

SOME REACTIONS OF DI-*n*-BUTYLTIN DIHYDRIDE

BERNARD R. LALIBERTE, WENZEL DAVIDSOHN AND MALCOLM C. HENRY

U.S. Army Natick Laboratories, Natick, Massachusetts (U.S.A.)

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INTRODUCTION

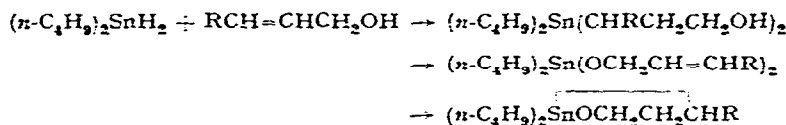
In recent years considerable research dealing with the addition of organotin hydrides to olefins has been reported^{*.2}. Many organotin compounds containing functional groups, *e.g.*, -CHO, -OC(O)CH₃, -COOH, -CONH₂, -CH(OC₂H₅)₂, -OH, -OC₆H₅, -OC(O)C₆H₅, -OC(CO)CH₃ etc., have been prepared by the addition of organotin hydrides to the corresponding functionally substituted olefins. In certain cases organotin hydrides in the presence of aldehydes and ketones act as selective reducing agents^{3,4}.

There appears to be little indication in the literature that organotin hydrides undergo reaction with the hydroxyl group of olefinic alcohols. Thus, triphenyltin hydride, for example, has been reported to react quantitatively with allyl alcohol via the expected addition reaction yielding (3-hydroxypropyl)triphenyltin⁵. Similarly, triphenyltin hydride and tri-*n*-propyltin hydride undergo addition reactions with propargyl alcohol² to form (3-hydroxypropenyl)triphenyl- and -tripropyltin respectively. The same workers also reported the addition of triphenyltin hydride to 2-methyl-2-propen-1-ol in the expected manner to yield (3-hydroxy-2-methylpropyl)-triphenyltin. Of interest was the report that tripropyltin hydride does not undergo the expected addition reaction with allyl alcohol².

We noticed that the reaction of dibutyltin dihydride and allyl alcohol resulted in the liberation of hydrogen. Prompted by this observation, we undertook an investigation of the nature of the reaction between dibutyltin dihydride and of certain olefinic alcohols as well as one unsaturated mercaptan, namely, allyl mercaptan.

RESULTS AND DISCUSSION

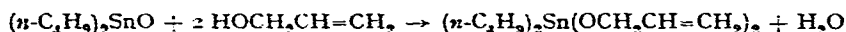
A summation of the results obtained from the reactions of dibutyltin dihydride with olefinic alcohols can be expressed conveniently as follows:



where: R = H, CH₃, C₆H₅.

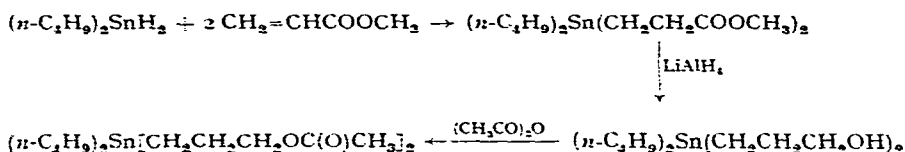
* For reviews in this field see ref. 1.

The reaction between di-*n*-butyltin dihydride and allyl alcohol yielded two products, a viscous liquid, di-*n*-butylbis(allyloxy)tin^{6,7} and crystalline 2,2-di-*n*-butyl-1-oxa-2-stannacyclopentane. The former was also prepared by an alternate route⁶:

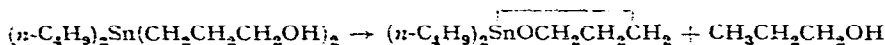


The infrared spectrum of di-*n*-butylbis(allyloxy)tin prepared by this alternate route was identical with that prepared by reaction of dibutyltin dihydride with allyl alcohol. Further analyses could not be carried out due to rapid hydrolysis and/or polymerization of the compound.

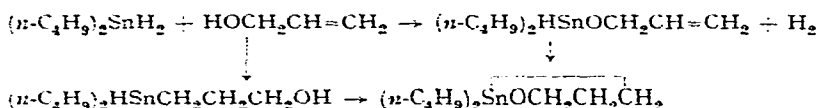
Since the reaction of allyl alcohol and dibutyltin dihydride did not yield bis-(3-hydroxypropyl)di-*n*-butyltin, this compound was prepared by a different route involving the addition of dibutyltin dihydride to methyl acrylate followed by a lithium aluminum hydride reduction as indicated below:



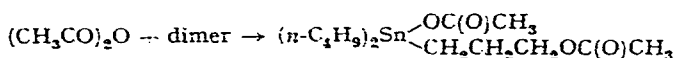
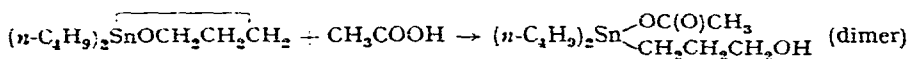
Acetylation of bis(3-hydroxypropyl)di-*n*-butyltin yielded the corresponding diacetate derivative, bis(3-carbomethoxypropyl)di-*n*-butyltin. Bis(3-hydroxypropyl)di-*n*-butyltin, in its pure state, is fairly stable. However, upon standing it slowly decomposes to 2,2-di-*n*-butyl-1-oxa-2-stannacyclopentane as follows:



Since the reaction of allyl alcohol and dibutyltin dihydride did not yield bis(3-hydroxypropyl)di-*n*-butyltin or propyl alcohol it can be assumed that 2,2-di-*n*-butyl-1-oxa-2-stannacyclopentane must have been formed via one of two alternative routes.



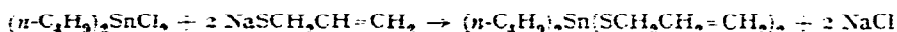
2,2-Di-*n*-butyl-1-oxa-2-stannacyclopentane is insoluble in most common organic solvents. However, it reacts in dilute acetic acid to yield acetoxy(3-hydroxypropyl)di-*n*-butyltin. The infrared spectrum of acetoxy(3-hydroxypropyl)di-*n*-butyltin, either in solution or neat, shows a strongly bonded hydroxyl group and a shifted carbonyl band in the 6.2 micron region. Molecular weight determinations yielded a value double that of the expected value, indicating a dimeric mixture. Acetylation of acetoxy(3-hydroxypropyl)di-*n*-butyltin yielded acetoxy(3-acetoxypropyl)di-*n*-butyltin with the expected molecular weight (see EXPERIMENTAL).



The main reaction product, bis(2-carbomethoxyethyl)di-*n*-butyltin obtained from the reaction of di-*n*-butyltin hydride and methyl acrylate, was accompanied by appreciable quantities of 2,2-di-*n*-butyl-1-oxa-2-stannacyclopentane. When the former was treated under similar experimental conditions with di-*n*-butyltin dihydride, no 2,2-di-*n*-butyl-1-oxa-2-stannacyclopentane was obtained, indicating that the di-*n*-butyltin dihydride probably reduced the methyl acrylate to form allyl alcohol prior to the addition reaction. The allyl alcohol thereby generated then reacted with di-*n*-butyltin dihydride to form 2,2-di-*n*-butyl-1-oxa-2-stannacyclopentane.

In attempts to further elucidate the nature of the assumed competitive reaction between an olefinic bond and a hydroxyl group in the presence of dibutyltin dihydride structural variations of allyl alcohol were selected which might vary the relative reactivity of the active sites concerned. Thus, crotyl alcohol, $\text{CH}_3\text{CH}=\text{CH}_2\text{CH}_2\text{OH}$, cinnamyl alcohol, $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2\text{OH}$, and allyl mercaptan, $\text{CH}_2=\text{CHCH}_2\text{SH}$, were selected as reactants with dibutyltin dihydride.

Allyl mercaptan, when treated with di-*n*-butyltin dihydride, yielded only bis(allylthio)di-*n*-butyltin whose structure was confirmed by an independent alternative synthesis.



The products obtained from the reaction of di-*n*-butyltin dihydride with both crotyl alcohol and cinnamyl alcohol were extremely prone to hydrolysis and thus bis(1-methyl-3-hydroxypropyl)di-*n*-butyltin and bis(1-phenyl-3-hydroxypropyl)-di-*n*-butyltin could not be isolated pure. Because of the evolution of hydrogen during the reaction it is assumed that both were formed but not stable enough to be isolated.

Separate experiments with di-*n*-butyltin dihydride and allyl alcohol were conducted making variations in the mode of addition of reactants, increased reaction temperatures, increased amounts of catalyst or free radical inhibitor (hydroquinone). No significant effects were noted on the products of the reaction or the relative amounts formed.

EXPERIMENTAL

General comments

All hydride addition reactions were carried out under an atmosphere of argon. Infrared spectra were recorded on a Perkin-Elmer 137 spectrophotometer. Reaction times for the hydride addition reactions were determined by the disappearance of the tin-hydrogen absorption band at 1835 cm^{-1} . Melting points are uncorrected. Refractive indices were measured on an Abbe-3L, Bausch and Lomb Refractometer. Vapor phase chromatographic studies were carried out on an Aerograph Autoprep Model A-700, fitted with a 6-ft. butyl glycol adipate resin packed column. Molecular weights, unless otherwise specified, were determined with a Mechrolab Model 301-A Osmometer. The purity of isolated products was followed by thin-layer chromatographic techniques⁸. Di-*n*-butyltin dihydride was prepared by the method described in the literature⁹.

Preparation of bis(2-carbomethoxyethyl)di-*n*-butyltin

To a mixture of di-*n*-butyltin dihydride (11.7 g, 0.05 mole) and methyl acrylate

(11.2 g, 0.125 mole) was added 2.5 mg of catalyst (AIBN). The reaction mixture, after its initial exothermic reaction, was refluxed for 1 h and then distilled at 126°/0.075 mm, 18.8 g (92 % yield); n_D^{25} 1.4808. (Found: C, 47.50; H, 7.89; Sn, 29.31; mol. wt. in benzene 406. $C_{16}H_{32}O_4Sn$ calcd.: C, 47.21; H, 7.93; Sn, 29.20 %; mol. wt., 407.)

Preparation of bis(3-hydroxypropyl)di-n-butyltin

Bis(2-carbomethoxyethyl)di-*n*-butyltin (15 g, 0.037 mole) dissolved in 25 ml of ether was added to 100 ml ethereal solution of lithium aluminum hydride (3.0 g, 0.079 mole). The addition rate was adjusted to maintain reflux. The reaction mixture was refluxed for a period of 1 h after the addition was completed and then slowly hydrolyzed with 10 ml of water and 25 ml of a saturated ammonium chloride solution. A sufficient amount of dilute hydrochloric acid was added during the hydrolysis to dissolve the precipitated aluminum hydroxide and the mixture extracted with ether. The ethereal solution was dried over anhydrous sodium sulfate, filtered, and evaporated. Yield 10.7 g (83 %) of nearly pure product; n_D^{25} 1.5005. (Found: C, 48.38; H, 9.21; Sn, 33.74; mol. wt. in benzene, 360. $C_{14}H_{32}O_2$ calcd.: C, 47.91; H, 9.18; Sn, 33.82 %; mol. wt., 351.) An attempted distillation of bis(3-hydroxypropyl)di-*n*-butyltin at 160° (0.0075 mm) resulted in decomposition to a white solid material, 2,2-di-*n*-butyl-1-oxa-2-stannacyclopentane, m.p. 219–226° (dec.). A clear liquid collected in a dry ice trap during the attempted distillation gave a red color in the presence of ceric nitrate¹⁰ reagent. Partial decomposition was observed when bis(3-hydroxypropyl)-di-*n*-butyltin was allowed to stand for one week at room temperature.

Bis(3-hydroxypropyl)di-*n*-butyltin, a clear thick liquid, was sealed in a glass tube at reduced pressure. The tube was placed in an oven at 140° for one week, opened at subambient temperatures, warmed to ambient temperature, and the volatile liquid was trapped in a cool trap under reduced pressure. The infrared spectrum and VPC chromatogram of the trapped liquid was identical to *n*-propyl alcohol. The white solid was characterized to be 2,2-di-*n*-butyl-1-oxa-2-stannacyclopentane as described below.

Acetylation of bis(3-hydroxypropyl)di-n-butyltin

The acetylation was carried out by the method of Shriner, Fuson and Curtin¹⁰, using sodium acetate and acetic anhydride. The resulting product, n_D^{25} 1.4748, gave one spot using TLC (ethanol). (Found: C, 49.80; H, 8.30; Sn, 26.94; mol. wt. in benzene, 426. $C_{13}H_{26}O_4Sn$ calcd.: C, 49.68; H, 8.34; Sn, 27.27 %; mol. wt., 435.)

Preparation of di-n-butylbis(allyloxy)tin (method described by Mack⁶)

Di-*n*-butyltin oxide (11.0 g, 0.044 mole) and allyl alcohol (4.7 g, 0.08 mole) were refluxed in 250 ml of benzene for a period of 2 h. The water formed during the reaction was collected in a Dean-Stark trap attached to the reaction flask, ca. 0.7 ml. The slight excess of di-*n*-butyltin oxide was removed by filtration. The filtrate was evaporated under reduced pressure, 11.3 g of di-*n*-butylbis(allyloxy)tin was obtained.

Preparation of 2,2-di-n-butyl-1-oxa-2-stannacyclopentane

To a mixture of di-*n*-butyltin dihydride (11.7 g, 0.05 mole) and allyl alcohol (11.6 g, 0.20 mole) was added 4.1 mg (AIBN) of catalyst. The reaction mixture was stirred with a magnetic stirrer at 40° for 48 h. A slow evolution of gas was observed

with the formation of a soft white mass. Fifty ml of petroleum ether was added to the mixture and the resultant white crystals were filtered, washed thoroughly with petroleum ether and dried; yield 3 g; m.p. 219–226° (dec.). (Found: C, 45.19; H, 8.10; Sn, 40.93; mol. wt. Rast in camphor, 338. $C_{11}H_{24}OSn$ calcd.: C, 45.39; H, 8.31; Sn, 40.80%; mol. wt., 291.) This compound can be sublimed at 190°/0.0075 mm with partial decomposition; the residue was dibutyltin oxide.

Precipitation took place in the filtrate after 48 h. The precipitate was filtered and the filtrate evaporated under reduced pressure to remove the petroleum ether and excess allyl alcohol, yielding a viscous liquid, di-*n*-butylbis(allyloxy)tin.

Reaction of 2,2-di-n-butyl-1-oxa-2-stannacyclopentane with acetic acid

Equimolar quantities of an acetic acid benzene solution and 2,2-di-*n*-butyl-1-oxa-2-stannacyclopentane (2.0 g, 0.069 mole) were mixed and stirred at room temperature until the solution became clear. Volatile substances were removed by distillation under reduced pressure, yielding dimeric acetoxyl(3-hydroxypropyl)di-*n*-butyltin (quantitative); n_D^{20} 1.4870. This dimer decomposed during an attempted vacuum distillation and when spotted on silica gel thin-layer chromatographic plates, did not move with non-polar or polar solvents. (Found: C, 44.16; H, 8.12; Sn, 33.81; mol. wt. in benzene, 738. $C_{13}H_{28}O_3Sn$ calcd.: C, 44.46; H, 8.04; Sn, 33.81%; mol. wt., 251.)

Acetylation of acetoxyl(3-hydroxypropyl)di-n-butyltin

The acetylation of acetoxyl(3-hydroxypropyl)di-*n*-butyltin was carried out by a method described by Shriner¹¹ using sodium acetate and acetic anhydride. The resulting crystals were purified by sublimation 120°/0.0075 mm; m.p. 41–42°; one spot, TLC (ethanol). (Found: C, 44.98; H, 7.89; Sn, 30.56; mol. wt. in carbon tetrachloride, 379. $C_{15}H_{20}O_4Sn$ calcd.: C, 45.84; H, 7.69; Sn, 30.20%; mol. wt., 393.)

Preparation of bis(allylthio)di-n-butyltin

(a). The reaction mixture of allyl mercaptan (12.5 g, 0.17 mole), di-*n*-butyltin dihydride (20.0 g, 0.085 mole) and 20 mg (AIBN) was heated at 60° for 10 h; a slow evolution of gas was observed. The product was distilled at 134–135°/0.075 mm; 5.0 g, (15% yield); one spot to TLC (benzene). A large percentage of bis(allylthio)di-*n*-butyltin polymerized during the distillation. (Found: C, 44.14; H, 7.90; S, 16.82; Sn, 31.27; mol. wt. in benzene, 374. $C_{14}H_{28}S_2Sn$ calcd.: C, 44.34; H, 7.44; S, 16.91; Sn, 31.30%; mol. wt., 379.)

(b). To a mixture of 5.8 g sodium hydride oil dispersion (50% concentration 0.12 mole) in 150 ml of anhydrous benzene, allyl mercaptan (9.0 g, 0.12 mole) was added dropwise during 30 minutes. The sodium mercaptide was heated at 55° for 0.5 h. The reaction mixture was stirred at room temperature for 1 h, then at 55° for 0.5 h. To the ice-cooled reaction mixture, 50 ml of water was added dropwise. The reaction mixture was filtered and the residue was washed thoroughly with benzene. The combined benzene portions were thoroughly washed with water, and the benzene extract dried over sodium sulfate. Yield 2.7 g (12%) of pure bis(allylthio)di-*n*-butyltin was obtained by distillation at 134–135°/0.075 mm.

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SUMMARY

The hydroxyl groups of allyl, crotyl and cinnamyl alcohol and the mercapto group of allyl mercaptan, are shown to be the main reaction sites for di-*n*-butyltin dihydride. Allyl alcohol, however, undergoes a competitive stepwise hydrostannation, typically anti-Markownikoff in nature, resulting in ring compound formation.

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