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SCHIFF BASE COMPLEXES OF ORGANOTIN(IV). REACTIONS OF TRIALKYLTIN(IV) CHLORIDES AND ALKOXIDES WITH *N*-SUBSTITUTED SALICYLIDENEIMINES

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Summary

Eighteen new volatile *N*-substituted salicylideneiminatotrialkyltin derivatives have been synthesized by the reactions of trialkyltin chlorides or alkoxides with the corresponding Schiff bases. On the basis of infrared and proton magnetic resonance measurements, five coordination is proposed for tin in these complexes.

Introduction

There has been much interest in the syntheses and structures of organotin(IV) complexes of anionic Schiff base ligands in recent years. Since the first reports by Barbieri and coworkers [1] on the synthesis of *N,N'*-ethylenebis(salicylideneiminato)dimethyltin, the work has been repeated by three different groups [2—4] and the structure of the compound has been fully elucidated [5—8]. Complexes of diorganotin(IV) moieties with dianionic terdentate Schiff base ligands have also been synthesized and characterized by various physico-chemical techniques [9—13]. In this paper, we describe the reactions of trialkyltin chlorides and alkoxides with *N*-substituted salicylideneimines.

Results and discussion

Reactions of trialkyltin alkoxides with *N*-substituted salicylideneimines in a 1 : 1 molar ratio in refluxing benzene proceed with the liberation of alcohol

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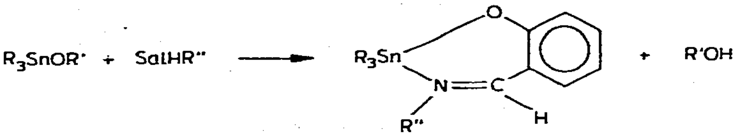
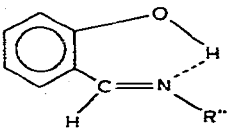
according to the following equation:



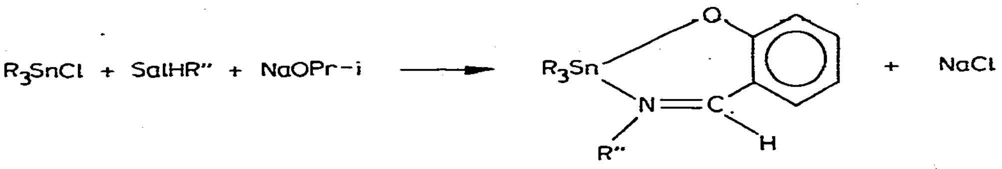
where SalHR'' =



(R = n-Pr,n-Bu,R'=Et,i-Pr; R''=Me,Et,i-Pr,Allyl,n-Bu)

The reactions were forced to completion by the fractionation out of the liberated alcohol (ethanol or isopropanol) azeotropically with benzene during 8—10 hours, and the completeness of the reaction was checked by the determination of alcohol in the azeotrope by an oxidimetric method [14].

Reactions of trialkyltin(IV) chlorides with the sodium salt of N-substituted salicylideneimines in dry isopropanol also yield similar products. The sodium salts of the salicylideneimines for these reactions were prepared by adding the requisite amount of ligand to a solution of sodium in isopropanol:



(R = Et,n-Pr,n-Bu,R''=Me,Et,i-Pr,Allyl,n-Bu,Ph)

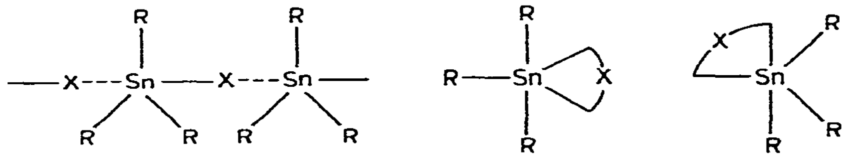
All these compounds are yellow, volatile liquids. These are highly sensitive to moisture. Molecular weight measurements of some of them in refluxing benzene show them to be monomeric. Infrared and proton magnetic resonance studies indicate that the tin atom has a coordination number five.

In the PMR spectra of the free ligands [15—18] the resonance signal due to intramolecularly hydrogen bonded OH, occurs at δ12.4—14.0 ppm. This signal is not present in the PMR spectra of these new organotin(IV) complexes. A weak broad band in the region 2800—2600 cm^{-1}, which has been assigned to the intramolecularly hydrogen bonded OH in the Schiff bases [19—21], is not observed in the infrared spectra of these complexes. The phenolic C—O stretching vibration of the ligands at 1280 cm^{-1}, which generally shifts towards higher frequencies on replacement of a hydrogen atom by a metal atom [22—24], appears at ~1300 cm^{-1} in the infrared spectra of complexes, indicating the formation of a Sn—O bond with the *ortho* hydroxy group of the Schiff base.

The C=N stretching vibration observed in the region 1616—1645 cm^{-1} in the IR spectra of the free ligands [17,18,24,25] occurs at almost unchanged positions in the spectra of these complexes. It has been reported that on chelation, the C=N stretching vibration of the Schiff base is very little changed [21]. However, a slight downfield shift for the —CH=N signal in the PMR spectra does indicate the coordination of azomethine nitrogen with the tin atom.

The Sn—C stretching vibrations generally occur in the range 610—450 cm^{-1}. The ν_{as}(Sn—C) and ν_s(Sn—C) in triethyltin compounds occur at 510 ± 10 and 485 ± 10 cm^{-1} as a strong intensity band and a shoulder, respectively [26]. The new triethyltin derivatives exhibit strong intensity bands at 510 ± 10 cm^{-1} for ν_{as}(Sn—C) vibrations. All the new tripropyltin and tributyltin derivatives exhibit two bands at 600 ± 10 and 510 ± 10 cm^{-1} which may be assigned to the Sn—C asymmetric stretching vibrations of *trans* and *gauche* conformations respectively [27]. Following the assignments made in the region 662—700 cm^{-1} in trialkyltin alkoxides [28] to Sn—CH_2 rocking vibrations, bands near 680 ± 10 and 660 ± 10 cm^{-1} in these new derivatives may also be assigned to Sn—CH_2 rocking vibrations associated with *gauche* and *trans* conformations, respectively. ν(Sn—O) has been empirically estimated by Poller [29] to occur at 570 cm^{-1} and the range 550—570 cm^{-1} has been suggested [30]. In trialkyltin alkoxides [28,31], the tin—oxygen stretching frequencies have been reported to occur as a strong band in the range 530—470 cm^{-1}. The intensity and broadness of the bands in the region 510 ± 10 cm^{-1} may be attributed to the coupling of ν(Sn—O) and ν(Sn—C) in these complexes.

Complexes of the type R_3SnX and R_3SnXY of five coordinate tin are known [32] to have trigonal bipyramidal structures with a planar trioganotin moiety and with the more electronegative groups occupying the axial positions. However, very recently, five coordinate trimethyltin and triphenyltin derivatives have been reported to have *mer-* and *all-cis* structures, respectively, on the basis of Mössbauer [33—36] and X-ray diffraction studies [36,37]:


planar mer all-cis

In view of the observed monomeric nature of the complexes synthesized during the present investigations, these may be assigned either the *cis* or the *mer* structures. A choice between the two would only be possible by further physicochemical studies, e.g. Mössbauer spectroscopy.

Experimental

Special precautions were taken to exclude moisture. Benzene, methanol, ethanol and isopropanol were dried by usual methods. Pr_3SnOEt and Bu_3SnOPr-i were prepared by the sodium method and Schiff bases by literature methods [16,17].

Molecular weights were determined ebullioscopically in boiling benzene with a semimicro Gallenkamp ebulliometer employing thermistor sensing. Refractive

(continued on p. 160)

TABLE 1

REACTIONS OF TRIALKYLTIN ALKOXIDES WITH SCHIFF BASES

$R_3Sn(OR')$ (g)	Schiff base SalHR″ (g)	Molar ratio of the reactants	Amount of alcohol in azeotrope (g) Found (calc.)	B.p. of the product (°C/mmHg)	Yield of distilled product Found (calc.) (g)	Product formed	Refractive index n_D^{36}	Analyses (Found (calcd.)) (%)	
								Sn	N
n-Pr_3SnOEt (2.33)	R″ = Me (1.07)	1 : 1	0.34 (0.37)	148/0.05	2.74 (3.03)	n-Pr_3SnSalMe	1.52732	31.20 (31.05)	3.40 (3.66)
n-Pr_3SnOEt (2.13)	R″ = Et (1.09)	1 : 1	0.30 (0.33)	142/0.01	2.49 (2.88)	n-Pr_3SnSalEt	1.52032	29.81 (29.96)	3.33 (3.53)
n-Pr_3SnOEt (2.07)	R″ = Allyl (1.34)	1 : 1	0. 30 (0.32)	172/0.05	2.60 (2.88)	n-Pr_3SnSalAllyl	1.53548	29.30 (29.08)	3.20 (3.43)
n-Pr_3SnOEt (2.22)	R″ = i-Pr (1.24)	1 : 1	0.30 (0.35)	142/0.01	2.40 (3.11)	n-Pr_3SnSaPr-i	1.51334	28.80 (28.94)	3.28 (3.41)
n-Pr_3SnOEt (2.02)	R″ = n-Bu (1.22)	1 : 1	0.28 (0.32)	176/0.2	2.77 (2.91)	n-Pr_3SnSalBu-n	1.52139	27.70 (27.98)	3.09 (3.30)
n-Bu_3SnOPr-i (2.02)	R″ = Me (0.78)	1 : 1	0.29 (0.35)	176/0.4	2.07 (2.46)	n-Bu_3SnSalMe	1.51333	27.85 (27.98)	3.22 (3.30)
n-Bu_3SnOPr-i (1.78)	R″ = Et (0.76)	1 : 1	0.26 (0.30)	146/0.1	1.90 (2.23)	n-Bu_3SnSalEt	1.51037	27.20 (27.09)	3.10 (3.20)
n-Bu_3SnOPr-i (1.95)	R″ = Allyl (0.72)	1 : 1	0.30 (0.34)	186/0.4	1.72 (2.33)	n-Bu_3SnSalAllyl	1.50442	26.50 (26.37)	3.01 (3.11)
n-Bu_3SnOPr-i (1.84)	R″ = i-Pr (0.86)	1 : 1	0.27 (0.32)	149/0.05	1.99 (2.37)	n-Bu_3SnSalPr-i	1.50439	26.10 (26.25)	3.20 (3.10)

TABLE 2

REACTIONS OF TRIALKYLTIN CHLORIDES WITH SCHIFF BASES IN PRESENCE OF NaOPr-i IN DRY ISOPROPANOL

R_3SnCl (g)	Schiff base SalHR″ R″ = (g)	Sodium (g)	Molar ratio of the reactants	B.p. of the product (°C/mmHg)	Yield of distilled product Found (Calc.) (g)	Product formed	Refractive index n_D^{36}	Analyses (found (calcd.)) (%)	
								Sn	N
Et_3SnCl (2,52)	R″ = Me (1,41)	0,24	1 : 1 : 1	144/0,2	2,95 (3,50)	$Et_3SnSalMe$	1,52735	34,75 (34,91)	4,30 (4,12)
Et_3SnCl (2,50)	R″ = Et (1,55)	0,24	1 : 1 : 1	162/0,4	3,30 (3,70)	$Et_3SnSalEt$	1,55025	33,40 (33,54)	3,72 (3,96)
Et_3SnCl (2,51)	R″ = Allyl (1,68)	0,24	1 : 1 : 1	160/0,4	2,60 (3,90)	$Et_3SnSalAllyl$	1,54437	32,27 (32,43)	3,89 (3,82)
Et_3SnCl (2,33)	R″ = i-Pr (1,57)	0,22	1 : 1 : 1	145/0,2	2,90 (3,54)	$Et_3SnSalPr$-i		32,41 (31,26)	3,65 (3,81)
Et_3SnCl (2,35)	R″ = n-Bu (1,73)	0,22	1 : 1 : 1	150/0,05	3,20 (3,73)	$Et_3SnSalBu$-n		31,20 (31,07)	3,50 (3,66)
Et_3SnCl (2,45)	R″ = Ph (2,00)	0,23	1 : 1 : 1	190/0,1	3,78 (4,09)	$Et_3SnSalPh$	1,59427	29,60 (29,53)	3,31 (3,48)
n-Pr_3SnCl (2,05)	R″ = Ph (1,43)	0,17	1 : 1 : 1	200/0,05	2,64 (3,22)	n-$Pr_3SnSalPh$	1,58025	26,62 (26,74)	3,01 (3,15)
n-Bu_3SnCl (2,53)	R″ = n-Bu (1,38)	0,18	1 : 1 : 1	178/0,05	3,10 (3,60)	n-$Bu_3SnSalBu$-n	1,50635	25,34 (25,46)	3,18 (3,00)
n-Bu_3SnCl (2,41)	R″ = Ph (1,46)	0,17	1 : 1 : 1	214/0,2	2,80 (3,60)	n-$Bu_3SnSalPh$	1,52733	24,35 (24,42)	2,74 (2,88)

indices were measured with a Carl Zeiss (Jena) Refractometer. Infrared spectra were recorded on a Perkin—Elmer 337 instrument in the range 4000—400 cm^{-1}, as neat liquids, using KBr optics. PMR spectra were run on a Perkin—Elmer R12B spectrometer working at 60 MHz, in carbon tetrachloride solutions using TMS as an external standard.

The ethanol and isopropanol in the azeotrope were estimated by an oxidimetric method [14]. Tin was estimated as SnO_2 by hydrolysing the weighed amount of sample with a few drops of conc. H_2SO_4 and HNO_3, the acids were evaporated on a low flame and finally, the residue was ignited to weigh as SnO_2. Nitrogen was estimated by the Kjeldahl method.

Reaction of tripropyltin ethoxide with N-methylsalicylideneimine in (1 : 1) molar ratio in dry benzene

A mixture of tripropyltin ethoxide and *N*-methylsalicylideneimine was refluxed in anhydrous benzene and the ethanol liberated was removed azeotropically and determined. Excess benzene was removed and the product was distilled under reduced pressure. Reactions of tributyltin isopropoxide with *N*-substituted salicylideneimines were carried out similarly. The results are shown in Table 1.

Reactions of triethyltin chloride with sodium salt of N-methylsalicylideneimine in 1 : 1 molar ratio in dry isopropanol

Sodium salt of *N*-methylsalicylideneimine was first prepared by adding a calculated amount of *N*-methylsalicylideneimine to a fresh solution of sodium in isopropanol. Methanol was added to dissolve the sodium salt and the solution was refluxed for an hour followed by the addition of triethyltin chloride. A vigorous reaction took place and sodium chloride precipitated instantaneously. The mixture was refluxed for one hour more and then cooled. Sodium chloride was filtered off and the filtrate was evaporated under vacuum. The crude product was purified by distillation under reduced pressure. Results are shown in Table 2.

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