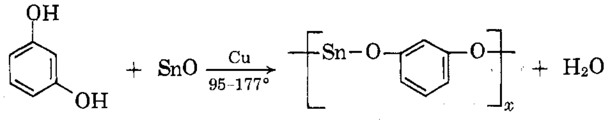
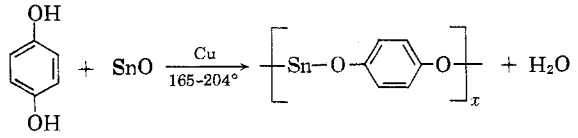
dine, in which solvent this compound was found to be monomeric. The state of aggregation in the solid would have to be higher to explain the low volatility, hydrolytic stability, and insolubility of these cyclic esters. A higher coordination number for tin in the solid state could be achieved through *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.*

Acknowledgments.—This investigation was supported by Public Health Service Research Grant CA-07064-01 from the National Cancer Institute. We are indebted to the National Science Foundation Summer Undergraduate Research Participation Program at Cornell University for a stipend to G. T. C.

CONTRIBUTION NO. 1266 FROM THE DEPARTMENT OF
CHEMISTRY, INDIANA UNIVERSITY, BLOOMINGTON, INDIANA

The Preparation of 2-Bromotetraborane-10[1]

BY JERRY DOBSON AND RILEY SCHAEFFER

Received November 13, 1964

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

---

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

no halogenated derivatives of tetraborane-10 have been well characterized. Since only relatively few derivatives of tetraborane-10 have been reported,[4,5] and since a halogen derivative was desired for other work in this laboratory, study of the reaction of bromine with tetraborane-10 was undertaken. Under controlled conditions at low temperatures, a 2-bromotetraborane-10 has been prepared and characterized.

Experimental

Preparation of B_4H_9Br.—Approximately 10 mmoles of bromine was introduced into a small glass flask using a hypodermic syringe to measure and transfer the liquid. The flask was chilled with liquid nitrogen, evacuated, and warmed, and the bromine was allowed to transfer by condensation into a 1-l. reaction flask. Tetraborane-10 from laboratory stock was purified by fractional condensation and an excess (approximately 30 mmoles) condensed into the flask on top of the solid bromine. The flask was sealed from the vacuum system, warmed slowly to near 0°, and then immersed in a salt–ice bath (about $-15°$) until the bromine color disappeared. From 12 to 18 hr. was generally required before the color had completely faded. The flask was reattached to the vacuum system, opened, evacuated, and subjected to a series of trap to trap fractional condensation steps. Hydrogen bromide and unreacted tetraborane-10 passed a $-80°$ trap which retained the desired product. The entire $-80°$ fraction was further fractionated through a special low-temperature column in which between 2 and 3 mmoles of 2-bromotetraborane was separated from boron tribromide and possible other impurities.[6]

Analysis.—Owing to the thermal instability of the compound an analysis of a weighed sample was not attempted. A suitable small sample of material was collected in a thin-walled ampoule placed at the exit of the fractionating column. The ampoule was sealed off and placed in a flask containing a similar ampoule of water. The flask was evacuated and sealed off, and both ampoules were broken by shaking. The hydrolysis was carried to completion by heating to 100° for 24 hr. Hydrogen was measured volumetrically, and both hydrogen bromide and boric acid were determined by titrating the strong acid produced, then adding *d*-mannitol and titrating the boric acid complex by the identical pH method. The ratio of boron to bromide to hydrogen was 4.01:1.00:10.01, in good agreement with the 4:1:10 required by the balanced equation for hydrolysis reaction.

To determine the molecular weight, a sample of the material was quickly vaporized in a calibrated U-tube, the pressure quickly measured, and the entire contents of the tube transferred to a weighing tube. The observed molecular weight, 135.2, agreed adequately with the theoretical 132.3.

Melting Point.—The melting point of 2-bromotetraborane was found to be $-37.1 \pm 0.5°$ in three determinations using the Stock plunger method.[2]

Vapor Pressures.—Freshly purified 2-bromotetraborane-10 was distilled directly from the fractionating column into a U-tube with attached manometer. Vapor pressures were measured at several temperatures with the U-tube cooled by suitable slush baths. The temperature of each bath was checked with a vapor pressure thermometer. The measured value at 25.5° was rendered somewhat uncertain by decomposition during the time necessary for measurement. The experimental points were used to determine the equation

$$\ln P_{\text{mm}} = 18.31 - 8822/RT$$

by a least-squares fit. The calculated boiling point is 110°, and Trouton's constant has a normal value of 23 cal. mole^{-1} deg.$^{-1}$. Experimental vapor pressures (given as mm.) were: $-36.2°$, 0.65; $-23.3°$, 1.55; $-19.0°$, 2.20; 0.0°, 9.90; 25.5°, 32.

Nuclear Magnetic Resonance Spectra.—Both proton and ^{11}B spectra were observed with a Varian DP-60 spectrometer operating at 60 and 19.3 Mc./sec., respectively. Samples were maintained at about $-20°$ in each case to avoid decomposition. As usual, the proton spectrum is complex and similar to that of tetraborane. In the absence of spin saturation studies, no further comments seem justified at the present time. The ^{11}B spectrum consists of a low-field doublet at δ +1.5 (relative to the diethyl etherate of boron trifluoride), J = 149 c.p.s.; a triplet at δ 10.0, J = 130 c.p.s.; and a high-field doublet at δ +34.7, J = 160 c.p.s., in relative intensities close to the 1:1:2 expected for a 2-substituted product. Both the triplet and the high-field doublet showed signs of further splitting of about 31 and 39 c.p.s., respectively, arising from the influence of bridge protons. This splitting was insufficient to resolve clearly the individual peaks but the coupling to the 1(3) borons clearly exceeded the coupling to the 2(4) borons. It is interesting to observe that the complex 1(3) resonance of tetraborane itself is reduced to a simpler structure in the substituted case. The cause of the complex splitting in tetraborane-10 itself is treated elsewhere and in any event is sufficiently complex so that no simple interpretation can be given of the reduction of fine structure in the substituted molecule.[7]

Discussion

The n.m.r. spectrum clearly establishes that this derivative is 2-substituted but it should be pointed out that in principle two isomers of 2-bromotetraborane-10 could exist. It seems likely that the more stable isomer will have the bromine in an equatorial (relative to the twofold axis of the unsubstituted molecule) position since considerable steric repulsion between the bromine and a 4 hydrogen might occur if the former were axial. On the other hand such stereochemistry might account for the rapid decomposition of the molecule. The argument is by no means clear and an X-ray study has been undertaken by others to clarify this point.

Acknowledgment.—Support of this work by a grant from the National Science Foundation is gratefully acknowledged.

---

(1) Studies of Boranes XV; for paper XIV of this series see R. Schaeffer, F. Tebbe, and C. Phillips, *Inorg. Chem.*, **3**, 1475 (1964).

(2) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

(3) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y.

(4) C. A. Lutz, and D. M. Ritter, *Can. J. Chem.*, **41**, 1344 (1963).

(5) B. C. Harrison, I. J. Solomon, R. D. Hites, and M. J. Klein, *J. Inorg. Nucl. Chem.*, **14**, 195 (1960).

(6) J. Dobson and R. Schaeffer, "Studies of Boron-Nitrogen Compounds. IX," to be published elsewhere.

(7) J. D. Baldeschweiler, *et al.*, to be published.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WASHINGTON, SEATTLE, WASHINGTON 98105

Role of Water in the Reaction of Fluorine with Trifluoroacetic Acid to Produce Trifluoroacetyl Hypofluorite

BY GARY L. GARD AND GEORGE H. CADY

Received November 6, 1964

Ever since it was found that water[1] increased the yield of trifluoroacetyl hypofluorite by the reaction of

---

(1) G. H. Cady and K. B. Kellogg, *J. Am. Chem. Soc.*, **75**, 2501 (1953).