ml. of 3%) in methanol (25 ml.) was then added and the mixture boiled for a few minutes. The dark red-brown solution was diluted with water until it became cloudy and allowed to cool when it was filtered free of a slight precipitate. The complex iodide was then precipitated by the addition of sodium iodide, collected and recrystallized from methanol with the help of ether. It came out in black nodular prisms, m.p. 239°, very sparingly soluble in water to a red-brown solution.

Anal. Calcd. for $[Co(C_{28}H_{22}N_2O_2S_2)]I$: Co, 50.3; H, 3.3; N, 4.2; Co, 8.8; I, 19.0. Found: C, 50.3; H, 3.4; N, 4.3; Co, 8.9; I, 19.1.

All attempts to resolve this salt proved abortive.

1-Phthalimido-6-(*o*-nitrophenyl)-3,6-dithiahexane.—Hot solutions of *o*-nitrothiophenol (11.6 g.) in absolute ethanol (125 ml.) and of 1-phthalimido-5-bromo-3-thiapentane (23.6 g.) in absolute ethanol (90 ml.) were added successively to a cooled solution of sodium ethoxide (from sodium (1.73 g.) and absolute ethanol (35 ml.)) and the mixture then refluxed for 3 hours. Most of the alcohol was then distilled off, water added and the washed solid product collected and recrystallized from acetone. It formed yellow needles, m.p. 122°, yield 82%.

Anal. Calcd. for $C_{18}H_{16}N_2O_4S_2$: C, 55.7; H, 4.2; N, 7.2. Found: C, 55.4; H, 4.3; N, 7.4.

1-Amino-6-(*o*-nitrophenyl)-3,6-dithiahexane.—The above described phthalimido compound (11.6 g.) was suspended in boiling ethanol (100 ml.), hydrazine hydrate (5.2 ml. of 50%) added and the boiling continued under reflux for 2 hours. Hydrochloric acid (10 ml., 10 *N*) was then added and the boiling continued for 0.5 hour after which as much alcohol as possible was distilled off and water added to the residue. The precipitated phthalhydrazide was removed and solid sodium hydroxide added to the filtrate until the base separated as a yellow oil which solidified on standing and scratching. It was difficult to purify but could be partially purified by solution in alcohol and then reprecipitation with aqueous sodium hydroxide solution; or by solution in ether in which it is somewhat soluble when impure, removal of most of the solvent and allowing to crystallize. The solid base becomes oily in a vacuum desiccator and solidifies again on exposure to air. For analysis it was converted to its 5-bromosalicylidene derivative; yellow needles, m.p. 85° from ethanol.

Anal. Calcd. for $C_{17}H_{17}N_2O_3S_2Br$: N, 6.3. Found: N, 6.5.

The picrate formed yellow needles, m.p. 169° from ethanol.

Anal. Calcd. for $C_{16}H_{17}N_6O_9S_2$: N, 14.2. Found: N, 14.4.

1-(5′-Bromosalicylideneamino)-6-(*o*-(5′-bromosalicylideneamino)-phenyl)-3,6-dithiahexane.—Zinc dust (11.5 g.) and a solution of calcium chloride (0.4 g.) in water (1.2 ml.) were added to a solution of 1-amino-6-(*o*-nitrophenyl)-3,6-dithiahexane (2.7 g.) in aqueous methanol (38 ml. of 80%). The mixture was then heated under reflux for 2 hours, filtered hot and the alcohol removed, leaving a brown oil (crude EEB base). A solution of 5′-bromosalicylaldehyde (2 moles) in ethanol was added to a hot ethanolic solution of this crude base (1 mole). After boiling for a minute or two the product separated as an oil which was induced to crystallize and was recrystallized from ethyl acetate; yellow prisms, m.p. 103°.

Anal. Calcd. for $C_{24}H_{22}N_2O_2S_2Br_2$: C, 48.5; H, 3.7; N, 4.7. Found: C, 48.5; H, 3.9; N, 5.2.

1-(5′-Bromosalicylideneamino)-6-(*o*-(5′-bromosalicylideneamino)-phenyl)-3,6-dithiahexane Cobalt(III) Iodide.—Cobalt(II) chloride hexahydrate (0.5 g.) was added to a boiling solution of the bis-5-bromosalicylidene derivative of EEB base just described (0.45 g.) in methanol (130 ml.) and then a solution of sodium acetate (0.5 g.) and hydrogen peroxide (4.5 ml. of 3%) in methanol (10 ml.) added. When the volume was reduced to about 50 ml. the solution was filtered and a strong aqueous solution of potassium iodide added to the filtrate. The precipitate was collected and recrystallized by allowing its solution in methanol containing a little water to evaporate slowly, when it came out in minute brown needles, m.p. 205°, which were soluble in chloroform.

Anal. Calcd. for $[Co(C_{24}H_{20}Br_2N_2O_2S_2)]I$: C, 37.1; H, 2.6; N, 3.6; Co, 7.57. Found: C, 37.6; H, 2.9; N, 3.8; Co, 7.7.

SYDNEY, AUSTRALIA

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

Chemistry of Arsenic–Boron Bonding: Arsine Borines and Arsinoborine Polymers

BY F. G. A. STONE AND ANTON B. BURG

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The methylarsines form borine complexes which are more easily dissociated than the corresponding phosphine borines, but show a similar increase of stability, and difficulty of losing hydrogen, with methylation. The existence of arsine borine could not be recognized. The protolytic reactions occur far more readily than those of the phosphine borines, with formation of fairly similar polymers, such as those of the $(CH_3)_2AsBH_2$ unit. The trimer of $(CH_3)_2AsBH_2$ (m.p. 50°, b.p. est. 250°, yield 80%) is stable up to 200°, and requires such a temperature for hydrolysis—some 100° lower than for trimeric $(CH_3)_2PBH_2$. The tetramer of $(CH_3)_2AsBH_2$ (m.p. 150°, b.p. est. 352°, yield 6%) is less stable than the trimer, to which it is partially converted at 180°. A higher polymer of $(CH_3)_2AsBH_2$, formed in far larger yield (14%) than the corresponding P compound (*ca.* 1%) is converted to trimer, with less tetramer, on heating. The trimer and tetramer can be recrystallized from organic solvents in the open air. Their lesser stability and greater reactivity, relative to the $(CH_3)_2PBH_2$ polymers, can be ascribed to the relative weakness of bonding electrons in the 4 quantum level of arsenic.

The discovery of some very stable boron hydride derivatives based upon P–B bonding,[1] such as the trimers of $(CH_3)_2PBH_2$ and $(CH_3)_2PB(CH_3)_2$, led to the question whether analogous arsinoborines also would be stable and chemically fairly inert. Inasmuch as trivalent arsenic compounds generally are less strongly bonded than the analogous phosphorus compounds, it was expected that the arsinoborines would have less thermal stability and higher chemical reactivity than the analogous phosphinoborines; also the arsine borine complexes were expected to be less stable than the corresponding phosphine borines. The results of the present study agree with such expectations, although the new arsinoborines are decidedly more stable and far less reactive than most of the previously known derivatives of the boron hydrides. The structural factors leading to the stabilization of the phosphinoborines have already been discussed,[1] and similar arguments presumably would apply to the arsinoborines.

Experimental Part

1. Preparation and Characterization of Methylarsines

Arsine.—A 70% yield of arsine was obtained by the reaction of arsenic trichloride with lithium aluminum hy-

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(1) A. B. Burg and R. I. Wagner, THIS JOURNAL, 75, 3872 (1953).

dride in ether. The vapor tensions of the fractionated product agreed with the literature.[2]

Methylarsine.—A one-stage methylation of arsine was accomplished by passing it into a solution of calcium in liquid ammonia to form the salt $Ca(AsH_2)_2$, which was treated with methyl chloride to form CH_3AsH_2 in 80% yield.[3] Its vapor tension at −45° was 10% lower than the literature value,[3] but its purity was affirmed by CuO combustion analysis.

Dimethylarsine.—The second stage of the methylation process—conversion of CH_3AsH_2 to its calcium salt and treating this with methyl chloride[4]—gave a 44% yield of $(CH_3)_2AsH$ along with a fair proportion of $(CH_3)_3As$.

The preparation of dimethylarsine by an ostensibly simpler method—the reaction of $(CH_3)_2AsCl$ with $LiAlH_4$ in tetrahydrofuran—was tried under widely varying conditions but the yields were very low except in one unrepeatable experiment in which addition of $(CH_3)_2AsCl$ to the $LiAlH_4$ solution led to a 30% yield. Much hydrogen always formed and it seemed that most of the arsenical material had gone to produce $(CH_3)_2As$–Al compounds from which no appreciable yield of dimethylarsine could be obtained by acidic or basic hydrolysis. Such arsenic–aluminum compounds may well be worthy of extensive study.

Characterization of Dimethylarsine.—Unlike methylarsine and trimethylarsine, dimethylarsine has received little attention since its discovery,[5,6] and accordingly its melting point and vapor tensions are given here. An especially pure sample was prepared through formation of the adduct $(CH_3)_2AsH\cdot BH_3$ (more fully described in Section II) from $(CH_3)_2AsH$ and B_2H_6. After removal of the more volatile impurities, the pure adduct was treated with triethylamine to form $(C_2H_5)_3NBH_3$, quantitatively liberating the $(CH_3)_2AsH$. After distillation to remove any excess triethylamine, the pure $(CH_3)_2AsH$ was found to melt at −136.1°. Its vapor tensions, shown in Table I, determined the equation $\log p_{mm} = 7.532 - 1443/T$, whence one calculates the boiling point as 37.1° and the Trouton constant as 21.3 cal./deg. mole.

Table I

Vapor Tensions of Liquid $(CH_3)_2AsH$

t, °C.	p_{mm} (obsd.)	p_{mm} (calcd.)	t	p (obsd.)	p (calcd.)
−78.5	1.3	1.32	−7.7	125.0	124.8
−64.0	4.1	4.3	−5.4	138.5	139.0
−31.4	36.6	36.6	0.0	178.7	177.6
−22.2	60.5	60.5	15.3	338.0	338.5
−15.6	85.2	85.0	17.4	368	368

II. The Arsine–Borine Complexes

Attempt to Make H_3AsBH_3.—Arsine and diborane (2:1 mole ratio) were brought together at −78.5°, with no reaction whatever during 48 hours. As the mixture was warmed, the first observable effect was the arsinolysis reaction described in Section III.

Methylarsine Borine.—Samples of CH_3AsH_2 (35.6 cc.[7]) and diborane (35.25 cc.) were brought together in an immersible tensimeter[8] at −78.5°. A reaction was indicated by a decrease of pressure and the formation of a white solid. After half an hour, with the tensimeter maintained at −78.5°, the excess reactants were removed and separated: 4.95 cc. of CH_3AsH_2 and 19.80 cc. of B_2H_6. Hence the reaction ratio of CH_3AsH_2 to B_2H_6 was 1.99, indicating the formation of $CH_3AsH_2\cdot BH_3$. During 60 hours at −78.5° the complex developed a dissociation pressure of 10.5 mm., indicating a far lower stability than that of the corresponding phosphorus compound.[1] On warming to room temperature the complex dissociated entirely, and the diborane and methylarsine then reacted slowly to form hydrogen as described in Section III.

Dimethylarsine Borine.—The 2:1 addition reaction between dimethylarsine and diborane occurred smoothly at −78.5°. Thus 55.1 cc. of $(CH_3)_2AsH$ and 42.0 cc. of B_2H_6 were brought together, with subsequent recovery of 14.62 cc. of B_2H_6: the reaction ratio thus was 2.01, or in other experiments 2.02 and 1.98. The adduct melted in the range −22.4 to −21.5°. Its vapor tensions, measured in an immersible tensimeter,[8] are given in Table II.

Table II

Vapor Tensions of Liquid $(CH_3)_2AsH\cdot BH_3$

t, °C.	p_{mm} (obsd.)	p_{mm} (calcd.)	t	p (obsd.)	p (calcd.)
−14.5	2.78	2.77	24.7	39.4	39.2
0.0	8.11	8.06	30.6	55.1	55.1
6.8	12.82	12.82	36.1	74.6	74.8
15.5	22.3	22.4	43.7	111.7	111.7
19.8	30.0	29.2	49.0	147.3	147.1

They determine the equation $\log p_{mm} = 9.191 - 2263/T$, from which the normal boiling point is calculated as 85.5° and the Trouton constant as 28.9 cal./deg. mole. The high value of the latter meant that the average molecular weight of the vapor was considerably less than that of the liquid. Accordingly the vapor density was measured, indicating an average molecular weight of 82.0 at 24° and 23 mm., or 81.6 at 24° and 15 mm. These results correspond to 94–96% dissociation of the adduct into $(CH_3)_2AsH$ and B_2H_6. Since this is a higher degree of dissociation than that indicated by the Trouton constant, it would appear that considerable dissociation occurred even in the liquid state. Hence the adduct $(CH_3)_2AsH\cdot BH_3$ is far less stable than the corresponding $(CH_3)_2PH\cdot BH_3$, the vapor of which was undissociated up to 150°.[1] The loss of hydrogen from $(CH_3)_2AsH\cdot BH_3$, to form polymers of $(CH_3)_2AsBH_2$, is described in Section IV.

Trimethylarsine Borine.—A 34.7-cc. sample of $(CH_3)_3As$, treated with 35.65 cc. of B_2H_6 at −78.5°, at once formed a white solid. The residual gas consisted of 18.3 cc. of pure B_2H_6; hence the arsine:diborane reaction ratio was just 2.00, corresponding to $(CH_3)_3AsBH_3$. This adduct melted in the range 73.5–74.5°.

The decomposition of the 34.7-cc. sample of $(CH_3)_3AsBH_3$ was studied by heating it for 24 hours at 120°. It yielded 32.4 cc. of H_2 (purity demonstrated by CuO combustion), and 24.8 cc. of $(CH_3)_3As$ (71.6%). The accompanying nonvolatile solid corresponded to the decomposition of diborane. No methane was formed even though the remaining $(CH_3)_3AsBH_3$ was heated for 24 hours at 155°, yielding an additional 4.5 cc. of H_2 and 2.52 cc. of $(CH_3)_3As$.

At 80° a 28.2-cc. sample of $(CH_3)_3AsBH_3$ yielded no hydrogen and only a trace (0.8 cc.) of $(CH_3)_3As$ during two hours. Hence it was considered feasible to measure the vapor tensions of $(CH_3)_3AsBH_3$ up to 110°, especially by working very rapidly at temperatures above 80°. The values for the solid, given in Table III, determine the equation $\log p_{mm} = 9.966 - 2920/T$. The equation $\log p_{mm} = 8.553 - 2420/T$ represents the values for the liquid, given in Table IV, due allowance being made for slight decomposition at the highest temperatures.

Table III

Vapor Tensions of Solid $(CH_3)_3AsBH_3$

t, °C.	32.3	39.9	46.4	52.6	58.1	71.2
p_{mm} (obsd.)	2.57	4.35	6.68	10.13	14.5	30.1
p_{mm} (calcd.)	2.55	4.35	6.73	10.05	14.2	30.6

Table IV

Vapor Tensions of Liquid $(CH_3)_3AsBH_3$

t, °C.	78.0	83.9	86.1	89.5	97.2	110.5
p_{mm} (obsd.)	45.9	59.4	65.0	76.9	106.6	177.5
p_{mm} (calcd).	45.9	59.6	65.0	75.9	104.5	175.9

The latter equation implies that the normal boiling point would be 154° and the Trouton constant 26.0 cal./deg. mole. The molar heat of fusion is estimated as 2.29 kcal.

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[2] W. C. Johnson and A. Pechukas, This Journal, **59**, 2068 (1937).

[3] Method similar to that of Johnson and Pechukas: ref. 2.

[4] Like the preparation of $(CH_3)_2PH$: R. I. Wagner and A. B. Burg, This Journal, **75**, 3869 (1953).

[5] A. W. Palmer, *Ber.*, **27**, 1378 (1894).

[6] W. M. Dehn, *Am. Chem. J.*, **35**, 1 (1906).

[7] Throughout this paper the abbreviation cc. refers to gases at standard conditions or the equivalent amount of a non-volatile substance.

[8] A. B. Burg and H. I. Schlesinger, This Journal, **59**, 785 (1937).

III. The Highly Polymerized Arsino- and Methylarsinoborines

The Reaction between Arsine and Diborane.—Although diborane and arsine form no observable adduct, they react at room temperature to form hydrogen and a white solid product usually somewhat lower in hydrogen than the ideal formula H_2AsBH_2. For example, 48.5 cc. of AsH_3 and 24.05 cc. of B_2H_6 were left together in a sealed 60-cc. bulb for 5 days at room temperature; then the H_2 was measured as 33.25 cc. and the mixture of condensable gases was shown by hydrolysis to contain 10.08 cc. of B_2H_6 and 19.85 cc. of AsH_3. Hence the non-volatile solid could be represented empirically as $BAs_{1.03}H_{3.70}$. This product proved to be insoluble in ether, benzene, acetone or water, and accordingly is regarded as highly polymerized. It reacted slowly with water at room temperature to form arsine, hydrogen and boric acid. Upon exposure to the open air, it turned black. On heating in a closed bulb to 80°, a similar sample turned brown and lost hydrogen slowly, approaching an apparent limit corresponding to $BAsH_{2.8}$ in three days; but more hydrogen was lost on further heating at higher temperatures, and no definite substance could be recognized during the process. Formulas as degraded as $BAsH_{1.7}$ have been reached at 100°, but the effects of heating of different samples were highly variable, since one sample arrived at the composition $BAsH_{2.22}$ only after extended heating at 150°. It would appear that a highly polymeric $BAsH_n$ (n almost = 4) was first formed and was self-protolytic, losing hydrogen to establish cross-links between long chains, in a manner governed by the opportunities of geometry. The chief differences from the phosphine borine case were (1) the absence of the original arsine borine complex, and (2) the far greater ease of protolysis.

A sample having the composition $BAs_{1.03}H_{3.70}$ was hydrolyzed at 80–110° (15 hours, plain water), yielding 94% of the As as AsH_3 and hydrogen (53.1 cc.) in amount indicating 1.90 B–H bonds per B. Titration of the resulting boric acid indicated only 80% of the known B content; the rest apparently was in an As–B compound of minimal H content. This appeared as a dark precipitate which vanished upon treatment with nitric acid. A titration now showed 104% of the expected value for total boron.

The Reaction Between Methylarsine and Diborane.—The protolysis of diborane by methylarsine is very like that by arsine, except that the degradation cannot be so extensive, for lack of active hydrogen. In a typical experiment, 16.6 cc. of B_2H_6 and 34.6 cc. of CH_3AsH_2 were left together in a sealed bulb at room temperature for 13 days, after which the volatile contents consisted of 35.1 cc. of H_2 and 1.87 cc. of CH_3AsH_2. Hence the composition of the non-volatile product could be represented as $CH_3AsB_{1.01}H_{2.90}$. This evidently polymeric material was colorless, viscous, water-repellent, and insoluble in acetone or benzene. Hydrolysis was attempted by heating the sample with water at 80° for 15 hours, forming 4.5 cc. of CH_3AsH_2 and 14.69 cc. of H_2. Then hydrogen chloride was added in sufficient amount to bring the acidity to 1 *M* and the reaction vessel was maintained at 100° for 4 days; thus a further 24.65 cc. of CH_3AsH_2 and 43.4 cc. of H_2 were obtained. The low recovery of CH_3AsH_2 paralleled the hydrolysis of the polymer obtained from B_2H_6 and AsH_3 and, as in that case, there was a brown precipitate. This was dissolved in nitric acid and the solution was titrated to show a boron content of 32.4 cc. (98%).

Another sample of the polymer (composition $CH_3AsB_{1.03}H_{2.83}$) lost hydrogen on heating for 48 hours at 80°, arriving at the composition $CH_3AsB_{1.03}H_{2.14}$. Further heating for 10 days at 100° and 45 hours at 150° gave a dark brown solid of composition $CH_3AsB_{1.03}H_{0.79}$. During this process there was no discontinuity in the evolution of hydrogen, such as would indicate the formation of a definite compound.

IV. The Dimethylarsinoborine Polymers

Formation.—The adduct $(CH_3)_2AsHBH_3$ began to lose hydrogen noticeably at 50°, producing 0.75 mole of H_2 per mole of adduct in four hours, and a total of 0.97 H_2 per mole after 36 hours at 130°. In earlier experiments extensive decomposition to dark products occurred when $(CH_3)_2AsH{\cdot}BH_3$ was heated at 150°. In the most definitive experiment, 162 cc. of $(CH_3)_2AsH{\cdot}BH_3$, heated for 24 hours at 75°, yielded 147 cc. of H_2; after 48 hours at 100°, it had produced a total of 160.5 cc. of H_2, or 99.1% of the expected quantity. The white solid product was composed of at least three fractions: 665.7 mg. (80%) was barely sublimable under high vacuum at 50°, and was later identified as the trimeric form of $(CH_3)_2AsBH_2$; 50.7 mg. (6.0%) could be sublimed out by slightly stronger heating, and corresponded to the tetramer; the apparently non-volatile residue, amounting to 14% of the whole solid product, evidently was a higher polymer, occurring in a far larger proportion than the corresponding high polymer of $(CH_3)_2PBH_2$.[1] On heating *in vacuo* by a free flame, it changed to the trimer, some tetramer, and a non-volatile brown residue. The trimer and tetramer proved to be readily soluble in methanol, acetone or carbon tetrachloride, but insoluble in water. They were easily purified by recrystallization in the open air.

Proof of Formula of the Trimer.—A sample of the most volatile of the solid products was analyzed by combustion to show 20.15% C and 6.93% H (calcd. for Me_2AsBH_2, 20.4 and 6.81). For analyses of arsenic and boron, weighed samples approximating 20 mg. were burned in an enclosed oxygen–hydrogen flame.[1] The arsenic was determined by reducing the resulting oxides to the element by means of a hypophosphite solution, and titrating by ceric ammonium sulfate solution.[9] The boron was determined in the usual manner (titration of the mannitol acid–spirane) after removal of the arsenic as the sulfide. Found: As, 63.2, 64.1%; B, 9.8, 9.5% (calcd.: As, 63.6; B, 9.2).

Molecular weight determinations by the Rast camphor method gave the values 329 and 365; calcd. for trimer, 353.1.

Hydrolysis of the Trimer.—The conditions and results of an experiment on the hydrolysis of a 40.0-mg. (2.54-cc.) sample, by means of 12 *M* hydrochloric acid, are shown in Table V. The methane–hydrogen mixtures were analyzed by CuO combustion.

TABLE V

HYDROLYSIS OF 2.54 CC. OF $[(CH_3)_2AsBH_2]_3$

Time intervals, hours	Temp., °C.	Total products H_2, cc.	Total products CH_4, cc.	H_2 ratio found/calcd.[a]
15	110	0.36	...	0.024
45	200	2.49	...	0.164
15	250	17.13	1.11	1.125
15	250	17.86	2.22	1.173
96	250	18.31	13.17	1.203

[a] Calcd. value 15.24 cc., based only on the hydrolysis of B–H bonds.

The production of nearly two moles of methane per $(CH_3)_2As$ unit is an effect not paralleled in the hydrolysis of the dimethylphosphinoborines. Also different is the failure of arsenic to be oxidized completely to the pentavalent state, although the 20.3% excess production of hydrogen indicates some of this reaction. Methane accounted for only 86.4% of the carbon; the rest was recovered in the form of 1.02 cc. of $(CH_3)_2AsH$, bringing the total carbon to 99.8% of the calculated value.

Characterization of the Trimer.—The compound $[(CH_3)_2AsBH_2]_3$ melted in the range 49.7–50.6°. The vapor tensions, shown in Table VI, were obtained by means of an immersible tensimeter designed for automatic correction for mercury vapor.[10] The resulting equation, $\log p_{mm} = 8.752 - 3074/T$, indicates the normal boiling point as 250° and the Trouton constant as 26.7 cal./deg. mole. It is interesting that the trimer of $(CH_3)_2PBH_2$ also has a high value: 26.0 cal./deg. mole.[1]

TABLE VI

VAPOR TENSIONS OF LIQUID $[(CH_3)_2AsBH_2]_3$

t, °C.	p_{mm} (obsd.)	p_{mm} (calcd.)	t	p (obsd.)	p (calcd.)
94.0	2.40	2.40	127.7	11.90	12.12
102.2	3.67	3.66	129.2	13.17	12.94
110.6	5.46	5.52	136.7	18.2	17.9
118.1	7.92	7.86	146.1	26.0	26.3

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[9] I. M. Kolthoff and E. Amdur, *Ind. Eng. Chem., Anal. Ed.*, **12**, 177 (1940).

[10] C. L. Randolph, Jr., Ph.D. Dissertation, University of Southern California Libraries, 1949, p. 37.

The vapor of a 44.9-mg. sample of the trimer at 140.1°, in a volume of 222.2 cc., registered a pressure of 14.08 mm. The molecular weight thus was indicated as 370, calcd. 353.1.

Proof of Formula of the Tetramer.—Samples of the less volatile solid obtained by the protolysis of dimethylarsine borine gave values of 492 and 453 for the molecular weight by the Rast method; calcd. for $[(CH_3)_2AsBH_2]_4$, 471. Arsenic and boron were determined by the same procedures as described for the trimer. Found: As, 63.25, 61.6%; B%, 9.8% (calcd.: As, 63.6; B, 9.2).

Characterization of the Tetramer.—The compound $[(CH_3)_2AsBH_2]_4$ melted in the range 149.5–150.5°. Its vapor tensions, determined by means of the special tensimeter[10] and shown in Tables VII and VIII, determine the equation $\log p_{mm} = 18.635 - 7692/T$ for the solid and for the liquid $\log p_{mm} = 7.973 - 3179/T$. Hence the normal boiling point is estimated as 352° and the Trouton constant as 23.3 cal./deg. mole. The molar heat of fusion is computed as 20.65 kcal. and the melting point as 150.1°, near the middle of the observed range.

TABLE VII

VAPOR TENSIONS OF SOLID $[(CH_3)_2AsBH_2]_4$

t, °C.	130.3	135.8	137.8	140.3	145.2	147.6
p_{mm} (obsd.)	0.37	0.67	0.83	1.06	1.72	2.28
p_{mm} (calcd.)	0.37	0.67	0.83	1.07	1.77	2.26

TABLE VIII

VAPOR TENSIONS OF LIQUID $[(CH_3)_2AsBH_2]_4$

t, °C.	149.3	160.2	166.2	170.3	175.5	185.0
p_{mm} (obsd.)	2.84	4.30	5.50	6.39	7.68	10.8
p_{mm} (calcd.)	2.81	4.34	5.46	6.37	7.72	10.8

Thermal Stability and Interconversion of Trimer and Tetramer.—The tetramer of dimethylarsinoborine begins to convert to the trimer quite observably at 180°—a temperature at which the tetramer of dimethylphosphinoborine is quite stable, although it is known to form some trimer at 350°.[1] In one experiment a 52-mg. sample of the dimethylarsinoborine tetramer, after being heated somewhat longer than an hour at 180°, showed a vapor tension of 13.2 mm. at 180° (calcd. from equation, 9.1 mm.); and after a further 3 hours at 181°, it showed the still higher value 15.1 mm. at that temperature. The sample now could be separated into two fractions, the more volatile of which melted at 49° (trimer 49.7–50.6°).

A sample of the trimer was unchanged during a week at 150°, but another sample (48.3 mg., or 3.06 cc.) formed brown material and 1.26 cc. of hydrogen, on heating for 8 days at 200°. A trace (0.13 cc.) of CH_4 also was found, along with 0.26 cc. of a condensable gas (probably dimethylarsine) which formed 0.51 cc. of CO_2 by CuO combustion. The recoverable trimer amounted to 5.0 mg. (10.3%), m.p. 50°. There was no evidence of any tetramer; this apparently is not formed in any appreciable yield from the trimer.

Discussion

From the results of this and a preceding paper,[1] it is clear that the As–B compounds are similar to the corresponding P–B compounds except that all bonds involving arsenic are weaker than those of phosphorus, permitting some reactions to occur which are not known for the phosphorus compounds, or increasing the ease of occurrence of other reactions which are parallel to those of the phosphorus compounds. A summary of such comparisons is given in Table IX.

TABLE IX

COMPARISON OF BORINE COMPOUNDS OF PHOSPHORUS AND ARSENIC

Phosphorus compound	Arsenic compound
"$PH_3 \cdot BH_3$": P→B bonding stable at −78.5°; slow evolution of H_2 at 65° to form $(PBH_{3.75})_x$; further degradation difficult.	$AsH_3 \cdot BH_3$ non-existent at −78.5°; $2AsH_3 + B_2H_6$ at 25° easily form H_2 and $(AsBH_{3.7})_x$; further degradation easy.
$CH_3PH_2 \cdot BH_3$: P→B bonding stable at 80°; slow H_2 loss at 80°; strong heating forms $(CH_3PBH)_x$.	$CH_3AsH_2 \cdot BH_3$: dissoc. p = 10.5 mm. at −78.5°. Components at 25° form H_2 and $(CH_3AsBH_{2.3})_x$; further degradation easy.
$(CH_3)_2PH \cdot BH_3$: P→B bonding stable at 150°, where H_2 is formed.	$(CH_3)_2AsH \cdot BH_3$: 95% dissoc. (24°, 20 mm.) H_2 evolution appreciable at 50°.
$(CH_3)_3P \cdot BH_3$: slow destruction of BH_3 group at 200°, probably through P–B dissociation.	$(CH_3)_3As \cdot BH_3$: destruction of BH_3 at 120° faster than $(CH_3)_3PBH_3$ case at 260°.
$[(CH_3)_2PBH_2]_3$: stable and formed from tetramer at 350°; slow hydrolysis at 300–325° yields H_2 and $(CH_3)_2POOH$ but no CH_4.	$[(CH_3)_2AsBH_2]_3$: formed from tetramer at 180°; slow decomp. at 200°; hydrolysis at comparable rate (200–250°) yields H_2, CH_4, and little As(V).
$[(CH_3)_2PBH_2]_4$: stable at 255° but wholly dec. at 350°; hydrolysis slightly easier than for trimer.	$[(CH_3)_2AsBH_2]_4$: slow decomp. at 180°.
$[(CH_3)_2PBH_2]_x$: converted to trimer at 173°; original yield slight.	$[(CH_3)_2AsBH_2]_x$: easily converted to trimer and some tetramer; original yield moderate.

This table shows also that increasing replacement of H by CH_3 on As increases the stability of As–B bonding, in a manner quite parallel to the effect on P. The greater ease of arsinolysis than phosphinolysis can be ascribed to the higher protic acid strength of the arsines—an effect which clearly decreases with the increasing base strength due to methylation. The rates of protolytic reactions do not correlate, except in a rough negative manner, with the stability of the P–B or As–B complex bonding.

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LOS ANGELES 7, CALIFORNIA