The spectrum is similar to that of methyl dimethylphenylsilanecarboxylate, with the same change in intensities associated with the replacement of a methyl by a phenyl group.

*Reduction of methyl dimethylphenylsilanecarboxylate with lithium aluminum hydride.* Lithium aluminum hydride, 3.26 g. (0.086 mole), was added in small portions to 20.0 g. (0.013 mole) of methyl dimethylphenylsilanecarboxylate dissolved in 200 ml. of ether and cooled to ice-bath temperature. Vigorous refluxing occurred as each portion was added. The ice bath was removed upon completion of addition, and the reaction mixture was allowed to stir at room temperature for 4.5 hr. The solution was then poured onto crushed ice acidified with sulfuric acid. The usual work-up was employed. Distillation of the solvent left a colorless oil which was distilled at reduced pressure to give 13.55 g. (79.3%) of a colorless oil later shown to be dimethylphenylhydroxymethylsilane, b.p. 130–135° (30 mm.), $n_D^{20}$ 1.5220. This was redistilled to give 12.05 g. (70.4%), b.p. 132–135° (27 mm.), $n_D^{20}$ 1.5225, $d_{20}^{20}$ 0.9899.

*Anal.* Calcd. for $C_9H_{14}OSi$: C, 65.00; H, 8.48; $MR_D$, 51.65. Found: C, 64.39, 64.56; H, 7.57, 7.74; $MR_D$, 51.24.

The infrared spectrum in carbon disulfide showed the absorption bands mentioned previously for C—H aromatic and aliphatic, Si-methyl, and Si-phenyl, and, in addition, bands at 2.97 and 10.00 $\mu$ indicative of an associated OH and hydroxymethyl, respectively.

*Reaction of dimethylphenylsilyllithium with formaldehyde.* Formaldehyde gas, prepared by heating 20.0 g. of paraformaldehyde, was passed over a rapidly stirred solution of 0.148 mole of dimethylphenylsilyllithium in tetrahydrofuran solution. The reaction mixture became quite warm and mild refluxing occurred. A water bath was applied to avoid overheating. The solution became lighter in color, until after 1 hr. it was light brown-orange. Color Test I[9] was then negative. Stirring at room temperature was continued for 2 hr. Hydrolysis was effected with water and the usual work-up employed. Evaporation of the solvent left a colorless oil which was distilled at reduced pressure to give 11.15 g. (45.3%) of dimethylphenylhydroxymethylsilane, b.p. 111–117° (11 mm.), $n_D^{20}$ 1.5256. This oil was redistilled to give 8.80 g. (35.8%), b.p. 113–117° (11 mm.), $n_D^{20}$ 1.5251.

*Anal.* Calcd. for $C_9H_{14}OSi$: C, 65.0; H, 8.48; $MR_D$, 51.65. Found: C, 64.43, 64.57; H, 8.02, 8.19; $MR_D$, 50.35.

The infrared spectrum is superimposable with that of the oil obtained in the lithium aluminum hydride reduction of methyl dimethylphenylsilanecarboxylate.

*Acknowledgment.* This research was supported in part by the United States Air Force under Contract AF 33(616)-3510 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Division, Wright-Patterson Air Force Base, Ohio.

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[9] H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

# Hydrogenolyses of Aromatic Halides with Triphenyltin Hydride[1]

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*Received February 1, 1960*

Triphenyltin hydride is postulated to be a by-product of the intermediate in the Diels-Alder reaction between triphenylvinyltin and tetracyclone. The hydride serves as a reducing agent for tetracyclone and is also capable of hydrogenolyzing aromatic halides selectively.

Tetracyclone, (tetraphenylcyclopentadienone, I) has been reported to undergo a Diels-Alder reaction with organomercury[5,6] and organoarsenic[6] compounds. With a view toward preparing new organometallic compounds *via* this reaction, I was treated with triphenylvinyltin (II). No evidence of reaction was obtained when the components were heated in benzene, but in refluxing bromobenzene (IX) the color of I was discharged and a reducing gas was evolved. From the reaction mixture, tetraphenyltin (III), 2,3,4,5-tetraphenylcyclopent-2-enone (IV), triphenyltin bromide (V), and 1,2,3,4-tetraphenylbenzene (VI) were isolated by fractional crystallization. When the reaction was conducted in refluxing nitrobenzene III and VI were isolated.

In order to understand the appearance of these products, II was heated in refluxing bromobenzene and it slowly disproportionated to give III. That V had not been obtained suggested that another tin containing compound had reacted with the solvent.

It was then assumed that I underwent the Diels Alder reaction with II and afforded an unstable adduct (A) which eliminated carbon monoxide (the reducing gas?) and triphenyltin hydride (VII) to give fully aromatic VI. Hydrogenolysis of the solvent by VII would give V and reduction of I would give IV. In support of this suggested

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[1] A preliminary report of part of this work appeared in *J. Org. Chem.*, **24**, 294 (1959).

[2] Taken from a portion of the dissertation presented to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June 1960.

[3] To whom inquiries should be sent.

[4] Sponsored in part by the Office of Ordnance Research, U. S. Army.

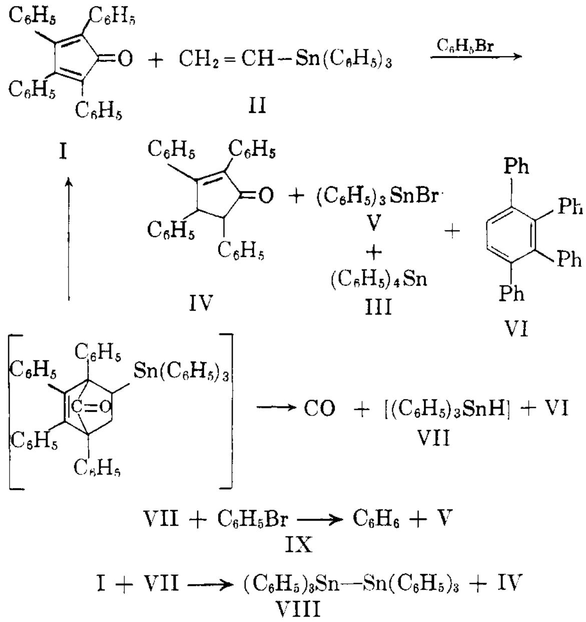
[5] V. S. Abramov and L. V. Shapshinskaya, *Doklady Akad. Nauk S.S.S.R.*, **59**, 1291 (1948).

[6] V. S. Abramov, *Bull. acad. sci. U.R.S.S., Classe sci. chim.*, **1945**, 330.

route was the reported reduction of ketones with tin hydrides.[7,8]

To test these assumptions, a solution of VII and IX was refluxed and afforded V and benzene. Reduction of I gave IV and hexaphenyldistannane (VIII) (Chart). During the course of these investigations, van der Kerk also reported that the reduction of bromobenzene afforded V.[8]

CHART



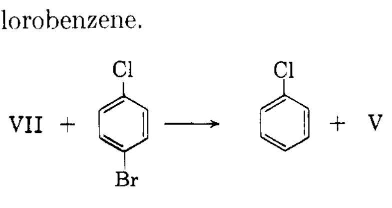
$$\text{VII} + \underset{\text{IX}}{C_6H_5Br} \longrightarrow C_6H_6 + \text{V}$$

$$\text{I} + \text{VII} \longrightarrow \underset{\text{VIII}}{(C_6H_5)_3Sn{-}Sn(C_6H_5)_3} + \text{IV}$$

Some reactions of VII were investigated. Benzophenone was reduced to benzhydrol and aromatic halides were hydrogenolyzed by VII. No solvent was employed for these reactions.

Similar yields of V were obtained from the reduction of bromobenzene when the reaction was heated for two, six or thirteen hours or when either VII or bromobenzene was present in excess.

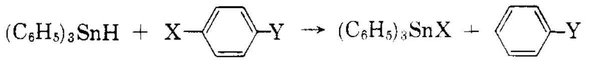
Iodobenzene could be hydrogenolyzed at a lower temperature than bromobenzene, which in turn was more reactive than chlorobenzene. These differences in ease of reduction permitted the selective removal of halogen atoms from an aromatic system. 1-Bromo-4-chlorobenzene afforded V and chlorobenzene.



A series of *para*-substituted bromobenzenes along with iodobenzene were treated with VII and in each case afforded the parent hydrocarbon and the triphenyltin halide. The extent of hydrogenolysis was determined by titration (Table I) at 154°. The reaction proceeded nearly to completion affording yields of better than 90%. At 124° the reaction was more selective, affording smaller yields with those compounds substituted in the *para* position with electron donating groups. At 95°, only iodobenzene was hydrogenolyzed readily.

TABLE I

YIELDS FROM THE HYDROGENOLYSES OF AROMATIC HALIDES



| X | Y | Yield, %, at 95° | 124° | 154° |
|---|---|---|---|---|
| Br | $OCH_3$ | 7% | 34% | 98% |
| Br | $CH_3$ | 10 | 50 | 91 |
| Br | H | 12 | 55 | 90 |
| Br | Cl | 16 | 82 | 97 |
| Br | $C_6H_5$ | 23 | 93 | 95 |
| I | H | 84 | 90 | 91 |

Benzene, tetraphenyltin, and tin were found as by-products of the hydrogenolysis reaction. The latter two have been reported[9] to arise from the thermal decomposition of VII. Benzene, in turn, was found when a mixture of V and VII was heated.

Heating a mixture of triphenyltin hydride and triphenyltin bromide under the conditions of the hydrogenolysis experiments did not consume triphenyltin bromide. Thus, the yields of triphenyltin bromide or iodide corresponded to the yield of hydrogenolyzed halobenzene (see Table II).

TABLE II

TESTS FOR INTERACTION OF TRIPHENYLTIN BROMIDE WITH TRIPHENYLTIN HYDRIDE AND FOR INTERFERENCE OF THE LATTER WITH ANALYSIS FOR THE FORMER

| Temp. | $(C_6H_5)_3SnH$, g. | Triphenyltin Halide Taken, g. | Triphenyltin Halide by Titration, g. |
|---|---|---|---|
| | | $(C_6H_5)_3SnBr$ | |
| 25 | 1.01 | 0.45 | 0.46 |
| 25 | 1.0 | 0.27 | 0.28 |
| 125 | 1.1 | 1.08 | 1.08 |
| 125 | 1.0 | 0.32 | 0.33 |
| 155 | 1.02 | 0.43 | 0.43 |
| 155 | 1.03 | 1.01 | 1.01 |
| 155 | 1.13 | 1.09 | 1.10 |
| 158 | 1.00 | 1.04 | 1.04 |
| 159 | 1.0 | 0.53 | 0.54 |
| | | $(C_6H_5)_3SnI$ | |
| 25 | 1.4 | 0.20 | 0.20 |
| 155 | 1.10 | 1.10 | 1.11 |
| 157 | 1.02 | 1.21 | 1.20 |
| 159 | 1.0 | 0.11 | 0.12 |

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(7) H. G. Kuivila and O. F. Beumel, Jr., *J. Am. Chem. Soc.*, **80**, 3798 (1958).

(8) J. G. Noltes and G. J. M. van der Kerk, *Chemistry & Industry*, 9, 294 (1959).

(9) H. Gilman and J. Eisch, *J. Org. Chem.*, **20**, 763 (1955).

## EXPERIMENTAL

*Diels-Alder reaction between tetracyclone and triphenylvinyltin. Procedure A.* A solution of 0.72 g. (1.87 mmoles) of I and 0.92 g. (2.44 mmoles) of II in 15 ml. of benzene was refluxed for 40 hr. A test for carbon monoxide was not obtained and the color of I was not discharged.

*Procedure B.* A solution of 3.0 g. (7.8 mmoles) of I and 3.42 g. (9.1 mmoles) of II in 10 ml. of bromobenzene was refluxed for 20 hr. A strip of paper moistened with palladium(II) chloride held in the effluent gases turned black, indicating the evolution of a reducing gas. The color of tetracyclone was also discharged. At the end of this time, the solution was cooled and the reaction products were separated by fractional crystallization, using heptane as the solvent, affording 0.3 g. (0.70 mmole) of III, m.p. 228–229° (reported,[10] m.p. 229°), 1.1 g. (2.9 mmoles) of VI, m.p. 192.5–193.5° (reported,[11] m.p. 193–194°), 0.3 g. (0.78 mmole) of IV, m.p. 160–162° (reported,[12] m.p. 160–162° and 162–163°), and 0.1 g. (0.23 mmole) of V, m.p. 121.5–122.5° (reported,[13] m.p. 121–122°). Admixture of each compound with a known sample showed no depression. Infrared spectra of corresponding knowns and unknowns were superimposable.

*Procedure C.* A solution of 3.03 g. (7.9 mmoles) of I and 3.40 g. (9.0 mmoles) of II in 10 ml. of nitrobenzene was refluxed for 13 hr., giving a positive test for a reducing gas. After allowing the mixture to cool, 0.8 g. (1.9 mmoles) of III, m.p. 227.5–229.5°, were obtained. A mixture melting point with a known sample of tetraphenyltin was not depressed.

*Anal.* Calcd. for $C_{24}H_{20}Sn$: C, 67.49; H, 4.72. Found: C, 67.35; H, 4.66.

The filtrate was concentrated and afforded 0.7 g. (1.8 mmoles) of VI, m.p. 192–193° (recrystallized from heptane). A mixture melting point with a known sample of tetraphenylbenzene was not depressed.

*Thermal disproportionation of* II. A solution of 0.8 g. (2.1 mmoles) of II in 3 ml. (29 mmoles) of bromobenzene was refluxed for 102 hr. A reducing gas was not evolved. After removal of the solvent, crystallization of the residue from benzene afforded 0.1 g. (0.23 mmole) of III, m.p. 228–229°. Adding 1-propanol to the filtrate gave 0.1 g. (0.26 mmole) of II, m.p. 37.6–39.2°. Mixture melting points of each of these compounds with known samples were not depressed. A negative Beilstein test for halogen, after the removal of bromobenzene, indicated that triphenyltin bromide had not been formed in this reaction.

*Triphenyltin hydride* (VII) *and bromobenzene* (IX). A solution of 13.4 g. (0.0382 mole) of VII in 15 ml. (0.143 mole) of bromobenzene was refluxed for 13 hr. Distillation of the reaction mixture gave 2.22 g. (75%) of a liquid, b.p. 79–82°, $n_D^{22}$ 1.5010. Its dinitro derivative melted at 89–90.5° (no depression in admixture with authentic *m*-dinitrobenzene, m.p. 90–91°).

After removal of the benzene, the remaining solvent was evaporated on a steam bath, and the residue was extracted with ether and filtered, leaving 1.3 g. of gray insoluble material. This was extracted with boiling benzene leaving 0.1 g. of grey material, identified as metallic tin by x-ray analysis.

The benzene extract gave 0.9 g. (2.1 mmoles, 7%) of tetraphenyltin, m.p. 228–229°. A mixture melting point with a known sample was not depressed. Infrared spectra were superimposable.

The ether extract was evaporated and the residue recrystallized from heptane to afford 11.8 g. (72%) of V, m.p. 117–121°. Another recrystallization gave 11.2 g., (68%), m.p. 121.5–122.5°. The sample gave a positive Beilstein test for halogen and did not depress the melting point of a known sample.

A second experiment in which VII and bromobenzene were refluxed for 2 hr. afforded 59% of V. The same yield was obtained after refluxing for 6 hr. When the reaction was run for 2 hr. in a flask protected from light, a 62% yield of V was obtained, m.p. 121–122.5°. A 61% yield of V, m.p. 120–122° was obtained when 1.57 g. of bromobenzene were heated with 4.15 g. of VII, which was present in excess.

*Tetracyclone* (I) *and triphenyltin hydride* (VII). One gram (2.67 mmoles) of I and 3.1 g. (8.8 mmoles) of VII were heated at 158° for 12 hr. The mixture was taken up in ether and filtered. The ether-insoluble residue was recrystallized from benzene to give 1.5 g. (81%) of VIII, m.p. 234–235° (reported,[14] m.p. 237°). The ether filtrate was evaporated and the residue recrystallized from methanol to give 0.2 g. (19%) of IV, m.p. 160–161.5°. A mixture melting point with authentic IV showed no depression.

*Triphenyltin hydride* (VII) *and iodobenzene.* A solution of 6 g. (17.1 mmoles) of VII and 6 ml. (54 mmoles) of iodobenzene was heated in an oil bath for 4 hr. at 160°. The mixture was distilled until the benzene, 0.76 g. (57%), was removed. The latter afforded a dinitro derivative, m.p. 89–90° which did not depress the melting point of a known sample. The residue in the distilling flask was recrystallized from heptane and afforded 3.6 g. (44%) of triphenyltin iodide, m.p. 123.5–124.5° (reported,[15] m.p. 123–123.2°). This gave a positive Beilstein test for halogen and a test for iodine with chlorine water and carbon tetrachloride.

*Triphenyltin hydride* (VII) *and 4-bromobiphenyl.* A mixture of 2.33 g. (0.0100 mole) of 4-bromobiphenyl and 7.02 g. (0.0200 mole) of VII was heated at 151° for 2 hr. After cooling to room temperature, a vacuum was applied to the system and 0.3 g. of liquid was distilled and collected in a Dry Ice trap. The distillate was identified as benzene by its index of refraction, $n_D^{27}$ 1.4985, vapor phase chromatograph and infrared spectrum.

The residue in the reaction flask was sublimed under vacuum at 70° and then at 126°. The first fraction gave 1.30 g. of biphenyl, m.p. 65–68°. Recrystallization from methanol gave 1.0 g. (65%) of biphenyl, m.p. 68–69°. This gave a negative Beilstein test for halogen, and a mixture melting point with known material was not depressed. The second fraction 2.6 g., m.p. 115.5–121°, after recrystallization from heptane, gave 2.1 g. (49%) of V, m.p. 120–122°. The product gave a positive Beilstein test for halogen; a mixture melting point with triphenyltin bromide was not depressed.

*Triphenyltin hydride* (VII) *and 1-bromo-4-chlorobenzene.* A solution of 4.68 g. (0.0131 mole) of VII and 1.91 g. (0.0100 mole) of 1-bromo-4-chlorobenzene was heated at 150° for 3.3 hr. After cooling to room temperature, the contents were distilled at reduced pressure to give 0.9 g. of liquid in a Dry Ice trap. This liquid gave a positive Beilstein test for halogen. Its dinitro derivative, m.p. 49.7–50.7°, did not depress the melting point of a known sample of 2,4-dinitrochlorobenzene and its infrared spectrum was superimposable on that of known chlorobenzene. A vapor phase chromatograph showed the presence of chlorobenzene and a smaller amount of benzene, but bromobenzene was not detected. From the index of refraction the liquid was calculated to contain 0.85 g. (75%) of chlorobenzene and 0.05 g. of benzene.

The material in the reaction flask was purified by recrystallization to give 0.01 g. of III, m.p. 229–230°, and 3.8 g. (88%) of V, m.p. 115–120.5°. The latter on recrystallization from heptane afforded 2.7 g. (63%) of V, m.p. 120–121.5°.

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(10) H. D. K. Drew and J. K. Landquist, *J. Chem. Soc.*, 1480 (1935).

(11) W. Dilthey and G. Hurtig, *Ber.*, **67B**, 495 (1934).

(12) N. O. V. Sonntag, S. Linder, E. I. Becker, and P. E. Spoerri, *J. Am. Chem. Soc.*, **75**, 2283 (1953).

(13) O. H. Johnson and J. R. Holum, *J. Org. Chem.*, **23**, 738 (1958).

(14) M. E. Krause and R. Becker, *Ber.*, **53**, 173 (1920).

(15) J. Boeseken and J. J. Rutgers, *Rec. trav. chim.*, **42**, 1017 (1923).

The melting point of III, and of V, was not depressed upon admixture with known materials.

*Triphenyltin hydride and the bromonaphthalenes.* A solution of 4.5 g. (0.0128 mmole) of VII and 2.1 g. (0.010 mole) of 2-bromonaphthalene was heated at 154° for 14 hr. in a flask equipped with a condenser. During this time 0.9 g. of naphthalene, m.p. 76–79° (69%), sublimed into the condenser, was recovered from the condenser and recrystallized from methanol-water to give 0.6 g. (46%), m.p. 79–81° of naphthalene. The product gave a negative Beilstein test for halogen, and a mixture melting point with a known sample of naphthalene was not depressed.

The residue in the reaction flask was recrystallized three times from heptane to give 2.5 g. (58%) of V, m.p. 122–123°, whose mixture melting point with known material was not depressed.

In a similar manner, 4.5 g. (0.0128 mole) of VII and 2.1 g. (0.010 mole) of 1-bromonaphthalene were heated for 15 hr. at 152° to afford 0.4 g. of naphthalene, (31%) m.p. 79–81°, and 1.9 g. (44%) of V, m.p. 122–123°.

*Triphenyltin hydride* (VII) *and p-bromotoluene.* A solution of 1.71 g. (0.0100 mole) of *p*-bromotoluene and 7.08 g. (0.0200 mole) of VII was heated for 2 hr. at 148–150° in a flask equipped with a reflux condenser. After cooling to room temperature, a vacuum was applied to the system and 0.78 g. of distillate were collected in a Dry Ice trap. The infrared spectrum and a vapor phase chromatograph showed that the distillate contained benzene and toluene. From the index of refraction, the mixture was calculated to have 0.6 g. of toluene (65%) and 0.18 g. of benzene.

The residue in the reaction flask was recrystallized from heptane to give 1.9 g. (44%) of V, m.p. 120–122°. This product gave a positive Beilstein test for halogen and did not depress the melting point of triphenyltin bromide.

*Triphenyltin hydride* (VII) *and p-bromoanisole.* A solution of 1.87 g. (0.0100 mole) of *p*-bromoanisole and 7.01 g. (0.0200 mole) of VII was heated at 140–160° for 2 hr. The reaction vessel was cooled to room temperature, and the product distilled at reduced pressure into a Dry Ice trap. A vapor phase chromatograph and the infrared spectrum showed that the distillate (1.3 g.) was composed of anisole and benzene. From the refractive index, the mixture was calculated to contain 0.8 g. of anisole (73%) and 0.5 g. of benzene.

The material in the reaction flask was recrystallized from heptane to give 2.1 g. (49%) of V, m.p. 120–123°. Another recrystallization afforded a product, m.p. 122–123°, whose mixture melting point with authentic V was not depressed.

*Formation of benzene upon heating* V *and* VII. Seven grams of VII were heated at 150° for 2.5 hr. Benzene was not isolated upon vacuum distillation. Similarly, no benzene was detected when 2.0 g. of V were heated at 150–158° for 7.3 hr.

A mixture of 2.01 g. (4.7 mmoles) of V and 7.00 g. (20 mmoles) of VII was heated at 150–155° for 14.3 hr. After cooling to room temperature, vacuum distillation afforded 0.16 g. of benzene, identified by its vapor phase chromatograph, infrared spectrum and index of refraction $n_{\mathrm{D}}^{25.4}$ 1.4979. Tin, III, V, and VIII were also isolated.

*Benzophenone and* VII. A mixture of 1.8 g. (0.010 mole) of benzophenone and 9.0 g. (0.0256 mole) of VII was heated at 153° for 2.5 hr. After cooling, the mixture was taken up in ether and filtered from 3.9 g. (56%) of VIII, m.p. 233–235°. The ether filtrate was evaporated and the residue recrystallized from heptane to give 0.5 g. (28%) of benzhydrol, m.p. 65.5–66.4°. A mixture melting point with known material was not depressed, and the infrared spectra were superimposable.

*Reaction between chlorobenzene and triphenyltin hydride* (VII). A solution of 7.1 g. (0.020 mole) of VII in 7 ml. (0.068 mole) of chlorobenzene was refluxed for 12 hr. Neither benzene nor triphenyltin chloride could be isolated.

In a second experiment, 1 g. (8.9 mmoles) of chlorobenzene and 1 g. (2.85 mmoles) of VII were heated at 125° for 2 hr. The solution was titrated with alkali; triphenyltin chloride was not detected.

*Analytical determination of triphenyltin hydrides. Series A.* Accurately weighed samples (0.1–0.2 g.) of V dissolved in 10 ml. of methanol were titrated with aqueous sodium hydroxide (0.0546*N*) to a phenolphthalein endpoint. The weights of V determined volumetrically agreed with the weights of V taken to between 0.2–0.7% error.

During the course of these titrations, a precipitate appeared, m.p. 121.5–123.7°. It gave a negative Beilstein test for halogen and a mixture melting point with V was depressed.

When 0.5 g. of V were employed in the titration, the endpoint was indefinite; probably too much aqueous alkali was needed and V was thrown out of solution.

*Series B.* From 0.1-g. to 1-g. samples of triphenyltin iodide, bromide, or chloride were titrated with 0.203*N* aqueous sodium hydroxide in from 75 to 150 ml. of methanol-water (2:1), using the larger quantity for the 1-g. samples, to within 2% accuracy.

*Series C.* In Table II are given weights of triphenyltin halide and of VII which were heated at the specified temperatures for 2 hr. The mixture was taken up in 100 ml. of boiling methanol. Fifty milliliters of water were added and then the solution was titrated with 0.198*N* sodium hydroxide to give the listed results.

*Acknowledgment.* We are pleased to acknowledge generous gifts of triphenylvinyltin and triphenyltin chloride from the Metal and Thermit Corporation.

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