113. *Some Organotin Compounds containing the* o-*Phenoxyphenyl Group.*

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The preparation and properties of some *o*-phenoxyphenyltin compounds are described. The hydrolysis of di-*o*-phenoxyphenyltin dichloride gives low-melting crystalline compounds in contrast to the polymeric amorphous oxides usually obtained from organotin dichlorides. The structures and significance of these products are discussed.

ALKALINE hydrolysis of disubstituted organotin dichlorides generally gives insoluble, polymeric, amorphous oxides of high melting point. Exceptions are the hydrolyses of dibenzyltin dichloride,[1] di-t-butyltin dichloride,[2] and di-isopentyltin dichloride [2] where soluble compounds of uncertain structure were isolated. These products probably arise from limited polymerisation, by loss of water, of the initially formed organotin dihydroxides.[1] Steric factors may be significant in preventing extended polymerisation and it was of interest to examine the products of hydrolysis of a compound R_2SnCl_2 when R is a bulky group and a stable dihydroxide might be formed; the case where R = *o*-phenoxyphenyl was chosen for study.

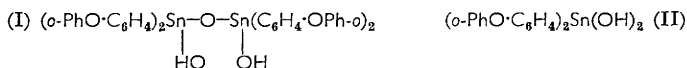Reaction of diphenyl ether with n-butyl-lithium gave *o*-lithiodiphenyl ether [3] and

[1] Smith and Kipping, *J.*, 1913, 2034.
[2] Krause and Weinberg, *Ber.*, 1930, **63**, 381.
[3] Gilman and Bebb, *J. Amer. Chem. Soc.*, 1939, **61**, 109.

treatment of this with stannic chloride gave tetra-*o*-phenoxyphenyltin. Cleavage by iodine gave *o*-iododiphenyl ether (confirming the point of attachment of the diphenyl ether residues to tin) and di-*o*-phenoxyphenyltin di-iodide. The di-iodide exists in an α-form, m. p. 121—122°, which, on being heated to just above 122°, is converted into the more stable β-form, m. p. 139—140°. Attempts to form tri-*o*-phenoxyphenyltin iodide by treatment of the tetra-substituted compound with one molecular proportion of iodine gave the di-iodide and unchanged starting material. The di-iodide proved resistant to hydrolysis and the very vigorous conditions necessary to bring about attack on the Sn–I bond caused more general decomposition.

When tetra-*o*-phenoxyphenyltin was heated with stannic chloride di-*o*-phenoxyphenyltin dichloride and *o*-phenoxyphenyltin trichloride were obtained. The products of hydrolysis of the dichloride varied according to the conditions used, but in no case was an insoluble or infusible product obtained. By analogy with the known organosilicon dihydroxides it was expected that an excess of acid or base would favour polymerisation [4] and, accordingly, the di-*o*-phenoxyphenyltin dichloride was hydrolysed by brief treatment with slightly more than the stoicheiometric quantity of aqueous sodium hydrogen carbonate at 0°. The product was a well-defined crystalline solid which showed an O–H stretching band at 3630 cm.[-1] and had an elemental analysis corresponding to bis(hydroxy-di-*o*-phenoxyphenyltin) oxide (I); estimation of hydroxyl groups by Karl Fischer titration [5] and by Zerewitinoff determination confirmed this structure. Cryoscopic

$$\text{(I) } (o\text{-PhO·C}_6\text{H}_4)_2\text{Sn–O–Sn(C}_6\text{H}_4\text{·OPh-}o)_2 \qquad (o\text{-PhO·C}_6\text{H}_4)_2\text{Sn(OH)}_2 \text{ (II)}$$
$$\qquad\qquad\qquad | \quad\quad |$$
$$\qquad\qquad\quad \text{HO} \quad \text{OH}$$

molecular-weight determinations gave erratic, high, values and it became apparent that solutions of the oxide in organic solvents were unstable. Thus a benzene solution of compound (I), after some days, deposited colourless crystals which had a similar infrared spectrum, elemental analysis, and hydroxyl content to those of the oxide and is, therefore, considered to be an associated form.

Although triethylsilanol gives urethanes with organic isocyanates [6] it was shown that triphenyltin hydroxide resembles triphenylsilanol [7] in undergoing preferential dehydration when treated with phenyl isocyanate. The oxide (I) should be less susceptible to dehydration but, nevertheless, attempts to form urethane derivatives were unsuccessful.

Hydrolysis of di-*o*-phenoxyphenyltin dichloride with an excess of 2N-sodium hydroxide gave colourless crystals. This product was stable in air but decomposed on warming or on dissolution in a solvent and all attempts at recrystallisation were unsuccessful. The infrared spectrum of this material showed an O–H stretching band at 3610 cm.[-1] and its elemental analysis and hydroxyl content indicated that it was largely di-*o*-phenoxyphenyltin dihydroxide (II). Its purity, based on hydroxyl content, was estimated at 72%, on the assumption that the contaminant is the oxide (I).

From the products of thermal decomposition of the dihydroxide, bis(tri-*o*-phenoxyphenyltin) oxide was isolated, whose infrared spectrum, compared with that of the dihydroxide, shows an additional absorption band at 828 cm.[-1] corresponding to that found at 777 cm.[-1] in bis(triphenyltin) oxide and tentatively associated [8] with the Sn–O–Sn group.

Treatment of the dihydroxide with hydrogen sulphide in acetone gave di-*o*-phenoxyphenyltin sulphide; molecular-weight determinations indicated that, like the corresponding dialkyl- [9] and diphenyl-tin [10] sulphides, this compound is a cyclic trimer.

[4] George, Sommer, and Whitmore, *J. Amer. Chem. Soc.*, 1953, **75**, 1585.

[5] Gilman and Miller, *J. Amer. Chem. Soc.*, 1951, **73**, 2367.

[6] Atakhin, Losev, and Andrianov, *Doklady Akad. Nauk S.S.S.R.*, 1957, **113**, 581 (*Chem. Abs.*, 1957, **51**, 14582).

[7] Dolgov and Volnov, *Zhur. obshchei Khim.*, 1931, **1**, 91 (*Chem. Abs.*, 1931, **25**, 4535).

[8] Poller, *J. Inorg. Nuclear Chem.*, 1962, in the press.

[9] Harada, *Bull. Chem. Soc. Japan*, 1942, **17**, 283.

[10] Reichle, *J. Polymer Sci.*, 1961, **49**, 521.

The marked contrast in physical properties between the silicones and the generally insoluble and infusible disubstituted organotin oxides, has been attributed [8] to cross-linking of the Sn–O–Sn chains by co-ordination of oxygen atoms in one chain to tin atoms in neighbouring chains. The isolation of bis(hydroxydi-o-phenoxyphenyltin) oxide (I) and of the crude dihydroxide (II) indicates that the presence of large groups on tin inhibits the extended condensation polymerisation of a dihydroxide $R_2Sn(OH)_2$ and the isolation of an associated form of (I) supports the view that co-ordination is a significant factor in the structure of the organotin oxides.

EXPERIMENTAL

Infrared absorption spectra were measured with an Infracord model 137 spectrophotometer by the potassium bromide disc technique. The positions of hydroxyl stretching bands were checked on carbon disulphide solutions with a Unicam S.P. 700 spectrophotometer.

Organolithium compounds were manipulated in an atmosphere of nitrogen.

Tetra-o-phenoxyphenyltin.—Diphenyl ether (52·0 g.) in dry ether (100 ml.) was added to a solution of n-butyl-lithium (from 8·6 g. of lithium and 84·0 g. of n-butyl bromide) in ether (300 ml.). The mixture was boiled under reflux for 2 hr. and then stirred at room temperature overnight. Anhydrous stannic chloride (20·0 g.) in dry benzene (100 ml.) was added dropwise and the mixture boiled under reflux for 1 hr. The ether and benzene were removed by distillation and the residue added, in portions, to water (600 ml.). The aqueous mixture was shaken with benzene (250 ml.), then filtered, and the residue crystallised from xylene to give *tetra*-o-*phenoxyphenyltin* (11·0 g.), m. p. 233—234°. The benzene was separated from the filtrate, dried (Na_2SO_4), and concentrated, giving a further 5·4 g. of product, m. p. 228—234° (total yield 16·4 g., 27% based on stannic chloride). Further crystallisation from xylene gave the analytical specimen, m. p. 234—235° (Found: C, 72·9; H, 4·9; Sn, 14·8. $C_{48}H_{36}O_4Sn$ requires C, 72·5; H, 4·6; Sn, 14·9%).

Di-o-phenoxyphenyltin Di-iodide.—Tetra-o-phenoxyphenyltin (10·0 g.) was ground with iodine (6·38 g., 2 mol.) and the mixture heated at 65° for 2 hr. and then at 120° for 1 hr. Distillation under reduced pressure gave o-iododiphenyl ether (4·1 g., 55%), b. p. 136—138°/0·6 mm., m. p. 53·5—56°. After recrystallisation from light petroleum (b. p. 40—60°) this material had m. p. and mixed m. p. 55—56° and its infrared spectrum was identical with that of an authentic [11] specimen.

The involatile residue solidified and crystallisation from nitromethane gave the *di-iodide* (6·6 g., 74%), m. p. 119—121°. Further crystallisation gave, arbitrarily, either the pure α-form, m. p. 121—122°, or the pure β-form, m. p. 139—140°; these forms showed similar analyses and identical infrared spectra (Found: C, 40·7; H, 2·6; Sn, 16·6. $C_{24}H_{18}I_2O_2Sn$ requires C, 40·6; H, 2·6; Sn, 16·7%). When the α-form was heated to just above 122° it re-solidified, melting again at 139—140°.

Attempted Preparation of Tri-o-phenoxyphenyltin Iodide.—Tetra-o-phenoxyphenyltin (5·00 g.) was ground with iodine (1·60 g., 1 mol.) and the mixture heated at 75° for 1·5 hr. and then at 145° for 1 hr. The o-iododiphenyl ether was removed by distillation under reduced pressure and the involatile residue crystallised from nitromethane (400 ml.) to give unchanged tetra-o-phenoxyphenyltin (1·81 g.), m. p. 229—232°, which after further crystallisation had m. p. and mixed m. p. 234—235°. Evaporation of the mother-liquor gave crude di-o-phenoxyphenyltin di-iodide (2·40 g.) which after crystallisation from nitromethane (30 ml.) had m. p. 121—122° and 139—140°.

Di-o-phenoxyphenyltin Dichloride.—A mixture of tetra-o-phenoxyphenyltin (10·00 g.), anhydrous stannic chloride (3·62 g., 1·1 mol.), and xylene (10 ml.) was boiled under reflux for 1 hr. The xylene was distilled off and the resulting mixture heated at 280°/0·5 mm. to remove any trichloride formed. The residue crystallised from light petroleum (b. p. 60—80°), to give the pure *dichloride* (10·44 g., 79%), m. p. 98—99° (Found: C, 55·0; H, 3·4; Sn, 22·4. $C_{24}H_{18}Cl_2O_2Sn$ requires C, 54·6; H, 3·4; Sn, 22·5%).

o-*Phenoxyphenyltin Trichloride.*—Anhydrous stannic chloride (7·4 g., 4·5 mol.) in toluene (10 ml.) was added to tetra-o-phenoxyphenyltin (5·0 g.), and the mixture boiled under reflux

[11] Clarkson and Gomberg, *J. Amer. Chem. Soc.*, 1930, **52**, 2881.

for 30 min. After being left overnight at room temperature the toluene and the excess of stannic chloride were removed at 100°/15 mm. The residue was distilled, to give the *trichloride* (3·6 g., 36%), b. p. 184—186°/0·7 mm., m. p. 69—72°. Recrystallisation from light petroleum (b. p. 40—60°) raised the m. p. to 71—72° (Found: C, 36·4; H, 2·4; Sn, 30·0. $C_{12}H_9Cl_3OSn$ requires C, 36·6; H, 2·3; Sn, 30·1%).

*Hydrolysis of Di-*o-*phenoxyphenyltin Dichloride.*—(a) *By sodium hydrogen carbonate.* A solution of sodium hydrogen carbonate (2·1 g.) in water (100 ml.) was added to a stirred solution of the dichloride (6·0 g.) in ether (100 ml.), cooled in ice–salt. Rapid crystallisation occurred and, 2 minutes after the addition was complete, the product was filtered off, washed with water and ether, and air-dried, to give *bis(hydroxydi-*o-*phenoxyphenyltin) oxide* (5·0 g.), m. p. 164°. Recrystallisation by the addition of an excess of light petroleum (b. p. 60—80°) to a chloroform solution of the product raised the m. p. to 165—166° [Found: C, 59·9; H, 4·5; Sn, 24·3; OH, 3·3 (Karl Fischer), 3·9 (Zerewitinoff). $C_{48}H_{38}O_7Sn_2$ requires C, 59·8; H, 4·0; Sn, 24·6; OH, 3·5%]. The infrared spectrum of this compound showed a sharp OH band at 3630 cm.⁻¹; the corresponding frequency for the OH band in triphenyltin hydroxide, measured in carbon tetrachloride solution, is 3647 cm.⁻¹.[12]

The oxide (1·00 g.) was dissolved, at room temperature, in " AnalaR " benzene (25 ml.), and the solution set aside in a stoppered flask for 3 days. Slow crystallisation occurred and filtration gave a co-ordination polymer of the oxide (0·82 g.), m. p. 162—180° [Found: C, 60·1; H, 3·9; OH, 3·6% (Karl Fischer)].

(b) *By sodium hydroxide.* To a filtered solution of di-o-phenoxyphenyltin dichloride (2·00 g.) in ether (30 ml.) was added filtered 2N-sodium hydroxide (40 ml.), and the mixture was shaken for several minutes and then set aside for 1 hr. Filtration, washing with water and ether, and drying in the air gave crude di-o-phenoxyphenyltin dihydroxide as colourless crystals (1·35 g.), m. p. 141—142° (decomp.) (Found: C, 59·1; H, 4·1; Sn, 24·0; OH, 5·95. $C_{24}H_{20}O_4Sn$ requires C, 58·7; H, 4·1; Sn, 24·2; OH, 6·9%). The OH stretching frequency for this material was 3610 cm.⁻¹.

The dihydroxide (1·0 g.) was heated at 145°/15 mm. for 1 hr. The resulting glass appeared to be a complex mixture but chromatography on alumina followed by crystallisation from cyclohexane gave *bis(triphenoxyphenyltin) oxide* (0·17 g.), m. p. 143—144° (Found: C, 68·5; H, 4·7. $C_{72}H_{54}O_7Sn_2$ requires C, 68·2; H, 4·3%). This oxide undoubtedly arises from a disproportionation, and small amounts of a second product having an analysis approximating to that required for o-phenoxyphenylstannonic acid were isolated but could not be obtained pure.

*Di-*o-*phenoxyphenyltin Sulphide.*—Hydrogen sulphide was passed into a warm solution of crude di-o-phenoxyphenyltin dihydroxide (1·00 g.) in acetone (25 ml.) for 30 min. Evaporation gave a colourless glass which was crystallised from light petroleum (b. p. 80—100°) to give the *sulphide* (0·57 g.), m. p. 144—148°. Further crystallisation from light petroleum raised the m. p. to 148—149·5° [Found: C, 58·7; H, 3·85%; *M*, 1470, 1450. $(C_{24}H_{18}O_2SSn)_3$ requires C, 58·9; H, 3·85%; *M*, 1467].

Reaction of Triphenyltin Hydroxide with Phenyl Isocyanate.—Phenyl isocyanate (3·0 ml.) was added to triphenyltin hydroxide (1·0 g.); heat was evolved; the mixture was set aside for 20 min. Heating at 100°/15 mm. removed unchanged phenyl isocyanate and crystallisation of the residue from nitromethane gave *NN′*-diphenylurea (0·37 g.), m. p. 238—242°, raised, on recrystallisation, to 241—243° (lit.,[13] m. p. 238—239°: this compound showed the expected infrared absorptions). Evaporation of the original nitromethane mother liquor gave bis(triphenyltin) oxide (0·55 g., m. p. 119—125°); after recrystallisation from light petroleum (b. p. 80—100°) this material had m. p. and mixed m. p. 121—123°.

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[12] West and Baney, *J. Phys. Chem.*, 1960, **64**, 822.
[13] Young and Clark, *J.*, 1898, **83**, 361.