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SCHIFF BASE COMPLEXES OF ORGANOTIN(IV): REACTIONS OF TRIMETHYLTIN HYDROXIDE AND TRIALKYLTIN ETHOXIDES WITH BENZOTHIAZOLINES

B.S. SARASWAT, G. SRIVASTAVA and R.C. MEHROTRA *
Chemical Laboratories, University of Rajasthan, Jaipur-302004 (India)
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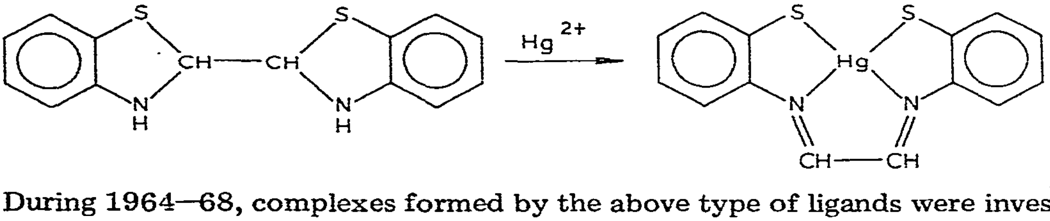
Summary

Twenty-three new volatile trialkyltin derivatives of sulphur containing Schiff bases have been synthesized by the reactions of trimethyltin hydroxide and trialkyltin ethoxides with 2,2-disubstituted benzothiazolines. On the basis of molecular weight measurements and infrared and proton magnetic resonance spectra, five coordination at tin is proposed for these complexes.

Introduction

It has been known for a long time that the condensation of *o*-aminobenzenethiol with carbonyl compounds yields benzothiazolines or benzothiazoles depending upon the nature of the carbonyl compound and the reaction conditions [1—10]. Bayer [11] first reported in 1961 that in the presence of mercuric ions, bis-benzothiazoline rearranged to the corresponding Schiff base and the mercury complex of the Schiff base could be isolated (eq. 1).



(1)

During 1964—68, complexes formed by the above type of ligands were investigated [12—15] for a number of metals (Ni, Zn and Cd). More recently (1970—74), the work was extended to the derivatives of diorganotin(IV) and monoorganotin(IV) with benzothiazolines, synthesized by the condensation of *o*-amino-

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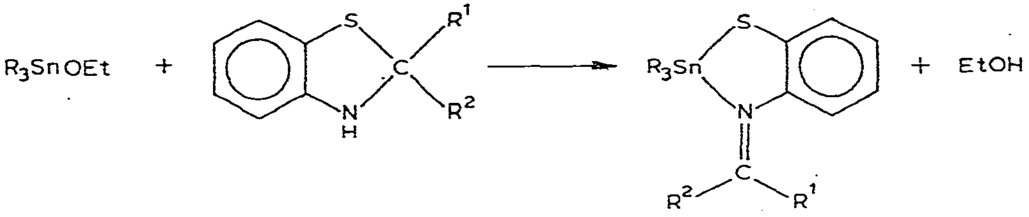
* All enquiries should be addrressed to this author at his present address: Vice-Chancellor, University of Delhi, Delhi-110007 (India).

benzenethiol with salicylaldehyde and acetylacetone [10,16,17] by IR, PMR and Mössbauer spectroscopy; the crystal structure of diphenyltin-2-[{(2-sulphidophenyl)imino}methyl]phenolate was also elucidated [18].

In continuation of our previous work [19] on the synthesis of *N*-substituted salicylideneiminatotrialkyltin(IV) derivatives, we report here the results of our studies on trialkyltin(IV) derivatives of 2,2-disubstituted benzothiazolines derived from *o*-aminobenzenethiol and simple ketones.

Results and discussion

Reactions of trialkyltin ethoxides with 2,2-disubstituted benzothiazolines in 1/1 molar ratio in refluxing benzene proceed with the liberation of ethanol according to equation 2. The completion of the reaction was checked by the estimation (by an oxidemetric method [20]) of ethanol in the azeotrope collected during 6—8 h of fractionation.

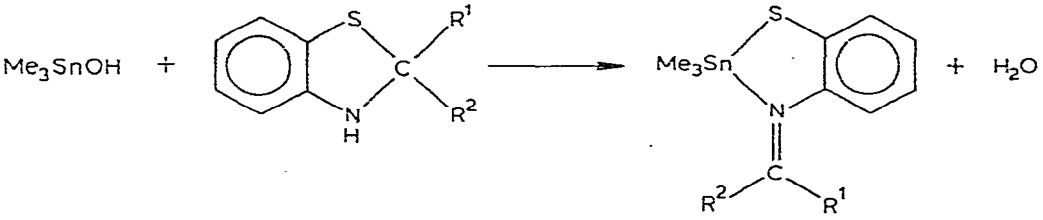


(2)

(R = Et, n-Pr, n-Bu; R^1 = Me, R^2 = Me, Et, i-Bu, Ph;

R^1 = Et, R^2 = Et, n-Bu)

Trimethylin derivatives of the above benzothiazolines were synthesized by the reactions of trimethyltin hydroxide with benzothiazolines in 1/1 molar ratio in refluxing benzene. The reactions were comparatively slow, but could be taken to completion by continuous removal of water as an azeotrope with benzene (eq. 3).



(3)

(R^1 = Me, R^2 = Me, Et, i-Bu, Ph; R^1 = Et, R^2 = Et, n-Bu)

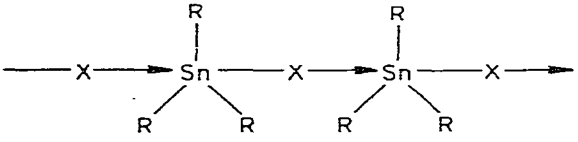
All these compounds are yellow- to green-coloured liquids, except for the trimethyltin derivative of 2-methyl-2-phenylbenzothiazoline which is a low melting solid. They could be distilled unchanged under reduced pressure. Molecular weight measurements on some of them in refluxing benzene show them to be monomeric. IR and PMR studies indicate that tin has a coordination number of five in these complexes.

In the infrared spectra of the ligands, a strong broad band at ~3350 cm^{-1} is assigned to N—H stretching vibration [7,9,14] and a sharp strong band at

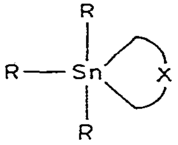
1675—1700 cm^{-1} to the N—H deformation. The spectra of the ligands do not show any band at 2500—2600 cm^{-1} attributable to ν(S—H). These data together with PMR data indicate that the ligands exist as benzothiazolines. The spectra of the complexes do not show these bands and a new band appears at 1650—1670 cm^{-1}, which may be assigned to the ν(C=N) of the Schiff bases [21].

The broad signal at δ 3.80—4.0 ppm in the PMR spectra of the ligands has been assigned to the nitrogen-bound protons of benzothiazolines [8,14]; this signal does not appear in the spectra of the complexes. In the spectra of trialkyltin complexes of 2,2-dimethylbenzothiazoline, the resonances due to $=CMe_2$ protons appear as two singlets of equal height at $\delta \sim 1.75$ ppm and $\delta \sim 2.20$ ppm, while one singlet at δ 1.70 ppm is observed in the spectrum of the ligand. Similarly in the spectra of 2,2-diethylbenzothiazoline derivatives, a set of two triplets and two quartets are observed at δ 0.9—1.4 ppm and δ 2—2.5 ppm, respectively, whereas only a single triplet and a single quartet appear at δ 1.0 and 1.85 ppm in the ligand itself. This indicates that both the $=CMe_2$ methyls and $=CEt_2$ ethyls are not magnetically equivalent in trialkyltin derivatives, in contrast to the situation in the free ligand.

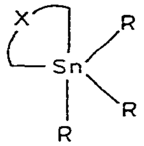
Complexes of the five-coordinate tin of the type R_3SnX, where X is a chelating ligand, may have one of the three structures A, B and C. In view of the monomeric nature of the new derivatives, structures of the type A could immediately be ruled out, leaving structures B and C.



(A) planar



(B) *mer*



(C) all *cis*

Assignments of stretching vibrations due to Sn—C, Sn—N and Sn—S bonds would be helpful in elucidating the structure of these complexes, but was not possible because of the complex nature of the spectra below 700 cm^{-1}.

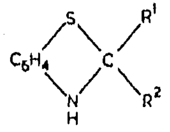
In the PMR spectra of trimethyltin derivatives the proton resonance signal due to the trimethyltin moiety appears as a singlet at $\delta \sim 0.40$ ppm together with a single set of tin-117 and tin-119 satellites. Single peak resonances have also been reported previously for a number of trimethyltin compounds, e.g., oxinate [22], oximes [23], β-diketonates [24] and hydroxylamine derivatives [25]. In view of the non-equivalence of the three methyl groups in both the possible structures, B and C, the appearance of only one resonance may be attributed either to a fast intra- or inter-molecular conversion or to a distortion making the three methyl groups almost equivalent.

The values of tin—proton coupling constants have been suggested to be closely related to the coordination number of tin in organotin compounds. A value of 58—56 cps for coupling constant $J(^{119}Sn—CH_3)$ was observed in the PMR spectra of our complexes; similar values, i.e., 57 and 59.2 cps were reported for trimethyltin oxinate [22] and (2,3-diphenylpropane-1,3-dionato)trimethyltin [24], respectively. On the basis of IR data and quadrupole splitting values in Mössbauer spectra, a *mer* structure has been assigned to the latter and other trimethyltin β-diketonate compounds [24]. In view of this, the newly synthesized

(continued on p. 307)

TABLE 1

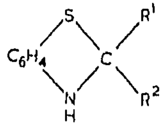
REACTIONS OF TRIALKYLTIN ETHOXIDES WITH BENZOTHIAZOLINES IN 1/1 MOLAR RATIO

R_3SnOEt (g)	Benzothiazoline  (g) R^1	R^2	Amount of ethanol in azeotrope (g) (Found (calcd.))	B.p. of the product (°C/mmHg)	Yield of the distilled pruduct (%)	Product formed	Analyses (Found (calcd.) (%)) Sn	N	S
Et_3SnOEt 2.18	Me 1.43	Me	0.36 (0.40)	128/0.3	94	$Et_3SnSC_6H_4N{=}CMe_2$	32.22 (32.08)	3.83 (3.78)	8.78 (8.66)
Et_3SnOEt 2.52	Et 1.80	Me	0.44 (0.48)	130/0.1	91	$Et_3SnSC_6H_4N{=}CMeEt$	30.85 (30.90)	3.69 (3.65)	8.48 (8.35)
Et_3SnOEt 2.04	Me 1.68	i-Bu	0.34 (0.37)	158/0.5	90	$Et_3SnSC_6H_4N{=}CMeBu$-i	28.93 (28.80)	3.50 (3.40)	7.91 (7.78)
Et_3SnOEt 2.07	Me 1.88	Ph	0.34 (0.38)	186/0.4	90	$Et_3SnSC_6H_4N{=}CMePh$	27.33 (27.47)	3.17 (3.24)	—
Et_3SnOEt 1.98	Et 1.54	Et	0.32 (0.36)	136/0.1	93	$Et_3SnSC_6H_4N{=}CEt_2$	29.94 (29.82)	3.47 (3.52)	8.14 (8.05)
Et_3SnOEt 1.79	Et 1.58	n-Bu	0.30 (0.33)	138/0.5	95	$Et_3SnSC_6H_4N{=}CEtBu$-n	27.70 (27.85)	3.33 (3.29)	—

n-Pr_3SnOEt	Me		Me	0.31	132/0.05		n-$Pr_3SnSC_6H_4N=CMe_2$	28.98	3.45	7.85
2.09		1.18		(0.33)		96		(28.80)	(3.40)	(7.78)
n-Pr_3SnOEt	Me		Et	0.31	164/0.3		n-$Pr_3SnSC_6H_4N=CMeEt$	27.95	3.25	7.66
2.11		1.29		(0.33)		91		(27.85)	(3.29)	(7.52)
n-Pr_3SnOEt	Me		i-Bu	0.30	148/0.1		n-$Pr_3SnSC_6H_4N=CMeBu$-i	26.02	3.03	—
2.06		1.47		(0.32)		91		(26.13)	(3.08)	
n-Pr_3SnOEt	Me		Ph	0.27	184/0.1		n-$Pr_3SnSC_6H_4N=CMePh$	25.08	2.91	6.87
1.81		1.41		(0.29)		92		(25.02)	(2.95)	(6.76)
n-Pr_3SnOEt	Et		Et	0.29	160/0.3		n-$Pr_3SnSC_6H_4N=CEt_2$	26.90	3.22	7.42
2.05		1.36		(0.32)		93		(26.96)	(3.18)	(7.28)
n-Pr_3SnOEt	Et		n-Bu	0.29	156/0.2		n-$Pr_3SnSC_6H_4N=CEtBu$-n	25.48	2.93	—
1.99		1.50		(0.31)		96		(25.35)	(2.99)	
n-Bu_3SnOEt	Me		Me	0.30	152/0.1		n-$Bu_3SnSC_6H_4N=CMe_2$	26.01	3.13	7.14
2.32		1.14		(0.32)		96		(26.13)	(3.08)	(7.06)
n-Bu_3SnOEt	Me		Et	0.32	162/0.1		n-$Bu_3SnSC_6H_4N=CMeEt$	25.29	2.90	—
2.62		1.40		(0.36)		91		(25.35)	(2.99)	
n-Bu_3SnOEt	Me		i-Bu	0.28	174/0.2		n-$Bu_3SnSC_6H_4N=CMeBu$-i	23.98	2.80	6.29
2.22		1.37		(0.31)		91		(23.92)	(2.82)	(6.46)
n-Bu_3SnOEt	Et		Et	0.27	178/0.5		n-$Bu_3SnSC_6H_4N=CEt_2$	24.56	2.93	6.72
2.19		1.26		(0.30)		90		(24.61)	(2.90)	(6.65)
n-Bu_3SnOEt	Et		n-Bu	0.28	164/0.05		n-$Bu_3SnSC_6H_4N=CEtBu$-n	23.19	2.69	—
2.24		1.48		(0.31)		94		(23.26)	(2.74)	

TABLE 2

REACTIONS OF TRIMETHYLTIN HYDROXIDE WITH BENZOTHIAZOLINES IN 1/1 MOLAR RATIO

Me_3SnOH (g)	Benzothiazoline  (g)			B.p. of the product (°C/mmHg)	Yield of the distilled product (%)	Product formed	Analyses (Found (calcd.) (%))		
	R^1		R^2				Sn	N	S
1.84	Me	1.68	Me	94/0.1	95	$Me_3SnSC_6H_4N{=}CMe_2$	36.24 (36.17)	4.32 (4.27)	9.89 (9.77)
1.71	Me	1.70	Et	102/0.1	93	$Me_3SnSC_6H_4N{=}CMeEt$	34.86 (34.70)	4.01 (4.00)	—
1.59	Me	1.82	i-Bu	118/0.1	90	$Me_3SnSC_6H_4N{=}CMeBu$-i	32.16 (32.07)	3.70 (3.78)	8.78 (8.66)
1.48	Me	1.86	Ph	174/0.4	91	$Me_3SnSC_6H_4N{=}CMePh$	30.30 (30.42)	3.52 (3.59)	8.08 (8.22)
1.69	Et	1.81	Et	118/0.1	92	$Me_3SnSC_6H_4N{=}CEt_2$	33.45 (33.32)	3.86 (3.93)	9.12 (9.00)
1.65	Et	1.97	n-Bu	120/0.05	93	$Me_3SnSC_6H_4N{=}CEtBu$-n	30.98 (30.89)	3.56 (3.64)	8.44 (8.35)

complexes may also be tentatively assigned the *mer* structures, although an unequivocal choice between the two structures would only be possible after further physico-chemical studies, e.g., Mössbauer spectroscopy.

Experimental

Special precautions were taken to exclude moisture during the reactions. Benzene and ethanol were dried by standard methods. Et_3SnOEt, n-Pr_3SnOEt and n-Bu_3SnOEt were prepared by the sodium method [26]. Benzothiazolines [see refs 4—6,8] were prepared by the condensation of *o*-aminobenzenethiol with an excess of ketone in the presence of a drop of concentrated HCl. Water was removed azeotropically with benzene. The products were purified by distillation under reduced pressure.

Molecular weights, IR and PMR spectra were determined as previously described [19]. The ethanol in the azeotrope, nitrogen in the ligands as well as in the complexes and tin in the complexes were estimated as previously decribed [19,20].

Initial attempts to estimate sulphur in the ligands as well as in the complexes by alkaline $KMnO_4$ were not successful. However, oxidation of sulphur was made quantitative by employing alkaline H_2O_2 and $KMnO_4$ successively. 0.15—0.20 g of the compound was taken in 20 ml of 30% H_2O_2 to which 2 g of KOH was added. When the initial reaction slowed down, the mixture was refluxed for 2 h. After cooling, a further 20 ml of H_2O_2 were cautiously added and the mixture was again refluxed for 2 h. 0.5 g $KMnO_4$ was then added and the mixture refluxed for another 4 h to ensure complete oxidation of the sulphur in the compound. Subsequent treatment was similar to that used in the conventional alkaline $KMnO_4$ method. Sulphur was finally weighted as $BaSO_4$.

Reaction of triethyltin ethoxide with 2,2-dimethylbenzothiazoline in 1/1 molar ratio in dry benzene

A mixture of triethyltin ethoxide and 2,2-dimethylbenzothiazoline was refluxed in dry benzene and the ethanol liberated was removed azeotropically and determined. The residue benzene was removed and the product was distilled under reduced pressure. Reactions of tripropyltin- and tributyltin-ethoxides were carried out similarly. The results are shown in Table 1.

Reaction of trimethyltin hydroxide with 2,2-dimethylbenzothiazoline in 1/1 molar ratio in benzene

Stoichiometric amounts of trimethyltin hydroxide and 2,2-dimethylbenzothiazoline were taken in benzene and the mixture was refluxed to remove water as azeotrope. After complete removal of water (8—10 h), the remaining benzene was removed and the product was purified by distillation under reduced pressure. Results of this and other reactions of trimethyltin hydroxide with benzothiazolines are shown in Table 2.

Acknowledgement

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