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DIPHENYLTIN DINITRATE AND sym-TETRAPHENYLDINITRATODISTANNOXANE

A. N. FENSTER AND E. I. BECKER
Department of Chemistry, University of Massachusetts, Boston, Massachusetts 02116 (U.S.A.)

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SUMMARY

Diphenyltin dinitrate has been previously reported to be an intermediate in the thermal decomposition of triphenyltin nitrate. However, in agreement with Simpson's recent report, we could not detect diphenyltin dinitrate as a product of the decomposition of triphenyltin nitrate. In the present work, diphenyltin dinitrate was prepared unequivocally by the metathetical reaction between diphenyltin dichloride or diiodide and silver nitrate and characterized by elemental analysis, molecular weight determination, infrared spectrum, and preparation and analysis of its 1,10-phenanthroline derivative. Diphenyltin dinitrate is sensitive to moisture, equivalent quantities of water converting it to sym-tetraphenyldinitratodistannoxane. Triphenyltin nitrate also yields sym-tetraphenyldinitratodistannoxane when warmed in chloroform with access to air. Exploratory experiments suggest that oxygen is probably necessary for the conversion.

INTRODUCTION

According to Tsai and co-workers[1], diphenyltin dinitrate is an intermediate in the thermal decomposition of triphenyltin nitrate, a reaction which has been reported earlier[2]. Yet, recently Simpson[3] has indicated that attempts to characterize diphenyltin dinitrate in the solid residue of the decomposition products have failed. We are prompted at this point to confirm Simpson's observations and to report on the preparation and properties of diphenyltin dinitrate. We also will report on the synthesis and properties of sym-tetraphenyldinitratodistannoxane, an unexpected reaction product of triphenyltin nitrate.

RESULTS AND DISCUSSION

Diphenyltin dinitrate was prepared by treating either diphenyltin dichloride in acetonitrile or diphenyltin diiodide[4] in acetone/acetonitrile with silver nitrate under nitrogen. The product is a white, crystalline solid melting at 195–197° (dec.). Analogous to the dialkyltin dinitrates[5], it is soluble in polar organic solvents and slowly decomposes at room temperature. However, it may be refrigerated without appreciable decomposition for several weeks and is stable as its 1 : 1 reaction product with 1,10-

phenanthroline. On the other hand, the product reported by Tsai did not melt up to 310° and no derivative was reported.

In several experiments diphenyltin diiodide in acetone was treated with silver nitrate with access to air and under these conditions a new product was obtained in good yields. The compound was found to be sym-tetraphenyldinitratodistannoxane by analysis of its infrared spectrum, elemental analysis and molecular weight. Eqn. (1) suggests the reaction sequence:

$$2\,(C_6H_5)_2SnI_2+4\,AgNO_3 \rightarrow [2\,(C_6H_5)_2Sn(NO_3)_2] \xrightarrow{H_2O} [(C_6H_5)_2Sn(NO_3)]_2O+2\,HNO_3 \quad (1)$$

It was also found that when diphenyltin dinitrate was stirred in ether at room temperature in an open vessel or treated with an equivalent amount of water, sym-tetraphenyldinitratodistannoxane was produced in excellent yields and the reaction mixture became acidic. The product is a white crystalline solid melting at 288–290° (dec.), soluble in polar organic solvents, recrystallizable from chloroform, and stable at room temperature. If diphenyltin dinitrate is added to an excess of water, a material is obtained which appears to be amorphous and does not melt below 310°. The water layer gives a positive brown ring test for nitrate ion. When sym-tetraphenyldinitratodistannoxane is added to water, a similar material is obtained.

Okawara and co-workers[6] have suggested, on the basis of infrared analysis and molecular weight determinations, that the analogous sym-tetraalkyldinitratodistannoxanes are dimeric in benzene. On the other hand, we have found that sym-tetraphenyldinitratodistannoxane is monomeric in acetone. Both results are in accord with the findings of Considine *et al.*[7] that related compounds are monomeric in cyclopentadecanone and in camphor, more highly associated in benzene, and dimeric in carbon tetrachloride[6]. The broad band for Sn–O–Sn stretching vibrations characteristic of dimeric stannoxanes[8-10] near 600 cm^{-1} was not present. Instead, two sharp bands at 600 and 550 cm^{-1} were observed. This class of compounds, the sym-tetraalkyl- or tetraaryldinitratodistannoxanes, is related to the sym-tetraalkyldichloro- and dibromodistannoxanes prepared by Davies and co-workers[11,12].

Quite aside from the experiments above, we inadvertently obtained the distannoxane from triphenyltin nitrate. When triphenyltin nitrate was heated in chloroform and allowed to stand in an open vessel for several days, a solid was obtained in high yield. The product proved to be identical in all respects to sym-tetraphenyldinitratodistannoxane obtained in the preparation of diphenyltin dinitrate. Its derivation from triphenyltin nitrate raised the question of how it was formed and a few preliminary experiments were carried out. Table 1 summarizes part of this work and points out that exclusion of oxygen prevents formation of the stannoxane as would be predicted from the consideration of the oxygen requirement in the conversion. Also, reflux in chloroform was not necessary, only standing with access to the oxygen in the air. No phenol was detected, although it was looked for, but benzene was found. The solvent chloroform was assumed to be the source for the hydrogen needed for the production of benzene. To test this hypothesis, deuterated chloroform was used. Under these conditions, no deuterated benzene was found, but benzene was obtained. Rigorous precautions were then taken to dry the solvent, the oxygen, and the triphenyltin nitrate to exclude the possibility of adventitious moisture. After the elimination of the balloon, and the use of an all glass apparatus the results became more consistent. Under these

TABLE 1

CONVERSION OF TRIPHENYLTIN NITRATE IN CHLOROFORM

Run	Reaction conditions[a]	Product yields (%)		
		$(C_6H_5)_3SnNO_3$	$[(C_6H_5)_2Sn(NO_3)]_2O$	C_6H_6[b]
1	Refluxed under air for 0.5 h	100		
2	Refluxed under air for 0.2 h, then sealed in a flask for 7 days	96		3.3
3	Refluxed under air for 0.2 h, then sealed in a flask for 10 days	92		6.3
4	Refluxed under air for 2 h	98		1.6
5	Refluxed under air for 24 h	81	10	17.2
6	Refluxed under air for 70 h		96	89
7	Refluxed under air for 72 h, then allowed to stand at r.t. for 4 days		96	92
8	No reflux, allowed to stand at r.t. for 10 days	39	50	46
9	Refluxed under air for 0.2 h, then allowed to stand at r.t. for 7 days		96	[c]
10	Refluxed under O_2[d] for 1 h	98		1.0
11	Allowed to stand under O_2[d] at r.t. for 3 days	98		0.8
12	Refluxed under O_2[e] for 0.2 h, then allowed to stand at r.t. under O_2 for 7 days	50	45	46
13	Refluxed under O_2[e] for 72 h	40	55	52
14	No reflux, allowed to stand at r.t. for 7 days under O_2[d]	55	40	43
15	No reflux, allowed to stand dry at r.t. for 50 h under N_2[d]	96		
16	No reflux, allowed to stand dry at r.t. for 7 days under N_2[d]	95		

[a] To a filter flask which has been previously flamed out and cooled in a desiccator was added 2.0 g (4.8 mmoles) of purified triphenyltin nitrate and 50 cc of purified chloroform as outlined in *Procedure A*. A rubber balloon was attached at the side arm and a rubber septum used to stopper the other opening. The atmosphere in the flask was as described in Table 1 for each experiment and the isolation of products was in accord with those of *Procedure A*. [b] Benzene was determined by programmed temperature gas chromatography. Analyses were done on a Varian Aerograph, Model 1520-B, using a 5% SE-30 on 60–80 mesh Chromosorb W (6 ft. × 0.25 in.) column. [c] Identified but unable to determine yield. [d] Under a balloon. [e] Bubbling gas.

conditions the products were the distannoxane and biphenyl, no benzene was detected in the vapor phase chromatogram. However, it was found that the reaction proceeded faster when a small amount of water was present. When dried ethanol was substituted for water, benzene and the distannoxane were obtained, albeit, not in such good yields as with water. To determine whether oxygen is a genuine requirement in this conversion, a reaction was conducted with water in a flask sealed under vacuum. After workup of this reaction only starting material was obtained. The slower reaction in pure oxygen appears to be due to the absence of water under these conditions.

It is important to note the purity of triphenyltin nitrate because it is known to undergo complex thermal decomposition[1-3,13] and even to decompose upon standing at room temperature when impure. Triphenyltin nitrate was prepared from triphenyltin chloride and silver nitrate in anhydrous acetonitrile. It was tested for purity by means of titration by base, melting point, and comparison of its infrared spectrum with that reported by Clark and Goel[13]. The well defined bands for ν_4 and ν_1 indicate the high purity and anhydrous condition of the triphenyltin nitrate.

When triphenyltin nitrate was added to excess water, hexaphenyldistannoxane and nitric acid in nearly equimolar quantities were formed. If nitric acid was added to hexaphenyldistannoxane in chloroform, triphenyltin nitrate was obtained in good yields as Srivastava[14] has found.

$$2\,(C_6H_5)_3SnONO_2 \underset{CHCl_3}{\overset{H_2O}{\rightleftharpoons}} (C_6H_5)_3Sn\text{–}O\text{–}Sn(C_6H_5)_3 + 2\,HNO_3 \qquad (2)$$

EXPERIMENTAL

Tin analyses were performed according to Gilman and King[15]. Elemental microanalyses were done by Galbraith Laboratories, Inc., Knoxville, Tennessee, and by Alfred Bernhardt, West Germany.

Diphenyl dinitrate

Either diphenyltin dichloride[16] or diphenyltin diiodide[17] can be used under the following conditions to prepare diphenyltin dinitrate*. To a solution of 21 g (0.060 moles) of diphenyltin dichloride in 50 cc of distilled acetonitrile (acetone was used in the case of diphenyltin diiodide) cooled to 0° under an atmosphere of nitrogen, was added a solution of 13.6 g (0.80 moles) of silver nitrate in 50 cc of acetonitrile. The solution was allowed to stir for an additional 0.5 h and filtered. Dissolved silver chloride was precipitated from the filtrate by addition of acetone and filtered. After concentrating the filtrate on a rotary evaporator without heating, the residue was washed with a mixture of hot chloroform/petroleum ether, filtered and washed again in the same way to give 14.65 g of colorless diphenyltin dinitrate (91 %), m.p. 195–197° (dec.). (Found: C, 36.95, 37.03; H, 2.73, 2.83; N, 6.18, 6.30; Sn, 30.34, 30.42, 30.01,

TABLE 2[a]

ASSIGNMENT OF INFRARED BANDS[b]

Compounds	NO stretch	NO_2 out of plane	NO_2 sym. stretch	NO_2 asym. stretch	Sn–O–Sn stretch
$(C_6H_5)_3SnNO_3$	995 (s, sp) 980 (w)	800 (m)	1288 (sh) 1270 (s) 1250 (sh)	1510 (m) 1495 (sp)	
$(C_6H_5)_2Sn(NO_3)_2$	1000 (m, sp) 995 (s)	800 (m, sh) 798 (m, sp)	1312 (s) 1265 (w) 1235 (s, sp)	1560 (sh) 1550 (s, sp)	
$[(C_6H_5)_2Sn(NO_3)]_2O$	998 (m) 960 (s, b)	790 (m, s)	1275 (s, b)	1550 (s, sh) 1530 (s, sp)	600 (s, sp) 550 (s, sp)
$(C_6H_5)_2Sn(NO_3)_2 \cdot L^c$	998 (m, b)	800 (m)	1280 (s, sp)	1495 (s, sp)	

[a] See refs. 6, 8–10, 13, 18, 19. [b] All frequencies are given in cm^{-1}; w = weak, m = medium, sh = shoulder, s = strong, sp = sharp, b = broad. [c] L = 1,10-phenanthroline.

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* Srivastava and Bhattacharya[4] reported failure to obtain diphenyltin dinitrate this way. As will be discussed further on, their failure may have been due to adventitious moisture since they did not mention operating under a dry, inert gas.

29.23, 29.12; vapor pressure mol. wt. in acetone, 382. $C_{12}H_{10}N_2O_6Sn$ calcd.: C, 36.28; H, 2.54; N, 7.06; Sn, 29.91%; mol. wt., 397.) Infrared absorption bands of this compound are listed in Table 2.

(1,10-Phenanthroline)diphenyltin dinitrate

To 0.36 g (2.0 mmole) of 1,10-phenanthroline dissolved in 10 cc of absolute ethanol was added 0.80 g (2.0 mmole) of diphenyltin dinitrate. To the mixture about 25 cc of acetone was added and the precipitate was filtered, washed with two 10-cc portions of acetone and then dried giving 1.1 g (95%) of the complex, m.p. 276–278° (dec.). (Found: C, 50.45; H, 3.36; N, 9.23; Sn, 20.59. $C_{24}H_{18}N_4O_6Sn$ calcd.: C, 49.95; H, 3.15; N, 9.71; Sn, 20.57%.) Infrared absorption bands of this compound are listed in Table 2.

sym-Tetraphenyldinitratodistannoxane

A mixture of 5.0 g (9.5 mmole) of diphenyltin diiodide and 4.0 g (0.0235 mole) of silver nitrate in 50 cc of distilled acetone was stirred for 1 h at room temperature. The precipitated silver iodide and excess silver nitrate was filtered and the solvent distilled at reduced pressure. The residue was then washed with petroleum ether leaving 3.2 g of sym-tetraphenyldinitratodistannoxane, m.p. 265–270°. Two recrystallizations from chloroform gave an analytical sample in 87% yield, m.p. 288–290° (dec.). (Found: C, 42.09; H, 3.10; N, 4.12; Sn, 34.80; vapor pressure mol. wt. in acetone, 673. $C_{24}H_{20}N_2O_7Sn_2$ calcd.: C, 42.02; H, 2.92; N, 4.08; Sn, 34.64%; mol. wt., 686.) Infrared absorption bands of this compound are given in Table 2.

Conversion of diphenyltin dinitrate to sym-tetraphenyldinitratodistannoxane

A suspension of 4.14 g (0.0104 moles) of diphenyltin dinitrate in 50 cc of ether was stirred overnight in a flask open to the atmosphere. Filtration and recrystallization from chloroform yielded 3.2 g of sym-tetraphenyldinitratodistannoxane, m.p. 287–289° (dec.). The infrared spectrum of this compound was identical with that of the previously prepared sample.

Preparation of triphenyltin nitrate

To 100 g (0.260 moles) of purified triphenyltin chloride in 250 cc of dried, distilled acetonitrile was added 42 g (0.252 mole) of silver nitrate in a minimum of acetonitrile (350 cc) in a 1-l erlenmeyer flask. The mixture was stirred vigorously with a magnetic stirrer from 15–30 min. The silver chloride was filtered. Dry acetone was added to the filtrate until no further precipitation occurred and the suspension was filtered again. The resulting filtrate was concentrated to dryness under vacuum (using a roto-evaporator). The residue was a white crystalline material weighing 100 g and melted 160–170° (dec.). Three recrystallizations from a chloroform/petroleum ether mixture afforded 84 g (0.204 moles) of triphenyltin nitrate (81%), m.p.* 184–186°. The sample did not immediately decompose upon melting, but did decompose when kept at that temperature for 2 or 3 min. This compound is stable for several months at

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* Simpson[3] has reported a melting point of 170°, and Tsai and co-workers[1] have reported a melting point of 181–182° for triphenyltin nitrate. We have found that any decrease in melting point of sample indicates a degree of impurity and decomposition.

room temperature. (Found: Sn, 28.75; saponification equivalent 412. $C_{18}H_{15}NO_3Sn$ calcd.: Sn, 28.83 %; saponification equivalent, 412.) Infrared absorption bands of this compound are given in Table 2.

Conversion of triphenyltin nitrate to sym-tetraphenyldinitratodistannoxane

A mixture of 15 g (0.0365 moles) of triphenyltin nitrate was boiled for about 15 min in chloroform. The resulting solution was filtered hot, cooled, and filtered to collect 5.2 g (0.0125 moles) of triphenyltin nitrate, m.p. 184–185°. After standing for five days, the filtrate deposited a precipitate weighing 7.0 g, m.p. 287–288° (dec.). A mixed melting point with sym-tetraphenyldinitratodistannoxane obtained previously was not depressed and an infrared spectrum of this compound was superimposable upon that of a known sample of sym-tetraphenyldinitratodistannoxane.

Reaction of triphenyltin nitrate in chloroform under oxygen

Procedure A. To a preheated flask connected to another flask by ground glass joints was added 2.0 g (4.8 mmoles) of purified triphenyltin nitrate and 50 cc of chloroform which was dried over calcium chloride, and distilled twice. The solvent was checked for absolute purity by means of gas chromatography. The system was evacuated, and oxygen, which was passed through phosphorus pentoxide, was allowed to saturate the system. After being stirred at room temperature for six days, the system was analyzed by gas chromatography. Chloroform and 0.063 g (17 %) biphenyl were detected. After concentration of the mixture and continuous extraction of the residue with chloroform/petroleum ether, 0.33 g (20 %) sym-tetraphenyldinitratodistannoxane and 1.50 g (75 %) triphenyltin nitrate were obtained.

Reaction of triphenyltin nitrate in chloroform under oxygen with water

The reaction was conducted according to *Procedure A*, except that the system contained 0.1 ml of water. Upon workup of the reaction mixture 1.64 g (99 %) sym-tetraphenyldinitratodistannoxane and 0.35 g (94 %) benzene were obtained.

Reaction of triphenyltin nitrate in chloroform under oxygen with ethanol

The ethanol used was dried with magnesium according to Fieser[20]. *Procedure A* was used. Upon workup of the reaction mixture 0.68 g (34 %) triphenyltin nitrate, 0.94 g (58 %) sym-tetraphenyldinitratodistannoxane, and 0.20 g (52 %) benzene were obtained.

Reaction of triphenyltin nitrate in chloroform under vacuum with water

A mixture of 0.65 g of purified triphenyltin nitrate, 15 cc of dried chloroform and 0.1 cc of water in a test tube was cooled in dry ice/acetone, evacuated, and sealed under vacuum. After standing for 6 days at room temperature, the system was opened and the reaction mixture worked up yielding 0.60 g (94 %) starting material.

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