

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA]

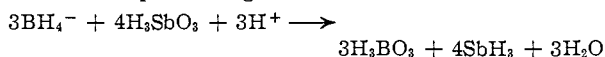
The Preparation of the Volatile Hydrides of Groups IV-A and V-A by Means of Aqueous Hydroborate

BY WILLAM L. JOLLY

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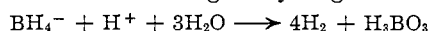
By the dropwise addition of an alkaline solution of hydroborate and either arsenite, antimonite, germanate or stannite to aqueous acid, good yields of either arsine, stibine, germane or stannane, respectively, were obtained. Small amounts of diarsine, digermane and the heretofore unknown distannane formed with the arsine, germane and stannane, respectively. No silane was obtained by a similar procedure using a solution of sodium silicate, and only traces of phosphine were obtained by similar procedures involving phosphite and hypophosphite. Distannane readily decomposes into the elements at room temperature. The infrared absorption spectrum of solid distannane was determined and a partial frequency assignment was made.

The convenience of working with only aqueous solutions stimulated our exploitation of the aqueous hydroborate method for the preparation of volatile hydrides. In general, our aim was to increase as far as possible the yields with respect to the hydroborate consumed. We have assumed that all four hydrogens of the hydroborate ion are potentially available for hydride formation. Thus, for the stibine-producing reaction, we write



Experimental Results

Stibine.—In a recent study of the preparation of stibine by the dropwise addition of a hydroborate solution to an acidic solution of antimony (III), yields of about 25% (based on the hydroborate consumed) were obtained.¹ In these experiments, it was impossible to reduce the ratio of $\text{H}^+/\text{Sb(III)}$ much below 0.5 without causing basic antimony salts to precipitate. Therefore an appreciable amount of hydroborate was wasted in the reaction with H^+ to give hydrogen

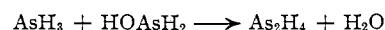


Since antimonite is completely unreactive with hydroborate in alkaline solutions, it was considered of interest to study the process wherein a concentrated solution of both antimonite and hydroborate is added dropwise to aqueous acid. It was expected that the precipitation of insoluble antimony salts would be slower than the stibine-producing reaction. Since the latter reaction could then take place in a zone where the H^+ concentration was very low and where the Sb(III) concentration was very high, it was hoped that an improvement in the yield of stibine (based on hydroborate) would be achieved. Indeed the yield was improved by a factor of two; stibine was prepared in 51% yield by this procedure.²

Arsine and Diarsine.—By using arsenite in a procedure similar to that used with antimonite, a 60% yield of arsine was obtained.³ It was found that the concentration of the acid had practically no effect on the yield of arsine. This is what one might expect if the reaction were occurring in a zone between the bulk of the entering drop and the bulk of the acid solution, where the acid con-

centration was very low. The concentration of acid in this zone would be essentially independent of the concentration of acid in the bulk of the solution. It was also demonstrated that the yield of arsine increased as the concentration of arsenite increased. This is the result which one would expect from a simple consideration of the competition between H^+ ions and arsenite ions for hydroborate ions.

It was observed that, at high concentrations of arsenite, relatively large amounts of diarsine (As_2H_4) were formed. This result might be explained by assuming that, at high concentrations of As(III) , the steady-state concentration of partially reduced species such as HOAsH_2 would be high. Under these conditions reactions of the type



would be favored. No special attempt was made to isolate the diarsine which formed with the arsine; it was identified only by its solid decomposition product, As_2H_3 .³

Germane and Digermane.—Piper and Wilson⁴ and Macklen⁵ prepared germane by the dropwise addition of aqueous hydroborate to acid solutions of germanium(IV). We wished to see whether better yields could be obtained by adding a solution of hydroborate and germanate to acid, and we wished to investigate the effect of changing the ratio of hydroborate to germanate on the relative amounts of germane and digermane. Since germanium is much more expensive than hydroborate, we were concerned with the yield of germane with respect to germanate, rather than with respect to hydroborate. Our results are presented with those of the previous investigators in Table I. (We have chosen the best aqueous solution data of Macklen.) It will be noted that, in each investigation, the best yield of germane (based on Ge(IV)) was around 70%. The fact that Macklen required much less hydroborate to achieve this yield than did Piper and Wilson may be explainable by the fact that the former investigator employed a much higher Ge(IV) concentration in the reaction flask than did the latter investigators. There is little to choose between our method and that of Macklen, either from a consideration of the percentage conversion of germanium to germane or from a consideration of the amount of hydroborate consumed.

(1) L. Berka, T. Briggs, M. Millard and W. Jolly, *J. Inorg. & Nuclear Chem.*, **14**, 190 (1960).

(2) The experimental procedures which were found best for the preparation of stibine and arsine are described in S. R. Gunn, W. L. Jolly and L. G. Green, *J. Phys. Chem.*, **64**, 1334 (1960).

(3) R. Nast, *Chem. Ber.*, **81**, 271 (1948).

(4) T. S. Piper and M. K. Wilson, *J. Inorg. & Nuclear Chem.*, **4**, 22 (1957).

(5) E. D. Macklen, *J. Chem. Soc.*, 1989 (1959).

TABLE I
 GERMANE SYNTHESSES

Investig.	Conc. Ge(IV) (mole/l.)	Mole ratio BH ₄ ⁻ / Ge(IV)	% Con- version Ge(IV) to GeH ₄	Mole ratio GeH ₄ / Ge ₂ H ₆
Piper and Wilson ⁴	0.019	18.5	42	...
	.019	37.0	67	...
	.019	55.5	73	167
Macklen ⁵	ca. .05	1.53	17	...
	ca. .05	3.06	39	...
	ca. .05	4.95	65	...
This work	1.14	0.65	27	11.2
	0.76	0.97	31	...
	0.38	5.82	68	38

Unfortunately, Macklen did not determine his yields of digermene, and so no comparison is possible here. Our results indicate, as one might expect, that a higher proportion of digermene is formed when the concentration of Ge(IV) is higher.

The data in the bottom row of Table I were collected by the following experimental procedure. A solution of 20 ml. of concentrated sulfuric acid in 100 ml. of water was placed in a 300-ml. three-neck round-bottom flask equipped with a magnetic stirrer, a nitrogen inlet tube (dipping beneath the solution), a dropping funnel and an outlet tube. The outlet tube led to two efficient liquid nitrogen traps followed by a stopcock leading to the vacuum pump. The flask was immersed in an ice-bath. Two g. of 85% potassium hydroxide, 1.0 g. of germanium(IV) oxide and 3.0 g. of potassium hydroborate were dissolved, in that order, in 25 ml. of water. This solution was added from the dropping funnel, over a period of 20 minutes, to the sulfuric acid solution. During the run, nitrogen was continuously bubbled through the sulfuric acid solution and the pressure was maintained at approximately 100 mm. by adjustment of the stopcock leading to the vacuum pump. A brown, germanium-containing precipitate formed in the flask.

The crude product which collected in the liquid nitrogen traps was distilled *in vacuo* through a -63.5° trap (to collect water and trigermene) and a -112° trap (to collect digermene). Germene and carbon dioxide collected in a final liquid nitrogen trap. Only a very small amount of trigermene was collected, and this was discarded. The digermene (0.17 mmole) was identified by its infrared spectrum⁶ and its vapor pressure of 6 mm. at -63.5° (lit.,⁷ 8 mm.). The germane (6.53 mmoles) was separated from carbon dioxide by passage through Ascarite followed by a -112° trap. Its vapor pressure at the melting point of carbon disulfide was 181 mm. (lit.,⁸ 182 mm.).

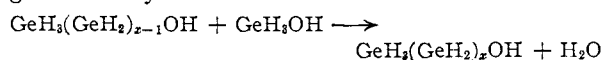
It is significant that, in our runs with BH₄⁻/Ge(IV) ratios of 0.65 and 0.97, an enormous amount of brown foam formed in the reaction vessel. The addition of silicone anti-foam agents to the reaction flask did not help. It was therefore necessary to interpose a Kjeldahl-type foam trap between the flask outlet and the liquid nitrogen traps.

(6) D. A. Dows and R. M. Hexter, *J. Chem. Phys.*, **24**, 1029 (1956).

(7) K. K. Kelley, U. S. Bureau of Mines Bulletin 383.

(8) A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach and H. I. Schlesinger, *THIS JOURNAL*, **69**, 2692 (1947).

We suspect that the foam was caused by soap-like molecules of the type GeH₃(GeH₂)_xOH, which formed when there was insufficient reducing agent present to form germane. Such species may be generated by reactions such as



No foaming occurred when the BH₄⁻/Ge(IV) ratio was 5.82.

Stannane and Distannane.—Schaeffer and Emilius⁹ studied the formation of stannane by the dropwise addition of aqueous hydroborate to acid solutions of tin(II). Their highest yield of stannane (based on the hydroborate consumed) was 1.3%. By adding a solution of hydroborate and stannite to acid, we have only been able to increase this yield to 1.9%. However, we have been able to isolate distannane from the volatile reaction products in an amount equal to about 5 mole % of the stannane formed.

The stannanes were prepared with the same apparatus and general procedure as used for the germane preparations. The procedural details for one of the more successful runs follow. The reaction flask was charged with 150 ml. of 6 M HCl. The solution which was added from the dropping funnel was prepared immediately before use as follows. An ice-cold solution of 36 g. of 85% potassium hydroxide in 60 ml. of water was added, with stirring, to an ice-cold solution of 15 g. of tin(II) chloride 2-hydrate in 60 ml. of water. Potassium hydroborate (1.5 g.) was dissolved in this solution. During the reaction, a brown precipitate (which soon turned grey-black) formed in the flask. The volatile material which collected in the liquid nitrogen traps was distilled *in vacuo* through a -63.5° trap (to collect water) and a -112° trap (to collect 0.02 mmole of distannane). Stannane (0.70 mmole), carbon dioxide and perhaps some hydrogen chloride collected in a final liquid nitrogen trap.

Whenever a trap containing distannane was allowed to warm up to room temperature, the distannane completely decomposed to the elements, forming a mirror on the inner walls of the trap. However, distannane could be readily distilled from a trap without decomposition when the distillation was carried out at very low pressures and when the trap was allowed to warm up very slowly. In two separate experiments, samples of distannane were allowed to decompose, and the hydrogen and tin formed were measured (by P, V, T measurements and by weighing, respectively). The observed atom ratios of H to Sn were 3.01 and 3.09, as compared with the theoretical value 3.00 for distannane.

A sample of distannane was allowed to distil at low pressure onto a NaCl plate cooled to approximately -180° in a special infrared absorption cell.¹⁰ The spectrum of the frozen sample was measured with a Perkin-Elmer Model 21 Spectrophotometer in the frequency range 600-4000 cm.⁻¹. Absorption peaks were observed at these frequen-

(9) G. W. Schaeffer and M. Emilius, *ibid.*, **76**, 1203 (1954).

(10) Special thanks are due Prof. G. C. Pimentel for the use of this cell.

cies (in cm.^{-1}): 690(s), 880(w), 1040(w), 1840(vs), 2010(w), 2220(w), 2280(vw), 2420(vw), 3620(m). It is believed that the 690 cm.^{-1} and 880 cm.^{-1} peaks correspond to ν_6 and ν_8 , respectively, since the corresponding peaks for digermane⁶ and disilane¹¹ are of similar intensity and frequency. It is believed that the very strong peak at 1840 cm.^{-1} is an unresolved pair of peaks corresponding to ν_5 and ν_7 . The corresponding close pairs of peaks for digermane and disilane are of similar intensity and frequency. The 3620 cm.^{-1} peak probably corresponds to the combination $\nu_1 + \nu_5$. It is perplexing that we found no peak corresponding to $\nu_8 + \nu_{11}$, which should occur around 1600 cm.^{-1} .

No attempt was made to separate the stannane from the carbon dioxide and any hydrogen chloride which might have been present. However, each sample of stannane was decomposed by flaming its glass container; the evolved hydrogen was pumped off and measured, and the change in volume of the condensable gases was noted. The data from a typical experiment indicate that one volume of stannane gave 2.15 volumes of hydrogen, as opposed to the theoretical value of 2.00 volumes of hydrogen. The evolved hydrogen was taken as a measure of the stannane.

Unsuccessful Experiments.—We found no bismuth compounds soluble in alkaline solution, so we were unable to use our method for the preparation of bismuthine. When a solution of hydroborate and plumbite was added to acid, we were unable to detect any trace of plumbane. Similarly, when a solution of hydroborate and silicate (water glass) was added to acid, no trace of silane was detected. Only very small amounts of phosphine were obtained from the addition of solutions of hydroborate and either hypophosphite or phosphite to acid.¹²

(11) G. W. Bethke and M. K. Wilson, *J. Chem. Phys.*, **26**, 1107 (1957).

Discussion

It is particularly interesting that neither the silicate, the hypophosphite, nor the phosphite ion is appreciably reduced by hydroborate. It seems likely that, in each of these species, the central atom is too well protected by its four surrounding atoms to permit approach of a hydride ion. If germanium(IV), tin(II), arsenic(III) and antimony(III) have coordination numbers of four (as do Si(IV), P(I) and P(III)), then the greater size of the central atoms in these cases would explain their greater accessibility to hydride ions. Recent work has shown that sulfite (or sulfurous acid) is readily reduced to hydrogen sulfide by hydroborate.¹³ Here the sulfur atom has a coordination number of only three and is accessible to hydride ions. The sulfate ion, with four coordinated oxygen atoms, is inert to hydroborate. The nitrous acid molecule, with only two oxygen atoms, is readily reduced to ammonium ion by aqueous hydroborate.¹⁴ However, the three oxygen atoms of the nitrate ion are apparently enough to protect the nitrogen atom from attack by hydroborate, inasmuch as nitrate is inert to hydroborate in acid solution.¹⁴

The inability to detect any plumbane in the reduction of lead(II) by hydroborate may be explained by the extreme instability of plumbane. Since lead metal formed in the reaction flask, it is apparent that reduction took place; but any plumbane which may have formed underwent immediate decomposition to the elements.

Acknowledgments.—It is a pleasure to acknowledge helpful discussions with Professors R. E. Connick, R. E. Powell and G. C. Pimentel. This work was supported in part by the Atomic Energy Commission.

(12) Unpublished observations of J. D. Macomber, 1959.

(13) Unpublished observations of Floris Y. Tsang, 1959.

(14) M. E. Kramer, Ph.D. Thesis, Saint Louis University, 1954.

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The Formation of Bitropyl in the Radiolysis of Carbon-14 Labeled Cycloheptatriene¹

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The irradiation of carbon-14 labeled cycloheptatriene in a nuclear reactor or in a beam of 1.95 Mev. electrons from a Van de Graaff generator leads to the formation of labeled bitropyl among other products. Ozonization of bitropyl leads to dicyclopropyltetracarboxylic acid. Permanganate oxidation of bitropyl leads to benzoic acid. The extent of labeling in these degradation products suggests a symmetrical intermediate as a precursor of the dimer.

Introduction

Radicals, ions and molecule ions have been suggested as precursors for the numerous products one obtains on radiolysis of organic compounds.³ The primary processes occurring in radiation chem-

istry are usually not product determining. The many secondary reactions which can occur as a result of the primary processes bear a formal analogy to carbanion, carbonium ion and radical reactions.⁴

One of the commonly observed products in radiation chemistry is a dimer containing two hydrogens less than the starting material. Bicyclohexyl from cyclohexane⁵ and biphenyl from ben-

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) Research associate BNL 1958-1960; present address: Hahn-Meitner Institut für Kernforschung, Berlin, Germany, Dept. of Radiation Chemistry.

(3) Cf. A. Charlesby and A. J. Swallow, *Ann. Rev. Phys. Chem.*, **10**, 89 (1959).

(4) Cf. A. Henglein, *Ang. Chem.*, **71**, 15 (1959).

(5) H. A. Dewhurst, *J. Phys. Chem.*, **63**, 813 (1959).