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SYNTHESIS OF TIN(IV) -OXYGEN AND SULFUR HETEROCYCLES AND THEIR --ETC(U)
JUL 78 W D HONNICK, J J ZUCKERMAN N00014-77-C-0432
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Condensation of diorganotin oxides with diols, carboxylic acids and thiols releases water to form tin(IV)-oxygen and sulfur heterocycles with five-, six-, and seven-membered rings. In this way new diorganotin(IV) ortho-phenylenedioxy-, oxybenzoyloxy-, thiolatobenzoyloxy-, pyridinedioxy- and acetanilidoxy-heterocycles, the structure of the last of which is assigned to a seven-membered ring isomer, and derivatives of mandelic acid are synthesized. Reaction with tin(II) chloride transforms the heterocycles into

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their tin(II) analogues, while treatment with catechol and salicylic acid results in the ortho-phenylenedioxy- and oxybenzoyloxy- derivatives, respectively. The heterocycles react with di-n-butyltin dichloride to give open chain ditin dichlorides, while acetyl chloride gives the diacetylated diol plus the corresponding diorganotin dichloride. The compounds are characterized by infrared and tin-119m Mössbauer spectroscopies.

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Synthesis of Tin(IV)-Oxygen and Sulfur Heterocycles and Their Transformation to Tin(II) Analogues

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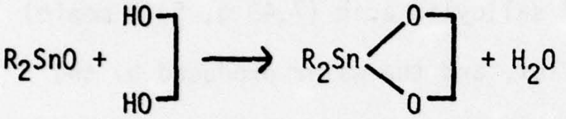
Abstract: Condensation of diorganotin oxides with diols, carboxylic acids and thiols releases water to form tin(IV)-oxygen and sulfur heterocycles with five-, six-, and seven-membered rings. In this way new diorganotin(IV) *ortho*-phenylenedioxy-, oxybenzoyloxy-, thiolatobenzoyloxy-, pyridinedioxy- and acetanilidoxy-heterocycles, the structure of the last of which is assigned to a seven-membered ring isomer, and derivatives of mandelic acid are synthesized. Reaction with tin(II) chloride transforms the heterocycles into their tin(II) analogues, while treatment with catechol and salicylic acid results in the *ortho*-phenylenedioxy- and oxybenzoyloxy- derivatives, respectively. The heterocycles react with di-*n*-butyltin dichloride to give open chain ditin dichlorides, while acetyl chloride gives the diacetylated diol plus the corresponding diorganotin dichloride. The compounds are characterized by infrared and tin-119m Mössbauer spectroscopies.

Heterocyclic organotin(IV)-oxygen compounds have been prepared from aliphatic diols,[1-3] cis- and trans-cyclohexanediol,[4] catechol,[4-5] 2,2'-dihydroxybiphenyl,[5] Schiff bases[6-11] and dicarboxylic acids.[12-14] The species are generally associated through intermolecular tin(IV)-oxygen bonding as shown by tin-119 nmr studies of their solutions[4] and by X-ray diffraction data on analogous solids.[15] The most satisfactory method of preparing these compounds is the reaction between an organotin oxide and a diol to release water:



$$R_2SnO + \left.\begin{matrix}HO\\HO\end{matrix}\right] \longrightarrow R_2Sn\left\langle\begin{matrix}O\\O\end{matrix}\right] + H_2O \tag{1}$$

The cyclic products display a high degree of thermal and hydrolytic stability in contrast to the reactive organotin alkoxides.[16]

This paper reports the characterization of several novel tin(IV)-oxygen and sulfur heterocycles and their transformation reactions.

Experimental Section:

Reagent grade chemicals and solvents were used as received, except for 2,3-dihydroxypyridine which was recrystallized from water. Infrared spectra were recorded as Nujol and halocarbon mulls on a Beckman IR-12 spectrophotometer. Tin-119m Mössbauer spectra were recorded at 77K on a cam-drive, constant acceleration spectrometer previously described,[17] using $Ba^{119m}SnO_3$ (New England Nuclear Corp.) as both source and zero Isomer Shift reference standard. Tin was analyzed for as tin(IV) oxide by treatment with concentrated nitric and sulfuric acids. Carbon and hydrogen analyses were performed by Instranal Laboratory, Rensselaer, New York.

Syntheses. New compounds are listed with their yields, melting points and microanalytical data in Table 1. Tin-119m Mössbauer data are listed in Table 2.

(ortho-Oxybenzoyloxy)dimethyltin(IV). Dimethyltin oxide (11.9 g, 72.2 mmole) was suspended in benzene solution of salicylic acid (10.0 g, 72.4 mmole). The mixture was heated to reflux, and the water liberated in the reaction removed by azeotropic distillation by means of a Dean and Stark separator. The product (19.5 g) was insoluble in benzene and was filtered, washed with pentane and dried.

(ortho-Oxybenzoyloxy)di-n-butyltin(IV). Di-n-butyltin oxide (13.45 g, 54.0 mmole) was suspended in a solution of salicylic acid (7.49 g, 54.0 mmole) in benzene. The mixture was heated to reflux, and the water produced by the reaction was removed by azeotropic distillation by means of a Dean and Stark separator (0.9 ml found, 1.0 ml calculated). As the di-n-butyltin oxide reacted it dissolved. The solution was cooled and concentrated by removal of benzene by rotary evaporation. The product, (ortho-oxybenzoyloxy)-di-n-butyltin(IV) (the analogous silicon heterocycle has been named benzo-2,2-dimethyl-2-sila-1,3-dioxanon-(4)[18]), precipitated, and was filtered and washed with pentane.

(ortho-Oxybenzoyloxy)di-n-octyltin(IV). Di-n-octyltin oxide (5.00 g, 13.8 mmole) was suspended in a benzene solution of salicylic acid (1.91 g, 13.8 mmole). The mixture was heated to reflux, and the water liberated by the reaction removed by azeotropic distillation by means of a Dean and Stark separator. The resulting clear solution was cooled, and the solvent stripped by rotary evaporation to leave a viscous liquid. The liquid was taken up in petroleum ether, the solution filtered, and allowed to stand for 1 day during which time a white solid precipitated. The product was filtered and dried.

(ortho-Oxybenzoyloxy)phenyltin(IV) Hydroxide. Diphenyltin oxide (3.50 g, 12.1 mmole) was suspended in a benzene solution of salicylic acid (1.68 g, 12.2 mmole). The mixture was heated to reflux and the water liberated by the reaction was removed by means of a Dean and Stark separator. The mixture was cooled and the product filtered, washed with petroleum ether and dried in vacuo at 90° for 1 hour.

(ortho-Thiolatobenzoyloxy)dimethyltin(IV). Dimethyltin oxide (5.00 g, 30.3 mmole) was suspended in a benzene solution of ortho-mercaptobenzoic acid (5.35 g, 34.7 mmole). The suspension was heated to reflux, and the water liberated by the reaction was removed by azeotropic distillation by means of a Dean and Stark separator. The crude product was filtered, and then purified by Soxhlet extraction using methanol.

(ortho-Thiolatobenzoyloxy)di-n-butyltin(IV). Di-n-butyltin oxide (13.5 g, 54.0 mmole) was suspended in a benzene solution of ortho-mercaptobenzoic acid (8.25 g, 53.5 mmole). The mixture was heated to reflux, and the water liberated was removed by azeotropic distillation by means of a Dean and Stark separator. The light yellow solution was cooled, and the solvent removed by rotary evaporation, leaving a viscous oil. Petroleum ether was added, and the mixture was stirred for ca. 1 hour, during which time a light yellow solid precipitated, which was filtered, washed with petroleum ether and dried.

(ortho-Thiolatobenzoyloxy)diphenyltin(IV). Diphenyltin oxide (4.00 g, 13.8 mmole) was suspended in a benzene solution of ortho-mercaptobenzoic acid (2.14 g, 13.9 mmole). The suspension was heated to reflux, and the water liberated by the reaction was removed by azeotropic distillation by means of a Dean and Stark separator. The resulting solution was cooled, and its volume reduced to ca. 50 ml by rotary evaporation. Petroleum ether was then added, and the product (5.57 g) precipitated. The solid was filtered and dried.

(2,3-pyridinedioxy)di-n-butyltin(IV). Di-n-butyltin oxide (6.00 g, 24.1 mmole) was suspended in a benzene solution of 2,3-dihydroxypyridine (2.08 g, 24.1 mmole). The suspension was heated to reflux, and the water liberated was removed by azeotropic distillation by means of a Dean and Stark separator. The resulting solution was cooled, and the solvent was removed by rotary evaporation. Petroleum ether was added and the solution was filtered to remove undissolved solids. The product (7.39 g) was crystallized from the petroleum ether solution and dried *in vacuo* at 90° for 2 hours.

(ortho-Oxybenzoyloxy)di-n-butyltin(IV)·Pyridine. Pyridine was slowly added to (*ortho*-oxybenzoyloxy)di-*n*-butyltin(IV) until the compound had dissolved. Pentane was slowly added to the solution, and a white precipitate formed which was filtered, washed with pentane and dried.

Dimethyltin Oxide with Mandelic Acid. Dimethyltin oxide (4.00 g, 24.3 mmole) was suspended in a benzene solution of mandelic acid (3.70 g, 24.3 mmole). The mixture was heated to reflux, and the water liberated from the reaction was removed by azeotropic distillation by means of a Dean and Stark separator. The product (7.06 g), which was insoluble in benzene, was filtered, washed with petroleum ether and dried.

Di-n-butyltin Oxide with Mandelic Acid. Di-*n*-butyltin oxide (7.00 g, 28.1 mmole) was suspended in a benzene solution of mandelic acid (4.30 g, 28.3 mmole). The mixture was heated to reflux, and the water produced by the reaction was removed by azeotropic distillation by means of a Dean and Stark separator. The resulting solution was cooled, and its volume reduced to *ca*. 50 ml by rotary evaporation. Petroleum ether was added and the product precipitated as a white solid (10.22 g) which was filtered, washed with petroleum ether and dried.

Dimethyltin Oxide with ortho-Hydroxyacetanilide. Dimethyltin Oxide (3.00 g, 18.2 mmole) was suspended in a benzene solution of *ortho*-hydroxyacetanilide

(2.76 g, 18.3 mmole). The mixture was heated to reflux, and the water liberated by the reaction was removed by azeotropic distillation by means of a Dean and Stark separator. The product (5.20 g), which was insoluble in benzene, was filtered, washed with petroleum ether and dried.

Di-n-butyltin Oxide with ortho-Hydroxyacetanilide. Di-n-butyltin oxide (5.00 g, 20.1 mmole) was suspended in a benzene solution of ortho-hydroxyacetanilide (3.04 g, 20.1 mmole). The mixture was heated to reflux, and the water liberated by the reaction was removed by means of a Dean and Stark separator. The volume of the resulting solution was reduced to ca. 50 ml, and petroleum ether added to precipitate the product (7.30 g) which was filtered, washed with petroleum ether and dried.

Di-n-butyltin(IV) Salen. Di-n-butyltin oxide (10.0 g, 40.2 mmole) was suspended in a benzene solution of bis(salicylaldehyde)ethylenediamine (10.8 g, 40.3 mmole). The mixture was heated to reflux, and the water liberated by the reaction was removed by azeotropic distillation by means of a Dean and Stark separator. The resulting yellow solution was cooled, and the solvent removed by rotary evaporation. The bright yellow product was filtered, washed with petroleum ether and dried.

Transformations: Tin(IV) to Tin(II) Catecholate. (ortho-Phenylenedioxy)di-n-butyltin(IV) (1.00 g, 2.9 mmole) and tin(II) chloride (0.56 g, 2.9 mmole) were mixed in acetone and refluxed for ca. 3 hours. The solid product was filtered and its infrared spectrum identified it as ortho-phenylenedioxytin(II) by comparison with the spectrum of an authentic sample.[19]

Tin(IV) to Tin(II) ortho-Oxybenzoylate. (ortho-Oxybenzoyloxy)di-n-butyltin(IV) (1.00 g, 2.6 mmole) and tin(II) chloride (0.49 g, 2.6 mmole) were mixed together in acetone and refluxed ca. 3 hours. The solid product was filtered and its infrared spectrum identified it as ortho-oxybenzoyloxytin(II) by comparison with the spectrum of an authentic sample.[20]

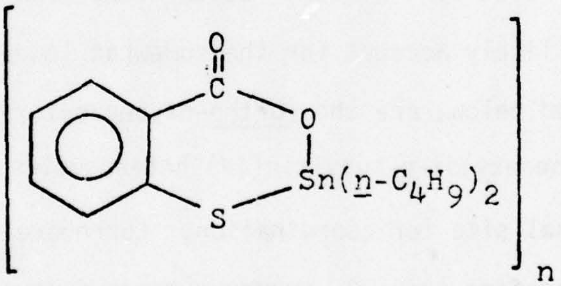
Tin(IV) (*ortho*-Phenylenedioxy)dimethyltin(IV) to Diacetoxy Catecholate. (*ortho*-Phenylenedioxy)dimethyltin(IV) (3.00 g, 10.9 mmole) was suspended in benzene and acetyl chloride (1.71 g, 21.8 mmole) added. The mixture was heated to reflux, during which time all the (*ortho*-phenylenedioxy)dimethyltin(IV) dissolved. After the solution had refluxed *ca*. ½ hour and was cooled to room temperature, pyridine (1.75 g, 22.2 mmole) was added. The dimethyltin dichloride-pyridine complex formed an immediate precipitate and was filtered. Benzene was removed from the filtrate by rotary evaporation and the product, diacetoxy catecholate, was recrystallized from a 1:1 solution of ethanol and water, m.p. 61.5-62.5° (lit.: 62-64°).[21]

Tin(IV) *ortho*-Oxybenzoyloxate to Catecholate. (*ortho*-Oxybenzoyloxy)di-*n*-butyltin(IV) (1.00 g, 2.9 mmole) and catechol (0.32 g, 2.9 mmole) were mixed in benzene and refluxed *ca*. 1 hour. The solid product was filtered and its infrared spectrum identified it as (*ortho*-phenylenedioxy)di-*n*-butyltin(IV).[5]

Results and Discussion

The syntheses of heterocyclic organotin(IV) compounds by reaction of diorganotin oxides according to Eq. (1) proceed rapidly and in high yield. The compounds, which are listed with their melting points, yields and microanalytical data in Table 1, display high thermal and hydrolytic stability, properties attributable to their presumed high degree of association in the solid state. Water is carried off as the benzene azeotrope. The oxygen in the water molecule can originate in either of the two reactants, but in the syntheses involving *ortho*-mercaptobenzoic acid only water was liberated. We assume that the water oxygen originates in the diorganotin(IV) oxide, just as it does in the case of the tin(II) oxide[20] and dimethoxytin(II) reactions.[22]

Evidence for the associated nature of ortho-oxybenzoyloxy- and (ortho-thiolatobenzoyloxy)diorganotin(IV) compounds is found in their infrared spectra listed in Tables 3 and 4, respectively. In the carbonyl stretching frequency region there are a number of strong absorption bands, with those in the range 1530-1500 cm^{-1} assigned to $\nu_{asym}(CO_2)$. These low values of $\nu_{asym}(CO_2)$ suggest that association occurs through coordination of the carbonyl oxygen to tin. The spectrum of (ortho-oxybenzoyloxy)di-n-butyltin(IV) in chloroform shows a new absorption band of medium intensity at 1630 cm^{-1} in addition to the associated carbonyl absorption band, presumably an absorption arising from a free carbonyl group. The spectrum of the sulfur analogue in chloroform, on the other hand, is identical to its solid-state spectrum. A molecular weight measurement by vapor pressure osometry extrapolated to infinite dilution in chloroform indicates that for



n = ca. 7, association apparently persisting in solution. The association in the solid (ortho-phenylenedioxy)di-n-butyltin(IV) is broken up in the strong base pyridine, in which the compound is monomeric.[5]

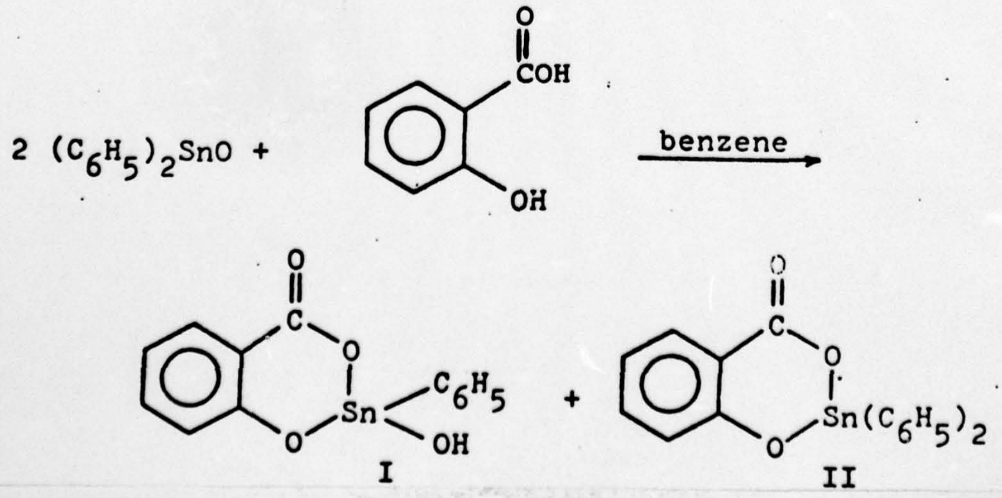
ortho-Oxybenzoyloxy- and (ortho-thiolatobenzoyloxy)di-n-butyltin(IV) differ from (ortho-phenylenedioxy)di-n-butyltin(IV) in other ways as well. Neither of the former are vacuum sublimable, but both are soluble in common organic solvents. (ortho-Oxybenzoyloxy)di-n-butyltin(IV) is fairly soluble initially, but with aging its solubility decreases, requiring refluxing to effect dissolution. The aging of the solid however, has no effect on its melting point or infrared spectrum. (ortho-Thiolatobenzoyloxy)di-n-butyltin(IV), on the other hand, is remarkable for its solubility. Crystallization of a concentrated chloroform solution could not be achieved, even when cooled to Dry Ice temperatures. Precipitation could only be brought about by addition of pentane.

Evidence for the association of the heterocycles is also given by the ^{119m}Sn Mössbauer data listed in Table 2. The ratios of the Quadrupole Splitting to the Isomer Shifts values are all greater than 2.1, reflecting higher coordination at tin.[23] The magnitude of the Quadrupole Splitting values, 3.1-3.9 mm/s for the heterocycles prepared here, also rules out a four-coordinated structure. A trans-diorganotin octahedral arrangement would demand a Q.S. value of 4 mm/s.[23] Distortions from the perfect trans-O_h symmetry would most likely account for the somewhat lowered values. Two exceptions, discussed below, are the (ortho-oxybenzoyloxy)phenyltin(III) hydroxide and the (2,3-pyridinedoxy)di-n-butyltin(IV) heterocycles, in each of which there is an additional site for coordination. Corroboration for the departure from the perfect trans-O_h symmetry comes from the infrared spectra of the dimethyltin derivatives in the region of the ν(Sn-C) stretching frequency. In each of the four such derivatives prepared (from mandelic, salicylic and ortho-mercaptobenzoic acids and ortho-hydroxyacetanilide) both ν_{sym} and ν_{asym}(Sn-C) absorptions can be assigned, indicating that the methyl groups are not linearly disposed about the central tin atom. Potentially interfering absorptions are seen in the tin(II) derivatives of salicylic and ortho-mercaptobenzoic acids,[22] but these bands do not block the ν_{sym}(Sn-C) at 535-528 cm^{-1} crucial to this analysis.

The infrared and ^{119m}Sn Mössbauer data for (ortho-oxybenzoyloxy)-dimethyltin(IV) differ from the other ortho-oxybenzoyloxy- and (ortho-thiolatobenzoyloxy)diorganotin(IV) compounds in that $\nu_{asym}(CO_2)$ is found at a higher frequency, 1630 cm^{-1}, and its Quadrupole Splitting value of 3.85 mm/s is significantly higher than for the other analogous heterocycles. The value of $\nu_{asym}(CO_2)$ is surprising, since this is usually associated with an uncoordinated carbonyl oxygen. However, the high melting point and insolubility, even in boiling pyridine, and the observation of a weak ambient temperature Mössbauer spectrum, usually indicative of a large recoil-free fraction arising from a polymeric lattice,[23,24] are all evidence for association.

The five-membered sulfur heterocycle $(CH_3)_2\overline{SnS(CH_2)_2S}$ has been shown by X-ray crystallographic studies to be monomeric in the solid with four-coordinated tin atoms,[25] in contrast to the related six-membered oxygen heterocycle, $(n\text{-}C_4H_9)_2\overline{SnO(CH_2)_3O}$, which is intermolecularly coordinated to form octahedra at tin.[26]

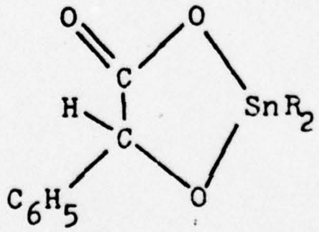
Diphenyltin oxide reacts with ortho-mercaptobenzoic acid to give (ortho-thiolatobenzoyloxy)diphenyltin(IV), but the reaction with salicylic acid produces only half the required amount of water and gives an insoluble solid whose infrared, spectrum given in Table 5, shows a broad absorption band arising from $\nu(OH)$ at 3290 cm^{-1}. The Mössbauer parameters are similar to those reported for monoalkylstannoic acids,[23,27,28] which, along with the elemental analysis data, suggest that the reaction occurs as



(2)

with compound (I) isolated as an insoluble product. A solid was recovered from the benzene solution which may be compound (II), but this material could not be obtained analytically pure. The low Quadrupole Splitting value observed for (I) is consistent with a tetrahedral geometry about the tin atom. The Isomer Shift value is very small owing to the low s-electron density at the tin atom resulting from the electron attraction by the three surrounding oxygen atoms. Close analogues are the phenylstannanoic acid, $[C_6H_5Sn(O)OH]_n$ and the phenylstannatrane, $C_6H_5Sn(OCH_2CH_2)_3N$, with Isomer Shift and Quadrupole Splitting values of 0.78; 1.83 and 0.43; 1.18 mm/s, respectively.[28] These compounds, like ours, are infusible, air-stable solids, but the tin atom is generally thought to be four-coordinated in a tetrahedral environment of the type $RSnX_3$,[28] as in methyltin sesquisulfide, $(CH_3Sn)_4S_6$ in which the tin atoms have been shown to be tetrahedral in an X-ray crystal structure.[29] The $\nu_{asym}(CO_2)$ at 1625 cm^{-1} corresponds to a free, unassociated carbonyl group and is confirmatory. The broad, low energy $\nu(OH)$ band at 3290 contrasts with the sharp absorptions above 3600 cm^{-1} in other organotin hydroxides,[30] and suggests hydrogen bonding in the solid.

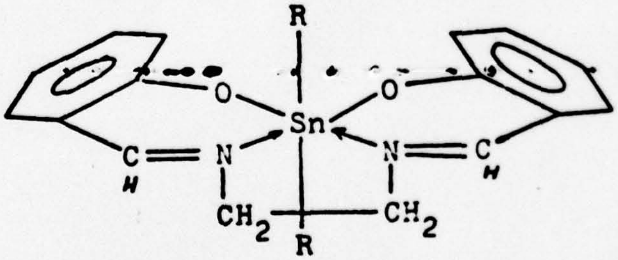
The reaction of dimethyl- and di-n-butyltin oxides with mandelic acid gives the heterocycles



whose infrared spectra and Mössbauer data resemble those of (ortho-oxybenzoyloxy)-dimethyltin(IV). In the dimethyltin(IV) heterocycle, $\nu_{asym}(CO_2)$ is split into two bands at 1654 and 1630 cm^{-1}, and is found at 1613 cm^{-1} for the di-n-butyltin heterocycle.

The reaction of di-n-butyltin oxide with 2,3-dihydroxypyridine gives a heterocycle whose structure is analogous to that of (ortho-phenylenedioxy)di-n-butyltin(IV),[5] but whose melting point is much lower (by ca. 70°) and whose solubility is much greater. These data suggest that in (2,3-pyridinedioxy)di-n-butyltin(IV), intermolecular coordination through the pyridyl nitrogen breaks the oxygen-tin coordination in the analogous phenylene derivative to give a more tractable compound. The lower Quadrupole Splitting value (2.86 vs. 3.40 mm/s[4,31,32]) is corroboratory. The reaction of dimethyltin oxide with 2,3-dihydroxypyridine, on the other hand, yields a solid that is insoluble in all solvents, and could not be obtained pure, as indicated by elemental analysis and the complexity of its Mössbauer spectrum.

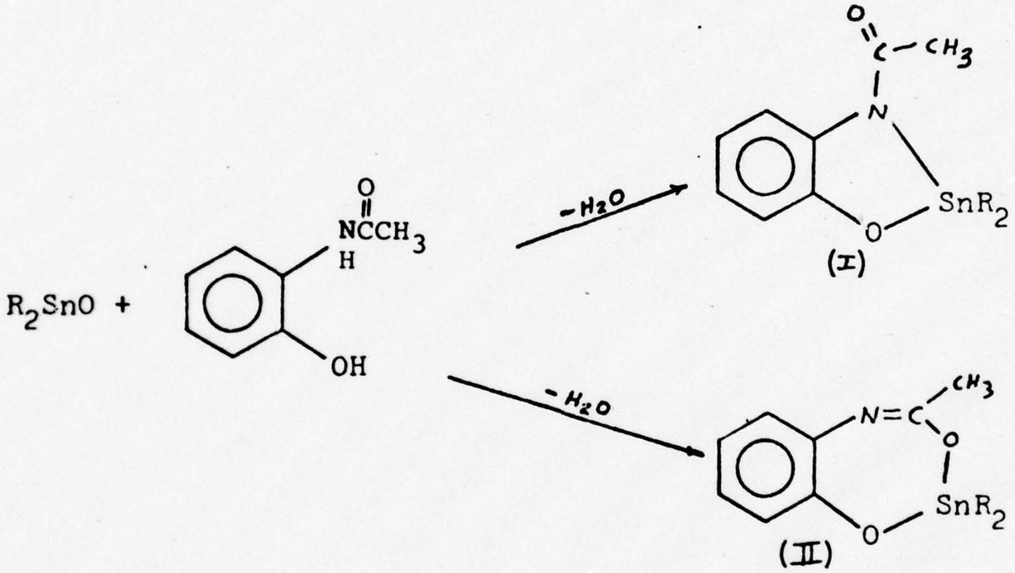
A number of diorganotin(IV) compounds have been derived from the dianion of bis(salicylaldehyde)ethylenediimine, usually abbreviated Salen.[6-11] The structure of the R_2SnSalen compounds where R = CH_3 has been found by X-ray crystallography to be octahedral about the tin atom with trans-R groups (<C-Sn-C = 160°)[33]



The reaction of di-n-butyltin oxide with H_2Salen gives a compound whose infrared spectrum is comparable with those of the known R_2SnSalen compounds, usually prepared from the sodium or thallium salts of the H_2Salen dianion. Mössbauer

Isomer Shift and Quadrupole Splitting values for the dimethyltin derivative of known structure are also similar,[10,11] suggesting that the n-butyl analogue also takes a distorted octahedral structure.

Hexalkyldistannoxanes react with amides, such as succinimide to form tin(IV)-nitrogen bonds.[34] However, the reaction of dimethyl- and di-*n*-butyltin oxide with *ortho*-hydroxyacetanilide could yield heterocycles with two possible structures:



(3)

Distinguishing the two possible heterocycles is difficult. Heterocycle (III) contains an amide carbonyl group which would be expected to be coordinated to the tin atom of an adjacent molecule. Dimethylformamide shows a lowering of *ca*. 50 cm^{-1} on complexation with tin(IV) chloride[35] from the n-hexane solution value of 1696 cm^{-1}.[36] However, the most prominent absorption in the region associated with either ν(C=O) or ν(C=N) is found at *ca*. 1556 cm^{-1} for both our dimethyl- and dibutyltin derivatives, a value which can only be assigned to an intracyclic ν(C=N) absorption. In addition, the compounds are stable toward atmospheric moisture, suggesting that they adopt the structure shown for heterocycle (IV), while (III) would not be expected to be as stable, owing to the high reactivity of tin-nitrogen bonds toward protic reagents.[37]

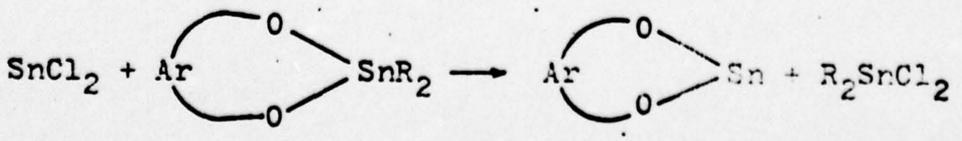
One heterocycle, (ortho-oxybenzoyloxy)di-n-butyltin(IV), when recrystallized from pyridine, forms a stable 1:1 adduct. The infrared spectrum shows that $\nu_{asym}(CO_2)$ is shifted to 1624 cm^{-1}, and the Quadrupole Splitting value increases to 3.75 mm/s, as compared to values of 1512 cm^{-1} and 3.18 mm/s for the uncomplexed heterocycle. All the other heterocycles studied are either insoluble in pyridine, or when recrystallized from pyridine, do not form a stable complex.

A general class of organometallic transformation reactions can be represented by the Equation:

$$M\text{-}E + Q\text{-}X \longrightarrow M\text{-}X + Q\text{-}E \qquad (4)$$

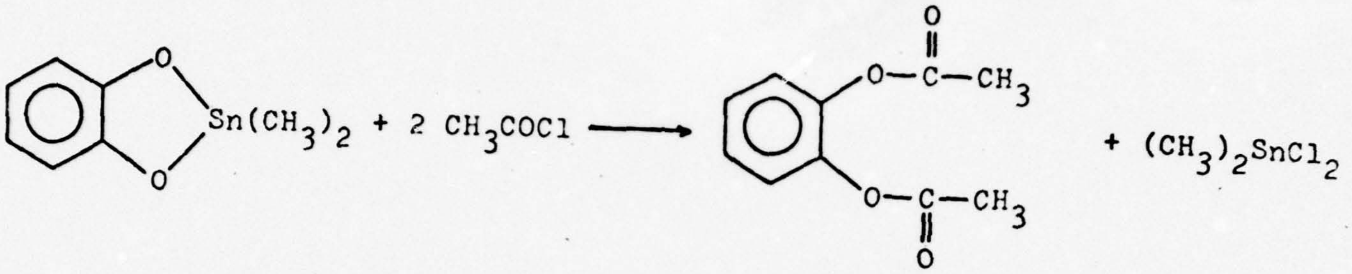
where M and Q are metals or metalloids, X is a halogen, and E an organic grouping RO-, R_2N-, etc.[38] Our heterocyclic organotin(IV) compounds also participate in these transformation reactions, and we have shown that this scheme can be extended to a system where M and Q are the element tin in different oxidation states.

Tin(II) chloride, for example, reacts with the ortho-phenylenedioxy- and ortho-oxybenzoyloxytin(IV) heterocycles in acetone to give the corresponding tin(II) heterocycles:



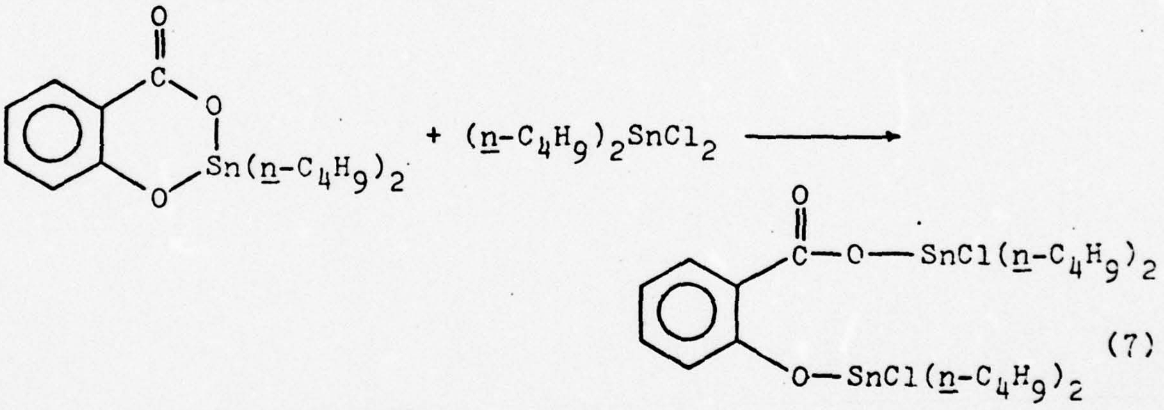
(5)

The insoluble tin(II) heterocycle precipitates from the reaction medium in each case. Acetyl chloride also reacts with (ortho-phenylenedioxy)dimethyltin in benzene to give diacetoxycatechol:



(6)

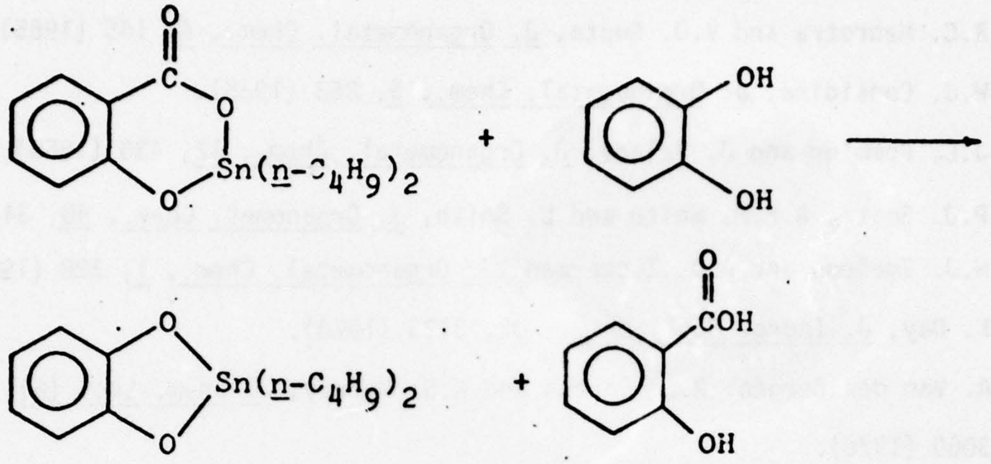
In this case the organotin halide was precipitated from the reaction medium as the pyridine complex. Di-n-butyltin dichloride reacts with (ortho-oxybenzoyloxy)di-n-butyltin(IV) in refluxing benzene according to the equation:



(7)

The product of the reaction is a viscous liquid, which upon vacuum distillation gives only di-n-butyltin dichloride, illustrating the reversibility of the transformation reactions.

Transformations can also be accomplished from one heterocycle to another, for example:



(8)

This transformation is presumably due to the greater insolubility of the ortho-phenylenedioxytin(IV) heterocycle. An attempt to exchange organotin moieties based on the greater insolubility of (ortho-oxybenzoyloxy)dimethyltin(IV) relative to its di-$\underline{n}$-butyltin analogue failed, owing to the formation of a ditin compound by a reaction similar to that shown in Eq. (7).

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References and Notes

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24. The recent observation of ambient-temperature tin-119m Mössbauer spectra for certain molecular solids such as tetraphenyltin (m.p. 229°) does not effect our conclusion which is based upon a variety of physical evidence and upon close analogies with other associated tin(IV)-oxygen and sulfur solids whose structures are known.[14]

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Table 1

Heterocyclic Organotin(IV) Compounds

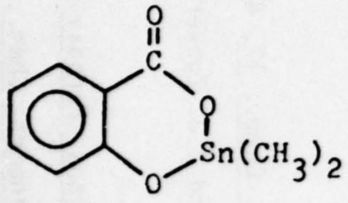
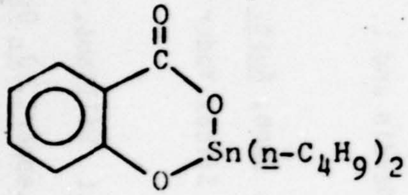
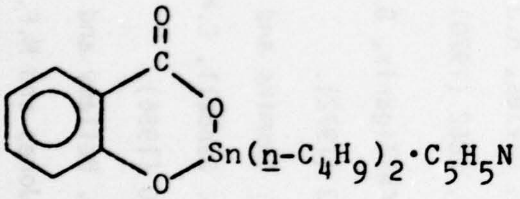
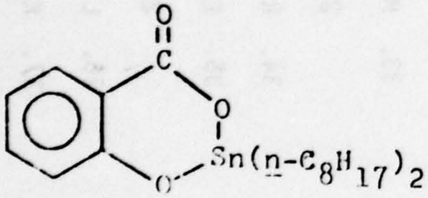
Compound	Yield,%	m.p.	Anal. Found(Calc.) Sn,%	 C,%	 H,%
	95	285-288°a	40.93(41.67)	38.66(37.95)	3.50(3.54)
	94	226-229°	31.66(32.16)	48.95(48.82)	6.00(6.01)
		231-233°	26.92(26.49)		
	45	162-164°	25.01(24.66)	56.61(57.40)	8.08(7.96)

Table 1 (cont'd)

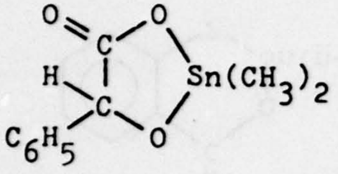
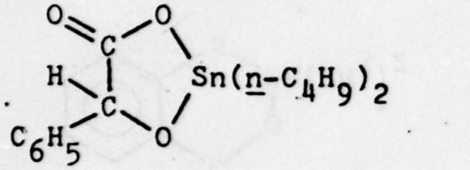
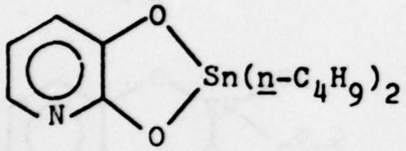
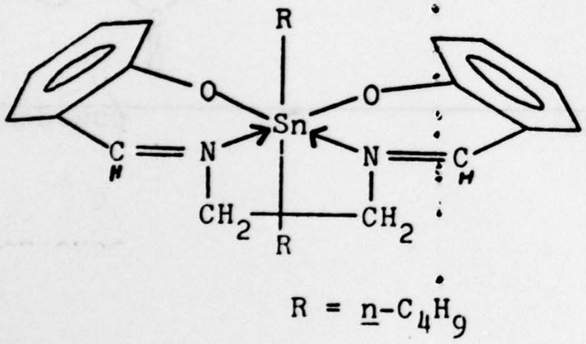
Compound	Yield,%	m.p.	Sn,%	C,%	H,%
	97	287-290°	38.37(39.71)		
	93	194-195°	30.22(30.98)	50.53(50.17)	6.41(6.31)
	90	199-201°	33.86(34.70)	45.84(45.66)	6.37(6.18)
	96	151-153°	23.68(23.57)	57.67(57.74)	6.51(6.46)

Table 1 (cont'd)

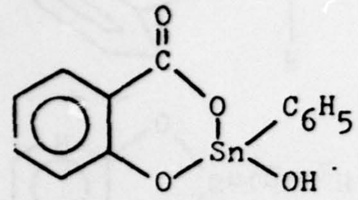
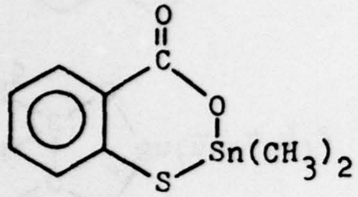
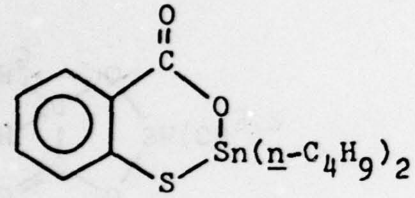
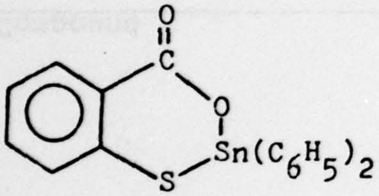
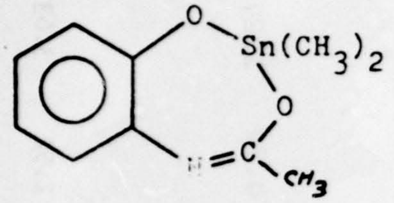
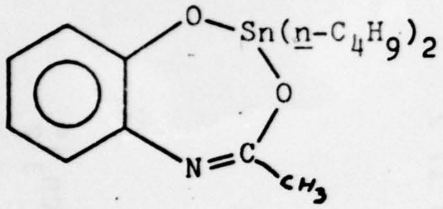
Compound	Yield,%	m.p.	Sn,%	C,%	H,%
	47	>300°	33.19(34.02)	46.70(44.75)	3.08(2.89)
	62	290-292°	40.03(39.44)	35.63(35.92)	3.45(3.35)
	75	185-186°	30.36(30.82)	47.42(46.79)	6.10(5.76)
	94	295-296°	27.57(27.92)	53.52(53.67)	3.36(3.32)

Table 1 (cont'd)

Compound	Yield,%	m.p.	Sn,%	C,%	H,%
	95	280-283°	40.30(39.84)		
	95	208-210°[a]	31.06(31.06)	49.98(50.30)	6.87(6.60)

[a] Melts with decomposition.

Table 2

^{119m}Sn Mössbauer Data at 77K

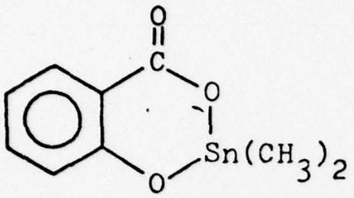
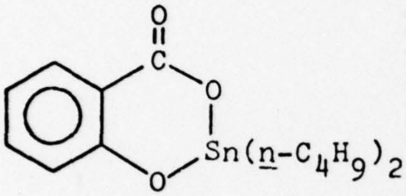
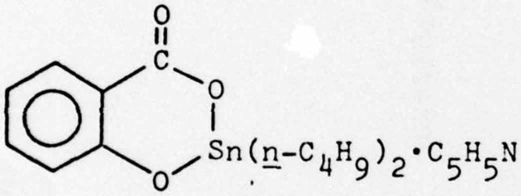
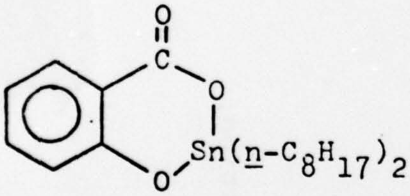
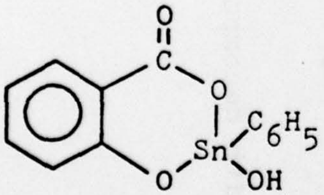
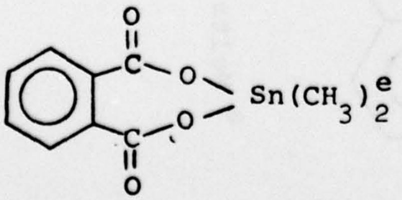
Compound	I.S.[a]	Q.S.[b]	Γ_1	Γ_2	ρ[c]
	1.38[d]	3.85	1.46	1.53	2.80
	1.26	3.18	1.38	1.32	2.52
	1.38	3.75	0.95	1.03	2.72
	1.29	3.13	1.47	1.16	2.43
	0.70	1.27	1.44	1.55	1.81
	1.52	3.63	1.15	1.28	2.39

Table 2 (cont'd)

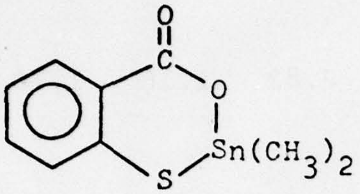
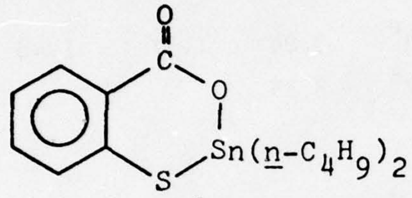
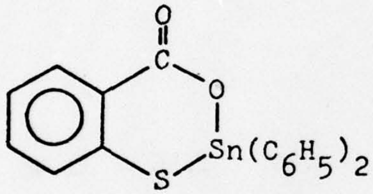
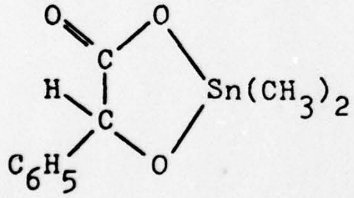
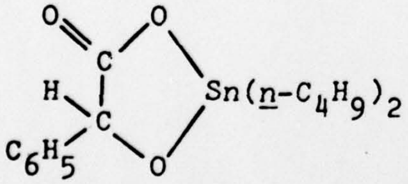
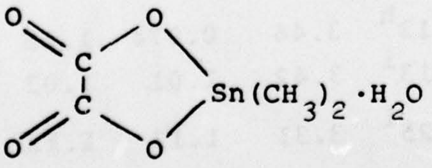
Compound	I.S.[a]	Q.S.[b]	Γ_1	Γ_2	ρ[c]
	1.32	3.08	1.22	1.15	2.33
	1.46	3.24	1.32	1.18	2.22
	1.27	2.86	1.50	1.20	2.25
	1.26	3.63	1.52	1.50	2.88
	1.36	3.71	1.33	1.26	2.73
	1.47[e] (-0.55)[f]	4.41 4.65	1.27	1.29	3.00

Table 2 (cont'd)

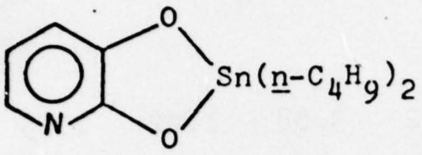
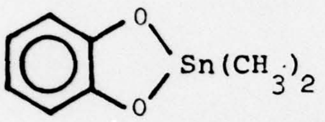
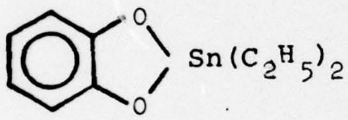
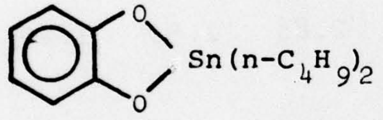
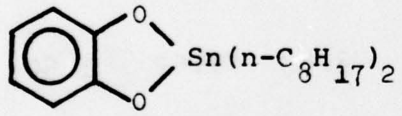
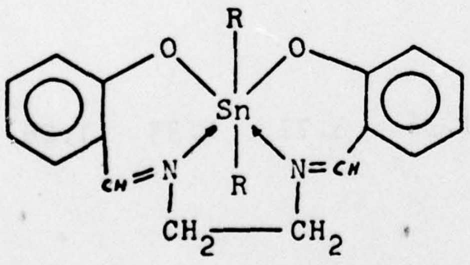
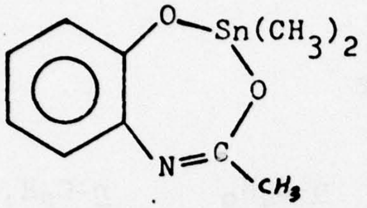
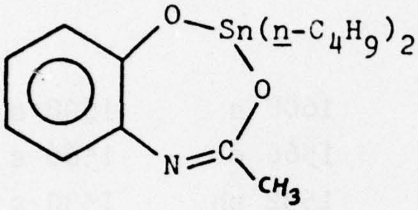
Compound	I.S.[a]	Q.S.[b]	Γ_1	Γ_2	ρ[c]
	1.26	2.82	1.16	1.10	2.24
	1.14[e] 1.32[g]	3.24 3.35	1.57	1.48	2.84 2.53
	1.50[g]	3.60			2.40
	1.29[e] 1.52[g]	3.40 3.62	1.56	1.48	2.64 2.38
	1.36[g]	3.41			2.51
					
R=CH_3	1.13[h]	3.46	0.874	1.02	3.06
	1.13[i]	3.42	1.01	1.02	3.03
C_2H_5	1.25[i]	3.31	1.13	1.13	2.65
n-C_4H_9	1.27	3.50	1.31	1.26	2.76

Table 2 (cont'd)

Compound	I.S.[a]	Q.S.[b]	Γ_1	Γ_2	ρ^c
	1.23	3.18	1.04	1.30	2.59
	1.39	3.30	1.13	1.14	2.37

[a] ±0.06 mm/s.

[b] ±0.12 mm/s.

[c] ρ = I.S./Q.S.

[d] Shows a weak spectrum at ambient temperatures.

[e] From ref. 31.

[f] Run _vs_. grey tin in ref. 39.

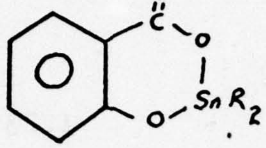
[g] From ref. 32.

[h] From ref. 10.

[i] From ref. 11.

TABLE 3

Infrared Spectra of (*ortho*-Oxybenzoyloxy)dialkyltin(IV),



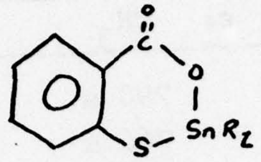
Assignment	R= CH_3	n-C_4H_9	n-C_8H_{17}
$\nu_{asym}(CO_2)$	1622 vs		
	1612 s		
	1595 s	1608 s	1608 s
		1566 s	1566 s
	1520 w	1532 sh	1530 s
$\nu_{asym}(CO_2)$		1512 vs	1512 vs
	1473 s	1466 sh	1467 sh
	1457 s	1448 s	1447 s
		1419 sh	1419 sh
	1406 w		
$\nu_{sym}(CO_2)$	1352 s	1403 s	1404 s
		1330 m	1330 m
	1312 sh	1313 w	1314 w
	1252 m	1257 sh	1258 sh
	1224 s	1233 s	1235 s
	1202 w	1198 w	1203 w
	1162 s	1163 m	1165 m
	1140 s	1144 s	1147 s
	1100 w	1104 m	1106 m
	1042 s	1038 s	1040 m
	969 w	968 m	968 w
	897 m	890 s	890 s
	874 m	875 m	875 m
	846 s	831 s	830 s
	806 sh	811 m	812 m

TABLE 3 (cont'd)

Assignment	R: CH_3	n-C_4H_9	n-C_8H_{17}
δ(Sn-CH_3) rock	790 s		
	766 s	766 s	767 s
	706 m	711 s	709 m
δ(CO_2)	670 s	670 s	672 s
	630 m	642 m	642 m
		618 w	622 w
	590 s	585 s	587 s
		555 w	
	535 m	535 m	534 m
	506 m	493 m	493 m
	452 s	460 m	
	436 m	425 m	436 sh
			425 m
	403 s		
		395 m	
		349 s	349 s
	317 m	300 sh	300 sh
	282 s	275 s	269 s
		224 w	217 w

TABLE 4

Infrared Spectra of (ortho-Thiolatobenzoyloxy)diorganotin(IV),



Assignment	R= CH_3	$\underline{n}$-C_4H_9	C_6H_5
	1596 s	1590 s	1591 s
	1568 s	1566 s	1566 s
$\nu_{asym}(CO_2)$	1530 vs	1527 vs	1527 vs
			1482 m
			1462 m
	1429 m	1428 m	1430 m
$\nu_{sym}(CO_2)$	1410 vs	1406 vs	1408 vs
	1276 w	1278 w	1279 w
	1255 w	1255 w	
	1155 w	1157 w	
	1118 vw	1120 vw	
			1080 w
	1059 m	1060 m	1061 m
	1038 m	1040 m	1039 m
			1024 w
			1001 m
	957 w	959 w	960 w
	870 s	867 s	870 m
	808 sh	810 w	811 w
$\delta(Sn-CH_3)$ rock	788 s		
	747 s	749 s	751 s
	729 s	732 s	733 s
	707 w	705 m	
	680 s	678 m	698 s

TABLE 4 (Cont'd)

Assignment	R=	CH_3	$\underline{n}$-C_4H_9	C_6H_5
		653 s	654 s	652 m
		577 m	577 m	575 w
		563 m		
		528 m	524 w	
		498 m	498 m	492 sh
		477 m	480 m	482 m
				449 m
		428 w	427 w	
		394 sh	396 m	402 m
		378 m	377 w	375 w
ν(Sn-S)		336 m	334 m	335 m
				280 m
		251 m	246 m	263 m
				235 sh
				221 s

TABLE 5

Infrared Spectra of Diorganotin(IV) Heterocycles

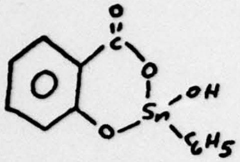
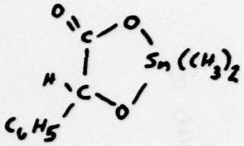
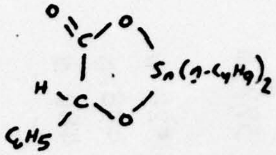
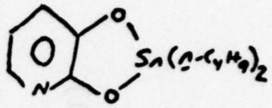
			
3290 m,br	1653^{a} vs	1642 sh	1609 s
1625 s	1630 vs	1613^{a} vs	1558 s
			1488 vs
1588 s	1497 w	1496 w	1420 m
1541^{a} vs	1407 w	1466 w	1352 m
		1453 m	
1485 s	1349^{b} vs	1362^{b} s	1300 s
1466 s			
1433 m	1290 m	1194 m	1271 s
1388^{b} s	1260 w	1080 m	1238 w
1321 w	1197 m	1055 s	1206 s
1248 s	1085 m	1027 m	1124 s
1162 m	1045 s	1003 w	1081 w
1148 m	1030 m	953 m	1064 m
1078 m	994 w	920 w	1028 m
1034 m	956 m	875 w	967 w
999 w	867 w	795 m	944 w
967 m	803 s	764 s	904 w
808 w	765 s	705 s	882 m
757 s	705 s	690 w	852 w
732 s	638 w	623 m	823 s
698 s	623 m	578 m	790 w

TABLE 5 (cont'd)

674 s	586 s	523 m	770 s
596 s	528 m	480 m	691 m
564 m	480 m		654 s
530 m	399 m		627 s
447 m			592 sh
			512 m
			476 m

[a] $\nu_{asym}(CO_2)$.

[b] $\nu_{sym}(CO_2)$.

TABLE 5 (cont'd)

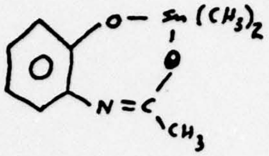
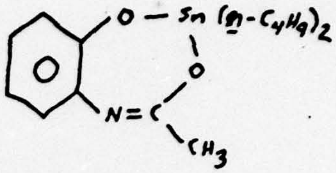
$(\underline{n}\text{-}C_4H_9)_2$Sn Salen		
1624 vs	1594 w	1595 w
1602 sh	1554 s	1555 s
1536 s	1500 s	1499 s
1451 s	1416 s	1420 s
1403 sh	1352 w	1352 w
1397 m	1315 m	1317 m
1346 m	1288 m	1289 m
1324 m	1241 s	1248 s
1262 w	1213 m	1216 m
1243 m	1195 w	1198 w
1192 m	1163 w	1164 w
1147 s	1120 m	1120 m
1129 m	1051 m	1080 w
1092 m	1039 m	1052 m
1048 m	1014 m	1038 m
1029 m	975 m	1016 m
988 w	919 w	974 m
955 w	827 s	917 w
909 m	740 s	876 w
883 w	667 m	828 s
848 w	636 m	738 s

TABLE 5 (cont'd)

$(\underline{n}\text{-}C_4H_9)_2Sn$ Salen		
792 w	597 m	687 m
759 s	582 m	666 s
740 m	562 m	634 m
694 w	529 w	598 m
677 w		561 m
607 m		
571 m		
522 w		
462 m		