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Preparation of di(n-butyl)tin and di(n-octyl)tin dihalides by the direct synthesis method

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The direct synthesis of the two industrially important organotin intermediates, di(n-butyl)tin and di(n-octyl)tin dihalides, has been investigated by reacting the appropriate alkyl halide with metallic tin under varying conditions. Observations were made on the influences of temperature, pressure, reaction time, nature of the tin metal, organic halide/tin reactant ratios and the presence of catalysts on the extent of tin conversion and yields of the organotin products. The efficacy of the onium halides, notably n-Bu_4NI, Me_3SI and Ph_3MeAsI, either singly or in binary combinations with iodine or inorganic iodine compounds, in catalysing the synthesis of the above dialkyltins as well as higher di(n-alkyl)tin analogues is described.

Keywords: Direct synthesis, di(n-butyl)tin dibromide, di(n-octyl)tin dihalides, onium catalysts, pressure reactor

INTRODUCTION

Diorganotin(IV) dihalides containing the hydrocarbon groups methyl, n-butyl, n-octyl and 2-butoxycarbonylethyl are important intermediates in the manufacture of diorganotin stabilizers for poly(vinyl chloride) (PVC).[1] Of these, only the methyl- and 2-butoxycarbonylethyltins are produced by direct synthesis routes from tin metal.[2,3] The direct synthesis for the n-butyl- and n-octyl-tins, involving the interaction of tin with n-butyl and n-octyl halides, proceeds satisfactorily only with the iodides and requires the presence of catalysts to achieve lower operational temperatures that minimize alkene- and distannane-forming side reactions.[4] Developmental interest in catalysts has been intense in recent years, especially in the reactions involving the less reactive but cheaper n-butyl and n-octyl chlorides and bromides.

The chemical and patent literature on the direct synthesis of diorganotins is vast and has been well reviewed by Murphy and Poller.[5] A wide variety of catalyst systems have been reported which include iodine, metals such as magnesium, lithium, sodium and copper or their salts (often in combination with higher alcohols or ethers or aprotic solvents), tetra-alkylammonium halides, and organo Group V element derivatives, notably triorganostibines and tetraorganophosphonium halides. Either singly or in binary and ternary combinations, these catalysts have been used particularly in the case of the reactions of tin with n-butyl chloride and bromide along with small amounts (usually *ca* 4 mol % of tin used) of n-butyl iodide.†

We report here our results on the use of a selected range of catalysts, in particular the onium halides, Me_3SI, n-Bu_4NI, Ph_3MeAsI and Ph_3MePBr, in the direct synthesis of n-Bu_2SnBr_2, n-Oct_2SnX_2 (X = Cl, Br), (n-decyl)$_2SnBr_2$ and (n-dodecyl)$_2SnBr_2$.

EXPERIMENTAL METHODS

Tin powder of particle size $< 71\ \mu m$ (mesh no. 215) was used throughout the experiments. The alkyl halides, catalysts and solvents (AR grade) used were commercial supplies of acceptable purity. The preparations, typified in the two examples described below, were carried out at least twice in most cases to ensure reproducibility. Many experiments of a similar nature were carried out with systematic variations in experimental conditions, as noted in the tables.

Trimethylsulphonium iodide-catalysed synthesis of di(n-butyl)tin dibromide using a high-pressure reactor

Tin powder (10 g, 84.8 mmol), n-butyl bromide (33 g, 241.0 mmol), n-butyl iodide (1.6 g, 8.8 mmol), and trimethylsulphonium iodide (0.64 g, 3.1 mmol) were introduced into a Parr

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†See *Note added in proof*, p 114.

(model 452 HC) Pressure Reactor of 300 cm^3 capacity equipped with high-speed stirring and temperature-control facilities. The initial internal pressure of the reactor was charged with oxygen-free, dry nitrogen to 100 psi (690 kPa), and the mixture was heated at 180°C under high-speed stirring. During the reaction the pressure rose to 280 psi (1930 kPa) and this was maintained for 6 h. At the end of this period, the reactor was allowed to cool to room temperature and the internal pressure carefully released. The contents of the reactor vessel were poured into 250 cm^3 ethanol in a large beaker with stirring, and the whole quantitatively filtered to remove unreacted tin. The tin was thoroughly washed, dried and its weight (0.9 g) recorded. A sample of the ethanol filtrate was analysed by TLC (silica gel) using two different eluting solvents—chloroform/glacial acetic acid (10:1 v/v) and n-hexane/acetone (10:7 v/v)—to determine the types of butyltin compounds present. n-Bu_2SnX_2 was detected as the predominant product; mono- and tri-butyltins were present only in trace amounts.

The ethanolic filtrate was next treated with 150 cm^3 sodium hydroxide solution containing 20 g solid sodium hydroxide. A white solid immediately precipitated. This was filtered, washed thoroughly with distilled water until the washings were no longer alkaline and, following further washings with ethanol, air-dried. The solid was finally dried in an oven at 80–90°C to constant weight (15.3 g). It was identified as di(n-butyl)tin oxide, m.p. 237–240°C (dec.).

Analysis: Found: C, 38.55; H, 7.20. Calcd for $C_8H_{18}SnO$: C, 38.62; H, 7.24%.

The mono-n-butyltin content in the oxide formed was investigated by the EDTA titrimetric method of Efer *et al.*[6] Thus a 0.5 g sample of the oxide was dissolved in 5 cm^3 methanolic hydrochloric acid (prepared by passing gaseous hydrogen chloride into methanol) with brief warming on a water bath, and following addition of about 15 drops of a 0.1% solution of pyrocatechol violet in methanol, the solution was titrated with 0.05 mol dm^{-3} EDTA until a colour change from blue to reddish-violet occurred. The titration was carried out in triplicate, and revealed in this case negligible contamination of the dibutyltin oxide by monobutyltin oxide.

The percentage yield of the n-Bu_2SnBr_2 originally formed in the reaction was calculated based on the tin consumed.

The percentage tin consumed and yield of n-Bu_2SnBr_2 using the pressure reactor were found to be 91 and 80 respectively.

Synthesis of dioctyltin dichloride at atmospheric pressure using the catalyst combination Ph_3MeAsI/iodine

Tin powder (2.5 g, 21.2 mmol), n-octyl chloride (9.5 g, 63.6 mmol), n-octyl iodide (0.5 g, 2.1 mmol), Ph_3MeAsI (0.38 g, 0.84 mmol), and iodine (0.1 g, 0.84 mmol) were placed in a 100 cm^3 round-bottomed flask equipped with a reflux condenser. The mixture was heated on a oil bath at 200°C for 6 h with high-speed stirring. At the end of this period, the mixture was allowed to cool to room temperature, treated with 60 cm^3 ethanol and the whole filtered to remove unreacted tin (0.21 g). The ethanolic filtrate was next treated with 40 cm^3 of sodium hydroxide containing 5 g NaOH. An immediate white precipitate resulted, which was washed thoroughly with distilled water, filtered and dried to constant weight (5.3 g). The solid was identified as di(n-octyl)tin oxide, m.p. 245–248°C (dec.).

EDTA titration revealed *ca* 1% of mono-octyltin content in the oxide formed. The percentage tin consumed and yield of n-Oct_2SnCl_2 originally formed in the reaction mixture were calculated to be 92 and 75 respectively.

RESULTS AND DISCUSSION

Dialkyltin(IV) dihalide formation in the direct synthesis experiments was quantitatively assessed by conversion to the oxide, $(R_2SnO)_n$, by addition of excess alkali to the reaction mixture at the end of the reaction. Thin-layer chromatographic analysis of the reaction mixture revealed the presence of only trace amounts of trialkyltin halides; tetra-alkyltin was not detected. The presence of mono-alkyltin oxide in the isolated dialkyltin oxide $(R_2SnO)_n$ was selectivity estimated by EDTA titrimetric analysis: only in the reaction with n-octyl halides were mono-n-octyltin(IV) species detected (less than 10% for most cases). Generally, tin powder of particle size $<71\,\mu m$ was used throughout the experiments and its effective dispersion in the organic halide was ensured using high-speed stirring.

Direct synthesis of di(n-butyl)tin dibromide

The percentage tin conversion and yields of n-Bu_2SnBr_2 under the influence of various catalysts at atmospheric pressure are shown in Table 1. The optimal oil-bath temperature was 200°C and the reaction period 24 h. Relative to the uncatalysed reaction, the use of a catalyst such as magnesium resulted in increased tin consumption but was without effect on the yield of n-Bu_2SnBr_2. Similar observations were noted using iodine, n-Bu_4NI and hexamethylphosphoramide (HMPA) as catalysts. The use of magnesium together with a co-catalyst such as HMPA or DMF (dimethylformamide) caused significant enhancements in the values for tin conversion and n-Bu_2SnBr_2 product yields. Moderate increases, however, were obtained in the presence of n-BuOH.

It is speculated that the added magnesium catalyses the reaction by activation of the tin surface as well as through incipient formation of a Grignard reagent, which is stabilized by the aprotic solvent. The role of Grignard reagents in promoting direct synthesis has previously been demonstrated.[7] A generalized scheme (Eqns [1]–[4]) for the direct synthesis has been advanced by Murphy and Poller:[5]

$$\dot{Sn} + R{-}X \rightarrow \dot{Sn}^{+} + R^{\cdot} + X^{-} \quad [1]$$

$$\dot{Sn}^{+} + X^{-} \rightarrow \dot{Sn}X \quad [2]$$

$$\dot{Sn}X + R^{\cdot} \rightarrow RSnX \quad [3]$$

$$RSnX + RX \rightarrow R_2SnX_2 \quad [4]$$

The high tin consumption obtained with HMPA is probably attributable to the polar reaction medium that it provides and its role in stabilizing the reaction intermediates in Eqn [1] of the above scheme. Mechanistic aspects have also been discussed recently by Holland.[8]

Tetra(n-butyl)ammonium iodide is seen to be more effective in bringing about increased tin consumption compared with iodine or magnesium. This is probably due to the availability of an alternative path[9] for tin consumption (Eqn [5]):

$$Bu_4NI + Sn \rightarrow BuSnI \cdot NBu_3 \quad [5]$$

However, for this reaction the yield of n-Bu_2SnBr_2 product was observed to be low. The addition of iodine or HMPA or magnesium as co-catalyst caused a marked increase in the yield of n-Bu_2SnBr_2 while maintaining the high tin consumption. Conceivably, in the presence of iodine, the dissociation of n-Bu_4NI is favoured, since tributylamine (n-Bu_3N) could be stabilized by the iodine present (Eqn [6]).

$$\text{n-}Bu_4N^{+}I^{-} \rightleftharpoons \text{n-}Bu_3N + \text{n-BuI}$$
$$\downarrow I_2 \quad [6]$$
$$\text{n-}Bu_3N \cdot I_2$$

The consequent higher n-butyl iodide (n-BuI) concentration in the reaction mixture could then favour an increase in the formation of n-Bu_2SnBr_2 both stoichiometrically and catalytically.[5,10] The latter presumably through promotion of the oxidative addition (Eqn [4]) of alkyl halide to [RSnX]. The influence of added n-butyl iodide on the reaction is clearly seen from the data in Table 1 for the magnesium/n-Bu_4NI catalyst system.

To obtain reasonable reaction rates, the use of the high-pressure reactor was next explored for the n-butyl bromide/tin direct reaction using a

Table 1 Direct synthesis[a] of di(n-butyl)tin dibromide from n-BuBr and tin at atmosphere pressure in the presence of various catalysts

Catalyst[b]	Tin conversion (%)	Di(n-butyl)tin[c] (%)
None	24	33
Iodine	62	34
HMPA (1 cm^3)	96	23
Magnesium	64	31
Magnesium/HMPA (1 cm^3)	92	80
Magnesium/DMF	90	76
Magnesium/n-BuOH (1 cm^3)	88	52
n-Bu_4NI	92	35
Magnesium/n-Bu_4NI	100 (78)[d]	88 (48)[d]
Ph_3Sb/magnesium	100	44
Ph_3Sb/iodine	80	45
n-Oct_3N/iodine	64	44
Me_3SI/SnI_2	24	33
Ph_3MeAsI/iodine	32	25

[a]Reaction conditions: T (oil bath) = 200°C; t = 24 h; n-BuBr (8.1 g, 63.1 mmol), n-BuI (0.4 g, 2.1 mmol), tin powder (2.5 g, 21.0 mmol). [b]Amounts used are *ca* 4 mol% based on tin used: magnesium (0.02 g); n-Bu_4NI (0.31 g); Ph_3Sb (0.30 g); iodine (0.1 g); n-Oct_3N (0.30 g); Ph_3MeAsI (0.38 g); Me_3SI (0.17 g); SnI_2 (0.16 g). [c]Estimated as n-Bu_2SnO and based on the amount of tin reacted. [d]In the absence of n-BuI.

similar range of catalysts. The reactor was operated at 280 psi (1930 kPa) and heated at a temperature of 180°C for 6 h. Using n-Bu_4NI as the catalyst, high tin consumption and high yields of n-Bu_2SnBr_2 were obtained using the above reaction conditions (Table 2). Me_3SI proved equally effective, but triphenylstibine (Ph_3Sb) and trioctylamine (n-Oct_3N) showed only moderate activity. As with the reaction carried out at atmospheric pressure, the importance of adding n-BuI was again demonstrated in these reactions. The generally improved tin consumption and product yields achieved in the high-pressure reaction is probably due to the increased dissolution of the metal in the reaction medium and the promotion[5] of the oxidative addition step (Eqn [4]) which is likely to proceed by a free-radical pathway.

Direct synthesis of di(n-octyl)tin dihalides

The direct synthesis of n-Oct_2SnBr_2 was carried out by heating at 200°C with high-speed stirring at atmospheric pressure over 6 h, in the presence of n-octyl iodide (n-OctI) (4 wt% of n-OctBr used). The results of the influence of the various catalysts and reaction conditions, including variations in the physical state of the tin used, are summarized in Table 3.

Table 2 Direct synthesis of di(n-butyl)tin dibromide using the high-pressure reactor[a]

Catalyst[b]	Tin conversion (%)	Di(n-butyl)tin[c] (%)
None	78	29
n-Bu_4NI	64 (130°C)	52 (130°C)
	80 (160°C)	66 (160°C)
	95	81
	92[d]	59[d]
	65[e]	23[e]
	88 (200°C)	78 (200°C)
n-Bu_4NI/iodine	92	78
	65[e]	33[e]
Me_3SI	91	80
	77[e]	39[e]
Ph_3MePBr	62	8
Ph_3Sb	78	60
Ph_3Sb/iodine	93	60
n-Oct_3N	96	58
n-Oct_3N/iodine	94	76

[a]Model: Parr 452 HC; T (bath) = 180°C; t = 6 h; P_{final} 280 psi (1930 kPa); n-BuBr (32.3 g, 252.6 mmol); n-BuI (1.6 g, 8.4 mmol); tin powder (particle size < 71 μm, 10 g, 84.2 mmol) unless otherwise specified. [b]n-Bu_4NI (1.2 g); iodine (0.2 g); others (0.64 g). [c]Estimated as the dibutyltin oxide and based on the amount of tin reacted. [d]t = 4 h. [e]Without added n-BuI.

Table 3 Direct synthesis[a] of di(n-octyl)tin dibromide from n-OctBr and tin at atmospheric pressure in the presence of various catalysts

Catalyst[b]	Tin conversion (%)	Di(n-octyl)tin[c] (%)
None	84	47[d]
HMPA (1 cm^3)	100/100[e]/100[f]	83/34[e]/50[f]
Iodine	80	80
Magnesium	81	62
Magnesium/iodine	96 (72)[g]	76 (26)[g]
Magnesium/HMPA (1 cm^3)	96	81
Magnesium/DMF (1 cm^3)	96	80
Me_3SI	96 (98)[i]/68[g]	67[h] (51)[i]/35[g]
Me_3SI/SnI_2	100/28[j]/10[k]	70[l]/14[j]/10[k]
n-Bu_4NI	98 (98)[g]	72 (86)[g]
n-Bu_4NI/iodine	94	85
Ph_3Sb	98 (68)[i]	79 (38)[i]
Ph_3Sb/iodine	98	71
n-Oct_3N	98	66
n-Oct_3N/iodine	96	67
Ph_3MeAsI	98	84
Ph_3MePBr	92	65
SnI_2	80	80
CuI	60	77
$HgCl_2$	46	56

[a]Reaction conditions: T (bath) = 200°C; t = 6 h; n-OctBr (12 g, 63 mmol); n-OctI (0.5 g, 2.1 mmol); tin powder (particle size < 71 μm, 2.5 g, 21.0 mmol). [b]Amounts used are *ca* 4 mol% based on tin used: iodine (0.1 g); magnesium (0.02 g); Me_3SI (0.17 g); Ph_3Sb (0.30 g); Ph_3MeAsI (0.38 g); Ph_3MePBr (0.30 g); n-Oct_3N (0.30 g); n-Bu_4NI (0.31 g); SnI_2 (0.16 g); CuI (0.13 g); $HgCl_2$ (0.11 g). [c]Estimated as n-Oct_2SnO) and based on the amount of tin reacted. [d]Estimated mono-octyltin content in n-Oct_2SnO is 12%. [e]For n-OctBr/Sn mol ratio 1.8. [f]For n-OctBr/Sn mol ratio 4.0. [g]In the absence of n-OctI. [h]Estimated mono-octyltin content in n-Oct_2SnO is 16%. [i]T (bath) = 160°C. [j]Using tin foil. [k]Using pelletized tin. [l]Estimated mono-octyltin content in n-Oct_2SnO is 13%.

In sharp contrast to the dibutyltin case, a high tin conversion (84%) was noted for the uncatalysed reaction, but the yield of n-Oct_2SnBr_2 formed was low (47%). The isolated n-Oct_2SnO contained 12% mono-octyltin as contaminant. In the presence of catalytic amounts of iodine or HMPA, a higher yield (*ca* 80%) of n-Oct_2SnBr_2 was obtained along with increased tin consumption. With magnesium, the yield of n-Oct_2SnBr_2 was moderate, but increased in the presence of iodine or aprotic solvents. Reasonably high yields of product and near-total

tin consumption were obtained using the onium salts, n-Bu_4NI, Me_3SI, Ph_3MeAsI and Ph_3MePBr, with the co-addition of iodine for n-Bu_4NI and SnI_2 for Me_3SI tending to enhance further the yields of n-Oct_2SnBr_2.

In contrast to the n-octylbromide case, the reaction with n-octyl chloride (n-OctCl) under similar conditions proceeded negligibly in the absence of catalyst (Table 4). As in the case of n-BuBr and n-OctBr reactions, HMPA again proved to be an effective catalyst, yielding 78% n-Oct_2SnCl_2. The use of HMPA together with iodine or inorganic iodine compounds (among other co-catalysts) in the presence of an organic medium such as alcohol, thioalcohol, ether, thioether or ester has been previously described in the patent literature[11] to yield mixtures of mono-, di- and tri-n-octyltin chlorides whilst favouring total tin conversion. Magnesium, either alone or in combination with iodine, was not as effective in the n-OctCl reaction as in the n-OctBr case, but the catalyst combination magnesium/HMPA considerably improved both tin consumption and the yield of n-Oct_2SnCl_2.

The use of Ph_3MeAsI resulted in very low tin conversion (14%), but the yield of n-Oct_2SnCl_2 formed was high (74%). However, the use of iodine as co-catalyst significantly increased the rate of tin conversion to 92%.

As in the n-OctBr reaction, the use of n-Bu_4NI was found to enhance tin consumption as well as formation of the n-Oct_2SnCl_2 product. The co-presence of iodine was not detrimental to the reaction but a higher tin consumption was achieved when the reaction time was extended to 24 h. Only moderate activity was shown by Me_3SI, which required an extended reaction time; the use of the high-pressure reactor (73% Sn conversion; yields 56% n-Oct_2SnCl_2, 23% n-$OctSnCl_3$) under conditions described previously did not significantly improve the catalytic performance. Improved reaction rates, however, were achieved when Me_3SI was used with iodine or tin(II) iodide (SnI_2). Although high tin conversion (88%) was observed with Ph_3Sb as catalyst, the yield of n-Oct_2SnCl_2 was low (21%). The results contrast with those of the n-OctBr case where relatively higher tin consumption and more favourable product yields were obtained. The use of iodine as co-catalyst again markedly improved the yield of n-Oct_2SnCl_2.

The efficacies of the two onium catalyst combinations, n-Bu_4NI/iodine and Me_3SI/SnI_2, are compared in Table 5. As indicated by the results, high tin consumptions and high yields of diorganotin products were achieved with long-chain alkyl halides using both catalyst systems. However, low yields and poor tin consumption characterized the reactions of cycloalkyl, phenyl and benzyl halides. In the case of isobutyl bromide (i-BuBr), it was found that the use of the high-pressure reactor allowed attainment of high

Table 4 Direct synthesis[a] of di(n-octyl)tin dichloride from n-OctCl and tin at atmospheric pressure in the presence of various catalysts

Catalyst[b]	Tin conversion (%)	n-Octyltin[c] (%)	
		Dioctyltin	Mono-octyltin
None	12	40	5
HMPA (1 cm^3)	76	78	6
Magnesium/iodine	44[d]	56[d]	19[d]
Magnesium/HMPA (1 cm^3)	84	81	8
Me_3SI	52[d]	68[d]	7[d]
Me_3SI/iodine	80	51	6
Me_3SI/SnI_2	72[d]	70[d]	12[d]
n-Oct_3N	48	33	2
n-Oct_3N/iodine	92[d]	63[d]	14[d]
n-Bu_4NI	72	78	6
n-Bu_4NI/iodine	68 (84)[d]	78 (82)[d]	2 (11)[d]
Ph_3Sb	88	21	5
Ph_3Sb/iodine	90[d]	63[d]	16[d]
Ph_3MeAsI	14	74	10
Ph_3MeAsI/iodine	92 (96)[d]	75 (71)[d]	1 (13)[d]

[a, b, c]See footnotes a, b, c of Table 3; n-OctCl, 9.5 g. [d]$t = 24$ h.

Table 5 Direct synthesis[a] of diorganotin dihalides: influence of the organic halide reactant

RX (g)	Tin conversion (%)	Diorganotin (%)
Catalyst system: Me_3SI (0.17 g)/SnI_2 (0.16 g)		
n-BuBr (8.2)	24 (24 h)	73 (24 h)
n-BuBr (32.8)	91[b]	80[b]
i-BuBr (8.2)	15 (24 h)	20 (24 h)
i-BuBr (32.8)	86[b]	74[b]
n-OctBr (12.0)	100	70
n-OctCl (9.5)	72 (24 h)	70 (24 h)
n-$C_{10}H_{21}$Br (13.1)	92	78
n-$C_{12}H_{25}$Br (14.8)	100	85
C_6H_5Br (10.0)	14 (24 h)	10 (24 h)
c-C_5H_9Br (9.5)	68 (24 h)	10 (24 h)
c-C_6H_{11}I (13.3)	65 (24 h)	30 (24 h)
$C_6H_5CH_2Cl$ (8.1)	73 (24 h)	48 (24 h)
Catalyst system: n-Bu_4NI (0.16 g)/I_2 (0.1 g)		
n-BuBr (8.2)	98 (24 h)	72 (24 h)
n-BuBr (32.8)	95[b]	81[b]
i-BuBr (8.2)	60 (24 h)	51 (24 h)
i-BuBr (32.8)	93[b]	83[b]
n-OctBr (12.0)	94	85
n-OctCl (9.5)	87	72
n-$C_{10}H_{21}$Br (13.1)	98	83
n-$C_{12}H_{25}$Br (14.8)	96	81
c-C_5H_9Br (9.5)	73 (24 h)	48 (24 h)

[a]Reaction conditions: T (bath) = 200°C; t = 6 h (unless otherwise indicated): tin (2.5 g), OctI (0.5 g), RX (as shown). [b]Using the high-pressure reactor at 180°C for 6 h; P_{final} 280 psi (1930 kPa). Amounts of tin, OctI and catalyst scaled proportionally to four-fold those indicated for atmospheric-pressure synthesis.

tin consumption and high product yields in the presence of these catalysts. At normal pressures, however, the tin consumption and yields were low compared with the n-BuBr case.

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