

salt, and solvent, if any. The desired quantity of ammonia was introduced by way of a transfer bomb. The reaction mixture was then heated as desired, subsequently cooled, and vented to atmospheric pressure. The contents of the autoclave were extracted with ether to recover unchanged nitrile and then with hot acetonitrile or ethanol to separate the amidine salt from unreacted ammonium salt. Most of the significant data is presented in Table I. Pressures in the absence of solvent ranged from about 1300 p.s.i.g. at 125° or 6500 p.s.i.g. at 180°. With solvent present, pressure at 150° was of the order of 350–400 p.s.i.g.

p-Chlorobenzamidine thiocyanate. A mixture of 5.50 g. (0.040 mole) of *p*-chlorobenzonitrile and 12.2 g. (0.16 mole)

of thiourea was heated at 190–200° for 5 hr. The mass was then cooled and extracted with ether from which 9% of the starting nitrile was recovered. The insoluble material was suspended in ice water, additional ammonium thiocyanate was added to near saturation, and the insoluble amidine thiocyanate was collected by filtration. The crude yield was 90% m.p. 160–195°. After recrystallization from water the melting point was 202–203°.

Anal. Calcd. for C₈H₈N₃ClS: C, 44.96; H, 3.77; N, 19.67. Found: C, 45.23; H, 3.74; N, 19.85.

STAMFORD, CONN.

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

Reactions of Triphenyltin Hydride with Thiophene Compounds and Certain Carboxylic Acids¹

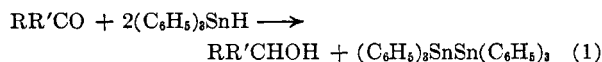
STUART WEBER AND ERNEST I. BECKER^{2a, b}

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Triphenyltin hydride reduces methyl and phenyl 2-thienyl ketones to the corresponding alcohols. Triphenyltin hydride reacts with acetic and propionic acids to give the corresponding triphenyltin esters, while with furoic and thenoic acids it gives both the triphenyltin ester and also the *sym*-tetraphenyldiaroyloxyditin, and with benzoic acid only the *sym*-tetraphenyldibenzoyloxyditin.

Kuivila and Beumel have found that triphenyltin hydride (I) reduces ketones to the corresponding alcohols,^{3,4} but no heterocyclic ketones were examined. The purpose of the present work was to report on some similar reactions with heterocyclic compounds.

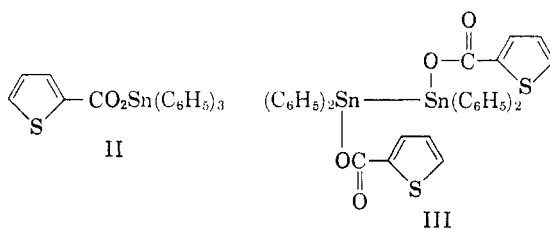
Thiophene derivatives were first to be examined. It was first ascertained that thiophene is not reduced at reflux nor at 130° in a sealed tube. Then a number of reactions were tried in which the ratio of I:ketone was varied. With a molar ratio of 1:1, methyl 2-thienyl ketone afforded 7% of methyl-2-thienylcarbinol, while a 2:1 ratio gave 15% of the carbinol. With phenyl 2-thienyl ketone ratios of 1:1, 2:1, and 5:1 were carried out, with the best yield (20%) of phenyl-2-thienylcarbinol being formed with the highest ratio. Appreciable quantities of hexaphenylditin were also recovered, suggesting equation 1 for the stoichiometry.



Related to the reduction of the ketones, it was

ascertained that the carbinols are not reduced to the methylene group under similar conditions.

The attempted reduction was next extended to 2-thenoic acid. The reaction of I and 2-thenoic acid gave triphenyltin 2-thenoate (II) in 32% yield at a molar ratio of 1:1 and *sym*-tetraphenyldithenoxyloxyditin (III) in 20% yield. With a 2:1 ratio of I:thenoic acid, 42% of III was obtained, while II could not be isolated from the reaction mixture.



Obtaining III from the reaction with triphenyltin hydride was surprising. Structural assignment was based upon ultimate analysis, which was in agreement with the expected values, and the isolation of diphenyltin oxide and thenoic acid from the reaction of III with cold concentrated sodium hydroxide solution. No bistrisphenyltin oxide was found. Owing to solubility difficulties, a molecular weight could not be obtained on III, but it was obtained, and the value agreed with that expected, for the corresponding product with benzoic acid.

Accompanying the reaction during which III appeared, were hydrogen and benzene. However, the precise origins of these by-products were not investigated, although several paths may be writ-

(1) From the thesis of S. W. submitted to the faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the Master of Science degree, 1962.

(2) (a) To whom inquiries should be directed. (b) Supported in part by the U. S. Army Research Office (Durham) under Grant DA-ORD-31 124-61-G39.

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

(4) H. G. Kuivila and O. F. Beumel, Jr., *J. Am. Chem. Soc.*, **83**, 1246 (1961).

ten for them. These points are under further study.

The unusual appearance of a diphenyltin group from the reaction with a triphenyltin molecule suggested testing the generality of the formation of the ditin. Accordingly, it was found that acetic and propionic acids in various ratios with I gave only esters analogous to II. Furoic acid gave compounds analogous to both II and III, with III increasing proportionately as the ratio of I:furoic acid increased. With benzoic acid only the compound corresponding to III was isolated. *sym*-Tetraphenyldibenzoyloxyditin has been prepared previously in the reaction between diphenyltin and benzoyl peroxide,⁵ and also in reaction between triphenyltin hydride and benzoyl peroxide.⁶

A peculiarity of the three *sym*-tetraphenyldiaroyloxyditins is that they show no carbonyl absorption in the infrared as solids or in solution. This has been previously mentioned by Gilman and Eisch⁶ for *sym*-tetraphenyldibenzoyloxyditin, but without reference to the physical state of the sample. However, that tetravalent tin can coordinate strongly to oxygen atoms in adjacent molecules has been indicated for tetraalkoxy tins.⁷

From the results obtained here it may be tentatively concluded that aromatic acids lead to compounds analogous to II and III, while aliphatic acids lead only to compounds of type II.

EXPERIMENTAL

All hydrogenolyses were run under nitrogen.

Triphenyltin hydride and thiophene. A. A solution of 2.0 g. (0.024 mole) of thiophene and 12.6 g. (0.036 mole) of I was refluxed (about 84°) for 21 hr. Distillation of the reaction mixture gave 1.7 g. (85%) of recovered thiophene, b.p. 83–84°, n_D^{20} 1.5282 (reported⁸: n_D^{20} 1.5287). The remaining residue, recrystallized from xylene, gave tetraphenyltin, m.p. 224.6–225.0°, (reported⁹: m.p. 226°).

B. An 8-in. Carius tube containing 1.0 g. (0.012 mole) of thiophene and 8.42 g. (0.24 mole) of I was sealed and heated for 24 hr. at 130°. Fractional distillation of the reaction mixture gave 0.7 g. (70%) of recovered thiophene, n_D^{20} 1.5284. No test was obtained for hydrogen sulfide.

Triphenyltin hydride and methyl 2-thienyl ketone. A solution of 2.0 g. (0.016 mole) of methyl 2-thienyl ketone and 11.22 g. (0.032 mole) of I was heated for 2 hr. at 146°. Fractional distillation with a 30-cm. Widmer column produced a water white liquid (0.30 g., 15%) boiling at 87–88.4° (5.7 mm.) n_D^{20} 1.5420 (reported¹⁰: n_D^{20} 1.5422). The phenylurethane

(5) H. G. Kuivila and A. K. Sawyer, *J. Am. Chem. Soc.*, **82**, 5958 (1960).

(6) H. Gilman and J. Eisch, *J. Org. Chem.*, **20**, 763 (1955). The authors described the compound but were unable to assign a structure to it, merely pointing out that physical properties and infrared analysis precluded that the compound melting at 184–185° could be tetraphenyltin, hexaphenylditin, diphenyltin oxide, bistrisphenyltin oxide, or *p*-carboxyphenyltriphenyltin.

(7) D. C. Bradley, E. V. Caldwell, and W. Wardlaw, *J. Chem. Soc.*, 4775 (1957).

(8) H. D. Hartough, "Thiophene and Its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1952, p. 66.

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

derivative prepared from this sample melted at 84.2–84.9° (reported¹¹: m.p. 85°).

Triphenyltin hydride and phenyl 2-thienyl ketone. A mixture of 1.0 g. (0.005 mole) of phenyl 2-thienyl ketone and 8.75 g. (0.025 mole) of I was heated for 19 hr. at 145°. Three extractions with 50-ml. portions of ether gave a yellow ethereal solution and a grey-white residue. Crystallization of the residue from chloroform gave 4.5 g. of tetraphenyltin, m.p. 223.5–224.5°. With 5.0 g. (0.025 moles) of phenyl 2-thienyl ketone and 8.9 g. (0.025 moles) of I, 2.3 g. of hexaphenylditin, m.p. 229–231°, was obtained.

Evaporation of the ether gave a yellow viscous oil giving no infrared absorption in the region 1660–1700 cm.⁻¹. Chromatography on grade I alumina and collecting fractions as follows: 400 ml. of benzene, 100 ml. of chloroform, 100 ml. of ether, 50 ml. of 1:1 ether-alcohol, 125 ml. of alcohol, and finally 90 ml. of water-alcohol, gave trace amounts of material in all but the last flask from which 0.2 g. (20%) of phenyl-2-thienylcarbinol, m.p. 57.2–57.6°, (reported¹²: m.p. 57–58°), was isolated. A mixture melting point with the ketone was depressed. The compound showed strong absorption at 3500 cm.⁻¹.

Triphenyltin hydride and thenoic acid. A. A solution of 5.0 g. (0.045 mole) of thenoic acid and 15.8 g. (0.045 mole) of I was allowed to react for 19 hr. in heptane at reflux temperature (about 98°). A gas was evolved simultaneously with the formation of an insoluble solid. The solid was filtered, extracted with ether, the ether distilled, and the residue recrystallized from benzene to give 6.7 g. (31%) of II, m.p. 111.0–111.8°.

Anal. Calcd. for C₂₃H₁₈O₂SSn: C, 59.89; H, 3.80; S, 6.72; Sn, 24.87; molecular weight, 477. Found: C, 59.08; H, 3.94; S, 7.02; Sn, 25.09; mol. wt., 471 (cryoscopic in benzene).

The residue from the ether extraction was recrystallized from benzene, producing 3.8 g. (21%) of III, m.p. 177–178° (dec.).

Anal. Calcd. for C₃₄H₂₆O₄S₂Sn₂: C, 51.04; H, 3.27; S, 8.01; Sn, 29.67. Found: C, 50.79; H, 3.22; S, 8.33; Sn, 30.04.

Addition of III to concentrated sodium hydroxide solution produced an infusible solid (diphenyltin oxide). The filtrate was acidified with hydrochloric acid and extracted with ether. Distillation of the ether left thenoic acid.

B. A solution of 10.4 g. (0.029 mole) of I and 2.0 g. (0.014 mole) of thenoic acid was allowed to react for 4 hr. in heptane at reflux temperature. The mixture was filtered and the solid was extracted with 300 ml. of ether. Distillation of the ether left a droplet of yellow oil.

The residue from the ether extraction was recrystallized from chloroform to give 1.3 g. of III, m.p. 177–178° (dec.). The filtered heptane from the initial reaction mixture deposited a yellow solid on standing. Recrystallization from benzene gave 1.0 g. of III, m.p. 176–177° (dec.) for a total yield of 42%. Diphenyltin oxide (0.3 g.) was found to be the remaining isolatable material, m.p. > 300° (reported¹³: infusible).

Concentrated sodium hydroxide and III. A cold concentrated (pH = 12) sodium hydroxide solution and 0.1613 g. of III was stirred vigorously for 5 min. The solid formed was collected quantitatively and dried to give 0.114 g. (99.0%, based upon diphenyltin oxide as the product).

Anal. Calcd. for C₁₂H₁₀OSn: Sn, 41.09. Found: Sn, 40.78.

Triphenyltin hydride and acetic acid. A. A solution of 10.0 g. (0.0285 mole) of I and 3.42 g. (0.0570 mole) of acetic acid was allowed to react for 30 min. at 70°. A solid separated simultaneously with evolution of a flammable gas. Extraction of the reaction mixture with 250 ml. of ether left a waxy residue, while distillation of the ether and recrystallization of the solid from benzene gave 1.9 g. (17%) of tri-

(10) Footnote 8, p. 304.

(11) R. Kuhn and O. Dann, *Ann.*, **547**, 293 (1941).

(12) Footnote 8, p. 305.

(13) "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1959.

phenyltin acetate, m.p. 122–124° (reported¹⁴: m.p. 122–124°).

Anal. Calcd. for $C_{24}H_{18}O_2Sn$: molecular weight, 409. Found: mol. wt., 398 (ebullioscopic in benzene).

Extraction of the initial waxy residue with benzene gave 0.29 g. of diphenyltin oxide, infusible.

B. A solution of 20.0 g. (0.0570 mole) of I and 1.71 g. (0.0285 mole) of acetic acid was allowed to react in heptane at reflux temperature for 2 hr. The solvent was removed by distillation and the residue extracted with 250 ml. of ether, leaving a pasty residue.

Distillation of the ether and two recrystallizations of the residue from benzene gave 9.6 g. (85%) of triphenyltin acetate, m.p. 123.0–124.8°. No further compounds could be isolated.

Triphenyltin hydride and benzoic acid. *A.* A solution of 10.0 g. (0.0285 mole) of I and 1.75 g. (0.0142 mole) of benzoic acid was allowed to react for 3 hr. in heptane at 60°. The solvent was distilled, and the remaining solid extracted with 300 ml. of ether, leaving an oily residue. The ether was removed by distillation and the solid, 2.1 g., m.p. 177–183° (dec.), recrystallized from benzene to give 1.6 g. (46%) of *sym*-tetraphenyldibenzoyl oxydinitin m.p. 184–185° (dec.) [reported¹⁵: m.p. 184–185° (dec.)].

Anal. Calcd. for $C_{38}H_{30}O_4Sn_2$: Sn, 30.13; molecular weight, 788. Found: Sn, 30.10; mol. wt., 820 (ebullioscopic in chloroform).

A flammable gas (hydrogen) was observed during the first 30 to 45-minutes' reaction. In a parallel experiment the heptane was distilled and subjected to vapor phase chromatographic analysis. Peaks for benzene and for heptane were observed.

The oily residue was extracted with benzene, which, upon standing, deposited 0.1 g. of infusible diphenyltin oxide. The mother liquor was concentrated, leaving an intractable oil (8 g.).

B. A solution of 10.0 g. (0.0285 mole) of I and 3.47 g. (0.0285 mole) of benzoic acid was allowed to react in heptane at 60° for 3 hr. The solvent was removed by distillation and the white residue extracted with 300 ml. of ether leaving a yellow waxy residue. Distillation of the ether left 1.5 g. of a white solid, m.p. 180–185° (dec.), which was recrystallized from benzene to give 1.2 g. (10%) of *sym*-tetraphenyldibenzoyloxydinitin, m.p. 184–185° (dec.).

The yellow residue was dissolved in benzene and kept in an ice bath for 4 hr. Filtration afforded 1.2 g., (10%) of the

ditin, m.p. 184–185° (dec.). The remaining solution was concentrated to a yellow oil (7 g.). Infrared analysis indicated the presence of I and trace amounts of carbonyl containing compounds. Attempts at isolation were unsuccessful. The total yield of the ditin was 20%.

Triphenyltin hydride and furoic acid. *A.* A solution of 10 g. (0.0284 mole) of I and 3.2 g. (0.0284 mole) of furoic acid was allowed to react in heptane for 2 hr. at 65°. The reaction mixture was cooled and the mixture filtered. Concentration of the solvent left a clear oil. An infrared spectrum indicated the presence of I and carbonyl compounds. Standing at Dry Ice temperature for 6 hr. produced 1.5 g. of a white solid, m.p. 175–180° (dec.). Recrystallization from chloroform gave 1.3 g. (17%) of *sym*-tetraphenyldifuroxydinitin, m.p. 184–186° (dec.).

Anal. Calcd. for $C_{34}H_{26}O_6Sn_2$: Sn, 30.91. Found: Sn, 30.72.

The remaining oil was left at Dry Ice temperature overnight. Filtration afforded 3.4 g. of impure triphenyltin furoate, m.p. 190°. Recrystallization from benzene gave 3.25 g. (70%) of white solid, m.p. 192–193° (dec.).

Anal. Calcd. for $C_{28}H_{18}O_6Sn$: Sn, 25.74. Found: Sn, 25.72.

The original residue from the solvent filtration was recrystallized from benzene to give 1.0 g. of white needles, m.p. 131–133°. A mixture melting point with furoic acid was not depressed. The oily residue was dissolved in 10 ml. of benzene and allowed to stand at Dry Ice temperature for 2 hr. Filtration afforded 1.0 g. of hexaphenylditin, m.p. 229–231° (reported¹²: 231°).

B. A solution of 5.0 g. (0.0142 mole) of I and 0.8 g. (0.0071 mole) of furoic acid was allowed to react in heptane for 19 hr. at 65°. The solvent was distilled and the residue extracted with ether leaving a residue. The ether was distilled and the solid recrystallized from benzene to give 1.0 g. (31%) of the furoate, m.p. 192–193° (dec.).

The residue was recrystallized from chloroform to give 1.9 g. (35%) of the ditin, m.p. 184–186° (dec.). The mother liquor from this recrystallization was concentrated to an intractable oil (1.5 g.).

Triphenyltin hydride and propionic acid. A solution of 10.0 g. (0.0285 mole) of I and 1.0 g. (0.0142 mole) of propionic acid was heated in heptane for 3 hr. at 60°. The solvent was removed by filtration to leave a white solid. This was extracted with ether leaving a residue. Crystallization of the solid from ether gave 5.5 g. (90%) of triphenyltin propionate, m.p. 122–124°. An infrared spectrum of the inextractable concentrated solvent indicated I and decomposition products of I.

Anal. Calcd. for $C_{21}H_{20}O_2Sn$: Sn, 28.05. Found: Sn, 27.84.

BROOKLYN 1, N.Y.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF IOWA STATE UNIVERSITY]

Metalation Reactions by Organolithium Derivatives of Triaryl Group IV-B Elements

H. GILMAN, O. L. MARRS, W. J. TREPKA, AND J. W. DIEHL

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The relative reactivity of triphenylsilyl-, triphenylgermyl-, triphenyltin-, and triphenylleadlithium has been studied by allowing tetrahydrofuran solutions of these anions to metalate fluorene under similar conditions. Fluorene-9-carboxylic acid was obtained after carbonation decreasing in the order $(C_6H_5)_3Si^-$, $(C_6H_5)_3Ge^-$, $(C_6H_5)_3Sn^-$, $(C_6H_5)_3Pb^-$. Compared to other organometallic reagents, triphenylsilyllithium has been found to be of moderate metalating ability.

Although the lithium derivatives of triaryl group IVb elements of the general formula $(C_6H_5)_3MLi$, where $M=Si, Ge, Sn,$ and Pb , have been utilized in numerous studies,¹ little is known about the relative

reactivity of these four anions.^{1a} Until recently, the triaryl group IVb lithium derivatives were prepared under different conditions, and, therefore, a fair comparison of their reactivity could not