

Investigation of the infrared spectra of a series of dialkyltin dihalides R_2SnX_2 ($X = Cl, Br$ and I) in the $600-50\text{ cm}^{-1}$ region has permitted unambiguous assignment of Sn-C and Sn-halogen modes.

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Short Communication

A cyclic tetramer of di-*tert*-butyltin

It is now becoming clear that the so-called "dialkyltins" and "diaryltins" are mixtures of polymers¹. These contain both straight and branched chains, but when prepared by certain routes, well-defined cyclic compounds are also present. Thus a cyclic 6-mer and 9-mer have been isolated from crude "diethyltin"², and cyclic 5- and 6-mers from "diphenyltin"². We now report a cyclic 4-mer of di-*tert*-butyltin, which was formed unexpectedly during attempts to prepare tetra-*tert*-butyltin.

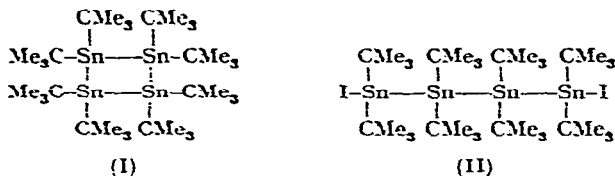
Krause and Weinberg studied the reaction of *tert*-butylmagnesium chloride with tin(IV) chloride in diethyl ether, and obtained a red ethereal solution, which they supposed to contain "di-*tert*-butyltin", since on addition of bromine, di-*tert*-butyltin dibromide was formed. In our hands the same reaction, but carried out in tetrahydrofuran solvent, gave a good yield of di-*tert*-butyltin dichloride, without formation of a red solution. Traces of a bright yellow crystalline by-product were noticed, however, and this became the main product when di-*tert*-butyltin dichloride was allowed to react with an excess of *tert*-butylmagnesium chloride in boiling tetrahydrofuran.

Elementary analysis showed the yellow compound had empirical formula $C_8H_{16}Sn$. On heating, the substance decomposed without melting at *ca.* $205^\circ C$; it also proved to be only sparingly soluble in the usual solvents at room temperature.

An X-ray analysis of the crystal showed that the unit cell is monoclinic ($a = 18.42 \text{ \AA}$, $b = 12.70 \text{ \AA}$, $c = 9.53 \text{ \AA}$, $\beta = 115^\circ 2'$) and contains 8 monomer ($C_8H_{16}Sn$) units. Systematic absences indicate a C centred cell, and allow $C2$, Cm and C_m^2 as possible spacegroups. It follows that di-*tert*-butyltin may be monomeric, dimeric, or tetrameric; it is not possible to have molecules larger than tetramers.

J. Organometal. Chem., 1 (1964) 434-436

Evidence that the compound is the cyclic tetramer (I) came from a study of its reaction with iodine.



A cold solution of I_2 in benzene rapidly dissolved the compound (I), forming an iodine-containing substance whose analysis and molecular weight corresponded to (II). Further addition of iodine to (II), under less mild conditions gave di-*tert*-butyltin diiodide.

During these studies, a cyclic tetramer of "diphenylgermanium" was reported⁵, and was stated to react with iodine to give a compound analogous to (II).

The reaction of dicyclohexyltin dichloride⁶ with cyclohexylmagnesium bromide or with *tert*-butylmagnesium chloride in boiling tetrahydrofuran did not give a compound analogous to (I). The reaction of *tert*-butylmagnesium chloride with lead(II) chloride in tetrahydrofuran precipitated a mass of "spongy" lead.

EXPERIMENTAL

Octa-tert-butyltetraastannacyclobutane (I)

A solution of *tert*-butylmagnesium chloride was prepared from magnesium (14 g) and *tert*-butyl chloride (47 g) in tetrahydrofuran (200 ml). (A trace of methyl iodide was added as a "starter".) After filtering from unreacted magnesium, the solution was treated with di-*tert*-butyltin dichloride⁴ (10 g) in portions, with stirring, over 20 minutes. The mixture was then refluxed for 4 hours, cooled, and filtered. The solid product (4.3 g, 56%) was washed with dilute hydrochloric acid, and then with acetone, and dried.

The tetramer (I) formed bright yellow crystals, which decomposed rather suddenly at 205°C (Kofler block) without melting, and leaving a black residue which was not metallic tin. The yellow colour faded on exposure to sunlight. The substance was slightly soluble in hot pyridine and hot di-*n*-butyl ether, from which small quantities could be recrystallised; otherwise, it was virtually insoluble. (Found: C, 41.1; H, 7.45; Sn, 52.0. $\text{C}_8\text{H}_{18}\text{Sn}$ calcd.: C, 41.2; H, 7.7; Sn, 51.0%.)

Reaction with iodine

A solution of iodine in benzene was added dropwise to a suspension (3.0 g) of (I) in the same solvent at 20°C. The iodine was decolorised, and (I) went into solution. After adding 0.7 g iodine, the benzene was allowed to evaporate leaving 1,4-diiodoocta-*tert*-butyltetra-*tin* (II) (3.7 g), as pale yellow prisms, m.p. 160°C. This substance could be crystallised from light petroleum, but appeared to be unstable in hot solvents, slowly depositing a sandy, amorphous powder. (Found: C, 32.9; H, 6.0%; mol. wt., 1150 ± 75. $\text{C}_{32}\text{H}_{72}\text{I}_2\text{Sn}_4$ calcd.: C, 32.4; H, 6.1%; mol. wt., 1185.4.) The molecular weight was measured using the Mecrolab vapour-pressure osmometer, with solutions of (II) in benzene ranging from 1–5% in concentration (g/l).

A benzene suspension of (I) was treated with sufficient iodine for complete reaction and refluxed for 20 minutes. The iodine had by then almost disappeared; after allowing the benzene to evaporate, a residue of slightly impure di-*tert*-butyltin diiodide was obtained. This sample, m.p. 80–84°, did not depress the m.p. (95°) of a pure specimen obtained from the dichloride and sodium iodide in acetone. (Found: C, 20.65; H, 3.75. $C_8H_{18}I_2Sn$ calcd.: C, 19.7; H, 3.7%).

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