Experimental

Materials.—Triethylgermanium acetate,[6] diisopropylgermanium diacetate,[3] and tri-*n*-butylgermanium trifluoroacetate[11] served in the preparation of new alkylgermanium alkanesulfonates. In Table II di-*n*-butylgermanium dibromide,[11] triethyltin fluoride,[12] triphenylisocyanatosilane,[13] and antimony(III) fluoride were special preparations; some commercial products required drying or dehydration.

Triethylgermanium Methanesulfonate, Triethylgermanium Ethanesulfonate, Diisopropylgermanium Bis(methanesulfonate), Tri-*n*-butylgermanium Methanesulfonate, and Tri-*n*-butylgermanium Ethanesulfonate.—Typically, 5.70 g. or 15.9 mmoles of tri-*n*-butylgermanium trifluoroacetate and 1.39 g. or 14.5 mmoles of methanesulfonic acid in a 10-min. reflux with distillation furnished approximately 1.36 g. or 12.0 mmoles of trifluoroacetic acid, b.p. 73°, then 0.40 g. of excess tri-*n*-butylgermanium trifluoroacetate distilled at 29 mm., next 0.45 g. of crude tri-*n*-butylgermanium methanesulfonate distilled under 1 mm. pressure, and finally 4.35 g. of fair grade tri-*n*-butylgermanium methanesulfonate at approximately 150° (1 mm.), leaving 0.4 g. undistilled. The yield was 89%. Redistillation of the 4.35-g. fraction furnished a 2.6-g. center cut of b.p. 150–152° (1 mm.) for measurements. The analyses and properties of these five new compounds are in Table I.

Infrared Measurements.—A Perkin-Elmer Model 421 spectrophotometer served for the measurements, which indicated strong asymmetric sulfonate stretch[14–16]: triethylgermanium methanesulfonate, 1152 cm.$^{-1}$; diisopropylgermanium bis(methanesulfonate), 1157 cm.$^{-1}$; tri-*n*-butylgermanium methanesulfonate, 1151 cm.$^{-1}$; also, tri-*n*-butylgermanium ethanesulfonate, 1150 cm.$^{-1}$. Weak absorptions at 1078 and 1079 cm.$^{-1}$, possibly symmetric sulfonate stretch, appeared only in the butylgermanium derivatives. Flat circular plates of silver chloride (under study by Dr. L. L. Pytlewski at this institute) proved inert to thin films of pure liquid alkylgermanium alkanesulfonates at 25°; sodium chloride or potassium bromide plates were too reactive at 25° to be of any use.

Hydrolysis.—A 0.0310 *M* solution of tri-*n*-butylgermanium ethanesulfonate in 59% aqueous ethanol had a pH of 1.90 and thus 0.0125 mole of hydrogen ion per liter. This is approximately 40% hydrolysis.

Conductance.—The molar conductance of 0.060 *F* tri-*n*-butylgermanium ethanesulfonate in 99.7% acetic acid was only 8.2 × 10^{-3} cm.^{2} ohm^{-1} mole^{-1}.

Solubility.—Tri-*n*-butylgermanium methanesulfonate was easily soluble in an equal volume of petroleum ether (100–115°) or carbon tetrachloride at 25°.

Exchange Reactions (Table II).—Sixteen reactions, with distillation under reduced pressure, were complete in 10 min. or less and used very small distilling units with ground joints, calibrated receivers, and calibrated thermometers. Typically, after reflux under atmospheric pressure for 8 min., distillation under 1–150 mm. pressure followed; identification of each alkylgermanium product included a later measurement of boiling point and a qualitative test for the halide or halogenoid. However, the slow reaction with silver chloride furnished 0.14 g. of triethylgermanium chloride in the first 30 min. of reflux and then distillation; the second 30 min. of reflux and then distillation supplied another 0.14 g. of triethylgermanium chloride, while unchanged triethylgermanium ethanesulfonate still persisted. The average difference between the observed boiling point of each alkylgermanium chief product in Table II and the published boiling point is 1.5°, with a maximum difference of 3°. Nine of these compounds appearing as alkylgermanium chief products are compounds prepared for the first time at an earlier date by the present author. There was no further study of other reaction products.

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CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
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Volatile *n*-Butyltin and Phenyltin Tricarboxylates. Organotin Oxymonocarboxylates[1]

BY HERBERT H. ANDERSON

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No mention of volatile alkyltin tricarboxylates or aryltin tricarboxylates occurs in a recent organotin review.[2] Recent publications carry the names of compounds such as phenyltin triacetate (without data),[3] *n*-butyltin tris(2-ethylhexoate) as a catalyst (without physical properties),[4] *n*-butyltin S,S′,S″-tris(mercaptoacetate) (with analyses),[5] *n*-butyltin trioctoate catalyst (without physical properties),[6] phenyltin trilaurate stabilizer,[7] and also methyltin triacetate, ethyltin trihexoate, phenyltin tristearate, and other catalysts (without physical properties).[8]

Crystalline $CH_3Sn(OCOR)_2OSn(CH_3)(OCOR)OSn(OCOR)_2$ is the product[9] of the reaction of the corresponding aliphatic carboxylic acid with either methanestannonic acid or $[CH_3Sn(O)OCOR]_6$ and then crystallization. However, the present publication reports successful distillation at 1 mm. pressure of *n*-butyltin tricarboxylates, starting with the corresponding aliphatic carboxylic acids and *n*-butyltin oxacetate, *n*-butyltin oxy-*n*-butyrate, or *n*-butanestannonic acid anhydride. This surprising difference may result from the use of distillation instead of crystallization, or from the longer length of the *n*-butyl group as compared to methyl. Also, the preparation and properties of $[CH_3Sn(O)OCOR]_6$[9] are in agreement with those of the five new related polymeric organotin oxycarboxylates in this publication.

In the present publication an excess of the silver carboxylate converts *n*-butyltin trichloride, phenyltin trichloride, or tin(IV) chloride, in carbon tetrachloride solution, into nine organotin tricarboxylates and one tin tetracarboxylate; distillation is possible at 1 mm. pressure. Analyses in Table I establish the formulas.

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[5] E. L. Weinberg and E. W. Johnson, U. S. Patent 2,832,750 (April 29, 1958).

[6] H. J. Leavitt, U. S. Patent 2,985,546 (May 23, 1961).

[7] C. W. Montgomery and R. C. Ryan, Jr., U. S. Patent 2,895,941 (July 21, 1959).

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[9] H. Lambourne, *J. Chem. Soc.*, **121**, 2533 (1921).

TABLE I

PROPERTIES OF VOLATILE ORGANOTIN CARBOXYLATES

Compound	B.p.,[a] °C.	M.p., °C.	d^{20}_4[b]	n^{20}	Mol. refr.		Tin[c]		OCOR[d]		Temp. distilled at, °C. (1 mm.)
					Calcd.	Found	Calcd.	Found	Calcd.	Found	
n-$C_4H_9Sn(OCOCH_3)_3$[e]	273	46	1.474[f]	1.476[f]	66.88[f]	67.54	33.6	33.7	50.2	49.7	117–119
n-$C_4H_9Sn(OCOC_2H_5)_3$[g]	289	...	1.360	1.470	80.82	81.04	30.0	30.1	55.5	55.7	133–135
n-$C_4H_9Sn(OCO$-n-$C_3H_7)_3$	311	...	1.281	1.463	94.76	93.98	27.2	27.1	59.8	60.1	156–158
n-$C_4H_9Sn(OCO$-i-$C_3H_7)_3$	309	...	1.262	1.4556	94.76	94.08	27.2	27.4	59.8	60.1	139–141
n-$C_4H_9Sn(OCO$-n-$C_4H_9)_3$	331	...	1.213	1.4627	108.71	108.75	24.8	24.9	63.3	63.2	182–184
$C_6H_5Sn(OCOCH_3)_3$	268	76	...	...	...	...	31.6	32.0	47.5	47.6	*ca.* 180[h]
$C_6H_5Sn(OCOC_2H_5)_3$	290	67.5	...	...	...	...	28.6	28.6	52.8	52.7	*ca.* 195[i]
C_6H_5SnOCO-n-$C_3H_7)_3$	300	...	1.355	1.5105	100.12	100.98	26.0	25.8	57.2	57.0	193–196
$C_6H_5Sn(OCO$-i-$C_3H_7)_3$	300	50.5	1.336[f]	1.4925[f]	100.12	99.07	26.0	25.9	57.2	56.7	171–173[j]
$Sn(OCO$-i-$C_3H_7)_4$	305	116	...	...	...	...	25.4	25.6	74.6	74.1	*ca.* 167[j]

[a] All compounds decomposed at the normal boiling points. [b] In white light; all compounds are colorless. [c] Weighing of tin as stannic oxide after use of fuming nitric and sulfuric acids. [d] Average of two titrations of available acid using sodium hydroxide in absolute ethanol, with phenolphthalein indicator; chlorophenol red was indicator with tin tetraisobutyrate. [e] Calcd.: mol. wt., 352.9. Found: mol. wt. (camphor), 330. [f] On supercooled liquid; bond refraction Sn–O taken as 3.13. [g] Calcd.: mol. wt., 395.0. Found: mol. wt. (camphor), 390. [h] Then five crystallizations from 1-chlorobutane followed. [i] One crystallization from benzene and two from 1-chlorobutane followed. [j] Then four purifications by fractional freezing followed.

As a whole, the organotin tricarboxylates are relatively covalent and easily hydrolyzed; n-butyltin triacetate and n-butyltin tripropionate are monomeric in camphor solution. Seven observed molar refractions agree to within 0.61% with values calculated using 3.13 for the Sn–O bond refraction rather than the earliest value of 3.84,[10] or a recent value of (approximately) 2.928.[11]

Organotin tricarboxylates hydrolyze easily in 97% ethanol. This hydrolysis is reversible

$$n\text{-}C_4H_9Sn(OCOR)_3 + H_2O \rightleftarrows [n\text{-}C_4H_9Sn(O)OCOR]_n + 2RCOOH$$

boiling pure excess aliphatic carboxylic acid forces the equilibrium to the left and gives pure alkyltin tricarboxylate. However, phenyltin oxycarboxylates and boiling carboxylic acid yield a tin tetracarboxylate

$$[C_6H_5Sn(O)OCO\text{-}i\text{-}C_3H_7]_n + 3i\text{-}C_3H_7COOH = Sn(OCO\text{-}i\text{-}C_3H_7)_4 + C_6H_6 + H_2O$$

Infrared absorptions include strong antisymmetric carboxylate and slightly weaker symmetric carboxylate, while the carbonyl of organic esters, around 1700 cm.$^{-1}$, is completely missing from organotin oxymonocarboxylates and is usually weak in organotin tricarboxylates. All this is in general agreement with published spectra in the solid state for trialkyltin carboxylates and dialkyltin dicarboxylates.[12,13]

Closely related ethylgermanium triformate, triacetate, tripropionate, tri-n-butyrate, and tri-n-valerate often decompose at the normal boiling points.[14]

Experimental

n-Butyltin Triacetate, n-Butyltin Tripropionate, n-Butyltin Tri-n-butyrate, n-Butyltin Triisobutyrate, and n-Butyltin Tri-n-valerate.—Typically, 9.0 g. of n-butyltin trichloride and 26 g. (33% excess) of silver isobutyrate finally furnished 11.6 g. (83% yield) of crude, chlorine-free, very easily hydrolyzed n-butyltin triisobutyrate. The preparation included the following respective steps: 90 min. reflux in 50 g. of carbon tetrachloride in equipment with ground joints; filtration and washing of silver salts; careful removal of solvent under 60 mm. pressure in a filter flask on a hot plate; transfer to distilling equipment; fractional distillation under 1 mm. pressure to get 2.9 g. of b.p. 137–139°, then a 6.3 g. center fraction of b.p. 139–141° for measurements, also 2.4 g. of slightly higher boiling point.

Phenyltin Triacetate, Phenyltin Tripropionate, Phenyltin Tri-n-butyrate, Phenyltin Triisobutyrate, and Tin Tetraisobutyrate.—Typically, 22 g. of phenyltin trichloride and 52 g. (30% excess) of silver propionate after 1 hr. of reflux in 100 g. of carbon tetrachloride, then filtration and washing of silver salts, next removal of solvent, and finally distillation under 1 mm. pressure and approximately 195° furnished 25 g. (82% yield) of supercooled liquid phenyltin tripropionate, which later crystallized at −78°. One crystallization from benzene and two from 1-chlorobutane gave chlorine-free crystals of m.p. 66–67° in a capillary. Phenyltin triacetate (69% yield) remained a supercooled liquid, but five crystallizations from 1-chlorobutane furnished chlorine-free material of m.p. 76°. Distilled phenyltin triisobutyrate had a m.p. of 49.5–49.8°, which became 50.5° after five fractional freezings. Phenyltin tri-n-butyrate remained an extremely viscous liquid at 23°. The purification of tin tetraisobutyrate involved distillation and then four fractional freezings.

n-Butyltin Oxyacetate, n-Butyltin Oxypropionate, n-Butyltin Oxy-n-butyrate, Phenyltin Oxyacetate, and Phenyltin Oxyisobutyrate.—Typically, 4.85 g. of n-butyltin tripropionate in 32 g. of absolute ethanol upon slow addition of 10 g. of 95% ethanol with stirring furnished 2.73 g. (84% yield) of white polymeric precipitate, $[n\text{-}C_4H_9Sn(O)OCOC_2H_5]_n$; filtration and then three washings with 95% ethanol followed; finally there was drying in air and then for 1 hr. at 100° under 1 mm. pressure. This polymer was essentially insoluble in boiling nitromethane, dimethylformamide, or dimethyl sulfoxide.

Anal. Calcd. for $[n\text{-}C_4H_9Sn(O)OCOCH_3]_n$: Sn, 47.3; $OCOCH_3$, 23.5. Found: Sn, 47.4; $OCOCH_3$, 23.5, 23.6, 23.4 by distillation with phosphoric acid.[15] Calcd. for $[n\text{-}C_4H_9Sn(O)OCOC_2H_5]_n$: Sn, 44.8; $OCOC_2H_5$, 27.6. Found: Sn, 44.9; $OCOC_2H_5$, 27.5, 27.7. Calcd. for $[n\text{-}C_4H_9Sn(O)OCO\text{-}n\text{-}C_3H_7]_n$: C, 34.5; H, 5.78; Sn, 42.6. Found: C, 34.8; H, 5.92; Sn, 42.3. Calcd. for $[C_6H_5Sn(O)OCOCH_3]_n$: Sn, 43.8. Found: Sn, 43.9. Calcd. for $[C_6H_5Sn(O)OCO\text{-}i\text{-}C_3H_7]_n$: Sn, 39.8;

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OCO-*i*-C_3H_7, 29.1. Found: Sn, 39.9; OCO-*i*-C_3H_7, 29.0, 29.2, 29.2.

Reactions of Organotin Oxymonocarboxylates.—Reflux of 0.26 g. of *n*-butyltin oxyacetate and 0.7 g. of glacial acetic acid (3 min.) and distillation at 1 mm. pressure furnished 0.33 g. (88% yield) of *n*-butyltin triacetate, with normal b.p. 278° dec. Similarly, *n*-butyltin oxy-*n*-butyrate and *n*-butyric acid gave a 60% yield of *n*-butyltin tri-*n*-butyrate, b.p. 315°, $d^{20}{}_4$ 1.281, and bearing 60.2% *n*-butyrate. However, 1.5 g. of phenyltin oxyisobutyrate and 10 g. of isobutyric acid upon slow evaporation on a hot plate yielded approximately 1.2 g. of crude tin tetraisobutyrate, m.p. *ca.* 106–107°, b.p. 160–170° (1 mm.); this involved elimination of the phenyl group. *Anal.* Found: Sn, 25.4; isobutyrate, 74.5.

Reactions of *n*-Butanestannonic Acid Anhydride.—Anhydride (5 g.) and 7 g. of glacial acetic acid upon 1 hr. of reflux, then careful distillation of aqueous carboxylic acid, next addition of 3 g. of acetic acid, followed by distillation of acetic acid and finally of *n*-butyltin triacetate furnished 7.4 g. (89% yield) of the latter, b.p. 125–129° (1 mm.). A similar reaction with propionic acid gave an 84% yield of *n*-butyltin tripropionate, b.p. 286° and n^{20} 1.467.

Conductance.—In absolute ethanol 0.0655 *M* *n*-butyltin triisobutyrate had a molar conductance of only 7.6×10^{-2} cm.^{2} ohm^{-1} mole^{-1}.

Infrared Absorptions.—A Perkin-Elmer Model 421 spectrophotometer served for measurements on organotin oxycarboxylates in KBr pellets (1%) and on organotin tricarboxylates (1%) in carbon tetrachloride. Carbonyl absorption as in organic esters at approximately 1700 cm.$^{-1}$ was completely absent from four organotin oxycarboxylates: *n*-butyltin oxyacetate, with strong antisymmetric carboxylate absorption at 1570, 1548, and 1533 cm.$^{-1}$ and strong symmetric carboxylate at 1421 cm.$^{-1}$; *n*-butyltin oxypropionate, with corresponding absorptions at 1532, 1424, and 1408 cm.$^{-1}$; *n*-butyltin oxy-*n*-valerate at 1560, 1548, 1530, 1420, and 1400 cm.$^{-1}$; phenyltin oxyisobutyrate at 1548, 1530, 1426, and 1416 cm.$^{-1}$. *n*-Butyltin triacetate had weak ester carbonyl absorption at 1705 cm.$^{-1}$, possibly due to slight hydrolysis, and strong absorptions at 1560, 1549, 1542, 1534, 1420, and 1410 cm.$^{-1}$; *n*-butyltin triisobutyrate also had weak ester carbonyl at 1699 cm.$^{-1}$ and strong absorptions at 1532 and 1426 cm.$^{-1}$. *n*-Butyltin tri-*n*-valerate had medium ester carbonyl at 1701 cm.$^{-1}$, strong absorptions at 1579, 1543, and 1533 cm.$^{-1}$, and medium absorption at 1412 cm.$^{-1}$. Phenyltin tripropionate had weak ester carbonyl at 1706 cm.$^{-1}$, strong absorptions at 1544 and 1532 cm.$^{-1}$, and medium absorptions at 1422 and 1410 cm.$^{-1}$. Phenyltin triisobutyrate had weak absorption at 1699 cm.$^{-1}$, strong at 1532 cm.$^{-1}$, and medium at 1426 cm.$^{-1}$. Antisymmetric carboxylate absorption was always stronger than that of symmetric carboxylate; CH_2 deformation gave strong absorption in the region 1441–1466 cm.$^{-1}$ with all eight compounds studied.

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CONTRIBUTION FROM THE EVANS LABORATORY
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Large Scale Synthesis of $H_2B(NH_3)_2{}^+BH_4{}^-$ and H_3NBH_3

BY S. G. SHORE AND K. W. BÖDDEKER

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Two compounds of empirical composition BNH_6 are known: the diammoniate of diborane, $H_2B(NH_3)_2{}^+BH_4{}^-$, and ammonia–borane, H_3NBH_3, the products of unsymmetrical and symmetrical cleavage, respectively, of diborane.[1] Previous synthetic procedures for $H_2B(NH_3)_2{}^+BH_4{}^-$ required slow, low temperature (below −100°) addition of diborane to ammonia in order to avoid vigorous reaction which could lead to side products.[1,2] Yields were restricted to several hundred milligrams (2–4 mmoles).

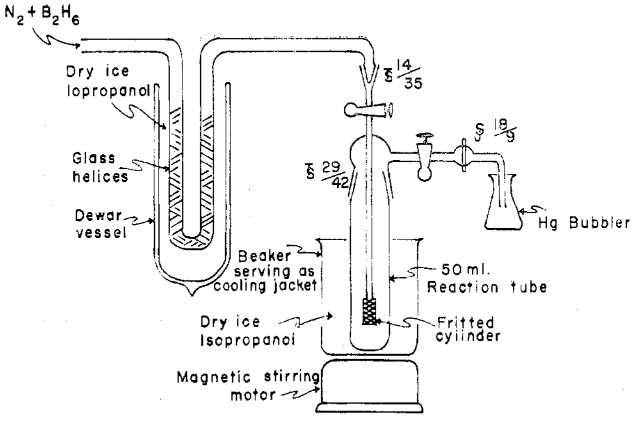

Fig. 1.—Reaction system.

We have found that by passing a stream of diborane, diluted in N_2, into liquid ammonia at −78°, an essentially quantitative yield of $H_2B(NH_3)_2{}^+BH_4{}^-$ is produced. The procedure described below is not only convenient, but is easily adaptable to relatively large scale runs. As much as 30 g. of diammoniate (0.5 mole) has been prepared at one time. However, the usual synthesis involves the preparation of 2 to 4 g. of product.

In a typical preparation of the diammoniate, diborane was generated according to the method of Shapiro and co-workers[3] by slowly dropping 15 ml. of $BF_3\cdot(C_2H_5)_2O$ into a suspension of 3 g. of $LiAlH_4$ in 150 ml. of ether. A continuous stream of N_2 flowing through the system carried the B_2H_6 from the generator to the reaction tube (Fig. 1), where it was dispersed through a frit beneath the surface of 20 ml. of liquid NH_3, at −78°. The solution was stirred continuously by means of a magnetic stirrer. One-half hour after the last drop of $BF_3\cdot(C_2H_5)_2O$ had been added to the $LiAlH_4$ solution, the side arm of the reaction tube was connected to a vacuum system; the solution was frozen in liquid nitrogen and NH_3 was sublimed away at −78°.

Diammoniate of diborane obtained from this procedure is a white, microcrystalline, free flowing solid. Its X-ray powder diffraction pattern is identical with that of diammoniate prepared in the conventional way. (Table I). No more than a trace amount of H_3NBH_3 can be extracted with ether from the solid product. Fresh samples of $LiAlH_4$, rated at 95+% (Metal

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