CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
DREXEL INSTITUTE OF TECHNOLOGY, PHILADELPHIA, PENNSYLVANIA

Alkyltin Methanesulfonates and Ethanesulfonates

BY HERBERT H. ANDERSON

Received June 20, 1963

Seven new dialkyltin bis(alkanesulfonates) and one new trialkyltin methanesulfonate result from one of the following preparative methods: best, from excess alkanesulfonic acid and a dialkyltin oxide, or sometimes a bis(trialkyltin) oxide; from excess alkanesulfuric acid and a dialkyltin bis(trifluoroacetate); less desirably, from a dialkyltin dihalide and excess silver alkanesulfonate. These partly ionic alkyltin alkanesulfonates melt above 240° with partial decomposition and also have infrared absorptions for asymmetric sulfonate stretch at 1188–1195 cm.$^{-1}$ and symmetric sulfonate stretch at 1050–1066 cm.$^{-1}$. Partial hydrolysis of the compounds in water gives acidic solutions. Solubilities are high in the polar solvents water, dimethylformamide, dimethyl sulfoxide, and alcohols with less than five carbon atoms; molar conductances in dimethylformamide are between 7 and 12.

Introduction

Di-*n*-butyltin bis-(*p*-toluenesulfonate)—apparently the only organotin arylsulfonate or alkylsulfonate known before the present syntheses of eight alkyltin alkanesulfonates—is a white solid melting above 320°, made from di-*n*-butyltin oxide and *p*-toluenesulfonic acid monohydrate in methanol, with evaporation to small volume and then extraction with ether.[1]

In contrast to this meager information there is much known about closely related alkylsilicon, alkylgermanium, and alkyltin sulfates. Known compounds include $[(C_2H_5)_3Ge]_2SO_4$, b.p. 342° and m.p. −4°,[2] $[(C_2H_5)_2GeSO_4]_2$, m.p. 116°,[2] $[(n\text{-}C_3H_7)_3Ge]_2SO_4$, b.p. 370°,[3] $[(i\text{-}C_3H_7)_3Ge]_2SO_4$, b.p. 380°,[4] $[(i\text{-}C_3H_7)_2GeSO_4]_2$, m.p. 115° dec.,[5] $[(C_2H_5)_3Si]_2SO_4$, b.p. 278°,[6] $[(CH_3)_3Si]_2SO_4$, b.p. 87–90° (4 mm.),[7] and $[(C_2H_5)_3Sn]_2SO_4$,[8] a solid melting much above 100°. A deficiency of 100% sulfuric acid causes the straightforward reaction

$$2(n\text{-}C_3H_7)_3GeOCOC_2H_5 + H_2SO_4 = [(n\text{-}C_3H_7)_3Ge]_2SO_4 + 2C_2H_5COOH$$

to occur under reflux.[3] This transesterification or ester exchange leads to later related preparations of alkylsilicon, alkyltin, and other alkylgermanium sulfates.[4–6,8]

Experimental

Materials.—M and T Chemical Co., Rahway, N. J., very kindly furnished numerous alkyltin chlorides and oxides, while alkanesulfonic acids were Eastman Kodak practical grade.

Diethyltin Bis(ethanesulfonate), Di-*n*-propyltin Bis(methanesulfonate), and Di-*n*-propyltin Bis(ethanesulfonate).—Typically, 4.0 g. of polymeric diethyltin oxide soon dissolved in a solution of 5.6 g. of ethanesulfonic acid in 20 g. of hot 95% ethanol in a 50-ml. beaker. Filtration and then three evaporations with 1-butanol on a hot plate and then crystallization followed. A second filtration and three careful washings of crystals with toluene came next. Further partial evaporation produced a second crop of crystals, later filtered and washed, for a total of 6.8 g. of $(C_2H_5)_2Sn(OSO_2C_2H_5)_2$, yield 83%. Then crystallization from 93% 1-butanol, 5% water, and 2% ethanesulfonic acid furnished a 4.7-g. first crop of crystals for study and then a 1.7-g. second crop. Drying was in air overnight and then for 2 hr. at 110° with all compounds.

Diisopropyltin Bis(methanesulfonate) and Di-*n*-butyltin Bis(methanesulfonate), by Dealkylation.—Five-hour heating of 10.0 g. of bis(triisopropyltin) oxide and 14.5 g. of methanesulfonic acid in 10 g. of 1-butanol in a 50-ml. beaker on a hot plate—mainly with little solvent, but adding 95% ethanol and a small amount of water to redissolve the solid when necessary—finally gave a 20-ml. hot solution. Addition of 10 g. of boiling toluene and slow crystallization followed. Filtration, washing of the crystals twice with benzene, and drying gave 13.5 g. of diisopropyltin bis(methanesulfonate) needles, an 88% yield. Crystallization from a mixture containing 23 g. of 1-butanol, 1.5 g. of water, and 0.5 g. of methanesulfonic acid and then a careful triple wash with benzene gave 5.4 g. of crystalline needles for study; further crystallization gave 5 g. more, used for work on solubility. Evaporation of a solution of 5.0 g. of bis(tri-*n*-butyltin) oxide and 7.4 g. of methanesulfonic acid in 17 g. of 95% ethanol in a 50-ml. beaker down to 10-ml. volume and heating 20 min. with little solvent and slow cooling produced tiny crystals, later filtered and washed with benzene. Two repetitions of the heating process followed; 6.5 g. (91% yield) of di-*n*-butyltin bis(methanesulfonate) resulted. Crystallization from 1-butanol with 1% methanesulfonic acid followed.

Triisopropyltin Methanesulfonate.—In equivalent quantities, 12.8 g. of bis(triisopropyltin) oxide and 4.8 g. of methanesulfonic acid in 14 g. of mixed 95% ethanol and 1-butanol reacted easily in a 50-ml. beaker on a hot plate; three crystallizations furnished 14 g. of crude triisopropyltin methanesulfonate. Further crystallizations of the 14 g. from 1-butanol bearing 2% water and 1.5% methanesulfonic acid furnished a 3.2-g. first crop of needles, carefully washed three times with benzene, and a discarded 3-g. second crop containing 28.9% methanesulfonate and some diisopropyltin bis(methanesulfonate).

Dimethyltin Bis(methanesulfonate) and Diethyltin Bis(methanesulfonate), Using Silver Methanesulfonate.—Typically, 4.1 g. of dimethyltin dichloride and 11 g. of silver methanesulfonate reacted easily in 32 g. of absolute ethanol in a 1.5-hr. reflux. Filtration, washing, and then crystallization from mixed 95% ethanol–1-butanol gave 3.9 g. or an 89% yield of crude dimethyltin bis(methanesulfonate). Another crystallization from the same solvents with 0.2% methanesulfonic acid and then washing with cold 1-butanol gave 1.70 g. of tiny white crystals for study.

Diethyltin Bis(methanesulfonate) from Diethyltin Bis(trifluoroacetate).—Exactly 3 g. of methanesulfonic acid and 4.3 g. of diethyltin bis(trifluoroacetate) reacted in a beaker on a hot plate while CF_3COOH escaped; two crystallizations from 1-butanol with 4% water gave a total of 3.6 g. of diethyltin bis(methanesulfonate), a 92% yield. Identification by KBr pellet showed alkanesulfonate and no carboxylate present.

---

[1] D. Seyferth and F. G. A. Stone, *J. Am. Chem. Soc.*, **79**, 515 (1957).

[2] H. H. Anderson, *ibid.*, **72**, 194 (1950).

[3] H. H. Anderson, *ibid.*, **73**, 5798 (1951).

[4] H. H. Anderson, *J. Org. Chem.*, **20**, 536 (1955).

[5] H. H. Anderson, *J. Am. Chem. Soc.*, **78**, 1692 (1956).

[6] H. H. Anderson and G. M. Stanislow, *J. Org. Chem.*, **18**, 1721 (1953).

[7] W. I. Patnode and F. C. Schmidt, *J. Am. Chem. Soc.*, **67**, 2272 (1945).

[8] G. S. Sasin and R. Sasin, *J. Org. Chem.*, **20**, 387 (1955).

TABLE I
PROPERTIES OF NEW COMPOUNDS

Compound	M.p., °C.[d]	Tin[a]		OSO_2R[b]			Infrared absorption, cm.$^{-1}$[c]	
		Calcd.	Found	Calcd.	Found		Asymm. sulfonate	Symm. sulfonate
$(CH_3)_2Sn(OSO_2CH_3)_2$	325	35.0	35.4	56.1	55.9	56.1	1195	1053, 1059
$(C_2H_5)_2Sn(OSO_2CH_3)_2$	334	32.3	32.8	51.8	51.7		1195	1051, 1061
$(C_2H_5)_2Sn(OSO_2C_2H_5)_2$	309	30.0	30.2	55.2	54.9	55.0	1188	1064
$(n\text{-}C_3H_7)_2Sn(OSO_2CH_3)_2$	307	30.0	29.9	48.1	48.3	48.2	1195	1051, 1059, 1061
$(n\text{-}C_3H_7)_2Sn(OSO_2C_2H_5)_2$	298	28.1	27.8	51.6	51.7	51.8	1188	1066
$(i\text{-}C_3H_7)_2Sn(OSO_2CH_3)_2$	275	30.0	30.0	48.1	48.1	48.2	1195	1053, 1059, 1063
$(i\text{-}C_3H_7)_3SnOSO_2CH_3$	244	34.6	34.6	27.7	28.1	28.2	1193	1051, 1059
$(n\text{-}C_4H_9)_2Sn(OSO_2CH_3)_2$	312	28.1	28.1	45.0	45.1	44.9	1190	1050, 1059

[a] Conversion to stannic oxide using fuming nitric and fuming sulfuric acids. [b] Acid titrating with sodium hydroxide in 80% ethanol to blue color of brom thymol blue indicator. [c] Concentration about 0.8 wt. % in KBr pellets, with Perkin-Elmer Model 421 spectrophotometer; asymmetric sulfonate stretch absorption was always strong, while symmetric sulfonate stretch absorptions were medium. [d] Melting points, taken in capillaries in an aluminum block, all involved partial decomposition with some escape of a gas. Averages of two or three determinations, with corrections of temperatures. All compounds are crystalline white solids.

Solubilities.—Dissolving of $(i\text{-}C_3H_7)_2Sn(OSO_2CH_3)_2$ in the solvent in a 5-ml. beaker on a hot plate was followed by partial evaporation of solvent and then by slow crystallization at 22°; evaporation of 1.00 ml. or less of the clear supernatant on a tared 25-mm. watchglass furnished the weight of solute per ml. Solubilities of diisopropyltin bis(methanesulfonate) in g./l. of saturated solution at 22° were: nitromethane, 1.0; acetonitrile, 3.0; glacial acetic acid, 15; trifluoroacetic acid, 400; absolute ethanol, 38; 1-butanol, 20; dimethylformamide, 500; dimethyl sulfoxide, 290; ethyl acetate, very little. Water and alcohols were very good solvents for dimethyltin bis(methanesulfonate), but nitromethane, bromoethane, di-*n*-butyl ether, carbon tetrachloride, and butanone were poor solvents. Di-*n*-butyltin bis(methanesulfonate) dissolved poorly in water or molten camphor.

Conductances.—At a concentration of 0.065 mole of solute per liter of dimethylformamide the molar conductances were 11.5 cm.^{2} ohm^{-1} mole^{-1} for diisopropyltin bis(methanesulfonate), 8.8 for dimethyltin bis(methanesulfonate), and 7.7 for triisopropyltin methanesulfonate.

Thermal Decomposition.—A preliminary macro investigation of the melting point of diethyltin bis(ethanesulfonate) showed that odoriferous gas escaped, the liquid darkened, and the observed melting point dropped when the compound remained at 310°.

Results and Discussion

Table I includes the properties of seven new dialkyltin bis(alkanesulfonates) and one trialkyltin alkanesulfonate; these are compounds of a type little investigated previously. All these compounds have strong absorption for asymmetric sulfonate stretch at 1188–1195 cm.$^{-1}$ and medium absorptions for symmetric sulfonate stretch at 1050–1066 cm.$^{-1}$, in good agreement with 8.4 and 9.44 μ, respectively, reported for methanesulfonic acid.[9]

All these compounds melt above 240° with decomposition. This resembles the autoxidation of $[(CH_3)_3Si]_2SO_4$ in an attempted distillation at a pressure above 4 mm.[7]

Comparatively polar solvents such as water, lower alcohols, trifluoroacetic acid, dimethyl sulfoxide, and dimethylformamide are very good solvents for these alkyltin alkanesulfonates, while molten camphor, nitromethane, and acetonitrile are poor solvents. Some hydrolysis occurs in aqueous solution, since a pH of 2.2 and a $[H^+]$ of 6×10^{-3} *m* for a 0.053 formal aqueous solution of $(CH_3)_2Sn(OSO_2CH_3)_2$ correspond to 0.11 mole of H^+ per mole of compound. A recent study of the hydrolysis of $(CH_3)_2Sn(ClO_4)_2$ reports the existence of five complexes[10] including $(CH_3)_2Sn(OH)^+$, among others.

Taken as a whole, the infrared absorptions,[9,11,12] melting points, molar conductances, and solubilities clearly indicate a partly ionic character of the alkyltin alkanesulfonates, much of which may be due to the alkanesulfonate group.

The abstract summarizes the preparative methods, the least desirable of which involves silver alkanesulfonates.

---

(9) R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 4228 (1954).

(10) R. S. Tobias, I. Ogrins, and B. A. Nevett, *Inorg. Chem.*, **1**, 638 (1962).

(11) K. C. Schreiber, *Anal. Chem.*, **21**, 1168 (1949).

(12) N. B. Colthup, *J. Opt. Soc. Am.*, **40**, 397 (1950).