[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

DICHLOROTETRABUTYLDISTANNANE[1]

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The preparation and some of the properties of dichlorotetrabutyldistannane are reported. Since previous references to dihalodistannanes have not been found it is believed that this is the first recorded preparation of compounds of this nature.

The compound is intriguing because of the theoretical possibilities for linkage offered by the two chlorine atoms. The butyl compound was prepared for the simple reason that the tetrabutylstannane used as a starting material was the only compound of this type commercially available. Preparations of compounds containing other organo groups are in progress.

Mixing tetrabutylstannane with tin (IV) chloride and warming causes disproportionation with dichlorodibutylstannane as the principal product. Treating a solution of dichlorodibutylstannane in ethanol with sodium ethoxide yields dichlorotetrabutyldistannane which may be separated as white crystals.

The reactions of dichlorotetrabutyldistannane with a number of other compounds were studied. Butyl and phenyl Grignard reagents formed tetrabutylstannane and diphenyldibutylstannane, respectively. Treatment of the dichlorotetrabutyldistannane with chlorine yielded the original dichlorodibutylstannane. With bromine the previously unknown mixed halide, bromochlorodibutylstannane was formed. The only reference found for mixed halides was the preparation of bromochlorodiphenylstannane and chloroiododiphenylstannane (1). With silver nitrate a substance tentatively identified as tetrabutyldistannanylenedinitrate[2] was formed. Attempts to couple the dichlorodistannane by means of sodium ethoxide apparently yielded a tetrastannane compound but this substance was difficult to purify and has not been definitely characterized.

EXPERIMENTAL

Dichlorodi-n-butylstannane. Tetra-*n*-butylstannane (174 g., 165 ml., 0.5 mole), was carefully added to 130 g. (59 ml., 0.5 mole) of anhydrous tin (IV) chloride and the mixture heated to 200–215° for three hours with periodic shaking. The solution was then cooled at 50°, poured into 125 ml. of 60–68° petroleum ether, and chilled. The resulting crystals were separated by filtration and washed twice with cold (60–68°) petroleum ether. Yield, 154 g. Concentration of the filtrate and then chilling gave additional yields of 59 g. and 13 g. Total yield, 226 g., 74%. m.p.[3] 40.5° (2).

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[2] $O_3N—Sn(bu)_2Sn(bu)_2NO_3$. The Committee on Nomenclature, Spelling, and Pronounciation of the American Chemical Society: *Chem. Eng. News*, **24**, 1233 (1946) has given the name "disilanylene" to the radical, $—H_2SiSiH_2—$. By analogy the radical, $—H_2SnSnH_2—$, then becomes "distannanylene."

[3] All melting points uncorrected.

Anal. Calc'd for $(C_4H_9)_2SnCl_2$: C, 31.62; H, 5.97.
Found: C, 31.64; H, 6.10.

1,2-Dichlorotetra-n-butyldistannane. Dichlorodi-*n*-butylstannane (150 g., 0.495 mole), was dissolved in 250 ml. of absolute ethanol and placed in a one-liter flask equipped with a stirrer, dropping-funnel, and a reflux condenser with a drying tube. In another flask, 11.4 g. (0.495 mole) of sodium metal was added to 300 ml. of absolute ethanol. The sodium ethoxide solution was added with vigorous stirring within 55 seconds to the stannane solution, and the reaction mixture was stirred for one hour and then allowed to stand overnight. The alcohol was distilled from the reaction mixture and 500 ml. of anhydrous ether was added; then the mixture was again allowed to stand overnight. The sodium chloride was removed by filtration using diatomaceous earth as a filter aid. The ether was distilled from the filtrate leaving a residue of 145 g. which crystallized on cooling. Acetone, 250 ml., was added, and the 1,2-dichlorotetra-*n*-butyldistannane was recrystallized as glistening white crystals. The first crystallization yielded 89.1 g., m.p. 114.5–115.5°. By concentrating the filtrates additional yields of 25.8 g. and 6.5 g. were obtained. Total yield, 121.4 g., 91%. The analytical sample, recrystallized three times from acetone, melted at 115–116°.

Anal. Calc'd for $(C_4H_9)_4Sn_2Cl_2$: C, 35.80; H, 6.76; Sn, 44.23; Cl, 13.21.
Found: C, 35.19; H, 6.70; Sn (3) 44.15, 43.97; Cl[4]: 13.06, 12.85.

The calculated molecular weight for $(C_4H_9)_4Sn_2Cl_2$ is 536.77. The molecular weight as found by the lowering of the freezing point and the elevation of the boiling point of benzene solutions was 1068. Reactions and other properties indicate the monomeric formula. The dimerization in benzene is being investigated.

Tetra-n-butyldistannanylenedinitrate. A solution of 9.0 g. (0.017 mole) at 1,2-dichlorotetra-*n*-butyldistannane in 25 ml. of warm absolute ethanol was mixed with an excess of a warm saturated ethanol solution of silver nitrate. The silver chloride was removed and the filtrate was distilled yielding a crystalline residue. Recrystallization from methanol gave white crystals. Yield, 5.0 g., 50%. m.p. 222–225°. After three recrystallizations from methanol the white crystals melted at 220–225° turning slightly yellow at 225°. Further recrystallization decomposed the compound.

Anal. Calc'd for $(C_4H_9)_4Sn_2(NO_3)_2$: C, 32.58; H, 6.15.
Found: C, 33.46; H, 6.28.

Bromochlorodi-n-butylstannane. A solution of 1.6 g. (0.01 mole) of bromine dissolved in 10 ml. of carbon tetrachloride was added to a solution of 5.4 g. (0.01 mole) of 1,2-dichlorotetra-*n*-butyldistannane in 25 ml. of carbon tetrachloride and the mixture was heated gently on a steam-bath. The bromine color disappeared in approximately ten minutes. The carbon tetrachloride was distilled at atmospheric pressure, leaving the bromochlorodi-*n*-butylstannane as a colorless liquid. Distillation at 0.5 mm. yielded 5 g. (72%) of product, which crystallized in long prisms, m.p. 34–34.5°, b.p. 104–106°/0.55 mm., n_D^{27} 1.5252.

Anal. Calc'd for $(C_4H_9)_2Sn(Cl)Br$: C, 27.59; H, 5.21.
Found: C, 27.71; H, 5.34.

No reaction was observed when iodine and 1,2-dichlorotetra-*n*-butyldistannane in carbon tetrachloride were heated on a steam-bath for one week.

Dichlorodi-n-butylstannane from 1,2-dichlorotetra-n-butyldistannane. Chlorine gas (1.05 g., 0.0148 mole), was dissolved in a solution of 8.0 g. (0.015 mole) of 1,2-dichlorotetra-*n*-butyldistannane in 30 ml. of carbon tetrachloride. About 1.5 g. of an insoluble white solid formed. The mixture was filtered and the filtrate was distilled, leaving a residue of 6.0 g. which solidified on cooling. Recrystallization from 5 ml. of (60–68°) petroleum ether gave 3 g. of a white solid which melted at 38–40° and gave no lowering of the melting point with

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[4] Determined by dissolving 0.6 to 0.8 g. of 1,2-dichlorotetra-*n*-butyldistannane in 25 ml. of warm (*ca.* 50°) absolute ethanol, adding an excess (*ca.* 50 ml.) of saturated warm ethanol solution of silver nitrate, filtering on a sintered glass crucible, washing five times with 20-ml. portions of absolute ethanol, and drying at 100° for one hour.

known dichlorodi-*n*-butylstannane. The product selected for analysis distilled between 89–91°/0.2 mm. (4).

Anal. Calc'd for $(C_4H_9)_2SnCl_2$: C, 31.62; H, 5.97.

Found: C, 31.30; H, 5.67.

Reaction with a Grignard reagent. n-Butylmagnesium bromide was prepared from 11.0 g. (0.08 mole) of *n*-butyl bromide and 2.0 g. (0.082 mole) of magnesium turnings in 50 ml. of ether. To this reagent was added drop-wise a solution of 10.7 gm. (0.02 mole) of 1,2-dichlorotetra-*n*-butyldistannane dissolved in 50 ml. of anhydrous ether. A white precipitate formed during the addition of the distannane solution. The reaction mixture was stirred for an additional 30 minutes and the ether was removed by distillation. The white semisolid residue was heated on a steam-bath for one hour. After cooling, 200 ml. of ether and 50 ml. of saturated ammonium chloride were added, and the mixture was stirred for one hour. The ether layer was separated and dried over magnesium sulfate. The solvent was removed by distillation and the residue was distilled at reduced pressure. The tetra-*n*-butylstannane weighed 8.5 g., 61%. b.p. 96–98°/0.35 mm., $n_D^{23.5}$ 1.4734. Redistillation yielded 7.2 g., b.p. 94.5–96°/0.28 mm., n_D^{24} 1.4731. The compound was soluble in ether, acetone, ethyl acetate, and absolute ethanol and insoluble in methanol and water. There was no apparent reaction with water.

Anal. Calc'd for $(C_4H_9)_4Sn$: C, 55.35; H, 10.45.

Found: C, 54.92; H, 10.46.

Diphenyldi-n-butylstannane. Using the same method as above, the Grignard reagent prepared from 15.7 g. (0.10 mole) of bromobenzene and 2.43 g. (0.10 mole) of magnesium turnings was treated with 10.7 g. (0.02 mole) of 1,2-dichlorotetra-*n*-butyldistannane to give 11.2 g. (74%) of diphenyldi-*n*-butylstannane. This compound was a light yellow liquid, b.p. 143–149°/0.38 mm., n_D^{23} 1.5605. Redistillation yielded a colorless liquid, b.p. 137°/0.2 mm.

Anal. Calc'd for $(C_6H_5)_2Sn(n\text{-}C_4H_9)_2$: C, 62.06; H, 7.29.

Found: C, 62.70; H, 7.86.

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