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THE DEPROTONATION OF WEAK ACIDS WITH POTASSIUM HYDROXIDE

$$2KOH_{(s)} + HA \rightarrow K^{+} + A^{-} + KOH \cdot H_2O_{(s)}$$

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$$2KOH_{(s)} + HA \rightarrow K^+ + A^- + KOH{\cdot}H_2O_{(s)}$$

Submitted by William L. Jolly,* Douglas S. Rustad* (CH_3GeH_3), Thomas Birchall* (CH_3GeH_3), and David J. Chazan* ($Ni(C_5H_5)_2$)

March 1967

Potassium hydroxide may be used to deprotonate extremely weak† acids if hydroxylic solvents such as water and alcohols are avoided.[1] The following syntheses illustrate the general applicability of this procedure to inorganic syntheses.

The methyl cyclopentadienylmolybdenum tricarbonyl synthesis illustrates how a potassium cyclopentadienyl solution may be prepared and then used to prepare a typical transition metal cyclopentadienyl complex. By analogous procedures, one may prepare a wide variety of metal complexes of the anions of cyclopentadiene, indene, etc.

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† Although it has been calculated that KOH should only be able to deprotonate acids having aqueous pK values less than 31, it has been observed that even triphenylmethane (pK ≈ 32.5) is at least 95% deprotonated using dimethylsulfoxide as the solvent for the triphenylmethane and its salt.[1]

The ferrocene and nickelocene syntheses illustrate how the procedure may be adapted to the simultaneous deprotonation of cyclopentadiene and the dehydration of a transition metal salt.

The methylphosphine and dimethylphosphine syntheses show how alkyl derivatives of a volatile hydride may be prepared in amounts as great as 0.05 mole. The methylgermane synthesis shows a somewhat simpler procedure applicable to amounts less than 0.005 mole.

General Deprotonation Procedure

Potassium hydroxide which is to be used for deprotonation of a weak acid must be finely pulverized. For this purpose, pellets of reagent grade potassium hydroxide (85% KOH) are quickly ground to a powder with a mortar and pestle and transferred for temporary storage to a tared wide-mouthed bottle which can be capped to prevent absorption of moisture by the KOH. The KOH should be ground sufficiently fine so that the largest particles are less than 0.5 mm. in diameter. It is very difficult to pulverize a large quantity of KOH at one time; therefore it is recommended that the pulverization be done in batches whenever more than 15 g. of powdered KOH is required. The amount of KOH used is generally determined by the amount of acid to be deprotonated. Good results are usually obtained when the KOH powder is used in the proportion of 25 g. per 0.1 mole of acid, however very weak acids, with aqueous pK values greater than 25, may require a KOH/acid ratio two or three times as great in order to obtain complete deprotonation in a reasonable time. The KOH serves as a drying agent for the solvent as

well as a deprotonating agent; consequently no less than 10 g. of KOH powder should be used per 100 ml. of solvent unless the solvent is carefully dried beforehand.

The amount of solvent used is generally dictated by the solubility of the potassium salt. But even in the case of highly soluble potassium salts, the ratio of KOH to solvent should not be allowed to exceed 80 g. to 100 ml. – otherwise the slurry will be too difficult to stir, and too large a fraction of the solution will be held back during subsequent filtration.

The reaction is conveniently carried out in a round-bottomed flask having a capacity about double the volume of the solvent. If less than 80 g. of KOH is used, a magnetic stirring bar is adequate; however, larger amounts of KOH require a paddle stirrer. Often the anion of the weak acid is susceptible to autoxidation, requiring that the reaction flask be sealed and that oxygen be eliminated. With liquid and solid acids, this is best accomplished by providing a nitrogen atmosphere. It is convenient to use a 3-necked, ground-glass flask, with one of the side necks connected to a source of nitrogen. The tubing leading to the source of nitrogen should be connected via a T-connection to a mercury bubbler set to maintain a pressure differential of 5-10 mm. With gaseous acids, the use of a vacuum line is most convenient.

In the case of a relatively strong acid such as cyclopentadiene, the solution of the acid is vigorously stirred with the KOH for about 1 hour. Weaker acids, such as fluorene and triphenylmethane, require 10-15 hours, or even longer, to effect complete deprotonation. The reaction times are not appreciably reduced by increasing the temperature.

The rates are somewhat controlled by the choice of solvent. For example, it has been observed that deprotonations proceed much more rapidly in dimethyl sulfoxide than in 1,2-dimethoxyethane. However, dimethyl sulfoxide can sometimes be disadvantageous because of its high viscosity, its low volatility, or its oxidizing power.

A. σ-METHYL-π-CYCLOPENTADIENYLMOLYBDENUM TRICARBONYL

$$2KOH + C_5H_6 \rightarrow K^+ + C_5H_5^- + KOH \cdot H_2O$$

$$Mo(CO)_6 + C_5H_5^- \rightarrow Mo(CO)_3C_5H_5^- + 3CO$$

$$CH_3I + Mo(CO)_3C_5H_5^- \rightarrow CH_3Mo(CO)_3C_5H_5 + I^-$$

The anion $Mo(CO)_3C_5H_5^-$ has been prepared by the reaction of the cyclopentadienyl anion with molybdenum hexacarbonyl[2,3] and by the reaction of dicyclopentadiene with molybdenum hexacarbonyl to form $[C_5H_5Mo(CO)_3]_2$, followed by reduction of the latter compound with sodium amalgam.[4] In view of the simplicity of the present method of preparing potassium cyclopentadienyl, the former method is preferable and is described below. The $Mo(CO)_3C_5H_5^-$ anion may be converted to the hydride $HMo(CO)_3C_5H_5$[2,3,5] or to any of a series of alkyl derivatives, $RMo(CO)_3C_5H_5$.[2] The preparation of the methyl compound is described here. Many other cyclopentadienylmolybdenum tricarbonyl derivatives are known; synthetic methods for some of these are discussed by Pruett.[6]

Procedure

A 300-ml. 3-necked flask, equipped with a magnetic stirring bar and a connection from one side neck to a source of nitrogen, is charged with 150 ml. of 1,2-dimethoxyethane and 50 g. of KOH powder. While slowly stirring the mixture, and while flushing the flask with a stream of nitrogen, 16.4 ml. (0.20 mole) of cyclopentadiene* is added. The other side neck and the main neck of the flask are loosely stoppered, and when it is judged that 99% of the air has been flushed from the flask, the flask is tightly stoppered. The stirring rate is then increased as much as possible without causing undue splashing.

After one hour, the stopper in the side neck is removed and replaced with a coarse-porosity filter tube leading to the side neck of another 300-ml. 3-necked flask. (See Figure 1.) The main neck of the receiver flask should be stoppered and the other side neck should be closed with a stopper having a stopcock permitting evacuation of the flask. The filtering apparatus is flushed with nitrogen, and the apparatus is slowly tipped so as to decant the solution through the filter into the receiver flask. Occasional application of a vacuum through this stopcock will hasten the filtration. When about 130 ml.

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* Cyclopentadiene is obtained by the thermal cracking of dicyclopentadiene. Dicyclopentadiene is slowly distilled through a short fractionating column, collecting only that which refluxes below 44°. (Cyclopentadiene boils at 42.5°, dicyclopentadiene at 170°.) This cyclopentadiene must be used within two or three hours, or stored at -78° until use, because slow dimerization occurs at room temperature.

of the solution has collected in the receiver flask, the first flask is righted and about 25 ml. of dry 1,2-dimethoxyethane is added to wash the remaining KOH. After collecting another 30 ml. of filtrate, the washing procedure is repeated. About 190 ml. of solution should be obtained.

In a fume hood, the main stopper of the flask containing the filtrate is removed, and, while flushing with nitrogen, 45 g. (0.17 mole) of molybdenum hexacarbonyl is added. (CAUTION: Molybdenum hexacarbonyl is somewhat volatile and extremely toxic.) The main neck of the flask is then fitted with a water-cooled reflux condenser. After flushing the condenser with nitrogen, the top of the condenser is connected to the source of nitrogen, and the side necks of the flask are stoppered. Using a heating mantle, the mixture is refluxed for at least 12 hr. Carbon monoxide is evolved during this time, and it will escape through the mercury bubbler.

The resulting solution of $KMo(CO)_3C_5H_5$ is cooled to room temperature, the reflux condenser is replaced with a dropping funnel containing 12.5 ml. (0.20 mole) of methyl iodide, and a magnetic stirring bar is placed in the flask. During a 5-minute period, the methyl iodide is added dropwise to the stirred solution. Stirring is continued for five hours. Two necks of the flask are then stoppered and the third is fitted with a stopcock leading to a large Dry Ice-cooled trap and a vacuum pump. While stirring, the solvent is removed <u>in vacuo</u> at room temperature. (About 3-4 hours are required.)

After complete removal of the solvent, the stopcock is closed and the flask is placed in a nitrogen-flushed dry bag. The flask is opened, and the solid contents are scraped out and transferred to a large vacuum sublimation apparatus. (If a sufficiently large sublimation apparatus is not available, the sublimation may be accomplished batchwise using a smaller apparatus.) Using circulated ice-water in the condenser of the sublimation apparatus, the $CH_3Mo(CO)_3C_5H_5$ is sublimed using a bath temperature of 80-90° and a pressure less than 0.1 mm. The vacuum is broken with nitrogen, inasmuch as the residue is usually pyrophoric. The residue is discarded in a place where it may safely burn. Yield: 35.5 g. (80%) of yellow $CH_3Mo(CO)_3C_5H_5$, melting at 121-124° (dec.).

Properties

In σ-Methyl-π-cyclopentadienylmolybdenum tricarbonyl, the methyl group is attached to the molybdenum by a metal-to-carbon σ bond, and the cyclopentadienyl group is attached by π-type bonding as in sandwich compounds. The material forms yellow crystals, m.p. 124° (dec.), that are soluble in organic solvents and slowly oxidized by air. Purification is readily effected by vacuum sublimation. The infrared and n.m.r. spectra have been described.[2]

B. BISCYCLOPENTADIENYLIRON (FERROCENE)

$$8KOH + 2C_5H_6 + FeCl_2 \cdot 4H_2O \rightarrow Fe(C_5H_5) + 2KCl + 6KOH \cdot H_2O$$

Of the wide variety of methods which have been used for the preparation of ferrocene,[7] one of the most straightforward is the reaction of an alkali metal cyclopentadienyl with iron(II) chloride.[8] The present procedure, although analogous in principle, is superior because of the simplified method of deprotonating cyclopentadiene and because ordinary hydrated iron(II) chloride may be used. The potassium hydroxide serves not only as a deprotonating agent, but also as a dehydrating agent.

Procedure

A 300-ml. 3-necked flask, equipped with a magnetic stirring bar and a connection from one side neck to a source of nitrogen, is charged with 120 ml. of 1,2-dimethoxyethane and 50 g. of KOH powder. While slowly stirring the mixture, and while flushing the flask with a stream of nitrogen, 11.0 ml. (0.134 mole) of cyclopentadiene is added. The other side neck is stoppered, and the main neck is fitted with a 100-ml. dropping funnel with its stopcock open. When it is judged that 99% of the air has been flushed from the flask, the stopcock is closed, and a solution of 13.0 g. (0.065 mole) of iron(II) chloride 4-hydrate* in 50 ml. of dimethyl sulfoxide†

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* The iron(II) chloride should be pulverized in a mortar and pestle in order to aid dissolution.

† Dimethyl sulfoxide should not be allowed to contact the skin because it is absorbed very rapidly.

is placed in the dropping funnel. The vent tube in the mercury bubbler is lifted above the mercury surface so that the pressure within the reaction vessel is atmospheric. The mixture is stirred vigorously. After about 10 minutes of vigorous stirring, dropwise addition of the iron(II) chloride solution is begun. The rate of addition is adjusted so that the entire solution is added in 45 minutes. At this point, the stopcock of the dropping funnel is closed, and the stirring is continued for another 30 minutes. Then the flow of nitrogen is stopped, and the mixture is added to a mixture of 180 ml. of 6 M HCl and approximately 200 g. of ice. Some of the resulting slurry may be used to wash the residual material out the flask. After stirring the slurry for about 15 minutes, the precipitate is collected on a coarse sintered glass funnel and washed with four 25-ml. portions of water.* The product is spread out on a large watch glass and allowed to air-dry overnight. Yield: 11.9 g. (98.4%) of ferrocene melting at 173-4°. Material prepared in this manner is quite satisfactory as an intermediate for subsequent syntheses. If an extremely pure product is desired, this material should be sublimed.

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* Sometimes the filtrate is deep blue because of formation of the ferricinium ion. If desired, the latter may be reduced to a relatively impure form of ferrocene by the addition of tin(II) chloride. However this recovery is seldom worthwhile, because the amount of ferricinium ion seldom accounts for more than 4% of the total yield of ferrocene.

Properties

Ferrocene forms orange crystals (m.p. 173-174°) which are soluble in most organic solvents but essentially insoluble in water. The compound readily sublimes at temperatures above 100°. The infrared spectrum has been recorded and interpreted.[9] The ultraviolet spectrum in ethanol or hexane shows maxima at 325 mμ (ϵ = 50) and 440 mμ (ϵ = 87), and rising short-wavelength absorption (ϵ = 5250 at 225 mμ).[10]

C. BISCYCLOPENTADIENYLNICKEL (NICKELOCENE)

$$10KOH + 2C_5H_6 + NiCl_2 \cdot 6H_2O \rightarrow Ni(C_5H_5)_2 + 2KCl + 8KOH \cdot H_2O$$

Most of the published methods for preparing nickelocene[11] are analogous to methods used for preparing ferrocene. The following procedure is analogous to the preceding ferrocene procedure, except that some extra precautions are necessary in order to avoid oxidation of the product.

Many derivatives of nickelocene can be prepared.[11] A particularly useful reaction is that between nickelocene and nickel tetracarbonyl, leading to $[C_5H_5NiCO]_2$ and $(C_5H_5)_3Ni_3(CO)_2$.[12]

Procedure

The procedure is identical to that described under the ferrocene procedure except for the following changes. Only 8.5 ml. (0.104 mole) of cyclopentadiene is used, and a solution of 11.9 g. (0.05 mole) of

nickel(II) chloride 6-hydrate in 65 ml. of dimethyl sulfoxide* is used instead of the iron(II) chloride solution. The 6 M HCl used in the precipitation step and the wash water are deaerated with a stream of nitrogen before use. The product is collected on a sintered glass funnel (under a stream of nitrogen), washed, and then dried overnight in a vacuum desiccator. Yield: 5.2 g. (55%) of nickelocene melting† at 173-4°.

Properties

Nickelocene forms dark green crystals (m.p. 173-174°) which are soluble in most organic solvents but essentially insoluble in water. The microcrystalline material formed in the above synthesis undergoes oxidation on standing in air and should be kept in an inert atmosphere. Purification can be effected by vacuum sublimation at 100°.

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* Dimethyl sulfoxide should not be allowed to contact the skin because it is absorbed very rapidly.

† The melting point should be determined using a sample under a nitrogen atmosphere in a sealed capillary.

D. METHYLPHOSPHINE

$$2KOH + PH_3 \rightarrow K^+ + PH_2^- + KOH \cdot H_2O$$

$$CH_3I + PH_2^- \rightarrow CH_3PH_2 + I^-$$

Both methylphosphine (this synthesis) and dimethylphosphine (the following synthesis) are considerably stronger Lewis bases than phosphine, and their reactions with various Lewis acids,[13] including boranes,[14,15] have been the subject of recent studies. Both methylphosphine and dimethylphosphine are readily oxidized by air and thus can serve as sources of methylphosphonous acid, $CH_3PHO(OH)$, and dimethylphosphonic acid, $(CH_3)_2PO(OH)$.[13]

A commonly used synthetic method for these substituted phosphines involves the deprotonation of phosphine[14,16] (or methylphosphine[14]) by a sodium-ammonia solution, followed by treatment with a methylhalide. More recently,[15] methylphosphine has been produced by the reduction of CH_3PCl_2 (unfortunately not a readily-available compound) by $LiAlH_4$. The present method is essentially the deprotonation-methylation procedure, but instead of sodium-ammonia solutions, relatively easily-handled KOH-dimethyl sulfoxide suspensions are used.

Procedure

CAUTION: Phosphine and methyl phosphine are toxic materials which must be handled with great care, using vacuum-line manipulation. Dimethyl sulfoxide should not be allowed to contact the skin because it is absorbed very rapidly.

A magnetic stirring bar, 30 g. of KOH powder, and 40 ml. of dimethyl sulfoxide are placed in a 200-ml. 3-necked round-bottomed flask with standard taper joints. One side neck is stoppered, the other is fitted with a small dropping funnel, and the main neck is fitted with an adapter connected to a 0-760 mm. manometer and a stopcock leading to a vacuum line. The joints are greased with Dow Corning silicone grease. The flask is thoroughly evacuated while stirring the mixture, and the stopcock is then closed. About 0.012 mole of pure phosphine[17] is transferred to a 300 ml. bulb connected to the vacuum line just beyond the stopcock, and the stopcock is opened so as to allow the phosphine to be absorbed by the stirred KOH suspension. The dimethyl sulfoxide becomes yellow because of the formation of the PH_2^- ion. When the manometer indicates that about 99% of the phosphine has been absorbed (after about 25 minutes) the system is again thoroughly evacuated. The stopcock is closed, a solution of 1.0 ml. (0.016 mole) of methyl iodide in 10 ml. of dimethyl sulfoxide is placed in the dropping funnel, and a trap between the stopcock and the vacuum pump is immersed in liquid nitrogen.

About 2 ml. of the methyl iodide solution is added to the stirred mixture, and, after about ten seconds, the stopcock is opened for a minute. This process is repeated until the dimethyl sulfoxide solution is colorless. The crude methyl phosphine which collects in the liquid nitrogen-cooled trap is then purified by fractional condensation in traps cooled to -112° (CS_2 slush), -130° (n-pentane slush), and -196°

(liquid nitrogen). The material which collects in the -112° and -196° traps is discarded. About 0.009 mole (75% yield) of purified methyl phosphine collects in the -130° trap.

Properties

Methylphosphine is an evil-smelling material which is probably very poisonous. The vapor pressure may be represented[16] by the equation $\log P_{mm} = 7.402 - 1158/T$, where T = °K. The extrapolated boiling point is -17.1°, and the vapor pressures at -78.5° (28 mm.), -63.5° (73 mm.) and -45.2° (210 mm.) may be used as criteria of purity. The infrared spectrum of the gas has been reported;[18] the appearance of a band at 1252 cm^{-1} indicates the presence of methyl iodide, and the appearance of a band at 1170 cm^{-1} indicates the presence of dimethyl ether.

The methylphosphine prepared by this procedure has a vapor pressure at -78.5° (dry ice slush) of 29 mm. The principal impurity is dimethyl ether, estimated by mass spectrometry and infrared spectrometry to amount to less than 1%.

E. DIMETHYLPHOSPHINE

$$2KOH + PH_3 \rightarrow K^+ + PH_2^- + KOH \cdot H_2O$$

$$CH_3I + PH_2^- \rightarrow CH_3PH_2 + I^-$$

$$2KOH + CH_3PH_2 \rightarrow K^+ + CH_3PH^- + KOH \cdot H_2O$$

$$CH_3I + CH_3PH^- \rightarrow (CH_3)_2PH + I^-$$

Procedure

CAUTION: Phosphine and the methylphosphines are toxic materials which must be handled with great care, using vacuum-line manipulation. Dimethyl sulfoxide should not be allowed to contact the skin because it is absorbed very rapidly.

The procedure is the same as that used for the preparation of methyl phosphine up to the point where the methyl iodide solution is added. A solution of 1.5 ml. (0.024 mmole) of methyl iodide in 10 ml. of dimethyl sulfoxide is placed in the dropping funnel, and the stopcock connecting the system to the vacuum line is closed. The methyl iodide solution is added, during a period less than one minute, until the solution is colorless. If, during the addition, the pressure in the flask exceeds 600 mm., the volume of the system should be increased by opening the stopcock to an evacuated volume of several hundred ml. so as to keep the pressure below 600 mm. However, the volume of the system should not be unduly expanded, or the deprotonation of the methyl phosphine will proceed too slowly. The slurry is vigorously stirred for an hour, during which time the pressure of methyl phosphine should markedly decrease. Then the remainder of the methyl iodide solution

is added (leaving a drop of solution to ensure that air does not enter the flask), and stirring is continued for another half hour. The volatile material is collected in a liquid nitrogen-cooled trap and is then fractionally condensed in traps cooled to -78° (dry ice slush), -112° (CS_2 slush) and -196° (liquid nitrogen). The material which collects in the -78° and -196° traps is discarded. The dimethylphosphine in the -112° trap usually contains an appreciable amount of methyl iodide as an impurity. However this impurity may be readily eliminated by simply allowing the mixture to stand in the liquid state at 0° for about one hour, during which time the methyl iodide is converted to the relatively non-volatile salt, $(CH_3)_3PHI$. About 0.0078 mole (65% yield) of purified dimethylphosphine remains.

Properties

Like methylphosphine, dimethylphosphine has a disgusting odor and is probably very poisonous. The vapor pressure may be represented[19] by the equation $\log P_{mm} = 7.539 - 1370/T$, where T = °K. The extrapolated boiling point is 21.1°, and the vapor pressure at 0° (338 mm.) may be used as a criterion of purity. Dimethylphosphine prepared by this procedure has a vapor pressure at 0° of 339 mm.

F. METHYLGERMANE

$$2KOH + GeH_4 \rightarrow K^+ + GeH_3^- + KOH \cdot H_2O$$

$$CH_3I + GeH_3^- \rightarrow CH_3GeH_3 + I^-$$

As in the case of alkylphosphines (see the preceding synthesis) alkylgermanes are generally prepared by either of two methods — a method based on the deprotonation and subsequent alkylation of germane,[20] and a method based on the reduction of germanium-halogen bonds with $LiAlH_4$ or hydroborates.[21,22] In view of the ease of preparation of germane[23] and the simple KOH deprotonation procedure, the deprotonation-alkylation method is believed to be superior and is described here for the synthesis of methylgermane. In this procedure, 1,2-dimethoxyethane is used as solvent, but, in analogous procedures, dimethylsulfoxide has been used in the preparation of dimethylgermane,[24] and liquid ammonia has been used in the preparation of 2-butylgermane and methylethylgermane.[25]

Procedure

Potassium hydroxide powder (2.8 g.) and 10 ml. of 1,2-dimethoxyethane are placed in a 50-ml. round-bottomed flask with a standard taper neck. The flask is fitted with an adapter having a stopcock for connecting to the vacuum line. With the flask in a -78° bath (dry ice slush), the mixture is degassed by pumping for about 5 minutes. Then the -78° bath is replaced with a -196° bath (liquid nitrogen), and the reactor is thoroughly evacuated. About 0.002 mole of pure germane is condensed into the reactor, and the stopcock is closed. The reactor is warmed in air to room temperature and is shaken for a half hour.

The shaking should be very vigorous in order to increase the surface area of the solution as much as possible. The reactor is then placed in a -196° bath and the very small amount of hydrogen gas (from the slow decomposition of potassium germyl) is pumped out. Approximately 0.003 mole of methyl iodide is condensed into the reactor. The reactor is allowed to warm up to room temperature in air, while shaking occasionally, until a white precipitate forms near room temperature. Then the reactor is immediately quenched in a -78° bath. If the reaction mixture is allowed to stand after formation of the precipitate, a secondary reaction of methyl iodide with potassium hydroxide to form dimethyl ether occurs. With the reactor in series with -78° and -196° traps, it is allowed to warm in air. Half or more of the monoglyme is allowed to distill into the -78° trap. The crude methylgermane which collects in the -196° trap is purified by fractional condensation in traps cooled to -130° (n-pentane slush), -160° (isopentane slush) and -196°. The material which collects in the -160° trap is pure methylgermane. A yield of about 0.0016 mole (80%) is obtained.

Properties

The vapor pressure of methylgermane may be represented[21] by the equation $\log P_{mm} = 3.9624 - 0.003034T + 1.75 \log T - 1080.3/T$, from which one calculates a boiling point of -34.1°. The vapor pressures at -83.9° (ethylacetate slush), -78.5° (dry ice slush), and -63.8° (chloroform slush) are 46.3 mm., 67.7 mm. and 169.4 mm., respectively. The infrared spectrum of the gas has been reported.[26]

The methylgermane prepared by this procedure has vapor pressures of 46 mm. at the ethyl acetate slush temperature and 168 mm. at the chloroform slush temperature.

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