The Synthesis of Alkyltin Halides by Direct Reaction between Tin and Alkyl Halides[1]

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Organotin compounds are widely used as stabilizers for polyvinylchloride or as antifungicides, and many patents or reports have been published about the synthesis of alkyltin halides, R_nSnX_{4-n}, which are the most important intermediates of these organotin compounds.

To obtain dialkyltin or trialkyltin halides, the redistribution reaction between tetraalkyltin and stannic chloride or the halogenation of tetraalkyltin has conveniently been employed. There have been, however, a few studies attempting to prepare these compounds from tin and alkyl halides by direct methods; with these, however, a considerable yield could be obtained only in the limited case where an alloy of tin was used.

In this report a modified direct synthesis of alkyltin halides will be described in which the reaction is carried out by adding a trace of magnesium or zinc and a small amount of alcohol, ester or an ether such as tetrahydrofuran. For its ease and the high yield of alkyltin halides, this method can be considered the most excellent one among the direct methods reported thus far.

For example, tin foil and butyl iodide were reacted at ordinary pressure in the presence of magnesium (0.2~0.3% to tin) and *n*-butanol (3% to butyl iodide); then almost all the tin foil was converted to dibutyltin diiodide.

By a similar reaction, alkyl bromide could convert tin almost completely to R_nSnBr_{4-n} (n=1—3) in an autoclave, but in this case it was found neccessary to add alkyl iodide (ca. 5% to alkyl bromide) besides magnesium and *n*-butanol.

The reaction of an alkyl chloride, for example, methyl chloride, with tin foil in the presence of magnesium, *n*-butanol or tetrahydrofuran and butyl iodide gave dimethyltin dichloride in a high yield of ca. 92%.

When aryl halides were used instead of alkyl halides, no reaction product was obtained.

Experimental

Materials.—The tin foil and the metals used as additives were 99.99 and 99.9% pure respectively. The alkyl halides and solvents used were purified by distillation.

Typical examples of the precedures are as follows.

Reaction of Tin and Butyl Iodide.—In a three-necked flask of 1 l. were placed 100 g. (0.843 mol.) of tin foil, 372 g. (0.843×2.4 mol.) of butyl iodide, 0.3 g. (0.3% to tin) of magnesium, and 11.2 g. (3% to butyl iodide) of *n*-butanol; then the mixture was heated to 130~135°C for three hours with being stirred. After the reaction, a small amount of solid was filtered off (98% of the tin was consumed). The fractionation of the remaining liquid gave unreacted butyl iodide and dibutyltin diiodide (b. p. 143~145°C/3 mmHg; yield 381 g., 95% to the reacted tin).

Reaction of Tin and Butyl Bromide.—A mixture of tin foil (30 g. : 0.253 mol.), butyl bromide (83~104 g. : 0.253×(2.4~3.0)mol.) and a catalytic amount of magnesium, butyl iodide and *n*-butanol was heated at 135~170°C in a stainless autoclave of 500 ml. After the reaction, the solid, which mainly consisted of unreacted tin, was filtered off. Fractionations through a helices-packed column of about thirty theoretical plates gave three fractions: unreacted butyl bromide, fraction I (95~100°C/2 mmHg) and fraction II (120~125°C/2 mmHg). Fraction I consisted of butyltin tribromide, while fraction II was a mixture of dibutyltin dibromide and tributyltin bromide.

The added butyl iodide was considered to have been converted to higher boiling substances.

Under optimum conditions (tin 30 g., butyl bromide 104 g., butyl iodide 5 g., *n*-butanol 2.5 g., and magnesium 0.12 g. were allowed to react at 160°C for 8 hr.), the tin was consumed completely and 27 g. of butyltin tribromide, 60 g. of dibutyltin dibromide and 6 g. of tributyltin bromide were obtained (yields: 26, 60 and 7% respectively).

Reaction of Tin and Methyl Chloride.—Methyl chloride 50~60 g. (ca. 1.0~1.2 mol.) was introduced into a stainless autoclave of 100 ml. in which 20 g. (0.169 mol.) of tin foil, magnesium, butyl iodide and *n*-butanol or tetrahydrofuran were charged. The temperature was kept at 190°C for six hours; then the reaction product was separated from the unreacted tin by filtration or sublimation under reduced pressure. The white crystal thus obtained was found to be dimethyltin dichloride. M. p. 105~106.5°C.

Found: Sn, 54.35; Cl, 32.32. Calcd. for $C_2H_6SnCl_2$: Sn, 54.03; Cl, 32.28%.

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[1] This paper is a summarized report of four articles published in Japanese: S. Matsuda and H. Matsuda, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **63**, 114 (1960); H. Matsuda and S. Matsuda, ibid., **63**, 1958, 1965 (1960); H. Matsuda, H. Taniguchi and S. Matsuda, idid., **64**, 541 (1961).

Analyses.—Halogen was determined by high frequency titration²⁾ with an aqueous silver nitrate solution. Gas chromatography was also applied³⁾ for identification of some of the products.

Results

Alkyltin Iodides.—In the reaction of tin and butyl iodide, the effect of the amount of magnesium and *n*-butanol vs. the tin conversion (see A and B), as well as the amount of the tin conversions by using various kinds of metal additives and solvents, are shown in Fig. 1. Usually 90~95% of dibutyltin diiodide was found in the reaction product.

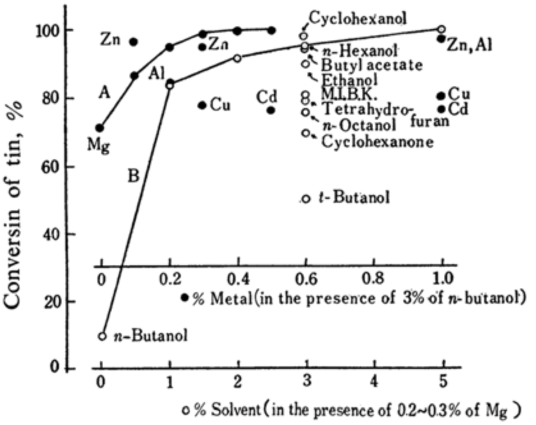

Fig. 1. The effect of the additives for the conversion of tin.

Figure 1 also shows that magnesium and zinc are two of the most effective additives in cooperation with alcohols such as *n*-butanol or cyclohexanol. The preferable amount of the metal seemed to be 0.1~0.3% to tin; an excessive addition caused an unfavourable discoloring of the product.

Methyl iodide and tin could be reacted completely in an autoclave within two hours in the presence of magnesium and methanol or *n*-butanol. Vacuum distillation gave a mixture of trimethyltin iodide, dimethyltin diiodide and methyltin triiodide in yields of 25~30, 40~46 and 20~27% respectively, and no appreciable change in composition was observed after changing the ratios of the reaction components, the amount of the additives, the reaction temperature or the reaction time.

Similarly, from tin and ethyl iodide, triethyltin iodide, diethyltin diiodide and ethyltin triiodide were obtained in yields of 14~18, 63~67 and 3~6% respectively.

Other alkyl iodides could be used as well as butyl iodide. In these reactions almost the same conversions were obtained as in the case

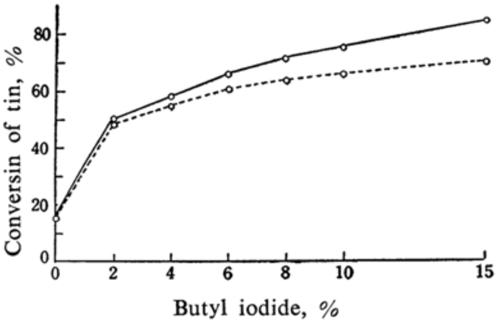

Fig. 2. The effect of butyl iodide for the reaction of tin and butyl bromide.
Butyl bromide (mol.)/tin (mol.) = 2.4, magnesium 0.06 g. (0.2% to tin), *n*-butanol 2.5 g. (6% to butyl bromide), reaction temperature 170°C, reaction time 4 hr.
—— The observed conversion of tin by butyl bromide and added butyl iodide.
---- The calculated conversion of tin by butyl bromide.

TABLE I. THE EFFECT OF ADDITIVES IN THE REACTION BETWEEN TIN AND METHYL CHLORIDE

Tin, 20 g.; Methyl chloride, 50~60 g.; Reaction temp., 190°C; Reaction time, 6 hr.

Amount of additives						
Magnesium	*n*-Butanol	Tetrahydrofuran	Butyl iodide	Tin conversion	$(CH_3)_2SnCl_2$	Yield
g.	g.	g.	g.	%	g.	%
0.06	1.7	14	3.4	100	34.3	92.7
0.06	1.7	0	3.4	100	33.5	90.6
0.06	0	14	3.4	100	34.4	92.8
0.06	0	14	0	45.0	—	—
0.06	0	0	3.4	21.0	—	—
0.06	1.7	0	0	4.0	—	—
0	1.7	0	3.4	26.0	—	—
0.06	0	7	3.4	100	33.8	91.3
0.06	0	3.5	3.4	74.0	—	—

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2) H. Matsuda and S. Matsuda, ibid., **64**, 539 (1961).

3) H. Matsuda and S. Matsuda, ibid., **63**, 1960 (1960).

TABLE II. PHYSICAL PROPERTIES[a] OF ALKYLTIN HALIDES

Compound	B. p., °C/mmHg	M. p., °C	n_D^{20}	d_4^{20}	Anal. Sn% (Calcd.)
$(CH_3)_3SnI$	61~62/14 (67~68/15)		1.5726 (1.5724)	2.1205	40.52[c] (40.83)
$(C_2H_5)_3SnCl$	147~149/130 (94/13)		1.5072 (1.5055)	1.4396	49.60 (49.18)
$(C_2H_5)_3SnI$	78~80/3 (117.5/13)		1.5615[b]	1.8232	35.98[d] (35.67)
$(n\text{-}C_4H_9)_3SnCl$	147~149/130 (145~147/5)		1.4909[b]	1.2072	36.23 (36.47)
$(n\text{-}C_4H_9)_3SnBr$	139~140/4.5 (163/12)		1.5028[b]	1.3421[b]	31.48 (32.08)
$(n\text{-}C_4H_9)_3SnI$	138~140/2.5 (168/8)		1.5302 (1.5345)	1.4810	28.03 (28.47)
$(n\text{-}C_3H_7)_2SnI_2$	103~104/2.5 (166~167/10)		1.6309	2.2099	—
$(i\text{-}C_3H_7)_2SnI_2$	95.5~96/2 (153~156/5)		1.6350	2.2088	—
$(n\text{-}C_4H_9)_2SnI_2$	143~145/3		1.6054	2.0198	24.93[e] (24.39)
$(i\text{-}C_4H_9)_2SnCl_2$	107/3.9 (135.5/15)		1.5090	1.4213	39.77 (39.07)
$(i\text{-}C_4H_9)_2SnBr_2$	118/4 (144/15)		1.5424	1.7578	29.85 (30.22)
$(i\text{-}C_4H_9)_2SnI_2$	124~126/3 (290~295/760)		1.6127	2.0738	—
$(s\text{-}C_4H_9)_2SnCl_2$	113/4		1.5218	1.4357	38.39 (39.07)
$(s\text{-}C_4H_9)_2SnBr_2$	122~124/4.5		1.5575	1.7836	29.93 (30.22)
$(s\text{-}C_4H_9)_2SnI_2$	113.5/3		1.6294	2.0999	25.42 (24.39)
$(i\text{-}C_5H_{11})_2SnCl_2$	129~135/4		1.5072	1.3402	35.18 (35.76)
$(i\text{-}C_5H_{11})_2SnBr_2$	137~139/4		1.5357	1.6688	28.72 (28.21)
$(i\text{-}C_5H_{11})_2SnI_2$	120.5~121/2 (202~205/8)		1.5964	1.9237	23.50 (23.06)
$(n\text{-}C_6H_{13})_2SnBr_2$	149~151/2				26.50 (26.45)
$(n\text{-}C_8H_{17})_2SnBr_2$	183~185/1.5	22~24			24.14 (23.41)
$(n\text{-}C_{10}H_{21})_2SnCl_2$	220~223/3.5	45~48			24.85 (25.16)
$(n\text{-}C_{10}H_{21})SnBr_2$	215~218/2	35~36			20.41 (21.17)
$(n\text{-}C_{12}H_{25})_2SnI_2$		46.5~48			
CH_3SnI_3	122~125/5.5	86.5~88.0 (86.5)			23.09 (23.07)
$n\text{-}C_4H_9SnBr_3$	120/8		1.5933	2.3652	28.79[f] (28.56)

a) Data in parenthesis are cited from Ref. 4.
b) Data at other temperatures were reported in Ref. 4.
c) Anal. Found: C, 12.94; H, 3.22. Calcd.: C, 12.39; H, 3.12
d) Anal. Found: C, 21.08; H, 4.80. Calcd.: C, 21.65; H, 4.54
e) Anal. Found: C, 20.22; H, 4.07. Calcd.: C, 19.74; H, 3.74
f) Anal. Found: C, 11.85; H, 2.29. Calcd.: C, 11.56; H, 2.18

of adding *n*-butanol by adding the alcohol with the same alkyl group as the iodide.

However, the rate of conversion of tin and the yield of dialkyltin diiodides decreased with the increasing size of the alkyl group. For example, *n*-dodecyl iodide converted 49% of tin and yielded di(*n*-dodecyl)tin diiodide corresponding to 59% of the tin consumed.

Alkyltin Bromides.—The reaction of tin with butyl bromide in the presence of magnesium and *n*-butanol can be carried out by adding alkyl iodide. The effect of butyl iodide is shown in Fig. 2.

The reactions shown in Fig. 2 were carried out at 170°C for four hours, but the highest conversion of tin was observed in the experiment at 160°C for eight hours. It was also found that in this reaction the metal additives were not as effective as in the reaction of tin and butyl iodide; the amount of magnesium neccessary increased slightly, and zinc was found to be practically ineffective.

The reaction product from tin and butyl bromide, in contrast that of butyl iodide, was a mixture of three alkyltin bromides.

Ethyl bromide could react with tin under similar conditions; thus, from 30 g. of tin were obtained 34 g. of diethyltin dibromide and 32 g. of a mixture of triethyltin bromide (ca. 30%) and ethyltin tribromide (ca. 70%).

Long chain alkyl bromides such as *n*-octyl bromide could be reacted under ordinary pressure as well as in an autoclave, but the amount of conversion decreased with the increasing size of the alkyl group.

Alkyltin Chlorides.—The effect ot additives in the reaction between tin and methyl chloride is shown in Table I.

It can easily be seen from Table I that the three additives, magnesium, alkyl iodide and *n*-butanol or tetrahydrofuran, are indispensable for this reaction to proceed.

The high yield of dimethyltin dichloride obtained by this method is of special note.

Butyl chloride was treated with tin by a similar procedure, but the reaction was found to be unsuccessful because of side reactions.

The physical properties of the alkyltin halides obtained in these experiments are listed in Table II, together with the data which appeared also in a recent article[4].

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[4] R. K. Ingham, S. D. Rosenberg and H. Gilman, *Chem. Revs.*, **60**, 459 (1961).