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The Esterification of Tin(II) Oxide[1]

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Aromatic o-*hydroxy-ethers react with blue-black stannous oxide (1) to give o-phenylenedioxytin(II), water and the corresponding* o-*dialkoxy-benzene. Salicylic acid also reacts to produce a novel, six-membered, tin(II)-containing ring system (3) for which infrared evidence shows intermolecular bonding through the carbonyl oxygen in the solid. (3) dissolves in and forms a 1:1 complex with triethylamine where the tin(II) atom is three-coordinate. Catechol produces (2) and hydrogen sulfide from stannous sulfide, suggesting (1) as the origin of the water oxygen in these reactions. The esterification of hydrous tin(II) oxide (4) by catechol and* o-*methoxyphenol proceeds uncatalyzed to produce (2). Monofunctional alcohols (which require a catalyst) and phenols also react with (4) to produce products of the composition* $RO(SnO)_nR$ *where* $n = 1$, *2 or 3 as shown by microanalytical and molecular weight data. These compounds hydrolyze to regenerate the starting alcohol or phenol. Ethylene glycol gives a polymer of the backbone structure* $-[-O-CH_2CH_2-O-Sn-]_n-$. *The presence of tin(II) is established by treatment with mercuric chloride and by* Sn^{119m} *Mössbauer spectroscopy. Mössbauer data indicate that slow hydrolysis in air is accompanied by oxidation to tin(IV) oxide. Catalysis in the alcohol reactions increases in effectiveness* $Cu > CuO > 1{:}1\,Cu + Cu_2O > Cu_2O$ *in competition with the dehydration of (4). Alkyl and arylthiols give tetrathiotin(IV) derivatives with (4), but with (1) thiophenol produces the simple tin(II) mercaptide. The insertion reactions of phenyl isocyanate with tin(II) dimethoxide and phenoxide yield tin(II) carbamate compounds with a tin(II)-nitrogen bond. The insertion of phenyl isocyanate into the tin(II)-oxygen bonds of 2,2'-biphenylenedioxytin(II) results in ring expansion to a novel eleven-membered heterocycle. The reactions of tin(II) acetate with alcohols and phenols are also described.*

Introduction

The recent renascence of organotin(IV) chemistry results in large measure from the ready availability of tractable starting materials, and the formation of products soluble in common organic solvents. Soluble starting materials are necessary for conventional organometallic syntheses, and solubility is a requirement of the study of novel products by nmr spectroscopy. An investigation directed toward the synthesis of soluble organotin(II) systems[3] is under way in this laboratory.

Synthesis of tin(II)-oxygen heterocycles directly from stannous oxide has been reported by us.[4] These compounds, first obtained by the action of dihydric phenols on tin metal at elevated temperatures,[5] can also be prepared by reaction of dihydric phenols with a slurry of anhydrous stannous chloride and sodamide powders in ether.[6] Cyclic esters thus obtained are chiefly notable for their low volatility and very high thermal and hydrolytic stability, all pointing to the associated nature of these materials. Sn^{119m} Mössbauer spectroscopy confirms the presence of stannous tin, and serves to rule out a polymerization through the formation of tin-tin bonds, in contrast to the known behavior of diorganotin(II) compounds. It was also shown that slow hydrolysis in air is accompanied by oxidation to tin(IV) oxide.[7]

Experimental Section

Materials used were of reagent grade purity. Microanalyses were performed by the Linde Analytical Laboratory, Union Carbide Corporation, the Schwartzkopf Microanalytical Laboratory and Galbraith Laboratories, Inc. Total tin content was analyzed by reduction to tin(II) with iron metal in hydrochloric acid and titration against standard iodine with a starch indicator. Tin(II) was analyzed by titration against iodine with tin(IV) obtained as a difference. Nmr data were obtained using a Varian A—60 spectrometer; infrared spectra were run on Perkin-Elmer

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(1) Portions of this investigation have already appeared: P. G. Harrison and J. J. Zuckerman, *Abstr.* 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April, 1969; *Chem. Comm.*, 321 (1969).

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(3) An excellent review of tin(II) chemistry has recently appeared [J. D. Donaldson, *Prog. Inorg. Chem.*, *8*, 287 (1967)].

(4) G. T. Cocks and J. J. Zuckerman, *Inorg. Chem.*, *4*, 592 (1965).

(5) (a) J. J. Zuckerman, *J. Chem. Soc.*, 1322 (1963); (b) *Advan Inorg. Chem. Radiochem.*, *6*, 383 (1964).

(6) H. J. Emeléus and J. J. Zuckerman, *J. Organometal. Chem.*, *1*, 328 (1964).

(7) A. J. Bearden, H. S. Marsh, and J. J. Zuckerman, *Inorg. Chem.*, *5*, 1260 (1966).

Infracord machines and calibrated with polystyrene. Our constant-acceleration, cam-drive Mössbauer spectrometer and method of data refinement has been previously described.[7]

Catechol with Tin(II) Sulfide. Catechol (0.138 mol) was mixed with tin(II) sulfide powder (0.138 mol) containing *ca.* 10% w/w copper metal powder in a glass tube of approximately 500 ml capacity, in which a magnetic stirring bar had been placed. The tube was heated to 125-135° with a slow stream of dry nitrogen gas passing through for two days. Lead sulfide precipitated in a trap of aqueous lead acetate. The solid reaction product was washed with ether to remove unreacted catechol and sublimed *in vacuo* at 300-400° to give *o*-phenylenedioxytin(II) in 4.3% yield. The product was identified by comparison of its infrared spectrum with that of an authentic sample. Analysis of the tin(II) sulfide used indicated that it was free of tin(II) oxide. *Anal.* Calcd. for SnS: Sn, 78.73; S, 21.27. Found: Sn, 78.78; S, 21.36.

o-*Methoxyphenol with Tin(II) Oxide.* To *o*-methoxyphenol (0.25 mol) was added powdered blue-black tin(II) oxide (0.25 mol) and the mixture refluxed under a slow stream of dry nitrogen for 38 hrs. Water was driven off during the reaction and collected. The reaction mixture was filtered, the residue washed with ether to remove unreacted starting material, and sublimed *in vacuo* at 300-350° to give *o*-phenylenedioxytin(II), identified by comparison of its infrared spectrum to that of an authentic sample. The filtrate was shown to contain *o*-dimethoxybenzene by comparison of the retention times in glc with an authentic sample on a Carbowax column both separately and by mixing *o*-dimethoxybenzene with the filtrate as well as by boiling point and infrared. Repetition of the procedure as above with stannous oxide containing *ca.* 10% w/w of copper metal failed to increase the yield.

o-*Ethoxyphenol with Tin(II) Oxide.* To *o*-ethoxyphenol (0.15 mol) was added powdered, blue-black tin(II) oxide (0.075 mol) containing *ca.* 10% w/w copper metal powder, and the mixture was refluxed under nitrogen for 18 hrs. The reaction mixture was filtered, the residue washed with ether to remove unreacted starting material and sublimed *in vacuo* at 300-350° to give *o*-phenylenedioxytin(II), identified by comparison of its infrared spectrum with that of an authentic sample. *o*-Diethoxybenzene was crystallized from the filtrate and identified by infrared.

4-Methyl-2-methoxyphenol (Creosol) with Tin(II) Oxide. Creosol (0.25 mol) and powdered blue-black tin(II) oxide (0.15 mol) containing *ca.* 10% w/w copper metal powder were refluxed under nitrogen for 21 hrs. The reaction mixture was washed with ether, and sublimed *in vacuo* at 340° to give 4-methyl-1,2-phenylenedioxytin(II) which was identified by the similarity of its infrared spectrum to an authentic sample of the 3-methyl-1,2-phenylenedioxytin(II) isomer.[4]

Salicyclic Acid with Tin(II) Oxide. Salicylic acid (0.1 mol) and powdered, blue-black tin(II) oxide (0.1 mol(containing *ca.* 10% w/w copper metal powder were refluxed in xylene (100 ml) for 18 hrs under nitrogen. Water (0.9 ml) was collected in a Dean-Stark trap. The reaction product was washed with ether, and the residue sublimed *in vacuo.* At 310-320° a compound sublimed and was identified as xanthone, mp 173°. *Anal.* Calcd. for $C_{13}H_8O_2$: C, 79.58; H, 4.11; mol wt 196. Found: C, 79.29; H, 4.13; mol wt 192. Further sublimation at 350° gave a buff colored product whose analytical data agreed with the formula, $C_7H_4O_3Sn$. *Anal.* Calcd. for $C_7H_4O_3Sn$: C, 32.98; H, 1.57; Sn, 46.60. Found: C, 33.29; H, 1.67; Sn, 46.33. This reaction was repeated in the absence of copper powder with no change.

5-Sulfosalicylic Acid with Tin(II) Oxide. Blue-black tin(II) oxide (0.125 mol) and 5-sulfosalicylic acid dihydrate were stirred in water (200 cc) on the steam bath for 42 hrs under nitrogen and filtered to recover 5.4 gm of unreacted tin(II) oxide. Foaming accompanied desolvation of the filtrate. Tin(II) 5-seulfosalicylate was obtained as a white, crystalline powder, mp 310° with decomp. *Anal.* Calcd. for $C_7H_4O_6SSn$: C, 25.1; H, 1.2; S, 9.56; Sn, 35.5. Found: C, 24.8; H, 2.5; S, 8.4; Sn, 32.6.

o-*Methoxyphenol with Hydrous Tin(II) Oxide.* Hydrous tin(II) oxide [14.2 g, containing 0.105 mol of tin(II) oxide] was added to *o*-methoxyphenol (0.20 mol) in benzene (100 ml) in a flask with a condenser tube fitted with a Dean-Stark trap, and refluxed under nitrogen for 24 hrs to give 1.6 ml water (0.089 mol) and a solid which was soluble in organic solvents. *o*-Dimethoxybenzene, identified by its boiling point, and *o*-phenylenedioxytin(II) were released from the solid with some blue-black tin(II) oxide on melting at 198-218°. Separate portions of the solid hydrolyzed in cyclohexane to regenerate the starting phenol, but its infrared spectrum lacked absorptions due to –OH. Sn^{119m} Mössbauer spectra showed a broad resonance in the tin(II) region.

Phenol with Hydrous Tin(II) Oxide. A. Hydrous tin(II) oxide[8] [14.2 g, containing 0.105 mol of tin(II) oxide] was added to phenol (0.21 mol) in benzene (150 ml) in a flask with a condenser tube fitted with a Dean-Stark trap, and refluxed under nitrogen for 18 hrs. At the conclusion of this time no more water was collected, and the reaction mixture was filtered and the filtrate frozen. When the benzene melted a white solid remained which was washed free of unreacted starting material with benzene, filtered, and dried *in vacuo.* These operations were carried under nitrogen. The product, soluble in benzene, chloroform, and carbon disulfide underwent some melting at 235°, but remained solid for the most part until over 350°. Heating is accompanied by darkening to red-brown. *Anal.* Calcd. for $C_{12}H_{10}O_4Sn_3$: C, 25.09; H, 1.74; Sn, 62.02. Found: C, 25.92; H, 1.89; Sn, 60.75. Mol wt determinations (osmometry) gave 527 (chloroform), 628 and 720 (benzene); calcd. 574. A sample of the same product treated with ether on the filter melted at 220.5-224° with darkening. *Anal.* Calcd. for $C_{12}H_{10}O_3Sn_2$: C, 32.8; H, 2.27; Sn, 53.9; mol wt,

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(8) J. D. Donaldson and W. Moser, *J. Chem. Soc.*, 835 (1961).

439 (benzene): Found: C, 32.45; H. 2.52; Sn, 50.10; mol wt, 425: Both solids gave phenol on hydrolysis with water, and showed a positive tin(II) test with mercuric chloride.

B. Hydrous tin(II) oxide [containing 0.33 mol tin(II) oxide], copper powder (0.071 mol) and phenol (0.545 mol) were refluxed in xylene (900 ml) under nitrogen in a flask with a condenser fitted with a Dean-Stark trap. After 15 hrs at 134°, water evolution ceased, and the system was cooled and filtered under nitrogen. Desolvation *in vacuo* yielded a white, paste-like solid in *ca.* 88% yield. *Anal.* Calcd for $C_{12}H_{10}O_2Sn$: C, 47.2; H, 3.28; Sn, 39.0; mol wt 305: Found: C, 40.5; H, 3.4; total Sn 41.1; Sn^{II}, 40.7; mol wt 399 (osmometry in benzene).

2-Naphthol and Hydrous Tin(II) Oxide. Hydrous tin(II) oxide [7.1 g containing 0.05 mol tin(II) oxide] with *ca.* 10% w/w copper metal powder (the reaction also proceeds in the absence of copper) was mixed with 2-naphtol (0.10 mol) in benzene (150 ml) and allowed to reflux under nitrogen in a flask fitted a Dean-Stark trap for five days. Evaporation of solvent followed by washing with ether gave a white solid in *ca.* 8% yield based on tin, which gave a positive test for tin(II) with mercuric chloride. The material softened over a range 210-303°. *Anal.* Calcd for $C_{20}H_{14}O_4Sn_3$: C, 35.61; H, 2.09; Sn, 52.81. Found: C, 35.49; H, 2.40; Sn, 52.74. Lack of solubility prevented a molecular weight determination.

1-Naphthol and Hydrous Tin(II) Oxide. Hydrous tin(II) oxide [7.1 g, containing 0.05 mol tin(II) oxide] and 1-naphthol (0.10 mol) in benzene (100 ml) were allowed to reflux as above for 10½ hrs, then washed with ether to remove starting material. The white solid (44% yield based on tin) melted over a range 92-103° and gave a positive test for tin(II) with mercuric chloride. *Anal.* Calcd for $C_{20}H_{14}O_3Sn_2$: C, 43.99; H, 2.61; Sn, 44.46. Found: C, 42.55, H, 2.89; Sn, 44.09. Hydrolysis regenerated 1-naphthol.

2-Dimethylaminoethanol with Hydrous Tin(II) Oxide. Tin(II) oxide (0.15 mol) as hydrous tin(II) oxide, copper powder (0.035 mol) and 2-dimethylaminoethanol (0.32 mol) were refluxed in xylene (400 ml) under nitrogen in a flask fitted with a Dean-Stark trap, for 5 hrs. After cooling the contents of the flask were filtered under nitrogen and vacuum desolvation gave in about 90% yield a solid with elemental analyses consistent with $[(CH_3)_2NC_2H_4OSn]_2O$. *Anal.* Calcd. for $C_8H_{20}O_3N_2Sn_2$: C, 22.3; N, 6.5; Sn, 55.2. Found: C, 23.3; N, 5.2; Sn, 55.5; Sn^{II}, 54.6.

Di(2-ethylhexyl)phosphoric acid with Hydrous Tin(II) Oxide. Hydrous tin(II) oxide (0.05 mol) and di(2-ethylhexyl)phosphoric acid (0.1 mol) were stirred under nitrogen for 6 hrs at room temperature when ethanol was added and stirring continued overnight. After filtration the filtrate was stripped at 100°/1mm to give a grey-white, viscous liquid ($n_D^{25} = 1.4700$) in quantitative yield. *Anal.* Calcd. for $C_{32}H_{68}O_8P_2Sn$: C, 50.8; H, 9.0; P, 8.2; Sn, 15.7. Found: C, 50.9; H, 9.0; P, 8.4; Sn, 12.8.

Dodecylbenzene Sulfonic acid with Hydrous Tin(II) Oxide. Hydrous tin(II) oxide (0.099 mol) was slowly added to dodecylbenzene sulfonic acid (0.198 mol) with stirring on the steam bath where the mixture was heated for 24 hrs. The crude reaction mixture was slurried with acetone, filtered and the filtrate treated with decolorizing charcoal, refiltered and solvent stripped to produce a dark viscous fluid. *Anal.* Calcd. for $C_{36}H_{58}O_6S_2Sn$: C, 56.4; H, 7.5; S, 8.4; Sn, 15.5. Found: C, 53.2; H, 7.6; S, 8.4; Sn, 13.3.

Gluconic Acid with Hydrous Tin(II) Oxide. Hydrous tin(II) oxide (0.5 mol) was dissolved in 50% aqueous gluconic acid (1.0 mol). The filtered mixture was obtained as a yellow solution which deposited crystals of tin(II) gluconate[9] on standing and additional production on concentrating the aqueous solution. *Anal.* Calcd. for $C_{12}H_{22}O_{14}Sn$: C, 28.3; H, 4.3; Sn, 23.4. Found: C, 28.0; H, 4.5; Sn, 23.4.

Ethylene glycol with Hydrous Tin(II) Oxide. Tin(II) oxide (0.15 mol) as hydrous tin(II) oxide, copper powder (0.035 mol) and ethylene glycol (0.15 mol) were refluxed as above in xylene (473 ml). After initial water evolution during 3 hrs reflux there was little change in the appearance of the flask contents, and additional ethylene glycol (0.16 mol) was added. After 3 hrs of further reflux the mixture was cooled to room temperature and suction filtered under nitrogen The solids obtained (70% yield) were greyish-white, and analysis corresponded to the $-[-SnOCH_2CH_2O-]-$ structure. *Anal.* Calcd. for $C_2H_4O_2Sn$: C, 13.4; Sn, 66.5. Found: C, 12.3; Sn, 65.9; Sn^{II}, 63.3.

n-*Butanol with Hydrous Tin(II) Oxide.* Following the procedure outlined above, hydrous tin(II) oxide (1 mol) was allowed to react with n-butanol (3 mol) in xylene under nitrogen. After suction filtration the clear filtrate was desolvated *in vacuo* to leave a viscous fluid. A portion of this crude product was purified by sublimation (290°/0.1mm). *Anal.* Calcd. for $C_8H_{18}O_4Sn_3$: C, 17.9; H, 3.4; Sn, 66.7. Found: C, 15.6; H, 3.3; Sn, 66.6. A further portion was extracted with ether, and desolvation gave a solid of composition, C, 17.5; H, 3.3; Sn, 65.9

n-*Octanol with Hydrous Tin(II) Oxide.* The reaction of hydrous tin(II) oxide (0.25 mol) with n-octanol (0.50 mol) in the presence of cupric oxide (3.0 g) gave a viscous liquid product upon desolvation. *Anal.* Calcd. for $C_{16}H_{34}O_4Sn_3$: C, 29.7; H, 5.3; Sn, 55.1. Found: C, 29.0; H, 5.4; Sn, 54.6.

2-Ethylhexanol with Hydrous Tin(II) Oxide. Hydrous tin(II) oxide (0.125 mol) was slurried in toluene (600 ml) under nitrogen with 2-ethylhexanol (0.5 mol) and copper metal as a catalyst. The water was removed by azeotropic distillation, and the temperature allowed to rise to 115°. The cooled mixture was filtered and the filtrate desolvated to leave a hazy, slightly yellow fluid. *Anal.* Calcd. for $C_{16}H_{34}O_2Sn$: C, 50.9; H, 9.0; Sn, 31.5. Found: C, 51.4; H, 9.4; Sn, 24.4.

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(9) M. M. Soloman, U. S. Pat. 2,803,614, Aug. 20, 1957; *Chem. Abstr.*, *51*, 18698 (1957).

sec-Octanol with Hydrous Tin(II) Oxide. Hydrous tin(II) oxide (0.25 mol), copper metal powder and 2-octanol (1 mol) were allowed to reflux in toluene (900 ml) for 2 hrs under nitrogen. After most of the water had been removed, the contents had the appearance of a milky-white slurry which became a pale yellow color and clear. After 2 hrs of further heating the contents were cooled, filtered and the filtrate desolvated to leave a fluid, hazy, yellow product. *Anal.* Calcd. for $C_{16}H_{34}O_4Sn_3$: C, 29.7; H, 5.3; Sn, 55.1. Found: C, 27.9; H, 5.0; Sn, 53.4; Sn^{II}, 53.1.

Dodecanethiol with Hydrous Tin(II) Oxide. Hydrous tin(II) oxide from tin(II) chloride dihydrate (0.25 mol) was allowed to react with 1-dodecanethiol (0.5 mol) in refluxing xylene (472 ml) under nitrogen for 4 hrs. Water was collected in a Dean-Stark trap. The reaction mixture was filtered and the residue extracted with chloroform to leave a black, metallic solid, presumably blue-black tin(II) oxide from the dehydration of the hydrous form. The filtrate and extract were combined and desolvated to give a crude product which was recrystallized from 1:5 chloroform-ethanol (90% yield based on recovered SnO), mp 40°. *Anal.* Calcd. for $C_{48}H_{100}S_4Sn$: C, 62.5; H, 10.9; S, 13.9; Sn, 12.9. Found: C, 62.2; H, 10.9; S, 10.8; Sn, 12.8.

Tin(IV) chloride pentahydrate (0.075 mol) was allowed to react with 1-dodecanethiol (0.3 mol) in ethanol- benzene using pyridine as the promoter (24 ml). The product was freed from pyridinium chloride by slurrying with ethanol. Recrystallization from chloroform-ethanol gave tetrakis(1-dodecylthio)tin(IV), mp 38-39°. A mixed mp with the product from hydrous tin(II) oxide gave no depression. *Anal.* Calcd. for $C_{48}H_{100}S_4Sn$: C, 62.5; H, 10.9; S, 13.9; Sn, 12.9. Found: C, 62.3; H, 11.0; S, 13.8; Sn, 12.8.

Benzenethiol and Hydrous Tin(II) Oxide. Hydrous tin(II) oxide (0.25 mol) was allowed to reflux with benzenethiol (0.50 mol) in xylene (450 ml) with stirring under nitrogen. Water was collected by means of a Dean-Stark trap over 1.5 hrs, and as the reaction progressed a bright yellow semi-solid was formed. Desolvation, followed by extraction with chloroform and desolvation again, gave a yellow crystalline mass. Recrystallization from ethanol gave a sample, mp 67-68°, which gave a negative test for tin(II) with mercuric acetate. *Anal.* Calcd. for $C_{24}H_{20}S_4Sn$: C, 51.9; H, 3.6; S, 23.0; Sn, 21.4. Found: C, 51.7; H, 3.6; S, 23.0; Sn, 21.8.

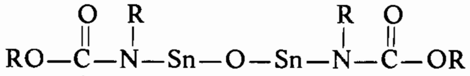
Benzenethiol with Tin(II) Oxide. In a three-necked, round bottomed flask, equipped with a stirrer and Dean-Stark trap was placed commercial, blue-black tin(II) oxide (0.25 mol), benzenethiol (1.4 mol) and xylene (450 ml). The mixture was heated to reflux for 3 hrs and water collected in the trap. The yellow mass of crude reaction product was extracted with xylene in a Soxhlet apparatus for three days. The purified product crystallized in the solvent flask during this time as long yellow needles, mp 160-162° with darkening. *Anal.* Calcd. for $C_{12}H_{10}S_2Sn$: C, 42.74; H, 2.99; S, 18.98; Sn, 35.29. Found: C, 42.8; H, 3.3; S, 18.9; Sn, 35.5. The residue in the Soxhlet thimble was fluffy and crystalline and appeared to be mostly crude $Sn(SC_6H_5)_2$. The concentrated xylene extract gave a yellow, low-melting solid, which appeared to be $Sn(SC_6H_5)_4$. *Anal.* Calcd. for $C_{24}H_{20}S_4Sn$: C, 51.9; H, 3.63; S, 23.05; Sn, 21.42. Found: C, 51.5; H, 3.8; S, 23.1; Sn, 18.4. This product melted below 60°. The yield of $Sn(SC_6H_5)_2$ was 74%; that of $Sn(SC_6H_5)_4$, 19%.

Bis(methyl N-phenylcarbamato)tin(II). A very exothermic reaction took place when phenyl isocyanate (7.0 ml, 64.2 mmol) was added to tin(II) methoxide (5.8 gm, 32.1 mmol) prepared by the method of Haenler, *et al.*[10] in petroleum ether (10 ml). The mixture was shaken vigorously until cool and the solvent removed under reduced pressure leaving the product as a white solid (in *ca.* quantitative yield), mp 109-114° (sealed tube). *Anal.* Calcd. for $C_{16}H_{16}O_4N_2Sn$: Sn, 28.3. Found: Sn, 28.0. The infrared spectrum exhibited strongbands at 1730 [ν(C=O)], 1070 and 1083 [ν(C–O)] cm^{-1}. The Sn^{119m} Mössbauer spectrum, recorded immediately after preparation, exhibited a doublet in the tin(II) region, I.S. = 3.11 ± 0.06; Q.S. = 1.88 ± 0.12 mm/sec. Hydrolysis, which was accompanied by yellowing, gave methyl N-phenylcarbamate, identified by comparison with an authentic sample.

Tin(II) Phenylcarbanilate. To tin(II) phenoxide (0.028 mol) in deäerated toluene (200 ml) phenyl isocyanate (0.056 mol) was added dropwise with agitation. No appreciable exotherm was observed. A copious precipitate appeared within minutes, and after 1-1½ hrs of agitation the contents were suction filtered under nitrogen. The clear yellow filtrate was desolvated *in vacuo,* yielding a slightly colored solid about 40% yield based on tin. *Anal.* Calcd. for $C_{26}H_{20}O_4N_2Sn$: C, 57.5; N, 5.2; Sn, 21.9. Found: C, 56.4; N, 5.7; Sn, 21.6; Sn^{II} 19.7.

In a similar experiment carried out with toluene/xylene as solvent, solids appeared after 10 minutes. After 90 min the mixture was suction filtered, and vacuum desolvation yielded $Sn[N(C_6H_5)(CO)OC_6H_5]_2$. *Anal.* Found: C, 54.1; N, 5.0; Sn, 24.1; Sn^{II}, 21.2.

In another experiment using the product prepared from tin(II) acetate shown to be of the n = 2 type, the filtered solids corresponded most closely to the double insertion into ROSnOSnOR to give



$$RO-\overset{\overset{O}{\|}}{C}-\overset{\overset{R}{|}}{N}-Sn-O-Sn-\overset{\overset{R}{|}}{N}-\overset{\overset{O}{\|}}{C}-OR$$

(R = C_6H_5). *Anal.* Calcd. for $C_{26}H_{20}O_5N_2Sn_2$; C, 50.2; H, 3; N, 4.1; Sn, 35. Found: C, 44.5; H, 3.4; N, 5.8; Sn, 34.

2,2′-Biphenylenedicarbamatotin(II). Phenyl isocyanate (2.17 ml, 19.9 mmol) was added to 2,2′-biphenylenedioxytin(II) (3.0 g, 9.9 mmol) freshly prepared by the method of Cocks and Zuckerman[4] and sublimed just before use, in toluene (20 ml). No reaction appeared to take place at room temperature. The mixture was refluxed for 50 hr, during which time all the isocyanate was consumed as shown by

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(10) J. S. Morrison and H. M. Haendler, *J. Inorg. Nucl. Chem.*, *29*, 393 (1967).

the loss of the very strong infrared ν(C=N=O) absorption at 2265 cm^{-1}. The mixture remained heterogeneous throughout. The product was collected as a grey-white solid on the filter in 97% yield and dried *in vacuo*, mp *ca.* 300° (decomp. in sealed tube). *Anal.* Calcd. for $C_{26}H_{18}O_4N_2Sn$: Sn, 21.95. Found: Sn, 21.35. The infrared spectrum contained a medium absorption at 1655 cm^{-1} [ν(C=O)]. The Sn^{119m} Mössbauer spectrum is a doublet in the region associated with tin(II): I.S. = 3.46±0.06; Q.S. = 1.56±0.12 mm/sec [Cf. for 2,2'-biphenylenedioxytin(II): I.S. = 3.13±0.06; Q.S. = 1.98±0.12 mm/sec].

Tin(II) acetate. A mixture of commercial, blue-black tin(II) oxide (0.36 mol), excess acetic acid (200 ml) and water (200 ml) were heated at reflux for 7 hrs. Filtration and desolvation of the filtrate gave the crude product as a white solid. The solid was slurried with benzene and desolvated again at 100°/1mm Hg. *Anal.* Calcd. for $C_4H_6O_2Sn$: C, 20.2; H, 2.5; Sn, 50.2. Found: C, 20.1; H, 2.4; Sn, 50.4.

n-*Octanol and Tin(II) Acetate.* A mixture of tin(II) acetate (0.185 mol) and *n*-octanol (1.04 mol) was heated to about 120°/48 mm Hg. The mixture became clear within an hr. Desolvation at 100°/1mm Hg gave the product as viscous, yellow fluid in 90% yield. *Anal.* Calcd. for $C_{16}H_{34}O_4Sn_3$: C, 29.7; H, 5.3; Sn, 55.1. Found: C, 30.0; H, 5.4; Sn, 54.0.

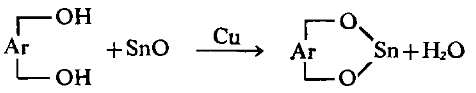
o-t-*Butylphenol with Tin(II) Acetate.* Tin(II) Acetate (0.31 mol) was added to *o-t*-butylphenol (1 mol) in refluxing xylene. Acetic acid was removed by azeotropic distillation, hexane added, the solvent stripped at 190°/3mm Hg and the flask contents extracted with toluene, filtered and solvent again stripped to yield the product as a brown, viscous liquid in 11% yield. *Anal.* Calcd. for $C_{20}H_{26}O_2Sn$: C, 57.6; H, 6.2; Sn, 28.5. Found: C, 51.6; H, 5.9; Sn, 26.7.

Phenol and Tin(II) Acetate. Tin(II) acetate (0.273 mol), phenol (1 mol) and xylene (600 ml) were heated at reflux for 5 hrs. About 450 ml of the acetic acid/xylene azeotrope were removed during this time. The residue deposited a solid on cooling. The mixture was filtered, and the pasty-white solid was slurried with dried hexane (250 ml) under nitrogen. The product was suction filtered and dried in a vacuum dessicator. *Anal.* Calcd. for $C_{12}H_{10}O_3Sn_3$: C, 32.8; H, 2.27; Sn, 53.9. Found: C, 33.8; H, 2.1; Sn, 49.2; Sn^{II}, 47.5.

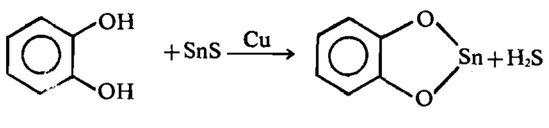
Phenylphosphonic Acid with Tin(II) Chloride Dihydrate. Phenylphosphonic acid (0.1 mol) in water (150 ml) was mixed with a solution of tin(II) chloride dihydrate (0.1 mol) in water (350 ml) acidified with concentrated hydrochloric acid (5 ml) to form a white product of composition $Sn(C_6H_5PO_3)\cdot 2H_2O$ immediately in quantitative yield (mp 360°). *Anal.* Calcd. for $C_6H_9O_5PSn$: C, 23.2; H, 2.9; P, 9.96; Sn, 38.2. Found: C, 23.1; H, 2.5; P, 10.0; Sn, 37.5.

Results and Discussion

Blue-black tin(II) oxide reacts with various dihydroxy-benzenes, naphthalenes and biphenyls in the presence of copper metal as a catalyst, either in a melt of the organic starting material or a suspension of the powders in refluxing xylene:

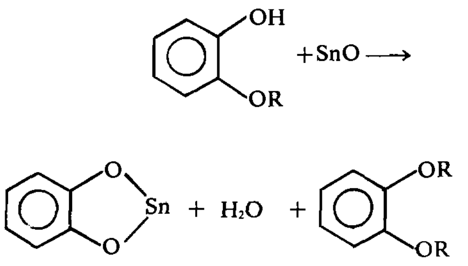

(1)

Water is carried off as the xylene azeotrope. The oxygen of this water molecule can originate in either of the two reactants; however, when catechol was allowed to react with stannous sufide, *o*-phenylenedioxytin(II) was again formed:

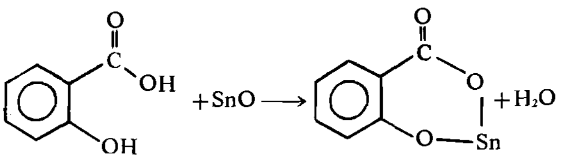

(2)

Hydrogen sulfide gas was swept out of the system and the sulfur precipitated as lead sulfide. No evidence for water, or for sulfur-containing tin compounds in the product could be obtained.[11] The water oxygen in the tin(II) oxide reactions, assuming a similar mechanism to operate, thus originates in the tin(II) oxide itself.

Aromatic *o*-hydroxyethers also operate in these reactions. For example, we find that *o*-alkoxyphenols react with blue-black tin(II) oxide to give *o*-phenylenedioxytin(II), water and the corresponding *o*-dialkoxybenzene:


(3)

The reactions are carried out in the refluxing *o*-alkoxyether; copper metal has no catalytic effect. *o*-Dimethoxybenzene fails to react with tin(II) oxide. The reaction is quenched by radical scavengers such as nitrobenzene and by air.


(4)

Metallic copper again shows no catalytic action. Some condensation of the organic acid to xanthone takes place under the conditions of the synthesis. The product is a white solid which sublimes *in vacuo*

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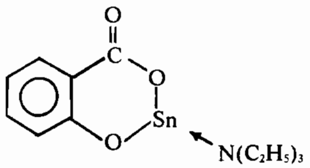
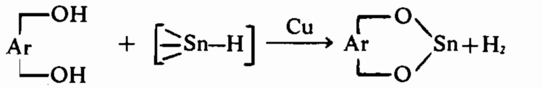
[11] Given the low yield of *o*-phenylenedioxytin(II) obtained in this reaction (*ca.* 4%), it is not possible to rule out unequivocally schemes involving the intermediate formation of sulfur-containing heterocycles and water, where subsequent hydrolysis of the heterocycle could produce tin(II) oxide which would also result from the direct action of water upon tin(II) sulfide.

at 350°. A shift in the infrared ν(C=O) in the direction of lower energy by *ca.* 75 cm^{-1} from the starting salicylic acid may be taken as evidence for some carbonyl oxygen-tin interaction in the solid. In an attempt to form the tin heterocycle free from this intermolecular self-association, the reaction product was washed continuously with triethylamine in a Soxhlet apparatus for 36 hrs to yield an involatile dark red-brown, waxy-oil, stable to 100°. The infrared spectra of the solid and oil were very similar, but a sharp absorption at 590 cm^{-1} present in the spectrum of the solid was absent in the oil. The carbonyl stretching frequency in the oil was found to be only slightly shifted from that of the starting material. The nmr spectrum of the oil establishes a 1:1 ratio of triethylamine to heterocycle on the basis of proton integration. The spectrum shows the methyl triplet at 8.8τ and the methylene quartet at 6.95τ with an internal chemical shift difference of Δ = 108 cps (compared with 85.2 cp for the free amine).[12] We have previously used this parameter as a measure of the donor role of triethylamine toward bis-(*o*-phenylenedioxy)-silane, where involving the nitrogen lone pair with silicon places the amine in a situation which differs little from that in a quaternary salt.[13] In the present case the tin atom (which shows no spin-spin coupling with the amine protons, presumably due to rapid intermolecular exchange) must be three-coordinated in the oil. The Sn^{119m} Mössbauer spectrum of the oil is a doublet in the tin(II) region (I.S. = 2.64±0.06; Q.S. = 1.89±0.12 mm/sec). The quadrupole splitting is similar to that observed for other tin(II)-oxygen heterocycles, but the isomer shift value is somewhat lower, presumably because of the shielding by nitrogen lone pairs occupying tin *p*- or *d*-orbitals. Exposure of the oil to the atmosphere results in the formation of a broad resonance at 0.00±0.06 mm/sec in the Mössbauer spectrum, presumably as a result of the hydrolysis-oxidation observed before.[7]



As we have noted previously, the esterification of blue-black tin(II) oxide does not proceed with cyclic ethers such as dibenzofuran, or with monofunctional phenols such as 2-naphthol or phenol itself.[4] Tin(II) oxide has a layer structure with the tin atom at the apex of a square pyramid formed by four oxygen atoms. The tin atoms in adjacent layers are separated by a distance similar to that found in tin metal itself[14] and may be in a situation not unlike that found at the surface of the metal. The cyclic tin(II) esters can be prepared directly from metallic tin under high pressures of hydrogen and may involve, by analogy with the similar reaction with silicon,[5,7,15] the intermediate formation under the conditions of the synthesis of a tin-hydrogen surface:



(5)

In the reaction with tin(II) oxide, the point of initial attack may again be the tin atom layer, excepting that in this case the hydrogens of the phenol appear in the product as water instead of molecular hydrogen. The structure of the tin(II) esters thus formed has been discussed in terms of a layer lattice, and studies in a furnace-equipped mass spectrometer have given evidence for the reverse process of abstraction of tin(II) oxide from the molecules.[7]

The type of esterification reaction more usually encountered involves a hydroxide with an alcohol. While no material of the composition Sn(OH)$_2$ is available, a recent crystallographic study has confirmed that the material known as hydrous tin(II) oxide, obtained when the pH of a tin(II) salt solution is raised by the addition of ammonia,[8] has the composition (SnO)$_3\cdot$H$_2$O, and that the analytical formula can be interpreted structurally as Sn$_6$O$_4$(OH)$_4$.[16] The structure contains Sn–OH units and is related to the trimeric Sn–O ring structure proposed for the Sn$_3$(OH)$_4^{2+}$ cation in solution.[17] The infrared spectrum of a sample prepared as described in Ref. 8 contains a broad band centered at 3350 cm^{-1}, presumably the Sn–OH ν(O–H).[18] The Sn^{119m} Mössbauer spectrum

Table I.[a] The Reactions of Alcohols, Phenols and Acids with Hydrous Tin(II) Oxide

$6ROH+(SnO)_3\,.\,H_2O \longrightarrow 3RO(SnO)R+4H_2O$	
	ROH = C$_6$H$_5$OH
	HOCH$_2$CH$_2$OH
	2-ethylhexanol
	di(2-ethylhexyl)phosphoric
	5-sulfosalicylic
	dodecylbenzene sulfonic
	CH$_2$OH(CHOH)$_4$COOH
$6ROH+2[(SnO)_3\,.\,H_2O] \longrightarrow 3RO(OSn)_2R+5H_2O$	
	ROH = C$_6$H$_5$OH
	1-naphthol
	(CH$_3$)$_2$NCH$_2$CH$_2$OH
$2ROH+(SnO)_3\,.\,H_2O \longrightarrow RO(OSn)_3R+2H_2O$	
	ROH = C$_6$H$_5$OH
	2-naphthol
	n-butanol
	n-octanol
	sec-octanol

[a] The compositions of the products of these reactions were distinguished in most cases on the basis of microanalytical data alone, which for some of the compounds was in only approximate agreement with the oligomeric formulas listed here.

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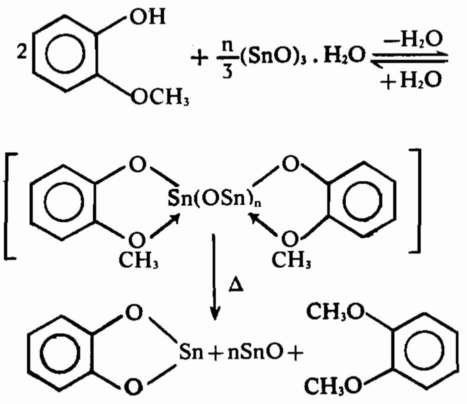
(12) A. G. Massey, E. W. Randall, and D. Shaw, *Spectrochim. Acta*, *20*, 379 (1964).
(13) C. M. Silcox Yoder and J. J. Zuckerman, *Inorg. Chem.*, *6*, 163 (1967).
(14) W. J. Moore and L. Pauling, *J. Am. Chem. Soc.*, *63*, 1392 (1941).
(15) J. J. Zuckerman, *J. Chem. Soc.*, 873 (1962).
(16) R. A. Howie and W. Moser, *Nature*, *219*, 372 (1968).
(17) R. S. Tobias, *Acta. Chem. Scand.*, *12*, 198 (1958).
(18) R. Okawara and K. Yasuda, *J. Organometal. Chem.*, *1*, 356 (1964).

confirms the presence of tin(II), and reflects the change in structure from blue-black tin(II) oxide [I.S. = 2.74±0.06; Q.S. = 2.19±0.12 mm/sec.].[19]

The esterification of hydrous tin(II) oxide proceeds with catechol in the manner we have previously described for reactions with blue-black tin(II) oxide,[4] but the reactions proceed under milder conditions, presumably due to the presence of the Sn–OH system in the material. Hydrous tin(II) oxide undergoes dehydration to the blue-black oxide at *ca.* 120° and the reaction can be followed by collecting the water azeotrope from a refluxing suspension of the material in xylene. In addition to the dihydric phenols, *o*-methoxyphenol also reacts with hydrous tin(II) oxide, but in this case an intermediate tin-containing material can be isolated during the course of the reaction. This material hydrolyzes to regenerate *o*-methoxyphenol, and produces on heating *o*-phenylenedioxytin(II), *o*-dimethoxybenzene and the blue-black oxide. Although we were not able to isolate an analytically pure sample of this material, infrared and Mössbauer spectra are consistent with the formulation of the reaction as:



(6)

It is possible that such an intermediate also plays a role in the action of *o*-methoxyphenol on blue-black tin(II) oxide.

We have also reinvestigated the action of monofunctional phenols which fail to react with blue-black tin(II) oxide.[4] We find that phenol reacts with the hydrous oxide to produce products characterized by the formula $RO(SnO)_nR$. Depending upon the conditions of the synthesis and work-up, products which are characterized predominantly by n = 1, 2 and 3 can be isolated separately. For example, when hydrous tin(II) oxide was refluxed in xylene for 15 hrs under nitrogen at 134° with phenol and copper metal powder in a flask fitted with a Dean-Stark trap, a white, paste-like solid precipitated in 88% yield on concentrating the filtrate whose microanalytical data best fit the formulation as tin(II) diphenoxide; probably somewhat contaminated with higher molecular weight oligomers.

$$6C_6H_5OH + (SnO)_3 . H_2O \xrightarrow{Cu} 3(C_6H_5O)_2Sn + 4H_2 \qquad (7)$$

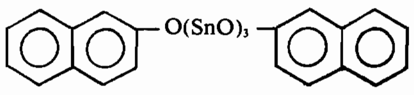
With benzene as the solvent and refluxing continued for 18 hrs the concentrated filtrate yielded a material of indefinite melting point, soluble in common organic solvents, whose microanalytical and molecular weight data best fit the formulation:

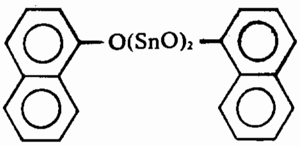
$$2C_6H_5OH + (SnO)_3 . H_2O \xrightarrow{Cu} C_6H_5O(SnO)_3C_6H_5 + 2H_2O \qquad (8)$$

In another experiment similar to the last described, treatment of the product with ether on the filter yielded:

$$6C_6H_5OH + 2[(SnO)_3 . H_2O] \xrightarrow{Cu} 3C_6H_5O(SnO)_2C_6H_5 + 5H_2O \qquad (9)$$

Similarly, naphthols react with hydrous tin(II) oxide in two ways: 2-naphthol gives the n = 3 product while 1-naphthol the n = 2





These reactions can be carried out using a variety of aliphatic alcohols as well, and the results are depicted in the Table. Carboxylic and substituted phosphoric and sulfonic acids react to give the n = 1 product in each case. Acidic amino compounds such as imidazole and *p*-toluene-sulfonamide fail to produce nitrogen derivatives although tin(IV)-nitrogen bonds are formed from dialkyltin oxides in an analogous reaction.[20]

The compounds are solids except for the *n*- and *sec*-octanol and 2-ethylhexanol derivatives which are viscous liquids. The product from ethylene glycol is most likely a polymer with the backbone structure $-[-O-CH_2CH_2-O-Sn-]_n-$. The compounds hydrolyze to regenerate the starting phenol or alcohol in all cases, and are shown by Mössbauer spectroscopy and by the classical Hg(II) chloride test to be compounds of tin(II). Sn^{119m} Mössbauer isomer shifts greater than that of β-tin are taken as confirmation of the presence of tin(II).[21] In the reaction of *n*-octanol with the hydrous oxide in xylene it was found that the effectiveness of various copper-containing catalysts, based on the relative amount of tin(II) oxide consumed, is Cu > CuO > 1 : 1 Cu + Cu_2O > Cu_2O. Alcohols do not react at a reasonable rate in the uncatalyzed reaction; dehydration to the blue-black oxide takes place instead. No catalyst is required for the phenols. It appears that hydrous tin(II) oxide is most stable in the range pH = 8–12; higher and lower pH's promote dehydration.

Tin(II) dialkoxides have been synthesized before from the pyrolysis of tin(IV) ethoxide,[22] from the action of sodium methoxide on tin(II) bromide in

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(19) J. J. Zuckerman, *J. Inorg. Nucl. Chem.*, *29*, 2191 (1967).

(20) K. Jones and M. F. Lappert, *J. Organometal. Chem.*, *3*, 295 (1965).

(21) J. J. Zuckerman, *Mössbauer Effect Methodology*, *3*, 15 (1967).

(22) H. Meerwein and E. Geschke, *J. Prakt. Chem.*, *147*, 203 (1936).

methanol[23] and by the action of alcohols on tin(II) chloride in the presence of tertiary amines.[9] The trimethylsilanolate of tin(II) has also been claimed from the reaction of the alkali metal trimethylsilanolates with tin(II) chloride.[24] A tin(II) silicone with the proposed backbone structure $-[-(CH_3)_2Si-O-Sn(II)-O-]_n-$ has also been claimed from the condensation of dimethyldiethoxysilane with tin(II) acetate.[25] The monomeric tin(II) esters are sensitive to moisture; presumably hydroxytin(II) species are intermediates in the hydrolysis:

$$\begin{tikzcd}
(RO)_2Sn+H_2O \arrow[r] & ROH+[ROSnOH] \arrow[r, "ROSnOH"] & ROSnOSnOR+H_2O \arrow[d, "H_2O"] \\
SnO+ROH & ROSnOSnOSnOR+H_2O \arrow[l, "etc."'] & ROSnOSnOH+ROH \arrow[l, "ROSnOH"']
\end{tikzcd} \tag{10}$$

The intermediate products corresponding to the formula $RO(SnO)_nR$ where n = 1, and 3 are reported here, and compounds of this sort where $R = CH_3$ and C_2H_5 and n = 2 have been isolated from the hydrolysis of tin(II) dimethoxide and diethoxide.[10] The unstable trimethylsiloxy derivative where $R = (CH_3)_3Si$ and n = 2 has been obtained from the cohydrolysis of trimethylchlorosilane and tin(II) chloride.[26] This series of compounds then would appear to be the low molecular weight oligomers of the tin(II) analogue of the silicones or tin(IV) stannoxanes. The solubility of these compounds in common organic solvents and their general tractability may be rationalized on the basis of the differences in Lewis acid acceptor strength between the Sn^{IV} and Sn^{II} atoms, and enable useful materials to be produced by further varying R and n.

Our isolation of compounds where n = 1, 2 and 3 from reactions involving hydrous tin(II) oxide is determined by the susceptibility of the n = 1 product and the products with higher tin-content to hydrolysis, and to the efficiency of the removal of the water formed in the reactions by the azeotropic technique. For example, the very sensitive tin(II) dimethoxide apparently undergoes complete hydrolysis *in situ* when methanol is refluxed with hydrous tin(IV) oxide in benzene. The Mössbauer data indicate that slow hydrolysis in air is accompanied by the formation of SnO_2.

Alkyl and aryl thiols react with hydrous tin(II) oxide in xylene in the absence of a catalyst to give the corresponding tin(IV) compound in high yield:

$$RSH+(SnO)_3 . H_2O \longrightarrow (RS)_4Sn \tag{11}$$

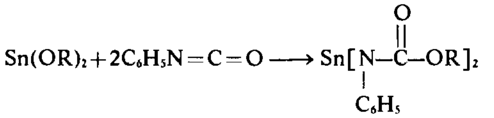
$$R = C_6H_5,\quad n{-}C_{12}H_{25}$$

The $R = n{-}C_{12}H_{25}$ product was shown to be identical to that prepared from tin(IV) chloride pentahydrate. A recent attempt to prepare 2-stanna-1,3-dithiacyclopentane from tin(II) chloride and ethane-1,2-dithiol gave the tin(IV) spiran as well.[27] Use of the blue-black oxide with thiophenol in refluxing xylene results in rapid reaction and the production of long, yellow needles (mp 160-162°) of tin(II) diphenylmercaptide in 74% yield:

$$2C_6H_5SH+SnO \longrightarrow (C_6H_5S)_2Sn+H_2O \tag{12}$$

This is the first example of a simple tin(II) mercaptide. From the xylene extract, the tin(IV) thiol was isolated in 19% yield.

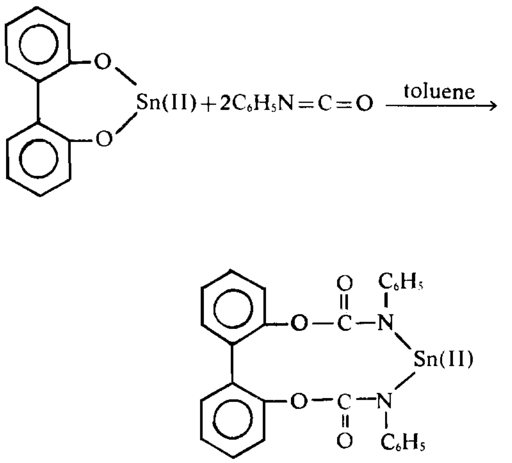
The addition of the tin(IV)-oxygen bond to multiply-bonded acceptor molecules such as isocyanates is well-known.[28] Tin(II) dimethoxide and diphenoxide react readily, exothermically in the case of the dimethoxide, to give bis(organo N-phenylcarbamato)tin(II) derivatives:



$$Sn(OR)_2+2C_6H_5N{=}C{=}O \longrightarrow Sn[N(C_6H_5)-C(=O)-OR]_2 \tag{13}$$

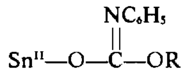
$$R = CH_3,\ C_6H_5$$

In a similar reaction, 2,2′-biphenylenedioxytin(II)[4] takes up two moles of phenyl isocyanate during 50 hrs in refluxing toluene to give 2,2′-biphenylenedioxytin(II)[4] takes up two moles of phenyl isocyanate during 50 hrs in refluxing toluene to give 2,2′-diphenylenedicarbamatotin(II) by a novel ring expansion reaction.



(14)

The Sn^{119m} Mössbauer spectra of the adducts exhibit a doublet in the region consistent with the presence of tin(II).[21] The infrared spectra contain absorptions assignable to $\nu(C{=}O)$, but our formulation of the structures in Equations 13 and 14 is by no means unequivocal since addition might conceivably take place across the C=O rather than the C=N bond of the isocyanate to produce the structural unit



$$Sn^{II}-O-C(=NC_6H_5)-OR$$

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(23) E. Amberger and M.-R. Kula, *Angew. Chem.*, *75*, 436 (1963); *Chem. Ber.*, *96*, 2562 (1963).

(24) W. S. Tatlock and E. G. Rochow, *J. Org. Chem.*, *17*, 1555 (1952).

(25) F. A. Henglein, R. Lang, and L. Schmack, *Makromol. Chem.*, *22*, 103 (1957).

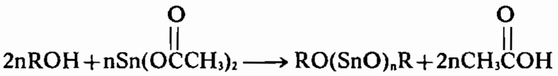
(26) R. Okawara, D. G. White, K. Fujitani, and H. Sato, *J. Am. Chem. Soc.*, *83*, 1342 (1961).

(27) E. W. Abel and D. B. Brady, *J. Chem. Soc.*, 1192 (1965).

(28) See A. J. Bloodworth and A. G. Davies, *J. Chem. Soc.*, 52238 (1965) and references therein.

in which case the absorption bands in the carbonyl region would then arise from $\nu(C{=}N)$. In the absence of further evidence, we chose to write the structures as shown above in conformity with the tin(IV) case.[28]

An alternative route to the tin(II) dialkoxides and diaryloxides is based on tin(II) acetate, prepared by dissolving tin(II) oxide in aqueous acetic acid.[29] Tin(II) acetate reacts to give the $n = 3$ product with *n*-octanol and the $n = 2$ product with phenol:



$$2n\mathrm{ROH} + n\mathrm{Sn}(\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3})_2 \longrightarrow \mathrm{RO(SnO)}_n\mathrm{R} + 2n\mathrm{CH_3}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OH} \qquad (15)$$

Acknowledgments. This work was supported by the National Sciences Foundation through Grants GP-5025 and 9249. We are indebted to the National Science Foundation Undergraduate Research Participation Program at Cornell University for summer stipends to R.R.G., T.B.H., III and K.C.-T.S. Sn^{119m} Mössbauer spectra were recorded by N. W. G. Debye. J. D. Strachan carried out some of the experimental work.

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(29) J. D. Donaldson, W. Moser and W. B. Simpson, *J. Chem. Soc.*, 5942 (1964).