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PREPARATION AND STABILITY OF SOME ORGANOTIN AND ORGANOLEAD COMPOUNDS

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The free-radical-catalyzed addition of various reagents to olefins has been extensively studied by Kharasch (1), Sommer (2) and their co-workers. Subsequently, the addition of trichlorosilane to olefins received wide attention (2-4). More recently, triphenylsilane was found to react in a similar manner with undecenoic acid (5), and with higher olefins (6) to yield long-chained organosilicon compounds.

In the present investigation some unsaturated organotin and organolead compounds were prepared and their ability to add triphenylsilane or triphenylgermane was examined. In addition, the photo- and thermo-stability of triphenyltin hydride and other tin and lead compounds was studied.

The general method of synthesizing the olefinic organometallic compounds was the interaction of the phenylmetallic halide with the olefinic organolithium or Grignard reagent. The synthetic scheme may be illustrated by the preparation of triphenylallyltin:

 $(\mathrm{C}_6\mathrm{H}_{\mathfrak{s}})_3\mathrm{SnCl} + \mathrm{CH}_2 = \mathrm{CHCH}_2\mathrm{MgBr} \rightarrow (\mathrm{C}_6\mathrm{H}_{\mathfrak{s}})_3\mathrm{SnCH}_2\mathrm{CH} = \mathrm{CH}_2 + \mathrm{MgBrCl}.$

Besides triphenylallyltin, diphenyldiallyltin, diphenyldi-4-pentenyltin and triphenylallyllead (7) were successfully prepared by this method. The attempted preparation of diphenyldiallyllead confirmed the observation of Towne (8) that the compound was too unstable to be characterized. The preparation of triphenyl-4-pentenyltin also proved troublesome. In the interaction of 4-pentenyl-lithium and triphenyltin chloride a sizable quantity of tetraphenyltin was formed. In a modification, cleavage of the product was avoided by employing 4-pentenyl-magnesium bromide, but attempts to purify the product by distillation caused disproportionation into tetraphenyltin.

The proposed addition of triphenylsilane (or triphenylgermane) would conceivably go thus with triphenylallyltin:

$$(C_{\mathfrak{e}}H_{\mathfrak{s}})_{\mathfrak{s}}\operatorname{SnCH}_{2}\operatorname{CH}=\operatorname{CH}_{2} + (C_{\mathfrak{e}}H_{\mathfrak{s}})_{\mathfrak{s}}\operatorname{SiH} \xrightarrow{\operatorname{Bz}_{2}O_{2}} (C_{\mathfrak{e}}H_{\mathfrak{s}})_{\mathfrak{s}}\operatorname{Sn}(\operatorname{CH}_{2})_{\mathfrak{s}}\operatorname{Si}(C_{\mathfrak{e}}H_{\mathfrak{s}})_{\mathfrak{s}}$$

Such an addition was also attempted with diphenyldiallyltin, triphenylallyllead, and diphenyldi-4-pentenyltin. In none of the cases examined, however, was any addition product isolated. After removal of the large excess of triphenylsilane by vacuum distillation, the residue yielded only starting material, together with thermal decomposition products, M and $(C_6H_5)_4M$ [M = Sn or Pb].

The behavior of triphenyltin hydride in such a free-radical type addition was also of interest. The compound could be prepared in 53-58% yield by reducing triphenyltin chloride with lithium aluminum hydride by the method of Wittig (9). Previous attempts using triphenyltin chloride by workers in these laboratories were unsuccessful, and the starting material was recovered in good yield (10).

The pure triphenyltin hydride, unfortunately, was too unstable to be used in such a free-radical type addition. Other workers (11) have shown that this compound must be stored under nitrogen to prevent the oxidation:

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$$(C_6H_5)_3SnH + O_2 \rightarrow 2 (C_6H_5)_3SnSn(C_6H_5)_3 + 2 H_2O$$

It was found, however, that even if the distillation and storage of the hydride were performed under oxygen-free nitrogen, the liquid hydride slowly deposited a gray solid upon exposure to light. The solid was identified as a mixture of tetraphenyltin and metallic tin. These substances also resulted from an attempted distillation of a sample which had stood exposed to light in ether solution for some time. A possible course of decomposition consistent with these observations is as follows:

$$(C_{6}H_{\delta})_{2}SnH \xrightarrow{h^{\nu} \text{ or Heat}} (C_{6}H_{\delta})_{3}Sn \cdot + H \cdot$$

$$2 (C_{6}H_{\delta})_{3}Sn \cdot \longrightarrow (C_{6}H_{\delta})_{2}Sn + (C_{6}H_{\delta})_{4}Sn$$

$$\xrightarrow{h^{\nu} \text{ or Heat}}$$

$$2 (C_{6}H_{\delta})_{2}Sn \xrightarrow{\text{Heat}} (C_{6}H_{\delta})_{4}Sn + Sn$$

In order to determine whether the decomposition would be facilitated by the presence of free radicals, the hydride and a small amount of benzoyl peroxide dissolved in hexane were irradiated with an ultraviolet lamp. In a short time the walls of the flask were covered with tetraphenyltin. Its amount was small, and no tin was formed. In the light of this the reaction may be written thus:

 $(C_6H_5)_3Sn \bullet \xrightarrow{C_6H_5 \bullet} (C_6H_5)_4Sn$

However, when triphenyltin hydride was refluxed in hexane solution with onehalf an equivalent of benzoyl peroxide, a solid was obtained which melted at 82-84°. This was shown to be the hitherto unknown triphenyltin benzoate by mixture melting point with an authentic specimen. The latter was prepared from triphenyltin iodide and sodium benzoate.

The other solid obtained from the peroxide reaction mixture was an organotin compound melting at 184–185° and analyzing for 30.41% tin. Although the colorless compound formed a bright yellow solid (m.p. > 360°) with sodium hydroxide, its infrared spectrum showed no carbonyl band and only a doubtful

hydroxyl band. There were bands indicative of mono- and di-substituted benzene rings, (probably *para*) however. Since it is possible that triphenyltin benzoate was formed in this manner:

$$\begin{array}{cccccccc} & & & & O \\ & & & \parallel \\ (C_6H_5)_5Sn_{\bullet} & + & C_6H_5C_{\bullet}O_{\bullet} & \longrightarrow & C_6H_5C_{\bullet}OSn(C_6H_5)_3 \end{array}$$

other conceivable products were considered in order to identify the unknown. It was shown not to be *p*-carboxyphenyltriphenyltin, tetraphenyltin, hexaphenylditin, diphenyltin oxide, triphenyltin oxide, or any mixture of these.

The thermal stabilities of the olefinic tin and lead compounds were investigated. It was mentioned that diphenyldiallyllead could not be purified due to its instability. Lead separated from the reaction mixture during its preparation and the clear, ethereal solution of the product deposited a brown, organolead solid and triphenylallyllead (8). When the crude diphenyldiallyllead was heated to 150°, lead, tetraphenyllead, and a liquid having the odor of diallyl were formed:

$$2 (C_6H_5)_2Pb(CH_2CH=CH_2)_2 \xrightarrow{} (C_6H_5)_4Pb + Pb$$

The difference in the stabilities of triphenylallyltin and triphenylallyllead was marked. The tin compound decomposed over the range $305-310^{\circ}$, whereas the lead compound decomposed over the range $165-175^{\circ}$ when both were heated at the same rate. In the tin series it might be noted that diphenyldi-4-pentenyltin could be smoothly vacuum-distilled but triphenyl-4-pentenyltin disproportionated upon distillation into tetraphenyltin.

EXPERIMENTAL

All operations involving free-radical reactions or organolithium and organomagnesium compounds were run in an oxygen-free nitrogen atmosphere. All melting points are corrected. The tin analyses were performed according to a recent procedure (12).

Starting materials. The tetraphenyltin was obtained from the Hooker Electrochemical Company. This was converted into triphenyltin chloride (13) and diphenyltin dichloride (14) by published procedures. The tetraphenyllead was prepared by the interaction of lead chloride and iodobenzene with phenylmagnesium bromide (15). This product was used to obtain triphenyllead chloride (16) and diphenyllead dibromide. The latter was made by adapting the directions given for the chloride (16).

Diphenyldiallyltin. Allylmagnesium bromide was prepared in an 84% yield by the addition of 40.8 g. (0.336 mole) of allyl bromide in 190 ml. of dry ether to 48.9 g. (2.02 g.-atoms) of magnesium turnings suspended in dry ether over the course of 2 hours (17). The reagent was analyzed by titration of an aliquot with standard acid (18). To 0.10 mole of the allylmagnesium bromide so prepared were added 17.2 g. (0.050 mole) of diphenyltin dichloride in 50 ml. of dry ether over 50 minutes. The addition was accompanied by smooth reflux and the formation of a white, gelatinous precipitate. After 1.5 hours of stirring Color Test I was negative (19). The reaction mixture then was hydrolyzed by pouring into cold ammonium chloride solution. The separated ether layer was dried over sodium sulfate and the ether was removed. The residue was distilled under a vacuum and a colorless fraction taken at 173-174° (5.5 mm.), n_p^{20} 1.6025. This weighed 12.5 g. and was a 70.3% yield.

Anal. Cale'd for C₁₈H₂₀Sn: Sn, 33.43. Found: Sn, 33.35, 33.29.

Triphenylallyltin. To 0.10 mole of allylmagnesium bromide in 190 ml. of dry ether was added 27.0 g. (0.0700 mole) of dry, powdered triphenyltin chloride by means of a rubber tube connecting a solids vessel to the flask. The addition required 30 minutes and a lively

reaction ensued. After stirring for 2 hours the reaction mixture was worked up in the usual manner. After drying the ether layer and removing the solvent there remained a pale yellow oil. This was refluxed with 100 ml. of petroleum ether (b.p. 77-115°) and then refrigerated. Filtration of the ether and concentration of the mother liquor gave a total yield of 24.0 g. (87.5%), melting at 73-75°. The analytical sample was obtained from 95% ethanol as colorless prisms and melted at 73.5-74.5°.

Anal. Calc'd for C₂₁H₂₀Sn: Sn, 30.34. Found: Sn, 30.21, 30.22.

Diphenyldi-4-pentenyltin. 4-Pentenyllithium was prepared in a 63% yield from 29.8 g. (0.200 mole) of 1-bromo-4-pentene and 3.1 g. (0.450 g.-atom) of lithium wire by following the directions for the preparation of *n*-butyllithium (20) and analyzing it by the double titration method (21). To 0.0550 mole of 4-pentenyllithium in 70 ml. of dry ether were added 8.6 g. (0.025 mole) of diphenyltin dichloride in 50 ml. of dry ether over 25 minutes. Lively reflux occurred and a white precipitate appeared. Stirring was continued for 1 hour and the reaction mixture was worked up in the usual manner (No tetraphenyltin was isolated; see below). The pale yellow liquid remaining after removal of the ether was distilled under a vacuum, and 5.9 g. (57.2%) were collected at 173-176° (1.5 mm.), n_p^{20} 1.5598. The analytical sample was obtained by redistilling and taking a fraction at 174-175° (1.5 mm.).

Anal. Calc'd for C₂₂H₂₈Sn: Sn, 28.87. Found: Sn, 28.97, 28.62.

Triphenyl-4-pentenyltin. The attempted preparation of this compound by the procedure used for diphenyldi-4-pentenyltin was unsuccessful due to extensive cleavage of the product by the organolithium compound. Use of the Grignard reagent did not cleave the product, but attempted purification by distillation caused disproportionation.

Using 4-pentenyllithium. To 19.3 g. (0.050 mole) of triphenyltin chloride partially dissolved in 100 ml. of dry ether was added 0.060 mole of 4-pentenyllithium in 70 ml. of dry ether over the course of 40 minutes. Gentle reflux occurred and a precipitate settled out of the pale yellow mixture. Hydrolysis with ammonium chloride solution left a white suspension. The solid was filtered off and dried. It weighed 4.5 g. and melted at 220-224°. Recrystallized from chloroform-petroleum ether (b.p. 77-115°) it gave glistening white needles melting at 227.0-228.5°. A mixture with authentic tetraphenyltin melted undepressed.

Attempted work-up of the ether solution by removal of the ether and vacuum-distillation of the residue gave a main fraction weighing 10.5 g. and boiling over the range 173-194° (2.5 mm.). This upon cooling gave more tetraphenyltin but no other solid.

Using 4-pentenylmagnesium bromide. 4-Pentenylmagnesium bromide was prepared in a 91% yield from 14.8 g. (0.0994 mole) of 1-bromo-4-pentene and 14.1 g. (0.595 g.-atom) of magnesium turnings in accordance with the directions for preparing allylmagnesium bromide (17). To 29.0 g. (0.0752 mole) of triphenyltin chloride suspended in 150 ml. of dry ether was added 0.077 mole of 4-pentenylmagnesium bromide in 90 ml. of dry ether over 90 minutes. After refluxing for 1 hour the mixture was stirred overnight at room temperature. The white slurry was worked up as usual. (No tetraphenyltin was isolated in this step.) The pale yellow oil was taken up in 40 ml. of anhydrous ethanol. Chilling gave some impure tetraphenyltin but no other product. Again, attempted vacuum distillation gave a product boiling over the range 180-190° (0.08 mm.) which deposited tetraphenyltin upon cooling.

Triphenylallyllead. Using the general procedure of Austin (7) triphenylallyllead was prepared in a 73% yield from triphenyllead chloride and allylmagnesium bromide.

Diphenyldiallyllead. The instability of diphenyldiallyllead, previously noted by Towne (8), was re-examined. The attempted preparation was conducted in the following manner. To 0.058 mole of allylmagnesium bromide in 52 ml. of dry ether was added 15.0 g. (0.0288 mole) of dry, powdered diphenyllead dibromide by the rubber tube arrangement used for triphenylallyltin. The addition required 25 minutes. The solution turned apple-green and a gray solid appeared after 1 hour of reflux. The reaction mixture was hydrolyzed with ammonium chloride solution and the gray solid was filtered off. It was a mixture of lead¹ and some organolead compound. The ether layer was dried over sodium sulfate, during which

¹ The lead was identified by solution in nitric acid and addition of sodium sulfide solution. Also, ignition proved it to be inorganic.

time an amorphous brown solid came down. The ether solution was filtered and the ether was removed to leave 5.0 g. of a viscous, pale yellow liquid. This was assumed to be crude diphenyldiallyllead. It was too unstable to be vacuum-distilled, and even while standing at room temperature under nitrogen it deposited more brown solid admixed with some cream-colored solid. The latter solid was identified as triphenylallyllead by a mixture melting point.

The thermal stability of the crude diphenyldiallyllead was studied by placing 2.6 g. of the yellow liquid in a test tube and heating it in an oil-bath at a rate of 4 degrees per minute. At 120° the liquid turned green, at 140° tan and at 150–160° the liquid turned black and effervesced. The liquid boiling off had the characteristic odor of diallyl. After 15 minutes decomposition was extensive. The residue was extracted with 20 ml. of hot chloroform and filtered. The black residue proved to be metallic lead.¹ The cooled chloroform solution deposited 0.3 g. of colorless needles melting at 227.0–228.5° and melting undepressed when mixed with an authentic sample of tetraphenyllead.

Triphenyltin hydride. The general preparative directions used are those of Wittig (9) who employed triphenyltin bromide on smaller-sized runs. On the first run using 88.4 g. (0.230 mole) of triphenyltin chloride and 14.0 g. (0.369 mole) of lithium aluminum hydride, the operation was extended over a period of a week with much exposure of the product to light. Consequently, even though all operations were carried out under nitrogen, no triphenyltin hydride could be obtained upon distillation. Instead, 0.5 g. of tin² and 28.2 g. of tetraphenyltin were isolated.³ The latter melted at 221-224° from the benzene used in the work-up. From chloroform-petroleum ether (b.p. 77-115°) it melted at 226.0-228.5° and melted undepressed with authentic tetraphenyltin.

In a second run employing 44.2 g. (0.115 mole) of triphenyltin chloride and 7.0 g. (0.185 mole) of lithium aluminum hydride the reaction mixture was worked up in 1.5 days to minimize decomposition. Distillation under nitrogen gave 20.6 g. (53%) of a water-white liquid boiling at 164–165° (0.3 mm.). Other runs gave up to 58% of triphenyltin hydride. A 3.9 g. residue of tin² was recovered from the distillation flask on one occasion.

This water-white liquid was stored under nitrogen. After 3 days of being exposed to light a gray solid began to deposit. (This deposition was slowed by storage in the dark.) After a considerable period of time this solid was separated and extracted with hot benzene. The gray residue proved to be tin² and the white needles from the cooled benzene were tetraphenyltin (mixture melting point).

Free-radical-catalyzed decomposition of triphenyltin hydride. Triphenyltin hydride (4.1 g., 0.0117 mole), 0.10 g. (0.0005 mole) of benzoyl peroxide, and 10 ml. of hexane were irradiated with an ultraviolet lamp under a nitrogen atmosphere. After 9 hours a white solid had precipitated, and after 25 hours a cream-colored solid coated the walls of the flask. This solid was filtered off and dried. It weighed 0.52 g. and melted over the range 165-210°. Solution in hot benzene and filtration left a trace (ca. 0.01 g.) of yellow solid on the filter paper. This organic substance contained tin and did not melt under 300°. Cooling of the benzene gave 0.30 g. of a solid, melting over the range 190-222°. Another recrystallization from benzene gave 0.17 g. of tetraphenyltin, m.p. 227-229° (mixture melting point).

Reaction of triphenyltin hydride with benzoyl peroxide. Six grams (0.0171 mole) of triphenyltin hydride, 2.0 g. (0.0084 mole) of benzoyl peroxide, and 30 ml. of hexane were refluxed and stirred under nitrogen for 96 hours. Upon cooling, the hexane solution deposited 2.0 g. of a colorless solid which melted at $168-170^{\circ}$. Several recrystallizations from benzene resulted in white needles which melted at $184-185^{\circ}$ (dec.). On one occasion cubic crystals, m.p. 166-167.5 (dec.), came down from benzene. This solid upon thorough drying, however, melted at $184-185^{\circ}$ (dec.). This compound analyzed for 30.41% tin and its infrared spectrum showed no carbonyl and only a doubtful hydroxyl band. Bands indicative of

² The tin was identified by melting point (230°), ignition and solution in hydrochloric acid. The resulting solution gave a gray precipitate with mercuric chloride solution.

³ Dr. R. Fuchs initiated the use of triphenyltin chloride in this preparation and also noticed the instability of triphenyltin hydride.

mono- and di-substituted benzenes (probably *para*) were present. Interestingly enough, the white solid did react with dilute sodium hydroxide to form a yellow sodium salt which did not melt under 360°.

A comparison was made with the infrared spectra⁴ of *p*-carboxyphenyltriphenyltin, tetraphenyltin, hexaphenylditin, diphenyltin oxide, and triphenyltin oxide, and mixtures of these. However, there was little similarity between these and that of the unknown.

The hexane filtrate from the above reaction mixture was concentrated to a pale yellow syrup weighing 4.0 g. Upon standing almost colorless crystals came down (1.4 g.). These were separated from the oil with the help of cold benzene. They melted at $81-84^{\circ}$ and upon recrystallization from a small amount of benzene melted at $82-84^{\circ}$. A mixture with an authentic sample of triphenyltin benzoate (m.p. $82.5-84^{\circ}$) melted undepressed.

Triphenyltin benzoate. Since this compound had not been reported, it was prepared and analyzed. Triphenyltin iodide (5.0 g., 0.0105 mole), 2.9 g. (0.0201 mole) of sodium benzoate, and 170 ml. of 95% ethanol were refluxed for 12 hours. The solution was reduced to one-half its volume by distillation of the ethanol. After dilution with one volume of water the solution was refrigerated. The solvent was decanted and the sticky residue was taken up in 95% ethanol. Concentration and cooling gave 2.8 g. (57%) of pale yellow prisms melting at 82-84°. Recrystallized from dilute ethanol the product melted at 82.5-84.0°.

Anal. Calc'd for C25H20O2Sn: Sn, 25.20. Found: Sn, 25.27, 25.33.

Attempted free-radical-catalyzed additions to olefinic organometallic compounds. Based on previous studies it was thought necessary to employ a large excess of triphenylsilane for optimum conditions of addition. However, triphenylgermane has given promising results in other cases employing a smaller excess (22). To illustrate the general procedure employed, the attempted additions of triphenylsilane and triphenylgermane to triphenylallyltin will be discussed.

Triphenylsilane and triphenylallyltin. Triphenylsilane (26.0 g., 0.100 mole), 6.3 g. (0.016 mole) of triphenylallyltin, 0.30 g. of benzoyl peroxide, and 30 ml. of hexane were stirred and refluxed under nitrogen for 19 hours. The pale yellow solution was stripped of the hexane and the residue was vacuum-distilled. Triphenylsilane (22.6 g., 87% recovery) was collected over the range 158-163° (1.6 mm.). The residue in the flask was extracted with 40 ml. of hot petroleum ether (b.p. 60-70°), leaving 0.12 g. of tin.² Refrigeration of the solution deposited 0.6 g. of a solid melting over the range 130-140°. Continued recrystallization finally gave 225-227° (undepressed when admixed with authentic tetraphenyltin). The first petroleum ether mother liquor was concentrated to a syrup and then taken up in hot 95% ethanol. Triphenylallyltin (0.4 g.) (melting range, 65-70°) came down. No other product was isolated.

In a similar procedure using only a slight molar excess of triphenylgermane, vacuum distillation and the resultant thermal decomposition could be avoided. Thus, 6.3 g. (0.0161 mole) of triphenylallyltin, 7.2 g. (0.024 mole) of triphenylgermane, 0.30 g. of benzoyl peroxide, and 30 ml. of hexane were heated under reflux for 19 hours. Removal of the solvent and solution of the residue in 40 ml. of hot, anhydrous ethanol gave upon cooling 3.4 g. of a white solid melting at 61-64°. An additional 1.1 g. melting over the range 60-65° was obtained from the mother liquor. Recrystallized from ethanol it melted at 71-72°. This is a 71% recovery of triphenylallyltin.

Thermal stability. A small sample was heated in a capillary tube in an electrically heated block at the rate of 5 degrees per minute. Triphenylallyltin decomposed over the range 305-310°, whereas triphenylallyllead decomposed over the range 165-175°.

SUMMARY

Diphenyldiallyltin, triphenylallyltin, and diphenyldi-4-pentenyltin have been prepared for the first time. Diphenyldiallyllead and triphenyl-4-pentenyltin were too unstable to be obtained pure.

⁴ The authors are grateful to Dr. V. A. Fassel and Messrs. R. Kross and R. McCord, of the Atomic Institute, for the infrared analyses.

The free-radical-catalyzed addition of triphenylsilane or triphenylgermane to olefinic organotin and organolead compounds was unsuccessful. Only starting material or thermal decomposition products were isolated.

Triphenyltin hydride was obtained from triphenyltin chloride and lithium aluminum hydride in improved yield. In sunlight it decomposed into tin and tetraphenyltin. With small amounts of benzoyl peroxide it gave tetraphenyltin but no tin. With large amounts triphenyltin benzoate and another, unidentified organotin compound were formed, but no tin or tetraphenyltin. An authentic sample of triphenyltin benzoate was obtained from triphenyltin iodide and sodium benzoate.

Crude diphenyldiallyllead decomposed into lead and tetraphenyllead upon heating. Triphenylallyltin was more thermally stable than triphenylallyllead.

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