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

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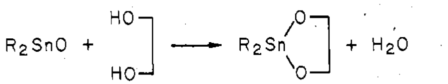
Condensation of diorganotin oxides with diols, carboxylic acids, and thiols releases water to form tin(IV)–oxygen and –sulfur heterocycles with five-, six-, and seven-membered rings. In this way new diorganotin(IV) *o*-phenylenedioxy, oxybenzoyloxy, thiolatobenzoyloxy, pyridinedioxy, and acetanilidoxy heterocycles, the structure of the last being 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 *o*-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.



(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 77 K on a cam-drive, constant-acceleration spectrometer previously described,[17] with $Ba^{119m}SnO_3$ (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, N.Y.

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

(*o*-Oxybenzoyloxy)dimethyltin(IV). Dimethyltin oxide (11.9 g, 72.2 mmol) was suspended in benzene solution of salicylic acid (10.0 g, 72.4 mmol). The mixture was heated to reflux, and the water liberated in the reaction was 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.

(*o*-Oxybenzoyloxy)di-*n*-butyltin(IV). Di-*n*-butyltin oxide (13.45 g, 54.0 mmol) was suspended in a solution of salicylic acid (7.49 g, 54.0 mmol) 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, (*o*-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.

(*o*-Oxybenzoyloxy)di-*n*-octyltin(IV). Di-*n*-octyltin oxide (5.00 g, 13.8 mmol) was suspended in a benzene solution of salicylic acid (1.91 g, 13.8 mmol). 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 clear solution was cooled and the solvent stripped by rotary evaporation to leave a viscous liquid. The liquid was taken up in petroleum ether and the solution filtered and allowed to stand for 1 day during which time a white solid precipitated. The product was filtered and dried.

(*o*-Oxybenzoyloxy)phenyltin(IV) Hydroxide. Diphenyltin oxide (3.50 g, 12.1 mmol) was suspended in a benzene solution of salicylic acid (1.68 g, 12.2 mmol). 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 °C for 1 h.

(*o*-Thiolatobenzoyloxy)dimethyltin(IV). Dimethyltin oxide (5.00 g, 30.3 mmol) was suspended in a benzene solution of *o*-mercaptobenzoic acid (5.35 g, 34.7 mmol). 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.

(*o*-Thiolatobenzoyloxy)di-*n*-butyltin(IV). Di-*n*-butyltin oxide (13.5 g, 54.0 mmol) was suspended in a benzene solution of *o*-mercaptobenzoic acid (8.25 g, 53.5 mmol). 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 was removed by rotary evaporation, leaving a viscous oil. Petroleum ether was added, and the mixture was stirred for ca. 1 h, during which time a light yellow solid precipitated, which was filtered, washed with petroleum ether, and dried.

(*o*-Thiolatobenzoyloxy)diphenyltin(IV). Diphenyltin oxide (4.00 g, 13.8 mmol) was suspended in a benzene solution of *o*-mercaptobenzoic acid (2.14 g, 13.9 mmol). 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 mmol) was suspended in a benzene solution of 2,3-dihydroxypyridine (2.08 g, 24.1 mmol). 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 °C for 2 h.

(*o*-Oxybenzoyloxy)di-*n*-butyltin(IV) Pyridine. Pyridine was slowly added to (*o*-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 mmol) was suspended in a benzene solution of *dl*-mandelic acid (3.70 g, 24.3 mmol). 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.

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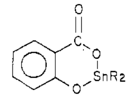
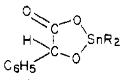
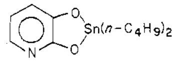
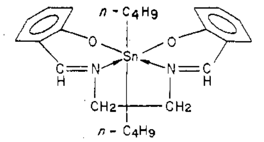
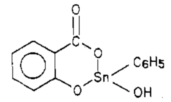
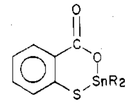
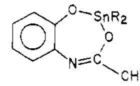
Table I. Heterocyclic Organotin(IV) Compounds

compound	yield, %	mp, °C	% Sn calcd	% Sn found	% C calcd	% C found	% H calcd	% H found
								
R = CH_3	95	285–288[a]	41.67	40.93	37.95	38.66	3.54	3.50
R = n-C_4H_9	94	226–229	32.16	31.66	48.82	48.95	6.01	6.00
pyridine addition		231–233	26.49	26.92				
R = C_4H_9	45	162–164	24.66	25.01	57.40	56.61	7.96	8.08
								
R = CH_3	97	287–290	39.71	38.37				
R = n-C_8H_{17}	93	194–195	30.98	30.22	50.17	50.53	6.31	6.41
	90	199–201	34.70	33.86	45.66	45.84	6.18	6.37
	96	151–153	23.57	23.68	57.74	57.67	6.46	6.51
	47	>300	34.02	33.19	44.75	46.70	2.89	3.08
								
R = CH_3	62	290–292	39.44	40.03	35.92	35.63	3.35	3.45
R = n-C_4H_9	75	185–186	30.82	30.36	46.79	47.42	5.76	6.10
R = C_6H_5	94	295–296	27.92	27.57	53.67	53.52	3.32	3.36
								
R = CH_3	95	280–283	39.84	40.30				
R = n-C_4H_9	95	208–210[a]	31.06	31.06	50.30	49.98	6.60	6.87

[a] Melts with decomposition.

Di-*n*-butyltin Oxide with Mandelic Acid. Di-*n*-butyltin oxide (7.00 g, 28.1 mmol) was suspended in a benzene solution of mandelic acid (4.30 g, 28.3 mmol). 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 *o*-Hydroxyacetanilide. Dimethyltin oxide (3.00 g, 18.2 mmol) was suspended in a benzene solution of *o*-hydroxyacetanilide (2.76 g, 18.3 mmol). 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 *o*-Hydroxyacetanilide. Di-*n*-butyltin oxide (5.00 g, 20.1 mmol) was suspended in a benzene solution of *o*-hydroxyacetanilide (3.04 g, 20.1 mmol). 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 was added to precipitate the product (7.30 g) which was filtered, washed with petroleum ether, and dried.

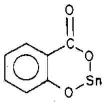
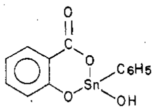
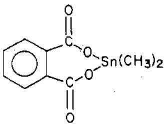
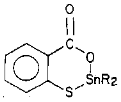
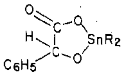
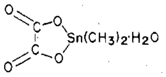
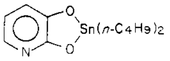
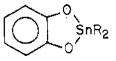
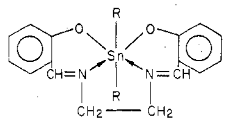
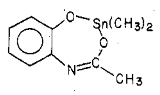
Di-*n*-butyltin(IV) Bis(salicylaldehyde) Ethylenediimine. Di-*n*-butyltin oxide (10.0 g, 40.2 mmol) was suspended in a benzene solution of bis(salicylaldehyde) ethylenediamine (10.8 g, 40.3 mmol). The mixture was heated to reflux, and the water liberated by the reaction was removed by azeotropic distillation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

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

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

Tin(IV) (*o*-Phenylenedioxy)dimethyltin(IV) to Diacetoxycatecholate. (*o*-Phenylenedioxy)dimethyltin(IV) (3.00 g, 10.9 mmol) was suspended in benzene and acetyl chloride (1.71 g, 21.8 mmol) added. The mixture was heated to reflux, during which time all the (*o*-phenylenedioxy)dimethyltin(IV) dissolved. After the solution had refluxed ca. 0.5 h and was cooled to room temperature, pyridine (1.75 g, 22.2 mmol) 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

Table II. ^{119m}Sn Mössbauer Data at 77 K

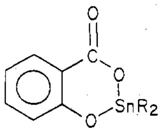
compound	IS,^{a} mm/s	QS,^{b} mm/s	Γ_1	Γ_2	ρ^c
					
R = CH_3	1.38^{d}	3.85	1.46	1.53	2.80
R = n-C_4H_9	1.26	3.18	1.38	1.32	2.52
pyridine addition	1.38	3.75	0.95	1.03	2.72
R = n-C_8H_{17}	1.29	3.13	1.47	1.16	2.43
	0.70	1.27	1.44	1.55	1.81
	1.52	3.63	1.15	1.28	2.39
					
R = CH_3	1.32	3.08	1.22	1.15	2.33
R = n-C_4H_9	1.46	3.24	1.32	1.18	2.22
R = C_6H_5	1.27	2.86	1.50	1.20	2.25
					
R = CH_3	1.26	3.63	1.52	1.50	2.88
R = n-C_4H_9	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
	1.26	2.82	1.16	1.10	2.24
					
R = CH_3	1.14^{e}	3.24	1.57	1.48	2.84
	1.32^{g}	3.35			2.53
R = C_2H_5	1.50^{g}	3.60			2.40
R = n-C_4H_9	1.29^{e}	3.40	1.56	1.48	2.64
	1.52^{g}	3.62			2.38
R = n-C_8H_{17}	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
R = C_2H_5	1.25^{i}	3.31	1.13	1.13	2.65
R = n-C_4H_9	1.27	3.50	1.31	1.26	2.76
					
R = CH_3	1.23	3.18	1.04	1.30	2.59
R = n-C_4H_9	1.39	3.30	1.13	1.14	2.37

[a] ±0.06 mm/s. [b] ±0.12 mm/s. [c] ρ = IS/QS. [d] Shows a weak spectrum at ambient temperatures. [e] From ref 31. [f] Run vs. gray tin in ref 39. [g] From ref 32. [h] From ref 10. [i] From ref 11.

and water; mp 61.5–62.5 °C (lit.[21] mp 62–64 °C).

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

Table III. Infrared Spectra of (*o*-Oxybenzoyloxy)dialkyltin(IV)



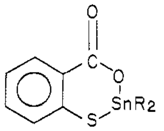
	R		
assignment	CH_3	n-C_4H_9	n-C_8H_{17}
$\nu_{asym}(CO_2)$	1622 vs		
	1612 s		
	1595 s	1608 s	1608 s
		1566 s	1566 s
	1520 w	1532 sh	1530 s
$\nu_{asym}(CO_2)$		1512 vs	1512 vs
	1473 s	1466 sh	1467 sh
	1457 s	1448 s	1447 s
		1419 sh	1419 sh
	1406 w		
$\nu_{sym}(CO_2)$	1352 s	1403 s	1404 s
		1330 m	1330 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
$\delta(Sn-CH_3)$ rock	790 s		
	766 s	766 s	767 s
	706 m	711 s	709 m
$\delta(CO_2)$	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

Results and Discussion

The syntheses of heterocyclic organotin(IV) compounds by reaction of diorganotin oxides according to eq 1 proceed rapidly, in high yield. The compounds, which are listed with their melting points, yields, and microanalytical data in Table I, 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 *o*-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]

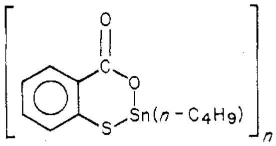
Evidence for the associated nature of (*o*-oxybenzoyloxy)- and (*o*-thiolatobenzoyloxy)diorganotin(IV) compounds is found in their infrared spectra listed in Tables III and IV, respectively. In the carbonyl stretching frequency region there are a number of strong absorption bands, with those in the range 1530–1500 cm^{-1} assigned to $\nu_{asym}(CO_2)$. These low values of $\nu_{asym}(CO_2)$ suggest that association occurs through

Table IV. Infrared Spectra of (*o*-Thiolatobenzoyloxy)diorganotin(IV)



assignment	R		
	CH_3	*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
	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
$\nu(Sn-S)$	336 m	334 m	335 m
			280 m
	251 m	246 m	263 m
			235 sh
			221 s

coordination of the carbonyl oxygen to tin. The spectrum of (*o*-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 with its solid-state spectrum. A molecular weight measurement by vapor pressure osmometry extrapolated to infinite dilution in chloroform indicates that for



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

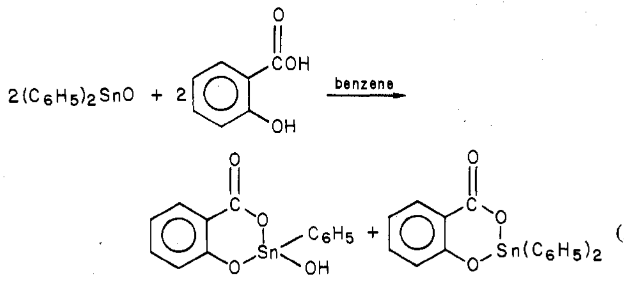
(*o*-Oxybenzoyloxy)- and (*o*-thiolatobenzoyloxy)di-*n*-butyltin(IV) differ from (*o*-phenylenedioxy)di-*n*-butyltin(IV) in other ways as well. Neither of the former are vacuum sublimable, but both are soluble in common organic solvents. (*o*-Oxybenzoyloxy)di-*n*-butyltin(IV) is fairly soluble initially, 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. (*o*-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 II. The ratios of the quadrupole splitting (QS) 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 QS 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 (*o*-oxybenzoyloxy)phenyltin(IV) hydroxide and the (2,3-pyridinedioxy)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 *o*-mercaptobenzoic acids and *o*-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 *o*-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 (*o*-oxybenzoyloxy)dimethyltin(IV) differ from the other (*o*-oxybenzoyloxy)- and (*o*-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 *o*-mercaptobenzoic acid to give (*o*-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 V, shows a broad absorption band arising from ν(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 shown in eq 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.

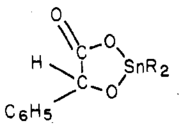


(2)

I II

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 ν(OH) band at 3290 cm^{-1} 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 (*o*-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 (*o*-phenylenedioxy)di-*n*-butyltin(IV),[5] but whose melting point is much lower (by ca. 70 °C) 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_2Sn(salen) 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]

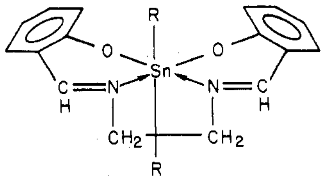
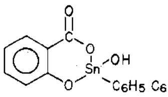
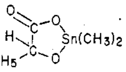
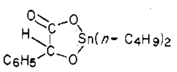
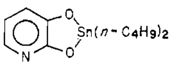
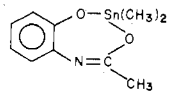
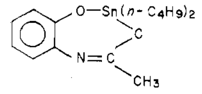


Table V. Infrared Spectra of Diorganotin(IV) Heterocycles

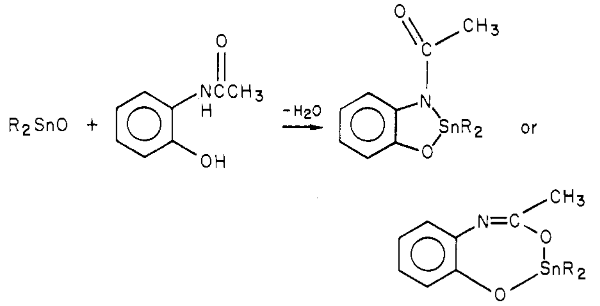
			
3290 m, br	1653^{a} vs	1642 sh	1609 s
1625 s	1630 vs	1613^{a} vs	1558 s
			1488 vs
1588 s	1497 w	1496 w	1420 m
1541^{a} vs	1407 w	1466 w	1352 m
		1453 m	
1485 s	1349^{b} vs	1362^{b} s	1300 s
1466 s			
1433 m	1290 m	1194 m	1271 s
1388^{b} s	1260 w	1080 m	1238 w
1321 w	1197 m	1055 s	1206 s
1248 s	1085 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
867 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
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

$(n\text{-}C_4H_9)$-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
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		

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

The reaction of di-*n*-butyltin oxide with H_2(salen) gives a compound whose infrared spectrum is comparable with those of the known R_2Sn(salen) compounds, usually prepared from the sodium or thallium salts of the H_2(salen) 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.

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



(3)

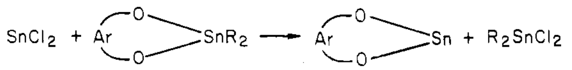
One heterocycle, (*o*-oxybenzoyloxy)di-*n*-butyltin(IV), when recrystallized from pyridine, forms a stable 1:1 adduct. The infrared spectrum shows that $\nu_{asym}(CO_2)$ is shifted to 1624 cm^{-1}, and the quadrupole splitting value increases to 3.75 mm/s, as compared to values of 1512 cm^{-1} and 3.18 mm/s for the uncomplexed heterocycle. All the other heterocycles studied either are 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

$$M\text{–}E + Q\text{–}X \rightarrow M\text{–}X + Q\text{–}E \qquad (4)$$

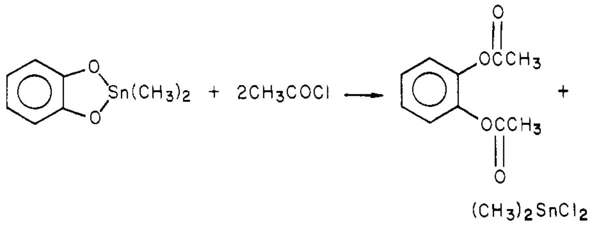
where M and Q are metals or metalloids, X is a halogen, and E an organic grouping RO–, R_2N–, etc.[38] Our heterocyclic organotin(IV) compounds also participate in these transformation reactions, and we have shown that this scheme can be extended to a system where M and Q are the element tin in different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

Tin(II) chloride, for example, reacts with the (*o*-phenylenedioxy)- and (*o*-oxybenzoyloxy)tin(IV) heterocycles in acetone to give the corresponding tin(II) heterocycles.



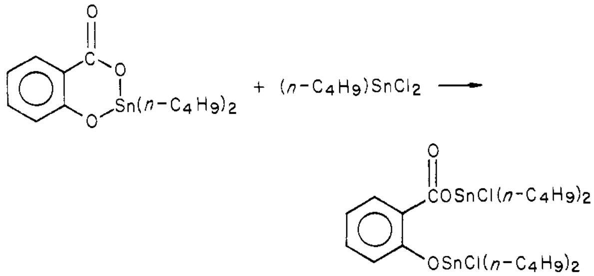
(5)

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



(6)

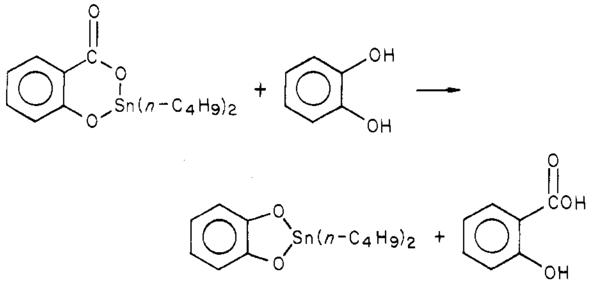
In this case the organotin halide was precipitated from the reaction medium as the pyridine complex. Di-*n*-butyltin dichloride reacts with (*o*-oxybenzoyloxy)di-*n*-butyltin(IV) in refluxing benzene according to the equation



(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 (*o*-phenylenedioxy)tin(IV) heterocycle. An attempt to exchange organotin moieties based on the greater insolubility of (*o*-oxybenzoyloxy)dimethyltin(IV) relative to its di-*n*-butyltin analogue failed, owing to the formation of a ditin compound by a reaction similar to that shown in eq 7.

Acknowledgment. Our work is supported by the National Science Foundation and by the Office of Naval Research. We are grateful to M & T Chemicals, Inc., for the donation of organotin starting materials.

Registry No. (*o*-Oxybenzoyloxy)dimethyltin(IV), 69706-04-3; (*o*-oxybenzoyloxy)di-*n*-butyltin(IV), 21807-90-9; (*o*-oxybenzoyloxy)di-*n*-octyltin(IV), 69706-05-4; (*o*-oxybenzoyloxy)phenyltin(IV) hydroxide, 69706-06-5; (*o*-thiolatobenzoyloxy)dimethyltin(IV), 69706-07-6; (*o*-thiolatobenzoyloxy)di-*n*-butyltin(IV), 15535-71-4; (*o*-thiolatobenzoyloxy)diphenyltin(IV), 69706-08-7; (2,3-pyridinedioxy)di-*n*-butyltin(IV), 69706-09-8; (*o*-oxybenzoyloxy)di-*n*-butyltin(IV) pyridine, 69706-31-6; $(CH_3)_2\overline{SnOCH(Ph)COO}$, 69706-10-1; $(n\text{-}C_4H_9)_2\overline{SnOCH(Ph)COO}$, 69706-11-2; $(CH_3)_2\overline{SnOC_6H_4N{=}C(CH_3)O}$, 69706-12-3; $(n\text{-}C_4H_9)_2\overline{SnOC_6H_4N{=}C(CH_3)O}$, 69706-13-4; di-*n*-butyltin(IV) salen, 35327-41-4; (*o*-phenylenedioxy)di-*n*-butyltin(IV), 36887-70-4; (*o*-phenylenedioxy)dimethyltin(IV), 4049-89-2; salicylic acid, 69-72-7; di-*n*-butyltin oxide, 818-08-6; di-*n*-octyltin oxide, 870-08-6; diphenyltin oxide, 2273-51-0; *o*-mercaptobenzoic acid, 147-93-3; 2,3-dihydroxypyridine, 16867-04-2; *o*-hydroxyacetanilide, 614-80-2; tin(II) chloride, 7772-99-8; dimethyltin oxide, 2273-45-2; mandelic acid, 90-64-2; acetyl chloride, 75-36-5; catechol, 120-80-9; diacetoxycatecholate, 635-67-6.

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Electrochemical Reduction Pathways of the Rhodocenium Ion. Dimerization and Reduction of Rhodocene

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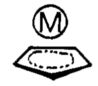
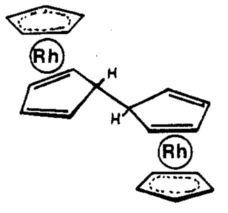
The electrochemical reduction of the rhodocenium ion, Cp_2Rh^+, and its dicarbollide analogue, $[(B_9C_2H_{11})_2Rh]^-$, has been studied in nonaqueous solvents by dc and ac polarography, cyclic voltammetry, and controlled potential coulometry. The starting Rh(III) complexes can both be reduced in two separate one-electron processes to Rh(II) and Rh(I) compounds which are very reactive. Cp_2Rh has a lifetime of about 2 s at room temperature but can be stabilized by performing the electrolysis at low temperatures. Rhodocene decomposes by dimerizing to form $[Cp_2Rh]_2$, which can be isolated in good yield by electrolysis of Cp_2Rh^+ solutions. Evidence is presented for the transient existence of the rhodocene anion, and comparison to the reduction of Cp_2Co^+ is made.

Introduction

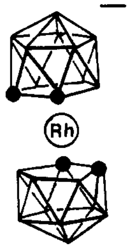
One interesting aspect of metallocene chemistry is the contrasting stabilities often found between a first-row transition-metal complex and its second- or third-row congener. For example, cobaltocene (**1**), Cp_2Co, is an air-sensitive but otherwise stable compound which can be oxidized or reduced by one electron to the very stable d^6 cobaltocenium ion, Cp_2Co^+, or the reactive cobaltocene anion, Cp_2Co^-, respectively.[1,2] However, the heavier analogues of cobaltocene, namely, rhodocene, Cp_2Rh (**2**), and iridocene, Cp_2Ir (**3**), are highly unstable, and no evidence of anions of these species has been reported.



2, M = Rh



4



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The neutral compounds **2** and **3** can be trapped at dry ice temperatures on a cold finger after reduction of $(\mathbf{2})^+$ or $(\mathbf{3})^+$ with molten sodium, but warming to room temperature produced a dimer with the postulated structure **4**,[3] shown for Rh. This dimer could be isolated only in low yields (ca. 8%).[3]

Because very little is known about the redox reactions of second- and third-row metal sandwich compounds, we have investigated the electrochemical reduction of Cp_2Rh^+ and its isoelectronic[4] carborane analogue $[(1,2\text{-}B_9C_2H_{11})_2Rh]^-$.[5]

The results confirm that Rh(II) is a highly reactive oxidation state for rhodium π complexes. Cp_2Rh is stable only for several seconds in solution and, under appropriate conditions, can be reduced to a (very reactive) anion, Cp_2Rh^-. The dimer **4** is isolated in high yield from electrolyzed solutions of Cp_2Rh^+.

Experimental Section

Electrochemical experiments were performed under an atmosphere of prepurified nitrogen by using solvents prepared by standard methods. The supporting electrolyte was Bu_4NPF_6, 0.1 M in each case. $Cp_2Rh^+PF_6^-$ was prepared by a method to be published.[17] The tetraethylammonium salt of $[(B_9C_2H_{11})_2Rh]^-$ was obtained from Dr. J. N. Francis and Professor M. F. Hawthorne. All potentials are reported vs. the aqueous saturated calomel electrode (SCE). The dimer $[Cp_2Rh]_2$ isolated from the electrolysis solutions melted (with decomposition) at 174 °C and gave an elemental analysis consistent with the dimeric structure. Anal. Calcd: C, 51.53; H, 4.32; Rh, 44.15. Found: C, 51.56; H, 4.34; Rh, 44.34. The infrared spectrum of this

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