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SILANE, STANNANE, SILANE-d_4, GERMANE-d_4, AND STANNANE-d_4

Submitted By: Arlan D. Norman,*† John R. Webster* and William L. Jolly*

Silane, germane, and stannane can be synthesized by the reduction of a variety of silicon, germanium, or tin compounds with active metal hydrides.[1,2] We have found that the general method described below, involving the lithium hydroaluminate ($LiAlH_4$) reduction of silicon tetrachloride and stannic chloride, is convenient for the efficient preparation of one to fifty millimoles of silane and stannane. The method is easily adapted to the synthesis of deuterio compounds, i.e. silane-d_4, germane-d_4, and stannane-d_4 by substituting lithium deuterioaluminate for lithium hydroaluminate in the appropriate reactions. Silane-d_4 and germane-d_4 are useful in structural and mechanistic studies, and undoubtedly stannane-d_4 will have similar applications.

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Normal germane (GeH_4) can also be prepared by reduction of germanium tetrachloride, although the previously reported reduction of germanate ion by potassium hydroborate in aqueous media gives significantly higher yields.[3] Because this latter method involves the use of relatively large quantities of water, acid, and a large excess of potassium hydroborate it is not economically feasible to adapt it to the preparation of deuterated germane.

General Procedure*

The apparatus shown in the figure is used for the preparation of SiH_4 and SnH_4. For the synthesis of SiD_4, GeD_4, and SnD_4 a similar apparatus without the addition funnel is used. A suspension of $LiAlH_4$ (or $LiAlD_4$) is placed in the 300 ml., 3-necked round bottom flask. The flask is equipped with an efficient magnetic stirrer, a cold finger condenser, and a 150-ml. addition funnel which contains the silicon tetrachlorine-ether solution or tin tetrachloride-ether slurry. For best results, all joints are greased with Dow-Corning Silicone grease. The apparatus is attached to a vacuum line in such a way that volatile reaction materials (products and some ether solvent) can be removed through a series of five U-traps.

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* These syntheses are based in part on reference 4. A detailed description of a vacuum line suitable for these syntheses is given in reference 3. For additional discussion of vacuum line techniques see reference 5.

The cold bath surrounding the reaction flask is maintained at the desired temperature by the controlled addition of powdered dry ice to the bath solvent and the cold-finger condenser is cooled to -78.5° (dry-ice slush).*

A. SILANE AND SILANE-d_4

$$SiCl_4 + LiAlH_4 \rightarrow LiCl + AlCl_3 + SiH_4$$

$$SiCl_4 + LiAlD_4 \rightarrow LiCl + AlCl_3 + SiD_4$$

Procedure (SiH_4)

The apparatus is assembled and prepared for the reaction as described under General Procedure, the reaction flask and addition funnel having been charged with 1.14 g (0.030 mole) of $LiAlH_4$ in 70 ml. of diethyl ether and 2.30 ml. (0.020 mole) of $SiCl_4$ in 50 ml. of ether, respectively. The cold bath and the cold finger condenser are maintained at -15 to -20° and -78.5° respectively, during this entire synthesis. After the apparatus is evacuated, care being taken to avoid excessive "bumping" of the solvent as ether refluxing begins, the U-trap nearest the reaction apparatus is cooled to -95° (toluene slush) and the remaining four traps are cooled to -196° (liquid nitrogen). The $SiCl_4$-ether solution is

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* A variety of solvents, i.e., ethanol, i-propanol, acetone, and trichloroethylene, can be used in preparing dry ice cooling baths. However, the low flammability of trichloroethylene makes it preferable to the others.

added through the addition funnel, over a 15 min. period, to the cooled, stirred $LiAlH_4$ suspension.* The silane is removed continuously at a moderate rate, in order to prevent violent refluxing of the ether. The rate is readily controlled by adjusting the opening of the stopcock between the reaction vessel and the vacuum line. The reaction mixture is stirred for 15-20 min. after $SiCl_4$ addition is completed, in order to ensure complete reaction. During this time the system can be closed off from the vacuum line to prevent excessive removal of ether. After the final quantity of silane is pumped into the vacuum line, the reaction vessel may be vented to the air and removed from the vacuum line.

The contents of the liquid nitrogen traps (silane and traces of ether) are combined in one trap and the material in the -95° trap (mainly diethyl ether) is discarded. The silane is freed of last traces of ether by passing it five times through a -130° trap into a -196° trap. Typically this procedure gives 0.016 mole of pure silane (80% based on $SiCl_4$).

Procedure (SiD_4)

The apparatus used is a 100 ml. round-bottom flask equipped with a cold-finger reflux condenser and a magnetic stirring bar. The apparatus is attached to the vacuum line along with two 100 ml. detachable bulbs

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* Caution: In order to prevent air from accidentally entering the system, stop the addition of $SiCl_4$-ether solution while a small amount of liquid is still present in the addition funnel. This is important since silane will inflame or explode upon exposure to oxygen.

from which dry ether solvent and silicon tetrachloride are distilled into the reactor. The entire system is pre-conditioned by allowing D_2O to stand in the line at its room temperature vapor pressure and exchange with H_2O present. The pre-conditioning is necessary to ensure the highest possible isotopic purity of the SiD_4 prepared in the synthesis. After one hour the D_2O is pumped from the system and the apparatus is thoroughly evacuated to remove last traces of D_2O.

After the pre-conditioning operation the reactor is opened and charged with 0.63 g. of $LiAlD_4$ (0.015 mole, > 98% D)* and re-evacuated. Thirty ml. of diethyl ether is dried in vacuo over $LiAlH_4$ in one of the detachable bulbs, then distilled into the reactor which is held at -196° (liquid nitrogen). A small plug of glass wool in the neck of the bulb will serve to keep small particles of $LiAlH_4$ from transferring into the reactor during distillation of the ether. Silicon tetrachloride (1.72 ml., 0.015 mole) is placed in the other detachable bulb, degassed by brief pumping, and then distilled into the reactor. The cold-finger condenser is cooled to -78.5° (dry ice slush), the U-trap nearest the reactor is cooled to -95°, and the remaining four traps are cooled to -196°. The reactor is allowed to warm slowly to 0° (over a 30 min. period), the volatile products being removed as they form at a rate slow enough to prevent violent refluxing of the ether. For best results

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* Alfa Inorganics, Inc., 8 Congress St., Beverly, Mass.

the reaction mixture should be stirred periodically during the reaction period. The reactor is allowed to stand at 0° for 30 min. to ensure complete reaction before last traces of SiD_4 are pumped into the vacuum line.

The contents of the liquid nitrogen traps (SiD_4 and traces of ether) are combined into one trap, and the material in the -95° trap (mainly diethyl ether) is discarded. The product is freed of last traces of ether by passing it five times through a -130° trap into a -196° trap. Thirteen mmoles of SiD_4 (87% yield based on $LiAlD_4$) having an isotopic purity of > 96% is obtained.

Properties

The infrared spectrum of SiH_4[6] gas in the NaCl region shows absorptions at 2191 (s) (Si-H stretching frequency) and 914 (s) cm^{-1}. The spectrum of SiD_4[7] shows absorptions at 1597 (s) (Si-D stretching frequency) and 681 cm^{-1}. The mass spectrum of SiH_4 has peaks at m/e 14-16 and 28-34, attributable to SiH_x^{2+} and SiH_x^{+} ions, respectively.[8] Peaks corresponding to the analogous ion fragments in the mass spectrum of SiD_4 occur at m/e 14-18 and 28-38. The presence of carbon dioxide impurity in the silane is indicated by an absorption at 2300 cm^{-1} in the infrared spectrum or by a peak at m/e = 44 in the mass spectrum.

Silane may be stored in the gas phase at room temperature for several months without noticeable decomposition. Since silane does not dissolve appreciably in grease, storage vessels equipped with greased stopcocks may be used.

B. GERMANE-d_4

$$GeCl_4 + LiAlD_4 \rightarrow LiCl + AlCl_3 + GeD_4$$

Procedure

The reactor consists of a 100-ml. round-bottomed flask equipped with a cold-finger condenser and a magnetic stirring bar. The apparatus is attached to the vacuum line along with two detachable bulbs from which dry diethyl ether and germanium tetrachloride are distilled into the reaction vessel. In order to obtain GeD_4 of the highest possible isotopic purity, the entire system is pre-conditioned with D_2O (see SiD_4 Procedure, above) prior to the synthesis.

After pre-conditioning the apparatus the reactor is opened and charged with 0.42 g. of $LiAlD_4$ (0.010 mole, > 98% D) and then re-evacuated. Twenty ml. of $LiAlH_4$-dried diethyl ether and 1.4 ml. (0.0123 mole) of $GeCl_4$ are distilled into the reactor which is cooled to -196°.* The cold-finger condenser is cooled to -78.5° (dry ice slush), the U-trap nearest the reactor is cooled to -95° (toluene slush), and the four remaining U-traps are cooled to -196°. The reaction mixture is allowed to warm slowly to room temperature over a 15-20 min. period, during which time the reaction mixture is periodically stirred

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* Details concerning these steps in the synthesis are given above under SiD_4 Procedure.

with a small magnet. While the reaction mixture is warming to room temperature, volatile reaction products are removed at a rate so as to maintain gentle reflux on the -78.5° cold finger. The reaction is complete when the reactor reaches room temperature.

The material in the -95° trap (mainly solvent) is discarded. The product in the -196° traps is freed of last traces of ether solvent by passing it five times through a -130° trap (n-pentane slush). The yield is 0.0019 mole of GeD_4 (19%, based on $LiAlD_4$) and the deuterium content of the product is > 96%.

Properties

The GeD_4 prepared has a vapor pressure of 186 mm. at -111.4°. The infrared spectrum of the gas shows absorptions at 1522 (Ge-D stretching frequency) and 596 cm^{-1}.[9] The mass spectrum shows peaks at m/e = 35 to 41 and m/e = 70 to 82 due to GeD_x^{2+} and GeD_x^{+} ions, respectively.[8] Traces of carbon dioxide impurity may be detected by a peak at m/e = 44 in the mass spectrum or by an absorption at 2300 cm^{-1} in the infrared spectrum.

Germane-d_4 may be stored at room temperature in a glass vessel equipped with a greased stopcock for several months without appreciable decomposition.

C. STANNANE AND STANNANE-d_4

$$SnCl_4 + LiAlH_4 \rightarrow LiCl + AlCl_3 + SnH_4$$

$$SnCl_4 + LiAlD_4 \rightarrow LiCl + AlCl_3 + SnD_4$$

Procedure (SnH_4)

The apparatus is assembled as described under General Procedure, except that a dewar flask is used instead of a crystallizing dish for holding the low-temperature bath around the reaction flask. The reaction flask is charged with 2.7 g. of $LiAlH_4$ (0.072 mole) and 70 ml. of anhydrous diethyl ether. The cold-finger reflux condenser and the dewar around the reaction flask are filled with -78.5° baths (dry ice slushes). The system is opened to the vacuum pump, and a -95° bath (toluene slush) is placed around the U-trap nearest the reaction vessel. The remaining four U-traps are cooled to -196° with liquid nitrogen. Eight ml. of $SnCl_4$ (0.068 mole) and 130 ml. of diethyl ether are carefully mixed together to make a slurry of the solid white etherate which forms. This slurry is slowly added from the dropping funnel over a period of about one hour. It is usually necessary to agitate the slurry in some manner since the solid etherate tends to settle to the bottom and hinder steady addition; stirring with a glass rod is sufficient. If stirring of the reaction flask cannot be accomplished while the dewar is around it, it may be done manually by removing the dewar momentarily every five minutes and moving the stirring bar with a small magnet. Addition of the slurry should be

sufficiently slow so that most of the SnH_4 traps out in the first three -196° traps. The appearance of much SnH_4 in the last trap is an indication that the rate of addition is too fast and that product is being swept through the condensation train. Considerable H_2 is also evolved in this preparation and it hinders the condensation of SnH_4. We have found that our best yields are obtained if a stopcock between the -196° traps and the vacuum pump is partially closed, thus maintaining the pressure in the reaction system around 50 to 100 mm Hg.

After the addition of the $SnCl_4$-etherate slurry is complete, the reaction mixture is allowed to warm slowly to -20°. The mixture is then quenched to -78°, and the reaction flask is removed from the vacuum line. The material in the -95° trap (mostly solvent) is discarded. The crude product in the -196° traps is combined and passed four times through a -112° trap (CS_2 slush) to remove traces of solvent. This procedure typically gives 0.020 mole (30% yield) of SnH_4 with a vapor pressure of 17 mm. Hg at -112°.

Procedure (SnD_4)

The apparatus used is a 100-ml. round-bottomed flask equipped with a cold-finger reflux condenser and a magnetic stirring bar. This system is connected to a vacuum line with five U-traps between the reactor and pump and two detachable bulbs from which reactants are distilled into the reactor. Prior to the synthesis the entire vacuum system is pre-conditioned with D_2O as has been described above (see SiD_4 Procedure).

After pre-conditioning and evacuating the system, the reactor is opened, charged with 0.270 g. of $LiAlD_4$ (0.0065 mole, > 98% D), and then evacuated again. Ten ml. of dried diethyl ether and 0.9 ml. anhydrous stannic chloride (0.0077 mole) are distilled into the reactor which is cooled to -196°C.* The cold finger reflux condenser and dewar around the reactor are filled with -78° baths (dry ice slushes). The U-trap nearest the reactor is cooled with a -95° bath (toluene slush) and the remaining four U-traps are cooled to -196°. The reactor and cold finger are allowed to warm slowly to room temperature (over a period of about 90 min.), and volatile products are taken off at five-minute intervals. Stirring is accomplished manually by using a small magnet to move the stirring bar. The reaction is stopped when the reactor reaches room temperature.

The material in the -95° traps (mostly solvent) is discarded. The product in the four -196° traps is combined and passed four times through a -112° trap (CS_2 slush) to remove traces of solvent. The yield is 0.0017 mole of SnD_4, or 25% based on $LiAlD_4$. Vapor pressure at -112° is 17.4 mm. Hg., and deuterium content is > 98%.

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* Details concerning these steps in the synthesis are given above under SiD_4 Procedure.

Properties

Stannane has a reported vapor pressure at -111.6° of 17.5 mm.[10] The infrared spectrum of the gas in the NaCl region shows absorptions at 1860(s) (Sn-H stretch), 760(m), 703(s), and 677(s) cm^{-1}.[11] The deuterio stannane prepared absorbed at 1455(s) cm^{-1}. The presence of carbon dioxide in the stannane may be detected by a peak at m/e = 44 in the mass spectrum or by an absorption at 2300 cm^{-1} in the infrared spectrum.

Stannane decomposes thermally in a few hours at room temperature. The decomposition is catalyzed by the metallic tin mirror which forms,[12] however traces of oxygen have been reported to inhibit the decomposition.[13] Thus stannane is best stored at room temperature with oxygen present or pure at liquid nitrogen temperature.

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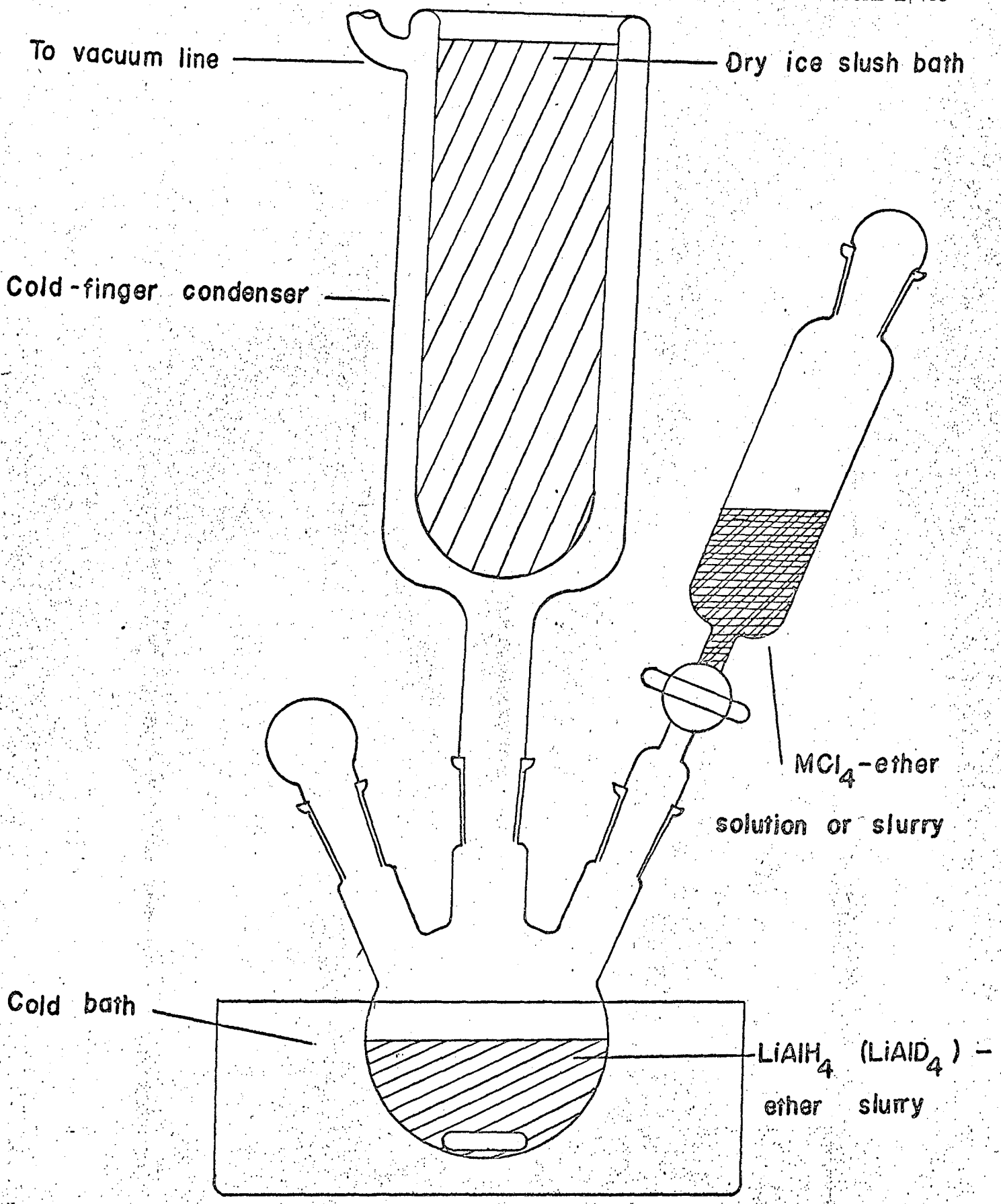

Apparatus for the preparation of silane, stannane, silane-d_4, germane-d_4, and stannane-d_4.