DECOMPOSITION STUDIES AND ADDITION REACTIONS OF TRIPHENYLTIN HYDRIDE*

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INTRODUCTION

The mechanisms of the addition reactions of organotin hydrides to unsaturated compounds has been the subject of considerable speculation[1-14,23]. An ionic mechanism was proposed on the basis of the observations that free radical inhibitors such as hydroquinone failed to inhibit the addition of triphenyltin hydride to styrene[2] and that benzoyl peroxide did not catalyze the addition of triphenyltin hydride to 1-octene[9].

In support of a free radical mechanism, it has been shown that the addition of alkyltin hydrides to olefins is promoted by ultraviolet light and by free radical catalysts[10-12,14]. Also, free radical inhibitors retarded the addition of triethyltin hydride to 1-octene and to styrene[23].

We have investigated the decomposition reactions of triphenyltin hydride and have studied the influence of free sources and of free radical inhibitors upon the addition of triphenyltin hydride to olefins. Our results suggest that both the decomposition reactions and the addition reactions are of a homolytic nature.

RESULTS

In order to distinguish those factors promoting the addition of triphenyltin hydride to double bonds from those causing decomposition of the hydride, comparable experiments were made in 1-octene solution and in *n*-octane solution. It was found that the triphenyltin hydride content of the reaction mixtures could be measured by means of the intensity of the infrared absorption band at 5.4 microns (1850 cm^{-1}) due to Sn–H stretching. A typical calibration curve is shown in Fig. 1.

Except where noted, reactions were run in sealed tubes. In a given series, several identical samples were subjected to the same treatment and the progress of the reactions were followed by means of infrared measurements. The ultimate course of the reactions was determined by separation and identification of the products.

Fig. 2 shows the influence of a commercial antioxidant on the rate of disappearance of triphenyltin hydride in 1-octene solutions at various temperatures. At 25°, the inhibitor effectively prevents the reaction of triphenyltin hydride for more

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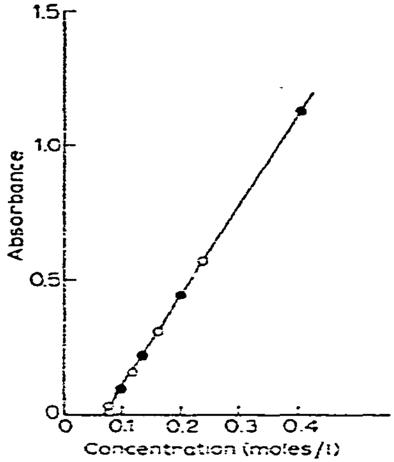

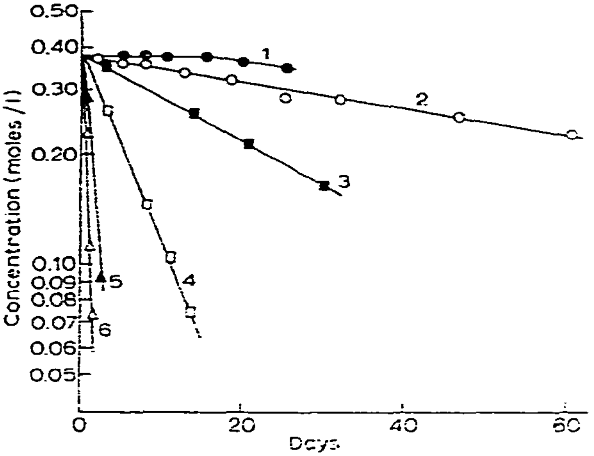

Fig. 1. Calibration curve for triphenyltin hydride solutions in: (○), 1-octene; (●), *n*-octane. Absorbance at 1850 cm^{-1}, (log I_0/I), *vs.* molar concentration. Sample thickness 0.2 mm.

Fig. 2. Influence of temperature and of inhibitor on the stability of $(C_6H_5)_3SnH$. Solutions aged for 5 days, sample tubes sealed in air. (○, □, △). No added inhibitor; (●, ■, ▲). 5% 2,2′-methylene-bis (4-ethyl-6-*tert*-butylphenol) added. (○, ●), 25°; (□, ■), 80°; (△, ▲), 120°.

than twenty days (curve 1). At 80°, the inhibitor retards the reaction (curve 3) compared to samples containing no inhibitor (curve 4). At 120°, there is essentially no difference between samples with and without inhibitor (curves 5 and 6). In all of these cases, the decrease of triphenyltin hydride concentration with time is logarithmic. Analyses of the reaction mixtures from the experiments run at 80° and at 120° revealed hexaphenylditin and the addition product, *n*-octyltriphenyltin.

Fig. 3 shows the results of aging the solutions of triphenyltin hydride at room temperature prior to reaction in 1-octene at 80°. Curve 1 represents the behavior of a freshly prepared solution. Curves 2 and 3 show the decay of solutions which had stood for 5 days and for 21 days, respectively, before heating. The rate of decay is faster in the aged solutions but in all cases the decay is logarithmic.

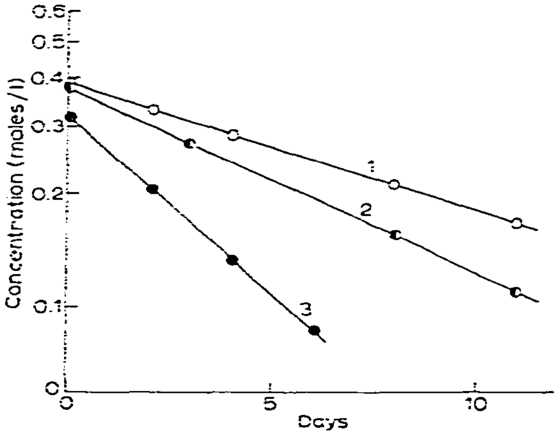

Fig. 3. Effect of aging on the reactivity of $(C_6H_5)_3SnH$ in octene solution at 80°. Sample tubes sealed in air; no added inhibitor. (1), Fresh solution; (2), aged 5 days; (3), aged 21 days.

Two sets of sample tubes were prepared from a stock solution of triphenyltin hydride in 1-octene. One set of tubes was purged of oxygen by bubbling in dry nitrogen for about 30 minutes prior to sealing. The other set was sealed in air. Similarly, four sets of tubes were prepared from a stock solution of triphenyltin hydride in *n*-octane. Two of these sets were purged with nitrogen and two sets were sealed in air. The tubes were then heated at 80° or at 120° and analyzed periodically. The results are shown in Fig. 4.

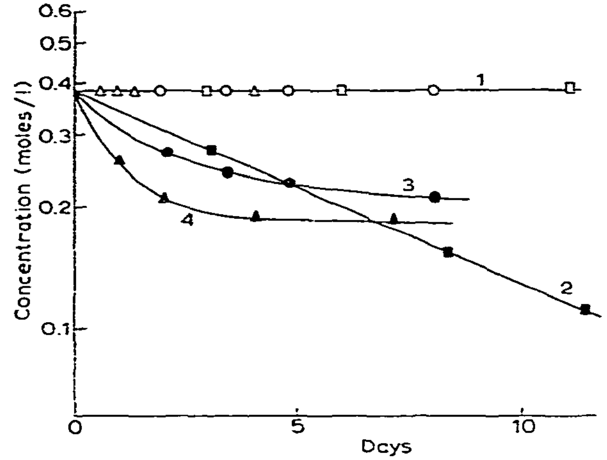

Fig. 4. Effect of oxygen on $(C_6H_5)_3SnH$ stability. (○, □, △), Samples purged with nitrogen before sealing; (●, ■, ▲), samples sealed in air. (□, ■), 1-Octene solns. at 80°; (○, ●), *n*-octane solns. at 80°; (△, ▲), *n*-octane solns. at 120°.

All of the samples which had been purged with nitrogen showed no loss of triphenyltin hydride in 11 days (curve 1). The 1-octene solutions which had been sealed in air showed a logarithmic decay (curve 2). On the other hand, the *n*-octane samples which were sealed in air showed an initial rapid decrease in hydride content but after a few days there was no further change (curves 3 and 4). Hexaphenylditin and *n*-octyltriphenyltin were isolated from the 1-octene solutions. In the octane solutions, the major product was hexaphenylditin.

The role of oxygen was further demonstrated in preparative scale experiments. Hexaphenylditin was the only product formed when dry oxygen gas was passed into solutions of triphenyltin hydride in absolute alcohol and in *n*-octane at room temperature for about three days. When oxygen was passed into a *n*-octane solution of the hydride at 125°, for 24 hours, hexaphenylditin, tetraphenyltin and some gray infusible materials were formed.

The results of experiments with free radical catalysts are shown in Fig. 5. The reaction mixtures were purged with nitrogen prior to heating at 80°. Curve 1 of Fig. 5 shows that samples containing no catalyst were not changed after 6 days. Samples containing azobisisobutyronitrile underwent a logarithmic decrease in hydride concentration (curves 3 and 4). In these cases the products were *n*-octyltriphenyltin from the 1-octene solution and hexaphenylditin from the *n*-octane solution. Samples containing benzoyl peroxide decreased in hydride content in a non-logarithmic manner (curve 2). After six days, the only materials isolated were unreacted triphenyltin hydride and solid products which were not identified.

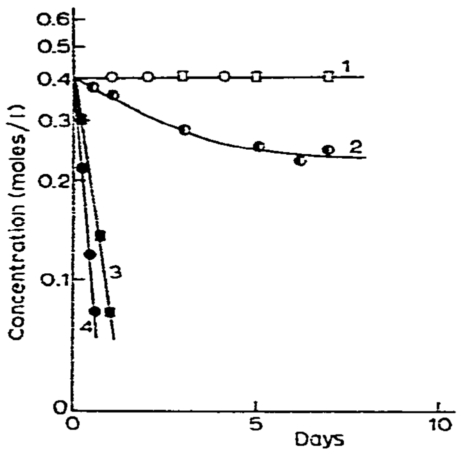

Fig. 5. Influence of free radical catalysts on the reactivity of $(C_6H_5)_3SnH$ at 80°. 0.05 moles of catalyst per mole of hydride; samples purged with nitrogen. (○, □), No added catalyst; (◑), added benzoyl peroxide; (●, ■), added azobisisobutyronitrile. (○, ◑, ●), *n*-Octane solns. (□, ■), 1-octene solns.

TABLE 1

DECOMPOSITION OF TRIPHENYLTIN HYDRIDE IN PRESENCE OF FREE RADICAL CATALYSTS IN REFLUXING SOLVENTS FOR TWENTY HOURS[a]

Solvent	*Catalyst*[b]	*Moles catalyst/ Mole hydride*	*Products isolated*
n-hexane	A	0.052	None. Decomposition was negligible
n-hexane	A	0.52	1,1,2,2-tetraphenyl-1,2-dibenzoyloxyditin, triphenyltin benzoate
n-hexane	B	0.052	hexaphenylditin, tetraphenyltin, polymers
benzene	B	0.052	hexaphenylditin, tetraphenyltin, polymers
benzene	B	0.52	hexaphenylditin, tetraphenyltin, polymers
n-octane[c]	C	—	hexaphenylditin, tetraphenyltin, polymers

[a] Initial concentration of solutions is 0.54 *M*. [b] A = benzoyl peroxide; B = azobisisobutyronitrile; C = ultraviolet radiation. [c] Reaction temperature 25–50°; decomposition was complete in 10 h.

Preparative scale decomposition reactions of triphenyltin hydride in the presence of free radical sources are summarized in Table 1. With a catalytic amount of benzoyl peroxide, there was no reaction of triphenyltin hydride in refluxing hexane in 20 hours. When a stoichiometric quantity of benzoyl peroxide was used, the products obtained were triphenyltin benzoate and 1,1',2,2'-tetraphenyl-1,2-dibenzoyloxyditin along with some polymeric material. In the presence of azobisisobutyronitrile in either hexane or benzene, triphenyltin hydride reacted to give hexaphenylditin, tetraphenyltin and a trace of polymers. Ultraviolet light also promoted the formation of hexaphenylditin and tetraphenyltin from triphenyltin hydride in *n*-octane solution.

Preparative scale addition reactions of triphenyltin hydride to olefins are summarized in Table 2. With no catalyst other than air, considerable hexaphenylditin was formed although some addition to 1-octene did occur at 120°. Quantitative yields of addition products were obtained at or near room temperature when triphenyltin

TABLE 2

FREE RADICAL CATALYZED ADDITION OF TRIPHENYLTIN HYDRIDE TO VARIOUS OLEFINS[a,b]

Olefin	*Catalyst*	*Temp. (°C)*	*Reaction time (hours)*	*Products isolated*	*% Yield of addition product*
1-octene	none- air present	75	13	Hexaphenylditin	0
1-octene	none, air present	120	31	Hexaphenylditin, octyltriphenyltin	50
1-octene	azobisisobutyronitrile	40	17	octyltriphenyltin	100
1-octene	ultraviolet light	25–50	18	octyltriphenyltin	100
1-pentene	ultraviolet light	25–50	18	pentyltriphenyltin	100
1-hexene	ultraviolet light	25–50	18	hexyltriphenyltin	100
1-heptene	ultraviolet light	25–50	18	heptyltriphenyltin	100
1-nonene	ultraviolet light	25–50	18	nonyltriphenyltin	100
cyclohexene	none, air present	83	24	hexaphenylditin	0
cyclopentene	ultraviolet light	25–40	24	hexaphenylditin	0
cyclohexene	ultraviolet light	25–40	24	hexaphenylditin	0

[a] 15 mmoles of triphenyltin hydride added to an excess of olefin. [b] All reactions run under nitrogen atmosphere except where noted.

hydride was reacted with α-olefins in the presence of azobisisobutyronitrile or ultraviolet light. On the other hand, when triphenyltin hydride was reacted with an excess of cyclic olefin, no addition reaction was observed.

It was found that free radical inhibitors were effective in retarding the addition reaction. For example, triphenyltin hydride reacted with styrene at 80°, without catalysts, to give a quantitative yield of phenethyltriphenyltin in 24 hours. However when a small quantity of the monomethyl ether of hydroquinone was added to a mixture of triphenyltin hydride and styrene, it required 48 hours at 80° to achieve a quantitative reaction.

DISCUSSION

The results presented here support the conclusion that both the decomposition reactions of triphenyltin hydride and the addition of triphenyltin hydride to olefins proceed via free radical mechanisms. The logarithmic curves obtained in Fig. 2, 3 and 4 suggest that triphenyltin hydride reacts in an excess of olefin according to a "pseudo first order" rate law. This would be expected for a free radical chain mechanism as is represented by the following equations:

$$(C_6H_5)_3SnH \longrightarrow (C_6H_5)_3Sn^\bullet + H^\bullet$$

$$(C_6H_5)_3Sn^\bullet + H_2C{=}CHR \longrightarrow (C_6H_5)_3SnCH_2CHR^\bullet$$

$$(C_6H_5)_3SnCH_2CHR^\bullet + (C_6H_5)_3SnH \longrightarrow (C_6H_5)_3SnCH_2CH_2R + (C_6H_5)_3Sn^\bullet$$

Hexaphenylditin results from the coupling of two triphenyltin free radicals. This occurs in solvents which do not undergo addition reactions as is shown in Table 2 and in the experiment in which ethyl alcohol was the solvent. Likewise, in the attempted additions to cyclic olefins, the rate of coupling was faster than the rate of addition to the internal double bonds.

Gilman and Eisch[9] have postulated that triphenyltin radicals may disproportionate into tetraphenyltin, diphenyltin and tin. Thus the formation of tetraphenyltin along with infusible solids is further evidence of a free radical mechanism for the decomposition of triphenyltin hydride.

The results obtained in this investigation confirm a previously given explanation of why benzoyl peroxide does not catalyze the addition of triphenyltin hydride to olefins[19]. Free radicals from benzoyl peroxide react to give benzoic acid as follows;

$$C_6H_5COO^\bullet + (C_6H_5)_3SnH \longrightarrow C_6H_5COOH + (C_6H_5)_3Sn^\bullet$$

Side reactions of benzoic acid with triphenyltin hydride are fast compared to the addition reaction and the products obtained are triphenyltin benzoate and 1,1',2,2'-tetraphenyl-1,2-dibenzoyloxyditin.

$$C_6H_5COOH + 2(C_6H_5)_3SnH \longrightarrow C_6H_5COOSn(C_6H_5)_3 + H_2$$

$$2C_6H_5COOH + 2(C_6H_5)_3SnH \longrightarrow [(C_6H_5)_2SnOOCC_6H_5]_2 + 2C_6H_6 + H_2$$

Also triphenyltin benzoate may be formed by means of the chain termination reaction,

$$C_6H_5COO^\bullet + (C_6H_5)_3Sn^\bullet \longrightarrow C_6H_5COOSn(C_6H_5)_3$$

Comparison of these results with those of Neumann and Sommer[23] suggests that triphenyltin free radicals are less susceptible to chain termination and undergo addition to olefins more readily than trialkyltin radicals. Thus the catalyzed addition of triphenyltin hydride to 1-octene proceeded smoothly to completion while in the case of the analogous reaction using triethyltin hydride, it required several charges of catalyst to maintain the reaction.

Free radical inhibitors effectively stop the addition of triethyltin hydride to olefins, whereas, at higher temperatures, the rate of addition of triphenyltin hydride to styrene is comparable to the rate of the inhibition reaction. Therefore addition is observed in the latter case.

EXPERIMENTAL

Instrumental methods and reagents

An Aerograph Chromatograph, Model A-100 was used to monitor the purity of the liquid reagents. Infrared measurements were made on a Perkin-Elmer Model 137-B spectrometer using NaCl optics. Microanalyses for C, H, and Sn were made at the Central Research Laboratories of the Interchemical Corporation.

Reagent chemicals were obtained from commercial sources and, where necessary, appropriately purified. Azobisisobutyronitrile, (Dupont, "Vazo"), and benzoyl peroxide, (Lucidol Corp.), were used as free radical catalysts. The inhibitor used in the sealed tube studies was 2,2'-methylenebis(4-ethyl-6-*tert*-butylphenol), (Cyanamid, "Anti-oxide 425").

Triphenyltin hydride and authentic samples of possible addition products of triphenyltin hydride to olefins were prepared by established procedures[2,9,16]. Two hitherto unreported compounds were prepared: cyclopentyltriphenyltin, m.p. 111–

112° (Found: C, 65.81; H, 5.68; Sn, 28.73. $C_{23}H_{24}Sn$ calcd.: C, 65.87; H, 5.73; Sn, 28.40 %.); *n*-pentyltriphenyltin, b.p. 209°/2 mm, n_D^{21} 1.5985 (Found: C, 65.43; H, 6.23; Sn, 28.15. $C_{23}H_{26}Sn$ calcd.: C, 65.56; H, 6.18; Sn, 28.26 %.).

Standardization of triphenyltin hydride solutions

Triphenyltin hydride was dissolved in 1-octene to give a 0.395 molar stock solution. Aliquots were diluted with 1-octene to obtain concentrations of 0.237, 0.158 and 0.079 molar, respectively. The absorbances of the solutions at 5.4 microns (1850 cm^{-1}) were measured against an appropriate thickness of 1-octene. Solutions of triphenyltin hydride in *n*-octane were prepared and measured similarly. Points for both types of solution fell on the same straight line.

Stability studies

The following general procedure was used to obtain the data shown in Figs. 2, 3, 4 and 5. Two-ml samples of the stock solutions were introduced into drawn pyrex tubes and, in appropriate cases, the tubes were purged with dry nitrogen for about 30 minutes prior to sealing. After various times in a constant temperature oven, the tubes were opened and the contents analyzed for unreacted triphenyltin hydride by infrared spectroscopy. A small amount of benzene was added to the reaction mixture and polymeric material (or metallic tin) was removed by filtration. The filtrate was then digested with charcoal, filtered and the solvent was removed by evaporation at room temperature. The residue was extracted with cold anhydrous methyl alcohol in order to remove soluble products from any hexaphenylditin or tetraphenyltin. Tetraphenyltin was then separated from hexaphenylditin by fractional crystallization from hot benzene. The separation could also be made by vacuum sublimation as tetraphenyltin is quite volatile. The identities of the reaction products were confirmed by mixed melting with authentic samples.

Reaction of triphenyltin hydride solutions with oxygen

Into separate flasks containing 5 ml of absolute ethyl alcohol and 5 ml of *n*-octane, respectively, were put 6.9 g (19.7 mmoles) samples of triphenyltin hydride. Dry oxygen gas was bubbled through the solutions at room temperature for 3 days. Infrared analysis revealed that considerable unreacted triphenyltin hydride remained. The precipitates formed were shown to be hexaphenylditin by mixed melting with authentic material and by tin analysis. (Found: Sn, 33.85. $C_{36}H_{30}Sn$ calcd.: 34.0 %.) No tetraphenyltin was detected in either reaction mixture. A total of 1.3 g of hexaphenylditin was obtained from the ethanol solution. The alcohol filtrate was treated with carbon tetrachloride and 4.5 g of triphenyltin chloride was obtained. Thus 15.5 mmoles of the initial triphenyltin hydride was accounted for.

In another experiment, oxygen was bubbled through a solution of 6.9 g of triphenyltin hydride in refluxing *n*-octane for 24 hours. The precipitate formed weighed 2.5 g and consisted of hexaphenylditin, tetraphenyltin and a small amount of gray infusible material.

Catalyzed decomposition reactions

In a typical experiment, 4.75 g (13.5 mmoles) of triphenyltin hydride and 0.1 g (0.7 mmole) of azobisisobutyronitrile in 50 ml of hexane was refluxed under a nitrogen atmosphere for 20 h. Work-up of the precipitate formed yielded 0.01 g of gray polymeric material, 0.35 g (0.82 mmole) of tetraphenyltin and 3.0 g (4.35 mmoles) of hexaphenylditin.

A reaction mixture consisting of 4.75 g (13.5 mmoles) of triphenyltin hydride in 50 ml of *n*-octane under nitrogen was irradiated with light of 3130–3600 Å wavelength from a Hanovia quartz mercury vapor lamp. During the irradiation, the temperature rose to 50°. After 10 h no unreacted hydride remained. Decomposition products found included 0.1 g of polymeric material, 0.2 g (0.47 mmole) of tetraphenyltin and 3.3 g (4.7 mmoles) of hexaphenylditin.

Reaction of triphenyltin hydride with benzoyl peroxide

A mixture of 4.75 g (13.5 mmoles) of triphenyltin hydride and 0.163 g (0.7 mmoles) of benzoyl peroxide in 50 ml of hexane were refluxed under a nitrogen atmosphere, in the dark, for 20 h. No precipitate was observed and triphenyltin hydride was quantitatively recovered.

In a second experiment, 4.75 g (13.5 mmoles) of triphenyltin hydride and 1.63 g (7 mmoles) of benzoyl peroxide in 50 ml of hexane was heated for 30 h at reflux. Infrared analysis revealed no unreacted hydride. Filtration yielded 1.7 g of crude 1,1′,2,2′-tetraphenyl-1,2-dibenzoyloxyditin[18, 19]. Recrystallization from benzene gave a melting point of 184–185°. (Found: Sn, 30.20. $C_{38}H_{30}O_4Sn_2$ calcd.: Sn, 30.13%. $C_{25}H_{20}O_2Sn$ calcd.: Sn, 25.2%.)

Addition reactions

A mixture of 3.5 g of triphenyltin hydride and 30 ml of 1-octene were heated at 75°, in air, for 13 h. Complete decomposition of the hydride occurred. The only product was 3.4 g of hexaphenylditin.

Identical quantities of reactants to those described above were heated at 120°, in air, for 31 h. The reaction mixture was filtered and the solvent was removed by evaporation. The residue was extracted with absolute methyl alcohol to obtain 2.3 g of *n*-octyltriphenyltin. The insoluble material was 1.5 g of hexaphenylditin.

In a third experiment, 5.3 g (15 mmoles) of triphenyltin hydride, 0.15 g of azobisisobutyronitrile and 50 ml of 1-octene were reacted under nitrogen at 40° for 17 h. Upon evaporation of the excess octene from the clear reaction mixture, 6.5 g (14 mmoles) of *n*-octyltriphenyltin (m.p. 54°) was obtained.

In a fourth experiment, 15 mmoles of triphenyltin hydride and 50 ml of 1-octene, under nitrogen, were irradiated with ultraviolet light for 18 h. During the irradiation, the temperature rose to about 50°. Upon evaporation of the excess 1-octene, *n*-octyltriphenyltin was obtained in quantitative yield.

Ultraviolet-catalyzed addition of 15 mmoles of triphenyltin hydride to an excess of α-olefin resulted in quantitative yields of products whose physical properties agreed with literature values and whose identities were confirmed by analysis for C, H and Sn. Thus prepared were *n*-pentyltriphenyltin (a new compound), *n*-hexyltriphenyltin[20], *n*-heptyltriphenyltin[21], and *n*-nonyltriphenyltin[22].

Attempts were made to add triphenyltin hydride to cyclopentene and to cyclohexene. Irradiation of the reaction mixtures with ultraviolet light for 24 h resulted in complete reaction of the hydride. However, hexaphenylditin was the only product obtained.

Inhibition of the addition reaction

A mixture of 10 mmoles of triphenyltin hydride, 30 ml of 1-octene and 0.2 g of hydroquinone was heated in air at 120° for 31 h. Unreacted triphenyltin hydride and 0.01 g of impure hexaphenylditin was recovered.

In another experiment, 10 mmoles of triphenyltin hydride was heated with 30 ml of 1-octene in the presence of 0.2 g of the monomethyl ether of hydroquinone for 70 hours at 120°. Products obtained were 3.1 mmoles of hexaphenylditin and 3.9 mmoles of *n*-octyltriphenyltin.

Two separate reaction mixtures were prepared each containing 4.2 g (40 mmoles) of purified styrene and 7.0 g (20 mmoles) of triphenyltin hydride. To one of the mixtures was added 0.2 g of the monomethyl ether of hydroquinone. The progress of the reactions at 80° was monitored by infrared analysis. After 24 h, the sample containing no inhibitor yielded 7.4 g (16.3 mmoles) of phenethyltriphenyltin[2]. It required 48 h for complete reaction of triphenyltin hydride in the sample-containing inhibitor. The addition product was also obtained in this case. Thus the rate of the addition reaction had been retarded but not stopped completely.

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SUMMARY

In octane, benzene or ethyl alcohol solution, at 80–120°, triphenyltin hydride decomposes by a free radical mechanism. Hexaphenylditin and tetraphenyltin are the principal products obtained. The decomposition is accelerated by oxygen, free radical catalysts and by products formed when triphenyltin hydride solutions are aged in air for several days at room temperature. The decomposition reaction is retarded by the addition of anti-oxidants or by removal of air from the system.

The addition of triphenyltin hydride to olefins also proceeds via a free radical mechanism. Additions to several α-olefins are described. Hydroquinone and the methyl ether of hydroquinone retard the addition reaction. Attempts to add triphenyltin hydride to cyclic olefins were not successful.

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