[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TENNESSEE A. AND I. STATE UNIVERSITY]

Synthesis and Properties of Some Tin Alkyls[1]

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Twelve tin tetra-alkyls and three ethyltin chlorides have been synthesized and various physical properties have been measured. Diethyldi-*n*-butyltin, diethyltin hydride and ethyltin hydride are reported for the first time. Hitherto unreported physical properties of the ethyltin chlorides also have been determined. Heats of combustion of eight tin tetra-alkyls have been measured in an an oxygen bomb calorimeter.

As part of a program involving the investigation of organic derivatives of tin hydride, SnH_4, a number of tin alkyls have been prepared and some of their properties have been studied. These compounds include tetramethyltin, tetraethyltin, tetrapropyltin, tetra-*n*-butyltin, tetra-*n*-hexyltin, diethyldi-*n*-butyltin, trimethylethyltin, dimethyldiethyltin, methyltriethyltin, triethyltin hydride, diethyltin hydride and ethyltin hydride. Diethyldi-*n*-butyltin, diethyltin hydride and ethyltin hydride are reported here for the first time. In the course of the investigation it was necessary to prepare some very pure samples of ethyltin trichloride, diethyltin dichloride and triethyltin chloride. Consequently, it was possible to determine several physical properties of these compounds which have not been reported previously.

Published values of the heats of combustion and formation of tin alkyls exist only in the case of tetramethyltin,[3] tetraethyltin, tetrapropyltin, tetra-*n*-butyltin and tetra-*n*-amyltin.[4] In this investigation, the heats of combustion of tetramethyltin, tetraethyltin and tetra-*n*-butyltin have been redetermined and the heats of combustion of five tin tetra-alkyls are reported for the first time.

Experimental

Synthesis.—Pure tin tetra-alkyls were prepared according to the method of Kozeschkow[5] as modified by Jones and co-workers.[4] Benzene solutions of stannic chloride were added to an excess of the appropriate Grignard reagent. The excess Grignard reagent was then destroyed by hydrolysis and the crude product was distilled repeatedly through an efficient fractionating column until a sample was obtained which showed no change in refractive index upon further distillation. The boiling points, densities and refractive indices of the pure compounds agreed closely with the literature data. In the cases of new compounds or compounds for which new data are reported here, details of the preparations are given below.

Diethyldi-*n*-butyltin.—To 0.37 mole of *n*-butylmagnesium bromide in about 500 ml. of anhydrous ether was added dropwise 0.185 mole of pure diethyltin dichloride which was dissolved in 250 ml. of 1:1 benzene–ether mixture. The reaction mixture was refluxed for 3 hours, then the excess Grignard reagent was destroyed by hydrolysis with a liter of 3.5 molar ammonium chloride solution. The ether layer was separated and dried over calcium chloride. The ether and benzene were removed by distillation at atmospheric pressure, then the crude product was distilled at a pressure of 10 mm. through a small Vigreux column; 18.36 g. of material boiling at 110–115° was collected as the desired product. The compound was given a final purification by fractionation through a Podbielniak column rated at 40 theoretical plates. Physical properties of the pure compound were b.p. 112° (10 mm.), $n^{20}\text{D}$ 1.4734, d^{20} 1.1035 g./ml.; molar refractivity, calcd. 73.7 ml., found 74.03 ml. *Anal.* Calcd. for $C_{12}H_{28}Sn$: Sn, 40.8; C, 49.5; H, 9.7. Found: Sn, 39.1; C, 48.9; H, 9.75.

Triethyltin Hydride.—In a typical preparation, 26.6 g. (0.11 mole) of triethyltin chloride in 50 ml. of ether was added dropwise to 1.81 g. of lithium aluminum hydride (0.048 mole) in a 3-neck flask equipped with a reflux condenser and stirrer. The reaction mixture was cooled in an ice-bath during the addition of the triethyltin chloride. The mixture was stirred at room temperature for about 3 hours. Then the reflux condenser was replaced by a distilling column and the bulk of the ether was removed at atmospheric pressure. During these operations dry nitrogen gas was passed continuously through the apparatus. The pressure was reduced to 3 mm. and all material volatile up to a temperature of 53° was collected; 18 g. of crude product was thus obtained. This was redistilled through a 6-inch Vigreux column at 20 mm. pressure; 11.5 g. (56%) of pure triethyltin hydride (b.p. 51.5–52° at 20 mm.) was obtained. *Anal.* Calcd. for $C_6H_{15}SnH$: Sn, 57.48; hydrolyzable H, 0.487. Found: Sn, 56.2; hydrolyzable H, 0.49.

Diethyltin Hydride.—Diethyltin hydride was prepared in a reaction system consisting of a three-neck flask fitted with a dropping funnel, reflux condenser, magnetic stirrer and inlet for dry nitrogen. The reflux condenser was connected to a series of traps cooled by Dry Ice and liquid air, respectively. All connections were by means of ground glass joints. The flask was immersed in an ice-bath and an ether solution of diethyltin dichloride was added to an ether solution of lithium aluminum hydride calculated to contain 100% excess of reducing agent. Then the mixture was stirred for 45 minutes at room temperature. The pressure was reduced to 10 mm. and all materials volatile at room temperature were distilled into the traps. The material caught at Dry Ice temperatures was transferred to a vacuum line and purified by distillation through traps at −45°, −95° and −185°. The mixture was thus separated into triethyltin hydride, crude diethyltin hydride and a mixture of ethyltin hydride and ether. The crude diethyltin hydride was purified by repeated distillation through traps at −25°, −45° and −185°, respectively. *Anal.* Calcd. for $C_4H_{10}SnH_2$: mol. wt., 178.7; hydrolyzable H, 1.1. Found: mol. wt., 176; hydrolyzable H, 1.1.

Ethyltin Hydride.—Ethyltin hydride was prepared by the reaction between lithium aluminum hydride and ethyltin trichloride in dibutyl ether solution. The apparatus and general procedure was essentially the same as that used in the preparation of diethyltin hydride. Emphasis was placed upon obtaining the desired product rather than high chemical yield; consequently the procedure was not followed quantitatively. After the reaction mixture was stirred for 1 hour at room temperature under a nitrogen atmosphere, the system was evacuated through traps at −80°, −112° and liquid air. The fraction condensing at −112° was analyzed as follows: mol. wt., 150.8; hydrolyzable H, 1.7; C_2H_5-, 19.0. Calcd. for $C_2H_5SnH_3$: mol. wt., 150.7; hydrolyzable H, 1.7; C_2H_5-, 19.3.

Ethyltin Chlorides.—The ethyltin chlorides were prepared by refluxing, according to the method of Kozeschkow,[6] calculated amounts of anhydrous stannic chloride and tetraethyltin for 10–12 hours. The crude materials were purified by repeated vacuum fractionation through a 10-inch Vigreux column until products were obtained which showed

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(1) Based in part on a thesis presented by Ella E. Holmes to the graduate school of Tennessee A. and I. State University in partial fulfillment of requirements for the Master of Science degree, August, 1950.

(2) Morgan State College, Baltimore 12, Md.

(3) E. R. Lippincott and M. C. Tobin, THIS JOURNAL, **75**, 4141 (1953).

(4) W. J. Jones, D. P. Evans, T. Gulwell and D. C. Griffiths, *J. Chem. Soc.*, 39 (1935).

(5) K. A. Kozeschkow, *J. Gen. Chem.* (*USSR*), **4**, 1359 (1934).

(6) K. A. Kozeschkow, *Ber.*, **66**, 1661 (1933).

no change in refractive index upon further distillation and which, upon analysis for tin and chlorine, agreed to within 1% of the theoretical. *Anal.* Calcd. for $C_2H_5SnCl_3$: Sn, 46.9; Cl, 41.8. Found: Sn, 46.1; Cl, 41.2. Calcd. for $C_4H_{10}SnCl_2$: Sn, 48; Cl, 28.6. Found: Sn, 47.8; Cl, 29.0. Calcd. for $C_6H_{15}SnCl$: Sn, 49.2; Cl, 14.7. Found: Sn, 49; Cl, 14.7.

Analyses.—Diethyldi-*n*-butyltin was analyzed for carbon and hydrogen by semimicro combustion methods using a Sargent micro-combustion assembly.

All of the compounds were analyzed for tin by digesting weighed samples for 4–6 hours in a mixture of fuming HNO_3 and 18 *M* H_2SO_4 thus oxidizing the alkyl substituents and precipitating the tin as stannic acid. The precipitates were collected on ashless filter paper and ignited to stannic oxide.

In the case of the ethyltin chlorides, chlorine was determined by hydrolyzing the compounds in 30% aq. NaOH followed by acidification and gravimetric determination of chlorine as AgCl.

Ethyltin hydride was analyzed for ethyl radicals by means of the reaction

$$C_2H_5SnH_3 + 4HCl \xrightarrow{AlCl_3} C_2H_6 + SnCl_4 + 3H_2.$$

A measured volume of the compound (10.7 cc.) was treated with an excess of anhydrous HCl in the presence of 2 g. of $AlCl_3$ in a sealed tube at 100° for 24 hours. The volatile reaction products were condensed over soda-lime to remove the excess HCl and 10.5 cc. of ethane was obtained. Its identity was confirmed by vapor pressure measurements and molecular weight determination.

In the case of the alkyltin hydrides, the number of Sn–H groups was determined by hydrolysis with 30% aq. NaOH in sealed tubes at 100° for 24 hours. The hydrogen obtained was pumped through traps at $-185°$ by means of a Toepler pump, and measured in a calibrated volume of the vacuum line.

Physical Properties. Density.—Densities of all compounds were measured at 20 ± 0.1° with a Sprengel-type pycnometer. Several determinations were made for each compound and the average deviation was ±0.0002 g./ml.

Index of Refraction.—Indices of refraction were measured at 20 ± 0.1° with an Abbe-type refractometer which was standardized against conductivity water.

Molecular weights of ethyltin hydride and diethyltin hydride were determined by the vapor density method. Measurements were made at several pressures and a counterpoise flask was used to minimize weighing errors.

Vapor Pressures.—Vapor pressures of ethyltin hydride and diethyltin hydride were measured in a static system of the type described by Sanderson.[7] The vapor pressure of diethyltin hydride was measured in an isoteniscope of special design. Pressures exerted by the vapor were balanced against dry air and the points of balance were determined to ±0.1 mm. by means of a cathetometer. For low temperatures, an ammonia vapor pressure thermometer was used and then a calibrated mercury thermometer for temperatures of 0° and above. Vapor pressures of the ethyltin chlorides were determined by the boiling point method in an ebulliometer of the type described by Swietoslawski.[8] In the boiling point method, the external pressures were maintained constant to ±0.5 mm. by use of a sensitive manostat.

Melting Points.—The melting point of diethyltin dichloride, which is a solid at room temperatures, was determined in a capillary tube in the conventional manner. The freezing points of the liquid ethyltin chlorides were read from the halt points in plots of temperature *versus* time curves for samples which were cooled at a uniform rate.

Heats of Combustion.—Heats of combustion were determined by standard methods in a Parr series 13051 plain jacket oxygen bomb calorimeter.[9] Temperature measurements were made with a mercury thermometer (calibrated by the Natl. Bur. Standards) which could be read to ±0.005°F. "Radiation" heat losses were corrected for by the method of Dickinson.[10]

The water equivalent of the calorimeter was determined by the combustion of benzoic acid (Natl. Bur. Standards Sample 39-g). Five determinations yielded a water equivalent of 2421 ± 2.1 calories per degree centigrade.

Samples of the tin tetra-alkyls were weighed directly into the sample cup of the bomb and the procedure used in the determination of their heats of combustion was identical with that used in the standardization of the calorimeter.

A slight modification was necessary in the case of the compounds containing methyl groups. Because of their comparatively high volatilities, these compounds were sealed in weighed soft glass ampoules. A 0.5 g. pellet of benzoic acid was placed in the bomb with each sample to ensure breakage of the ampoule and to initiate the combustion. In the calculations of the results, corrections were made for the heat of combustion of benzoic acid.

In most of the experiments, the combustion reaction went to completion as was evidenced by the consistent results and the fact that stannic oxide was left as a pure white residue. In cases where the residue was dark or discolored, it was obvious that the combustion reaction was incomplete.

Discussion of Results

The physical properties of the ethyltin hydrides are presented in Table I. Vapor pressure measurements were made at a minimum of twelve temperatures and plots of log *P* *versus* 1/*T* were linear from 10 mm. to atmospheric pressure. The experimental data are represented by equations of the type

$$\log P = -A/T + B$$

TABLE I

PHYSICAL PROPERTIES OF THE ETHYLTIN HYDRIDES

Compound	B.p., ° C. 760 mm.[a]	$n^{20}D$	d^{20}, g./ml.	Mol. wt.	Vapor pressure constants[b] *A*	*B*
$(C_2H_5)_3SnH$	142	1.4700	1.258	. . .	2273	8.36
$(C_2H_5)_2SnH_2$	99	. . . .		176	1576	7.09
$C_2H_5SnH_3$	35	. . . .		150.8	1470	7.65

[a] Determined by extrapolation of vapor pressure data. [b] Constants for the equation $\log P = -(A/T) + B$.

The preparation of triethyltin hydride has been reported recently by Anderson.[11] The results obtained in this investigation are in good agreement with the physical properties observed by him.

In thermal stability the ethyltin hydrides resemble the methyltin hydrides reported by Finholt and others,[12] in that the stabilities increase with the increasing substitution of alkyl groups for hydrogen. Thus only triethyltin hydride was appreciably stable at room temperatures. All of the compounds react readily with atmospheric oxygen forming white solids.

The physical properties of the ethyltin chlorides are presented in Table II. Those properties not previously reported in the literature are denoted by asterisks. Molecular refractions have been calculated using the systems of bond refractions devised by West and Rochow[13] and by Denbigh.[14]

The agreement between the calculated and experimental values reported in Table II is excellent.

Thermodynamic Properties.—The heats of combustion of several tin tetraalkyls are given in

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[7] R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 82.

[8] W. Swietoslawski, "Ebulliometric Measurements," Reinhold Publishing Corp., New York, N. Y., 1945, p. 6.

[9] "Oxygen Bomb Calorimetry and Oxygen Bomb Combustion Methods," Parr Manual No. 120, Parr Instrument Co., Moline, Ill.

[10] H. C. Dickinson, *Natl. Bur. Standards (U. S.) Bull.*, **11**, 189 (1915).

[11] H. H. Anderson, THIS JOURNAL, **79**, 1913 (1957).

[12] A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach and H. I. Schlesinger, *ibid.*, **69**, 2692 (1947).

[13] R. West and E. G. Rochow, *ibid.*, **74**, 2490 (1952).

[14] K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

TABLE II

PHYSICAL PROPERTIES OF THE ETHYLTIN CHLORIDES[a]

Formula	Density, g./ml. at 20°	Ref. index, n^{20}_D	Mole refraction Calcd.	Mole refraction Found	Melting point, °C.	Vapor pressure eqn. constants[b] *A*	Vapor pressure eqn. constants[b] *B*	Calcd. B.p., °C. at 1 atm.	Calcd. heat of vapori-zation, cal./mole	Trouton's const., cal./mole/degree
$C_2H_5SnCl_3$	1.965*	1.5408*	40.22	40.61*	−10	2554*	8.377*	192	11672*	25.1
$(C_2H_5)_2SnCl_2$					84	2753*	8.385*	227	12581*	25.2*
$(C_2H_5)_3SnCl$	1.429	1.5055	50.54	50.15	15	2652*	8.416*	206	12119*	25.3*

[a] For previously reported values, see E. Krause and A. V. Grosse, "Die Chemie der Metall-Organischen Verbindungen," Photolithoprint, Edwards Bros., Ann Arbor, Mich., 1943, pp. 336, 340. [b] Constants for the equation $\log P = -A/T + B$.

TABLE III

HEATS OF COMBUSTION AND HEATS OF FORMATION OF SEVERAL TIN TETRAALKYLS AT 300°K. AND 1 ATM.

Compound	$-\Delta H$comb., kcal./mole	Calcd. $-\Delta H$comb.	ΔHform, kcal./mole
$(CH_3)_4Sn$	934 ± 3 904 ± 10[a]	920	+9
$(CH_3)_3SnC_2H_5$	1034 ± 5	1077	+53
$(CH_3)_2Sn(C_2H_5)_2$	1221 ± 5	1234	+28
$CH_3Sn(C_2H_5)_3$	1358 ± 1	1391	+54
$(C_2H_5)_4Sn$	1547 ± 2 1521[b]	1548	−27 −39[b]
$(C_2H_5)_2Sn(C_4H_9)_2$	2170 ± 2	2176	−54
$(C_4H_9)_4Sn$	2816 ± 4 2773[b]	2804	−57 −111[b]
$(C_6H_{13})_4Sn$	4060 ± 3	4060	+119

[a] Data of Lippincott and Tobin.[3] [b] Data of Jones, *et al.*[4]

Table III. To obtain the values reported in the table, the following corrections were applied: (1) all weighings were reduced to weight *in vacuo;* (2) the bomb process was corrected to constant temperature (27°); (3) the combustion reaction was corrected from one at constant volume to one at a constant pressure of one atmosphere. The latter two corrections were made according to the method of Washburn.[15] The data show the expected increase in the observed heats of combustion with increased size of substituent alkyl radical. With the exception of compounds containing methyl radicals, the heats of combustion may be represented by the empirical equation

$$-\Delta H_{300} = 157n + 292$$

where *n* is the number of carbon atoms in the molecule.

The heats of formation given in Table III were calculated from the heats of combustion, taking the heats of formation of $H_2O(l)$, $CO_2(g)$ and $SnO_2(s)$ to be 68.317, 94.052 and 138.8 kcal. per mole, respectively.[16-18]

Comparison of the heats of combustion observed in this work with those of previous investigators[3,4] reveal that the results obtained in this investigation are consistently larger in magnitude. The principal source of error in experiments of this type, where one of the combustion products is a solid, is failure to obtain complete combustion. This would lead to low values for the observed heats of combustion. This fact, in addition to the checks between individual determinations and the agreement, within the limits of experimental error, of the observed heats of combustion with a single empirical equation, supports the higher values obtained in this investigation.

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(15) E. W. Washburn, *J. Research Natl. Bur. Standards*, **10**, 525 (1933).

(16) D. D. Wagman, J. E. Kilpatrick, W. U. Taylor, K. S. Pitzer and F. D. Rossini, *ibid.*, **34**, 143 (1945).

(17) E. J. Prosen, R. S. Jessup and F. D. Rossini, *ibid.*, **33**, 447 (1944).

(18) J. Moose and S. W. Parr, THIS JOURNAL, **46**, 2656 (1924).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Some Studies on the Preparation of Arylboronic Acids[1]

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The yields of boronic acids from the reaction of various organic derivatives of the Group II-B metals with tri-*n*-butyl borate are not as good as those obtained from the reaction of Grignard reagents with tri-*n*-butyl borate or from the reaction of organomercury compounds with boron trichloride. The course of the reaction of boron trichloride with organomercury compounds is dependent upon the groups substituted on the aromatic radical attached to the mercury.

An interest in boronic acids has developed recently because of the proposed use of boron-containing compounds in brain tumor therapy. The treatment involves the irradiation of carcinogenic tissue which has absorbed preferentially a compound containing boron-10.[3] Azo dyes which contain boron have been shown to be promising for this treatment,[4] but the work of several has shown

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(1) This work was supported in part by the United States Atomic Energy Commission under Contract No. AT(11-1)-59.

(2) Du Pont Teaching Fellow, 1956–1957.

(3) Naturally occurring boron contains 18.83% of this isotope. See NBS Circular No. 499, p. 7.

(4) H. Gilman, L. Santucci, D. R. Swayampati and R. O. Ranck, THIS JOURNAL, **79**, 2898 (1957).