ORGANOTIN COMPOUNDS

I. THE SYNTHESIS OF DIBUTYLTIN DIHALIDES

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INTRODUCTION

Dibutyltin and dioctyltin dihalides are essential intermediates in the synthesis of organotin stabilisers for polyvinyl chloride and, therefore, a great deal of attention has been given in recent years to finding simpler and cheaper methods for their preparation. Until recently, the established industrial method of preparation was to form tetraalkyltins from alkylmagnesium halides[1,2] and stannic chloride and then redistribute[3] the alkyl groups with more stannic chloride. A more recent development has been to alkylate stannic chloride with aluminium alkyls[4] to give tetraalkyltin or even dialkyltin dihalides directly. Both methods suffer the disadvantage that they involve use of molar quantities of a second metal.

For many years, attempts have been made to alkylate tin directly with both low[5–7] or higher[8] alkyl iodides but with poor results. The first modest success was obtained by Irmscher *et al.*[9] who brought about reaction between methyl bromide and powdered tin by heating them together at 100° and 19 atmospheres in the presence of traces of alcohols. Matsuda and his co-workers[10–13] extended this work to cover reaction between tin and a range of alkyl iodides from methyl to hexyl. They concluded that the reaction was catalysed by the presence of certain metals, particularly magnesium and zinc, together with alcohols, such as butanol or cyclohexanol, or with tetrahydrofuran. They suggested that a Grignard reagent was first formed and then converted into an alkoxymagnesium halide which was the effective catalyst. The mechanism of the catalysis was not defined.

Because of the successful results reported by Matsuda, we have studied the direct reaction between *n*-butyl iodide and tin systematically. Experiments were carried out to reveal the relative importance of the different components of the catalyst system in the hope that a clearer picture of the mechanism of the reaction might be obtained. Although this hope was not fully realised, we did find several new catalysts which were very effective in promoting reaction. It is possible that the direct reaction using such catalysts could provide a new industrial method for making dialkyltin compounds.

EXPERIMENTAL

Reaction of tin and n-butyl iodide catalysed by a metal and n-butanol

A series of experiments was carried out in which *n*-butanol was used as the

TABLE 1

REACTIONS CATALYZED BY A METAL AND *n*-BUTANOL

Metal	*Catalyst metal (g-atoms)*	*n-Butanol (moles)*	*Reaction time (hours)*	*Maximum reaction temp. (°C)*	*Percentage conversion*	*Percentage yield of Bu_2SnI_2 on tin consumed*
Magnesium	0.052	0.264	4.5	150	68%	88.5%
Lithium	0.086	0.242	4.5	164	100%	90.5%
Mercury	0.03	0.256	8.0	132	48%	77.1%
Sodium	0.049	0.272	11.5	136	63%	73.2%
Zinc	0.043	0.256	5.0	135	30%	87.0%
Lithium	0.056	—	5.0	120	9%	—
—	—	0.25	8.5	134	36%	79.0%

alcohol component of the catalyst system while the metal component was varied in order to demonstrate its importance. The results are shown in Table 1. The reaction conditions were as follows:

n-Butyl iodide (2.2 moles) and *n*-butanol (0.24 to 0.26 moles) were mixed together, a trace of the metal under investigation was added, followed by granulated tin (1 g-atom). The resulting mixture was heated under reflux for several hours during which time the temperature of the reaction mixture rose from approximately 120° to a maximum of 164°. The mixture was filtered to remove unreacted tin and the filtrate distilled under reduced pressure to give dibutyltin diiodide, b.p. 134–138°/1 mm, n_D^{20} 1.6055. (Found: Sn, 24.1; I, 52.5. $C_8H_{18}I_2Sn$ calcd.: Sn, 24.4; I, 52.7%.)

Attempted reaction of tin and n-butyl bromide catalysed by lithium and n-butanol

n-Butyl bromide (2.2 moles) and *n*-butanol (0.272 moles) were mixed together, lithium (0.056 g-atom) and granulated tin (1 g-atom) added and the mixture heated under reflux for 15 hours. No reaction took place.

Reaction between tin and n-butyl iodide catalysed by a metal and ethoxyethanol

In order to demonstrate the importance of the alcohol component of the catalyst system a second series of experiments was carried out in which ethoxyethanol was substituted for butanol. Several other metals were also examined in conjunction with this alcohol. The reaction conditions used were identical to those in the first series and the results are shown in Table 2.

TABLE 2

REACTIONS CATALYZED BY A METAL AND ETHOXYETHANOL

Metal	*Catalyst metal (g-atoms)*	*2-Ethoxyethanol (moles)*	*Reaction time (hours)*	*Percentage conversion*	*Percentage yield of Bu_2SnI_2 on tin consumed*
—	—	0.28	6.0	89.0%	72.0%
Lithium	0.056	0.28	2.25	76.4%	93.0%
Beryllium	0.04	0.28	5.0	79.4%	84.0%
Copper	0.121	0.28	4.5	83.2%	75.0% (oxide)
Aluminium	0.056	0.28	5.0	70.2%	56.5%

In one instance the resulting dibutyltin diiodide was not collected by distillation but was converted into the oxide by treatment with aqueous alcoholic caustic soda as follows. The residue of dibutyltin diiodide remaining after removal of excess tin and *n*-butyl iodide was dissolved in ethanol (400 ml), and added to a stirred solution of sodium hydroxide (100 g) in water (400 ml). After stirring for 1 hour the white precipitate formed was filtered off, washed with ethanol and water then dried at 80°.

Attempted reaction of tin and n-butyl iodide in presence of dioxane

Granulated tin (0.25 g-atom), *n*-butyl iodide (0.55 mole) and 1,4-dioxane (0.1 mole) were refluxed together for eight hours. No reaction took place and the reactants were recovered quantitatively.

Reaction of tin and n-butyl iodide catalysed by lithium and 2,5-hexanedione

In order to establish whether the presence of an alcohol was necessary for reaction, the following experiment was carried out.

Lithium (0.1 g) was added to a mixture of *n*-butyl iodide (101 g, 0.55 mol) and 2,5-hexanedione (10 g). Granulated tin (29.7 g, 0.25 g-atom) was then added and the mixture heated under reflux for 25 hours. The unreacted tin (4.5 g, 15.1 %) was removed by filtration and the filtrate stripped of excess *n*-butyl iodide. The residue was dissolved in ethanol (100 ml) and the solution added to a stirred solution of caustic soda (25 g) in water (100 ml). The resulting precipitate of dibutyltin oxide was collected by filtration, washed first with ethanol, then water and dried at 80°. Yield 68 g (68 % on tin).

Reaction between tin and butyl iodide catalysed by metal halides and oxygenated solvents

A series of experiments was carried out in order to determine whether metal halides in the presence of either ethoxyethanol or 2,5-hexanedione function as catalysts. The reaction conditions were identical to those described in the previous series except that metal halide was used instead of metal. The reaction product was collected as either the diiodide or the oxide by the methods previously described. The results are shown in Table 3.

Butylmagnesium iodide was made by heating a mixture of *n*-butyl iodide (3.6 g), magnesium (0.48 g) and tetrahydronaphthalene (10 ml) until reaction was complete.

TABLE 3

REACTIONS CATALYZED BY A METAL HALIDE AND OXYGENATED SOLVENTS

Catalyst		*2-Ethoxyethanol (moles)*	*2,5-Hexanedione (moles)*	*Reaction time (hours)*	*Percentage conversion*	*Percentage yield*
Metal halide	*Moles*					
Lithium bromide	0.056	—	—	22	2.0	0
Lithium bromide	0.056	0.28	—	3.25	80.9	68.0 (oxide)
Lithium bromide	0.056	—	0.28	6.25	83.0	64.0 (oxide)
Ferric bromide	0.04	0.28	—	4.0	89.9	85.0
Butylmagnesium iodide	0.08	—	—	6.0	0	0
Butylmagnesium iodide	0.02	0.28	—	3.75	75.0	75.2 (oxide)

The whole of this solution was added when used alone, but only 25 % of it was added when ethoxyethanol was used as a catalyst.

DISCUSSION

Several interesting features emerge from the results of these experiments. One important point established is that variation of either of the components in the catalyst system can affect the rate of reaction between tin and *n*-butyl iodide. The results in Table 1 demonstrate that metals alone will not promote reaction whereas *n*-butanol alone will, albeit poorly. It is considered unlikely that when using alcohols alone the trace metal impurities in the tin function as co-catalysts.

Two component catalyst systems are most satisfactory, and in these cases, the rate of reaction depends markedly on which metal is used as a co-catalyst (*cf.* Tables 1 and 2). Of the metals examined lithium was the best, and is far better than the magnesium and zinc suggested by Matsuda. The lithium/*n*-butanol system does not promote reaction between *n*-butyl bromide and tin, although this might be because of the lower reaction temperature used.

When ethoxyethanol is substituted for *n*-butanol in the catalyst system, the reaction rates are increased considerably (Table 2) which suggests that the ether linkage plays a part in the reaction. However, dioxane failed to promote reaction which means that the presence of an ether linkage alone is not sufficient for promotion.

Ethoxyethanol was a very active catalyst even when used on its own, being far better than *n*-butanol in this respect. The addition of lithium brought about a noticeable increase in activity but several other metals had little effect contrary to the results obtained with butanol (*cf.* Tables 1 and 2). The superiority of ethoxyethanol as a catalyst is similar to the results obtained in the alkylation of benzene with alkyl chlorides using magnesium with *n*-butanol or ethoxyethanol as co-catalyst[14].

Comparison of the results obtained for the lithium/butanol with those for the lithium/ethoxyethanol system suggests that the catalyst is a solvated salt of lithium in which the activity is dependent on the electron donor properties of the solvent used. With *n*-butanol and ethoxyethanol, the solvated salt is possibly a lithium alkoxide. The presence of an alkoxide is not necessary, however, as is demonstrated by the fact that lithium and 2,5-hexanedione promotes reaction, though much less effectively than the former systems. An interesting point with the lithium/2,5-hexanedione system is that there is a marked induction period before the reaction starts whereas with the hydroxylic solvents there is only a short induction period (*cf.* Fig. 1). From this evidence, it appears most likely that the catalyst is a solvated lithium iodide. This would be formed much more readily in the presence of alcohols in which the lithium dissolves than in the system using 2,5-hexanedione in which the lithium would be present as a suspension.

Confirmation of this suggestion was provided by the last series of experiments (*cf.* Table 3) in which metal halides and Grignard compounds were examined as catalysts either alone or in the presence of oxygenated solvents. When used alone neither the metal halides nor the unsolvated Grignard compound catalysed reaction, but in the presence of oxygenated solvent they exhibited powerful catalytic activity; in the case of the Grignard compound, the active catalyst could be either the solvated Grignard compound itself or solvated magnesium halide. The lithium bromide/2,5-

hexanedione system effected reaction with no induction period (*cf.* Fig. 1) which is in agreement with the suggestion that the induction period for the lithium/2,5-hexanedione system involved formation of lithium iodide. Comparison of the reactions using lithium bromide and ethoxyethanol with those using lithium bromide and 2,5-hexanedione shows that the former system is much more effective thereby confirming the previous observation that the catalytic activity is influenced by the electron availability of the chelating groups in the solvent.

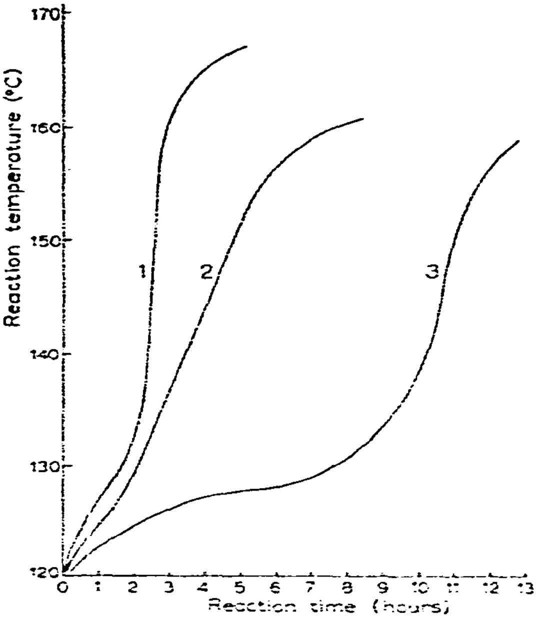

Fig. 1. Reaction of butyl iodide and tin in the presence of: (1), lithium/butanol; (2), lithium bromide/2,5-hexanedione; (3), lithium/2,5-hexanedione.

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SUMMARY

The direct reaction between butyl iodide and tin to give dibutyltin diiodide was investigated. It was found that extremely active catalysts for this reaction are provided by combinations of metal halides and oxygenated solvents. Either component alone has little or no catalytic effect but combination gives high yields of dibutyltin diiodide. The metal halide can be added as such, or alternatively a metal or salt which can readily be converted to a halide under the conditions of reaction may be used. Of the metals investigated, lithium appears to be the most active. The results suggest that all oxygen-containing solvents are effective co-catalysts with the metal halides, and that the oxygen-containing co-catalysts may have greater activity if they contain more than one oxygen atom in the molecule.

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