

## The Preparation and Reactions of Aryltin Pentachlorophenoxides

S. N. BHATTACHARYA\* and AHMAD S. PAKDAMAN

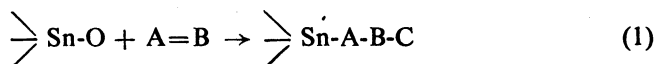
*Department of Chemistry  
University of Lucknow, Lucknow-226 007, India.*

The preparation of aryltin pentachlorophenoxides ( $C_6H_5$ )<sub>2</sub>SnOC<sub>6</sub>Cl<sub>5</sub>; (*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>SnOC<sub>6</sub>Cl<sub>5</sub> and ( $C_6H_5$ )<sub>2</sub>Sn(OC<sub>6</sub>O<sub>2</sub>Cl<sub>5</sub>)<sub>2</sub> are given along with their reactions with unsaturated substrates ( $C_6H_5N=C=O$ ,  $S=C=S$ ,  $O=S=O$ ) which add across the Sn-O bond of the alkoxides. The products have been identified and the details of reactions discussed.

### INTRODUCTION

The synthetic methods for obtaining trialkyltin perhalophenoxides  $R_3SnOC_6X_5$  (where  $R = CH_3$ ,  $C_6H_5$  and  $X = Br$  and  $F$ ) are reported<sup>1,2</sup>. Though the details of the preparations or characteristic properties were not mentioned, the corresponding perchloro derivatives have been used for its biocidal activity<sup>3</sup>. Similarly diphenylbis-(pentachlorophenoxy) tin has also been obtained as byproduct from the reaction of diphenylstannazosulfoxylarenes with pentachlorophenol<sup>4</sup> without any study of the properties. We now wish to report the syntheses of aryltin pentachlorophenoxides and the reactions of the Sn-O bond of these phenoxides.

The Sn-O bond of organotin phenoxides add to multiply bonded groups of acceptor molecules<sup>5-7</sup>.



(where  $A=B$ ,  $PhNCO$ ,  $PhNCS$ ,  $CS_2$ ,  $CO_2$ ,  $SO_2$  etc.)

### EXPERIMENTAL

#### Preparation

A typical preparation is described below. Further details of preparation are given in Table 1.

TABLE 1  
ORGANOTIN PENTACHLOROPHENOXIDE

Compounds	M.pt. °C	Yield (%)	Analysis (%)			
			Found		Calcd	
			C	H	C	H
( $C_6H_5$ ) <sub>2</sub> SnOC <sub>6</sub> Cl <sub>5</sub>	61-63	85.7	37.10	2.45	38.05	2.50
( <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> SnOC <sub>6</sub> Cl <sub>5</sub>	87-90	75.3	49.12	3.07	50.53	3.27
( $C_6H_5$ ) <sub>2</sub> Sn(OC <sub>6</sub> Cl <sub>5</sub> ) <sub>2</sub>	143-145	80.8	36.41	1.39	37.32	1.29

**Preparation of (pentachlorophenoxy) triphenyltin**

To a well stirred solution of triphenyltin chloride (7.70 g, 0.02 mol) in 50 ml of dry acetone was added sodium pentachlorophenoxide (5.77 g, 0.02 mol) dissolved in 50 ml of dry acetone. The sodium chloride was precipitated immediately. After 1 hr. it was centrifuged off and (pentachlorophenoxy) triphenyltin was purified by sublimation yield (10.55 g, 85.7%) m.pt. 61–63 (Found: C, 37.10; H, 2.45%. Calcd: for  $C_{24}H_{15}Cl_5O$  Sn, C, 38.05; H, 2.50%).

**Addition Reactions**

Preparative procedure of a representative sample is described below. Further details of similar reactions are given in Table 2.

TABLE 2

PRODUCTS OF THE REACTION OF VARIOUS ACCEPTOR MOLECULES WITH TRIALKYL TIN AND DIPHENYL TIN PENTACHLOROPHENOXIDE

Acceptor	Compound	Product	Yield (%)	M.pt. (C°)
phNCO	$ph_3SnOC_6Cl_5$	$ph_3Sn.N(Ph).CO.OC_6Cl_5$	80	98–100
CS <sub>2</sub>	$ph_3SnOC_6Cl_5$	$ph_3Sn.S.CS.OC_6Cl_5$	80	86–88
SO <sub>2</sub>	$ph_3SnOC_6Cl_5$	$ph_3Sn.O.SO.OC_6Cl_5$	95	90–92
CS <sub>2</sub>	$(p-CH_3C_6H_4)_3SnOC_6Cl_5$	$(p-CH_3C_6H_4)_3Sn.S.CS.OC_6Cl_5$	80	>300
SO <sub>2</sub>	$(p-CH_3C_6H_4)_3SnOC_6Cl_5$	$(p-CH_3C_6H_4)_3Sn.O.SO.OC_6Cl_5$	75	245 decomp
phNCO	$ph_2Sn(OC_6Cl_5)_2$	$ph_2Sn[N(ph)CO.OC_6Cl_5]_2$	90	170–2
CS <sub>2</sub>	$ph_2Sn(OC_6Cl_5)_2$	$ph_2Sn(S.CS.OC_6Cl_5)_2$	85	124–18
SO <sub>2</sub>	$ph_2Sn(OC_6Cl_5)_2$	$ph_2Sn(OC_6Cl_5)O.SO.OC_6Cl_5$	65	169–171

The addition of (pentachlorophenoxy) triphenyltin to acceptor molecules.

**I. Addition of phenyl isocyanate**

To a solution of pentachlorophenoxy triphenyltin (5.99 g, 0.01 mol) in dry benzene (200 ml) phenyl isocyanate (1.19 g, 0.01 mol) was added during 10 min. at refluxing. After complete addition it was further refluxed for 3 hrs. The reaction was freed from solvent under reduced pressure to yield (pentachlorophenyl) triphenyltin-N-1-phenyl carbamate ( $C_6H_5$ )<sub>3</sub>Sn.N( $C_6H_5$ ).CO.OC<sub>6</sub>Cl<sub>5</sub> as a white solid which was recrystallized from pet. ether yield (5.60 g, 80%) m.pt. 98–100° [Found C, 51.15; H, 2.60; N, 1.85%. Calcd. for  $C_{31}H_{20}Cl_5NO_2Sn$ , C, 50.67; H, 2.72; N, 1.99%).

## II. Addition of carbon disulphide

Carbon disulphide (0.76 g, 0.01 mol) was added to a solution of (pentachlorophenoxy) triphenyltin (5.99 g, 0.01 mol) in acetone during 10 min. After the complete addition the solution was further stirred for  $\frac{1}{2}$  hr. to ensure the completion of the reaction. It was freed from solvent at reduced pressure to yield S-triphenyltin-O-pentachlorophenyldithiocarbonate  $(C_6H_5)_3Sn.S.CS.O.C_6Cl_5$  as a white solid: m.pt. 86–88° (5.74 g, 85%) [Found C, 43.33; H, 2.10; S, 9.31%; calcd. for  $C_{25}H_{15}Cl_5CS_2Sn$ , C, 44.40; H, 2.14; S, 9.26%].

## III. Addition of sulphur dioxide

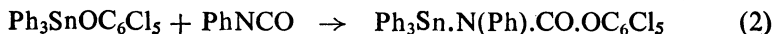
Heat was evolved when sulphur dioxide was passed through a solution of pentachlorophenoxytriphenyltin (5.99 g, 0.01 mol) in light petroleum. After *ca.* 1 hr. the solvent was removed by filtration to yield (pentachlorophenyl) triphenyltin sulphite  $[(C_6H_5)_3Sn.O.SO.O.C_6Cl_5]$  as a white solid which recrystallized from carbon tetrachloride (5.21 g, 78.6%) m.pt. 90–92° (Found C, 42.27; H, 2.40; S, 4.71%, Calcd. for  $C_{24}H_{15}Cl_5O_3S$ , Sn, C, 42.40; H, 2.21; S, 4.71%).

## RESULTS AND DISCUSSION

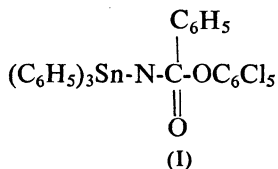
Trialkyltin alkoxide add, often reversibly to a variety of multiple bond acceptors to give 1 : 1 adducts<sup>8</sup>. Trialkyltin methoxides gave adducts which were usually oils and readily hydrolysed, but trialkyltin phenoxides gave adducts which were usually solid and less readily hydrolysed<sup>8</sup>. The trialkyl-lead alkoxides gave adducts which were usually oils and which decomposed with blackening during a few days at room temperature<sup>9</sup>. The adducts formed by triphenyl-lead methoxide on the other hand, were thermally stable solids which were purified by recrystallization<sup>10</sup>. The only alkoxide so far found to be inert to addition to isocyanates is tributyltin pentafluorophenoxide which did not react with phenyl isocyanate even after 5 hrs. at 100°C. This inactivity can be described due to the weak nucleophilicity of oxygen of the pentafluorophenoxy group<sup>10</sup>. Davies<sup>11</sup> concluded that the relative power of tin-oxygen bonded compounds to act as addenda by equation (1) decreases in the sequence  $R_3SnOMe > R_3SnOPh > R_3SnOC_6F_5$  which suggests that the nucleophilicity of oxygen bonded to tin is important. Accordingly it was observed that changing the alkyl groups on tin have little effect upon the reaction while a change of the alkoxy group has a more significant effect; thus oxygen of methoxide is more reactive than phenoxide and even more than pentafluorophenoxide.

The phenylisocyanate reacted exothermally with tributyltin methoxide to give methyl tributylstannyl-N-phenylcarbamate which could be distilled under reduced pressure, and was very sensitive to hydrolysis, the

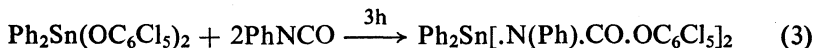
adduct formed from tributyltin phenoxide and phenyl isocyanate dissociated when heated<sup>12</sup>. In our case phenylisocyanate reacted with triphenyltin pentachlorophenoxide after 3 hrs. at 80°C, viz., nucleophilicity of the pentachlorophenoxy is not as weak as that of the pentafluorophenoxy group.



The structure of adducts formed between isocyanates and trialkyltin pentachlorophenoxide was open to argument<sup>12</sup>, for quite a while but the physical and chemical properties could now be reconciled with the pentachlorophenyltriphenylstannyl N-phenyl carbamate structure (I).



The reaction of bis(pentachlorophenoxy) diphenyltin with phenylisocyanate in 1 : 2 ratio molar took place according to equation (3) and the product isolated was N-diphenyl stannylene bis(pentachlorophenyl N-phenylcarbamate). Both the compounds showed characteristic C=O stretching in the IR absorption at  $1695 \pm 10 \text{ cm}^{-1}$ .

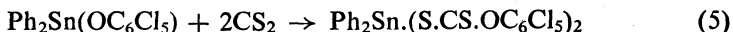


Carbon disulphide is one of the less reactive acceptor molecules, and have been reported not to react with triphenyltin phenoxide even after 6 days. Simple addition apparently occurred with tributyltin methoxide to give O-methyl S-tributyltin dithiocarbonate but the pure adduct could not be isolated<sup>12</sup>.

Carbon disulphide, however, reacted with triphenyltin pentachlorophenoxide at room temperature to give S-triphenyltin-O-pentachlorophenyldithiocarbonate



It also reacts with diphenyltin bis(pentachlorophenoxide) in 2 : 1 molar ratio to give S-diphenyltin-O-bis(pentachlorophenyldithiocarbonate). The IR spectra showed characteristic maxima at 1060, 1140 and  $1200 \text{ cm}^{-1}$  which agree well with those reported for thiocarbonates<sup>12</sup>.

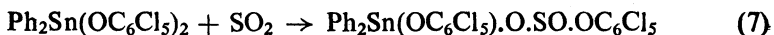


The reactions of sulphur dioxide were parallel to those of carbon dioxide. Tributyltin methoxide gave methyltributyltin sulphite as a viscous oil, which was rapidly converted in air into dibutyltin sulphite. Tributyltin phenoxide reacted only slowly with sulphur dioxide giving phenyltributyltin sulphite<sup>12</sup>.

Triphenyltin pentachlorophenoxide reacted readily with sulphur dioxide to give pentachlorophenyl triphenyltin sulphite.



Sulphur dioxide reacted with diphenyltin bis(pentachlorophenoxide) to give pentachlorophenyldiphenyl (pentachlorophenoxy)tin sulphate.



Only the mono insertion of  $\text{SO}_2$  was observed; even on prolonged passage of  $\text{SO}_2$ , no change in the product was observed.

The characteristic IR absorptions expected for sulphite complexes viz., at  $985 \pm 5 \text{ cm}^{-1}$  and  $843 \pm 5 \text{ cm}^{-1}$  <sup>12,13</sup> were observed in the sulphites.

TABLE 3  
ANALYTICAL DATA OF ARYL TIN PRODUCTS

Product	Found (%)				Calcd. (%)			
	C	H	N	S	C	H	N	S
$(\text{C}_6\text{H}_5)_3\text{Sn.N}(\text{C}_6\text{H}_5)\text{CO.OC}_6\text{Cl}_5$	51.15	2.60	1.85	—	50.67	2.72	1.99	—
$(\text{C}_6\text{H}_5)_3\text{Sn.S.CS.OC}_6\text{Cl}_5$	43.33	2.10	—	9.19	44.40	2.14	—	9.26
$(\text{C}_6\text{H}_5)_3\text{Sn.O.SO.OC}_6\text{Cl}_5$	42.27	2.10	—	4.61	42.40	2.21	—	4.71
$(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{Sn.S.CS.OC}_6\text{Cl}_5$	45.80	2.75	—	8.65	45.92	2.86	—	8.73
$(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{Sn.O.SO.OC}_6\text{Cl}_5$	44.81	2.80	—	4.34	45.92	2.91	—	4.42
$(\text{C}_6\text{H}_5)_2\text{Sn}[\text{N}(\text{C}_6\text{H}_5)\text{CO.OC}_6\text{Cl}_5]_2$	43.55	1.80	2.59	—	43.69	1.92	2.68	—
$(\text{C}_6\text{H}_5)_2\text{Sn}(\text{OC}_6\text{Cl}_5)(\text{O.SO.OC}_6\text{Cl}_5)$	32.90	1.65	—	1.55	33.11	1.15	—	1.61
$(\text{C}_6\text{H}_5)_2\text{Sn}(\text{S.CS.OC}_6\text{Cl}_5)_2$	32.40	1.05	—	13.25	32.58	1.05	—	13.36

### REFERENCES

1. A. J. Oliver and W. A. G. Graham, *J. Organometal Chem.*, **19**, 17 (1969).
2. Jeand'Aus and H. Gold, *Chem. Ber.*, **92**, 3076 (1959).
3. H. S. Hopf, J. Ducan, J. S. S. Berley, D. J. Weblcy and R. F. Sturrock. *Bull. World Health Organ.*, **36**, 955 (1967).
4. A. M. Khmaruk and A. M. Pinchuk, *Zh. Obshch. Khim.*, **48**, 1748 (1978), *Chem. Abstr.*, **89**, 180110 (1978).
5. A. G. Davies, *Synthesis*, **56** (1969).
6. J. C. Pommier and M. Pereyre, *Adv. Chem. Ser.*, **157**, 82 (1976).
7. ———, *J. Organometal Chem. Library*, **1**, 161 (1976).
8. A. J. Bloodworth and A. G. Davies, *J. Chem. Soc.*, 5238 (1965).

9. A. G. Davies and R. J. Puddephatt, *J. Chem. Soc. (C)*, 2663 (1967).
10. A. K. Sawyer, *Organotin compounds*, Marcel Dekker, Inc., New York, Vol. 1, p. 233 (1971).
11. A. G. Davies and W. R. Symes, *J. Chem. Soc. (C)*, 1009 (1967).
12. A. J. Bloodworth, A. G. Davies and S. C. Varishtha, *J. Chem. Soc. (C)*, 1309 (1967); A. G. Davies and P. G. Harrison. *J. Chem. Soc. (C)*, 1313 (1967).
13. E. Maslowsky, *Vibrational Spectra of Organometallic Compound*, Wiley-Interscience, New York, p. 172 (1977).

[Received: 10 February 1989; Accepted: 30 May 1989]

AJC-59

**NINTH INTERNATIONAL SYMPOSIUM ON HPLC OF  
PROTEINS, PEPTIDES AND POLYNUCLEOTIDES**

November, 6-8, 1989

Philadelphia, PA, U.S.A.

*Address for correspondence:*

Secretariat

Barr Enterprises

P.O. Box 279, Walkersville

MD-21793, U.S.A.