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Synthesis of Higher Alkyltin Compounds from Sodium-Tin Alloys

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n-Butyl chloride reacts with sodium-tin alloys at 150–180°C., resulting in 25–30% tin conversions to mixtures composed of 10–20% tetrabutyltin and 80–90% tributyltin chloride. *n*-Propyl chloride and *n*-amyl chloride react with NaSn (2% Zn) giving good conversions to the R_4Sn–R_3SnCl mixtures. Under milder conditions, reactions of ethyl chloride or *n*-butyl chloride with sodium-tin alloys result in substantial yields of R_2Sn, readily converted to the corresponding dialkyltin oxide by reaction with oxygen. Mixtures of tetrabutyltin and tributyltin chloride react readily with the theoretical quantity of stannic chloride, yielding dibutyltin dichloride quantitatively.

Reaction of methyl, ethyl, and some propyl halides with sodium-tin alloys is the oldest known method for synthesis of the corresponding alkyltin compounds. Löwig in 1852 reported the reaction of ethyl iodide with a sodium-tin alloy containing 14% sodium (composition NaSn) to form diethyltin.[1] Other reactions with alloys of similar composition and methyl or ethyl halides have appeared in the literature.[2,3,4] Reaction of an alloy of composition Na_2Sn with ethyl bromide has been reported to yield diethyltin,[5] tetraethyltin, or diethyltin dibromide.[6] Further, Harada has shown that NaSn alloy is activated by the presence of varying amounts of zinc in reactions with methyl iodide,[7] ethyl bromide,[8] and with propyl bromide.[9] Mixtures of R_4Sn and R_3SnX were obtained, the compositions varying with reaction conditions.

Reactions of butyl and higher alkyl chlorides with sodium-tin alloys have not been reported. The known references imply, moreover, that even though good yields are obtained with methyl and ethyl halides, the reaction is not satisfactory for higher molecular weight alkyl halides.[10] Reaction of *n*-butyl bromide with zinc-activated sodium-tin alloys has been reported, however, to give good yields of tributyltin bromide.[11]

We have found that *n*-butyl chloride reacts readily with the active ternary alloys NaSn (2% Zn) and $Na_{0.92}K_{0.08}Sn$ at 150–180°C. under autogenous pressure to give good yields of mixtures composed of 10–20 weight % tetrabutyltin and 80–90% tributyltin chloride. At lower reaction temperatures, and especially when the less active binary alloy NaSn is used, the organotin product contains substantial amounts of dibutyltin along with tetrabutyltin and tributyltin chloride. Satisfactory yields of R_4Sn–R_3SnCl mixtures are also obtained from *n*-propyl chloride and *n*-amyl chloride with the active ternary alloys under reaction conditions similar to those used for *n*-butyl chloride.

On the basis of the results of our work the following reactions are proposed to explain the products obtained:

$$2\ NaSn + 2\ RCl \longrightarrow R_2Sn + 2\ NaCl + Sn \qquad (1)$$

$$R_2Sn + RCl \longrightarrow R_3SnCl \qquad (2)$$

$$2\ R_2Sn \longrightarrow R_4Sn + Sn \qquad (3)$$

It appears that dialkyltin compounds are intermediates in the formation of R_4Sn and R_3SnCl. If the R_3SnCl–R_4Sn product contains 80 mole % R_3SnCl, summation of Equations (1)–(3) above would result in the total equation,

$$12\ NaSn + 16\ RCl \longrightarrow 4\ R_3SnCl + R_4Sn + 12\ NaCl + 7\ Sn \qquad (4)$$

for which the theoretical tin conversion to organotin product is 42.7%. We have obtained products apparently consisting of R_3SnCl and R_4Sn exclusively in tin conversions of 25–30%.

In reactions with *n*-butyl chloride and NaSn (2% Zn) carried out under mild conditions, *e.g.*, at temperatures below 130°C., or with the less active alloy NaSn, appearance of orange-brown colors in product solutions is taken to indicate intermediate dibutyltin formation, as in Equation (1). Preponderance of tributyltin chloride in the products when reaction conditions were more strenuous, along with absence of colors, and the fact that tin conversions were consistently higher than the theoretical 25% expected by the equation,

$$4\ NaSn + 4\ n\text{-}C_4H_9Cl \longrightarrow (n\text{-}C_4H_9)_4Sn + 3\ Sn + 4\ NaCl$$

suggest direct addition of *n*-butyl chloride to dibutyltin, as shown in Equation (2).

The dark colored solutions are decolorized by the action of chlorine, probably due to conversion of

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[1] Löwig, *Ann.*, **84**, 308 (1852).

[2] Cahours, *Ann.*, **122**, 198 (1862).

[3] Ladenburg, *Ann.*, **8** (Suppl.) 75 (1872).

[4] Kraus and Callis, U. S. Patent 1,639,947 (1927).

[5] Harada, *J. Sci. Research Inst.* (*Tokyo*), **43**, 31 (1948).

[6] Neiman and Shushunov, *Doklady Akad. Nauk S.S.S.R.*, **60**, 1347 (1950).

[7] Harada, *Bull. Chem. Soc. Japan*, **4**, 266 (1929).

[8] Harada, *Sci. Papers Inst. Phys. Chem. Research* (*Tokyo*), **35**, 290 (1939).

[9] Harada, *Repts. Sci. Research Inst.* (*Japan*), **24**, 177 (1948).

[10] van der Kerk and Luijten, *J. Applied Chem.*, **4**, 301 (1954).

[11] Gilman, PB No. 6004, National Defense Research Committee Report, May 2, 1942.

dibutyltin to colorless dibutyltin dichloride [Equation (5)]. However, no attempt was made to isolate dibutyltin dichloride from this reaction in this work. Also, the dark color is destroyed by aeration, forming white polymeric dibutyltin oxide [Equation (6)], which is converted to dibutyltin dichloride by treatment with hydrochloric acid [Equation (7)].

$$(n\text{-}C_4H_9)_2Sn + Cl_2 \longrightarrow (n\text{-}C_4H_9)_2SnCl_2 \qquad (5)$$

$$x\,(n\text{-}C_4H_9)_2Sn + \frac{x}{2}\,O_2 \longrightarrow [(n\text{-}C_4H_9)_2SnO]_x \qquad (6)$$

$$[(n\text{-}C_4H_9)_2SnO]_x + 2x\,HCl \longrightarrow x\,(n\text{-}C_4H_9)_2SnCl_2 + x\,H_2O \qquad (7)$$

In support of Equation (1), formation of dialkyltin compounds from NaSn and lower alkyl halides has been reported.[1] Formation of trialkyltin chlorides as in Equation 2 is also known.[12,13] Equation 3 has a precedent in the report of Frankland that diethyltin on distillation formed tin and tetraethyltin.[14] Pfeiffer *et al.* have demonstrated that diethyltin reacts with air to precipitate diethyltin oxide, and with halogens to form the corresponding diethyltin dihalide,[13] analogous to Equations (5) and (6). These authors also formed dialkyltin dihalides by the action of halogen acids on the corresponding dialkyltin oxide as in Equation (7).[15]

Tetrabutyltin–tributyltin chloride mixtures formed in sodium-tin alloy reactions are converted in essentially quantitative yields to dibutyltin dichloride by reaction with the calculated quantity of stannic chloride. Thus, for a mixture containing 80 mole % tributyltin chloride, reaction is expressed by the equation:

$$4\,(n\text{-}C_4H_9)_3SnCl + (n\text{-}C_4H_9)_4Sn + 3\,SnCl_4 \longrightarrow 8\,(n\text{-}C_4H_9)_2SnCl_2$$

van der Kerk and Luijten recommended temperatures of 230–240°C. for conversion of mixtures of high tetrabutyltin content to dibutyltin dichloride.[10] We have found in converting mixtures of high tributyltin chloride content that temperatures in excess of about 210°C. promote decomposition and undesirable by-product formation, and that a reaction temperature of 180°C. appears to be optimum for conversion to dibutyltin dichloride.

EXPERIMENTAL

Materials. *n*-Alkyl chlorides were all Eastman white label products, with the exception of ethyl chloride, which was redistilled Ethyl Corporation commercial grade. Metals from the following sources were used: tin, 1-lb. bars, Fisher Scientific Company; sodium, Ethyl Corporation, commercial grade; potassium, J. T. Baker Co., C.P.; and zinc, J. T. Baker Co., mossy. Stannic chloride was Fisher anhydrous reagent grade.

Alloy preparation. Alloys were prepared by stirring the calculated quantities of tin, sodium, and ternary metal (when used) at red heat for 15–20 min. in steel bombs under nitrogen. They were broken up by striking the cooled bomb with a hammer and were further comminuted in a large mortar under nitrogen until maximum particle size was about 0.25 inch. While well protected from the atmosphere, alloy samples were weighed into 4-oz. screw-cap bottles for storage prior to use. In this manner, NaSn, NaSn (2% Zn), and $Na_{0.92}K_{0.08}Sn$ were prepared. They were all shiny, gray, brittle solids, rapidly dulling in appearance when contacted with traces of atmospheric oxygen or moisture.

Anal: Calc'd for NaSn: Na, 16.2. Found: total Na, 16.3; active Na, 15.9. Calc'd for NaSn(2% Zn): Na, 15.9. Found: total Na, 15.2; active Na, 15.7. Calc'd for $Na_{0.92}K_{0.08}Sn$: Na, 14.8. Found: total Na, 14.7.

Tetrabutyltin-tributyltin chloride from NaSn (2% Zn). A small monel pressure reactor (170 ml. capacity) was charged under nitrogen with 60 g. of *n*-butyl chloride, 47.8 g. NaSn (2% Zn), and a 5/8-inch steel ball. The sealed bomb was tumbled for 5 hr. in an oil bath at 160–170°C. The bomb was cooled in a dry ice–acetone bath, after which it was opened. The uniform black slurry formed during reaction was washed onto a Büchner funnel with 200 ml. benzene. Filtration resulted in a black powdery solid (free of active sodium when tested with methanol) and a clear light yellow filtrate. Distillation in a Claisen flask yielded a benzene–butyl chloride fraction, and 25.7 g. of a main product fraction of tetrabutyltin–tributyltin chloride collected at 148–151°C. (10 mm.).

Anal: Calc'd for $(n\text{-}C_4H_9)_4Sn$: Sn, 34.2. Calc'd for $(n\text{-}C_4H_9)_3SnCl$: Sn, 36.5; Cl, 10.9. Found for product mixture: Sn, 34.5; Cl, 8.35.

Tin analyses were carried out by the method of Gilman and King.[16] From the analyses, the product mixture contained 23.3% tetrabutyltin and 76.7% tributyltin chloride (based on chlorine content). The calculated tin content of such a mixture is 35.8%. Tin conversion, calculated from the tin analysis, was 22.6%. In subsequent reactions, tin conversions averaged 25–30%. Small portions of a product mixture treated with $AgNO_3$ solution gave an immediate white AgCl precipitate (confirming the presence of tributyltin chloride), and gave no precipitate when treated with NH_4OH solutions (indicating the absence of dibutyltin dichloride which would be expected to form white dibutyltin oxide).

A 16.5-g. portion of the product mixture obtained above was redistilled in a 20-inch concentric tube column at 3–3.5 mm. Five fractions were taken though the boiling point varied only slightly. Data for the distillation are given in

TABLE I

DISTILLATION OF TETRABUTYLTIN-TRIBUTYLTIN CHLORIDE MIXTURE

Fraction No.	B.p., °C.[a]	Wt., g.	n_D^{20}[b]	Wt. % Cl
1	78.5–128.7	0.61	1.4739	
2	129	2.12	1.4853	7.97
3	128.7–129	10.64	1.4866	8.63
4	129 –131.2	2.03	1.4890	
5	131.2–131.4	0.80	1.4900	10.44
Residue	..	0.40	..	

[a] Pressure, 3–3.5 mm. [b] From the literature, n_D^{20} for tetrabutyltin is 1.4730[17]; n_D^{22} for tributyltin chloride is 1.4908.[18]

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(12) Krause and Pohland, *Ber.*, **57**, 532 (1924).

(13) Pfeiffer, *Ber.*, **44**, 1269 (1911).

(14) Frankland, *Ann.*, **85**, 340 (1853).

(15) Pfeiffer, Lehnardt, Lustensteiner, Prade, Schnurmann, and Truskier, *Z. anorg. Chem.*, **68**, 102 (1910).

(16) Gilman and King, *J. Am. Chem. Soc.*, **51**, 1213 (1929).

(17) Jones, Evans, Gilwell, and Griffith, *J. Chem. Soc.*, 39 (1935).

(18) Manulkin, *J. Gen. Chem. U.S.S.R.*, **20**, 2004 (1950).

Table I. Though a poor separation was obtained, refractive indices of the fractions vary from that found in the literature for tetrabutyltin to the literature value for tributyltin chloride. Chlorine analyses, also, increase almost to the calculated chlorine content of tributyltin chloride.

Tetrabutyltin–tributyltin chloride from $Na_{0.92}K_{0.08}Sn$. A reaction was carried out similar to the above reaction, using 60 g. of *n*-butyl chloride and 46.4 g. of $Na_{0.92}K_{0.08}Sn$ alloy. The mixture was heated for 4 hr. at 160–165°C. There was obtained on work-up 24.6 g. of crude tetrabutyltin–tributyltin chloride mixture, containing 5.8% chlorine and 38% tin, corresponding to a 53.2% tributyltin chloride content and a tin conversion of 24.2%.

Tetrabutyltin–tributyltin chloride from NaSn. By procedures similar to those described above for the ternary alloys, 69 g. of *n*-butyl chloride was allowed to react with 52.2 g. of NaSn alloy. The mixture was heated for 10 hr. at 140–155°C. The tetrabutyltin–tributyltin chloride product (37.2 g.) contained 9.4% chlorine and 36.3% tin. This corresponds to a tributyltin chloride content of 86.1% and a 30.9% tin conversion.

Other R_4Sn–R_3SnCl mixtures from NaSn(2% Zn). Mixtures of R_4Sn and R_3SnCl were obtained in reactions of NaSn(2% Zn) with *n*-propyl chloride and *n*-amyl chloride (Table II) by the procedures described above for *n*-butyl chloride. Reactants were used in the ratio of two moles of RCl per gram-atom of tin in the alloy. The crude products were not completely purified and identified. However, tin conversion calculated from tin analyses on the products serves as a measure of reaction efficiency. Chloride was shown to be present in the products by precipitation of silver chloride.

TABLE II

R_4Sn-R_3SnCl MIXTURES FROM REACTIONS OF RCl WITH NaSn(2% Zn)

			R_4Sn–R_3SnCl Product	
RCl	Temp., °C.	Time, Hr.	% Sn	% Sn conversion
n-C_3H_7Cl	160 140–145	0.3 4	40.3	18.2
n-$C_5H_{11}Cl$	162	4	31.6	27.2

Diethyltin, diethyltin oxide. An apparatus was constructed in which a 1-inch diameter Micrometallic filter disk ($^3/_{32}$-inch thickness, porosity "F") was welded into a steel pipe as a support for NaSn(2% Zn) alloy. After the pipe was charged with alloy (3.18 g.), 2.5 l. of ethyl chloride was passed through the heated reactor (89°C.) over a period of 173 min., under sufficient nitrogen pressure to maintain the ethyl chloride in the condensed phase. After a 30-min. induction period, the clear liquid collected from the reactor began to show a yellow color which gradually deepened to red. Maximum color intensity was obtained after 60 min. Ethyl chloride was distilled from the product solution and was replaced by 100 ml. of *n*-hexane. Aeration of the deep red *n*-hexane solution formed a colorless solution and precipitated 0.98 g. (45% yield) of white diethyltin oxide.

Anal: Calc'd for $[(C_2H_5)_2SnO]_x$: Sn, 61.5%. Found: Sn, 57.9%.

Distillation of *n*-hexane from the filtrate yielded 0.32 g. of colorless oil. The solids removed from the pipe after reaction were found to contain 86% of the expected chloride ion, based on sodium present in the original alloy.

Dibutyltin, dibutyltin oxide. A mixture of 47.7 g. NaSn alloy and 62.2 g. of *n*-butyl chloride was heated in an autoclave for 4 hr. at 162°C. On filtering the mixture and washing the solids with benzene (200 cc.), there was obtained a dark orange-brown product solution. Dry air was bubbled into the solution for 1.5 hr., resulting in a white precipitate of dibutyltin oxide (7.3 g., 8.6% tin conversion). A portion of the white precipitate was heated with concentrated hydrochloric acid, forming a white oil, dibutyltin dichloride, which on recrystallization from petroleum ether melted at 35–37.5°C., undepressed when mixed with an equal weight of authentic dibutyltin dichloride.

Benzene and *n*-butyl chloride were distilled from the clear filtrate from the precipitated dibutyltin oxide, leaving a residue of tetrabutyltin–tributyltin chloride mixture weighing 17.8 g. and containing 38% tin and 5.3% chlorine. This constituted a 16.9% tin conversion with 48.3% tributyltin chloride in the liquid organotin product mixture. Total tin conversion to organotin products was 25.5%.

A dark orange-brown benzene product solution from a second reaction similar to the above was treated with chlorine gas in the dark. The color was destroyed rapidly with evolution of heat, probably through formation of dibutyltin dichloride.

Dibutyltin dichloride. The quantity of stannic chloride necessary to convert 25 g. of a tetrabutytin–tributyltin chloride mixture to dibutyltin dichloride was calculated from the chlorine content of the mixture. The mixture contained 10.1% chlorine, or 92.6% tributyltin chloride. This corresponded to 0.0054 mole of tetrabutyltin and 0.0711 mole of tributyltin chloride. Consequently, 10.7 g. (0.0411 mole) of stannic chloride was pipetted into a 300 cc. flask fitted with a thermometer and reflux condenser and containing the butyltin mixture. The resulting mixture was heated from 160–207°C. over a period of 1.5 hr., after which the tan molten dibutyltin dichloride, obtained in essentially quantitative yield, was decanted into a distilling flask. A clear product was obtained on distillation; 94% of the charge was collected at 140–143°C. at 10 mm. pressure. Crystallization temperature of the distillate was 38.5°C. A small portion of the product, crystallized from petroleum ether, melted at 39.5–40°C. Identity of the product as dibutyltin dichloride was further verified by mixture melting point.

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