Journal of Organometallic Chemistry
Elsevier Publishing Company Amsterdam -
Printed in The Netherlands

DIRECT SYNTHESIS OF ORGANOTIN COMPOUNDS
V*. DI- AND TRIALKYLTIN CHLORIDES AND BROMIDES**

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(Received December 30th, 1966)

It has previously been reported from this Laboratory that di- and tribenzyltin chlorides[1] as well as diallyltin dibromide[2] can be prepared by a direct synthesis. Recently Matuda and Matuda[5] as well as Oakes and Hutton[6] have reported that dialkyltin diiodide is obtained by the direct reaction of alkyl iodide with metallic tin with the aids of catalysts such as the combination of alcohol and magnesium or lithium at 120–160°. Similar treatment of alkyl bromides, however, gave alkyltin bromides in poor yields, and that of alkyl chlorides gave only very little alkyltin chlorides. Smith and Rochow[7] had shown that at higher temperature (300–350°) only methyl chloride reacted with metallic tin to form methyltin chlorides, while ethyl chloride and the higher homologs hardly reacted even under drastic conditions.

Alkyltin chlorides were found to be produced in good yields by the direct reaction of alkyl chlorides at relatively low temperature (130–180°) when both an organic base and an iodine compound were used as the catalysts. Without either of these substances alkyltin compounds were scarcely obtained and almost all the starting materials were recovered (Table 1). When metallic tin powder and an excess

TABLE 1

REACTION OF n-BUTYL CHLORIDE WITH METALLIC TIN IN THE PRESENCE OF TRIETHYLAMINE AND IODINE[a]

Tin (g-atom)	*Triethylamine (mole)*	*Iodine (mole)*	*React. temp. (°C)*	*React. time (h)*	*Product (g)*		*Total yield (%)*
					n-Bu_2SnCl_2	*n-Bu_3SnCl*	
0.33	0.0	0.02	160	6	4.8	1.7	6.3[b]
0.33	0.1	0.0	160	6	0.1	2.5	2.4[b]
0.33	0.1	0.02	160	6	48.4	18.5	65.2[b]
0.67	0.1	0.02	160	6	37.4	33.3	55.2[c]
0.67	0.1	0.02	135	6	8.6	33.2	36.2[c]
0.67	0.1	0.02	180	6	64.6	0.0	42.4[c]
0.67	0.1	0.02	160	1	0.0	29.2	27.0[c]
0.67	0.1	0.02	160	3	49.9	24.6	55.0[c]
0.67	0.02	0.02	160	6	11.6	10.3	16.8[c]
0.67	0.05	0.02	160	6	30.3	8.0	27.4[c]
0.67	0.2	0.02	160	6	30.7	59.6	75.1[c]
0.67	1.0	0.02	160	6	2.0	54.6	51.9[c]

[a] All reactions were carried out with 1.0 mole of n-butyl chloride in an autoclave with a high speed rotatory stirrer (1000 rpm). [b] Yields are based on tin since the chloride was used in excess. [c] Yields are based on n-butyl chloride since tin was used in excess.

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* For Parts I–IV see refs. 1–4 respectively.

** Presented in part at the 19th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1966.

of n-butyl chloride were treated in the presence of a small amount of triethylamine and iodine at 160° for 6 h in an autoclave, di-n-butyltin dichloride mixed with a small amount of tri-n-butyltin chloride was obtained. Distribution of di- and tri-n-butyltin chlorides in the reaction product varied with the reaction time, the temperature, the amount of metallic tin and of triethylamine. Lower temperature (135°) and shorter time (1 h), favored the formation of tri-n-butyltin chloride. At higher temperature (180°), only di-n-butyltin dichloride was obtained. Increase of the amount of metallic tin or triethylamine raised the yield of tri-n-butyltin chloride at the expense of di-n-butyltin dichloride. In the extreme case, *i.e.*, when a large amount of triethylamine was used, the formation of di-n-butyltin dichloride could be avoided (Table 3). Addition of mercuric chloride* or magnesium** gave rather worse results. Replacement of triethylamine with diethylamine or n-butylamine caused the lowering of the yields. When n-butanol[5] or water[1] was used instead of amine, organotin compounds were scarcely obtained. Results of these experiments are summarized in Table 3.

TABLE 2

REACTION OF n-BUTYL CHLORIDE WITH METALLIC TIN IN THE PRESENCE OF ORGANIC BASES AND IODINE[a]

Tin (g-atom)	*Bases added (0.1 mole)*	*React. temp. (°C)*	*React. time (h)*	*Product (g)*		*Total yield (%)*
				n-Bu_2SnCl_2	*n-Bu_3SnCl*	
0.67	Pyridine	160	6	45.2	0.0	29.8[b]
0.33	Quinoline	160	6	61.2	0.0	60.3[c]
0.33	Aniline	160	3	31.1	0.0	31.2[c]
0.33	Piperidine	160	3	55.3	4.3	58.6[c]
0.33	Colidine	160	3	33.2	12.9	44.8[c]
0.33	N,N-Dimethylaniline	160	3	15.8	14.5	29.0[c]
0.33	Ethanolamine	160	3	15.5	15.6	29.7[c]
0.33	Tri-n-butylamine	160	3	20.1	27.5	45.0[c]
0.33	Diethylamine	130	6	1.9	23.7	23.8[c]
0.33	n-Butylamine	130	6	8.6	15.8	23.1[c]
0.33	Ammonia	160	6	28.1	25.1	50.8[c]
0.33	Morpholine	130	3	2.3	7.7	9.4[c]
0.67	N,N-Dimethylformamide	140	6	1.9	8.8	9.4[b]
0.33	Urea	160	3	Recovery of materials		
0.67	Triphenylphosphine	160	6	25.1	14.7	30.0[b]

[a] All reactions were carried out with 1.0 mole of n-butyl chloride and 0.02 mole of iodine in an autoclave with stirring (1000 rpm). [b] Yields are based on n-butyl chloride. [c] Yields are based on tin.

It has been shown that this direct preparation of n-butyltin chlorides was promoted not only by triethylamine but also by other organic bases such as pyridine, quinoline, aniline, N,N-dimethylaniline, piperidine, ethanolamine, tri-n-butylamine, diethylamine, n-butylamine, ammonia and triphenylphosphine in the presence of a small amount of iodine (Table 2). When pyridine or quinoline was used, pure di-n-butyltin dichloride was produced in good yields, while in the presence of other tertiary, secondary, primary amines or ammonia, a mixture of di- and tri-n-butyltin

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* In the direct reaction of allyl bromide with metallic tin, mercuric chloride acted as an effective catalyst[2].

** Presence of magnesium raised the yield of di-n-butyltin diiodide in the reaction of n-butyl iodide with metallic tin[5].

TABLE 3

PREPARATION OF TRI-n-BUTYLTIN CHLORIDE[a]

Amine, etc. (*100 ml*)	*Iodine* (*mole*)	*React. temp.* (*°C*)	*React. time* (*h*)	*Product* (*g*) *n-Bu$_3$SnCl*	*Yield*[b] (*%*)
Triethylamine	0.0	160	6	0.2	1
Triethylamine	0.004	160	6	11.1	51
Triethylamine[c]	0.004	160	6	10.2	47
Triethylamine[d]	0.004	160	6	8.9	41
Triethylamine	0.004	160	12	11.7	54
Triethylamine	0.004	180	6	10.8	50
Triethylamine	0.004	140	6	5.8	27
Triethylamine	0.004	140	12	11.4	53
Diethylamine	0.004	160	6	2.2	10
n-Butylamine	0.004	160	6	0.0	0
n-Butanol	0.004	160	6	1.6	7
Water	0.004	160	6	0.0	0

[a] All reactions were carried out with 0.2 mole of n-butyl chloride and 0.2 g-atom of tin powder in 100 ml of an amine in an autoclave with a high speed rotatory stirrer (1000 rpm). [b] Yields are based on n-butyl chloride. [c] Mercuric chloride (0.05 g) was added in this run. [d] Metallic magnesium powder (1.2 g) was used in this run.

chloride was obtained. The distribution of di- and trialkylated tin compounds delicately varied with the kind of amines.

It is known that iodine reacts with an equimolar amount of an amine to give a 1 : 1 intermolecular charge transfer complex[8-11]. This complex, as formed *in situ*, did not act as a catalyst efficiently (Table 1). Only when there was an excess of amine, that is, when the amine formed an organic ammonium iodide, a high yield of n-butyltin chloride was expected (Table 1). This suggested that the organic ammonium iodide was the effective catalyst of the reaction. There was no reaction between the organic ammonium iodide and alkyl chloride or metallic tin.

TABLE 4

REACTION OF n-BUTYL CHLORIDE WITH METALLIC TIN IN THE PRESENCE OF ORGANIC AMMONIUM HALIDES[a]

Ammonium halides (0.05 *mole*)	*React. time* (*h*)	*Product* (*g*)		*Yield*[b] (*%*)
		n-Bu$_2$SnCl$_2$	*n-Bu$_3$SnCl*	
Tetraethylammonium iodide[c]	6	46.5	0.0	46.3
Tetraethylammonium iodide[c]	3	30.7	7.2	37.1
Tetraethylammonium bromide[c]	6	0.0	17.7	14.7
Tetraethylammonium chloride[d]	6	0.0	3.8	3.5
Ethylpyridinium iodide[e]	6	49.7	0.0	49.5
n-Butylammonium iodide[f]	6	44.4	0.0	44.2
Ammonium iodide	6	0.0	4.3	4.0

[a] All reactions were carried out with 39.6 g (0.33 g-atom) of tin powder and 92.6 g (1.0 mole) of n-butyl chloride in the presence of 0.05 mole of the respective ammonium halide in an autoclave with vigorous stirring. [b] Yields are based on tin. [c] Tetraethylammonium iodide and bromide were prepared by the reaction of triethylamine with ethyl iodide and ethyl bromide, respectively[12]. [d] Prepared by the method of Phillips and Baltzly[13]. [e] Prepared from pyridine and ethyl iodide. [f] Prepared from n-butylamine and hydrogen iodide.

TABLE 5

REACTION OF ALKYL CHLORIDES WITH METALLIC TIN IN THE PRESENCE OF TRIETHYLAMINE AND SOME IODINE OR BROMINE COMPOUNDS[a]

Alkyl chloride (RCl)	*(mole)*	*Tin (g-atom)*	*Triethylamine (mole)*	*Iodine or bromine compounds*	*(mole)*	*React. time (h)*	*Product*		*Total yield (%)*
							R_2SnCl_2	R_3SnCl	
n-Butyl chloride	1.0	0.67	0.10	n-Butyl iodide	0.04	6	44.4	25.9	53.2[b]
n-Butyl chloride	1.0	0.33	0.10	Magnesium iodide	0.02	3	22.1	29.1	48.6[c]
n-Butyl chloride	0.20	0.20	1.0	Stannous iodide	0.004	6	0.0	7.8	36[c]
n-Butyl chloride	0.20	0.20	1.0	Sodium iodide	0.008	6	0.0	7.5	35[c]
Ethyl chloride	1.0	0.33	0.10	Iodine	0.02	6	33.8	8.4	50.1[c]
n-Octyl chloride	1.0	0.33	0.10	Iodine	0.02	6	26.6	29.8	37.7[c,d]
Chlorobenzene	1.0	0.33	0.10	Iodine	0.02	6	Recovery of materials		
n-Butyl chloride	1.0	0.67	0.10	Bromine	0.02	2	Recovery of materials		
n-Butyl chloride	1.0	0.33	0.10	n-Butyl bromide	0.04	6	1.0	19.7	19.4[c]

[a] All reactions were carried out in an autoclave with vigorous stirring at 160°. [b] Yields are based on alkyl chloride. [c] Yields are based on tin. [d] A fraction boiling at 162–201°/0.003 mm was collected.

It was found that in the presence of tetraethylammonium iodide, ethylpyridinium iodide or n-butylammonium iodide, the direct reaction of alkyl chloride with metallic tin proceeded to give dialkyltin dichloride in 40–50% yields. When, however, tetraethylammonium bromide or chloride was used instead of the iodide, only trialkylated tin compounds were formed in lower yields (Table 4). With simple ammonium iodide the yield was surprisingly poor and only tri-n-butyltin compound was produced.

Instead of iodine, alkyl iodide, magnesium iodide, stannous iodide, or sodium iodide could be used as an iodine source. Use of bromine instead of iodine did not catalyze the reaction, while n-butyl bromide added as a catalyst promoted the reaction of n-butyl chloride slightly.

Ethyl chloride and n-octyl chloride also reacted with metallic tin in the presence of triethylamine and iodine to produce ethyltin chlorides and n-octyltin chlorides in 50.1% and 37.7% yield, respectively. Chlorobenzene did not react with metallic tin under the same conditions. These results are tabulated in Table 5.

Alkyltin bromides could be prepared by the reaction of alkyl bromide with metallic tin in the presence of triethylamine (Table 6). The presence of iodine source was not necessary in this case. Bromobenzene did not afford phenyltin compounds under the same conditions, all the starting materials being recovered unchanged.

TABLE 6

REACTION OF ALKYL BROMIDE WITH METALLIC TIN IN THE PRESENCE OF TRIETHYLAMINE[a]

Alkyl bromide (RBr) (1.0 mole)	*Triethylamine (mole)*	*React. temp. (°C)*	*React. time (h)*	*Product (g)*		*Total yield[b] (%)*
				R_2SnBr_2	R_3SnBr	
n-Butyl bromide	0.1	160	6	85.0	0.0	64.9
n-Propyl bromide	0.1	160	6	67.2	0.0	55.3
Ethyl bromide	0.05	140	4	61.2	13.6	69.2
Bromobenzene	0.1	160	6	0.0	0.0	0.0

[a] All reactions were carried out with 39.6 g (0.33 g-atom) of tin powder and 1.0 mole of alkyl bromide in the presence of triethylamine in an autoclave with vigorous stirring. [b] Yields are based on tin.

EXPERIMENTAL

Analytical procedure

Distribution of di- and trialkyltin halides, except for n-octyltin halides, was determined by gas chromatography. For ethyltin halides, a 0.75-m column packed with "Succinate Polyester" was used at 150°. For n-propyltin and n-butyltin halides, a 3-m column packed with "High Vacuum Silicon Grease" was used at 200°. In the case of n-octyltin chlorides, the distribution was determined by chlorine content[14].

Reaction of alkyl chloride or bromide with metallic tin in the presence of organic base and iodine

A representative procedure is as follows. A mixture of 39.6 g (0.33 g-atom) of tin powder, 92.6 g (1.0 mole) of n-butyl chloride, 10.1 g (0.10 mole) of triethylamine and 5.1 g (0.02 mole) of iodine was heated in a stainless steel autoclave with a high speed rotatory stirrer (1000 rpm) at 160° for 6 h. Tin powder was completely consumed. To the reaction product was added 200 ml of water and 15 ml of 12 *N* hydrochloric acid in order to separate di-n-butyltin dichloride from the triethylamine adduct which is insoluble in ether and undistillable. n-Butyltin compounds were extracted three times with each 200 ml portion of ether. Combined ethereal solution was concentrated and the residue was distilled *in vacuo* to give 66.9 g of a product, b.p. 125–145°/5 mm, including 48.4 g of di-n-butyltin dichloride and 18.5 g of tri-n-butyltin chloride. Ethyltin compounds such as di-n-butylethyltin or n-butyldiethyltin halide were not detected even by gas chromatography.

In the case of ammonia as the base, liquid ammonia was added to a mixture of metallic tin, n-butyl chloride and iodine in an autoclave cooled at about −70° in dry ice/methanol bath and treated as above.

Reaction of n-butyl chloride with metallic tin in triethylamine in the presence of iodine. Tri-n-butyltin chloride

The ingredients were treated above and the reaction product, dissolved in 200 ml of methanol, was filtered to separate unchanged tin. Removal of methanol and triethylamine gave brown oil which was shaken with 200 ml of ether and 100 ml of 1 *N* hydrochloric acid to extract n-butyltin compounds. The aqueous layer was extracted twice with each 200 ml portion of ether and the combined ethereal layer was concentrated and the residue was distilled *in vacuo* to give 11.1 g (51 %) of tri-n-butyltin chloride, b.p. 140–142°/5 mm, n_D^{20} 1.4908 (lit.[15] b.p. 130–132°/4 mm, n_D^{20} 1.4903) in which no di-n-butyltin dichloride was found by gas chromatography. When n-butanol or water was used as the solvent, methanol was not added to the reaction mixture in the procedure.

Reaction of n-butyl chloride with metallic tin in the presence of organic ammonium halides

In the case of the reaction carried out with ammonium iodide, tetraethylammonium bromide and chloride, tin powder coagulated into a number of small hard balls after about 1 h so that the rotation speed of the stirrer slowed down from 1000 to 200–300 rpm. From the ethereal extraction of the reaction product n-butyltin halides were obtained by the analogous procedure described as above. The experimental results are summarized in Table 4.

Reaction of triethylamine/iodine complex with n-butyl chloride

To 10 ml of n-butyl chloride was added 7.1 g (0.020 mole) of triethylamine/iodine complex[8] and heated in a sealed glass bottle at 140° for 6 h. After cooling, n-butyl chloride layer was analyzed by gas chromatography (a 3-m column packed with "High Vacuum Silicone Grease" was used at 60°). In the n-butyl chloride layer, 1.2 g (17 %) of n-butyl iodide was present. The reaction mixture was shaken with 20 ml of methanol, 200 ml of water and 200 ml of ether. The aqueous layer was washed with ether, and evaporated *in vacuo* to give 1.2 g of pale yellow crystals. Although qualitative test for iodide anion[13] in the crystals was slightly positive, any ammonium iodides were not isolated by recrystallization which gave 0.7 g of triethylammonium chloride.

To 7.1 g (0.020 mole) of the complex in 20 ml of n-butyl chloride was added 8.0 g (0.08 mole) of triethylamine. The mixture was heated at 140° for 6 h to give no n-butyl iodide but 8.2 g (73%) of needles. Recrystallization from acetone gave 6.0 g of triethyl-n-butylammonium iodide.

Treatment of tetraethylammonium iodide with n-butyl chloride

On heating 3.2 g (0.0125 mole) of tetraethylammonium iodide in 4.6 g (0.05 mole) of n-butyl chloride in a glass sealed bottle at 140° for 9 h, all starting materials were recovered unchanged.

Treatment of tetraethylammonium iodide with metallic tin in toluene

On stirring 12.8 g (0.05 mole) of tetraethylammonium iodide and 39.6 g (0.33 g-atom) of tin powder in 100 ml of toluene in an autoclave at 160° for 6 h, 39.0 g (99%) of tin powder was recovered unchanged.

SUMMARY

Di- and trialkyltin chlorides were prepared in good yields by the direct reaction of alkyl chloride with metallic tin when organic ammonium halides or a mixture of organic base and iodine-compound was used as the catalysts. Distribution of di- and trialkyltin chlorides varied with the kind and the amount of organic base, and reaction conditions. In the presence of a large amount of organic base, pure trialkyltin chloride was obtained. For the direct synthesis of alkyltin bromides, iodine source was not necessary.

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