ACTION OF METAL HALIDES ON TETRA-, PENTA- AND HEXA-COORDINATED ORGANOTIN COMPOUNDS
I. THE REACTIONS OF MERCURIC HALIDES WITH BIS(TRIPHENYLTIN) OXIDE, AND SOME RELATED REACTIONS

DEBRANJAN DATTA*, BASUDEV MAJEE AND AMIYA KANTI GHOSH

Department of Chemistry, North Bengal University, Darjeeling (India)

(Received December 11th, 1970)

SUMMARY

Mercuric halides have been shown to react readily at room temperature with bis(triphenyltin) oxide to produce phenylmercury halides, triphenyltin halide and polymeric diphenyltin oxide, together with small amounts of tetraphenyltin. The action of mercuric chloride on the sodium salt of triphenyltin hydroxide has also been studied, and has provided evidence for the instability of compounds containing $\geq$Sn–O–Hg-system. Mercuric oxide has been shown to react with triphenyltin chloride in boiling benzene to give phenylmercuric chloride and polymeric diphenyltin oxide. Possible mechanisms are suggested for the reactions observed.

INTRODUCTION

The reactions of siloxanes with covalent halides and organometallic reagents have been extensively studied[1] and the reactions of organometallic halides and acetates derivatives of Hg, Tl, Si, Ge and Pb with dialkyltin oxide have recently been described by Davies and his co-workers[2]. Silicon, tin and phosphorus halides are known to react with organotin oxides to give organotin halides, but, on the other hand, the action of vinylmagnesium chloride on bis(tributyltin) oxide is known to produce tributylvinyltin. There have however, been no systematic study of the reactions of metal halides with organotin oxides and related compounds. Exploratory work revealed some metal halides, notably mercuric halides, are generally reactive towards organotin compounds containing $\geq$Sn–O linkages, and a systematic study of these reactions was undertaken. The present communication deals with the interaction of mercuric halides with bis(triphenyltin) oxide and with some related reactions.
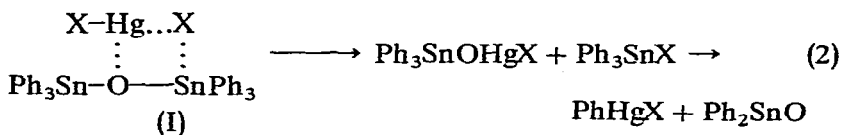
RESULTS AND DISCUSSION

When ethereal solutions of equimolar amounts of mercuric halide and bis-

* Present Address: Catalyst Section, Fertilizer Corporation of India Ltd., Sindri, Dhanbad, India.

(triphenyltin) oxide are mixed at room temperature, a white precipitate (mainly polymeric Ph_2SnO) immediately appears. (To ensure complete reaction the mixture was however stirred for several hours in each case.) All the mercuric halides react analogously to give $PhHgX$, Ph_3SnX (X=Cl, Br or I) and polymeric Ph_2SnO, together with small amounts of Ph_4Sn. The main reaction may be represented as:

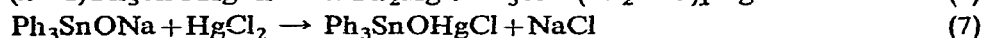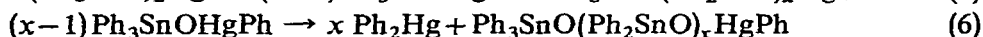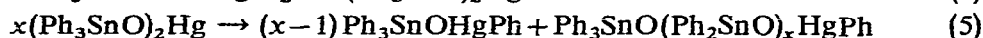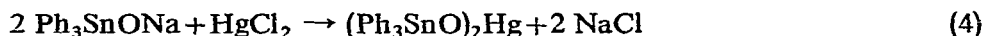$$(Ph_3Sn)_2O + HgX_2 \rightarrow PhHgX + Ph_3SnX + Ph_2SnO \tag{1}$$

These reactions may be explained by invoking a cyclic transition state (I) similar to that proposed for the reactions of siloxanes with $AlCl_3$[1].

$$
\begin{array}{c}
X\text{--}Hg...X \\
\vdots \quad \vdots \\
Ph_3Sn\text{--}O\text{---}SnPh_3 \\
(I)
\end{array}
\longrightarrow Ph_3SnOHgX + Ph_3SnX \rightarrow \tag{2}
$$

$$PhHgX + Ph_2SnO$$

Although the intermediate $R_3SiOAlX_2$ compounds have been isolated from the reaction of $(R_3Si)_2O$ with AlX_3[5,6], the intermediate in the present case *viz.* $Ph_3SnOHgX$ could not be isolated. All attempts to prepare this compound by other routes also proved futile. It is not surprising that compounds containing the $\gtrless$Sn–O–Hg-system are unstable in view of the instability of the analogous silicon compounds. Thus, $(Ph_3SiO)_2Hg$, $Ph_3SiOHgPh$ and $Ph_3SiOHgCl$ are known to undergo conversion into a polymeric material and Ph_2Hg or $PhHgCl$ by phenyl group migration from Si to Hg[7]. This tendency should be enhanced in the tin compounds because of the lower M–C (M = Si or Sn) bond energy, and this is supported by the results of the reaction of $HgCl_2$ with Ph_3SnONa. In view of the work of MacDiarmid[7] *et al.*, $(Ph_3SnO)_2Hg$ would be expected to be the initial product, with varying amounts of $Ph_3SnOHgPh$, Ph_2Hg and Ph_2SnO subsequently being formed depending on the stability of the $\gtrless$Sn–O–Hg-system. However, no $(Ph_3SnO)_2Hg$ or $Ph_3SnOHgPh$ could be isolated from the reaction and Ph_2Hg and polymeric diphenyltin oxide were the major products. Small amounts of $PhHgCl$, Ph_4Sn and $(Ph_3Sn)_2O$ were also isolated. Initial formation of an Sn–O–Hg bonded compound is, however, indicated by the fact that formation of sodium chloride was quite rapid, what would be consistent with a reaction of type (3), and also by the fact that polymeric material gradually separated from the initial clear filtrate. The latter observation can be rationalised by assuming initial formation of a soluble compound which undergoes rearrangement during concentration and recovery.

$$\gtrless Sn\text{--}O\text{--}Na + HgCl_2 \longrightarrow \gtrless Sn\text{--}O\text{--}HgCl + NaCl \tag{3}$$

By analogy with the reaction between Ph_3SiONa with $HgCl_2$, the formation of the observed products in the present case may be explained as follows:

$$2\,Ph_3SnONa + HgCl_2 \rightarrow (Ph_3SnO)_2Hg + 2\,NaCl \tag{4}$$

$$x(Ph_3SnO)_2Hg \rightarrow (x-1)Ph_3SnOHgPh + Ph_3SnO(Ph_2SnO)_xHgPh \tag{5}$$

$$(x-1)Ph_3SnOHgPh \rightarrow x\,Ph_2Hg + Ph_3SnO(Ph_2SnO)_xHgPh \tag{6}$$

$$Ph_3SnONa + HgCl_2 \rightarrow Ph_3SnOHgCl + NaCl \tag{7}$$

$$(x+1)Ph_3SnOHgCl \rightarrow x\,PhHgCl + Ph_3SnO(Ph_2SnO)_xHgCl \tag{8}$$
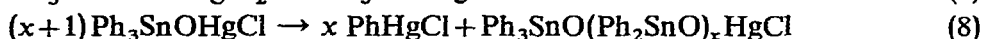
The rearrangement indicated in the equations (5), (6) and (8) may occur by

means of an intermolecular $O \rightarrow Sn$ interaction, *viz.*

$$-\text{Hg} \cdots \text{O-Sn} \lessdot$$
$$\text{Ph} \cdots \text{Sn} \lessdot$$
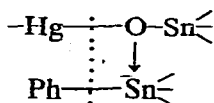
with cleavage as indicated by the dotted line. Such a process could then recur to give larger molecules.

The small amounts of Ph_4Sn and Ph_3SnCl formed probably come from the action of $HgCl_2$ on $(Ph_3Sn)_2O$ which may be formed during the preparation of Ph_3-SnONa, *viz.*:

$$Ph_3SnONa + Ph_3SnOH \rightarrow (Ph_3Sn)_2O + NaOH \tag{9}$$
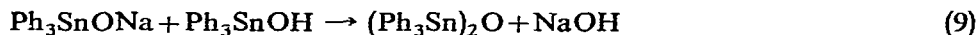
This conclusion is supported by the isolation of small amounts of $(Ph_3Sn)_2O$ from one of the experiments.

The instability of the $Sn-O-Hg$-system is reflected in yet another reaction. In contrast to the reaction of Ph_3SiCl with HgO, to give $(Ph_3Si)_2O^{8-10}$, the reaction involving the tin analogue gave $PhHgCl$ and polymeric Ph_2SnO. This may be accounted for by process (10):

$$Ph_3Sn-Cl$$
$$\uparrow \quad \vdots \quad \rightarrow Ph_3SnOHgCl \rightarrow PhHgCl + Ph_2SnO \tag{10}$$
$$O -Hg$$
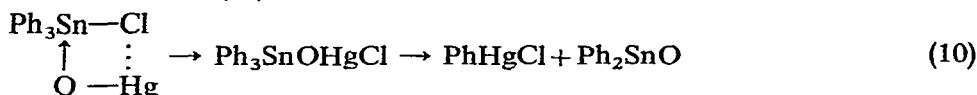
The detail of the mechanism of the rearrangement in the $\geqslant Sn-O-Hg$-system is, however, obscure. This, together with the mode of formation of small amounts of Ph_4Sn in the reaction of mercuric halides with $(Ph_3Sn)_2O$, will be discussed in subsequent papers.

It must be mentioned here that the elemental analysis of the polymeric materials were not always reliable because of considerable difficulty involved in their purification. In a few cases in which the material was digested with THF in a Soxhlet extractor for 24 h, or more, the analysis was very close to that of Ph_2SnO. In most cases the polymeric Ph_2SnO was identified by its IR spectrum[12], insolubility in organic solvents, its infusibility upto 360° and by its conversion to diphenyltin dioxinate[11].

EXPERIMENTAL

All solvents were purified and dried. The petroleum ether used had b.p. 60–80°. Mercuric chloride (B.D.H), mercuric bromide (Riedel) and mercuric iodide (E.M) were dried in an air oven at 110° for about 12 h and stored in a vacuum desiccator. Mercuric oxide (B.D.H) was used without further purification. Triphenyltin chloride was prepared by the method of Gilman *et al.*[13] and had m.p. 106° (Found: C, 56.30; H, 3.89; Cl, 9.12; $C_{18}H_{15}ClSn$ calcd: C, 56.10; H, 3.92; Cl, 9.23%.) Bis(triphenyltin) oxide was prepared from triphenyltin chloride by Van Rij's method[14], and had m.p. 122° (Found: C, 61.10; H, 4.46; $C_{36}H_{30}Sn_2O$ calcd.: C, 60.41; H, 4.42%.) Triphenyltin hydroxide (Alpha Inorganics) was thoroughly washed with ether to remove any bis-(triphenyltin) oxide and then dried in vacuum at room temperature.

All melting points are uncorrected. All reactions were carried out in diethyl ether at room temperature unless stated otherwise.

(1). The reaction of bis(triphenyltin) oxide with mercuric chloride

Mercuric chloride (2.7 g) in 2 0 ml ether was added slowly with stirring to a solution of 7.2 g of bis(triphenyltin) oxide in 300 ml ether. A white precipitate appeared immediately. The mixture was stirred for 2 h then filtered. The residue was digested with benzene for 12 h in a Soxhlet extractor to leave 2.8 g of a white residue, which was identified as polymeric diphenyltin oxide. The benzene extract on evaporation yielded 1.7 g of crude PhHgCl (m.p. 247°). The original filtrate was then subjected to fractional crystallisation by gradual evaporation. This process first yielded 0.7 g of crude Ph-HgCl, m.p. 249°–251° (identity confirmed by analysis after repeated crystallisation from benzene. (Found: C, 22.98; H, 1.53; C_6H_5HgCl calcd.: C, 23.01; H, 1.61%.) The subsequent fractions, 1.13 g of white crystalline solid, m.p. 180–190° and 2.8 g of white crystalline solid, m.p. 100–101°, were treated with petroleum ether. The petroleum ether extracts were mixed together, and 3.1 g of crude Ph_3SnCl, m.p. 103–104°, were obtained from them. Recrystallisation from ethanol furnished pure Ph_3SnCl, m.p. 106°, the identity of which was confirmed by mixed m.p. and IR spectra[12].

The fractions insoluble in petroleum ether were mixed together and treated with 15 ml benzene, boiled, and then cooled. A small amount of PhHgCl separated and was filtered off. The filtrate on complete evaporation yielded 0.6 g of crude Ph_4Sn, m.p. 220–222°. Repeated crystallization from benzene/petroleum ether mixture furnished pure Ph_4Sn, m.p. 226°, (identity confirmed by mixed m.p. and IR spectra[12]).

(2). The reaction of bistriphenyltin) oxide with mercuric bromide

To a suspension of 1.8 g of mercuric bromide in 200 ml ether was added slowly with vigorous stirring a solution of 3.6 g of bis(triphenyltin) oxide in 300 ml ether. After about 12 h stirring the mixture was worked up as described above and the following materials were isolated:

(i). Polymeric diphenyltin oxide (1.3 g)

(ii). Phenylmercuric bromide (1.5 g), m.p. 275–276°. (Found: C, 20.58; H, 1.36. C_6H_5HgBr calcd.: C, 20.47; H, 1.40%.)

(iii) Triphenyltin bromide (1.75 g), m.p. 122°. (Found: C, 50.99; H, 3.43; Br, 18.14. $C_{18}H_{15}SnBr$ calcd.: C, 50.29; H, 3.52, Br, 18.59%.)

(iv). Tetraphenyltin (0.27 g) m.p. 226°.

(3) The reaction of bis(triphenyltin) oxide with mercuric iodide:

Bis(triphenyltin) oxide (3.5 g) in 250 ml ether was added to a solution of 2.2 g, of mercuric iodide in 700 ml ether with stirring. The mixture was then filtered and the white residue (2.7 g) was digested successively with hot benzene and THF to leave 1.4 g of diphenyltin oxide as a residue. The benzene and THF extracts were evaporated to dryness, and the residue (1.3 g, m.p. 267°) after repeated crystallisation from benzene furnished pure phenylmercuric iodide, m.p. 269°. (Found: C, 17.83, H, 1.26, I, 31.85. C_6H_5HgI calcd.: C, 17.80: H, 1.20; I, 31.43%.)

The ethereal filtrate was fractionated as described above, and the following materials were obtained:

(i). Phenylmercuric iodide (0.35 g), m.p. 267–268°.

(ii). Triphenyltin iodide (1.8 g), m.p. 121°. (Found: C, 45.48; H, 3.09. $C_{18}H_{15}$-SnI calcd.: C, 45.34; H, 3.16%.)

(iii). Tetraphenyltin (very small amount), m.p. 226°.

(4) *The reaction of triphenyltin chloride with mercuric oxide*

Red mercuric oxide (1.0 g) and 1.8 g of Ph_3SnCl in 50 ml benzene were refluxed for 8 h, on a water bath. The filtrate was evaporated to dryness, treated with petroleum ether and filtered. The fraction insoluble in the petroleum ether (0.3 g, m.p. 247°) was crystallised from benzene several times to give pure PhHgCl, m.p. 251°, and the petroleum ether extract was evaporated to yield 1.42 g of crude Ph_3SnCl, m.p. 100–103°.

The benzene insoluble fraction was treated with aqueous potassium iodide to remove unreacted mercuric oxide. The residue was digested with benzene and the white insoluble mass was shown to be polymeric diphenyltin oxide.

(5) *The reaction of mercuric chloride with the sodium salt of triphenyltin hydroxide*

In a typical experiment, 8.0 g solid triphenyltin hydroxide was slowly added with stirring under dry nitrogen to 0.6 g of sodium dispersed in 200 ml ether. The stirring was continued for 7 h and the mixture was kept overnight. It was subsequently stirred again for 2 h and 2.0 g of mercuric chloride in 200 ml ether was then added with stirring during 30 min. After a further 30 min the white precipitate (6.0 g) which had formed was filtered off and thoroughly washed successively with ether, ethanol, and water. About 5.0 g of white infusible residue (A) was left, sodium chloride passing into the ethanol and water washings. The filtrate and the ether washings were combined and concentrated, and the precipitate formed was filtered off, about 1.0 g of a white infusible substance (B) being obtained. On complete evaporation the solution furnished 3.5 g of white solid (C), m.p. 115°. The infusible residues (A) and (B) were combined and digested with benzene in a Soxhlet extractor, to leave an infusible residue, which was identified as polymeric diphenyltin oxide. From the benzene extract PhHgCl and Ph_4Sn were isolated by fractional crystallisation and the residual mother liquor was completely evaporated. The residue, m.p. 115–116°, was mixed with the fraction (C) and treated with petroleum ether. The petroleum ether extract was fractionally crystallised to give diphenyl mercury, m.p. 125°, (identified by mixed m.p.) and a small amount of Ph_3SnCl, m.p. 105°. The fraction insoluble in petroleum ether was digested with benzene, and a small amount of an infusible polymer was again left as a residue. The benzene extract was concentrated to yield a small amount of bis(triphenyltin) oxide, m.p. 120° (confirmed by mixed m.p.)

The yields of the various products varied somewhat from one experiment to another, but Ph_2SnO and Ph_2Hg were always the major products.

REFERENCES

1. C. EABORN, *Organosilicon Compounds*, Butterworth, London, 1960, p. 264.
2. A. G. DAVIES AND P. G. HARRISON, *J. Organometal. Chem.*, 10 (1967) 31.
3. H. H. ANDERSON, *J. Org. Chem.*, 19 (1954) 766.
4. S. D. ROSENBURG, *J. Amer. Chem. Soc.*, 79 (1957) 2137.
5. N. F. ORLOV, *Chem. Abstr.*, 52 (1958) 2742.
6. A. H. COWLEY, F. FAIRBROTHER AND N. SCOLL, *J. Chem. Soc.*, (1959) 717.
7. A. K. GHOSH, C. E. HANSING, I. STUTZ AND A. G. MACDIARMID, *J. Chem. Soc.*, (1962) 403.
8. C. EABORN, *J. Chem. Soc.*, (1949) 2755.
9. L. R. VYLE AND F. S. KIPPING, *J. Chem. Soc.*, 125 (1924) 2616.
10. J. A. HYDE, *Chem. Abstr.*, 47 (1953) 5720.
11. E. J. KUPCHIK AND T. LANGIAN, *J. Org. Chem.*, 27 (1962) 3661.
12. R. A. CUMMINS AND P. DUNN, Report 266, Australian Defence Scientific Service, Defence Standard Laboratories, Victoria (1963).
13. H. GILMAN AND S. D. ROSENBERG, *J. Amer. Chem. Soc.*, 74 (1952) 5580.
14. J. H. VAN RIJ, Neth. Pat. 105,831 (1953); *Chem. Abstr.*, 60 (1964) 14539.