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REACTION OF BIS(TRIPHENYLTIN) OXIDE WITH THIOUREA AND SOME 1,3-DISUBSTITUTED THIOUREAS

RAYMOND A. CARDONA, EUGENE J. KUPCHIK* AND HANS E. HANKE
Department of Chemistry, St. John's University, Jamaica, New York 11432 (U.S.A.)

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SUMMARY

Bis(triphenyltin) oxide was found to react with thiourea in refluxing acetonitrile to give bis(triphenyltin) sulfide, bis(triphenylstannyl)carbodiimide, and dicyandiamide. Bis(triphenylstannyl)carbodiimide was prepared by the reaction of bis(triphenyltin) oxide with cyanamide in refluxing acetonitrile or benzene. Bis(triphenyltin) oxide was found to react with 1,3-disubstituted thioureas in refluxing acetonitrile or toluene to give bis(triphenyltin) sulfide and, with the exception of di-tert-butylthiourea, the corresponding 1,3-disubstituted urea.

INTRODUCTION

It has been reported that bis(tri-n-butyltin) oxide and thiourea react at 200° to give bis(tri-n-butyltin) sulfide (70%), tri-n-butyltin isothiocyanate (15%), and ammonia (20%)[1]. Bis(tri-n-butyltin) oxide has also been reported to react with 1,3-disubstituted thioureas in refluxing toluene to produce bis(tri-n-butyltin) sulfide and the corresponding 1,3-disubstituted urea[1]. In the case of 1,3-diphenylthiourea in refluxing benzene, a small amount of diphenylcarbodiimide was isolated also[2]. The suggestion was made that the urea is formed by the organotin-catalyzed reaction of the carbodiimide with water[2]. We now wish to report our results on the related reactions of bis(triphenyltin) oxide with thiourea and some 1,3-disubstituted thioureas.

RESULTS AND DISCUSSION

The reaction of bis(triphenyltin) oxide with thiourea in acetonitrile at 82° gave bis(triphenyltin) sulfide (57–69%), bis(triphenylstannyl)carbodiimide (20%), dicyandiamide, and unchanged thiourea (20%). The IR spectrum of the crude reaction product showed that the oxide was completely consumed.

Bis(triphenylstannyl)carbodiimide was prepared independently by allowing bis(triphenyltin) oxide to react with cyanamide in refluxing acetonitrile (57%) or benzene (62%). Its infrared spectrum shows a strong band at 4.80 μ, due to the carbodiimide linkage[3], and strong bands at 13.72 μ and 14.35 μ, due to monosubstituted

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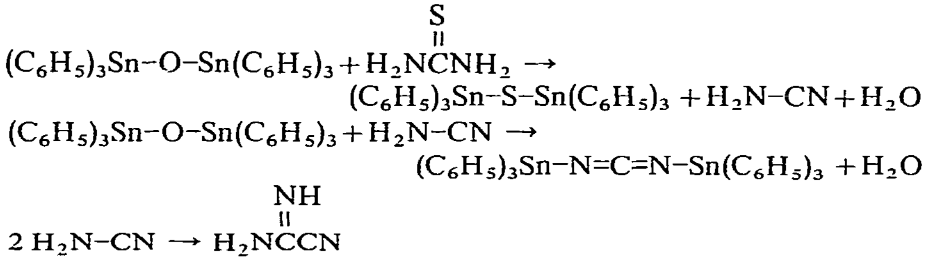
* To whom inquiries should be addressed.

phenyl groups[4]. The parent region of its mass spectrum shows a complex isotopic distribution which is expected for two tin atoms. The pattern is further complicated by the loss of hydrogen from the parent ion. The most abundant ion is expected to be $[(C_6H_5)_3{}^{120}SnNCN^{118}Sn(C_6H_5)_3]^{\dagger}$ with *m/e* equal to 740, which is found. The fragmentation mainly involves loss of phenyl groups with some rearrangements also taking place. It has been reported that bis(triphenylstannyl)carbodiimide results from the reaction of triphenyltin chloride with sodium cyanamide[5]; however, the melting point, elemental analysis, and infrared data were not given. More recently, bis(triethylstannyl)carbodiimide was obtained from the reaction of triethyltin chloride with cyanamide and triethylamine[6].

The dicyandiamide formed in our reaction very likely results from the dimerization of cyanamide, a reaction which is well-known[7]. The bis(triphenylstannyl)carbodiimide very likely results from the reaction of bis(triphenyltin) oxide with cyanamide, a reaction which we have demonstrated to occur. The fact that the yield of bis(triphenyltin) sulfide is not quantitative and that some of the thiourea remains unreacted, while all of the bis(triphenyltin) oxide is consumed, means that the bis(triphenyltin) oxide is more reactive towards the cyanamide produced in the reaction than towards thiourea. In summary, the reactions represented by eqns. (1)–(3) occur when an acetonitrile solution of bis(triphenyltin) oxide and thiourea is refluxed.



$$(C_6H_5)_3Sn{-}O{-}Sn(C_6H_5)_3 + H_2N\overset{\overset{S}{\|}}{C}NH_2 \rightarrow (C_6H_5)_3Sn{-}S{-}Sn(C_6H_5)_3 + H_2N{-}CN + H_2O \tag{1}$$

$$(C_6H_5)_3Sn{-}O{-}Sn(C_6H_5)_3 + H_2N{-}CN \rightarrow (C_6H_5)_3Sn{-}N{=}C{=}N{-}Sn(C_6H_5)_3 + H_2O \tag{2}$$

$$2\,H_2N{-}CN \rightarrow H_2N\overset{\overset{NH}{\|}}{C}CN \tag{3}$$

The products (except water) shown in eqn. (1) could conceivably result from the decomposition of an intermediate such as $(C_6H_5)_3Sn{-}S{-}C({=}NH){-}NH{-}Sn(C_6H_5)_3$. This intermediate might be expected to be formed also in the reaction of triphenyltin iodide with thiourea (2/1 mole ratio) in the presence of triethylamine. In fact, this latter reaction, carried out in refluxing acetonitrile, gave bis(triphenyltin) sulfide (87%), dicyandiamide, and triethylamine hydroiodide.

As expected, bis(triphenyltin) oxide was found to react with 1,3-disubstituted thioureas ($RNHC({=}S)NHR$, $R{=}CH_3$, n-C_3H_7, n-C_4H_9, cyclo-C_6H_{11}, $C_6H_5CH_2$, C_6H_5, or *p*-$CH_3C_6H_4$) in refluxing toluene to give, after 5 h, bis(triphenyltin) sulfide (84–89%) and the corresponding 1,3-disubstituted urea (38–92%). In two cases ($R{=}C_6H_5$ and *p*-$CH_3C_6H_4$) the reaction also proceeded well in refluxing acetonitrile. Although bis(triphenyltin) sulfide was obtained from the reaction of the oxide with 1,3-di-tert-butylthiourea in refluxing toluene (82%) or acetonitrile (83%), no 1,3-di-tert-butylurea could be detected or isolated. However, di-tert-butylcarbodiimide is very likely formed, since the IR spectrum of the solution remaining after reaction shows a very strong carbodiimide band at 4.75 μ. In this case, the bulky tert-butyl group may shield the nitrogen from the tin atom of the organotin compound, thus preventing the organotin compound from catalyzing the reaction of the di-tert-butylcarbodiimide with water.

EXPERIMENTAL

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York. The infrared data were obtained using KBr pellets with a Perkin–Elmer Infracord. The mass spectrum of bis (triphenylstannyl)carbodiimide was obtained with a Hitachi RMU-6D mass spectrometer by Morgan–Schaffer Corporation, Montreal 252, Quebec, Canada.

Reaction of bis(triphenyltin) oxide with thiourea

(*a*). *Isolation of bis(triphenyltin) sulfide, dicyandiamide, and thiourea.* A mixture of 7.16 g (0.01 mole) of bis(triphenyltin) oxide, 0.76 g (0.01 mole) of thiourea, and 100 ml of acetonitrile was refluxed with stirring for 12 h. The resulting clear solution was transferred to an Erlenmeyer flask resulting in the immediate formation of colorless needle-like crystals which were collected on a filter to give 5.02 g (69%) of bis(triphenyltin) sulfide, m.p. 141–143° (lit.[8] m.p. 145.5–147°). A single recrystallization from acetonitrile afforded 4.32 g (59%) of sulfide, m.p. 143–145°, no depression on admixture with an authentic sample, infrared spectrum superimposable on that of an authentic sample.

The filtrate was cooled to 4° and filtered to give 2.01 g of a white solid, m.p. 122–198°, which was dissolved in 10 ml of boiling chloroform. The solution was allowed to cool to room temperature, and the solid which separated was collected on a filter to give 0.022 g of dicyandiamide, m.p. 201–204° (lit.[9] m.p. 207–209°), no depression on admixture with an authentic sample, infrared spectrum superimposable on that of an authentic sample.

The filtrate remaining after removal of the material, m.p. 122–198°, was evaporated to dryness, the residue was stirred with hot chloroform, and the mixture was filtered to give 0.15 g (20%) of thiourea, m.p. 164–172°, no depression on admixture with an authentic sample, infrared spectrum superimpossable on that of an authentic sample.

(*b*). *Isolation of bis(triphenyltin) sulfide and bis(triphenylstannyl)carbodiimide. Thin-layer chromatographic identification of dicyandiamide and thiourea.* A mixture of 14.32 g (0.02 mole) of bis(triphenyltin) oxide, 1.52 g (0.02 mole) of thiourea, and 200 ml of acetonitrile was refluxed with stirring for 5 h. The resulting clear solution was transferred to an Erlenmeyer flask resulting in the immediate formation of colorless needle-like crystals which were collected on a filter to give 8.27 g (56%) of bis(triphenyltin) sulfide, m.p. 140–143°. A single recrystallization from acetonitrile afforded 6.96 g (48%) of sulfide, m.p. 144–145°.

The acetonitrile was evaporated from the filtrate, the residue was stirred with hot chloroform, and the mixture was filtered to give 0.59 g of a colorless solid, m.p. 143–172°, whose infrared spectrum was superimposable on that of an authentic mixture of thiourea and dicyandiamide. Thin-layer chromatography with silica gel and either acetonitrile or ethyl acetate as developing solvent also showed the mixture to be a composition of thiourea and dicyandiamide by comparison with authentic samples. Spots were detected by using a sodium nitroprusside-potassium ferricyanide spray for the detection of cyanamide and its derivatives[10].

The chloroform was evaporated from the filtrate, the residue was stirred with methanol, and the mixture was filtered to give 1.03 g (7%) of bis(triphenyltin) sulfide, m.p. 139–142°. A single recrystallization from acetonitrile afforded 0.78 g of sulfide, m.p. 143–145°.

The methanol was evaporated from the filtrate leaving 3.99 g of a solid, m.p. 93–100°. A single recrystallization from acetonitrile gave 3.03 g (20%) of bis(triphenylstannyl)carbodiimide, m.p. 92–98°, no depression on admixture with a sample, m.p. 95–97°, prepared by allowing bis(triphenyltin) oxide to react with cyanamide, as described below. Except for a very small additional band at 4.6 μ, the infrared spectrum was identical with that of the sample having m.p. 95–97°. Successive recrystallizations from acetonitrile and ethanol raised the m.p. to 96–99° and caused the band at 4.6 μ to disappear.

Reaction of bis(triphenyltin) oxide with cyanamide

(*a*). *In acetonitrile.* A mixture of 3.58 g (0.005 mole) of bis(triphenyltin) oxide, 0.42 g (0.01 mole) of cyanamide, 2 g of anhydrous magnesium sulfate, and 50 ml of acetonitrile was refluxed with stirring for 5 h. The mixture was filtered, and the acetonitrile was evaporated from the clear filtrate leaving a solid, m.p. 69–130°. Recrystallization of 1.5 g of the crude product from ethanol gave 0.86 g (57%) of bis(triphenylstannyl)carbodiimide, a white solid having m.p. 95–97°. (Found: C, 59.98; H, 4.32; N, 3.75; Sn, 31.84; mol.wt. by mass spectrometry, 740. $C_{37}H_{30}N_2Sn_2$ calcd.: C, 60.05; H, 4.09; N, 3.79; Sn, 32.08%; mol.wt., 740.045.) IR: 4.80 (N=C=N), 13.72 and 14.35 (C_6H_5) μ.

(*b*). *In benzene.* Into a single-neck flask equipped with a Dean-Stark trap was placed 3.58 g (0.005 mole) of bis(triphenyltin) oxide, 0.42 g (0.01 mole) of cyanamide, and 130 ml of benzene. The mixture was refluxed with stirring for 5 h, and a small amount of water was collected. The mixture was filtered, and the benzene was evaporated from the filtrate leaving white crystals, m.p. 43–55°. Recrystallization of 1.5 g of the crude product from ethanol afforded 0.93 g (62%) of bis(triphenylstannyl)carbodiimide, m.p. 97–99°.

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