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ORGANOTIN CHEMISTRY
X*. THE ALKALINE SAPONIFICATION OF TETRAKIS-(2-CYANOETHYL)TIN

GERALD H. REIFENBERG AND WILLIAM J. CONSIDINE
Corporate Research Department, M&T Chemicals Inc., Rahway, N.J. (U.S.A.)

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INTRODUCTION

The alkaline saponification of organotin compounds containing a 2-cyanoethyl group has been shown to proceed in the expected manner[1] yielding the sodium salts of the corresponding carboxylic acids (eqn. 1).

$$R_3SnCH_2CH_2CN + NaOH + H_2O \rightarrow \underset{(I)}{R_3SnCH_2CH_2COONa} + NH_3 \qquad R = \text{phenyl or butyl} \qquad (1)$$

The product obtained upon acidification of a solution of (I) depended on the nature of R. When R = phenyl, the free acid (II) was unstable and immediately decomposed with the loss of benzene to give diphenyl(2-carboxyethyl)tin inner salt (III).

$$n\,R_3SnCH_2COONa + n\,HCl \rightarrow n\,\underset{(II)}{(R_3SnCH_2CH_2COOH)} \rightarrow \underset{(III)}{(R_2SnCH_2CH_2COO)_n} + n\,RH \quad R = \text{phenyl or butyl} \qquad (2)$$

However, when R = butyl, the free acid could be isolated but it decomposed with the evolution of butane upon attempted distillation to form the butyl analog of (III).

Recently Kaabak and Tomilov[2] reported that alkaline saponification of tetrakis(2-cyanoethyl)tin proceeds normally, yielding the tetrasodium salt (IV) of tetrakis(2-carboxyethyl)tin.

$$Sn(CH_2CH_2CN)_4 + 4\,NaOH + 4\,H_2O \rightarrow \underset{(IV)}{Sn(CH_2CH_2COONa)_4} + 4\,NH_3 \qquad (3)$$

After acidification with hydrochloric acid (no experimental conditions were given), they obtained the inner salt, bis(2-carboxyethyl)(2-carboxylatoethyl)tin (V), as the only organotin compound (after recrystallization from hot water).

$$n\,Sn(CH_2CH_2COONa)_4 + 4n\,HCl \rightarrow [(HOOCCH_2CH_2)_2SnCH_2CH_2COO]_n + n\,CH_3CH_2COOH + 4n\,NaCl \qquad (4)$$

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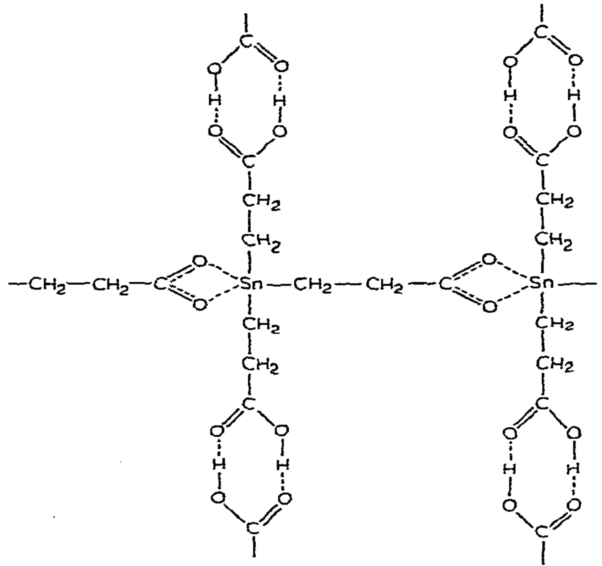
* For Part IX, see *Abstr. 148th Meeting Am. Chem. Soc., Chicago, Illinois*, 1964, p. 4s.



(V)

No mention is made by the authors of the formation of any intermediates, such as the free acid, tetrakis(2-carboxyethyl)tin.

It occurred to us that tetrakis(2-carboxyethyl)tin might be an isolable intermediate if the tetrasodium salt (IV) were to be acidified under suitable conditions. Therefore we decided to repeat the alkaline saponification of tetrakis(2-cyanoethyl)tin[2].

DISCUSSION

When the tetrasodium salt (IV) was carefully acidified at 0° with a stoichiometric quantity of aqueous hydrochloric acid, tetrakis(2-carboxyethyl)tin, (VI), precipitated. Attempts to purify this compound failed because of its thermal instability. The elemental analysis and the infrared spectrum of the product were in

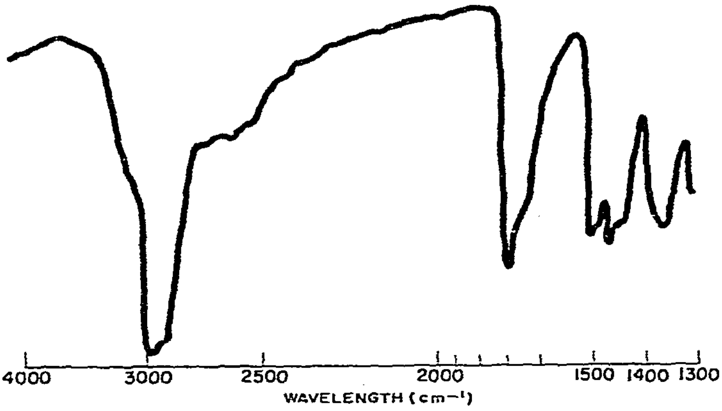


Fig. 1. Infrared spectrum of tetrakis(2-carboxyethyl)tin (VI) (Nujol mull).

agreement with this structure for (VI). The absorption in the infrared region between

$$\underset{\text{(IV)}}{\mathrm{Sn(CH_2CH_2COONa)_4}} + 4\,\mathrm{HCl} \xrightarrow{0°} \underset{\text{(VI)}}{\mathrm{Sn(CH_2CH_2COOH)_4}} + 4\,\mathrm{NaCl} \qquad (5)$$

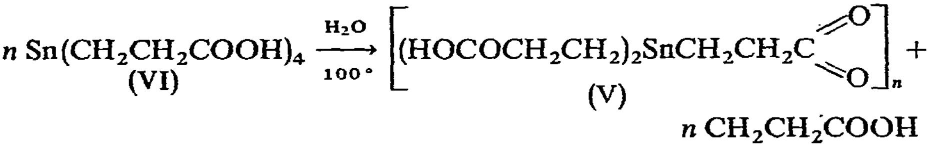
1250–4000 cm^{-1} was typical of that shown by an aliphatic carboxylic acid[3] (Fig. 1). In addition, no carbonyl absorption was observed at frequencies below 1700 cm^{-1}.

If the acidification of the tetrasodium salt (IV) with hydrochloric acid was conducted at room temperature instead of 0° no product precipitated. By concentrating the reaction mixture two white solids were isolated, one of which was identified as tris(2-carboxyethyl)tin chloride, $(HOOCCH_2CH_2)_3SnCl$ (VII). The elemental analysis and the infrared spectrum of the latter were in agreement with this structure for (VII). The absorption in the infrared region between 1250–4000 cm^{-1} was typical of that shown by aliphatic carboxylic acids[3] and similar to that shown in Fig. 1 for the tetraacid, (VI).

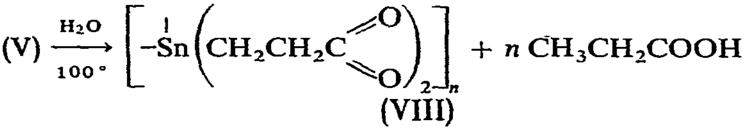
The formation of (VII) could occur by the electrophilic cleavage of a 2-carboxyethyl group from the initially formed tetrakis(2-carboxyethyl)tin by hydrochloric acid or by the protolysis of a tin carboxylate compound (V) (*vide infra*).

In an attempt to recrystallize the tetraacid (VI) from warm water (*ca.* 60°), partial decomposition occurred as evidenced by the strong odor of propionic acid. The recovered product, based on elemental analysis, appeared to be a mixture containing 80% of (VI) and 20% of the inner salt, (V). An infrared spectrum of the mixture indicated that (V) was present.

Refluxing an aqueous suspension of this 80–20 mixture for two hours completely decomposed the tetraacid. A 90% yield of polybis(2-carboxyethyl)(2-carboxylatoethyl)tin*, (V), m.p. 180° (dec.), was obtained in addition to a 5% yield of polybis(2-carboxylatoethyl)tin, (VIII), m.p. 280° (dec.), which precipitated during the reflux period.



$$n\,\underset{\text{(VI)}}{\mathrm{Sn(CH_2CH_2COOH)_4}} \xrightarrow[100°]{H_2O} \underset{\text{(V)}}{\left[\mathrm{(HOCOCH_2CH_2)_2SnCH_2CH_2C}\genfrac{}{}{0pt}{}{\nearrow \mathrm{O}}{\searrow \mathrm{O}}\right]_n} + n\,\mathrm{CH_2CH_2COOH} \qquad (6)$$



$$\text{(V)} \xrightarrow[100°]{H_2O} \underset{\text{(VIII)}}{\left[-\overset{|}{\mathrm{Sn}}\left(\mathrm{CH_2CH_2C}\genfrac{}{}{0pt}{}{\nearrow \mathrm{O}}{\searrow \mathrm{O}}\right)_2\right]_n} + n\,\mathrm{CH_3CH_2COOH} \qquad (7)$$

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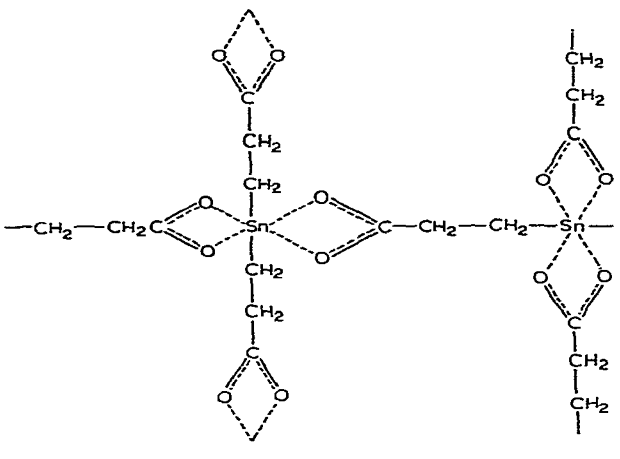
* The nomenclature used for (V) and also (VII) is based on its infrared spectrum which shows that the $-\mathrm{C}\genfrac{}{}{0pt}{}{\nearrow \mathrm{O}}{\searrow \mathrm{O}}$ residue is acting as either a bridging or a chelating group and is therefore designated 2-carboxylatoethyl.



(VIII)

The formation of (VIII) occurs by the loss of a second mole of propionic acid from (V), which itself was formed by the initial loss of one mole of propionic acid from (VI).

The infrared spectrum of (V) was obtained in the solid state and a reproduction of this spectrum between 1250–4000 cm^{-1} is shown in Fig. 2. This compound shows absorptions typical of both aliphatic carboxylic acids[3] (broad band centered at about 3000 cm^{-1} and a sharp peak at 1701 cm^{-1}) and of alkyltin carboxylates[4,5,6,7] (1530 and 1408 cm^{-1}). The carbonyl stretching frequencies at 1530 and 1408 cm^{-1} are in agreement with those reported by Okawara *et al.*[5] and Van der Kerk *et al.*[6] for trialkyltin acylates and dialkyltin diacylates. In these compounds, the carboxylate residue was shown to be, in the solid state, either a bridging group between two tin atoms or a chelating group[5,6], thereby increasing the coordination number of the tin atom from four to five in trialkyltin acylates and from four to six in dialkyltin diacylates. The 1530 and 1408 cm^{-1} peaks require a coordination of five for the tin atom. Since the normal frequencies of the carboxylic acid functions rule out any strong perturbation of these groups, a coordination number of six is unlikely. Equally unlikely is coordination number four. The carbonyl stretching frequencies of a tin acylate,

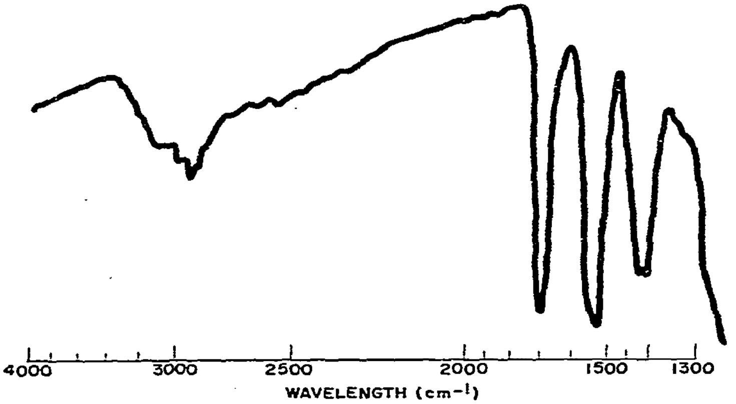


Fig. 2. Infrared spectrum of polybis(2-carboxyethyl)(2-carboxylatoethyl)tin (V) (Fluorolube mull).

where the carboxylate is unidentate has been assigned[6] at 1642–1655 cm^{-1}. On this basis we propose structure (V).

Because of our inability to find a solvent for (V), we could not make molecular weight measurements. This lack of solubility, of course, supports a polymeric structure. Van der Kerk and Noltes[1] were able to measure molecular weights for dibutyltin(2-carboxyethyl)tin inner salt (III, R = butyl) and showed that it was a polymer. Of course, it is predictable that (V) would be much less soluble because it is crosslinked through the strong hydrogen bonding involving the carboxyl groups. It is obvious from the IR spectra (Fig. 2) that the carboxyl groups in (V) are as strongly hydrogen bonded as those in any carboxylic acid dimer.

The infrared spectrum of polybis(2-carboxylatoethyl)tin, (VIII), between 1250–4000 cm^{-1} was obtained in the solid state and is shown in Fig. 3. This compound shows absorptions typical of alkyltin carboxylates[4,5,6,7] (1541 and 1428 cm^{-1}). The stretching frequencies which are typical of aliphatic carboxylic acids are absent.

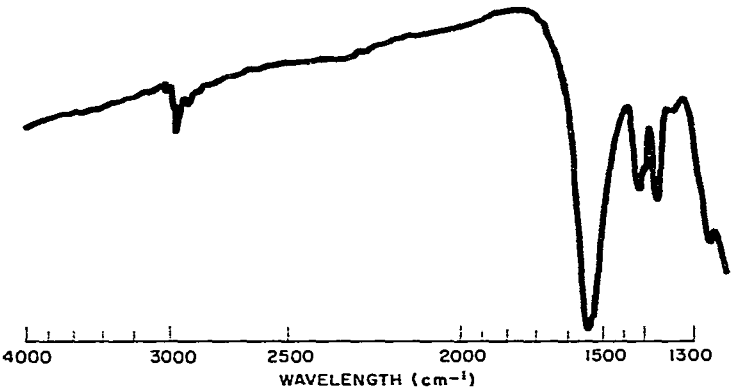


Fig. 3. Infrared spectrum of polybis(2-carboxylatoethyl)tin (VIII) (Fluorolube mull).

The low values (1541 and 1428 cm^{-1}) for the carboxylate stretching frequencies rules out unidentate bonding. Further, judging from the sharpness of these bands, it seems likely that only one type of carboxylate is present. On this basis, we propose structure (VIII) in which all the carboxylates are chelating and the coordination number of tin is six. Again the lack of solubility of (VIII) precluded molecular weight measurements and also requires a polymeric structure.

It is now evident why Kaabak and Tomilov[2] did not isolate any tetrakis(2-carboxyethyl)tin. Recrystallization from hot water of the product which precipitated after acidification of $Sn(CH_2CH_2COONa)_4$ completely decomposed any tetraacid, (VI), which might have been present.

The chemical evidence suggests that tetrakis(2-carboxyethyl)tin decomposes according to eqns. (6) and (7). To confirm this scheme, the thermogravimetric analyses (TGA) and differential thermal analyses (DTA) of the tetraacid (VI) and polybis-(2-carboxyethyl)(2-carboxylatoethyl)tin (V) were determined. Table 1 summarizes the TGA data and Figs. 4 and 5 are reproductions of the actual TGA curves.

The TGA results shows that (V) is more stable than the tetraacid (VI). In each case the first weight loss, although starting at different temperatures, ends at approximately the same temperature. These initial weight losses correspond closely to the

TABLE 1

THERMOGRAVIMETRIC ANALYSIS

Compound	(VI)	(V)
First wt. loss (%)[a]	38.0 (36.0)[b]	22.0 (22.0)[b]
Temperature range (°C)	35–185	78–190
Product formed after 1st wt. loss	(VIII)	(VIII)
Second wt. loss (%)[a]	24.1 (27.2)	33.6 (33.3)
Temperature range (°C)	185–350	190–350
Product formed after 2nd wt. loss	SnO_2	SnO_2
Total wt. loss, obs. (%)[c]	67.4 (63.3)	57.4 (55.2)

[a] Based on the starting material. [b] The first value is the actual % weight loss and the value in brackets is the weight loss calculated for the reaction. [c] The discrepancy between the sum of the first and second weight loss and the total weight loss is due to an inherent time lag in the instrument.

complete conversion of the starting materials to polybis(2-carboxylatoethyl)tin (VIII) (see eqns. 6 and 7) which strongly suggests that the initial decomposition product of the tetraacid, (VI), is (V). The second weight loss, in both cases, corresponds closely to the complete decomposition of (VII) to tin(IV) oxide.

Differential thermal analyses for tetrakis(2-carboxyethyl)tin (VI) and polybis-(2-carboxyethyl)(2-carboxylatoethyl)tin (V) confirm the melting point characteristics that had been observed visually. Tetrakis(2-carboxyethyl)tin shows a strong endotherm at *ca.* 106° and a very strong exotherm at 110–111°. These are in agreement with the melting point observed at 104–105° and complete solidification of the melt 109–110°. A small endotherm at 287° corresponds closely to the observed decomposition at 280° for polybis(2-carboxylatoethyl)tin.

For polybis(2-carboxyethyl)(2-carboxylatoethyl)tin (V), the endotherm at 175° and the exotherm at 180° correspond closely to its partial melting, observed at 180° and its complete solidification a few degrees higher (*ca.* 185°). A small exo-

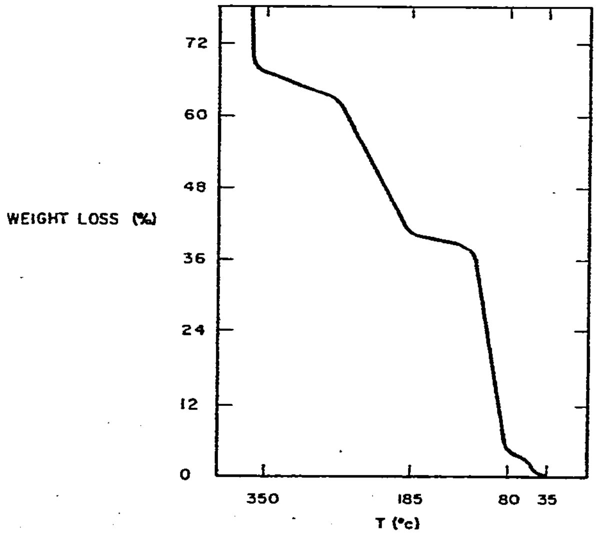


Fig. 4. Thermogravimetric analysis of tetrakis(2-carboxyethyl)tin (VI).

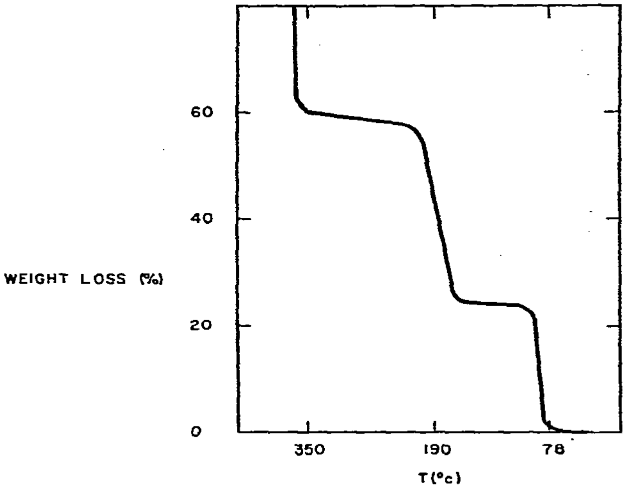


Fig. 5. Thermogravimetric analysis of polybis(2-carboxyethyl)(2-carboxylatoethyl)tin.

therm at 300° could correspond to the observed decomposition at 280° for polybis(2-carboxylatoethyl)tin (VIII).

Tris(2-carboxyethyl)tin chloride (VII), polybis(2-carboxyethyl)(2-carboxylatoethyl)tin (V), and polybis(2-carboxylatoethyl)tin (VIII), are stable at room temperature for at least 3–6 months (no odor of hydrogen chloride or propionic acid was detected). On the other hand, tetrakis(2-carboxyethyl)tin (VI) appeared to decompose after 5–6 days at room temperature as evidenced by a perceptible odor of propionic acid; however, at 0–5°, (VI) appears to be stable for at least 2–3 months.

EXPERIMENTAL

All melting points were uncorrected and were determined using an open capillary tube in a Mel-Temp Apparatus (Laboratory Devices, Cambridge, Mass.). Molecular weight determinations were carried out in a thermistor osmometer (Mechrolab Osmometer Model 301).

Thermogravimetric analyses were carried out in a self-constructed unit with the heating rates varying as follows: 20–180°, 6°/min; 180–300°, 8½°/min; 300–350°, 10°/min. Differential thermal analyses were determined using an Aminco Automatic Recording Thermoanalyzer (American Instrument Co., Inc., Silver Springs, Md.) at a uniform heating rate of 4°/min.

Infrared spectra were run on a Beckman IR-8 Infrared Spectrophotometer (Beckman Instruments, Inc., Fullerton, Cal.).

Tetrakis(2-carboxyethyl)tin

A mixture of tetrakis(2-cyanoethyl)tin (34.4 g, 0.103 mole), sodium hydroxide (31.0 g, 0.775 mole), methanol (240 ml), and water (100 ml) was refluxed (74°) for 2.5 h. During this period complete solution took place with the evolution of ammonia. White solids (77.6 g) were obtained as residue after the solvents had been distilled off under reduced pressure. The solid product was redissolved in 90 ml of water and filtered directly into a one liter, three-necked flask, equipped with an air motor and stirrer, addition funnel, Y-tube adapter, water condenser, and thermometer. The reaction flask was cooled with an ice/methanol bath in order to maintain the reaction temperature at 0°. Concentrated hydrochloric acid (67 ml, 0.804 mole) was added slowly, with stirring, into the reaction flask over a 70-minute period (the addition was controlled at such a rate that the pot temperature was maintained at 0°). When 30–35 ml of acid had been added (enough to just neutralize the excess of NaOH), a white precipitate appeared. The reaction mixture, while still cold, was filtered and the product collected. It was washed thoroughly with 50 ml of cold water (5°) and then allowed to air-dry for two days. Tetrakis(2-carboxyethyl)tin, m.p. 104–5°, (32.5 g) was obtained in 77% yield. Several attempts were made to purify the product by recrystallization. However, these were unsuccessful because of its instability. Analyses were therefore taken on the material as isolated. (Found: C, 35.95; H, 4.85; Sn, 28.70; mol.wt. in tetrahydrofuran, 380. $C_{12}H_{20}O_8Sn$ calcd.: C, 35.09; H, 4.91; Sn, 28.90%, mol.wt., 410.7.)

Preparation of Tetrakis(2-carboxyethyl)tin: polybis(2-carboxyethyl)(2-carboxylatoethyl)tin (80:20) *mixture*

A suspension of tetrakis(2-carboxyethyl)tin (47.0 g, 0.11 mole) in water (65 ml) was heated with stirring to 60°, at which point the acid completely dissolved and an odor of propionic acid was noticed. The warm solution was filtered and white solids crystallized from the filtrate as it was being cooled to room temperature. These solids, after washing with cold water (5°) and drying at 50° for 5 h weighed 34.0 g, m.p. 106° (cloudy). (Found: C, 34.24; H, 4.75; Sn, 30.19. 0.8 $C_{12}H_{20}O_8Sn+0.2\ C_9H_{14}O_6Sn$ calcd.: C, 34.49; H, 4.76; Sn, 30.20%.)

Polybis(2-carboxyethyl)(2-carboxylatoethyl)tin.

Thirty grams of a mixture of tetrakis(2-carboxyethyl)tin (VI) and polybis-(2-carboxyethyl)(2-carboxylatoethyl)tin (V) (80% VI and 20% V) was heated in boiling water (40 ml) for 2 h. Complete solution took place within a few minutes, but after 30 min some white solids precipitated. At the end of 2 h, the hot mixture was filtered and polybis(2-carboxylatoethyl)tin (VII) was collected (1.0 g) 5% yield, m.p. 280° (dec.). (Found: C, 27.41; H, 3.05; Sn, 44.32. $C_6H_8O_4Sn$ calcd.: C, 27.07; H, 3.14; Sn, 45.19%.)

The mother liquor, after cooling to room temperature, yielded 23.0 g (89%) of polybis(2-carboxyethyl)(2-carboxylatoethyl)tin (V), m.p. 180° (dec.)*. (Found: C, 32.12; H, 4.13; Sn, 35.40. $C_9H_{14}O_6Sn$ calcd.: C, 32.08; H, 4.16; Sn, 35.25%.)

Tris(2-carboxyethyl)tin chloride

A mixture of tetrakis(2-cyanoethyl)tin (51.6 g, 0.154 mole), sodium hydroxide (46.5 g, 1.16 moles), water (105 ml) and methanol (255 ml) was refluxed (76°) for 2 h. During this period, nearly complete solution took place with the evolution of ammonia. After filtering the solution, solvents were distilled off under reduced pressure

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* At *ca.* 185°, the partial melt completely solidified and finally turned tan at 280°. Kaabak and Tomilov[2] state that up to 280°, this product does not melt although darkening began at 240°. The differences between our results and theirs could be attributed to different heating rates.

to leave a white, semi-solid mixture of the tetrasodium salt, sodium hydroxide, and water as residue. The residue was redissolved in 180 ml of water and concentrated hydrochloric acid (100 ml, 1.22 moles) was added portionwise while the filtered solution was shaken vigorously. No solids precipitated and a strong odor of propionic acid was noted. The solution was concentrated on a steam bath at reduced pressure to about one-half of its original volume. Solids began to precipitate as the water was removed. A pink oil precipitated after the mixture was cooled to room temperature. The mixture was filtered and the solids were identified as sodium chloride. The pink oil which was separated from the aqueous layer was triturated with 50 ml of acetone in order to precipitate some occluded sodium chloride. After filtering off the sodium chloride and distilling away the acetone, 44.6 g of a pink oil remained.

Thirty-six grams of the latter was refluxed with ethyl acetate (85 ml). Upon cooling the solution to room temperature, 8.5 g of a white solid crystallized. Elemental analysis, after further treatment with ethyl acetate, indicated that the solid was a mixture of about 25% tetrakis(2-carboxyethyl)tin (VI) and 75% polybis(2-carboxyethyl)(2-carboxylatoethyl)tin (V). The ethyl acetate mother liquor was distilled to remove solvents. A yellow oil (25.0 g) was obtained as residue.

This oil was dissolved in 15 ml of ethyl ether. Upon the addition of toluene (200 ml), the entire mass appeared to solidify. The mixture was cooled to 5°, filtered, and the white solid collected and air dried. A 37% yield of tris(2-carboxyethyl)tin chloride (VII, 17.0 g) was obtained, m.p. 96.5–98.0. Repurification from an ethyl ether/toluene solvent pair caused no change in the melting point. (Found: C, 29.26; H, 3.96; Cl, 9.14; Sn, 31.63; mol.wt. in tetrahydrofuran, 380. $C_9H_{15}ClO_6Sn$ calcd.: C, 28.96; H, 4.05; Cl, 9.50; Sn, 31.80%; mol.wt., 373.2.)

ACKNOWLEDGEMENT

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SUMMARY

The alkaline saponification of tetrakis(2-cyanoethyl)tin yields the corresponding tetrasodium salt of tetra(2-carboxyethyl)tin in agreement with a previous report. Depending on the temperature at which the tetrasodium salt was acidified, four related compounds could be isolated: (1) tetrakis(2-carboxyethyl)tin (VI); (2) tris(2-carboxyethyl)tin chloride (VII); (3) polybis(2-carboxylatoethyl)tin (VIII); and (4) polybis(2-carboxyethyl)(2-carboxylatoethyl)tin (V). The preparation of three new compounds (VI), (VII), and (VIII) is described. The structural and chemical interrelationships are discussed on the basis of visual observation, infrared spectroscopy, differential thermal analysis, and thermogravimetric analysis.

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