the sharpness of the signal indicates that the compound is diamagnetic.

The infrared spectrum of the derivative (chloroform solution) in the metal carbonyl stretching frequency region consists of one weak (2123 cm.$^{-1}$) and three strong bands (2055, 1973, 1950 cm.$^{-1}$). The number of bands and their relative frequencies and intensities are in accord with the pattern predicted for a complex of the type *cis*-$M(CO)_4X_2$[14] (molecular symmetry C_{2v}) on the basis of symmetry and group theoretical considerations.[15]

Examination of the complete infrared spectrum of $Mn(CO)_4$(hfac) in a KBr pellet lends support to the bonding of the hexafluoroacetylacetonato group to the manganese in the usual bidentate manner, through the two equivalent oxygen atoms. Both the ketonic carbonyl stretching (1635 cm.$^{-1}$) and the C–H in-plane bending frequency (1142 cm.$^{-1}$) occur in the same regions as for the known bis- and tris(hexafluoroacetylacetonato) complexes.[12]

The attempted preparation of acetylacetonatotetracarbonylmanganese(I) from 2,4-pentanedione and chloropentacarbonylmanganese(I) yielded an unstable yellow solid. The infrared spectrum of this solid was in good agreement with that expected for the desired product; however, instability of the compound precluded consistent analytical data.

It is of interest to note that relative stabilities of the acetylacetonato- and hexafluoroacetylacetonatotetracarbonylmanganese(I) complexes parallel those of the alkyl and perfluoroalkyl metal carbonyls.[8] Greater stability of the fluorinated derivatives is most probably due to a high electronegativity of the trifluoromethyl group[16] which facilitates removal of the negative charge from a low-valent metal.

Acknowledgment.—The authors wish to gratefully acknowledge support of this work by the National Science Foundation.

[14] M = metal; X = unidentate ligand.

[15] See L. E. Orgel, *Inorg. Chem.*, **1**, 25 (1962); also, F. A. Cotton, *ibid.*, **3**, 702 (1964), and previous papers with C. S. Kraihanzel.

[16] W. R. Cullen and R. M. Hochstrasser, *J. Mol. Spectry.*, **5**, 118 (1960), and references therein.

CONTRIBUTION FROM THE BAKER LABORATORY,
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The Synthesis of Tin(II) Heterocycles Directly from Stannous Oxide[1a]

BY G. T. COCKS AND J. J. ZUCKERMAN[1b]

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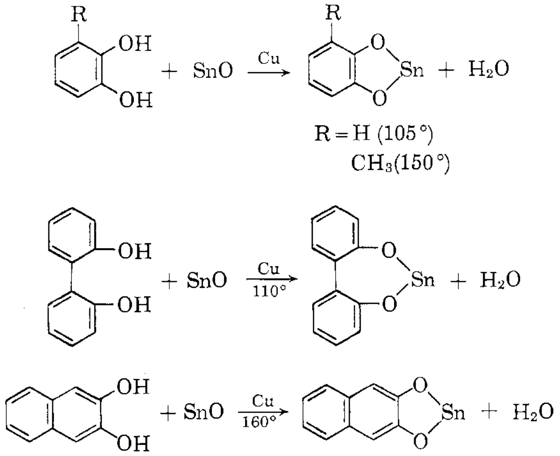
Dihydric phenols react directly with tin metal in the presence of copper as a catalyst to give tin(II) heterocycles. These cyclic esters of tin(II) are notable chiefly for their low volatility and very high thermal stability (*e.g.*, in air to *ca.* 500°).[2] They can also be obtained by reaction of dihydric phenols with a slurry of stannous chloride and sodamide powders in ether. Derivatives containing methyl and *n*-butyl groups attached to tin have been prepared, and these tin(IV) heterocycles exhibit similar properties.[3] It has been recently reported that stannous oxide reacts with methyl chloride to give dimethyltin dichloride.[4] Reaction conditions are said to be milder for this synthesis than for the direct synthesis of organotin halides from tin metal.[5] This paper describes the reaction of dihydric phenols with stannous oxide.

Dihydric phenols react with stannous oxide at pressures varying from 1500 p.s.i. of nitrogen gas to partial vacuum according to the following schemes.



A temperature high enough to melt the diol is sufficient to bring about reaction. Copper metal powder acts as a catalyst. The previously synthesized compounds *o*-phenylenedioxytin(II) and 2,2′-diphenylenedioxytin(II) were prepared by this new route, along with the novel compounds 3-methyl-1,2-phenylenedioxytin(II) and 2,3-naphthalenedioxytin(II). The reaction can also be carried out by refluxing a solution of the diol in an inert organic solvent in the presence of stannous oxide and copper powders. In addition, polymeric systems were produced when resorcinol and hydroquinone were employed as starting materials.

The cyclic tin(II) esters are white crystalline solids which possess high thermal and hydrolytic stability, especially when compared to the tin(IV) alkoxides[6] or with the recently reported tin(II) alkoxides.[7] They are insoluble in common organic solvents, but have some solubility in pyridine, triethylamine, and dimethyl sulfoxide from which they can be recovered unchanged. Because of their limited solubility, only the molecular weight of 3-methyl-1,2-phenylenedioxytin(II) could be determined ebullioscopically in pyri-

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[1] (a) Portions of this investigation were reported at the XIXth IUPAC Meeting, London, July 1963. (b) To whom all inquiries should be addressed.

[2] J. J. Zuckerman, *J. Chem. Soc.*, 1322 (1963).

[3] H. J. Emeléus and J. J. Zuckerman, *J. Organometal. Chem.*, **1**, 328 (1964).

[4] K. A. Andrianov, T. V. Vasil'eva, Z. N. Nudel'man, L. M. Khanashivili, A. S. Kochetkova, A. G. Cherednikova, *J. Gen. Chem. USSR*, **32**, 2275 (1962).

[5] J. J. Zuckerman, *Advan. Inorg. Chem. Radiochem.*, **6**, 383 (1964).

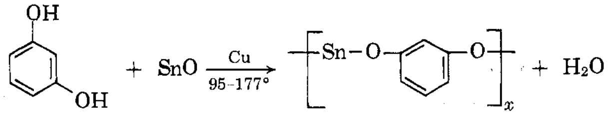
[6] J.-Cl. Maire, *Ann. Chim.* (Paris), **6**, 969 (1961).

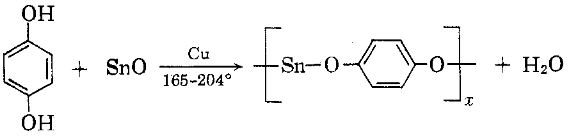
[7] E. Amberger and M.-R. Kula, *Chem. Ber.*, **96**, 2562 (1963).

dine, in which solvent this compound was found to be monomeric. The state of aggregation in the solid would have to be higher to explain the low volatility, hydrolytic stability, and insolubility of these cyclic esters. A higher coordination number for tin in the solid state could be achieved through *inter*molecular coordination of oxygen to tin, which is then presumably broken up by the action of strong Lewis bases such as pyridine.

Reactions were attempted under similar conditions with dibenzofuran, phenol, and 2-naphthol, but a study of these examples indicates that the method does not operate with cyclic ethers or monofunctional phenols. Benzyl chloride gave hydrated stannous chloride under the conditions of the synthesis (*cf.* ref. 8). The use of nitrobenzene as a radical scavenger in the solvent reactions had no apparent effect on the synthesis.

Resorcinol and hydroquinone react with stannous oxide to produce water and the expected polymeric materials. A very small amount of ill-defined material containing stannous tin sublimed at lower temperatures, but the bulk of the products were not volatile to above *ca.* 600° *in vacuo*. Some pyrolysis took place at these elevated temperatures. It is likely that the products in both cases are linear polymeric stannoxanes, probably further associated in the solid state by *inter*molecular oxygen–tin bonding.





Experimental

Materials used were of reagent grade purity. Microanalyses were performed by the Schwarzkopf Microanalytical Laboratory and the Scandinavian Microanalytical Laboratory.

2,2′-Diphenylenedioxytin(II).—Powdered stannous oxide (1.0 mole) containing 10% w./w. of copper metal powder was mixed with 2,2′-dihydroxydiphenyl (0.5 mole) in an autoclave, and the mixture was heated 12 hr. at 200° under an initial pressure of nitrogen gas at 1800 p.s.i. The product, a solid gray mass, was chipped out of the autoclave, ground in a mortar, and extracted with ether in a Soxhlet apparatus to recover the organic starting material. The gray powder remaining in the Soxhlet thimble was sublimed at 300° *in vacuo* to give a white crystalline material which gave a positive test for stannous tin with mercuric chloride and whose infrared spectrum was identical with that of an authentic sample of 2,2′-diphenylenedioxytin(II).

3-Methyl-1,2-phenylenedioxytin(II).—Preparation as above, using 3-methylcatechol (0.5 mole) as the starting material with 0.5 mole of stannous oxide. Analytical data agreed with the formula $C_7H_6O_2Sn$. *Anal.* Calcd. for $C_7H_6O_2Sn$: C, 34.91; H, 2.51; Sn, 49.29. Found: C, 34.42; H, 2.58; Sn, 47.92. The molecular weight determined ebullioscopically in pyridine gave 243 (calcd. for the monomer, 240.8) for a 0.045 *M* solution.

2,3-Naphthalenedioxytin(II).—Preparation as above, using 2,3-dihydroxynaphthalene (0.25 mole) as the starting material with 0.5 mole of stannous oxide. Analytical data fit the formula $C_{10}H_6O_2Sn$. *Anal.* Calcd. for $C_{10}H_6O_2Sn$: C, 42.90; H, 2.16; Sn, 43.37. Found: C, 42.95; H, 2.29; Sn, 43.21.

***o*-Phenylenedioxytin(II).**—Preparation as above, using catechol (0.50 mole) as the starting material. The infrared spectrum of the sublimed product was identical with that of an authentic sample of *o*-phenylenedioxytin (II).

Preparation in an Evacuated Tube.—Catechol (0.022 mole) was mixed with powdered stannous oxide (0.022 mole) containing 10% w./w. of copper metal powder in a glass tube of *ca.* 20 cc. capacity in which a stirring bar was placed. The tube was evacuated and heated in an oil bath at 120–140° for 2.5 hr. The catechol was liquid at these temperatures, and the stirrer kept the stannous oxide–copper powders suspended. After cooling, the contents were extracted with ether in a Soxhlet apparatus and sublimed *in vacuo*. The infrared spectrum of the product was identical with that of *o*-phenylenedioxytin(II).

To determine the effect of copper metal on the reaction, catechol and stannous oxide were stirred together in two tubes under identical conditions except that no copper metal was placed in one. In the presence of copper metal *o*-phenylenedioxytin(II) was recovered in 27% yield as compared with 7.6% in the absence of the catalyst.

Preparation in Solution.—Catechol (0.022 mole) was dissolved in 75 ml. of xylene and stannous oxide powder (0.022 mole) containing 10% w./w. of granulated copper metal was added. The mixture was refluxed with stirring for 19.5 hr. The gray residue was filtered and *o*-phenylenedioxytin(II) was separated by sublimation *in vacuo* at 300°. The method was seen to operate using benzene, toluene, decalin, and xylene as solvents in that order of increasing effectiveness with yields in xylene as high as 75%.

Phenol with Stannous Oxide.—Phenol was mixed with stannous oxide powder containing 10% w./w. of copper in a glass tube. The tube was evacuated and heated at 80° for 27 hr. After cooling, the resultant solid residue was washed with ether and sublimed *in vacuo*. No material sublimed to elevated temperatures, and phenol was recovered quantitatively. 2-Naphthol in 2:1 mole ratio behaved similarly.

Benzyl Chloride with Stannous Oxide.—Stannous oxide (0.15 mole) was placed with 150 ml. of toluene in a flask equipped with a stirrer and reflux condenser and the mixture heated to reflux. Benzyl chloride (0.15 mole) was added dropwise and the refluxing continued for 1.5 hr. The gray solid residue was treated with ether in a Soxhlet apparatus and gave positive tests for stannous tin and chloride ion with mercuric chloride and silver nitrate solutions. Its infrared spectrum was identical with that of an authentic sample of hydrated stannous chloride, and like this compound could be dehydrated by heating *in vacuo*.

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CONTRIBUTION NO. 1266 FROM THE DEPARTMENT OF
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The Preparation of 2-Bromotetraborane-10[1]

BY JERRY DOBSON AND RILEY SCHAEFFER

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Although halogenation of diborane, pentaborane-9, and decaborane-14 has been studied in some detail,[2,3]

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[8] K. Sisido, Y. Takeda, and Z. Kinugawa, *J. Am. Chem. Soc.*, **83**, 538 (1961).