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REACTION OF ALKYL HALIDES WITH DIALKYLTINS

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A crystalline dialkyltin, $(R_2Sn)_m$, is a polymeric substance containing a several-membered ring of tin–tin bonds[1-3]. In order to throw light on the mechanism of the direct reaction of alkyl halides with metallic tin, we have studied the reactions of the Sn–Sn bonds with alkyl halides. The reaction of one dialkyltin with an alkyl halide was investigated by Pfeiffer[4], who treated diethyltin with ethyl iodide to obtain triethyltin iodide.

The reaction of dialkyltins, $(R_2Sn)_m$, with alkyl halide, R'X, has been found to give two kinds of trialkyltin halides, $R_2R'SnX$ and R_3SnX. Diethyltin and an alkyl iodide at 140° gave the alkyldiethyltin iodide in about 50% yield (Table 1), and no triethyltin iodide. This reaction may be a useful method for preparing trialkyltin halides with two different kinds of alkyl groups; such compounds have been prepared hitherto by the cleavage of mixed tetraalkyltin compounds with halogen[5-8] or with hydrochloric acid[9]. When alkyl bromides were used in this reaction, both alkyldiethyltin and triethyltin bromides were produced (Table 2).

TABLE 1

REACTION OF DIALKYLTIN WITH ALKYL IODIDE[a]

Dialkyltin $(R_2Sn)_m$	*Alkyl iodide*[b] *R'X*	*Yield*[c] *of* $R_2R'SnI$ (%)	*B.p.* (°C/mm)
Diethyltin	Methyl iodide	49.3	90–92/35
Diethyltin	Ethyl iodide	53.6	108–110/18
Diethyltin	n-Propyl iodide	39.4	85–86/5
Diethyltin	n-Butyl iodide	41.2	100–102/5
Di-n-propyltin	Methyl iodide	63.0	85–87/4
Di-n-propyltin	Ethyl iodide	35.8	105–110/6
Di-n-propyltin	n-Butyl iodide	47.5	105–107/3
Di-n-butyltin	Methyl iodide	58.0	93–96/2.5
Di-n-butyltin	Ethyl iodide	56.0	102–104/1.5
Di-n-butyltin	n-Propyl iodide	64.0	110–115/0.8
Di-n-butyltin	n-Butyl iodide	65.0	118–120/0.85
Di-n-butyltin	Methyl iodide[d]	74.0	

[a] Reactions were carried out at 140° for 3 h. [b] Four molar proportions of alkyl iodide were used with dialkyltin prepared from one molar proportion of dialkyltin dihydride. [c] Yields are based on the content of the dialkyltin. [d] This reaction was carried out at 140° for 15 h.

As a representative of alkyl chlorides, n-butyl chloride was used, because of

TABLE 2

REACTION OF DIALKYLTIN WITH ALKYL BROMIDE[a]

Dialkyltin *$(R_2Sn)_m$*	*Alkyl bromide*[b] *$(R'X)$*	*Product yield*[c] (%)			
		R_3SnBr	*$R_2R'SnBr$*	*RR'_2SnBr*	*R'_3SnBr*
Diethyltin	n-Propyl bromide	14.1	12.2	1.2	0.0
Diethyltin	n-Butyl bromide	8.4	27.5	1.2	0.0
Di-n-propyltin	n-Butyl bromide	4.0	24.6	0.9	0.3
Di-n-butyltin	Ethyl bromide	9.5	26.2	0.7	0.3
Di-n-butyltin	n-Propyl bromide	9.0	23.2	0.5	0.9
Di-n-butyltin	n-Butyl bromide	28.1			
Di-n-butyltin	n-Butyl bromide[d]	70.0			

For footnotes see Table 1.

the volatility of the lower homologs. This gave no n-butyldiethyltin chloride, but formed triethyltin chloride in a poor yield even at higher temperature (160°). In the presence of triethylamine or quaternary ammonium iodide, both of which are effective catalysts for the direct reaction [10,11], the reaction of diethyltin and n-butyl chloride was found to give n-butyldiethyltin chloride and triethyltin chloride together with many other minor products (Table 3) as shown in eqn. 1.

$$(R_2Sn)_m + BuCl \xrightarrow[160°,\ 15\ h]{\text{Catalyst}} R_4Sn + R_3BuSn + R_2Bu_2Sn + R_3SnCl + R_2BuSnCl + RBu_2SnCl + Bu_3SnCl \quad (1)$$

Analogous results were obtained with di-n-propyltin and di-n-butyltin (Tables 1–3).

The mixed trialkyltin halide with two different kinds of alkyl groups, $R_2R'SnX$, are thought to be produced via an addition reaction involving dismemberment of the ring.

The simple trialkyltin halide, R_3SnX, must be formed via the disproportionation reaction, since all three alkyl groups in the compound originated from the dialkyltin and not from the alkyl halide. There are two possible pathways, A and B, both of which were shown to exist.

$$(R_2Sn)_m + R'X \rightarrow R_2SnX_2 \xrightarrow{(R_2Sn)_m} R_3SnX + Sn \quad (A)$$

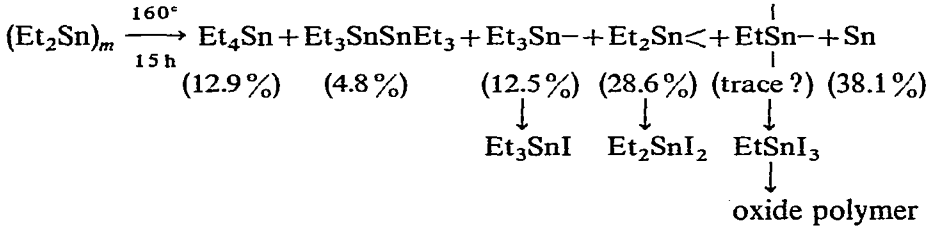
$$(R_2Sn)_m \rightarrow [R_3Sn-] \xrightarrow{R'X} R_3SnX \quad (B)$$

In sequence A, the chain of dialkyltin is broken and a halogen atom is abstracted from the alkyl halide to give dialkyltin dihalide, which reacts with dialkyltin to yield trialkyltin halide and metallic tin. This was confirmed by heating a mixture of diethyltin dichloride with di-n-butyltin, which gave di-n-butylethyltin chloride, n-butyldiethyltin chloride, tri-n-butyltin chloride and triethyltin chloride, as well as metallic tin (eqn. 2). All the diethyltin dichloride was consumed.

$$\begin{array}{lllllll} (Bu_2Sn)_m + Et_2SnCl_2 \xrightarrow[5\ h]{160°} & Bu_2EtSnCl + & BuEt_2SnCl + & Bu_3SnCl + & Et_3SnCl + & Sn & (2) \\ 2 : 1 & 12.4\% & 7.3\% & 5.0\% & 1.3\% & 48\% & \end{array}$$

When di-n-butyltin dichloride was used in place of diethyltin dichloride in this reaction, only tri-n-butyltin chloride and metallic tin were produced.

In sequence B, the ring form of dialkyltin is converted into some open-chain compound, the end-group of which is a trialkyltin fragment $[R_3Sn-]$[1]. This fragment, when it breaks away, abstracts a halogen atom from the alkyl halide to give trialkyltin halide. It is known that thermal decomposition of dialkyltin yields tetraalkyltin and metallic tin[12-14]. The detailed investigation of the pyrolysis of diethyltin gave, in addition to tetraethyltin and metallic tin, hexaethylditin (the lowest homolog of the open-chain compound) and some open-chain compounds. On treatment of these open-chain compounds with iodine, which breaks the tin–tin bonds to yield the corresponding iodides[1,3], there were obtained triethyltin iodide (from the end-groups) and diethyltin diiodide. Formation of ethyltin triiodide (as indicated by its conversion into its oxide-polymer hydrolyses products), which would result in a reaction at a chain-branching position, was negligible.



$$\begin{array}{lcccccc}
(Et_2Sn)_m \xrightarrow[15\,h]{160^\circ} & Et_4Sn + & Et_3SnSnEt_3 + & Et_3Sn{-} + & Et_2Sn{<} + & \overset{|}{\underset{|}{EtSn}}{-} + & Sn \\
& (12.9\%) & (4.8\%) & (12.5\%) & (28.6\%) & (\text{trace ?}) & (38.1\%) \\
 & & & \downarrow & \downarrow & \downarrow & \\
 & & & Et_3SnI & Et_2SnI_2 & EtSnI_3 & \\
 & & & & & \downarrow & \\
 & & & & & \text{oxide polymer} &
\end{array} \qquad (3)$$

The pyrolysis of di-n-butyltin, which decomposes less readily than diethyltin, gave tri-n-butyltin, di-n-butyltin and mono-n-butyltin fragments, identified as the corresponding iodides, together with traces of tetra-n-butyltin and metallic tin.

Triethyltin chloride may be produced from diethyltin via both the sequences A and B, and it is not clear which sequence predominates. Tri-n-butyltin chloride must be formed via sequence A predominantly, since the decomposition rate of di-n-butyltin into tri-n-butyltin fragment is comparatively slow.

Some of the minor products shown in Table 3 are considered to be formed according to eqn. 2. Alkyl halide, R'X, may react with metallic tin produced by the disproportionation and give dialkyltin dihalide, R'_2SnX_2[11], which, in turn, could react with dialkyltin, $(R_2Sn)_m$, to give the mixed and simple trialkyltin compounds.

EXPERIMENTAL

Analytical procedure

Determination and separation of all distillable products were carried out by gas chromatography with helium gas flowing at 50 ml/min through a stainless steel column of 3 m × 4 mm o.d. packed with "Polyethylene Glycol-6000" at 200°. Retention times of the products are summarized in Table 4. The main products of each experiment were isolated analytically pure by preparative gas chromatography using a stainless steel column of 2 m × 6 mm o.d. packed with "Thermaol-3" (Simazu Co. Ltd.) at 170°. Elemental analyses and refractive indices are shown in Table 4. Since di-n-butylalkyltin iodides tend to decompose during the gas-chromatographic analysis, they were converted into the corresponding chlorides by treatment with aqueous potassium hydroxide followed by hydrochloric acid.

Reaction of dialkyltin with alkyl halide

Dialkyltin was prepared from dialkyltin dihydride by the method of Neumann,

TABLE 3

REACTION OF DIALKYLTIN WITH n-BUTYL CHLORIDE[a]

Dialkyltin $(R_2Sn)_m$	*Reagent added*[b]	*Product yield*[c] (%)						
		R_4Sn	R_3BuSn	R_2Bu_2Sn	R_3SnCl	$R_2BuSnCl$	RBu_2SnCl	Bu_3SnCl
Diethyltin	None	0	0	0	17.4	0	0	0
Diethyltin	Triethylamine	7.3	6.5	2.0	17.9	13.7	2.8	0.4
Diethyltin	Tetraethylammonium iodide[d]	1.9	2.4	0.9	25.1	31.0	6.3	2.8
Di-n-propyltin	None	0	0	0	12.7	0	0	0
Di-n-propyltin	Triethylamine	3.5	2.3	0.8	31.5	26.3	4.1	1.3
Di-n-propyltin	Tetraethylammonium iodide[d]	0	0	0	19.8	32.8	4.9	2.8
Di-n-propyltin	Tetraethylammonium bromide[d]	0.5	1.0	0.5	23.8	29.6	7.0	2.5
Di-n-propyltin	Tetraethylammonium chloride[e]	0.2	0.2	0	30.4	15.3	1.7	0.4
Di-n-butyltin	None	0	0	0	3.5	0	0	0
Di-n-butyltin	Triethylamine	4.5	0	0	59.7	0	0	0

[a] All reactions were carried out with n-butyl chloride and dialkyltin at 160° for 15 h. Four molar proportions of n-butyl chloride were used with dialkyltin prepared from one molar proportion of dialkyltin dihydride. [b] Ten mole % of n-butyl chloride. [c] Yields are based on the tin content of dialkyltin. [d] Prepared according to Vernon and Sheard[15]. [e] Prepared by the method of Phillips and Baltzly[16].

TABLE 4

ANALYSES AND PROPERTIES OF TRIALKYLATED TIN COMPOUNDS

Compounds	*Refractive index* (n_D^{20})	*Retention time* (*min*)[a]	*C* (%)		*H* (%)	
			Found	*Calcd.*	*Found*	*Calcd.*
Et_2MeSnI	1.5607	3.8	19.01	18.84	4.38	4.11
Et_3SnI	1.5590	4.5				
Et_2PrSnI	1.5470	6.9	23.99	24.23	4.90	4.94
Pr_2MeSnI	1.5468	6.9	24.50	24.23	5.15	4.94
Et_2BuSnI	1.5411	10.2	26.70	26.63	5.55	5.30
$EtPr_2SnI$	1.5419	10.2	26.80	26.63	5.56	5.30
Pr_2BuSnI	1.5309	13.5	30.80	30.89	5.80	5.96
Et_3SnBr	1.5240	3.8				
$Et_2PrSnBr$	1.5182	4.7	28.32	28.04	5.74	5.72
$Et_2BuSnBr$	1.5150	5.8	30.60	30.61	6.19	6.10
$EtBu_2SnBr$	1.5103	8.2	35.10	35.13	6.70	6.78
$Pr_2BuSnBr$	1.5092	8.2	34.89	35.13	7.06	6.78
$PrBu_2SnBr$	1.5058	9.4	36.95	37.11	7.00	7.07
Et_3SnCl	1.5055	3.5				
$Et_2BuSnCl$	1.4998	5.3	35.81	35.66	7.13	7.10
$EtBu_2SnCl$	1.4940	8.0	40.45	40.39	7.95	7.79
$Pr_2BuSnCl$	1.4938	8.0	40.30	40.39	8.00	7.79
$PrBu_2SnCl$	1.4912	10.1	42.49	42.41	8.15	8.09

[a] Conditions of gas chromatography are described in the text.

Pedain and Sommer[3]. In all experiments four molar proportions of alkyl halide were used with dialkyltin prepared from one molar proportion of dialkyltin dihydride.

In a typical procedure, a mixture of 4.38 g of di-n-butyltin and 10.6 g of ethyl iodide was heated in a sealed glass bottle at 140° for 3 h. The product was distilled *in vacuo* to give 4.10 g (56.0%) of pure di-n-butylethyltin iodide, b.p. 102–104°/1.5 mm, n_D^{20} 1.5431, which was identified as the corresponding chloride by gas chromatography, elemental analysis and infrared spectrum. When the distillation residue (1.4 g) was treated successively with iodine, aqueous sodium hydroxide and hydrochloric acid, 1.8 g of di-n-butyltin dichloride was obtained, but no tri-n-butyltin chloride.

In the case of n-butyl chloride, the reactions were carried out at 160° for 15 h. The experimental results are summarized in Table 1–3.

Reaction of diethyltin dichloride with di-n-butyltin

A mixture of 2.50 g (0.010 mole) of diethyltin dichloride, 4.75 g di-n-butyltin, and 0.80 g (0.0080 mole) of triethylamine was heated in a sealed glass bottle at 160° for 15 h. The reaction mixture was dissolved in 100 ml of tetrahydrofuran, and 1.72 g (48%) of metallic tin was separated by filtration. The filtrate was distilled *in vacuo* to give 2.41 g of liquid which included 1.14 g (12.4%) of di-n-butylethyltin chloride, 0.60 g (7.3%) of n-butyldiethyltin chloride, 0.50 g (5.0%) of tri-n-butyltin chloride, 0.094 g (1.3%) of triethyltin chloride and traces of n-butyltriethyltin and di-n-butyldiethyltin (eqn. 2).

Reaction of di-n-butyltin dichloride with di-n-butyltin

A mixture of 3.03 g (0.010 mole) of di-n-butyltin dichloride, 4.70 g of di-n-butyltin and 0.80 g (0.0080 mole) of triethylamine was heated in a sealed glass bottle at 160° for 15 h. The product dissolved in 100 ml of tetrahydrofuran was filtered to remove 1.53 g (43 %) of metallic tin. The filtrate was distilled *in vacuo* to give 2.90 g (29.6 %) of pure tri-n-butyltin chloride.

Thermal decomposition of diethyltin

A mixture of diethyltin (2.62 g) and triethylamine (0.60 g) was heated in a sealed glass bottle at 160° for 15 h. The product was dissolved in tetrahydrofuran and 0.61 g (38.1 %) of metallic tin was separated by filtration. The filtrate was distilled *in vacuo* to give 0.45 g (12.9 %) of tetraethyltin, 0.29 g (4.8 %) of hexaethylditin and 1.15 g of distillation residue. To the residue dissolved in tetrahydrofuran was added tetrahydrofuran solution of iodine until no more discoloration of iodine occurred. Tetrahydrofuran was distilled off and the residue was dissolved in ether. The ethereal layer was shaken with water to remove the soluble monoethyltin triiodide. When aqueous ammonia was added to the aqueous layer to convert monoethyltin triiodide into the corresponding oxide, which is insoluble in water, a trace of white precipitate was observed. The ethereal layer was concentrated and the residue was distilled *in vacuo* to give 3.30 g of a pale-yellowish liquid distillate containing crystals, b.p. 110–117°/13 mm, including 0.62 g (12.5 %) of triethyltin iodide and 2.68 g (28.6 %) of diethyltin diiodide.

Thermal decomposition of di-n-butyltin

Di-n-butyltin (3.42 g) was heated at 160° for 15 h in a similar way to give 0.008 g (0.2 %) of tetra-n-butyltin, trace of metallic tin, 0.40 g (6.6 %) of tri-n-butyltin iodide, 0.14 g (4.5 %) of mono-n-butyltin oxide and 6.10 g (85.6 %) of di-n-butyltin diiodide. These were determined by the method used for the diethyltin decomposition.

SUMMARY

Treatment of a dialkyltin, $(R_2Sn)_m$, with an alkyl halide, R′X, gives the halides $R_2R'SnX$ and R_3SnX. Alkyl iodides give only $R_2R'SnI$ compounds, alkyl bromides give both $R_2R'SnBr$ and R_3SnBr compounds, while alkyl chlorides give only R_3SnCl compounds. In the presence of amine or quaternary ammonium halide, however, alkyl chlorides give a mixture of $R_2R'SnCl$ and R_3SnCl compounds. The routes by which R_3SnX products are formed have been established.

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