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A NEW ROUTE TO TETRAORGANOTIN COMPOUNDS

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Summary

A new direct synthesis suitable for the preparation of straight-chain tetraalkyltins is described.

Discussion

There continues to be considerable interest in the direct synthesis of organotin compounds from free tin [1—3], but such syntheses usually yield mixtures of di- and tri-organotin halides. To prepare tetraorganotins, on the other hand, it has usually been necessary to produce an alloy of tin with stoichiometric amounts of a second metal [1,4—6]. Recently, a new reaction has been discovered [7,8] in which it was not necessary to have tin combined as an alloy with the second metal in order to produce tetraalkyltins. We now report results of our investigations into the range of materials for which this reaction is applicable.

The reaction (eq. 1) was carried out using n-butyl, n-heptyl, n-octyl and n-decyl chlorides to give the yields of tetraalkyltin reported in Table 1. This reaction was previously used to prepare tetramethyltin from gaseous methyl chloride [7], and is thus suitable for a wide variety of alkyl chain lengths (eq. 1). For the synthesis of tetrabutyltin, following the isolation of the organotin compound it was possible to recover a mixture of unreacted metal powders in sufficient quantity to imply that the yield was close to 100% based on the tin consumed.

$$4RX + Sn + 2Zn \xrightarrow[160\text{—}170^\circ C]{Bu_4NI} R_4Sn + 2\ ZnX_2 \qquad (1)$$

TABLE 1

YIELDS OF TETRA-n-ALKYLTINS FROM VARIOUS n-ALKYL CHLORIDES

n-Alkyl chloride	Chain length	Yield of R_4Sn (on tin taken) (%)
Butyl	C_4	32.5
Heptyl	C_7	27.7
Octyl	C_8	26.9
Decyl	C_{10}	12.8

The products of the reaction of longer chain organic halides were contaminated by substantial quantities of unreacted n-alkyl chloride, due to the longer reaction time required by these compounds. The products were analysed for trialkyltin chloride by acidimetric titration *, and generally contained less than 1.0% of R_3SnCl. The samples of tetrabutyltin were also analysed by GLC *, and this technique confirmed the high purity of the products.

Previously, it was shown that when the alkyl groups of the chloride were different from those of the tetraalkylammonium iodide, there was a trace of mixed tetraalkyltins among the products [9]. It has also been shown that tetraalkylphosphonium iodides may be used in place of the tetraalkylammonium iodide [7,9]. It is essential that iodine be present in the reaction medium: attempts to prepare tetrabutyltin from butyl chloride, tin and zinc in the presence of either tributylamine or tetrabutylammonium bromide failed, and no reaction took place. Adding potassium iodide in the latter case (mol ratio KI/Bu_4NBr 1/1) led to production of tetrabutyltin in 20.6% yield. Halides other than the chloride could be used in the reaction, though they gave lower yields of tetraalkyltin (see Table 2). That the sequence of yields did not follow an orderly pattern, such as increasing in the direction $BuI > BuBr > BuCl$ as might perhaps be expected, is probably a reflection of the complexity of the reactions taking place [10].

The effect of alkyl chain branching on the reaction was investigated using t-, s- and i-butyl chlorides. In each case, the butyl chloride underwent a reaction, but yielded no tetrabutyltin; the butyl groups were instead lost from the reaction mixture, presumably in the form of products or as free-radical processes.

Similarly, the difunctional halides 1,4-dichlorobutane and 1,2-dibromoethane underwent a reaction, but gave no organotin product, the organic fragments again being lost from the reaction mixture. By contrast, chlorobenzene failed to undergo any reaction, thus showing that the reaction is not suitable for the synthesis of tetraphenyltin, and probably not for tetraaryltins in general.

Attempts to replace zinc as auxiliary metal in the preparation of tetrabutyltin from butyl chloride by copper, iron or aluminium were unsuccessful. In each case no tetrabutyltin was produced. Replacing zinc by magnesium led to the production of a trace of impure tetrabutyltin, which was difficult to extract,

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* For details, see ref. [10].

TABLE 2

YIELD OF TETRA-n-BUTYLTIN FROM VARIOUS n-BUTYL HALIDES

Butyl halide	Yield of n-Bu_4Sn (on tin taken) (%)
n-BuCl	32.5
n-BuBr	19.3
n-BuI	25.1

due to the formation of a voluminous waxy solid when extraction with light petroleum was attempted. The use of ternary mixture of tin, zinc and copper, suggested by early results in this field [11], was less successful than that of the usual binary tin-zinc mixture. The mixed metal powers (composition: Sn 43.2%, Zn 47.6%, Cu 9.2% by weight; mol ratio = 5/10/2) were treated with butyl chloride, and gave tetrabutyltin in only 9% yield.

Finally, attempts to prepare organic derivatives of silicon and lead by this process, using the finely divided elements, failed. In each case, it was possible to recover the element quantitatively from the reaction mixtures.

Experimental

The standard procedure for preparing tetraalkyltin from alkyl halide was as follows: To a 500 cm^3 round-bottomed flask fitted with a reflux condensor and a glass stirrer paddle was added tetrabutylammonium iodide (24.7 g, 0.067 mol), zinc dust (26.1 g, 0.400 mol Analar Zinc dust, ex. Fisons Ltd) and tin powder (23.7 g, 0.200 mol G.P.R. tin powder, weight-average particle size 8μ, ex. Hopkin & Williams Ltd). The air inside the flask was removed by passing in dry nitrogen, and the contents of the flask were heated to 160° C, the minimum temperature for reaction [8,9], with continual stirring. At this point, the mixture appeared as a dark grey, mobile liquid, and the dropwise addition of alkyl halide (0.400 mol) was begun. This was continued slowly until it had all been added to the reaction flask, a process which generally took 2 h. The mixture was then heated with continued stirring for a further 3 h, after which it was cooled slightly, and the isolation procedure begun. When adding a low boiling point alkyl chloride (e.g. BuCl, b.p. 78° C), care had to be taken, since too rapid an addition, i.e. faster than it was consumed, led to a reduction in the temperature inside the flask, and to refluxing of the alkyl chloride.

Isolation of the tetraalkyltin was carried out by adding light petroleum (100 ml, b.p. 40—60° C) slowly to the reaction mixture, thus gradually bringing the temperature inside the flask down to the reflux temperature of the petroleum, where it was maintained for 45 min. During this time, the flask contained two phases, a brittle grey solid one, and a highly mobile petroleum one. After the heating the flask was cooled, and the petroleum layer was removed by decantation. The residue was then washed with further small portions of petroleum, and the washings combined with the main extract. The petroleum was then distilled off to leave the organotin product. In a typical preparation of tetrabutyltin from butyl chloride, 23.0 g of Bu_4Sn was obtained, a yield of 33.1% on tin taken (close to 100% on tin consumed).

In order to examine the effectiveness of metals other than zinc in the reaction, zinc was replaced in the initial reaction mixture by the relevant metal (0.400 mol). Similarly, in order to discover whether this process was suitable for the synthesis of organometallic compounds of other Group IVB elements, tin was replaced by either silicon (0.200 mol) or lead (0.200 mol).

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