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Abstract

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DIALKYL TIN*

Whereas in the aromatic series compounds of the type Ar_2Sn have been rather well studied, dialkyl derivatives of tin have scarcely been characterized. The reason for this is that, for this type of compound, no acceptable method of synthesis has been developed that would make it possible to obtain them in sufficient quantity and with complete analysis for all the elements entering into their composition. Hence the contradictions in descriptions even of appearance, physical state, and other properties.

Indeed, Levin (^{1}) was the first to obtain diethyltin, by the action of ethyl iodide on an alloy of tin with sodium (without indicating the yield, but with a complete analysis), in the form of a dark-colored oil, and he expressed the supposition that in the pure state it should be colorless. Later, Frankland (^{2}) isolated from the reaction products of diethylzinc and stannic chloride a yellow-red liquid. Pfeiffer (^{3}), however, could not reproduce Frankland' s experiments and obtained diethyltin by reduction of dichlorodiethyltin with sodium amalgam. For the yellowish oil described by him he did not give an analysis for tin. By the same method of reduction of dialkyltin dihalides, Kraus and Greer (^{4}) proceeded (dimethyltin—a yellow powder without analysis), as did Harada (^{5}) (diethyltin—a yellow-orange powder without analysis). In a later work, Kettle (^{6}) treated dimethyltin dihydride with sodium, followed by addition of ammonium bromide (dimethyltin—a yellow-green powder without analysis for tin). We do not mention here those cases in which dialkyl compounds were not isolated as such and were characterized indirectly by converting them into one or another derivative (^{3},^{7}). Finally, quite recently a brief communication appeared (^{8}) (without experiment) concerning the synthesis of diethyltin by decomposition of diethyltin dihydride with amines.

In the present work we succeeded in developing a method for obtaining analytically pure di-*n*-butyltin and diethyltin by the reaction (cf. (^{9}))

$$SnCl_2 + 2C_4H_9Li \rightarrow (C_4H_9)_2Sn + 2LiCl.$$

When a suspension of anhydrous stannous chloride (0.25 mole) in a mixture of ether with benzene (1:4) is allowed to react at -10° with *n*-butyllithium (0.5 mole) in ether, the solution becomes dark cherry-red. The reaction mixture is decomposed with a small amount of water (temperature not above 2°). The precipitate that separates is filtered off, washed with hot benzene, and the filtrate is evaporated in vacuo. The residue is a dark-red oil with a small amount of precipitate. Hexane is added, the mixture is filtered once more, and the hexane is removed in vacuo ($1 \cdot 10^{-2}$ mm), while the remaining impurities are removed on a boiling water bath in vacuo at $5–7 \cdot 10^{-6}$ mm. There is obtained 37 g (63.7%) of a dark-red oil, which is pure di-*n*-butyltin.

Found, %: C 41.12; 41.22; H 7.64; 7.73; Sn 51.07; 51.19
$C_8H_{18}Sn$. Calculated, %: C 41.26; H 7.77; Sn 50.97

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* We use here the generally accepted term "dialkyltin," although the substance can be assigned a more complex structure.

Di-*n*-butyltin dissolves well in hexane, benzene, toluene, ether, chloroform, and carbon tetrachloride; poorly in alcohol and acetone.

Diethyltin was obtained analogously in 40.8% yield as a dark-cherry-colored oil.

	Found, %:	C 27.18, 27.21;	H 5.51, 5.55;	Sn 67.36, 67.40
$C_4H_{10}Sn$.	Calculated, %:	C 27.17;	H 5.70;	Sn 67.13

The solubility of diethyltin is analogous.

Diethyl- and di-*n*-butyltin are oxidized in air with the eventual formation of a solid white product (in solution the oxidation proceeds considerably more rapidly), which with hydrochloric acid gives dichloro-di-*n*-butyltin with m.p. 42–43° (mixed sample without depression). The formation of diethyltin oxide has been described by various authors, but the oxidation process of R_2Sn probably proceeds more complexly and deserves special study. On treating a solution of di-*n*-butyltin in carbon tetrachloride with a calculated amount of bromine in the same solvent, quantitative formation of dibromo-di-*n*-butyltin occurs (m.p. 18.5–19.5°; literature m.p. data 20°). There is little information on the disproportionation of R_2Sn. According to Pfeiffer’ s data (3), diethyltin decomposes without distilling. According to our experiments, di-*n*-butyltin in a sealed ampoule (in argon) begins to liberate metal at 230°.

Table 1

	Found: cryoscopy (phenone 112)	Found: ebullioscopy (toluene)	Calculated for R_2Sn
Diethyltin	1780	1633	176.8
Di-*n*-butyltin	1921	1745	232.9

Undoubtedly, the compounds R_2Sn are polymeric. We carried out measurements of the molecular weights of the di-*n*-butyltin and diethyltin obtained by us (Table 1).

Neumann (^{8}) assigned to diethyltin a cyclic structure corresponding to 7–9 units (the method by which he determined the molecular weight is not indicated in the work).

Now having an accessible method for preparing aliphatic compounds of the type described above, we have the opportunity to study their chemical reactions (especially the polymerization reaction) and to investigate their structure more closely.

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Note: Figure translations are in progress. See original paper for figures.