Journal of Organometallic Chemistry, 84 (1975) 231–238

THE ACTION OF METAL HALIDES ON TETRA-, PENTA-, AND HEXA-COORDINATED ORGANOTIN COMPOUNDS

III. THE ACTION OF MERCURIC HALIDES ON ORGANOTIN OXINATES

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(Received July 15th, 1974)

Summary

The reactions of mercuric halides with some organotin oxinates have been examined. The penta-coordinated compound triphenyltin oxinate, Ph_3SnOx (Ox = Oxinate), has been shown to react readily with mercuric halides at room temperature to produce halo(phenyl)tin dioxinates, $PhSn(Ox)_2X$, phenylmercuric halides, PhHgX, and triphenyltin halides, Ph_3SnX. Similarly, the penta-coordinated compound, chloro(diphenyl)tin oxinate, $Ph_2Sn(Ox)Cl$, reacts with mercuric chloride to give dichlorotin dioxinates, $Sn(Ox)_2Cl_2$, phenylmercuric chloride and diphenyltin dichloride. The hexa-coordinated compound diphenyltin dioxinate, $Ph_2Sn(Ox)_2$, is attacked by mercuric halides only when refluxed in benzene or ether to produce halo(phenyl)tin dioxinate, $PhSn(Ox)_2X$, and phenylmercuric halides, PhHgX.

Introduction

In previous communications [1-2] the reactions of some covalent metal halides with bis(triorganotin) oxides have been discussed. The high reactivity of bis(triorganotin) oxides, in contrast to that of tetraorganotin compounds and organotin halides, towards mercuric halides has been explained by the presence in the system of the Sn—O moiety which is very suitable for the formation of transition complexes with Lewis acids [1-2]. It was, therefore, thought worthwhile to investigate the action of mercuric halides on organotin complexes such as the organotin oxinates where a similar moiety is present. Although various other chelates, e.g. those of β-diketones, salicylaldehyde, contain similar moiet-

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ies, the oxinates were preferred for the present study because of ease of preparation and stability. Another reason for this choice is the appreciable polar character of the Sn—O bonds [3] in organotin oxinates as demonstrated by the low Sn—O stretching frequency in these complexes. Polarity increases the probability of electron donation to the Lewis acid by oxygen and increases the acceptor properties of the tin atom. This favours the formation of a cyclic transition structure as proposed earlier [1-2]. The present study describes the interaction between different organotin oxinates with mercuric halides and the subsequent isolation of three halo(phenyl)tin dioxinates, viz. chloro(phenyl)tin dioxinate, bromo(phenyl)tin dioxinate and iodo(phenyl)tin dioxinate. The organotin oxinates studied were penta-coordinated triphenyltin oxinate (Ph_3SnOx, Ox = oxinate chloro(diphenyl)tin oxinate ($Ph_2Sn(Ox)Cl$) and hexa-coordinated diphenyltin dioxinate ($Ph_2Sn(Ox)_2$). The action of mercuric halides on the penta-coordinated complex has been observed to occur readily at room temperature whereas the hexa-coordinated complex reacts with mercuric halides only when refluxed in ether or benzene.

Results and discussion

From the reaction of triphenyltin oxinate and mercuric halides, HgX_2 (X = Cl, Br or I) in equimolar quantities in ether, phenylmercuric halides, triphenyltin halides and halo(phenyl)tin dioxinates have been isolated. The overall reaction in this case may be represented by eqn. 1.

$$Ph_3SnOx + HgX_2 = \frac{1}{2}Ph_3SnX + PhHgX + \frac{1}{2}PhSn(Ox)_2X \quad (1)$$

This reaction may probably proceed in the steps 2-4.

$$Ph_3SnOx + HgX_2 \rightarrow Ph_2Sn(Ox)X + PhHgX \quad (2)$$

$$Ph_2Sn(Ox)X + HgX_2 \rightarrow PhSn(Ox)X_2 + PhHgX \quad (3)$$

$$PhSn(Ox)X_2 + Ph_3SnOx \rightarrow PhSn(Ox)_2X + Ph_3SnX \quad (4)$$

Although quantitative recovery of the products from this sort of reaction is rarely possible, the separation procedure in the reaction of mercuric chloride with triphenyltin oxinate was quite simple. In this case the yields of phenylmercuric chloride, triphenyltin chloride and chloro(phenyl)tin dioxinate were in the approximate molar ratio of 2/1/1, as is consistent with the above mechanism.

As in the case of bis(triorganotin) oxides [1-2], the formation of a cyclic transition structure as shown below (Fig. 1) is likely to be the crucial step in these reactions. Such a transition state will be highly favoured for the following reasons. 1. Coordination of the mercury by the oxygen atom will decrease the electron density at the tin atom, and enhance the donating ability of the halogen atom of the mercuric halide by the increased coordination number of the mercury. The decrease of electron density at the tin atom also enhances its acceptor ability and the coordination number may then be readily increased to six. 2. The ability of the halogen atom to form $p\pi-d\pi$ bonds will stabilise the intermediate. 3. The existence of $Ph_3SnOx \cdot MeOH$ in methanolic solutions of triphenyltin oxinate [4] has been indicated from spectrophotometric investigations.

Similar intermediates have also been postulated in siloxane chemistry [5].

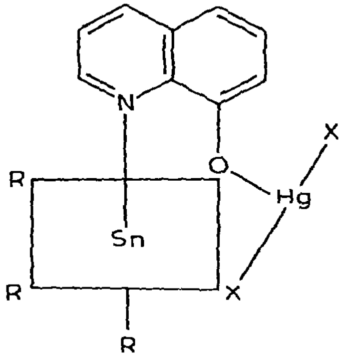

Fig. 1.

This intermediate may then undergo rearrangement similar to that of the bis(triorganotin) oxides [1-2] leading to the formation of phenylmercuric halides and halo(diphenyl)tin oxinate. The reactivity of chloro(diphenyl)tin oxinate ($Ph_2Sn(Ox)Cl$) towards mercuric chloride suggests that another phenyl group is rapidly replaced by chlorine by a similar process resulting in the formation of dichloro(phenyl)tin oxinate ($PhSn(Ox)Cl_2$). This compound may then undergo a halogen—oxinate exchange reaction with triphenyltin oxinate to form chloro(phenyl)tin dioxinate and triphenyltin chloride. Many examples of similar exchange reactions have been given by Westlake and Martin [6].

The reaction of chloro(diphenyl)tin oxinate with mercuric chloride produced dichlorotin dioxinate and diphenyltin dichloride together with phenylmercuric chloride, according to eqn. 5.

$$Ph_2Sn(Ox)Cl + HgCl_2 = \tfrac{1}{2}Sn(Ox)_2Cl_2 + PhHgCl + \tfrac{1}{2}Ph_2SnCl_2 \qquad (5)$$

The various products, as well as their relative amounts, may similarly be explained by reactions 6-8.

$$Ph_2Sn(Ox)Cl + HgCl_2 \rightarrow PhSn(Ox)Cl_2 + PhHgCl \qquad (6)$$

$$PhSn(Ox)Cl_2 + HgCl_2 \rightarrow Sn(Ox)Cl_3 + PhHgCl \qquad (7)$$

$$Sn(Ox)Cl_3 + Ph_2Sn(Ox)Cl \rightarrow Sn(Ox)_2Cl_2 + Ph_2SnCl_2 \qquad (8)$$

Unlike triphenyltin oxinate, in which the oxinate group is readily replaced by halide ions, chloro(diphenyl)tin oxinate does not easily exchange the oxinate group, rather the chlorine can be exchanged with a variety of anions. It is probably for this reason that chloro(phenyl)tin dioxinate is not formed in this reaction, since the exchange is likely to take place only after all the phenyl groups of chloro(diphenyl)tin oxinate are replaced by chlorine atoms.

The reactions of the hexa-coordinated compound diphenyltin dioxinate with the mercuric halides produces halo(phenyl)tin dioxinate, phenylmercuric halides and small amounts of dichlorotin dioxinate when refluxed in benzene. These reactions may be represented as in eqn. 9. The isolation of dichlorotin

$$Ph_2Sn(Ox)_2 + HgX_2 \rightarrow PhSn(Ox)_2X + PhHgX \qquad (9)$$

dioxinate in very small amounts is probably due to cleavage of the Sn—Ph bond

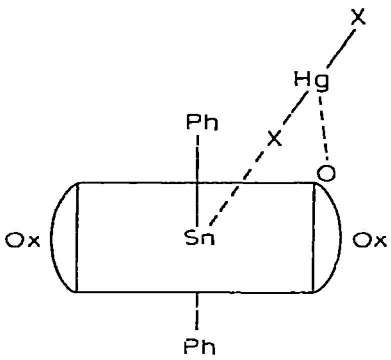

Fig. 2

of chloro(phenyl)tin dioxinate by mercuric chloride because of the higher temperature, since no dichlorotin dioxinate is formed in refluxing ether. Although the penta-coordinated organotin oxinates, like the bis(triorganotin) oxides [1-2], react readily with mercuric halides at room temperature, the hexa-coordinated diphenyltin dioxinate shows an appreciable rate of reaction only at higher temperatures. This relative inertness of diphenyltin dioxinate towards mercuric halides is consistent with the mechanism advanced. A transition state in this case would require hepta-coordination for tin which will be energetically much less favourable in comparison with the tetra-and penta-coordinated compounds. However, S_N2 type front attack as shown in Fig. 2 is more favourable than a dissociative mechanism as the formation of a weak donor-acceptor complex with the mercuric halides through the oxygen atom of the oxinate group is possible also in this case. In such a case the configuration at the tin atom will be retained. This contention is supported by the close similarity between the UV, visible and IR spectra of diphenyltin dioxinate and chloro(phenyl)tin dioxinate.

Of particular interest in the present study is the isolation of three halo(phenyl)tin dioxinates viz. chloro(phenyl)tin dioxinate, bromo(phenyl)tin dioxinate and iodo(phenyl)tin dioxinate. Of these compounds, chloro(phenyl)tin dioxinate has been reported earlier by both Faraglia et al. [7] and Nelson and Martin [8]. The chloro(phenyl)tin dioxinate obtained by us is identical in both colour and melting point to that prepared by Faraglia et al. [7] whereas it differs both in melting point and colour from the one reported by Nelson and Martin [8]. This is rather unusual since all other known organotin oxinates appear to exist in only in one form, irrespective of the method of preparation. Further, it is to be noted that it was not possible to isolate chloro(phenyl)tin dioxinate in our laboratory by the method described by Nelson and Martin [8].

The electronic absorption spectra of the three halo(phenyl)tin dioxinates, diphenyltin dioxinate and dichlorotin dioxinate are characterised by an intense absorption band in the region 245 to 270 nm and a broad band around 380 nm. The visible absorption bands were measured in benzene solution because of solubility considerations; cyclohexane was employed as a solvent for the UV region. Due to the very low solubility of the halo(phenyl) dioxinates in cyclohexane the molar extinctions could not be estimated for the UV absorption bands. These data are shown in Table 1.

TABLE 1 [a]

Compound	λmax (nm)
$PhSn(Ox)_2Cl$	262,380 (3.71)
$PhSn(Ox)_2Br$	260,380 (3.75)
$PhSn(Ox)_2I$	260,380 (3.77)
$Ph_2Sn(Ox)_2$	260,380 (3.76)
$Sn(Ox_2)Cl_2$	245,385

[a] Figures in parentheses are log ϵ max.

The close similarity in the spectra of the halo(phenyl)tin dioxinates and diphenyltin dioxinate indicates not only hexa-coordination [9] but also a general similarity in their structures. The spectra of dichlorotin dioxinate is, however, slightly different. Although the detailed structures of diphenyltin dioxinate and dichlorotin dioxinate are not known, *trans* configuration has been suggested for the former on the basis of IR, NMR, dipole moment [11] and optical resolution studies [8] and a *cis* configuration for the latter from IR studies [9]. These considerations suggest the *trans* configuration for the halo(phenyl)tin dioxinates. However, the existence of rigorously defined *cis* and *trans* forms is probably meaningless in view of the recent structural determination of dimethyltin dioxinate by Schlemper [12]. This compound, which was believed to have a *trans* geometry from various physico-chemical studies, has been shown to possess a highly distorted structure where the terms *cis* and *trans* have little relevance. In fact, Schlemper [12] deduced that dimethyltin dioxinate has a distorted tetrahedral structure. The possibility of the variation in the angle between the planes of the two oxinate groups cannot be ruled out. Such a variation will alter the extent of interaction between the two oxinate groups resulting in slight changes in the UV and visible spectra.

The spectra of all the oxinate derivatives are very similar in the region 300 to 4000 cm^{-1} except for two broad bands at 311 and 325 cm^{-1} in the case of dichlorotin dioxinate which have been assigned to Sn—Cl stretching modes by Douek et al. [11]. A broad strong band at 302 cm^{-1} is also present in the spectra of chloro(phenyl)tin dioxinate. This band, which is not present in the spectra of any other oxinate derivatives, may be assigned to ν(Sn—Cl). Since the Sn—Br and Sn—I modes are known to appear at much lower frequencies (below 250 cm^{-1} in most cases) the spectra of bromo(phenyl)tin dioxinate and iodo(phenyl)tin dioxinate are very similar to that of diphenyltin dioxinate in the region studied. The strong band in the region 500-530 cm^{-1} has been assigned to the Sn—O frequency as no strong band is present in this region in the spectra of phenyltin halides or of oxine. The same bands have been assigned to Sn—O stretching modes by Okawara et al. [3].

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. Diphenyltin dichloride (Theodore Schuchardt, München) was used without further purification. Triphenyltin oxinate was prepared by the reaction of bis(triphenyltin) oxide with oxine in methanol. The product was recrystallised several times from methanol and dried in vacuum for 48 h, m.p. 150°. (Found: C, 65.31; H, 4.25; N, 2.90. $C_{27}H_{21}NOSn$ calcd.: C, 65.64; H, 4.28; N, 2.84%.) Chloro(diphenyl)tin dioxinate was prepared according to the method of Westlake and Martin [6]. All melting points are uncorrected. All reactions were carried out in diethyl ether at room temperature unless stated otherwise.

The reaction of triphenyltin oxinate with mercuric chloride

A solution of mercuric chloride (2.2 g) in 200 ml ether was added slowly with stirring to a solution of triphenyltin oxinate (4.0 g) in 400 ml ether at room temperature. After 2 h stirring the mixture was filtered to obtain 3.4 g yellow residue, m.p. 195° (Ia). The filtrate on gradual concentration yielded successively impure phenylmercuric chloride (0.37 g, m.p. 247°) and a yellow crystalline solid, m.p. 198° (Ib). Finally, the filtrate was evaporated to dryness, treated with cold petroleum ether and filtered. The petroleum ether solution produced triphenyltin chloride (1.5 g, m.p. 105°) on evaporation. The petroleum ether-insoluble fraction and fractions Ia and Ib were mixed together, boiled with ethanol and quickly filtered while hot to obtain a yellow residue (0.5 g, m.p. 217°) which on repeated crystallisation from benzene/petroleum ether mixture afforded a crystalline solid, m.p. 218°, identified as chloro(phenyl)tin dioxinate as described earlier. (Found: C, 55.68; H, 3.04; N, 5.16. $C_{24}H_{17}ClN_2O_2Sn$ calcd.: C, 55.50; H, 3.30; N, 5.39%.) The ethanolic filtrate on concentration yielded phenylmercuric chloride (1.9 g, m.p. 247°) and crude chloro(phenyl)tin dioxinate (m.p. 213°).

The reaction of chloro(diphenyl)tin oxinate with mercuric chloride

Mercuric chloride (1.0 g) in 100 ml ether was added to a solution of chloro(diphenyl)tin oxinate in 100 ml ether with stirring. The mixture was stirred for 8 h then filtered to produce 1.37 g of a yellow residue (IIa). The ethereal filtrate was fractionated to yield phenylmercuric chloride (0.5 g, m.p. 247°) and a pale yellow solid (0.7 g) which was further treated with cold petroleum ether and filtered. The petroleum ether-insoluble yellow residue (0.1 g) was mixed with the yellow solid (IIa) and repeatedly digested with hot ether. On evaporation the ether extracts yielded crude phenylmercuric chloride (0.62 g, m.p. 241°). The ether-insoluble residue was characterised as dichlorotin dioxinate from elemental analysis. (Found: C, 44.10; H, 2.44; Cl, 14.79; N, 5.58. $C_{18}H_{12}Cl_2N_2O_2Sn$ calcd.: C, 45.26; H, 2.53; Cl, 14.85; N, 5.87%.) IR and UV spectra were run after crystallisation from dimethyl formamide/chloroform mixture. The petroleum ether extract was concentrated to low volume and cooled in ice to yield diphenyltin dichloride (0.58 g, m.p. 43°).

The reaction of diphenyltin dioxinate with mercuric chloride

A mixture of diphenyltin dioxinate (1.12 g) and mercuric chloride (0.54 g) in 100 ml benzene was refluxed for 6 h over a water bath and then filtered. The yellow residue (III) was digested with ether and filtered to afford dichlorotin dioxinate (0.13 g) (infusible up to 360°), identity confirmed by analysis after repeated crystallisation from dimethyl formamide/chloroform mixture. (Found: C, 44.86; H, 2.90; N, 5.72. $C_8H_{12}Cl_2O_2Sn$ *calcd.*: C, 45.26; H, 2.53; N, 5.87%.) The benzene filtrate and ether extract together were subjected to fractionation to yield phenylmercuric chloride (0.3 g, m.p. 249°) and a yellow solid (1.2 g) which was treated with methanol/chloroform mixture (4/1) and filtered. The white residue was identified as crude phenylmercuric chloride (0.4 g, m.p. 249°). The filtrate on evaporation afforded chloro(phenyl)tin dioxinate (0.78 g, m.p. 217-218°, identity confirmed by mixed m.p. and IR spectra).

The same reaction when carried out in refluxing ether gave identical products except for the fact that no dichlorotin dioxinate was formed.

The reaction of triphenyltin oxinate with mercuric bromide

1.0 g mercuric bromide was added to a solution of 1.4 g of triphenyltin oxinate in 300 ml ether. The mixture was stirred for 8 h at room temperature and then filtered. 0.8 g pale yellow residue, m.p. 235° (IVa) obtained was washed with petroleum ether. The original filtrate was subjected to fractional crystallisation by gradual evaporation. This process first yielded 0.85 g pale yellow crystals m.p. 190° (IVb) and then a solid (0.68 g, m.p. 115°, IVc). Fraction IVb was also washed with petroleum ether. The petroleum ether washings from fractions IVa and IVb were added to the fraction IVc, boiled, cooled and then filtered. The filtrate on evaporation produced crude triphenyltin bromide, m.p. 118° (0.57 g, identity confirmed by mixed m.p. after recrystallisation from petroleum ether, m.p. 122°). Residue IVa was digested with 10 ml hot benzene and cooled to leave a crude phenylmercuric bromide, m.p. 270° (0.65 g, identity confirmed by mixed m.p. after crystallisation from benzene). Fraction IVb and the petroleum ether-insoluble fraction from fraction IVc were added to the benzene filtrate, boiled, cooled and filtered. The residue (0.3 g, m.p. 265°) was crude phenylmercuric bromide. The filtrate was treated with petroleum ether to obtain a yellow precipitate. This precipitate was further dissolved in the minimum volume of benzene and petroleum ether was then added to precipitate the yellow substance again. On repeating this procedure twice further a yellow solid (m.p. 157-158°) was obtained which was characterised as bromo(phenyl)tin dioxinate from elemental analysis (Found: C, 51.16; H, 3.15; N, 4.66. $C_{24}H_{17}BrN_2O_2Sn$ calcd.: C, 51.21; H, 3.04; N, 4.98%), UV, IR spectra as discussed before.

The reaction of diphenyltin dioxinate with mercuric bromide

1.4 g of diphenyltin dioxinate and 0.9 g of mercuric bromide in 300 ml ether was refluxed for 12 h on a water bath. The solvent was removed by slow evaporation and the residue was dissolved in benzene, filtered, concentrated to a small volume (10 ml) and filtered again after cooling. The white crystalline residue (0.7 g, m.p. 270°) was washed with cold benzene and identified as phenylmercuric chloride (mixed m.p.). The filtrate was concentrated further and a second crop of phenylmercuric bromide was separated. It was filtered off and to the filtrate petroleum ether was added to produce crude bromo(phenyl)tin dioxinate (m.p. 150°-157°, identity confirmed by mixed m.p. and IR spectra after purification by reprecipitation as described in the previous section).

The reaction of triphenyltin oxinate with mercuric iodide

A mixture of solutions of 1.66 g of triphenyltin oxinate in 200 ml ether and 1.5 g of mercuric iodide in 600 ml ether was stirred for 6 h at room temperature and then filtered. The filtrate was slowly evaporated to dryness and further treated with petroleum ether. The petroleum ether-soluble fraction gave 0.65 g triphenyltin iodide, m.p. 121° (identify confirmed by mixed m.p.). The petroleum ether-insoluble residue and initial ether-insoluble residues were mixed together and dissolved in benzene. On concentration of the benzene solution first phenylmercuric iodide (1.2 g, m.p. 268-269°) was separated out (identified by mixed m.p.). Finally, the filtrate was treated with cold petroleum ether when a yellow solid (0.82 g, m.p. 208-210°) was separated out. It was again dissolved in the minimum volume of benzene and reprecipitated by the addition of petroleum ether. This yellow solid was characterized as iodo(phenyl)tin dioxinate (m.p. 212°) from elemental analysis (Found: C, 46.67; H, 2.97; N, 4.18. $C_{24}H_{17}IN_2O_2Sn$ calcd.: C, 47.21; H, 2.81; N, 4.59%) and IR and electronic spectra as described earlier.

The reaction of diphenyltin dioxinate with mercuric iodide

A mixture of diphenyltin dioxinate (1.4 g) and mercuric iodide (1.16 g) in 300 ml ether was refluxed for 3 h on a water bath and then filtered. The filtrate was evaporated to dryness, and the solid obtained was dissolved in the minimum volume of hot benzene, cooled and filtered. From the benzene filtrate iodo(phenyl)tin dioxinate (m.p. 212°, identity by mixed m.p. and IR spectra) was recovered by petroleum ether treatment as described in the previous reaction. The initial residue and benzene-insoluble residue together were treated with benzene, boiled, and cooled. On cooling, phenylmercuric iodide (m.p. 268-269°) separated out (identified by mixed m.p.). From the benzene filtrate another crop of iodo(phenyl)tin dioxinate was isolated by petroleum ether treatment as before.

Acknowledgements

The authors are indebted to Dr. A.D.E. Pullin, Department of Chemistry, Monash University, Clayton, Victoria, Australia, and Dr. A. Chakraborty, I.I.T. Kanpur, India for the IR spectra and Dr. J. Das, Chemistry Dept., Burdwan University, Burdwan, India for the UV spectra. Thanks are also due to the University of North Bengal for the award of a research scholarship to D.D.

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