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HYDRIDES OF GERMANIUM, TIN, ARSENIC AND ANTIMONY

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HYDRIDES OF GERMANIUM, TIN, ARSENIC AND ANTIMONY

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Volatile hydrides may be prepared from ether solutions by the reaction of the appropriate chlorides with lithium hydroaluminate.[1] In this general method, it is necessary to work with strictly anhydrous reagents and solvents because of the great reactivity of lithium hydroaluminate toward water. The procedures described below are believed to be much more convenient because the reducing agent employed is potassium hydroborate, which is relatively insensitive toward water. Since only aqueous solutions are involved, there are no solvent-purification steps and there is no dissolution or contamination of stopcock grease, etc.

General Procedure**

The apparatus shown in Fig. 1 may be used for the preparation of the hydrides of either germanium, tin, arsenic, or antimony. Aqueous acid is placed in a 500-ml three-neck round-bottom flask equipped with a magnetic stirrer, an inlet tube for nitrogen or argon (dipping beneath the solution), a 100-ml dropping funnel and an outlet tube leading to a vacuum line. The flask is partially immersed in an ice-water bath. During a run, nitrogen

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**These syntheses are based in part on references 2 and 3. For a discussion of general vacuum technique, see reference 4.

or argon is continuously bubbled (at a rate of approximately 500 cc/min, S.T.P.) through the magnetically-stirred acid solution and passed through a series of three traps (numbered 1, 2 and 3 in Fig. 1). The pressure in the system is maintained at approximately 100 mm by adjustment of the stopcock leading to the vacuum pump on the right side of the line. Two of the traps are immersed in Dewar flasks containing liquid nitrogen.

A. GERMANE AND DIGERMANE

$$HGeO_3^- + BH_4^- + 2H^+ \longrightarrow GeH_4 + H_3BO_3$$

$$8HGeO_3^- + 7BH_4^- + 15H^+ \longrightarrow 4Ge_2H_6 + 7H_3BO_3 + 3H_2O$$

Procedure

The apparatus used is similar to that described under General Procedure except that the ice-bath is not included. The reaction flask is charged with 120 ml of glacial acetic acid and is flushed with nitrogen or argon. In 25 ml of water are dissolved successively, 2 g of potassium hydroxide pellets, 1 g of germanium dioxide and 1.5 g of potassium hydroborate, giving a ratio of BH_4^-/Ge(IV) of 2.9. This solution is added, over a period of 10 minutes, to the glacial acetic acid. A small quantity of yellow, polymeric GeH_x forms in the reaction flask. The flow of inert gas is maintained for a further 5 minutes after all the solution has been added, and then the stopcock connecting the reaction flask to the vacuum line is closed. The line is evacuated thoroughly.

The contents of the liquid nitrogen traps are germane, digermane, a trace of trigermane, water, acetic acid, and carbon dioxide. The material is distilled through a chloroform-slush trap (-63.5°) to remove trigermane, water and acetic acid. The carbon dioxide is readily removed by passing the gases through successive traps of ascarite and magnesium perchlorate. Finally, by distilling the gases through a carbon disulfide slush bath (-111.6°) to remove digermane, pure samples of both germane and digermane are obtained.

Typically, this procedure gives 7.0 mmoles, or about 160 c.c. (S.T.P.), of pure germane, corresponding to a germanium conversion of 73%. The amount of digermane prepared is 0.31 m. moles, or about 7 c.c. (S.T.P.), corresponding to a germanium conversion of 6.5%. The yield of digermane is improved if a lower concentration of hydroborate is used; the best result being a germanium conversion of 9.1% when the $BH_4^-/Ge(IV)$ ratio is 1.5. However, the yield of germane is decreased by any appreciable variation in the quoted amount of hydroborate.

Properties

The germane prepared has a vapor pressure of 181 mm. at -111.6° (lit. 182 mm.[5]). The infra-red spectrum of the gas in the NaCl region shows the fundamental frequencies ν_3, ν_2 and ν_4 at 2105, 943 and 815 cm^{-1} respectively.[6] Germane is stored in a glass vessel with a greased stopcock.

The digermane prepared by this procedure has vapor pressures of 6 mm at -63.5°, 77 mm at -22.9° and 221 mm at 0° (lit. ca 9 mm, ca 85 mm and

243 mm respectively[7]). The infra-red spectrum of the gas in the NaCl region shows the fundamental frequencies ν_5, ν_8 and ν_6 at 2069, 885 and 759 cm^{-1} respectively.[8] Digermane is absorbed by stopcock grease and should be kept in a vessel sealed with a mercury float valve or in an all-glass ampoule. On heating it decomposes violently to its elements.

B. TRIGERMANE AND POLYMERIC GeH_x*

$$6HGeO_3^- + 5BH_4^- + 11H^+ \longrightarrow 2Ge_3H_8 + 5H_3BO_3 + 3H_2O$$

$$8HGeO_3^- + (4 + x)BH_4^- + (12 + x)H^+ \longrightarrow 8GeH_x + (4 + x)H_3BO_3 + (12-3x)H_2O$$

Procedure

The procedure described for the production of germane and digermane gives very poor yields of trigermane and polymeric GeH_x, and changes must be made in the procedure to obtain better yield of these latter compounds. The apparatus used is identical to that described under General Procedure. The flask is charged with 120 ml. of 3 M sulfuric acid; the system is cooled in the ice-bath, and the flask is flushed with nitrogen or argon. In 25 ml. of water are dissolved successively, 2 g. of potassium hydroxide pellets, 1.0 g. of germanium dioxide and 3.0 g. of potassium hydroborate, corresponding to a ratio of BH_4^-/Ge(IV) of 5.8. This solution is added, over a period of 15 minutes, to the sulfuric acid. During the addition some foaming occurs and an appreciable amount of yellow polymeric GeH_x

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* where $x \approx 1.0$

is deposited. On completing the addition, the flow of inert gas is maintained for a further 5 minutes before the line is thoroughly evacuated.

The trigermane and water present in the liquid nitrogen traps can be separated from germane, digermane and carbon dioxide by distilling the materials through a chloroform slush bath (-63.5°). The germane and digermane may be separated as described previously, but the yields are not as good as those obtained with acetic acid. The trigermane is easily separated from the water by passage through a trap containing magnesium perchlorate.

Typically, this procedure gives 0.07 mmoles, or 1.6 cc (S.T.P.), of pure trigermane, corresponding to a germanium conversion of 2.2%.

The contents of the reaction flask are filtered immediately after the reaction is complete and the yellow polymeric GeH_x is thoroughly washed with water. It is then dried by pumping it on the vacuum line.

Typically, this procedure gives 1.6 mmoles, or about 0.1 g. of polymeric GeH_x, corresponding to a germanium conversion of 17%.

Properties

The trigermane prepared has a vapor pressure of 9.5 mm. at 0° (lit. 14 mm.[7]). The infra-red spectrum in the NaCl region shows two bands at 2041 and 794 cm^{-1}. Trigermane, like digermane, is absorbed by stopcock grease and should be kept in an all-glass ampoule.

The polymeric GeH_x prepared is a yellow solid which turns orange-brown without change of composition on treatment with concentrated alkali, but is decomposed by concentrated acids. It must be handled with care since on exposure to air it sometimes decomposes explosively to its elements. Both the yellow and the orange-brown materials explode on heating to give germanium, hydrogen and a trace of germane. The value of x is usually close to unity (values between 0.95 and 1.10 are usually found); thus the product prepared by this procedure appears to resemble the polymeric compounds $(GeH)_n$ described by earlier workers.[9,10] The infra-red spectrum (KBr pellet) in the NaCl region shows three main bands at 2062, 833 and 775 cm^{-1}.

C. STANNANE AND DISTANNANE

$$H_2O + 4HSnO_2^- + 3BH_4^- + 7H^+ \longrightarrow 4SnH_4 + 3H_3BO_3$$

$$8HSnO_2^- + 5BH_4^- + 13H^+ \longrightarrow 4Sn_2H_6 + 5H_3BO_3 + H_2O$$

Procedure

The apparatus is assembled as described under General Procedure. The reaction flask is charged with 150 ml. of 6 M HCl and is flushed with nitrogen or argon. The solution which is to be added from the dropping funnel is prepared immediately before use as follows. An ice-cold solution of 36 g. of 85% potassium hydroxide in 60 ml. of water is added, with stirring, to an ice-cold solution of 15 g. of tin(II) chloride 2-hydrate in 60 ml. of water. A solution of 1.5 g. of potassium hydroborate in 20 ml. of water is then added to the solution. The resulting stannite- hydroborate solution is added, over a period of about 30 minutes, to the stirred hydrochloric acid solution. During the reaction, a brown precipitate (which soon turns grey-black) forms in the flask. The flow of inert gas is continued for several minutes after the complete addition of the stannite-hydroborate solution. The stopcock connecting the reaction vessel with the vacuum line is then closed and the line is thoroughly evacuated.

During subsequent operations, it is best to keep the stopcock above the mercury manometers closed except when it is necessary that they be open for pressure measurements. The crude product is distilled into trap 3 preparatory to its purification by fractional condensation. If only stannane is sought, the material is distilled through a CS_2-slush trap (-111.6°) to remove both water and distannane. The stannane which passes through this trap is highly contaminated with carbon dioxide originating from the carbonate impurity in the potassium hydroxide. This impurity may be removed by distilling the stannane several times through a trap containing 1/16-in. pellets of Linde Molecular Seive, Type 4A*, at 0°. A small amount of stannane decomposes in this process, so it is necessary to pump on the system during each distillation. Typically, 1.0 mmole, or about 22 cc. (S.T.P.), of purified stannane is prepared by this procedure. This yield corresponds to 2.7% yield, based on the hydroborate consumed.

If it is desired to isolate the distannane, the crude product is

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*Obtainable from the Linde Air Products Company, Division of Union Carbide Corporation. The molecular seive pellets should first be heated in the trap to 200° for several minutes while pumping to desorb highly volatile materials.

distilled through a chloroform-slush trap (-63.5°) to collect water and a CS_2-slush trap to collect distannane. The distillation must not be prolonged, or appreciable amounts of water will pass through the -63.5° trap. Typically, 0.02 mmole, or about 0.4 cc. (S.T.P.), of distannane is prepared by this procedure. Slightly better yields may be obtained by making the stannite-hydroborate solution more concentrated.*

Properties

Stannane, prepared as described, has a vapor pressure of 17 mm. at -111.6°, in good agreement with the literature[11] value of 17.5 mm. The melting and boiling points of stannane are reported as -150° and -51.8°, respectively.[12] The infrared spectrum in the NaCl region shows a prominent triple band (the Sn-H stretching vibration[13], ν_3) at 1900 cm^{-1}, a medium band at 760 cm^{-1}, and strong bands at 700 and 675 cm^{-1} [14]. The presence of carbon dioxide in stannane may be readily determined from the infrared spectrum; carbon dioxide has a strong absorption band at 2300 cm^{-1}. Stannane has been stored without decomposition in clean glass vessels in the absence of mercury for periods of several weeks. Traces of oxygen are reported to inhibit the decomposition.[15] Decomposition, once started, is usually quite rapid and results in the formation of a beautiful tin mirror on the walls of the vessel. Stannane is best stored in a glass bulb with an extended tip immersed in liquid nitrogen.

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* It is possible to dissolve the reagents in a total of 110 ml., rather than 140 ml., of water.

Distannane is an extremely unstable substance which, when warmed to room temperature, completely decomposes to the elements, forming a mirror on the walls of the container. However, distannane may be readily distilled from a trap without decomposition if the distillation is carried out at very low pressures and if the trap is allowed to warm up very slowly.[3]

D. ARSINE

$$4As(OH)_4^- + 3BH_4^- + 7H^+ \longrightarrow 4AsH_3 + 3H_3BO_3 + 7H_2O$$

Procedure

The apparatus is assembled as described under General Procedure. The reaction flask is charged with a solution of 25 ml. of concentrated sulfuric acid in 200 ml. of water and is flushed with nitrogen or argon. Four g. of sodium hydroxide, 8.0 g. of arsenic(III) oxide and 2.0 g. of potassium hydroborate are dissolved, in that order, in 20 ml. of water. This solution should be prepared immediately before its use, because it decomposes with evolution of arsine and precipitation of arsenic. The solution is added through the dropping funnel, over a period of 15 minutes, to the sulfuric acid solution. An orange precipitate of arsenic forms in the flask. A small amount of yellow, polymeric As_2H forms at the entrance to each of the liquid nitrogen traps. This material forms as the result of the decomposition of diarsine, As_2H_4.[16] The flow of inert gas is continued for several minutes after the complete addition of the arsenite-hydroborate solution. The stopcock connecting the reaction vessel with the vacuum line is then closed and the line is thoroughly evacuated.

The crude arsine is distilled into trap 1 (Fig.1), a U-tube packed with Ascarite is substituted for trap 2 and the arsine is then distilled through the Ascarite into trap 3. Trap 2 is replaced and immersed in a CS_2-slush bath (-111.6°), and the arsine is distilled into trap 1. Typically, 29 mmoles, or 650 cc. (S.T.P.), of purified arsine is prepared by this procedure. This corresponds to 59% yield, based on the hydroborate consumed.

Properties

Arsine has a vapor pressure of 35 mm. at -111.6°[17], a melting point of -116.93°[18] and a boiling point of -62.48°[18]. The infrared spectrum in the NaCl region shows a triple band at 2122 cm^{-1} (v_1 and v_2) and bands at 1005 and 906 cm^{-1} (v_4 and v_3, respectively).[19] Arsine is a relatively stable gas which may be stored in glass vessels for several months with less than 5% decomposition. Ordinary stopcock grease is blackened by prolonged exposure to the gas.

E. STIBINE

$$4Sb(OH)_4^- + 3BH_4^- + 7H^+ \longrightarrow 4SbH_3 + 3H_3BO_3 + 7H_2O$$

Procedure

The apparatus is assembled as described under <u>General Procedure</u>.

The reaction flask is charged with a solution of 25 ml. of concentrated sulfuric acid in 200 ml. of water and is flushed with nitrogen or argon. Twelve g. of 85% potassium hydroxide, 15 g. of potassium antimony tartrate and 2.0 g. of potassium hydroborate are dissolved, in that order, in 100 ml. of water. This solution is added through the dropping funnel, over a period of 15 minutes, to the sulfuric acid solution. A black precipitate of antimony forms in the flask. The flow of inert gas is continued for several minutes after the complete addition of the antimonite-hydroborate solution. The stopcock connecting the reaction vessel with the vacuum line is then closed and the line is thoroughly evacuated.

The crude stibine, with its impurities of water and carbon dioxide, is distilled into an ampoule attached to the ball joint which was previously connected to the reaction vessel. Trap 1 is immersed in a toluene-slush bath (-95°); trap 2 is immersed in an n-pentane-slush bath (-130°), and trap 3 is immersed in liquid nitrogen. By slowly distilling the crude stibine through these traps, the water plus traces of stibine are condensed out in the -95° trap, pure stibine is collected in the -130° trap, and the carbon dioxide plus traces of stibine are collected in the liquid nitrogen trap. With suitable precautions (because of the poisonous nature of stibine), the contents of traps 1 and 3 are discarded. Typically, 25 mmoles, or 560 cc. (S.T.P.), of purified stibine is prepared by this procedure. This corresponds to 51% yield, based on the hydroborate consumed.

Properties

Stibine has vapor pressures of 81 mm. and 224 mm. at the melting points of chloroform (-63.5°) and chlorobenzene (-45.2°), respectively.[20] The boiling point is -18.4°.[20] The infrared spectrum in the NaCl region shows a triple band at 1890 cm^{-1} (ν_1 and ν_3) and bands at 831 and 781 cm^{-1} (ν_4 and ν_2, respectively).[21] Stibine lies between arsine and stannane in its stability toward decomposition to the elements. If it is to be stored longer than two or three days, it should be kept frozen with liquid nitrogen.

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