (4.4%) is a tin(IV) acetate.

Table II. Vapor Pressure of Stannane (mm)

temp (°C)	present work	lit.[17]
−66 to −65	399	387 (−66.7 °C) 407 (−65.6 °C)
−82	154	157
−95	66.8	66 (−95.5 °C)

Table III. Other Attempted Reactions

	amt of reactant		amt of stannane	
material	charged g (mol)	recovered g	charged g (mol)	recovered g
$CH_3C(O)NHC_2H_5$	20.2 (0.20)	19.8	2.8 (0.025)	2.7
$(C_2H_5)_3N$	30.8 (0.30)	30.6	2.65 (0.021)	2.15
$CH_2{=}CHC(O)OCH_3$[a]	22.1 (0.26)	21.3	2.8 (0.023)	2.7
$PhNH_2$	48.7 (0.52)	48.4	2.7 (0.022)	2.3
$CH_3C(O)N(CH_3)_2$	33.0 (0.28)	32.5	2.8 (0.023)	2.6

[a] Methyl acrylate was freshly distilled to eliminate the polymerization inhibitor. Evaporation of the recovered liquid showed no polymer residue. No VPC analysis was done in this instance.

nitrogen containing 0.1% of oxygen in order to inhibit decomposition of SnH_4.

For measuring the temperature in the reaction vessel, a thermocouple was inserted into a thermowell of the flask. $SnCl_4$ (6.5 g, 0.025 mol) and another portion of dry diethyl ether (50 mL) were added in that order, and the entire mass became frozen. At this point, no signs of a reaction were evident. The temperature of the reaction flask was gradually warmed to −78 °C (dry ice–acetone temperature), at which point the reaction mixture became liquid. There were also some signs of a reaction, as evidenced by gas bubbles leaving the surface. As the temperature was increased further, reaction became more rapid. At −50 °C the reaction proceeded at a very rapid pace. Not until 0–10 °C was reached did the reaction subside. A total of 2.7 g (88%) of SnH_4 was collected in the last four traps as a white solid. Over a series of 20 preparations, yields ranging from 87 to 95% were realized; mp −146 °C (lit.[17] −150 °C); bp −52.5 °C (lit.[17] −51.8 °C).

Elemental analysis was effected by allowing a sample of SnH_4 (1.18 g, 0.0096 mol) to decompose slowly in a closed vessel overnight at ambient temperature. A gray residue was obtained which weighed, after venting the vessel, 1.16 g. The calculated value is 1.14 g. Analysis showed the residue to be tin metal.

For confirmation, the vapor pressure of SnH_4 was measured at several temperatures, close to or at those reported in the literature.[17] Our results tabulated in Table II are close to the published values.

The traps used to collect and store SnH_4 consisted of tubes fitted with two side arms each with a stopcock (Schlenk tubes). This arrangement facilitated the transfer of SnH_4 to a suitable reaction vessel. In all cases, the organic substrate was used in excess. Any unreacted SnH_4 was recovered by collection in a series of these traps (immersed in liquid nitrogen) connected to the reaction vessel.

Determination of the Solubility of SnH_4 at −78 °C. The solubility of SnH_4 was determined in several different solvents at −78 °C. The method is given for *n*-hexane below.

SnH_4 was generated as described above and collected in four traps immersed in liquid nitrogen. In this case the first two traps contained 10.9 and 10.0 g of *n*-hexane, respectively. After the generation of SnH_4 was completed, the traps containing *n*-hexane were found to have undergone a 0.94-g increase in weight. The stopcock on the first trap nearest to the reaction vessel was closed, and the liquid nitrogen baths under the first two traps were replaced by a dry ice–acetone bath (−78 °C). After a 1-h period to allow equilibration, the weight the two tubes containing *n*-hexane decreased to 0.6 g. On the basis of this weight gain the solubility of SnH_4 in *n*-hexane is 2.7 g of SnH_4/100 g of *n*-hexane at −78 °C.

The solubility of SnH_4 in several other solvents was found to be as follows: diethyl ether (1.9 g/100 g); tetrahydrofuran (2.7 g/100 g); carbon disulfide (6.1 g/100 g). In none of these solvents was there any sign of a reaction as would be evidenced by a tin metal deposit.

Reaction of $BF_3{\cdot}(C_2H_5)_2O$ with SnH_4. For this and the following reactions of SnH_4 with organic substrates the following general procedure was used. The reaction vessel was a special trap as described above but with a removable head to facilitate workup. After the 99.9% N_2:0.1% O_2 atmosphere was established, reactants, in this case, $BF_3{\cdot}(C_2H_5)_2O$ (3.55 g, 0.027 mol) and 1-octene (9.9 g, 0.088 mol) were charged and the vessel was immersed in a liquid nitrogen bath. To one of the arms of this trap were attached two other traps in series. These were also immersed in liquid nitrogen and were used to collect any unreacted SnH_4. SnH_4 (2.7 g, 0.022 mol) was condensed into the reaction vessel over a 1-h period. The temperature inside the reaction vessel, after 15 min, was allowed to rise gradually to room temperature. This was accomplished by changing the immersion baths every 15 min and keeping the reaction vessel in each bath for 10 min. The baths used were in the following sequence: liquid nitrogen; dry ice–acetone (−78 °C); ice–methanol (−23 °C); ice–water (0 °C).

At the end of the reaction period, the reaction mixture contained a light yellow liquid and a white solid. The mixture was filtered with suction, under nitrogen. The filtrate, which fumed, was discarded. The white solid was collected, washed once with 50 mL of diethyl ether, and dried under vacuum. The solid weighed 2.3 g and was identified as SnF_4 by comparing its X-ray diffraction pattern with that of authentic material and by analysis. Anal. Calcd for SnF_4: Sn, 60.97. Found: Sn, 60.54. The weight of SnH_4 recovered was 1.2 g. The yield of SnF_4 based on reacted SnH_4 was quantitative.

Attempted Reaction of Ethyl Acetate wtih SnH_4. This experiment was carried out in the same manner as the previous one with 2.8 g (0.023 mol) of SnH_4 and 22.2 g (0.25 mol) of ethyl acetate. At the end of the reaction period 21.4 g of ethyl acetate and 2.7 g of SnH_4 were recovered. Analysis of recovered ethyl acetate by VPC showed only one peak.

Additional attempted reactions of SnH_4 with the indicated substrates are summarized in Table III. In each case, except the one noted, gas chromatographic analysis of the recovered reactant showed only the one peak of the starting material.

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Reaction of Acetone with SnH_4. This reaction was carried out as above with 21.7 g (0.37 mol) of acetone and 2.7 g (0.022 mol) of SnH_4. At the end of the reaction a clear, colorless liquid containing a suspended gray-black solid was obtained. The mixture was filtered by gravity and the gray-black solid was collected. After air drying, 1.50 g of tin metal was obtained.

The filtrate (22.4 g) was analyzed by VPC which showed that it contained 4.5% (1.01 g) of isopropyl alcohol and 95.5% of unreacted acetone as the only products. The yield of isopropyl alcohol based on recovered tin metal was 71%. In addition, 1.0 g of SnH_4 was recovered.

Reaction of Isopropylamine with SnH_4. This reaction was carried out as in previous examples except that the initial temperature was 24 °C. Isopropylamine (38.9 g, 0.66 mol) was charged into the reaction vessel. SnH_4 (2.70 g, 0.022 mol) was slowly bubbled through the amine over a 2-h period. A vigorous reaction occurred with the formation of tin metal. After all the SnH_4 was added, the reaction mixture was filtered and the collected tin powder was air dried. Weight of the tin powder was 2.57 g, corresponding to 95% decomposition of the hydride. The amine (37.3 g) was also recovered to the extent of 95%. Gas chromatographic analysis of the recovered amine showed only one peak.

Reaction of Glacial Acetic Acid with SnH_4. This reaction was carried out as the previous example (isopropylamine) with 60.4 g (1.0 mol) of glacial acetic acid and 2.9 g (0.024 mol) of SnH_4. Tin metal formed during the addition of SnH_4. The mixture was decanted and gray-black tin powder was collected, washed with 50 mL of anhydrous diethyl ether, and air dried to give a recovery of 2.4 g (86%). The decanted liquid (58.7 g) was analyzed by VPC and by elemental analysis. Gas chromatographic analysis of the liquid acid showed only one peak due to acetic acid.

In order to ensure the completeness of the tin balance the recovered acetic acid was analyzed for the metal. Of the total tin charged, 0.19% was found with a Sn(IV):Sn(II) ratio of 95%: 5%. The only tin(IV) compounds possible are tin tetraacetate or a basic tin(IV) acetate. The yield of tin(IV) acetates is 4% based on reacted SnH_4. In addition, a small amount (0.3 g) of unreacted SnH_4 was recovered.

Reaction of Benzaldehyde with SnH_4. Benzaldehyde (51.2 g, 0.48 mol) was charged into the reaction vessel which was immersed in an ice–water bath. SnH_4 (2.9 g, 0.024 mol) was bubbled through the aldehyde over a 2.25-h period. During this time tin powder precipitated. The tin powder which was collected by filtration and air dried weighed 1.5 g. The filtrate (50.0 g) upon gas chromatographic analysis was found to contain 5.5% benzyl alcohol (2.75 g) and 94.5% unreacted benzaldehyde as the only products. The yield of benzyl alcohol based on recovered tin powder was quantitative. In addition, 1.3 g of SnH_4 was recovered.

Reaction of Nitrobenzene with SnH_4. Nitrobenzene (44.5 g, 0.36 mol) was charged into the reaction vessel at room temperature. SnH_4 (2.7 g, 0.022 mol) was bubbled through the liquid over a 2-h period. During the reaction tin powder precipitated. The nitro compound, which was very pale yellow at the beginning, became darker in color. The mixture was filtered with suction, and the tin powder which was collected weighed 0.7 g after drying in a vacuum oven at 50 °C. The filtrate, which contained suspended water droplets, weighed 44.2 g. A sample of the dried filtrate was analyzed by VPC. Gas chromatographic analysis showed aniline as the only product in 94% yield based on the tin powder isolated. In addition 1.9 g of unreacted SnH_4 was recovered.

Reaction of 2-Nitropropane with SnH_4. 2-Nitropropane (59.2 g, 0.60 mol) was charged into the reaction vessel at room temperature. This was connected to a trap containing 54.3 g of a 1.6% aqueous HCl solution to absorb any isopropylamine which might evaporate during the addition of SnH_4. SnH_4 (2.8 g, 0.023 mol) was bubbled through the liquid over a 2-h period. During the course of the reaction, tin powder precipitated. The clear liquid, which was decanted from the tin powder, contained a small number of liquid beads (H_2O). The weight of the tin powder, after drying in a vacuum oven at 50 °C, was 2.5 g. The clarified yellow filtrate (58.8 g) was shown by gas chromatographic analysis to be virtually all 2-nitropropane with only a trace of isopropylamine. Basic titration of the HCl solution showed that 0.83 g of isopropylamine had been absorbed. The yield of amine, based on the tin powder isolated, was 29%.

Reaction of Benzyl Chloride with SnH_4. Benzyl chloride (38.0 g, 0.30 mol) was charged into the reaction vessel which was immersed in a liquid nitrogen bath. SnH_4 (2.9 g, 0.024 mol) was condensed into the vessel. Two traps, each containing 100 mL of a 0.1 M NaOH solution, were connected in series. The temperature was allowed to rise slowly using the sequence of baths previously described. When the temperature reached *ca.* −23 °C (ice–methanol bath) a vigorous evolution of gas commenced accompanied by a gradual darkening in color of the reaction mixture. After the evolution of gas ceased (*ca.* 3 h), 30.3 g of a syrupy red liquid, which fumed in air ($SnCl_4$), was obtained as the reaction product. An aliquot of the liquid (24.3 g) was extracted once with 25 mL of distilled water. Both the organic phase (21.6 g) and the water phase (26.4 g) were analyzed for tin and chlorine. Gas chromatographic analysis of the organic phase gave the following results: toluene (9.9%, 3.0 g); $SnCl_4$ (5.3%, 1.6 g); polyarylmethanes (78.7%); unknown fractions (6.1%). No benzyl chloride was found.

Elemental analysis of the aqueous and organic phases gave the following results. Aqueous phase: Sn, 5.21%; Cl, 5.83%. Organic phase: Sn, 2.05%; Cl, 2.83%. On the basis of the elemental analyses, 3.7 g of $SnCl_4$ was found in both phases and 0.4 g of HCl in the aqueous phase. The first NaOH (108.3 g) trap contained 0.37% Sn and 5.72% Cl which is equivalent to 0.9 g of $SnCl_4$ and 5.9 g of HCl. An overall 92% tin balance was obtained.

Reaction of Acrylonitrile with SnH_4. To a 200-mL three-necked flask equipped with a gas inlet tube and a cold finger containing liquid nitrogen was added 10.6 g (0.2 mol) of distilled acrylonitrile (inhibitor-free). This flask was placed in a liquid nitrogen bath, and SnH_4 (2.8 g, 0.023 mol) was slowly condensed into the flask. After the liquid nitrogen cold finger was replaced with one containing an ethanol–liquid nitrogen slurry and the liquid nitrogen bath was removed, the temperature was permitted to rise gradually to ambient over a 1.5-h period. The resulting yellow liquid, which contained suspended grayish-black solids, was filtered. These solids dissolved readily in concentrated HCl, indicating they were metallic tin. The resulting HCl solution (50.0 g) was found to contain 0.5 g of tin.

The filtrate was distilled at reduced pressure, leaving tetrakis(2-cyanoethyl)tin as a pale yellow liquid residue. The weight of the product was 2.6 g (34%, 0.008 mol). An infrared spectrum of the neat product, with the characteristic nitrile absorption at 2242 cm^{-1}, was identical to that of an authentic sample.[18]

Elemental analysis showed that the compound was impure. Anal. Calcd for $C_{12}H_{16}N_4Sn$: Sn, 35.43; N, 16.71. Found: Sn, 31.2; N, 16.6.

Acknowledgment. The authors are grateful to Mr. John Saraka for his technical assistance. Analyses were performed by the Central Analytical Department of M&T Chemicals Inc. The efforts of Messrs. I. L. Simmons and P. D. Branigan were especially valuable. We benefited from the opportunity to discuss this work while ongoing with Professor Dietmar Seyferth. We are especially grateful for his encouragement and help in preparing the manuscript for publication. We thank the management of Elf Atochem North America, Inc., the successor to M&T Chemicals Inc., for permission to publish this manuscript.

OM9301445

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