weighed 12.4 g. of 97% finely ground sodium hydroxide (0.30 mole). The tightly sealed liner was quickly transferred to a standard, 1-l., stirred autoclave under a positive flow of dry nitrogen. To the sealed autoclave then was added 320 ml. of liquid ammonia in the usual manner,[7] followed by 40 g. (0.48 mole) of methylbutynol at a temperature of 14–20°. The reaction mixture was stirred for 3.5 hr. and isolated in the usual manner using hexane as inert diluent.

The isolated adduct, vacuum dried to constant weight (26.0 g.), was a fluffy, white solid showing no tendency to absorb water. The excess (0.18 mole) methylbutynol used solubilized some of the complex in the hexane layer. This was determined by decomposing the adduct to sodium bicarbonate and free acetylenic carbinol by carbonation (Dry Ice) of the hexane layer, followed by filtration of the solid sodium bicarbonate. A total of 4.5 g. of white, air-dried solid was obtained which contained 73.7% $NaHCO_3$ by acid titration, and was equivalent to 4.9 g. (0.040 mole) of MB–NaOH complex (total conversion of purity to MB–NaOH complex, 83.1%).

Anal. Calcd. for $C_5H_9NaO_2$: C, 48.4; H, 7.26. Found: C, 39.0. H, 9.11; per cent purity based on carbon analysis, 80.6.

Isolation of Dimethylhexynediol (DMH) from MB–NaOH Adduct.—An aliquot (16.6 g.) of the powdered adduct which had been standing for 23 days at 3° in a refrigerator desiccator under anhydrous conditions, was slurried in 150 ml. of cold diethyl ether and carbonated with small pieces of Dry Ice, and filtered from $NaHCO_3$. The diol was freed from ether by evaporation. The yield of unrecrystallized, dry DMH was 5.2 g. (m.p. 92–94°, lit. 95°).

The MB–NaOH adduct from an initial MB content of 67.6% contained only 17.5% MB 6 days before isolation. Loss of MB during this time due to disproportionation was 74.2%. This adduct was considerably less stable than the KOH adduct. The theoretical yield of DMH from 16.6 g. (0.134 mole) of MB–NaOH was 4.96 g. (0.067 mole). The slightly higher (105%) than theory yield of unrecrystallized DMH was probably due to occluded solvent, water, and sodium bicarbonate.

Catalytic Formation of 3-Methyl-1-butyn-3-ol Using the Methylbutynol–KOH Adduct as Catalyst.—A 1-l. stirred autoclave was used for the reaction. This scaled-down run corresponded to a high-concentration (loading) ethynylation of acetone (18 moles of acetone, 24 moles of acetylene, and 1.5 moles of KOH) with the exception that 200 ml. of ammonia was used instead of the calculated 33 ml.[15] The larger volume of ammonia was used to stir the batch more efficiently and to ensure good thermal contact between the reaction mixture and the thermocouple well.

The following reaction charge was employed: 0.10 mole of methylbutynol–KOH adduct,[16] 1.2 moles of acetone, 1.6 moles of acetylene, and 200 ml. of liquid ammonia. The total reaction time was 1.5 hr. at 30–32 using 0.5-hr. addition time for introducing acetone into the NH_3–KOH–C_2H_2 reaction mixture. The total pressure in the autoclave averaged 160–185 p.s.i.g.

Isolation of product was effected in the usual manner,[7] employing dry CO_2 gas to neutralize the catalyst complex to $KHCO_3$ and methylbutynol after venting off ammonia. The total conversion to methylbutynol before distillation was 97%, and the catalytic conversion of (moles of MB per mole of KOH) was 1170%. The conversion to pure methylbutynol was 88% (88 g.), b.p. 103–104° (lit. 104°).

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[15] High-concentration (loading) runs described earlier[7] would have used 33 ml. of ammonia instead of 200 ml. of ammonia in an exact, scaled-down run.

[16] Adduct prepared in isopropyl ether according to method is described in ref. 7; dry, isolated adduct was used.

Properties of Triphenyltin Nitrate

Tsu Tzu Tsai, A. Cutler, and W. L. Lehn

The Polymer Branch, Nonmetallic Materials Division, Air Force Laboratory, Wright-Patterson Air Forces Base, Ohio

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The properties of triphenyltin nitrate are described. The thermal decomposition of this compound was investigated by heating in both the presence and absence of solvent. Two independent modes of decomposition, decomposition by a distribution reaction and by heterolytic dissociation of the β-oxygen–nitrogen bond, were found.

According to a recent report in the literature,[1] triphenyltin nitrate is a relatively unstable material decomposing readily to a mixture of products. However, we have found, during the course of an investigation of a variety of organotin compounds, that this material is in fact quite stable at ordinary temperatures and can easily be prepared, purified, and studied. Trimethyltin nitrate[2] and dimethyltin dinitrate[3] have also recently been reported and found to be thermally stable at ordinary temperatures. It is the purpose of this paper to report the results of this investigation.

We have found that triphenyltin nitrate can be obtained either from the reaction of hexaphenylditin with silver nitrate in acetone or from the method of Shapiro and Becker[1] as a white crystalline solid which melts at 182–184° with some decomposition to a reddish brown liquid. It will sublime slowly under a high vacuum. It is very soluble in polar solvents but not in water and less soluble in benzene, chloroform, and many others from which it readily crystallizes. When it was taken up in commercialan hydrous methanol, no solvolysis could be observed as indicated by the infrared spectrum of the solid collected after removal of the methanol in air at room temperatures. However, a mixed solvent of methanol and water hydrolyzed it partially to a mixture of triphenyltin nitrate and triphenyltin hydroxide. The absence of any brown nitrogen oxide fumes and a negative test for nitrite ions was taken to indicate that no homolytic dissociation[4] had occurred during the hydrolysis reaction. Titration of the nitric acid produced by the hydrolysis of the triphenyltin nitrate was found to be an effective and satisfactory method for determining the quality of the material. Although wet triphenyltin nitrate turns yellow in a few days, a well-dried sample, in analogy to trimethyltin nitrate,[2] is not affected by exposure to air.

The infrared spectrum of triphenyltin nitrate in Nujol consists of absorption bands arising from the phenyltin groups and nitrate group. The bands from the phenyltin group[5] were the same as those of other phenyltin compounds. Bands from the nitrate are listed in Table I along with those found for covalently

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[1] P. J. Shapiro and E. I. Becker, *J. Org. Chem.*, **27**, 4668 (1962).

[2] H. C. Clark and R. J. O'Brien, *Inorg. Chem.*, **2**, 740 (1963).

[3] C. C. Addison, W. B. Simpson, and A. Walker, *J. Chem. Soc.*, 2360 (1964).

[4] C. C. Addison, Advances in Chemistry Series, No. 36, American Chemical Society, Washington, D. C., 1962, p. 131.

[5] V. S. Griffiths and G. A. W. Derwish, *J. Mol. Spectry.*, **5**, 148 (1960).

TABLE I

ASSIGNMENT OF INFRARED BANDS[a]

	Type					
Compd.	$v_1(A_1)$, NO stretch, 1034–970	$v_6(B_2)$, NO_3 out of plane, 800–781	$v_1(A_1)$, NO_2 stretch sym., 1290–1253	$v_4(B_1)$, NO_2 stretch asym., 1531–1481	$v_3(A_1)$, NO_2 bend sym., 739	$v_5(B_1)$, NO_2, bend asym., 713
Ph_3SnNO_3	1047 (w, sh) 980 (s, sp)	800 (m, b)	1282 (s) 1265 (sp) 1250	1512 (m) 1493 (sp)	Overlapped by PhSn absorptions	
Me_3SnNO_3	1031	780	1268	1488		

[a] All frequencies are given in reciprocal centimeters; w = weak, m = medium, s = strong, sh = shoulder, sp = sharp.

bound nitrates[6] and those from trimethyltin nitrate[2] and have been tentatively assigned. For triphenyltin nitrate there are two bands in the v_4 range and three in v_1 in contrast to trimethyltin nitrate and clearly indicates that the nitrate group is covalently bound. When the potassium bromide pellet technique was used to obtain the infrared spectrum of triphenyltin nitrate, the spectrum obtained was very similar to that obtained for a mixture of triphenyltin chloride and silver nitrate. The benzene extract of the potassium bromide pellet gave a positive test for bromide ion indicating that a benzene-soluble bromide, *i.e.*, triphenyltin bromide, had been formed.

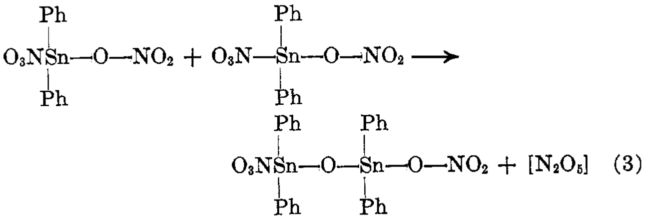
The thermal stability of triphenyltin nitrate was investigated by heating in both the presence and absence of solvent. Two independent modes of decomposition, decomposition by a distribution reaction and by heterolytic dissociation of the β-oxygen–nitrogen bond, were found.

Distribution reactions occurred when a solution of triphenyltin nitrate in *o*-dichlorobenzene was heated under reflux (180°) and under an atmosphere of nitrogen for 3 hr. No brown nitrogen oxide fumes were observed. A small amount of tetraphenyltin, unreacted triphenyltin nitrate, and a high-melting phenyltin nitrate compound were obtained as products. Elemental analysis of the high-melting solid indicated a composition close to that required for diphenyltin dinitrate, except for the nitrogen value being out of line. When the heating period was increased to 15 hr., brown nitrogen oxide fumes were evolved. Tetraphenyltin (52%), crude diphenyltin oxide (87%), and what was probably nitrobenzene were isolated and identified as products. The yields are based upon eq. 1 and 2. The reaction sequence is supported by the

$$2Ph_3SnNO_3 \longrightarrow Ph_4Sn + Ph_2Sn(NO_3)_2 \qquad (1)$$

$$2Ph_2Sn(NO_3)_2 \longrightarrow (Ph_2SnO)_n + \text{nitrogen oxides} \qquad (2)$$

presence of a small band characteristic of the nitrate group in the infrared spectrum of the diphenyltin oxide and indicates that the following intermolecular condensation reaction had occurred. This type of condensation reaction has been reported for benzhydryl nitrate.[7]



$$O_3NSn(Ph)_2{-}O{-}NO_2 + O_3N{-}Sn(Ph)_2{-}O{-}NO_2 \longrightarrow O_3NSn(Ph)_2{-}O{-}Sn(Ph)_2{-}O{-}NO_2 + [N_2O_5] \qquad (3)$$

When triphenyltin nitrate is rapidly heated to a temperature above its melting point in the absence of any solvent, decomposition occurs to give as products diphenyltin oxide, nitrobenzene, brown fumes of nitrogen oxide, and a small amount of tetraphenyltin. The absence of any bis(triphenyltin) oxide among the products indicates that a condensation of the type depicted in eq. 3 did not occur. In addition, none of the products which might be expected from a homolytic dissociation, such as hexaphenylditin, biphenyl, or triphenyltin phenoxide, were obtained. In the literature[8–11] the homolytic dissociation of the β-oxygen–nitrogen bond is generally suggested as the first step of the thermal decomposition of covalent organic and inorganic nitrates. The decomposition of triphenyltin nitrate was further investigated by studying the reaction in the presence of triphenylmethane and diphenylamine in order to trap the triphenyltin oxide radical and be able to identify it as triphenyltin hydroxide.

When triphenyltin nitrate and triphenylmethane are heated, it was found that decomposition commenced at a lower temperature, 160°, than when triphenyltin nitrate is heated alone, 190°. The products isolated and identified were triphenylcarbinol, triphenyltin hydroxide, tetraphenyltin, and nitrogen oxides. When triphenyltin nitrate was heated in the presence of diphenylamine the results were quite different. Benzene, diphenyltin oxide, tetraphenyltin, nitrogen oxides, and a black tar were isolated as products. Control experiments were performed by heating both tetraphenyltin and triphenyltin hydroxide with diphenylamine under the conditions of the reaction. In neither case was benzene identified as a major product of the reaction. Diphenylamine is known to be effective as an activator or inhibitor for free-radical chain reactions and experimental evidence[12] has been presented to demonstrate the occurrence of the reactions 4 and 5.

$$Me_3CO{-}OCMe_3 \longrightarrow 2Me_3CO\cdot \qquad (4)$$

$$Me_3CO\cdot + Ph_2NH \longrightarrow Ph_2N\cdot + Me_3COH \qquad (5)$$

It seems reasonable to believe that triphenyltin hydroxide should have formed if a homolytic dissociation of the β-oxygen–nitrogen bond occurred. On reviewing all of the results it appears clear that the decomposition of triphenyltin nitrate involves a heterolytic dissociation of the β-oxygen–nitrogen bond as its first step and that the reaction then proceeds according to the following equations.

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[6] C. C. Addison and B. M. Gatehouse, *J. Chem. Soc.*, 613 (1960).

[7] R. T. Merrow and R. H. Boschan, *J. Am. Chem. Soc.*, **76**, 4622 (1954).

[8] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 528.

[9] S. J. Cristol and J. E. Leffler, *J. Am. Chem. Soc.*, **76**, 4468 (1954).

[10] M. F. Hawthorne, *ibid.*, **77**, 5523 (1955).

[11] R. M. Topping and N. Kharasch, *J. Org. Chem.*, **27**, 4353 (1962).

[12] J. Pannell, *Mol. Phys.*, **5**, 291 (1962).

$$Ph_3SnO{-}NO_2 \longrightarrow Ph_3SnO^- + NO_2^+ \quad (6)$$

$$Ph_3SnO^- + Ph_3CH \longrightarrow Ph_3SnOH + \text{other products} \quad (7)$$

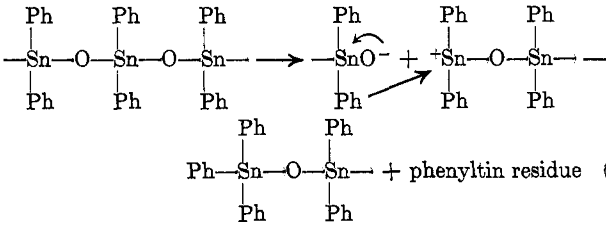
$$Ph_3SnO^- \longrightarrow (Ph_2SnO)_n + Ph^- \quad (8)$$

$$Ph^- + NO_2^+ \longrightarrow PhNO_2 \quad (9)$$

$$Ph^- + Ph_2NH \longrightarrow PhH + \text{other products} \quad (10)$$

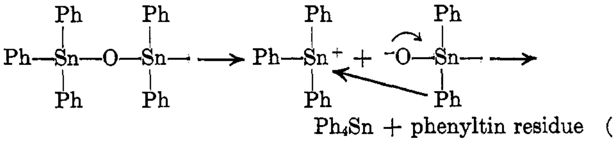
The formation of triphenyltin hydroxide in one case and benzene in the other indicates that there is a decided difference in proton availability between triphenylmethane and diphenylamine under the reaction conditions employed.

Inorganic nitrates of potassium and sodium are known to dissociate into ions[13,14] at high temperatures. It is felt that this heterolytic dissociation is characteristic of not only triphenyltin nitrate but other triphenyltin derivatives as well which involve a tin–oxygen bond. The thermal decomposition of bis(triphenyltin) oxide[15] and diphenyltin oxide[16] have been studied and in both cases tetraphenyltin was one of the products. The reactions leading to this product can be represented as occurring by an initial heterolytic dissociation of a tin–oxygen bond followed by the expulsion of a phenyl anion which is facilitated by the negative charge on the oxygen atom. West and co-workers[17] have studied the effects of π bonding from oxygen to an atom of group IV elements and concluded that there is no significant π bonding between the oxygen and tin or lead atoms in triphenyltin hydroxide or triphenyllead hydroxide. However, from the above observations it would seem that such an effect is present and is of enough significance that the over-all result appears as a shift from a free-radical to an ionic reaction.



$$-\underset{Ph}{\overset{Ph}{Sn}}-O-\underset{Ph}{\overset{Ph}{Sn}}-O-\underset{Ph}{\overset{Ph}{Sn}}- \longrightarrow -\underset{Ph}{\overset{Ph}{Sn}}O^- + {}^+\underset{Ph}{\overset{Ph}{Sn}}-O-\underset{Ph}{\overset{Ph}{Sn}}- \longrightarrow Ph-\underset{Ph}{\overset{Ph}{Sn}}-O-\underset{Ph}{\overset{Ph}{Sn}}- + \text{phenyltin residue}$$

(11)



$$Ph-\underset{Ph}{\overset{Ph}{Sn}}-O-\underset{Ph}{\overset{Ph}{Sn}}- \longrightarrow Ph-\underset{Ph}{\overset{Ph}{Sn^+}} + {}^-O-\underset{Ph}{\overset{Ph}{Sn}}- \longrightarrow Ph_4Sn + \text{phenyltin residue}$$

(12)

Experimental

Hexaphenylditin and triphenyltin chloride were obtained from Peninsular ChemResearch, Inc. Triphenylmethane and diphenylamine were obtained from Eastman Organic Chemicals. The diphenylamine was distilled before use. The *o*-dichlorobenzene was obtained from Matheson Coleman and Bell. All solvents were reagent grade chemicals obtained from Matheson Coleman and Bell and were used without further purification.

All melting points and boiling points are uncorrected.

Infrared spectra were obtained on a Model 137 Perkin-Elmer Infracord.

Microanalyses were made by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and by the Materials Physics Division, Air Force Materials Laboratory.

Preparation of Triphenyltin Nitrate. A. From Triphenyltin Chloride.—The procedure used was described in ref. 1. Before use the sample was purified as follows. A saturated solution of triphenyltin nitrate in boiling benzene was filtered through a jacketed funnel. Upon cooling, a white silky, crystalline precipitate appeared in the filtrate. It was removed by filtration and washed with petroleum ether (b.p. 30–60°). It melted at 182–185°. The quality of the sample was checked by titration and isolation of the product triphenyltin hydroxide as follows. Triphenyltin nitrate, 0.9275 g. (2.25 mmoles), was dissolved in 30 ml. of methanol, 10 ml. of distilled water and several drops of 0.1% phenolphthalein indicator solution were added, and the solution was titrated with 0.1000 *N* sodium hydroxide to the phenolphthalein end point. The sample required 23.30 ml. of base. The per cent purity of the triphenyltin nitrate is therefore 98.8%.

The titration solution was diluted with methanol until all of the solid which had appeared during the titration was dissolved. The solution was filtered and evaporated to dryness. The solid residue was repeatedly washed with water and collected on a Büchner funnel. After drying in air there was obtained 0.7562 g. of triphenyltin hydroxide, m.p. 118–124°, corresponding to a triphenyltin nitrate purity of 91.5%. A single recrystallization from methanol gave 0.72 g. of purified triphenyltin hydroxide, m.p. 122–124°.

B. From Hexaphenylditin.—To a solution of 24.0 g. (0.034 mole) of hexaphenylditin in 400 ml. of acetone was slowly added 11.60 g. (0.068 mole) of silver nitrate suspended in 100 ml. of acetone. The resulting mixture was stirred overnight at a temperature of approximately 0°, the unreacted hexaphenylditin and a black powder were removed by filtration in air, and the filtrate was concentrated in a rotary evaporator under reduced pressure. There was obtained 25.3 g. (90%) of yellowish triphenyltin nitrate. The material was purified as described above and, after two recrystallizations, it melted at 180–182°.

Anal. Calcd. for $C_{18}H_{15}NO_3Sn$: C, 52.47; H, 3.67; Sn, 28.83; mol. wt., 412.01. Found: C, 52.49, 52.63; H, 3.78, 3.94; Sn, 28.67, 28.76; mol. wt., 502, 535.

The sample was recrystallized and again submitted for analysis.

Anal. Found: C, 53.48, 53.41; H, 3.84, 3.76; Sn, 28.76, 29.00; mol. wt., 468, 479.

The Thermal Decomposition of Triphenyltin Nitrate in *o*-Dichlorobenzene. A.—A mixture of 3.79 g. (9.2 mmoles) of triphenyltin nitrate and 50 ml. of *o*-dichlorobenzene was heated at reflux under an atmosphere of nitrogen for 3 hr. After cooling to room temperature the reaction mixture was concentrated under reduced pressure. The infrared spectrum of the residue, 3.73 g., indicated only the presence of tin–phenyl groups and nitrate. The residue was treated with acetone and filtered. The insoluble precipitate, 0.13 g., was identified as tetraphenyltin by its melting point, 224–226° (lit.[18] m.p. 224–225°, 229°), and it did not fade the color of a dilute solution of iodine.

The acetone filtrate was evaporated to dryness in a rotary evaporator under reduced pressure and the residue was treated with boiling benzene and filtered. The benzene-insoluble precipitate was recrystallized from chloroform and there was obtained 0.89 g. of a crystalline material which does not melt up to 310°.

Anal. Calcd. for $C_{12}H_{10}N_2O_6Sn$: C, 36.31; H, 2.54; N, 7.06; Sn, 29.90. Found: C, 37.58, 37.45; H, 2.74, 2.58; N, 3.29, 3.14; Sn, 28.07, 27.75.

The remainder of the solid material obtained had a lower melting point and its infrared spectrum showed that only tin–phenyl and nitrate groups were present.

B.—A mixture of 4.3 g. (10.4 mmoles) of triphenyltin nitrate and 50 ml. of *o*-dichlorobenzene was heated at reflux for 15 hr. After cooling to room temperature the reaction mixture was concentrated under reduced pressure. The residue, 3.12 g., was treated with chloroform and filtered. There was obtained 0.47 g. of chloroform-insoluble material. The infrared spectrum of this material showed only tin–phenyl and nitrate absorption and was presumed to be diphenyltin oxide polymer with some nitrate as the end groups.

Concentration of the chloroform filtrate gave 2.65 g. of a solid material which was treated with boiling benzene and filtered. The precipitate, 0.79 g., had an infrared spectrum similar to that of the chloroform-insoluble material and was probably the same

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(13) F. R. Duke and M. L. Iverson, *J. Am. Chem. Soc.*, **80**, 5061 (1958).

(14) R. N. Kust and F. R. Duke, *ibid.*, **85**, 3338 (1963).

(15) R. F. Chambers and P. C. Scherer, *ibid.*, **48**, 1054 (1926).

(16) W. T. Reichle, *J. Polymer Sci.*, **No. 152**, 521 (1961).

(17) R. West, R. H. Baney, and D. L. Powell, *J. Am. Chem. Soc.*, **82**, 6269 (1960).

(18) R. K. Ingham, S. D. Rosenberg, and H. Gilman, *Chem. Rev.*, **60**, 459 (1960).

type of polymeric material. Total weight was 1.26 g., 87% yield calculated as diphenyltin oxide polymer.

The benzene filtrate was concentrated to dryness and the residue was washed with methanol. There was obtained 1.14 g., 52% yield of tetraphenyltin, m.p. 224–227°. The methanol gave a negative test for chloride indicating that the *o*-dichlorobenzene did not participate in the reaction.

Direct Thermal Decomposition of Triphenyltin Nitrate.—The apparatus used in the direct thermal decomposition of triphenyltin nitrate is described as follows. The sample was placed in a long test tube fitted with a standard taper joint and attached to an inverted U-shaped connecting tube. The connecting tube was equipped with a side arm for attachment to a vacuum system and was set up as for a distillation. A tube similar to the sample tube and cooled in a Dry Ice bath was attached to the other arm of the connecting tube and used as a receiver. This apparatus was used for the following experiments.

A. **Triphenyltin Nitrate.**—A sample of 0.65 g. of triphenyltin nitrate was rapidly heated by lowering the sample tube of the decomposition apparatus into an oil bath preheated to 160°. The temperature of the bath was then rapidly raised to 190°, during several minutes, at which point a brown gas was evolved and the clear molten sample turned brown and solidified. The reaction ceased in a few minutes. Nitrobenzene, identified by its infrared spectrum, was found in the receiver.

The residue in the sample tube was treated with boiling chloroform and filtered. The infrared spectrum of the chloroform-insoluble material, 0.35 g., indicated only the presence of phenyltin groups. The solid was suspended in methanol and treated with 6 *N* hydrochloric acid. Heat was evolved, the solution became clear, and the solution was extracted with ether. The ether extracts were dried over anhydrous magnesium sulfate and concentrated to give a low-melting solid. Recrystallization of this material from petroleum ether gave 0.25 g. of diphenyltin dichloride, m.p. 34° (lit.[18] m.p. 42–44°).

Concentration of the chloroform filtrate gave a yellow solid. Recrystallization from chloroform gave a small amount of tetraphenyltin, m.p. 224–226°; a sample did not discolor iodine solution.

B. **Triphenyltin Nitrate in the Presence of Triphenylmethane.**—A mixture of 2.0 g. of triphenyltin nitrate and 4.0 g. of triphenylmethane was rapidly heated by lowering the sample tube of the decomposition apparatus under reduced pressure into an oil bath preheated to 150°. The sample melted first, then gas was evolved and a precipitate gradually appeared. The oil-bath temperature was held at 150° for 1 hr. and then raised to 190°. After 5 min. the reaction tube was removed from the oil bath and allowed to cool in the air. Petroleum ether was added to the cooled reaction mixture before it had solidified and the resulting mixture was allowed to stand overnight. The precipitate which formed was removed by filtration and washed with more petroleum ether. The infrared spectrum of this solid material, 2.14 g., indicated that it was largely triphenylcarbinol. The sample was treated with methyl alcohol and filtered to obtain 0.59 g. of a methanol-insoluble material. Recrystallization of this material from chloroform gave 0.096 g. of tetraphenyltin, m.p. 222–224°.

Triphenylcarbinol, 1.54 g., was obtained from the methanolic filtrate, m.p. 110–145°. Recrystallization from carbon tetrachloride raised the melting point to 150° (lit.[19] m.p. 162°).

The petroleum ether filtrate was concentrated and the precipitate which formed removed by filtration. There was obtained 0.38 g. of triphenylcarbinol.

The filtrate was concentrated to dryness and there was obtained 3.12 g. of a solid material. The infrared spectrum of this material indicated the presence of triphenyltin hydroxide. The solid was washed with petroleum ether, leaving 0.82 g. of insoluble material. The infrared spectrum of this material exhibited a strong doublet at 910 and 897 cm.$^{-1}$ and a band at 774 cm.$^{-1}$ [20] characteristic of triphenyltin hydroxide and bis(triphenyltin) oxide, respectively. The solid was taken up in benzene and put on an alumina chromatographic column. The column was first eluted with benzene to remove triphenylmethane and then with a mixed solvent of methanol and benzene, 10:90. There was obtained 0.34 g. of bis(triphenyltin) oxide, m.p. 118–120°. Recrystallization from methanol water gave 0.21 g. of triphenyltin hydroxide, m.p. 121–123° (lit.[20] m.p. 121°).

No products other than nitrogen oxides were collected in the receiver.

C. **Triphenyltin Nitrate in the Presence of Diphenylamine.**—A mixture of 2.51 g. of triphenyltin nitrate and 4.0 g. of diphenylamine was rapidly heated by lowering the sample tube of the decomposition apparatus into an oil bath preheated to 185°. A brown gas was evolved. The temperature of the bath was raised to 195° and held there for a few minutes. The reaction mixture was black. The bath was removed and the sample tube was allowed to cool to room temperature. The liquid which was found in the receiver was identified as benzene by its infrared spectrum and through gas chromatographic analysis.

The reaction mixture was treated with petroleum ether and the resulting mixture was filtered. Concentration of the filtrate gave a solid material whose infrared spectrum contained no bands indicative of phenyltin compounds.

The petroleum ether insoluble material was treated with chloroform and filtered. On concentration of the filtrate a precipitate formed and it was removed by filtration. There was obtained 0.30 g. of a crystalline solid whose infrared spectrum did not contain bands indicative of either triphenyltin hydroxide or bis(triphenyltin) oxide. Recrystallization of this solid from chloroform gave tetraphenyltin, m.p. 220–226°.

Concentration of the chloroform filtrate from above to dryness gave a sample whose infrared spectrum indicated that neither triphenyltin hydroxide or triphenyltin nitrate were present.

Solvolysis of Triphenyltin Nitrate. A.—An anhydrous methanol solution of triphenyltin nitrate was evaporated to dryness while open to the atmosphere. The residue was treated with petroleum ether and collected on a Büchner funnel. The infrared spectrum indicated that only triphenyltin nitrate was present.

B.—A few milliliters of distilled water was added to an anhydrous methanol solution of triphenyltin nitrate. Upon evaporation of the solvent a beautiful crystalline substance was obtained. The infrared spectrum of this material indicated that it was a mixture of triphenyltin hydroxide and triphenyltin nitrate. No attempt was made to determine the ratio of the components in the mixture.

Control Experiments. A. Pyrolysis of Tetraphenyltin in the Presence of Diphenylamine.—A mixture of 2.87 g. of tetraphenyl tin and 5.20 g. of diphenylamine was rapidly heated by lowering the sample tube of the decomposition apparatus into an oil bath preheated to 165°. The temperature of the oil bath was increased to 195° and maintained at that temperature, the bath reaching that temperature 15 min. after the start of the experiment. The reaction mixture was kept in the bath for 1 hr. The reaction mixture turned brown but remained homogeneous throughout the heating period. No benzene was found in the cooling trap.

B. Pyrolysis of Triphenyltin Hydroxide in the Presence of Diphenylamine.—A mixture of 2.01 g. of triphenyltin hydroxide and 4.31 g. of diphenylamine was treated as above. The reaction mixture became brown and noticeably milky in appearance and a small amount of condensate formed on the walls of the cooling trap. Infrared analysis of the condensate indicated that the major component was water. The reaction mixture was repeatedly extracted with petroleum ether. Infrared analysis of the petroleum ether insoluble residue indicated the presence of unreacted triphenyltin hydroxide. No quantitative isolation was made.

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[19] A. I. Vogel, "A Textbook of Practical Organic Chemistry," 3rd Ed., Longmans, Green and Co., New York, N. Y., 1956, p. 816.

[20] B. Kushlefsky, I. Simmons, and A. Ross, *Inorg. Chem.*, **2**, 187 (1963).