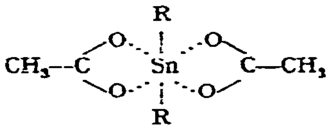
Preparation and properties of dialkyltin chloride carboxylates

The preparation of trialkyltin carboxylates and dialkyltin dicarboxylates has been well studied[1]. Increasing interest has recently been devoted to the question of the structure of these organotin derivatives, and the characteristic feature of penta- or hexacoordinated tin atom has been made clear in several reports. It was of interest to us to prepare and to determine the structure of another type of carboxylate, $ClR_2SnOOCR'$, in which one of the three alkyl groups in the trialkyltin carboxylate is replaced by a chlorine atom.

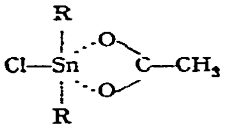
There is very little previous literature on the preparation of dialkyltin halide carboxylates, $XR_2SnOOCR'$. Okawara and Rochow[2] prepared dimethyltin chloride acetate, $ClMe_2SnOOCCH_3$, from dimethyltin dichloride and acetic anhydride, or from tetramethyl-1,3-dichlorodistannoxane, $ClMe_2SnOSnMe_2Cl$, and acetic acid. They also obtained dimethyltin chloride formate, $ClMe_2SnOOCH$, by the reaction of formic acid and sodium formate with dimethyltin dichloride, or by the reaction of formic acid and $ClMe_2SnOSnMe_2Cl$. Alleston and Davies[3] prepared dibutyltin bromide acetate by the reaction of dibutyltin dibromide and dibutyltin diacetate. We wish to report the preparation and properties of the other new dialkyltin chloride acetates and formates.

Each acetate investigated here is easily obtained in almost quantitative yield by refluxing $ClR_2SnOSnR_2Cl$ in acetic acid or acetic anhydride. By the analogous procedure with formic acid, we can obtain dimethyltin chloride formate, but in the case of ethyl-, *n*-propyl- and *n*-butyl-derivatives the corresponding chloride formate monohydrate, $ClR_2SnOOCH \cdot H_2O$, is obtained in good yield. Cryoscopic measurement of molecular weight in benzene shows that these ethyltin and *n*-propyltin acetates are monomeric. The hydrated compounds release their water in benzene, and it is difficult to measure their molecular weight.

It was found for trialkyltin acetate[4,5,6], laurate[6] and formate[4,5,7] in the solid state that a tin atom is weakly coordinated by two oxygen atoms, forming a linear chain in which the planar C_3Sn group is bridged by the –OCO– unit having C_{2v} symmetry. This weak bridging in the acetate[5] or the laurate[6] is destroyed in a non-polar solvent to give monomeric trialkyltin carboxylate with the ester type of carboxyl group, while in the case of the formate[7] a part of this bridging still remains in solution. On the other hand, dialkyltin dicarboxylates[5], which are liquid at room temperature and monomeric in benzene or cyclohexane, contain the hexa-coordinated tin atom with C_{2v} symmetry of –OCO– unit in carboxyl group, both in liquid state and in solution, and it was suggested that the diacetate has a chelate-type structure, at least in solution, as shown in (a). For the compounds investigated here, infrared spectra in the solid state show one of the characteristic bands associated with the acetoxy group at 1540–1565 cm^{-1} and the band associated with the formoxy group at 1595–1605 cm^{-1}. This band in acetates shifts to 1600 cm^{-1} in CCl_4 or benzene solution, indicating some structural changes on solution, but still suggesting a non-ester type of acetoxy group. Accordingly, we tentatively suggest that the structure of these acetates in solution is represented as shown in (b), in which the tin atom is penta-coordinated: two carbon atoms in alkyl groups, a chlorine atom and two oxygen atoms in acetoxy group.



(a)



(b)

Further details concerning the structure of these and the hydrated compounds are under being studied in our laboratory.

Experimental

Materials. The tetraalkyl-1,3-dichlorodistannoxanes (R = Et, *n*-Pr, *n*-Bu) were prepared as described elsewhere[8].

Preparation of dialkyltin chloride acetates. Tetraethyl-1,3-dichlorodistannoxane (1 g) in acetic acid (3 ml) was heated on water bath for ten minutes. From the clear solution obtained, an excess of acetic acid was distilled off under reduced pressure. The residual solid was either recrystallized from acetic acid or sublimed. Analysis of the product melting at 94° showed that it was $ClEt_2SnOOCCH_3$. The other dialkyltin chloride acetates shown in Table 1 could be obtained by this procedure.

TABLE 1

DIALKYLTIN CHLORIDE ACETATES: $ClR_2SnOOCCH_3$

R	*M.p. (°C)*	*% Sn Found (Calcd.)*	*% C Found (Calcd.)*	*% H Found (Calcd.)*
Et	94	43.81 (43.75)	26.59 (26.58)	4.90 (4.83)
n-Pr	73	39.86 (39.65)	31.97 (32.10)	5.70 (5.72)
n-Bu	61	36.53 (36.25)	36.39 (36.68)	6.39 (6.47)

Acetic anhydride could be used instead of acetic acid, giving the same results. Recrystallization of $Cl(n\text{-}Pr)_2SnOOCCH_3$ from methanol gave $Cl(n\text{-}Pr)_2SnOSn(n\text{-}Pr)_2Cl$ by hydrolysis.

Preparation of dialkyltin chloride formate monohydrates. Tetra-*n*-butyl-1,3-dichlorodistannoxane (1 g) was refluxed with formic acid (3 ml) for ten minutes, formic acid then being distilled off under reduced pressure. The residual solid was recrystallized from formic acid. Analysis of the product melting at 69° agreed well with $Cl(n\text{-}Bu)_2SnOOCH \cdot H_2O$, as shown in Table 2.

The spectra of the hydrated chloride formates in nujol show a very strong and broad band near 3140 cm^{-1}, indicating the existence of coordinated water. These compounds decompose in the course of sublimation, giving a solid of broad melting range.

Determination of molecular weight. The molecular weights were determined cryoscopically in benzene. Calcd. for $ClEt_2SnOOCCH_3$: M, 271.3; found: M, 288, 290, 281 at concentrations [w(sample)/W(solvent)], 0.018, 0.011 and 0.004, respectively. Calcd.

for $Cl(n\text{-}Pr)_2SnOOCCH_3$: M, 299.4; found: M, 319, 313, 315 at concentrations 0.033, 0.025 and 0.016, respectively.

TABLE 2

DIALKYLTIN CHLORIDE FORMATE MONOHYDRATES: $ClR_2SnOOCH \cdot H_2O$

R	*M.p. (°C)*	*% Sn Found (Calcd.)*	*% C Found (Calcd.)*	*% H Found (Calcd.)*
Et	82	43.27 (43.11)	21.47 (21.81)	4.67 (4.76)
n-Pr	81	39.22 (39.13)	27.99 (27.72)	6.00 (5.65)
n-Bu	69	35.89 (35.12)	33.09 (32.62)	6.53 (6.39)

Summary

The reactions of tetraalkyl-1,3-dichlorodistannoxanes, $ClR_2SnOSnR_2Cl$, (R = Et, *n*-Pr, *n*-Bu) with acetic acid, acetic anhydride or formic acid have been studied. Both acetic acid and acetic anhydride gave crystalline dialkyltin chloride acetates, $ClR_2SnOOCCH_3$, with good yield. Formic acid gave monohydrated dialkyltin chloride formates, $ClR_2SnOOCH \cdot H_2O$. They are all new compounds. From the results of infrared spectra and molecular weight determination in solution, the presence of penta-coordinated tin atom in a monomeric $ClR_2SnOOCCH_3$ was suggested.

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