

SYNTHESIS AND CONFIGURATIONS OF ORGANOTIN OXINATES

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INTRODUCTION

From the standpoint of structural considerations, interesting organotin compounds containing penta-coordinated tin atoms have been reported recently. The trimethyltin chloride pyridine adduct^{1,2} and trimethyltin hydroxide^{3,4}, for example, were found by the study of the infrared spectra and the X-ray crystallographic analysis to involve penta-coordinated tin with planar $(\text{CH}_3)_3\text{Sn}$ groups coordinated from both sides. There are many other examples of solid trimethyltin compounds involving planar $(\text{CH}_3)_3\text{Sn}$ groups bridged by various groups such as OOH and OOCCH_3 ⁵⁻⁷, BF_4 ⁸, AsF_6 ⁸, SbF_6 ⁸, ClO_4 ^{8,9} and NO_3 ^{10,11}. The occurrence of penta-coordinated tin in solution was also found. For example, *N*-(tributyltin)imidazole¹² and tri-*n*-propyl- and tri-*n*-butyltin formates⁵⁻⁷ have been found to form linear oligomers, and trimethyltin hydroxide¹³ is known to form dimers in anhydrous organic solvents. Neither of these, however, has a chelating structure.

Among organotin oxinates (*S*-hydroxyquinolinates) described in the literature^{14,15}, triphenyltin oxinate has been studied by means of UV spectra in 95 % ethanol and it was concluded that R_3Sn^+ cations could not form a chelate¹⁶. However, we have found that in anhydrous cyclohexane, triphenyltin oxinate is indeed chelated. Also we have synthesized a new type of dialkyltin chelate, $\text{R}_2\text{SnXOx}^{17}$ (Ox = oxinate).

During the course of our further study several papers¹⁸⁻²⁰ have appeared dealing with organotin oxinates. In this paper we will describe the syntheses and the configurations of several chelates of tri-, di-, and mono-organotin derivatives with oxine and will discuss the disproportionation reactions in polar solvents of dialkyltin halide oxinates in which the coordination number of the tin atom changes from five to six.

EXPERIMENTAL

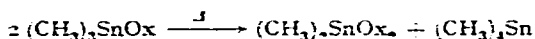
Materials

Organotin chlorides were purified according to standard methods described elsewhere²¹. Oxine was used after recrystallization of commercial materials.

Preparation and properties of organotin oxinates

Properties and analytical data of organotin oxinates used in this experiment are summarized in Table I.

Trialkyltin oxinates, R₃SnOx. (CH₃)₃SnOx. A cyclohexane solution (30 ml) of oxine (5.8 g; 0.04 mole) was dropped into a sodium methoxide solution prepared from sodium (1.0 g; 0.044 mole) and methanol (30 ml) under stirring; then trimethyltin chloride (8.0 g; 0.04 mole) in methanol (15 ml) was added dropwise and the mixture was stirred for one hour. Sodium chloride (1.9 g; 82 %) was filtered off, and the filtrate was concentrated and distilled under reduced pressure, giving a clear, yellow liquid distillate of (CH₃)₃SnOx, as shown in Table 1. The large amount of residue in the still was found to be dimethyltin dioxinate which was identified by its melting point²². The following disproportionation reaction might occur during the distillation.



Other trialkyltin oxinates were prepared in a manner similar to that described above.

Dialkyltin halide oxinates, R₂SnXOx. (CH₃)₂SnClOx. (i) To an absolute ethanol solution (5 ml) of dimethyltin dichloride (2.9 g; 13 mmole), was added under stirring crystalline oxine (1.9 g; 13 mmole). The crystals disappeared and a yellow precipitate was formed immediately. This was recrystallized from absolute ethanol to give 2.7 g (63 %) of yellow crystals, m.p. 137°. (ii) Dimethyltin dichloride (1.0 g; 4 mmole) and dimethyltin dioxinate (1.9 g; 4 mmole) were suspended in 130 ml of benzene and the mixture was refluxed for one hour to give a clear solution. The solvent was removed under reduced pressure and the residue was recrystallized from (1:1) ligroin/benzene mixture to give 2.0 g (70 %) of yellow crystals, m.p. 137°. Other dialkyltin halide oxinates were prepared in an analogous manner, mainly by this method.

Alkyltin chloride dioxinate, RSnClOx₂. CH₃SnClOx₂. Methyltin oxide (6.3 g; 0.04 mole) was stirred in an equimolar amount of dilute hydrochloric acid until all of the oxide was disappeared. To the filtrate, an ethanol solution (50 ml) of oxine (11.6 g; 0.08 mole) was added under stirring and followed by the addition of aqueous ammonia (5 ml). The fine yellow precipitate (16.8 g; 92 %) was filtered off and recrystallized from acetone to give bright yellow crystals, m.p. 246–247°.

n-C₄H₉SnClOx₂. An ethanol solution (20 ml) containing oxine (2.9 g; 0.02 mole) and n-butyltin trichloride (2.8 g; 0.01 mole) was concentrated on a water bath to a sticky liquid which, after solidification, was recrystallized from ethanol, m.p. 182–183°. The preparations of the other compounds used in this investigation have been described elsewhere^{16, 22}.

Molecular weight

Molecular weights of representative compounds were determined cryoscopically in benzene and cyclohexane. These compounds are monomeric as shown in Table 1.

Trialkyltin oxinates are clear, yellow liquids with high boiling points, stable in sealed tubes but they gradually turn brown on standing in air. The other organotin oxinates are bright yellow, crystalline compounds.

Disproportionation reactions

Reaction in pyridine. Dimethyltin chloride oxinate (0.66 g, 2 mmole) was added to anhydrous pyridine (3 ml) and upon heating gave a yellow solution. The precipitate which appeared on standing at room temperature was sublimed three times to give (CH₃)₂SnCl₂·2Py (0.15 g, 40 %), m.p. 158–161° (reported²³ m.p. 161°).

TABLE 1

ORGANOTIN OXINATES: R_3SnOx , R_2SnXOx AND $RSnClOx_2$
 $Ox = C_9H_6NO$, $X = \text{halogen or pseudohalogen}$.

<i>R</i>	<i>X</i>	<i>B.p.</i> ($^{\circ}C/mmHg$) or [<i>m.p.</i> ($^{\circ}C$)]	<i>C</i> (%) <i>found</i> (<i>calcd.</i>)	<i>H</i> <i>found</i> (<i>calcd.</i>)	<i>N</i> <i>found</i> (<i>calcd.</i>)	<i>Cl or (S)</i> <i>found</i> (<i>calcd.</i>)	<i>Sn</i> <i>found</i> (<i>calcd.</i>)	<i>Mol. Wt.</i> <i>found</i> (<i>calcd.</i>)
<i>R₃SnOx</i>								
CH_3		108.5–109.5/0.2	46.79 (46.81)	4.90 (4.91)	4.59 (4.55)		38.35 (38.54)	305 ^a (308)
C_2H_5		132–134/0.05	51.18 (51.47)	6.16 (6.05)	3.95 (4.00)			
$n-C_4H_9$		149–151/0.007	58.20 (58.09)	7.58 (7.66)	3.53 (3.69)		27.48 (27.34)	413 ^a (434)
C_6H_5		[145–146.5]	65.13 (65.62)	4.24 (4.82)	2.80 (2.84)			501 ^a 494 ^b (494)
<i>R₂SnXOx</i>								
CH_3	Cl	[137]	40.52 (40.24)	3.77 (3.68)	4.29 (4.24)	10.56 (10.86)	35.95 (36.15)	296 ^b (328)
C_2H_5	Cl	[119–120.5]	43.96 (43.81)	4.39 (4.53)	4.29 (3.93)	10.68 (9.95)		
$n-C_3H_7$	Cl	[90–91]	46.92 (46.86)	5.27 (5.24)				
CH_3	NCS	[124 (dec.)]	40.92 (41.06)	3.18 (3.45)	8.16 (7.98)	8.23(s) (9.14)		
$n-C_3H_7$	NCS	[134]	47.39 (47.21)	4.78 (4.95)	6.82 (6.88)	7.63(s) (7.88)		
<i>RSnXOx₂</i>								
CH_3	Cl	[246.5–247.5]	49.92 (49.88)	3.46 (3.30)	6.27 (6.12)	8.09 (7.75)	25.81 (25.94)	
$n-C_4H_9$	Cl	[182–183]	53.07 (52.89)	4.08 (4.24)	5.63 (5.61)	7.15 (7.10)	23.15 (23.76)	470 ^b (500)

^a In cyclohexane. ^b In benzene.

The filtrate was concentrated and cooled to give yellow crystals which were recrystallized from acetone to give dimethyltin dioxinate (0.16 g, 47%), m.p. 229–231° (reported²² m.p. 231–233°).

Reaction in water. Dimethyltin chloride oxinate (0.66 g; 2 mmole) was added to anhydrous dioxan (10 ml) and upon heating gave a yellow solution. A sufficient amount of water (50 ml) was added to precipitate yellow crystals which were recrystallized from acetone to give dimethyltin dioxinate (0.24 g; 55%), m.p. 230–232° (reported²² m.p. 231–233°).

Reaction by heating. Dimethyltin chloride oxinate (1.05 g; 3.2 mmole) and pyridine (0.26 ml) were heated in a sealed tube in an oil bath at 160° for one hour. The reaction mixture was washed with petroleum ether to give a yellow, crystalline solid, which was recrystallized from acetone to give methyltin chloride dioxinate (0.20 g; 55%), m.p. 246–247° (see Table 1). The characteristic, penetrating odor of the petroleum ether washings suggested the presence of trimethyltin chloride.

Other organotin chloride oxinates were found to disproportionate in a manner

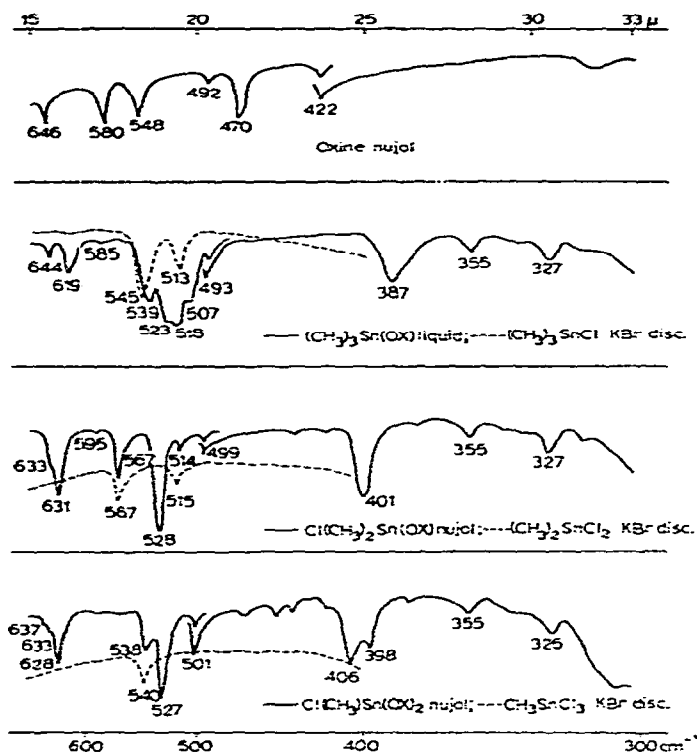


Fig. 1. Infrared spectra of oxine²², methyltin oxinates and methyltin chlorides⁵.

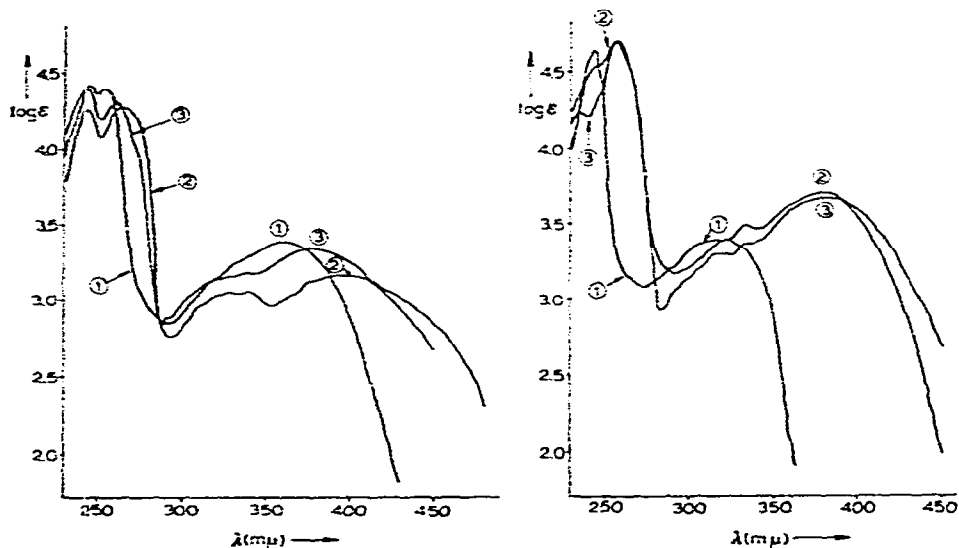


Fig. 2. Absorption spectra of $(\text{CH}_3)_3\text{SnOx}$ and $(\text{CH}_3)_2\text{SnClOx}$. The logarithm of the molecular extinction coefficient, $\log \epsilon$, is plotted against the wavelength, λ in $\text{m}\mu$. 1. $(\text{CH}_3)_3\text{SnOx}$ in cyclohexane; 2. $(\text{CH}_3)_2\text{SnClOx}$ in cyclohexane; 3. $(\text{CH}_3)_2\text{SnClOx}$ in dioxan.

Fig. 3. Absorption spectra of oxine, $(\text{CH}_3)_2\text{SnOx}_2$ and $\text{CH}_3\text{SnClOx}_2$. 1. Oxine in cyclohexane; 2. $(\text{CH}_3)_2\text{SnOx}_2$ in dioxan; 3. $\text{CH}_3\text{SnClOx}_2$ in dioxan.

TABLE 2

RELEVANT INFRARED STRETCHING FREQUENCIES OF METHYLTIN OXINATES
Positions of bands in cm^{-1} .

Compound	Sn-O	Sn-C	Sn-N
$(\text{CH}_3)_3\text{SnOx}$	523	539, 518, 507	387
$(\text{CH}_3)_2\text{SnClOx}$	528	567, 514	401
$(\text{CH}_3)_2\text{SnOx}_2$	517	526, 512	395
$\text{CH}_3\text{SnClOx}_2$	527	538	406

TABLE 3

ULTRAVIOLET ABSORPTION SPECTRA OF OXINE AND OF ORGANOTIN OXINATES

Compound	Solvent	λ_{max} (m μ)	$\epsilon(\text{M}^{-1}\cdot\text{cm}^2) \times 10^{-3}$
Oxine	cyclohexane	320	2.45
$(\text{CH}_3)_3\text{SnOx}$	cyclohexane	362	2.50
$(\text{n-C}_4\text{H}_9)_3\text{SnOx}$	cyclohexane	362	2.05
$(\text{C}_6\text{H}_5)_3\text{SnOx}$	cyclohexane	368	2.44
	dioxan	361	2.62
	95% aq. dioxan	318	2.43
$(\text{CH}_3)_2\text{SnClOx}$	cyclohexane	397	1.44 ^a
	dioxan	378	2.17
	pyridine	379	2.35
$(\text{CH}_3)_2\text{SnOx}_2$	benzene	380	4.86
	dioxan	378	4.97
	pyridine	379	5.20
$\text{CH}_3\text{SnClOx}_2$	benzene	383	4.07
	dioxan	381	4.68
	pyridine	383	4.55

^a The band broadening of this compound made the molecular extinction coefficient especially small compared with other types of the oxinates as shown in Fig. 2.

TABLE 4

TIN PROTON COUPLING CONSTANTS AND PROTON CHEMICAL SHIFTS FOR SEVERAL METHYLTIN CHELATES

Compound	$J(^{117}\text{Sn}-\text{CH}_3)$ (cps)	$J(^{119}\text{Sn}-\text{CH}_3)$ (cps)	$\tau(\text{Sn}-\text{CH}_3)$ (ppm) ^a	Solvent
$(\text{CH}_3)_3\text{SnOx}$	54.6	57.0	9.54	CHCl_3
	54.9	56.8	9.56	Direct
$(\text{CH}_3)_2\text{SnClOx}$	76.4	79.9	8.96	CDCl_3
$(\text{CH}_3)_2\text{SnOx}_2$	67.9	71.2	9.56	CDCl_3^b
	68.4	71.5	9.38	$\text{C}_2\text{H}_5\text{N}$
$\text{CH}_3\text{SnClOx}_2$	101.7	106.6	8.98	CHBr_3
$(\text{CH}_3)_2\text{Sn}(\text{acac})_2^b$	95.0	99.3	9.51	CDCl_3
$(\text{CH}_3)\text{SnCl}(\text{acac})_2^c$	111.5	120.9	9.12	CHCl_3

^a Tetramethylsilane = 10.0. ^b Ref. 24. ^c Ref. 25.

similar to those described above. In all cases the identities of the products were confirmed by infrared spectroscopy.

Infrared, ultraviolet and NMR spectra

The infrared spectra were measured using a Hitachi EPI-2G spectrophotometer equipped with gratings and a Leitz infrared spectrophotometer equipped with CsBr optics for the 15–25 μ and 15–35 μ regions, respectively. Spectra were obtained in Nujol mulls and in pyridine solutions. The typical spectra for methyltin oxinates are shown in Fig. 1 together with those of oxine and the methyltin chlorides in the 650–300 cm^{-1} region, and the relevant infrared frequencies are shown in Table 2.

The ultraviolet spectra were obtained with a Hitachi EPS-2 UV spectrophotometer, using 1 cm cells. Anhydrous cyclohexane, benzene, dioxan and pyridine and 95% aqueous dioxan were used as solvents. The concentrations of the solutions were such as to give optical densities in the range 0.05–1.20. The absorption spectra are shown in Figs. 2–4. The absorption maxima and the molecular extinction coefficients are summarized in Table 3.

Proton NMR spectra were determined with either a Varian A-60 or a Japan Electron Optics JNR-3H-60 spectrometer operating at 60 Mc/sec. with the room temperature at 20°. Coupling constants and chemical shifts were determined by the side band technique. The coupling constants are believed to be accurate to 1 cps and the chemical shifts to ± 0.02 ppm. Purified chloroform, bromoform and pyridine were used as solvents and tetramethylsilane as the internal standard throughout these experiments. The NMR data in various solvents of the methyltin oxinates together with those of acetylacetonates are given in Table 4.

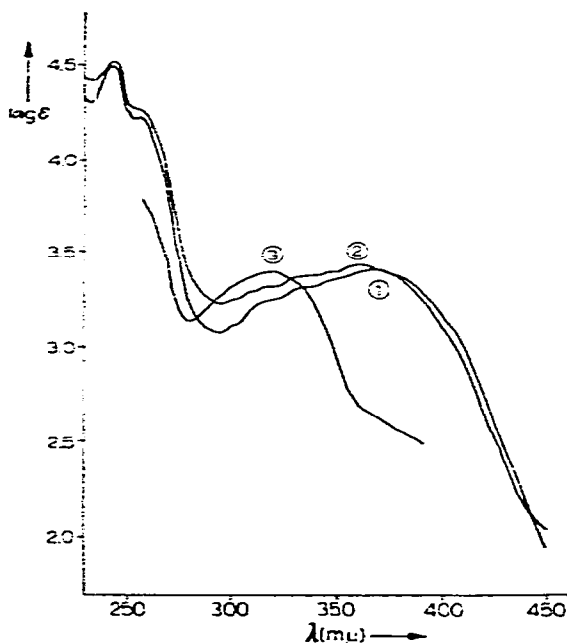


Fig. 4. Absorption spectra of $(\text{C}_6\text{H}_5)_2\text{SnOx}$. 1. In cyclohexane; 2. In dioxan; 3. In 95% aqueous dioxan.

RESULTS AND DISCUSSION

Infrared spectra

As shown in Fig. 1, all methyltin oxinates show two characteristic bands which are absent in the starting materials. One band is very strong and located at about 520 cm^{-1} , and the other band is of medium intensity and found near 400 cm^{-1} . The former can be assigned to the stretching vibration of Sn-O and the latter to that of Sn-N stretching²². These assignments could be supported further by comparing the spectra of the other analogous alkyltin oxinates shown in Table 1. Among the remaining bands are those which might be associated with the stretching vibrations of the Sn-C bonds by analogy with tetrahedral methyltin chlorides and octahedral dimethyltin bis(acetylacetonate) or methyltin chloride bis(acetylacetonate)²⁶.

Coordination around the tin atom

It has previously been known that the peak at $320\text{ m}\mu$ of oxine shifts to longer wavelength, $370\text{--}430\text{ m}\mu$ by chelation to metals²⁷⁻²⁹ and that the magnitude of this shift parallels the stability constant^{28, 29}. In the ultraviolet spectra of our compounds the absorption peaks are found in the $360\text{--}400\text{ m}\mu$ region as shown in Figs. 2-4. We therefore, believe that all of organotin oxinates in Table 1 are chelated in solution to form monomeric species. Thus R_3SnOx and R_2SnXOx form a new class of compounds containing a penta-coordinated tin atom and probably having a trigonal bipyramidal configuration. If the relationships between the band shift and stability constant are applicable in our compounds, the following sequences of stability constants in nonpolar solvents such as cyclohexane or benzene can be obtained from Table 3:



It is interesting to point out the parallelism between the order of stability constants of $(\text{CH}_3)_3\text{SnOx}$ and $(\text{CH}_3)_2\text{SnClOx}$ indicated in the above sequence and the strengths of the Sn-N bonds as indicated by their stretching frequencies (Table 2). The difference may be due to the difference in the acceptor properties of R_3Sn and R_2SnCl cationic groups in these compounds.

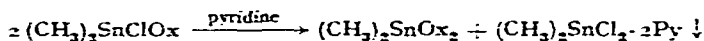
As far as trimethyltin oxinate is concerned, there is one more datum suggesting chelation. As shown in Fig. 1 and Table 2 the infrared spectra of trimethyltin oxinate shows four complicated bands at 539 , 523 , 518 and 507 cm^{-1} . If one strong band is assigned to the Sn-O stretching vibration, the remaining three bands would be associated with the Sn-C stretching modes. Since only two Sn-C stretching frequencies would be expected for a non-chelated structure, this seems to justify the contribution of the Sn-N bond, to disturb the C_{3v} local symmetry of the $(\text{CH}_3)_3\text{Sn}$ group.

The behavior of triorganotin and diorganotin cationic groups in polar media

We have investigated the UV spectra of triphenyltin oxinate in anhydrous cyclohexane¹⁷, anhydrous dioxan, and in 95% aqueous dioxan. Absorption peaks were observed at 368 , 361 and $318\text{ m}\mu$, respectively as shown in Fig. 4 and Table 3. In aqueous dioxan the peak at $361\text{ m}\mu$ was greatly reduced in intensity and appeared only as a shoulder. These findings suggest that although the nitrogen atom in oxine

does bond to the tin atom in a nonpolar solvent, the Sn-N coordination bond of triorganotin oxinates becomes weaker in a polar medium, and due to the comparatively low positive charge on the tin atom, is broken in the presence of a large amount of water*. This would explain why no chelation was observed in the case of the UV spectra in aqueous alcohol by Roncucci *et al.*¹⁶.

The absorption peak of dimethyltin chloride oxinate in anhydrous dioxan shifts to a shorter wavelength than that in cyclohexane (Fig. 2 and Table 3), indicating that the Sn-N bond is weakened in polar solvents. The spectrum of this compound in pyridine solution was exactly the same as that of dimethyltin dioxinate at half the concentration. The spectrum agreed in both the wavelengths of observed maxima and in the molecular extinction coefficients. Similarly the infrared and NMR spectra of $(\text{CH}_3)_2\text{SnClOx}$ in pyridine were identical with those of $(\text{CH}_3)_2\text{SnOx}_2$ in pyridine. These findings suggest that in pyridine a disproportionation reaction occurs in which the coordination number of tin atom changes from five to six.



Indeed from a solution of $(\text{CH}_3)_2\text{SnClOx}$ in pyridine both compounds were obtained in exactly corresponding yields. They were identified by their melting points and infrared spectra as shown in the experimental part. Compounds of the type R_2SnClOx were found to disproportionate to the corresponding R_2SnOx_2 type compounds in the presence of donor molecules such as pyridine and water. Thus in polar media the diorganotin group tends to form the most stable chelate containing a hexa-coordinated tin atom. As shown in Table 3, $(\text{CH}_3)_2\text{SnOx}_2$ and $\text{CH}_3\text{SnClOx}_2$, which have hexa-coordinated tin atoms, do not change the positions of their absorption peaks nor their molecular extinction coefficients in either nonpolar or in polar solvents.

Structure and bonding

The observation of only a single sharp resonance and only one set of spin-spin coupling constants between tin nuclei and methyl protons, as shown in Table 4 indicates that only one, probably the *trans* isomer, exists in solution in the case of dimethyltin dioxinate. The *trans* configuration has been suggested³⁰ and indeed often observed in dimethyltin complexes, such as $(\text{CH}_3)_2\text{SnCl}_2 \cdot 2\text{C}_3\text{H}_5\text{N}$ ²³ and $(\text{CH}_3)_2\text{Sn}(\text{acac})_2$ ^{24,31}.

It is rather surprising that only a single line is also obtained for trimethyltin oxinate in neat liquid and in chloroform. Three stereoisomers would be expected for a trigonal bipyramidal trimethyltin oxinate which would have two kinds of methyl groups. It can be concluded that the chemical shifts are identical for two types of methyl groups or that some rapid exchange makes the methyl protons equivalent in the NMR measurement. This exchange could not be intermolecular because spin-spin coupling between tin nuclei and methyl protons was observed; hence it is probably caused by a pseudorotation³² of methyl groups around the tin atom.

The Sn-CH₃ coupling constants of dimethyltin dioxinate and methyltin chloride dioxinate are surprisingly smaller than those of the corresponding acetylacetonates

* The experimental condition in 95% aqueous dioxan corresponds to 1 to 1.4×10^4 of the molar ratio of triphenyltin oxinate and water.

(Table 4). If the Fermi contact term dominates in the spin-spin coupling, the smaller values of the oxinates can be explained by an idea suggested by McGrady and Tobias²⁴ that the Sn-O and Sn-N bonds are more covalent than the Sn-O bonds in acetylacetonates and thus the tin *s* character has become more uniformly distributed among all six bonds*. In fact, the acetylacetonates in solution are less stable than the oxinates toward heating and their infrared spectra show the Sn-O stretching band²⁶ at a lower wave number than that of the oxinates.

The Sn-CH₃ coupling constants of chelated trimethyltin compounds containing a penta-coordinated tin atom are reported for the first time for trimethyltin oxinate as shown in Table 4. These values are smaller than those of (CH₃)₃SnBr·Py³³, namely $J(^{117}\text{Sn}-\text{CH}_3) = 59.8$ and $J(^{119}\text{Sn}-\text{CH}_3) = 62.1$ cps, and those of [(CH₃)₃SiOSn-(CH₃)₂OSn(CH₃)₂OSi(CH₃)₃]₂³⁴, namely, $J(^{117}\text{Sn}-\text{CH}_3) = 79.0$ and $J(^{119}\text{Sn}-\text{CH}_3) = 82.0$ cps. These results can also be explained by assuming the contribution of a more covalent character to the Sn-O and Sn-N bonds. The increase of about 23 cps of the $J(\text{Sn}-\text{CH}_3)$ of dimethyltin chloride oxinate compared with those of trimethyltin oxinate may be due to the electronegativity difference between the chlorine atom and the methyl group. The same effect is found in the case of methyltin chloride dioxinate and dimethyltin dioxinate.

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SUMMARY

A series of organotin oxinates of the general type R₃SnOx, R₂SnXOx and RSnClOx₂ (R = CH₃, C₂H₅, n-C₃H₇, n-C₄H₉ and C₆H₅; X = Cl and NCS; Ox = C₉H₆NO) has been synthesized. Studies of the ultraviolet spectra indicate that these compounds involve bidentate oxinato ligands and therefore R₃SnOx and R₂SnXOx contain pentavalent tin atoms. The order of the stability is also suggested by the ultraviolet spectra. An interesting disproportionation reaction is described in which the coordination number of the tin atom changes from five to six. The configurations of the organotin oxinates have been deduced from their NMR and infrared spectra.

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* McGrady and Tobias²⁴ have suggested from NMR data of dimethyltin dioxinate that oxine may be coordinated primarily through oxygen.

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