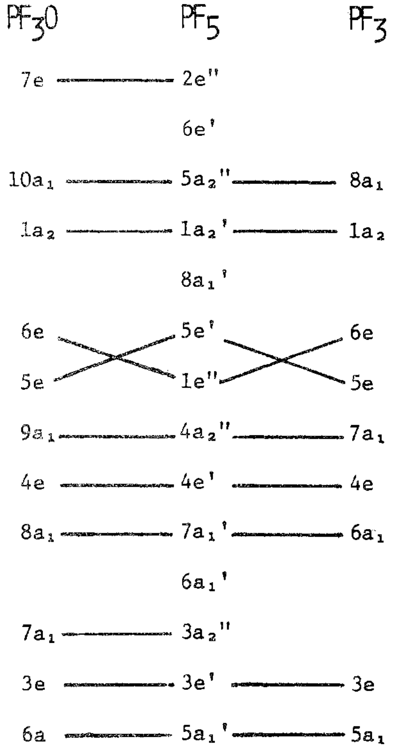

Figure 3. A correlation plot based on detailed electron density matching for the valence-shell molecular orbitals of phosphorus pentafluoride with those of phosphorus trifluoride and of phosphoryl fluoride. Note that the orbitals are listed downward in order of increasing stability but that the distance between them bears no relationship to the difference in their orbital energies.

and thiophosphoryl fluorohydrides.

Mulliken correlations were carried out for PF_5 with PF_3 and for PF_5 with OPF_3, using the following hypothetical reactions: $2F + PF_3 \rightarrow PF_5$ and $2F + OPF_3 = PF_5 + O$, maintaining C_{3v} symmetry throughout the transformation. Not surprisingly, orbitals 2e″, $8a_1'$, and 6e′ of PF_5 were found to correlate with the 2p atomic orbitals of the fluorine atom reactants in the Mulliken scheme. Likewise, orbitals $6a_1'$ and $3a_2''$ of PF_5 were found to correlate with the 2s orbitals of these fluorine atoms and orbital $7a_1$ of OPF_3 correlated with the 2s orbital of the oxygen atom product. Thus, the correlation orbitals 2e″ and $3a_2''$ of PF_5 with 7e and $7a_1$ of OPF_3 in our electron density scheme obviously represent the somewhat formal relationship whereby the oxygen of the OPF_3 molecule is replaced by a pair of fluorine atoms in PF_5.

The only key difference between the Mulliken correlation scheme and our scheme based on detailed electron density distributions is found in a switching of the correlation of orbitals 6e and 5e of either the PF_3 or OPF_3 molecules with orbitals 1e″ and 5e′ of PF_5. This switch simply means that mixing between the closely lying 6e and 5e orbitals of either PF_5 or OPF_3 leads to an interchange of the bonding characteristics in the Mulliken scheme. From the viewpoint of the chemist, it would seem that our correlation through electron density distributions (*i.e.*, the bonding characteristics) is more germane.

In comparing the electron density plots for the valence-shell orbitals of PF_3 and OPF_3 with those of PF_5, it was clear that the equatorial fluorine atoms of the latter molecule were closely related to the three fluorine atoms of the PF_3 and OPF_3 molecules and that the orbital of PF_3 dominated by the phosphorus lone pair transformed into the orbital dominated by P–O bonding in OPF_3 which in turn is closely related to the $P–F_{ax}$ bonding orbitals.

Acknowledgment. We wish to thank the Air Force Office of Scientific Research, Air Force Systems Command, United States Air Force, under AFOSR Contract No. AFOSR-72-2265, for partial financial support of this work.

Registry No. PF_5, 7647-19-0; PF_4H, 51262-44-3.

Contribution from the Department of Chemistry,
The University of Mississippi, University, Mississippi 38677

Group V Boranes. I. Synthesis of Arsaboranes from Decaborane[1]

J. L. LITTLE,* S. S. PAO, and K. K. SUGATHAN

Received November 14, 1973 AIC30838U

In the presence of a base and a reducing agent, decaborane reacts with $AsCl_3$ to give 7-$B_{10}H_{12}As^-$. Excess base and $AsCl_3$ produce 1,2-$B_{10}H_{10}As_2$, also obtained from the reaction of purified $B_{10}H_{12}As^-$ with $AsCl_3$ in the presence of a base. Piperidine removes a boron from 1,2-$B_{10}H_{10}As_2$ to produce 7,8-$B_9H_{10}As_2^-$. $B_{11}H_{11}As^-$ is produced from the reaction of $B_{10}H_{12}As^-$ with triethylamine-borane at 160° or by pyrolysis of $CsB_{10}H_{12}As$. The arsenic in $B_{10}H_{12}As^-$ quaternizes with methyl iodide to give $B_{10}H_{12}AsCH_3$, which dissolves in dilute ammonia to give $B_{10}H_{11}AsCH_3^-$. Sodium in liquid ammonia removes the methyl group from $B_{10}H_{12}AsCH_3$. Decaborane and $C_6H_5AsCl_2$ in the presence of base give $B_{10}H_{11}AsC_6H_5^-$. Acidification of solutions of $B_{10}H_{11}AsC_6H_5^-$ gives $B_{10}H_{12}AsC_6H_5$.

In recent years several papers have appeared reporting borohydrides containing a group V atom in the polyhedral framework. Carboranes containing a group V atom,[2,3] as well as their transition metal complexes,[3,4] and P-substituted phosphaboranes[5,6] have been reported.

---

[1] (a) Presented in part at the 162nd and 165th National Meetings of the American Chemical Society, Washington, D. C., Sept 1971, and Dallas, Tex., April 1973. (b) Taken in part from the M.S. thesis of S. S. Pao, The University of Mississippi, 1973.

[2] L. J. Todd, J. L. Little, and H. T. Silverstein, *Inorg. Chem.*, 8, 1698 (1969).

[3] L. J. Todd, A. R. Burke, A. R. Garber, H. T. Silverstein, and B. N. Storhoff, *Inorg. Chem.*, 9, 2175 (1970).

[4] J. L. Little, P. S. Welcher, N. J. Loy, and L. J. Todd, *Inorg. Chem.*, 9, 63 (1970).

[5] J. L. Little, J. T. Moran, and L. J. Todd, *J. Amer. Chem. Soc.*, 89, 5495 (1967).

Table I. Analytical Data of Nido and Closo Arsaboranes

			Calcd					Found				
No.	Compd	Mp, °C	% C	% H	% B	% As	Mol wt	% C	% H	% B	% As	Mol wt
I	$(CH_3)_4NB_{10}H_{12}As$		17.84	8.98	40.15	27.82		17.68	8.98	39.75	28.24	
II	1,2-$B_{10}H_{10}As_2$	222–224		3.83	40.97	55.22	264		4.28	40.06	55.26	266[a]
III	$(CH_3)_4N$-7,8-$B_9H_{10}As_2$		14.49	6.69				14.29	6.64			
IV	$(CH_3)_4NB_{11}H_{11}As$		17.21	8.30	42.63			16.84	8.49	42.80		
V	$B_{10}H_{12}AsCH_3$	113–115	5.71	7.20	51.45	35.62	210	5.91	7.20	50.85	35.67	218[a]
VI	$(CH_3)_4NB_{10}H_{11}AsCH_3$		21.19	9.25		26.44		21.39	9.54		26.80	
VII	$B_{10}H_{12}AsC_6H_5$	145–146	26.46	6.30	39.73	27.51	272	26.51	6.75	39.66	27.65	282[a]
VIII	$(CH_3)_4NB_{10}H_{11}AsC_6H_5$		34.78	8.17	31.30	21.69		34.73	8.27	31.00	22.01	

[a] Osmometric in benzene.

We wish to report the facile synthesis and some chemistry of higher nido and closo arsaboranes and arsaborates.

Results and Discussion

Decaborane reacts with arsenic trichloride in the presence of excess sodium hydride or sodium borohydride with diethyl ether as solvent to produce 7-$B_{10}H_{12}As^-$ (I) in low or moderate yield. The sodium hydride product is also of low purity. We have found that if triethylamine is substituted as base, zinc dust as reducing agent, and tetrahydrofuran (THF) as solvent, much purer $B_{10}H_{12}As^-$ is formed, although in lower yield than from the sodium borohydride reaction.

Boron (^{11}B) nmr of I at 70.6 MHz (Figure 1) exhibits a 1:2:2:2:1:2 pattern of doublets characteristic of C_s ion symmetry resulting from simple addition of an arsenic atom to one of the two vacant positions in the decaborane framework. Although the nmr data do not distinguish 7-$B_{10}H_{12}As^-$ and 2-$B_{10}H_{12}As^-$, it is probably safe to assume that no rearrangement of the cage would take place at the mild conditions of preparation. The nmr spectrum is broad, as has been noted for other uncomplexed 11-particle icosahedral fragments containing one or two heteroatoms. Analytical data for all compounds are presented in Table I.

Compound I is probably formed *via* a bridged intermediate similar to the product from reaction of $NaB_{10}H_{13}$ and $(C_6H_5)_2PCl$ (to produce $B_{10}H_{13}P(C_6H_5)_2$),[7] for which structural data have recently become available.[8] $(C_6H_5)_2AsCl$ and $B_{10}H_{13}MgI$ react to give a product[9] with properties similar to those of the bridged phosphinoborane. The bridged intermediate could then eliminate HCl and the reaction sequence would be

$$B_{10}H_{13}^- + AsCl_3 \rightarrow B_{10}H_{13}AsCl_2 + Cl^-$$

$$B_{10}H_{13}AsCl_2 + (C_2H_5)_3N \rightarrow (C_2H_5)_3NHCl + B_{10}H_{12}AsCl$$

$$B_{10}H_{12}AsCl + Zn \rightarrow B_{10}H_{12}As^- + Zn^{2+} + Cl^-$$

Alternatively, the base may be forming an adduct with either $B_{10}H_{14}$ or $B_{10}H_{13}^-$. Arsenic trichloride could then react with the base adduct, *i.e.*

$$B_{10}H_{14} + (C_2H_5)_3N \rightarrow B_{10}H_{13}^- + (C_2H_5)_3NH^+$$

$$B_{10}H_{13}^- + (C_2H_5)_3N \rightarrow B_{10}H_{13}\cdot N(C_2H_5)_3^-$$

$$B_{10}H_{13}\cdot N(C_2H_5)_3^- + AsCl_3 \rightarrow B_{10}H_{12}AsCl + (C_2H_5)_3NH^+ + 2Cl^-$$

The presence of the complexed base could be assisting the reaction either by enhancing the electron density at the reaction site or merely by its close proximity to the reaction site (*i.e.*, proton abstraction).

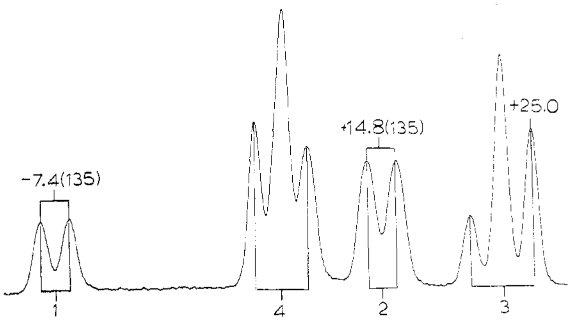

Figure 1. Boron (^{11}B) nmr of $(CH_3)_4N$-7-$B_{10}H_{12}As$ (DMF) at 70.6 MHz. The numbers above are δ in ppm (J_{BH} in Hz) relative to $BF_3\cdot O(C_2H_5)_2$, while the numbers below are relative areas.

In the presence of a twofold excess of triethylamine and arsenic trichloride, 1,2-$B_{10}H_{10}As_2$ (II, mp 222–224°) is formed in yields comparable with that of I. However, if a fourfold excess of the reagents is used, no I is obtained and II is of low purity and in low yield. Compound II is also found in the $NaBH_4$ reaction in about 1% yield and may be prepared in about 30% yield from purified $B_{10}H_{12}As^-$ in the presence of excess triethylamine and arsenic trichloride with THF as solvent.

The low-resolution mass spectrum of II cuts off at *m/e* 270, corresponding to the $^{11}B_{10}{}^1H_{10}{}^{75}As_2{}^+$ parent ion. Boron (^{11}B) nmr at 70.6 MHz (Figure 2) shows a 1:1:4:4 pattern, interpretable as the expected distribution for C_{2v} cage symmetry with each of two pairs of boron atoms accidentally degenerate.

Like 1,2-carborane, II is thermally stable to high temperatures. However, II must be heated to relatively high temperatures to bring about isomerization. Heating II in a sealed, evacuated tube at 575° for 1.5 hr gives only 14% yield of a volatile mixture still containing 67% II by glpc analysis. In addition, five other peaks are seen, one of them showing a longer retention time than II. The major product is probably 1,7-$B_{10}H_{10}As_2$, and we are presently investigating the nature of this material and the other four pyrolysis products.

As in the case of other icosahedral heteroboranes containing two heteroatoms,[2,4,10] piperidine removes a boron from II to give 7,8-$B_9H_{10}As_2^-$ (III) in high yield. The boron nmr spectrum at 70.6 MHz (Figure 3) is in a pattern (2:2:1:2:1:1) expected for C_s cage symmetry and is very similar to that of 7,8-$B_9C_2H_{12}^-$ at 60 MHz reported by Hawthorne and coworkers.[10] The doublet of area 1 at 32.1 ppm in the 60-MHz spectrum of 7,8-$B_9C_2H_{12}^-$ shows secondary splitting attributed to the bridging ("extra") proton, while the comparable resonance (16.0 ppm) in the 70.6-MHz spectrum of 7,8-$B_9H_{10}As_2^-$ shows significant broadening. Thus, these

---

(6) J. L. Little and A. C. Wong, *J. Amer. Chem. Soc.*, 93, 522 (1971).

(7) H. Schroeder, *Inorg. Chem.*, 2, 390 (1963).

(8) L. B. Friedman and S. L. Perry, *Inorg. Chem.*, 12, 288 (1973).

(9) E. L. Muetterties and V. D. Aftandilian, *Inorg. Chem.*, 1, 731 (1962).

(10) M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe, and P. A. Wegner, *J. Amer. Chem., Soc.*, 90, 862 (1968).

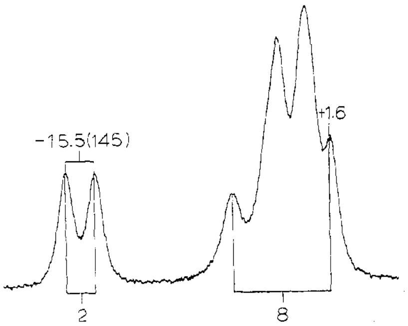

Figure 2. Boron (^{11}B) nmr of 1,2-$B_{10}H_{10}As_2$ (DMSO) at 70.6 MHz. The numbers above are δ in ppm (J_{BH} in Hz) relative to $BF_3 \cdot O(C_2H_5)_2$, while the numbers below are relative areas.

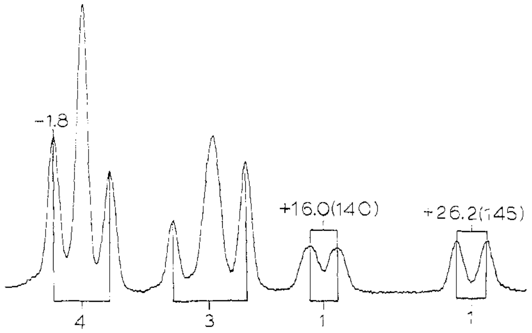

Figure 3. Boron (^{11}B) nmr of $(CH_3)_4N$-7,8-$B_9H_{10}As_2$ (acetone) at 70.6 MHz. The numbers above are δ in ppm (J_{BH} in Hz) relative to $BF_3 \cdot O(C_2H_5)_2$, while the numbers below are relative areas.

doublets can probably be assigned to the boron atom in the mirror plane on the open pentagonal face of each ion.

Attempts to quaternize one or both of the arsenic atoms of III using methyl iodide have thus far not been successful.

Compound I is similar to its one carbon analog[11] $B_{10}H_{12}CH^-$ in many of its physical and chemical properties. For example, boron may be inserted using triethylamine-borane

$$B_{10}H_{12}As^- + (C_2H_5)_3N \cdot BH_3 \xrightarrow[160°]{\text{diglyme}} B_{11}H_{11}As^- \text{ (IV)} + 2H_2 + (C_2H_5)_3N$$

Excess triethylamine-borane must be used or the product is contaminated with unreacted I.

Resonances in the boron (^{11}B) nmr spectrum of IV at 70.6 MHz appear at −8.0 (1 B, J_{BH} = 135 Hz), 7.6 (5 B, J_{BH} = 125 Hz), and 8.6 ppm (5 B, J_{BH} = 140 Hz), externally referenced to $(C_2H_5)_2O \cdot BF_3$. The low-field doublet is assigned to the boron para to arsenic, and the other two are assigned to the two five-membered rings.

Synthesis may also be carried out by maintaining $CsB_{10}H_{12}As$ under nitrogen at 375° until H_2 evolution ceases. The product is of very low quality and must be purified by liquid chromatography as a tetramethylammonium salt. No $B_9H_9As^-$ can be detected in the product mixture, in contrast to the monocarbon carborane system,[11] which, when heated, forms both $B_{11}H_{11}CH^-$ and $B_9H_9CH^-$. $B_9H_9As^-$ is probably formed and then rapidly decomposed at the reaction temperature. Reaction of IV with methyl iodide in THF resulted in cage disruption.

Methyl iodide in THF reacts with I to give $B_{10}H_{12}AsCH_3$ (V) in high yield. Boron nmr (see Experimental Section) exhibits a 1:2:2:2:1:2 pattern (C_s symmetry) and is very similar to that of I. The low-resolution mass spectrum cuts off at *m/e* 212, corresponding to the parent ion $^{11}B_{10}H_{15}{}^{12}C^{75}As^+$. The proton nmr shows only a singlet ($AsCH_3$) at τ 7.9.

Compound V is quite similar in physical and chemical properties to the analogous phosphaborane $B_{10}H_{12}PCH_3$[6] and the thiaborane $B_{10}H_{12}S$.[12] Compound V is acidic, readily losing a proton in dilute aqueous ammonia to form $B_{10}H_{11}AsCH_3^-$, which may be precipitated as the salt of a large cation.

Boron nmr of $(CH_3)_4NB_{10}H_{11}AsCH_3$ (VI, Figure 4) is in a C_s 2:2:2:2:1:1 pattern. Thus the bridging proton in this anion either could be on the mirror plane (proposed structure: Figure 5) or could be rapidly tautomerizing in solution. Resonances in the proton nmr of VI appear at τ 6.62 (12 H) and 7.99 (3 H), assignable to the tetramethylammonium and methyl protons, respectively.

Compound VI is easily converted to V in high yield by dissolving it in acetonitrile-water, acidifying, and extracting with diethyl ether. Compound V is demethylated in high yield to I by sodium in liquid ammonia. The boron nmr spectrum of this product is identical with that of authentic $B_{10}H_{12}As^-$. Thus samples of impure I may be purified by methylation to V, purification of V by vacuum sublimation, and subsequent demethylation of pure V.

We wished to see if using mild base with decaborane in THF could be extended as a synthetic method to substituted arsines. Thus $C_6H_5AsCl_2$ reacts with decaborane in THF in the presence of 2 equiv of triethylamine to produce $B_{10}H_{12}AsC_6H_5$ (VII, mp 145–146°) in 5% yield. We had tried unsuccessfully to synthesize VII by both the NaH and $NaBH_4$ methods cited earlier.

As expected, VII is very similar in physical and chemical properties to $B_{10}H_{12}PC_6H_5$.[6] Its boron nmr spectrum (see Experimental Section) is quite similar to that of the methyl analog and is in the familiar C_s pattern. Proton nmr shows a multiplet at τ 2.4, assigned to the phenyl protons. The low-resolution mass spectrum cuts off at *m/e* 274 corresponding to the parent ion $^{11}B_{10}H_{17}{}^{12}C_5{}^{75}As^+$.

Like its methyl analog, a proton on VII can be readily removed and replaced. The boron nmr spectrum (see Experimental Section) of $(CH_3)_4NB_{10}H_{11}AsC_6H_5$ (VIII) is very similar to that of the methyl analog VI. The proton nmr spectrum shows a complex multiplet centered at τ 2.7 (5 H) and a singlet at τ 6.66 (12 H), assigned to the phenyl and tetramethylammonium protons, respectively.

We are currently exploring some of the chemistry of 1,2-$B_{10}H_{10}As_2$ and the transition metal chemistry of $B_{10}H_{12}As^-$, as well as extending our synthetic method to group V elements other than arsenic, and will report our results later.

Experimental Section

Boron (^{11}B) nmr spectra at 70.6 MHz were obtained with a Varian HR-220 spectrometer and are externally referenced to $(C_2H_5)_2O \cdot BF_3$. Proton nmr spectra were obtained with a Varian A-60A or HR-220 spectrometer. Carbon, hydrogen, boron, and arsenic analyses and osmometric molecular weight determinations were performed at Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Analytical data of all compounds are summarized in Table I. Low-resolution mass spectra were obtained with an Atlas CH-7 instrument. Infrared spectra were obtained with the Perkin-Elmer 621 instrument. Spectra were obtained from KBr disks and spectral intensities were reported as very strong (vs), strong (s), medium (m), or weak (w). Gas-phase chromatographic analyses were carried out with an HP 700 laboratory chromatograph employing a 4-ft column ($^1/_4$-in. diameter) packed with 10% SE-30 gum on 90% 60–80 mesh Chromosorb P.

---

(11) W. H. Knoth, *J. Amer. Chem. Soc.*, **89**, 1274 (1967).

(12) W. R. Hertler, F. Klanberg, and E. L. Muetterties, *Inorg. Chem.*, 6, 1696 (1967).

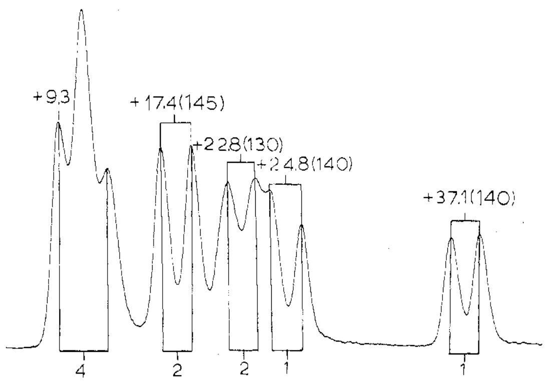

Figure 4. Boron (^{11}B) nmr of $(CH_3)_4$N-7-$B_{10}H_{11}AsCH_3$ (acetone-d_6) at 70.6 MHz. The numbers above are δ in ppm (J_{BH} in Hz) relative to $BF_3 \cdot O(C_2H_5)_2$, while the numbers below are relative areas.

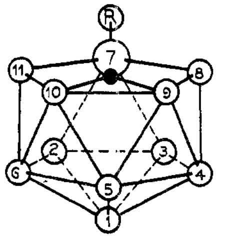

Figure 5. A proposed structure for 7-$B_{10}H_{11}AsR^-$ (R = CH_3 or C_6H_5). Each boron has a terminal H not shown, and the bridging H is shown as a black circle.

Liquid chromatography was carried out employing a Waters Associates ALC 201 with Poragel PS as the column-packing material. Melting points were obtained in evacuated, sealed capillaries and are uncorrected.

All preparations were carried out in a nitrogen atmosphere. Tetrahydrofuran (THF) was distilled from lithium hydroaluminate under an inert atmosphere. Arsenic trichloride ($AsCl_3$) was distilled prior to use. Decaborane was vacuum sublimed. All other reagents were used as received.

$(CH_3)_4NB_{10}H_{12}As$ (I). Method A. Anhydrous diethyl ether (100 ml) and $NaBH_4$ (12.2 g) were added to a 500-ml three-necked flask flushed with nitrogen and fitted with a pressure-equalized dropping funnel, overhead stirrer, and reflux condenser. $B_{10}H_{14}$ (12.2 g) was dissolved in diethyl ether in the dropping funnel and the solution was added dropwise with stirring. Then 12.6 ml of $AsCl_3$ in Et_2O was added dropwise over several hours and the solution was stirred and refluxed for about 2 days until the ceasing of the H_2 gas evolution. H_2O was then added very slowly. (*Caution*! Adding water too fast can cause a violent reaction.) The solvent was then removed *in vacuo* leaving a brown solid, which was extracted with water, and the extract was precipitated with aqueous tetramethylammonium chloride solution. The crude product was chromatographed on silica gel, eluting first with 10% acetone–90% ethanol and then with 30% acetone–70% ethanol. The white compound from the second chromatographic fraction was crystallized from acetone–methanol to give 9.2 g of $(CH_3)_4NB_{10}H_{12}As$ (34% yield).

Method B. To a 500-ml three-necked flask fitted with two pressure-equalized dropping funnels, magnetic stirrer, reflux condenser, and nitrogen inlet were added 2.4 g of $B_{10}H_{14}$ as a fine powder, 200 ml of THF, and 2.6 g of Zn dust. From one dropping funnel was added 14 ml of $(C_2H_5)_3N$ and the solution was stirred for a few minutes. Then from the other dropping funnel was added very slowly 3.4 ml of $AsCl_3$. After addition was complete, the solution was stirred at reflux for 24 hr. The solvent was removed *in vacuo* and the tacky red-brown residue was extracted several times with benzene to remove the 1,2-$B_{10}H_{10}As_2$ (*vide infra*). Extraction was then carried out with 10% NaOH solution, any solids were removed by filtration, and the solution was precipitated with tetramethylammonium chloride solution. The crude product was chromatographed on silica gel as described in part A followed by recrystallization from acetone–methanol to give 0.788 g (14.8% yield).

The infrared spectrum shows λ_{max} at 2520 (vs), 1473 (vs), 1100 (w), 1020 (s), 990 (m), 945 (s), 770 (w), 720 (w), and 705 (w) cm^{-1}.

The proton nmr spectrum (acetone-d_6 solution) shows a very sharp singlet at τ 6.6 ($(CH_3)_4N^+$).

1,2-$B_{10}H_{10}As_2$ (II). Method A. $(CH_3)_4NB_{10}H_{12}As$ (7.5 g) and 100 ml of THF were added to a three-necked flask fitted with reflux condenser, magnetic stirring bar, and two dropping funnels, one charged with 9.7 ml of triethylamine and the other with 2.5 ml of arsenic trichloride. With stirring the triethylamine was added rapidly and then the arsenic trichloride was added slowly. The mixture was then refluxed and stirred overnight. The solvent was then removed *in vacuo* and the product mixture was extracted with several 25-ml portions of benzene. All benzene fractions were combined and evaporated and the solid residue was sublimed at 110° and recrystallized from toluene or benzene to give 2.20 g (29% yield).

Method B. The benzene solution obtained in method B of the $(CH_3)_4NB_{10}H_{12}As$ synthesis was treated the same as the benzene solution in method A above to give 0.8 g (15.3% yield, mp 222–224°).

The infrared spectrum shows λ_{max} at 2550 (vs), 995 (s), 915 (w), 900 (m), 885 (m), 840 (m), 755 (m), 720 (s), 650 (w), 600 (w), and 420 (w) cm^{-1}.

$(CH_3)_4NB_9H_{10}As_2$ (III). To a 100-ml three-necked flask were added 1.00 g of 1,2-$B_{10}H_{10}As_2$ and 25 ml of piperidine. After stirring at room temperature overnight, the piperidine was removed *in vacuo* and the solid residue was dissolved in acetone. After filtration to remove any solids, water and then tetramethylammonium chloride solution were added to the acetone solution. The tetramethylammonium salt was recrystallized from acetone–methanol to give 1.09 g (85.9% yield).

The infrared spectrum includes absorptions at λ_{max} (KBr phase) 2450 (vs), 1440 (s), 980 (s), 935 (s), 760 (m), 720 (m), 615 (w), and 510 (m) cm^{-1}.

The proton nmr spectrum (acetone-d_6 shows a sharp singlet at τ 6.62 ($(CH_3)_4N^+$).

$(CH_3)_4NB_{11}H_{11}As$ (IV). Method A. Two grams of $CsB_{10}H_{12}As$ was pyrolyzed under nitrogen at 350–370° for 1 hr. The pyrolysate was dissolved in hot water and precipitated with $(CH_3)_4NCl$ solution. The precipitate was dried and liquid chromatographed, using 70% acetonitrile–30% water, with Poragel PS (Waters Associates) as the column-packing material to obtain 0.108 g (yield 12.7%).

Method B. Triethylamine–borane was prepared by dissolving 2.5 g of dried triethylammonium chloride and 1.5 g of $NaBH_4$ in diglyme and stirring at 95° overnight. Then 1.24 g of $(CH_3)_4NB_{10}H_{12}As$ was added and the solution was refluxed for 3 days. The diglyme was then removed *in vacuo* and the solids were recrystallized from acetone to obtain 0.67 g of $(CH_3)_4NB_{11}H_{11}As$ (52% yield).

The infrared spectrum includes absorptions at λ_{max} 2520 (vs), 1415 (w), 1025 (s), 945 (s), 865 (w), 725 (m), and 655 (w) cm^{-1}.

The proton nmr spectrum (acetone-d_6) shows a very sharp singlet at τ 6.6 ($(CH_3)_4N^+$). The boron (^{11}B) nmr spectrum at 70.6 MHz (DMF) exhibits doublets at −8.0 (1 B, J_{BH} = 135 Hz), 7.6 (5 B, J_{BH} = 125 Hz), and 8.6 ppm (5 B, J_{BH} = 140 Hz).

$B_{10}H_{12}AsCH_3$ (V). $(CH_3)_4NB_{10}H_{12}As$ (2.00 g) in THF was treated in reflux with methyl iodide (1.0 ml) for 24 hr. The solvent was removed and the solid residue was sublimed at 80° to obtain 1.19 g (76% yield). Purer product may be obtained by resublimation, first collecting a fraction at 50° and then collecting at 35° (mp 113–115°).

The infrared spectrum includes absorption at λ_{max} 2550 (s), 1240 (m), 1075 (m), 1005 (s), 970 (s), 905 (w), 925 (w), 820 (m), 760 (m), 640 (w), and 485 (w) cm^{-1}.

The proton nmr spectrum ($CDCl_3$ solution) shows a very sharp singlet at τ 7.9 ($AsCH_3$). The boron (^{11}B) nmr spectrum at 70.6 MHz (chloroform) exhibits resonances at (J_{BH} in parentheses) −4.6 (1 B, 145 Hz), 2.3 (2 B, 170 Hz), 4.7 (2 B, 165 Hz), 14.3 (2 B, 155 Hz), 17.4 (1 B, 160 Hz), and 23.4 ppm (2 B, 150 Hz), externally referenced to $BF_3 \cdot O(C_2H_5)_2$.

Demethylation of $B_{10}H_{12}AsCH_3$. $B_{10}H_{12}AsCH_3$ (0.31 g) was dissolved in liquid ammonia to form a pale yellow solution. Small pieces of sodium were added until the blue color persisted. The ammonia was allowed to evaporate and the solid residue was dissolved in water and precipitated with tetramethylammonium chloride solution. Recrystallization from acetone–methanol gave 0.355 g of $(CH_3)_4NB_{10}H_{12}As$ (90% yield).

$B_{10}H_{12}AsC_6H_5$ (VII). Decaborane (7.3 g) was added to a 250-ml three-necked flask containing 100 ml of THF and fitted with a pressure-equalized dropping funnel and a mechanical stirrer. Triethylamine (19 ml) was added by syringe and then $C_6H_5AsCl_2$ (10 g) was added slowly from the dropping funnel with stirring. The solution was refluxed 24 hr, the solvent removed *in vacuo*, and the residue dissolved in dilute NaOH solution. Precipitation was carried out with tetramethylammonium chloride solution and the crude solid was isolated by filtration and air-dried. The crude solid was dissolved in acetonitrile and passed through oven-dried (100°), strongly acidic ionexchange resin using acetonitrile as eluent. The acetonitrile was removed *in vacuo* and the residue sublimed at 40–45° to obtain 0.764 g (4.3 % yield, mp 145–146°).

The infrared spectrum (KBr phase) includes absorptions at λ_{max} 2545 (vs), 1570 (m), 1470 (s), 1435 (s), 1375 (m), 1320 (m), 1300 (w), 1260 (w), 1070 (m), 1060 (m), 1010 (s), 990 (s), 970 (s), 930 (m), 905 (m), 810 (m), 780 (m), 755 (m), 725 (s), 700 (m), 675 (s), 640 (w), 440 (m), and 390 (w) cm^{-1}.

The proton nmr spectrum ($CDCl_3$ solution) shows only a broadened resonance at τ 2.4 due to the C_6H_5 group. The boron nmr spectrum at 70.6 MHz (chloroform) exhibits resonances at (J_{BH} in parentheses) −4.4 (1 B, 140 Hz), 1.7 (2 B, 170 Hz), 5.6 (2 B, 165 Hz), 14.2 (2 B, 150 Hz), 17.7 (1 B, 155 Hz), and 23.3 ppm (2 B, 150 Hz), externally referenced to $BF_3 \cdot O(C_2H_5)_2$.

$(CH_3)_4NB_{10}H_{11}AsR$ (R = CH_3 (VI) or C_6H_5 (VIII)). $B_{10}H_{12}AsR$ was dissolved in 4 *M* NH_3 and precipitated with tetramethylammonium chloride solution. The precipitate was crystallized under a nitrogen blanket from 95% ethyl alcohol (yield 90–95%).

The infrared spectrum of $(CH_3)_4NB_{10}H_{11}AsCH_3$ indicates absorption at λ_{max} 3025 (w), 2520 (vs), 1475 (s), 1410 (w), 1315 (w), 1280 (w), 1245 (m), 1010 (m), 985 (m), 945 (s), 445 (w), and 410 (w) cm^{-1}, while that of $(CH_3)_4NB_{10}H_{11}C_6H_5$ includes absorptions at λ_{max} 3020 (m), 2500 (vs), 1475 (vs), 1440 (m), 1430 (s), 1410 (w), 1290 (w), 1270 (w), 1050 (s), 1000 (s), 980 (s), 935 (s), 725 (s), 680 (s), 550 (w), 520 (w), 465 (m), 430 (m), and 415 (m) cm^{-1}.

The proton nmr spectrum of $(CH_3)_4NB_{10}H_{11}AsCH_3$ (acetone-d_6) consists of a very sharp singlet (12 H) at τ 6.62 ($(CH_3)_4N^+$) and a singlet (3 H) at τ 7.99 (CH_3), while that of the phenyl derivative (acetone-d_6) consists of a sharp singlet at τ 6.66 ($(CH_3)_4N^+$) and a multiplet (5 H) centered at τ 2.7 (C_6H_5). The boron nmr spectrum at 70.6 MHz of $(CH_3)_4NB_{10}H_{11}AsC_6H_5$ (acetone-d_6) includes resonances at (J_{BH} in parentheses) 10.5 (2 B, 145 Hz), 17.1 (2 B, 150 Hz), and 36.8 ppm (1 B, 140 Hz), externally referenced to $BF_3 \cdot O(C_2H_5)_2$.

Acknowledgments. The authors gratefully acknowledge support by The Research Corp. We thank Professor L. J. Todd and coworkers (Indiana University) for the 70.6-MHz boron spectra and Dr. John H. Kindsvater for advice on liquid chromatography.

Registry No. I, 51292-89-8; II, 51292-90-1; III, 51668-00-9; IV, 51292-92-3; V, 51358-36-2; VI, 51292-94-5; VII, 51358-38-4; VIII, 51292-96-7; $B_{10}H_{14}$, 17702-41-9; $AsCl_3$, 7784-34-1; $CsB_{10}H_{12}As$, 51292-97-8; CH_3I, 74-88-4; $C_6H_5AsCl_2$, 696-28-6.

Contribution No. 2359 from the Department of Chemistry,
Indiana University, Bloomington, Indiana 47401

Chemical and Nuclear Magnetic Resonance Studies of the $B_9H_{12}^-$ and $B_9H_{12}S^-$ Ions

A. R. SIEDLE,[1a] G. M. BODNER,[1b] A. R. GARBER, and L. J. TODD*

Received December 20, 1973 AIC30910O

The 70.6-MHz ^{11}B nmr spectra of labeled $B_9H_{12}S^-$ derivatives indicate that a rearrangement process occurs during the formation of this thiaborane from decaborane(14). Treatment of $B_9H_{13} \cdot S(C_2H_5)_2$ or $B_9H_{12}^-$ with ammonium polysulfide forms $B_9H_{12}S^-$. Similar rearrangement of labeled molecules is also observed in these latter two chemical transformations. A unified mechanism which explains all the observed rearrangement reactions is proposed.

Introduction

Exclusive of the carboranes, the chemistry of nine-atom boranes and heteroatom boranes may be divided into three broad categories: (1) synthesis and reactions of the two neutral, isomeric B_9H_{15} hydrides,[2-7] (2) degradative reactions of decaborane to form $B_9H_{12}^-$,[8] $B_9H_{14}^-$,[9] and $B_9H_{13} \cdot$ligand species,[10,11] (3) insertion of heteroatoms into the B_9 framework to form $B_9H_{12}S^-$ and $B_9H_{12}NH^-$ [12] and metalloboranes such as $(R_3P)_2Pt(B_9H_{11} \cdot \text{ligand})$[13] and $(CO)_3Mn(B_9H_{13})^-$.[14] We have recently reported specific positional assignments of the ^{11}B nuclear magnetic resonance spectra of complex boron hydride species such as $B_{10}H_{13}^-$,[15] $B_{10}H_{15}^-$,[16] and $B_9H_{13} \cdot$ligand.[17] This paper reports the results of a 70.6-MHz ^{11}B nmr spectral study of $B_9H_{12}^-$, $B_9H_{12}S^-$, and their labeled derivatives.

Experimental Section

The ^{11}B nmr spectra were measured on equipment consisting of a pulsed nmr apparatus built in this department operating at 70.6 MHz, a Varian 51.7-kG superconducting magnet, and a 20K Nicolet 1080 series computer. Additional details have been reported elsewhere.[18] The ^{11}B nmr spectra were externally referenced to $BF_3 \cdot O(C_2H_5)_2$. Acetonitrile was the solvent for all ^{11}B nmr spectra except that of $B_9D_4H_{11} \cdot S(C_2H_5)_2$ where acetone was used. The proton nmr spectra were obtained with a Varian HR-220 spectrometer.

The method of Hertler and coworkers[12] was used to convert $B_{10}H_{14}$, 1,2,3,4-$B_{10}D_4H_{10}$, μ_4,5,6,7,8,9,10-$B_{10}D_{10}H_4$, and 2-$BrB_{10}H_{13}$ to $CsB_9H_{12}S$, $CsB_9D_4H_8S$, $CsB_9D_8H_4S$, and $(C_2H_5)_4N[B_9BrH_{11}S]$, respectively.

Synthesis of $(C_2H_5)_4N[B_9BrH_{11}S]$ from $B_9BrH_{12} \cdot S(C_2H_5)_2$. To a solution of 0.3 g of $BrB_9H_{12} \cdot S(C_2H_5)_2$[17] in 10 ml of warm ethanol was added 1 ml of a 10% aqueous ammonium polysulfide solution. The mixture was warmed at 65° on a steam bath for 15 min, then cooled, and filtered. Saturated aqueous tetraethylammonium bromide, 5 ml, and acetonitrile, 5 ml, were added. Small amounts of

---

(1) (a) NDEA Title IV Fellow, 1972; Procter and Gamble Fellow, 1972–1973; (b) NASA Predoctoral Fellow, 1969–1972.

(2) J. Dobson, P. C. Keller, and R. Schaeffer, *Inorg. Chem.*, 7, 399 (1968).

(3) J. Dobson and R. Schaeffer, *Inorg. Chem.*, 7, 402 (1968).

(4) D. B. MacLean, J. D. Odom, and R. Schaeffer, *Inorg. Chem.*, 7, 408 (1968).

(5) P. C. Keller and R. Schaeffer, *Inorg. Chem.*, 9, 390 (1970).

(6) A. B. Burg and R. Kratzer, *Inorg. Chem.*, 1, 725 (1962).

(7) W. V. Kotlensky and R. Schaeffer, *J. Amer. Chem. Soc.*, 80, 4157 (1958).

(8) B. M. Graybill, J. K. Ruff, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 83, 2669 (1961).

(9) L. E. Benjamin, S. F. Stafiej, and E. A. Takacs, *J. Amer. Chem. Soc.*, 85, 2674 (1963).

(10) B. M. Graybill, A. R. Pitochelli, and M. F. Hawthorne, *Inorg. Chem.*, 1, 626 (1962).

(11) E. L. Muetterties and W. H. Knoth, *Inorg. Chem.*, 4, 1498 (1965).

(12) W. R. Hertler, F. Klanberg, and E. L. Muetterties, *Inorg. Chem.*, 6, 1696 (1967).

(13) A. R. Kane, L. J. Guggenberger, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 92, 2571 (1970).

(14) J. W. Lott, D. F. Gaines, H. Shenhav, and R. Schaeffer, *J. Amer. Chem. Soc.*, 95, 3042 (1973).

(15) A. R. Siedle, G. M. Bodner, and L. J. Todd, *J. Inorg. Nucl. Chem.*, 33, 3671 (1971).

(16) R. R. Rietz, A. R. Siedle, R. O. Schaeffer, and L. J. Todd, *Inorg. Chem.*, 12, 2100 (1973).

(17) G. M. Bodner, F. R. Scholer, L. J. Todd, L. E. Senor, and J. C. Carter, *Inorg. Chem.*, 10, 942 (1971).

(18) A. Allerhand, D. Doddrell, and R. Komoroski, *J. Chem. Phys.*, 55, 189 (1971).