

ORGANOTIN COMPOUNDS

II. THE SYNTHESIS OF DIBUTYL- AND DIOCTYL TIN COMPOUNDS

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(Received December 14th, 1965)

INTRODUCTION

Dialkyltin halides are intermediates in the preparation of organotin stabilisers for polyvinyl chloride. The main industrial manufacturing method in use at present is to form crude tetraalkyltins from alkylmagnesium halides^{1,2} and stannic chloride and then redistribute³ the alkyl groups with more stannic chloride. This method is costly to operate on an industrial scale particularly for the higher alkyltin compounds which are formed in poor yield and of poor quality. The latter point is of great importance as the main outlet for the higher alkyltin compounds (*i.e.* di-*n*-octyltin compounds) is in non-toxic polyvinyl chloride applications because of their inherent low mammalian toxicity⁴. For this reason the formation of high purity products is essential.

In Part I⁵ of this series the possibility of synthesising di-*n*-butyltin diiodide directly from *n*-butyl iodide and tin was discussed. This work has been extended to the use of *n*-butyl iodide/bromide mixtures for *n*-butyltin compounds and *n*-octyl bromide for *n*-octyltin compounds. The results obtained form a satisfactory basis for the development of new industrial methods for the preparation of di-*n*-butyl and di-*n*-octyltin oxides.

EXPERIMENTAL

General procedure

The experiments carried out in these studies were of a standard type and the following description will serve as a typical example. Granulated tin (1.0 g-atom), alkyl halide (2.2 mole) and catalyst were heated under reflux (*n*-butyltins) or at 150–160° (*n*-octyltins) for a predetermined period of approximately 50 h in a nitrogen atmosphere. Unreacted tin was then filtered off, weighed and the filtrate stripped free of excess alkyl halide under reduced pressure. The residue was dissolved in ethanol (400 ml) which was added to a vigorously agitated solution of caustic soda (100 g) in water (400 ml). After being stirred for 1 h, the mixture was filtered, washed with ethanol, water, dried for 12 h at 80° and then weighed. Alternatively, the crude residue after stripping off the excess alkyl halide could be recrystallised from light petroleum.

DISCUSSION

In Part I of this series we had shown that mixtures of metals and oxygenated solvents were effective catalysts for promoting direct reaction between tin and *n*-butyl iodide to give di-*n*-butyltin diiodide. We had also shown lithium and ethoxyethanol to be particularly good examples of a suitable catalyst system and had suggested that the active catalyst was a solvated lithium iodide which was formed *in situ*.

An attempt (expt. 1) to use the lithium/ethoxyethanol combination to promote reaction between tin and *n*-butyl bromide met with failure although this could possibly be attributed to the low reaction temperature. The use of *n*-butyl bromide in the presence of a 10% molar excess of *n*-butyl iodide was far more successful and a series of experiments (2-7) was carried out to determine whether alteration of the lithium-to-ethoxyethanol ratio affected the yield. The results indicate that optimum yields are obtained around a 1:3 ratio and below a 1:2 ratio the yields fall dramatically (*cf.* Fig. 1). Based on this optimum ratio of 1:3 a series was carried out (8-11) in which the reactants were heated for different periods so as to obtain different percentage tin conversions. The results indicate that lower yields are obtained at lower conversions.

TABLE I

DI-*n*-BUTYL TIN COMPOUNDS BY CATALYSED REACTION OF TIN (1 g-atom) WITH *n*-BUTYL BROMIDE (2 mole)/*n*-BUTYL IODIDE MIXTURES

Expt. No.	Butyl iodide (mole)	Lithium (g-atom)	Ethoxy-ethanol (mole)	React. time (h)	Percent conversion	Yield ^a
1	—	0.05	0.25	15	0	0
2	0.2	0.05	0.30	50	88	63
3	0.2	0.05	0.25	50	79	63
4	0.2	0.05	0.20	52	84	63
5	0.2	0.05	0.15	52	85	70
6	0.2	0.05	0.10	50	75	62
7	0.2	0.05	0.05	50	2	0
8	0.2	0.05	0.15	20	11	0
9	0.2	0.05	0.15	28	37	45
10	0.2	0.05	0.15	32	70	52
11	0.2	0.05	0.15	52	85	70
12	0.2	0.25	0.075	25	11	49
13	0.2	0.25	0.075	44	41	64
14	0.2	0.25	0.075	68	75	63

^a Percent yield of oxide in tin.

This same trend is observed in the next three experiments (12-14) in which the lithium-to-tin ratio has been reduced to 50% although, perhaps surprisingly, the overall yields for a given conversion in these experiments are substantially higher than in expts. 8-11. This result suggests that the yield may be more related to the time of heating (Fig. 2) than to the conversion (*cf.* Fig. 3) as the results of all expts. 8-14 lie on one smooth curve when plotted using yield and time of heating as ordinates.

One difficulty in all the experimental work so far and later discussed is that the general method of preparation used was only designed to give results on the dialkyltin content of the initial reaction product by isolating this as the oxide. It is possible that in all cases, this reaction product contained a mixture of mono-, di- and trialkyltin

halides and it would have been preferable to establish the actual composition of the mixture. Unfortunately, however, although we investigated the possibility of using GLC for this purpose, at the time when the work was completed we were unsuccessful. The possibility of the existence of all three halides in the reaction mixture is supported to some extent by the higher yields of dialkyltin oxides obtained in the experiments having prolonged heating periods, for these conditions would favour redistribution of the alkyl groups to give predominantly dialkyltin halides.

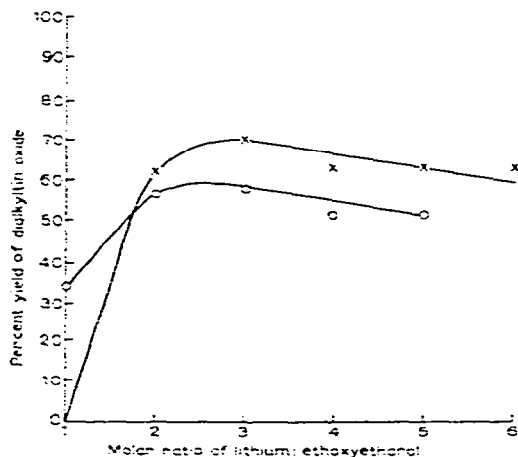


Fig. 1. The effect of alteration in the lithium-to-ethoxyethanol ratio on the yield of dialkyltin oxide. x dibutyltins, o dioctyltins.

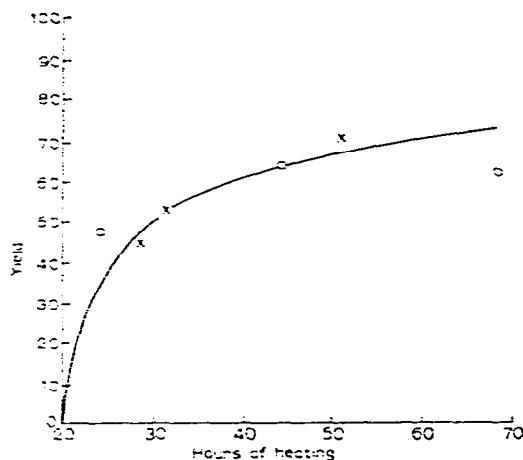


Fig. 2. Variation of yield of dibutyltin oxide with time of heating. x expts. 8-11, o expts. 12-14.

Lithium and ethoxyethanol were also examined as catalysts for the preparation of di-*n*-octyltin compounds. In the initial experiments a ratio of 1:5 was used and most experiments were carried out at 150°. The results showed that the combination of catalysts would not promote reaction with *n*-octyl chloride (expt. 15) but was successful with *n*-octyl bromide (expt. 16). Higher yields resulted in the *n*-octyl

bromide reaction when it was carried out in a nitrogen atmosphere (expt. 19) and, therefore, all further experiments were carried out under these conditions. Expts. 17 and 18 show that lithium and ethoxyethanol do not function as catalysts when used alone which is different from the results obtained in Part I⁵ where ethoxyethanol alone promoted reaction between tin and *n*-butyl iodide.

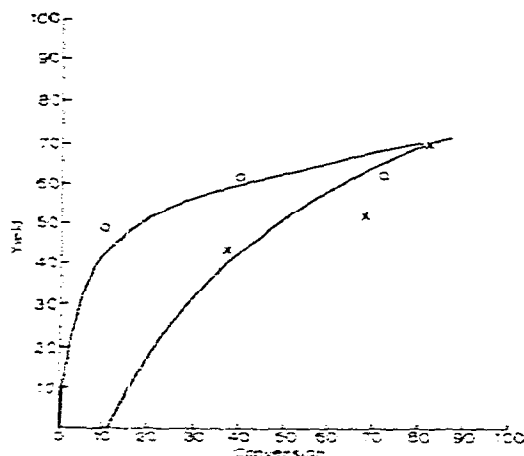


Fig. 3. Variation of yield of dibutyltin oxide with tin conversion. X expts. 8-11, O expts. 12-14.

A similar series of experiments (20-24) to those described earlier for *n*-butyltin compounds was carried out in order to determine whether an optimum ratio existed for the lithium and ethoxyethanol. The best results were obtained once again at ratios around 1:2 and 1:3. An isolated experiment (25) in which the lithium was reduced to 10% gave very poor yields. In a series of experiments (26-30) in which *n*-octyl iodide was introduced into the system at the expense of *n*-octyl bromide the results indicated that the yield and rate of reaction improved as the *n*-octyl iodide content increased.

TABLE 2

DI-*n*-OCTYL TIN COMPOUNDS BY CATALYSED REACTION OF TIN (1 MOLE) WITH OCTYL BROMIDE (2.2 MOLE)

Expt. No	Lithium (g-atom)	Ethoxy-ethanol (mole)	React. time (h)	React. temp.	Percent conversion	Yield ^a
15 ^{b,c}	0.056	0.28	65	160°	0	0
16 ^b	0.056	0.28	43	150°	73	56
17 ^b	—	0.28	45	150°	0	0
18 ^b	0.056	—	40	150°	0	0
19	0.056	0.28	40	150° ^c	73	64
20	0.2	0.2	40	150°	50	34
21	0.2	0.4	40	150°	85	56
22	0.2	0.6	40	150°	100	57
23	0.2	0.8	40	150°	100	50
24	0.2	1.0	40	150°	96	51
25	0.02	1.0	40	150°	34	5

^a Percent yield of oxide on tin. ^b Carried out in air, all others under nitrogen. ^c Octyl chloride used instead of octyl bromide.

TABLE 3

DI-*n*-OCTYL TIN COMPOUNDS BY CATALYSED REACTION OF TIN (1 mole) WITH *n*-OCTYL BROMIDE/*n*-OCTYL IODIDE MIXTURES

Lithium used 0.056 mole; ethoxyethanol used 0.28 mole; except expt. 34.

Expt. No.	Octyl iodide (mole)	Octyl bromide (mole)	React. time (h)	React. temp.	Percent conversion	Yield ^a
26	2.2	0	2.75	150°	76	56
27	0.4	1.8	8.0	150°	95	70
28	0.2	2.0	7.0	150°	81	67
29	0.1	2.1	23.0	150°	86	62
30	0	2.2	40.0	150°	73	63
31	0	3.0	20.0	150°	70	60
32	0.2	2.0	24.0	130°	69	71
33	0.2	2.0	24.0	120°	13	0
34	0.2	2.0	24.0	150°	0	0

^a Percent yield on tin consumed.

The only exception to this rule was when *n*-octyl iodide was used alone (expt. 26). This result might be attributable to the lower thermal stability of the di-*n*-octyltin diiodide. Expt. 31 showed that increase in the excess of *n*-octyl bromide in the reaction brought about a much faster reaction rate as would be expected. Investigations into conducting the reaction at lower temperatures (32-33) showed that for the *n*-octyl bromide/iodide system used little reaction took place at 120° although at 130° it proceeded smoothly. Use of this halide mixture at 150° in the absence of catalyst resulted in no reaction taking place (expt. 34).

The use of lithium bromide with ethoxyethanol and other solvents was also examined (expt. 35-38). Satisfactory reactions were obtained with ethoxyethanol and polyethylene glycol but no reaction took place with di-*n*-butyl ether and tetrahydrofuran although in the last instance the low reaction temperature was a probable contributory factor. These results confirm similar observations in Part I.

TABLE 4

DI-*n*-OCTYL TIN COMPOUNDS BY REACTION OF TIN (1 g-atom) AND OCTYL BROMIDE (2.2 mole) IN THE PRESENCE OF LITHIUM AND VARIOUS LIGANDS

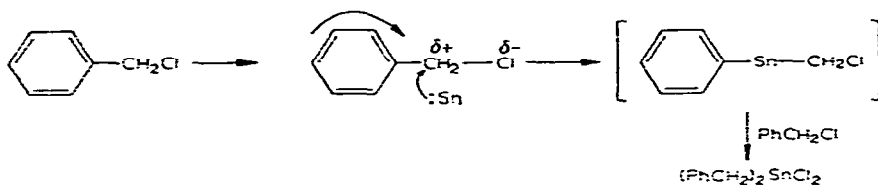
Expt. No.	Lithium bromide (mole)	Co-catalyst (mole)	React. time (h)	React. temp.	Percent conversion	Yield (%)
35	0.5	Ethoxyethanol, 1.5	16	150°	97	45
36	0.5	Polyethylene glycol 1000, 1.5 ^a	40	150°	82	52
37	0.5	Dibutyl ether, 1.5	40	150°	0	0
38	0.5	Tetrahydrofuran, 1.5	40	65°	0	0
39	0.056	Phenoxyethanol, 0.28	43	150°	49	57.5
40	0.056	Ethoxyethyl acetate, 0.28	40	150°	83	62
41	0.056	Ethoxymethyl methyl ketone, 0.28	40	150°	82	60
42	0.05	3-Ethoxy-propionitrile, 0.25	40	150°	77	68
43	0.056	<i>N,N</i> -dimethylformamide, 0.4	23	150°	87	32
44	0.056	Butyl acetate, 0.28	43	150°	35.4	39.5

^a The molar quantity was calculated on the unit $-(CH_2-CH_2-O)-$.

Six alternative solvents to ethoxyethanol were examined in expts. 39–44 and all promoted reaction between tin and *n*-octyl bromide in the presence of lithium. These results support previous statements that the active catalyst is a solvated lithium halide and the presence of a hydroxyl group in the solvent is not essential. Confirmation of this point may be obtained by comparing expt. 30 with 40, 41 and 42 when the results obtained are similar. Of particular interest is the good result obtained with 3-ethoxypropionitrile as a co-catalyst as this indicates that oxygen is not essential in the co-catalyst but more the presence of powerful electron donor groups. Comparison of expt. 30 with 44 suggests that the presence of two electron donor groups in the same molecule are an advantage. Similar comparison with 39 indicates that the electron availability of the group is an important factor governing the reaction as with phenoxyethanol the ether linkage will be deactivated by the neighbouring phenyl group. Based on these and previously reported observations it is of interest to postulate a possible mechanism for this reaction.

The only halogen compounds which have previously been reported as reacting with tin under mild conditions in the absence of catalysts are benzyl^{6,7} and allyl^{8,9} chloride. It has been suggested⁶ that reaction takes place by a free-radical mechanism as nitrobenzene inhibits reaction. It has also been shown⁶, however, that phenolic compounds do not inhibit the reaction between benzyl chloride and tin and in our hands similar use of phenols failed to inhibit a catalysed reaction between *n*-octyl bromide and tin.

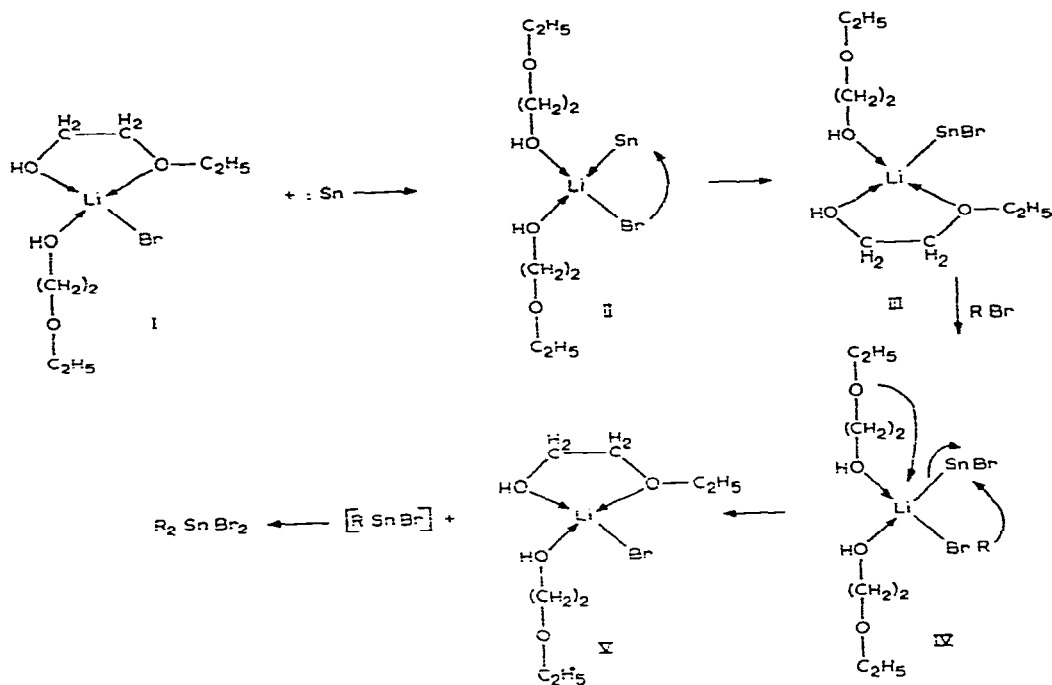
On this evidence we feel that doubt must be cast on the radical mechanism proposed and it is more likely that reaction takes place by a simple ionic mechanism. For benzyl and allyl halides such a reaction would be greatly facilitated by increased polarity of the carbon halogen bond as a result of the electron-donating properties of the neighbouring group. This property would allow attack of a tin atom on the carbon so that reaction could proceed by the mechanism shown below for benzyl chloride.



In the case of simple alkyl halides the carbon-halogen bond is not sufficiently polar to permit ready reaction and, therefore, catalysts for the reaction must either increase the polarity of this bond or modify the electron donor properties of the tin atom. We believe that to some extent both of these properties are affected by our catalysts.

Our results in Parts I and II of this series indicate the following points. (1) Active catalysts are formed from metal halides which are present as complexes with suitable ligands. (2) Either component of the catalyst is ineffective when used alone. (3) The most suitable ligands contain two chelating groups preferably of different donor ability. (4) With ethoxyethanol as the ligand, at least two moles are required per mole of lithium halide. (5) The effectiveness of the metal halides increases as its tendency towards complex formation improves.

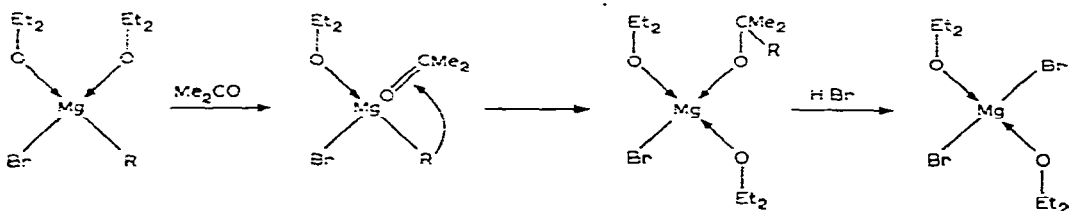
These several conditions suggest that the catalyst formed between lithium bromide and ethoxyethanol is as shown below (I) and the reaction proceeds as illustrated.



The intermediate $[\text{RSnBr}]$ can undergo a similar series of reactions replacing the tin atom at Stage (I).

This suggested mechanism meets all the conditions outlined earlier. In particular it meets the requirements of the minimum metal-to-ligand ratio and provides a reason why the chelating groups in the ligand should be of different chelating power with one of them being fairly weak so as to allow its replacement by a tin atom. It also meets the condition that lithium halides are the best catalysts and increase in order of effectiveness from lithium chloride through bromide to iodide as the energy involved on rupturing the lithium halogen bond at Stage (II) will decrease in the same order and as a general rule this energy is lower for lithium halogen bonds in this type of complex than for any other metal halogen bond¹⁰.

The mechanism suggested above may be likened to the established mechanism for alkylations using Grignard reagents¹¹.



ACKNOWLEDGEMENT

The authors express their thanks to the Directors of Pure Chemicals Limited for permission to publish this paper.

SUMMARY

Investigations were made into the catalysed reaction of *n*-butyl and *n*-octyl halides with tin so as to form dialkyltin dihalides which could be converted into their respective oxides. Lithium halides and a variety of ligands containing two chelating groups were demonstrated to be powerful catalysts: the most effective ratio being about 1:2. A possible mechanism for the reaction is discussed.

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