be drawn from the application of Badger's rule,[12] which relates the force constant to the bond length for diatomic molecules. The bond length value of 1.67 Å. and the corresponding force constant of 7.2 × 10^5 dynes/cm. give a value for Badger's constant for the vanadium–oxygen pair, which, taken with a bond length of 2.4 Å., yields a force constant of approximately 0.7 × 10^5 dynes/cm. This is reasonably close to the value of approximately 0.6 × 10^5 dynes/cm. which emerges from a diatomic molecule calculation using the 280 cm.$^{-1}$ value. The remaining observation, the solvent sensitivity, is adequately accounted for by the mass change in the ion.

These vibrational data do not, of course, determine the number of water molecules in the ion but they do prove that the water is closely bound.

It should be noted here that vibrational spectra are not very sensitive to weak ion–ion association. Thus, for example, the vibrational spectra[13] of aqueous solutions of a series of sulfates which are known from conductivity measurements to be associated to widely differing degrees[14] are indistinguishable. It is then quite likely that the chloride and the solvated vanadyl ion may be loosely associated in vanadyl chloride solutions.

The spectra of vanadyl fluoride solutions are very

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(13) J. C. Evans, unpublished data.
(14) C. W. Davies, in "The Structure of Electrolytic Solutions," edited by W. J. Hamer, J. Wiley and Sons, Inc., New York, N. Y., 1959, Chapter 3.

similar to those of the chloride. The higher frequency band is, however, broader in the fluoride and is shifted to lower wave number. This is indicative of considerably stronger ion–ion interaction between the vanadyl and the fluoride ions than is the case for the chloride ion.[9]

The infrared and Raman spectra of vanadyl perchlorate solutions are the same as the superposition of the spectra of the perchlorate ion and the solvated vanadyl ion; see Fig. 2 and Table III. Little or no ion–ion interaction is indicated.

Vanadyl sulfate solution spectra, however, show definite signs of complex formation between the sulfate and vanadyl ions. The spectra are concentration dependent with the more dilute solutions yielding spectra which indicate the dissociation of the complex to solvated vanadyl and sulfate ions; see Fig. 3. The structure of the complex cannot be determined unequivocally on the evidence available but the observations are in accord with the presumption that the sulfate ion displaces one of the water molecules from the vanadyl ion. Those bands indicated by arrows in Fig. 3 may be assigned to the sulfate ion bound in the complex and are reminiscent of the spectra of the HSO_4^- ion in aqueous solution, suggesting that the sulfate ion is bound at one point only. In solid $VOSO_4 \cdot 5H_2O$ this is the case.[11]

Monogermanes—Their Synthesis and Properties

BY JAMES E. GRIFFITHS

Germane and the methylgermanes CH_3GeH_3, CD_3GeH_3, $(CH_3)_2GeH_2$, $(CD_3)_2GeH_2$, and $(CH_3)_3GeH$ were conveniently prepared by the addition of an aqueous solution of sodium hydroborate to acidic solutions of GeO_2, CH_3GeBr_3, CD_3GeBr_3, $(CH_3)_2GeBr_2$, $(CD_3)_2GeBr_2$, and $(CH_3)_3GeBr$, respectively. At reaction temperatures of 30–55°, yields of 94–100% were obtained for the alkylgermanes and no side reactions were noticed. Physical properties of the CH_3 derivatives are reported. The yield of germane was virtually quantitative and temperature-independent in the 0–80° range.

Germane had been difficult to prepare until the reduction of GeO_2 with hydroborate was reported to give germane in 75% yield.[1] Other studies[2-4] under a variety of conditions failed to improve the yield and these failures were interpreted in terms of several effects. For example, a negative temperature coefficient of yield was attributed to nascent hydrogen reduction of Ge(IV) to the metal arising from the increas-

ing [H] concentration with increasing temperature. Since yields of over 90% were obtained recently at 35°, doubt was cast upon this speculation.[5]

A good method for the preparation of substituted germanes of the type R_nGeH_{4-n} ($n = 1$-3 and R = alkyl) seemed to be lacking,[6] although several methods appeared adequate.[7,8] These, however, required the use

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(2) E. D. Macklen, J. Chem. Soc., 1989 (1959).
(3) W. L. Jolly, J. Am. Chem. Soc., 83, 335 (1961).
(4) J. E. Drake, "The Preparation of Some Germanium Hydrides," Report UCRL 9709 from the Lawrence Radiation Laboratory, University of California, Berkeley, Calif., Contract No. W-7405-eng-48, U. S. Atomic Energy Commission.

(5) T. N. Srivastava, J. E. Griffiths, and M. Onyszchuk, Can. J. Chem., 40, 739 (1962).
(6) F. Rijkens, "Organogermanium Compounds, A Survey of the Literature from Jan., 1950 to July, 1960," Institute for Organic Chemistry T.N.O., Utrecht, Holland.
(7) J. Satgé, R. Mathis-Noel, and N. Lesbre, Compt. rend., 249, 131 (1959).
(8) H. H. Anderson, J. Am. Chem. Soc., 82, 3016 (1960).

of non-aqueous solvents or highly flammable metal hydrides or both and are not particularly promising for the preparation of germane itself. It seemed desirable, therefore, to extend the method used for the synthesis of germane by hydroborate to the preparation of the methyl-substituted germanes. Since these compounds represent prototypes of the entire class of alkyl-substituted germanes, the chemistry of which is not well understood at this time, their physical properties and their chemistry are of considerable importance. Furthermore, these compounds are of interest for spectroscopic studies. Accordingly, this paper is concerned with the synthesis and physical properties of methyl-, dimethyl-, and trimethylgermanes, and with a brief study of the factors affecting the yield of germane.

Experimental

The methylbromogermanes CH_3GeBr_3, CD_3GeBr_3, $(CH_3)_2$-$GeBr_2$, and $(CD_3)_2GeBr_2$ were prepared by passing methyl bromide (or CD_3Br) over a heated Cu–Ge alloy[9] and purified using a preparative scale gas chromatograph.[10] Trimethylbromogermane (95% purity) was obtained from the Chemicals Procurement Laboratories, College Point, N. Y. Bromine was removed by shaking with mercury before the sample was purified chromatographically. Sodium hydroborate (Metal Hydrides, Inc.) and GeO_2 (Eagle-Pitcher Co.) were used without further purification.

Synthesis.—The experimental procedure was similar in the preparation of all of the compounds and details are presented only for dimethylgermane. Results are listed in Table I.

TABLE I
SYNTHESIS OF ALKYLGERMANES

$(CX_3)_nGeBr_{4-n}$			$(CX_3)_nGeH_{4-n}$	Yield,	Reaction temp.,
n	X	mmoles	mmoles	%	°C.
1	H	3.22	3.21	99.7	35–45
2	H	5.75	5.38	93.7	35–50
3	H	2.38	2.26	95.3	35–40
1	D	1.99	1.89	95.6	35–50
2	D	5.73	5.70	99.4	30–55

Dimethylgermane.—A 5.75-mmole sample of $(CH_3)_2GeBr_2$ was stirred magnetically in a 500-ml. three-necked flask with 70 ml. of 1 M hydrobromic acid. The flask was fitted with a thermometer which reached into the solution, a dropping funnel, and a reflux condenser. The condenser had a cold finger maintained at $-78°$ and led to a series of *five* U-traps cooled with liquid nitrogen and then to a glass vacuum system. A solution of 5 g. of $NaBH_4$ in 100 ml. of water was added slowly to the stirred solution during 1 hr. and the effluent gases were collected in the cold U-traps. A pressure of about 400 mm. was maintained during the addition, after which it was reduced to 10 mm. to ensure recovery of the hydride.

The crude product from the liquid nitrogen cooled traps was allowed to pass through a series of traps maintained at -95, -150, and $-196°$. A small amount of HBr (0.283 mmole; v.p. at $-126.3°$ 5.7 mm., lit.[11] 5.7 mm.) was trapped at $-196°$ and any water which was carried past the $-78°$ condenser was stopped at $-96°$. Dimethylgermane (5.83 mmoles, mol. wt. 104.8 ± 0.3, calcd., 104.6; yield, 93.7%) was recovered from the trap cooled to $-150°$.

TABLE II

t, °C.	p (obsd.)	p (calcd.)	t, °C.	p (obsd.)	p (calcd.)
Equilibrium Vapor Pressures of CH_3GeH_3					
($\log p$ (mm.) = $3.9624 - 0.003034T + 1.75 \log T - 1080.3/T$)					
−118.9	2.06	2.09	−78.5	67.7	67.4
−111.8	4.25	4.40	−63.8	169.4	169.4
−95.0	19.55	19.83	−53.2	303.5	304.1
−83.9	46.3	46.3	−45.6	446.7	446.5
Equilibrium Vapor Pressures of $(CH_3)_2GeH_2$					
($\log p$ (mm.) = $5.4643 - 0.005872T + 1.75 \log T - 1445.2/T$)					
−95.0	1.73	1.76	−31.0	176.3	176.5
−84.0	4.90	4.99	−23.3	256.4	256.5
−63.8	24.70	24.75	−16.0	356.5	356.7
−45.5	80.6	80.3	−15.4	366.2	366.1
−35.9	137.0	137.0	−15.0	372.7	372.5
Equilibrium Vapor Pressures of $(CH_3)_3GeH$					
($\log p$ (mm.) = $5.4904 - 0.005544T + 1.75 \log T - 1594.4/T$)					
−78.5	1.79	1.76	−35.9	43.3	43.3
−73.1	2.92	2.88	−31.0	57.8	57.7
−70.0	3.75	3.76	−23.3	88.1	88.3
−63.8	6.28	6.27	−9.7	174.3	174.4
−58.9	9.10	9.18	0.0	269.7	269.8
−45.3	24.0	24.0	10.4	414.0	414.0

Product Purity.—For the presentation of physical constants a quantitative estimate of any impurities is essential. The existing data on the boiling point of methylgermane amply demonstrate the effect of impurities ($-22.2°$,[12] $-23.0°$,[13] $-23.5°$,[14] $-34.1°$ (this work), and $-35.1°$ [15]). Gas samples (0.1–0.2 cc.) were examined using a Barber-Coleman gas chromatograph with an argon ionization detector and a diethylhexyl sebacate on firebrick column. Operating at column and detector temperatures of 75 and 100°, respectively, methyl-, dimethyl-, and trimethylgermanes were eluted at 2.8 (34), 6.6 (24), and 8.9 (24) min., respectively. Argon carrier gas flow rates are given in parentheses. Although no impurity could be detected in trimethylgermane, methylgermane contained 0.1% dimethylgermane and the dimethylgermane contained 0.006% of the monomethyl derivative. Other impurities were below our level of detection ($<$ 0.001%).

Physical Properties.—Molecular weights were determined directly by weighing an accurately known volume of gas. Vapor pressures were measured in a tensimeter using a cathetometer capable of 0.05 mm. reproducibility at $p > 25$ mm. and 0.02 mm. at $p < 25$ mm. The mercury minisci in wide-bore arms of the tensimeter were illuminated with plane polarized light. Melting points were obtained using the Stock plunger technique and temperatures were measured with appropriate vapor pressure thermometers,[16] calibrated mercury thermometers, or a calibrated copper–constantan thermocouple and potentiometer. Results are listed in Table II.

Vapor pressure data are expressed by the standard Nernst equation of the form

$$\log p \text{ (mm.)} = A - BT + 1.75 \log T - C/T$$

rather than by the Clausius–Clapeyron or Antoine equations, which in many cases are inadequate. The constants given in the equations for the various germanes were determined by a least squares machine computation (IBM 7090) procedure involving two main operations.[17] Equilibrium vapor pressure data are given in Table II, from which the respective boiling points, heats of vaporization, and Trouton constants were calculated to be: methylgermane, $-34.1°$, 4981 cal. mole^{-1}, and 20.8 cal.

(9) E. G. Rochow, *J. Am. Chem. Soc.*, **69**, 1729 (1947).

(10) Beckman Megachrom gas chromatograph. The instrument was equipped with columns containing either Apiezon J grease on firebrick or Dow-Corning high vacuum silicone grease on Chromosorb-W. Operating at 180°, the bromides were easily separated from each other in at least 99.95% purity.

(11) D. R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).

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deg.$^{-1}$ mole^{-1}; dimethylgermane, 3.0°, 5525 cal. mole^{-1}, and 20.0 cal. deg.$^{-1}$ mole^{-1}; trimethylgermane, 27.0°, 6097 cal. mole^{-1}, and 20.3 cal. deg.$^{-1}$ mole^{-1}. The melting points of methyl-, dimethyl-, and trimethylgermane were -154.5 ± 0.2, -144.3 ± 0.2, and $-123.1 \pm 0.2°$, respectively. Observed molecular weights were: CH_3GeH_3, 90.7, calcd. 90.6; $(CH_3)_2$-GeH_2, 104.8, calcd. 104.6; $(CH_3)_3GeH$, 118.6, calcd. 118.6; CD_3GeH_3, 93.6, calcd. 93.6; $(CD_3)_2GeH_2$, 110.6, calcd. 110.6.

Germane.—Several experiments were conducted using the previously described procedure. Excess hydroborate solutions were added slowly to 20-ml. aliquots of GeO_2 (1.171 mmoles) dissolved in 1 M HBr and the product gas in the stream of evolved hydrogen was collected in *five* traps cooled to $-196°$. Pure germane was recovered in 96.0, 96.8, 96.2, 100.6, and 98.2% yields when the reaction temperatures were 0, 20, 40, 60, and 80°, respectively. Digermane was a minor product ($\leq 1\%$) at $t \leq 40°$. Experiments conducted at 40° using GeO_2 (1.245 mmoles) in 1 N HCl with *one*,[2] *two*,[1,3,4] and *five* traps at $-196°$ in the effluent gas stream gave yields of 56.4, 78.5, and 97.6%, respectively.

Discussion

The experimental results show that the reduction of an aqueous acid solution of a Ge(IV) compound with sodium hydroborate is the most efficient and general method of preparing monogermanium hydrides presently available. Germane and its alkyl derivatives $(CH_3)_nGeH_{4-n}$ ($n = 1$–3) were prepared in virtually quantitative yield and it is expected that the reaction could be further extended to include aryl and cyclo-alkyl derivatives. Furthermore, contrary to previous reports,[2] the yield of germane is temperature-independent in the range 0–80°, and earlier problems with yields appear to have arisen from the use of inefficient product collection techniques. This was demonstrated further by a parallel investigation[18] in which yields of 90 and only 70% were obtained in the preparation of trialkyl- and dialkylgermanes, respectively, using the hydroborate method.

A considerable body of evidence has now been collected[1-4,17] which suggests that an important species in the reaction may be represented by $\equiv GeBH_4$. Subsequent steps in the mechanism, however, are not known with certainty and, therefore, a definitive kinetic study of the process would be desirable.

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Phosphorus Nitrogen Chemistry. VI. Preparation and Properties of Thiophosphorus Tri-N-methylimide, $P_4S_4N_6(CH_3)_6$[1,2]

BY ROBERT R. HOLMES[3] AND JAMES A. FORSTNER

Thiophosphorus tri-N-methylimide, $P_4S_4N_6(CH_3)_6$, was prepared in high yield by the reaction of elemental sulfur and solid $P_4N_6(CH_3)_6$ at room temperature. Physical properties support a structure analogous to the cage structure for $P_4O_6S_4$. Additional properties of the related compounds, $P_4N_6(CH_3)_6$ and $As_4N_6(CH_3)_6$, are reported. Comparison of proton n.m.r. spectra and mass spectral cracking patterns substantiates a common structural basis for these molecules.

The properties of phosphorus tri-N-methylimide, $P_4N_6(CH_3)_6$, recently reported,[4,5] suggested a cage structure similar to the structure observed for phosphorus trioxide, P_4O_6. In later work[1] reaction of P_4N_6-$(CH_3)_6$ with oxygen led to an apparent polymeric material having the empirical composition $P_2O_2N_3(CH_3)_3$. One might anticipate the formation of a molecular derivative as well. The latter expectation was realized on studying the properties of thiophosphorus tri-N-methylimide, $P_4S_4N_6(CH_3)_6$, the subject of the present paper.

Experimental and Results

Apparatus.—The apparatus used for making physical measurements is the same as that reported previously.[1] Proton n.m.r. measurements were made at 60 Mc. at room temperature. For the most part vacuum line procedures were used in conducting the various reactions.

Materials.—Phosphorus tri-N-methylimide was prepared and purified according to our previous method.[5] Sulfur (Baker and Adamson, flowers) and arsenic trichloride (Baker and Adamson, reagent) were used directly. Tank hydrogen chloride (Matheson) was fractionated in the vacuum line. The vapor pressure at $-111.7°$ was 125 mm. Tank methylamine (Matheson, anhydrous) was dried with barium oxide before use. Benzene (Fisher certified reagent, anhydrous) was dried over calcium hydride. Petroleum ether (Hommel Company, 30–60°) was distilled and dried over sodium ribbon. Toluene (Hommel Company, C.P.) was distilled (b.p. 107.5–107.8° at 748 mm.) and dried over calcium hydride. Other solvents were dried with an appropriate agent and used directly.

Preparation of Thiophosphorus Tri-N-methylimide.—Freshly sublimed phosphorus tri-N-methylimide, $P_4N_6(CH_3)_6$, was pressed into pellets in a 6-mm. glass tube using a concentric glass rod. The operation was performed in a nitrogen-filled drybox. After the pellets had been placed in a weighing bottle and the total weight determined, the pellets were dropped into a reaction ampoule which consisted of a tube 25 mm. in diameter and 50 mm. in length connected to an 8 mm. tube ending in a male 12/30 ground-glass joint. The bottle was reweighed. A known amount of sulfur then was introduced in a similar fashion. One

(1) Previous paper in the series: R. R. Holmes and J. A. Forstner *Inorg. Chem.*, **1**, 89 (1962).

(2) Presented in part before the Inorganic Division at the 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962. This paper represents part of the work submitted by James A. Forstner in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology.

(3) Bell Telephone Laboratories, Inc., Murray Hill, N. J.

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