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Methyltetraboranes. I. 2-Methyl and 1,2-, 2,2-, and 2,4-Dimethyl Derivatives[1]

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Reaction between (dimethyl ether)–triborane(7) and 1,2-dimethyldiborane(6) gave an improved synthesis for 2-methyltetraborane(10). The isomeric 1,2-, 2,2-, and 2,4-dimethyltetraborane(10) derivatives were obtained in the same reaction. The substances were characterized by the glpc separation, by melting point, and by mass spectrometric analysis. Substituent locations were determined by interpretation of the ^{11}B nmr spectrum. Uniquely characteristic intensities for bridge stretching frequencies in the infrared spectra were found for each substance, as were also some characteristic relative abundances observed in the high-resolution mass spectra.

Introduction

Numerous exchange experiments show a lability of structure in many boranes with respect to the wandering of the constituent atoms.[3] This diminishes the prospect that isotopic labeling can be widely successful in the diagnosis of mechanism in boron hydride reactions; indeed there are few examples,[4] and these illustrate the limitation just cited. Less mobile markers might be found in the form of alkyl substituents of which methyl groups seem most convenient. To that end a program has been in progress for synthesis and characterization of methyl derivatives from the more reactive higher boranes with the results reported here as the most recent examples. Previously pentaborane(11) was methylated by a process based upon the isotopic exchange between that hydride and diborane(6).[5] The hypothesis of diminished mobility appeared supported by the methylation being confined to the 2,5 positions. That the mechanism might be traced was indicated by products of base-promoted conversions of 2-methylpentaborane(11). Possibly a methylhexaborane(10) was formed with diethyl ether,[5] and more definitely with water[6] there was prepared a methyltetraborane(10) apparently different from the one made previously by exchange.[5]

Neither the hydrolysis nor the exchange reactions could be expected to yield large amounts of methyltetraborane isomers as expeditiously as might some other method, and moreover other syntheses which were independent of the routes used for examining mechanisms would have a certain merit for matching purposes. The utility of the exchange process was limited by the low yield (8%) compared with the higher one (64%) found for pentaborane(11). This becomes understood when the isotopic exchange processes are examined in detail. The fraction of exchange from deuteriodiborane proposed to proceed by a path involving boron atom exchange[7] was only about 10% of the total for tetraborane(10) with a rate constant at 30.4° of 2.5×10^{-3} l.$^{1/2}$ (g-atom)$^{-1/2}$ min^{-1} compared with 8.6×10^{-2} l.$^{1/2}$ (g-atom)$^{-1/2}$ min^{-1} for pentaborane(11) exchange.[3] Accordingly any management of the exchange process in hope of higher yield would be fruitless, and need for a new method was apparent.

Results and Discussion

Preparative Data.—A process based upon the generation of triborane(7) and its subsequent reaction with 1,2-dimethyldiborane(6) was considered likely to give 2-methyltetraborane(10). The second step would be analogous to the one proposed for the assimilation of borane by tetraborane(8) in the exchange with pentaborane(11).[3] For this there was tried (dimethyl ether)–triborane(7)[8] from which triborane(7) might be formed by dissociation of the adduct or through abstraction of the base by a stronger acid such as boron trifluoride. In the latter case 2-methyltetraborane(10) was the only tetraborane derivative formed (45–53% yield), together with other boranes believed to be decomposition products of triborane(7).

Without an abstracting acid quite another result was obtained. A reaction at −16% between 1,2-dimethyldiborane(10) and (dimethyl ether)–triborane(7), which proceeded faster than the dissociation of the adduct, gave not only 2-methyltetraborane(10) (43.3%), but also three of the four possible isomeric dimethyltetraboranes—the 1,2- (10.2%), 2,4- (23.1%), and 2,2-dimethyl (3.2%) derivatives. Formation of any of these products, even 2-methyltetraborane, through adduct dissociation seems improbable. Instead competitive displacement reactions appear most likely. The products will then be determined by the leaving group. When this is the ether, the residue is effectively triborane(7), which will assimilate methylborane from the attacking molecule. When the leaving group is (dimethyl ether)–borane, the whole attacking molecule becomes assimilated, and whether the product becomes

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(1) Research supported by funds from National Science Foundation Grants GP-3459 and GP-7888.

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(3) W. S. Koski, "Borax to Boranes," Advances in Chemistry Series, No. 32, American Chemical Society, Washington, D. C., 1961, p 78.

(4) R. Schaeffer and R. O. Buttlar, Technical Note 59–258, Wright-Air Development Center, July 1959; R. Schaeffer and F. N. Tebbe, *J. Am. Chem. Soc.*, **84**, 3974 (1962).

(5) C. A. Lutz and D. M. Ritter, *Can. J. Chem.*, **41**, 1344 (1963).

(6) D. A. Phillips and D. M. Ritter, unpublished research.

(7) J. E. Todd and W. S. Koski, *J. Am. Chem. Soc.*, **81**, 2319 (1959).

(8) W. R. Deever and D. M. Ritter, *Inorg. Chem.*, **7**, 1036 (1968).

1,2- or 2,4-dimethyltetraborane may depend upon the stereoconfiguration of the transition state. As partial support for such a view another somewhat similar method,[9] where 1,2-dimethyldiborane attacks bis(trifluorophosphine)–diborane(4), gives a different proportion of products: tetraborane(10) (15.3%), 2-methyltetraborane (7.6%), and the 1,2- (22%), 2,4- (21%) and 2,2-dimethyl (7.6%) isomers. The lesser yield of monosubstituted species in the latter case and its exclusive formation in the procedure assisted by acid abstraction suggests the need for triborane(7) as an intermediate in the formation of 2-methyltetraborane. A small departure from the expected methyl group immobility is demonstrated by the appearance of 2,2-methyltetraborane(10) among the products. In the reaction with bis(trifluorophosphine)–diborane(4) formation of the minor amount of 2-methyltetraborane(10) and of somewhat more tetraborane(10) along with the 2,2 isomer must also be the result of methyl group transfer.

Characterization.—The composition and structure of the methylated tetraboranes were established through the correlative application of glpc parameters, melting points, and mass spectra as criteria for purity, of mass spectra for establishing molecularity and composition, and of nmr for determination of structure. Additionally some correlations appear possible in which intensities for high-resolution mass spectra and infrared spectra are linked with identity and structure.

The glpc process as described in this paper has a separation efficiency equivalent to a distillation column of 600–800 theoretical plates.[10] While this is enough to ensure separation of 2-methyltetraborane as a pure substance, as corroborated by the sharp melting point, the isomeric dimethyltetraboranes have retention times so closely spaced that multiple passes and peak-splitting were required for their separation. Nevertheless, the smooth, uninflected shapes of the final elution curves for the individual components showed the separation to be completed. The sharpness of the melting point for the 2,4 isomer gave additional assurance of its purity, but the chance to make this observation for the 1,2 isomer was lost because it would not crystallize, and the 2,2 isomer was obtained in too small quantity to obtain a good ring of crystals. As will be seen, the shapes of the ^{11}B nmr peaks give additional evidence that the samples dealt with have been those of pure substances.

The mass spectrum of 2-methyltetraborane has been described previously,[5] and the low-resolution polyisotopic spectra for the dimethyltetraboranes are given in Table I. These can be reduced to monoisotopic spectra found in Table II where the small value for R shows the purity of the sample and the correctness of the formulas.

There is a regularity to be found in the mass spectra of most boron hydrides, which might be called the $M - 2$ rule, whereby the first mass spectrometric abundance of significant intensity is found at two mass units below the parent mass.[11] Accordingly the molecular weights of monomethyltetraborane and the dimethyltetraboranes are correctly 68 and 82, respectively.

TABLE I
POLYISOTOPIC MASS SPECTRA OF THE DIMETHYLTETRABORANES

Mass no. *m/e*	Rel abundances			Mass no. *m/e*	Rel abundances		
	2,4	1,2	2,2		2,4	1,2	2,2
82	0.4	0.2	0.3	45	1.5	4.3	3.5
81	0.7	0.2	0.3	44	0.9	1.5	1.3
80	4.5	5.4	2.9	43	1.9	3.4	2.3
79	13.8	9.1	5.6	42	3.9	3.0	2.3
78	96.5	97.9	42.5	41	100.0	78.6	63.4
77	88.8	100.0	41.7	40	51.5	29.6	31.0
76	40.0	73.4	22.1	39	22.1	13.9	16.7
75	13.0	47.0	10.0	38	20.6	15.8	21.0
74	5.9	53.4	7.8	37	31.2	32.4	31.0
73	9.1	49.5	6.8	36	16.2	17.4	15.9
72	2.5	41.0	5.1	35	4.7	5.5	4.9
71	1.7	31.4	3.8	34	1.3	1.7	1.4
70	1.1	20.3	2.4	33	0.5	0.3	0.3
69	1.5	13.0	2.2	32			0.2
68	0.8	7.4	1.3	31			0.2
67	2.5	5.1	2.3	30			0.1
66	21.7	14.5	13.2	29	1.0	0.7	1.0
65	31.5	28.1	19.5	28	4.1	2.7	5.4
64	49.8	47.4	34.1	27	72.7	61.5	100.0
63	45.2	45.3	33.0	26	33.4	29.7	52.0
62	32.6	55.0	28.0	25	7.5	7.8	13.7
61	18.7	42.5	21.6	24	4.5	5.1	9.1
60	8.6	25.4	11.8	23	0.5	2.0	3.6
59	5.6	22.6	8.4	22		0.2	0.5
58	3.6	17.3	5.5	21			
57	2.5	12.3	4.0	20			
56	3.1	5.3	1.8	19			
55	1.5	3.5	1.8	18		0.6	
54	1.1	1.9	1.4	17			
53	9.3	6.7	6.5	16	1.0	0.8	1.1
52	66.0	46.6	43.0	15	1.2	1.1	2.2
51	63.3	47.5	44.6	14	0.5	0.4	0.7
50	56.6	47.6	44.3	13	1.9	1.9	5.3
49	44.9	45.6	39.6	12	0.7	0.8	1.3
48	27.6	40.4	26.1	11	2.3	2.0	2.9
47	13.3	26.5	15.8	10	0.6	0.5	0.7
46	5.1	12.2	6.2				

A few ions were observed under high resolution to compare isomers. The need for a mass spectrometric identification was particularly critical in the case of the isomer which was finally classified as 2,2, because too little of that substance was available for the more certain ^{11}B nmr structure determination. Because the 1,2 and 2,4 substitutions could be distinguished by nmr, the method was tested by high-resolution mass spectrometric examination of some crucial ions from those substances. As can be seen from the ion abundances in Table III, there are differences, many of which have qualitatively the relative relation to be expected as judged by the number of bonds which must be broken to produce the ions. The ion BH_3^+ should surely be more available from the 1,2-substituted molecule with a terminal BH_2 than from the 2,4 isomer with none, and

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[9] W. R. Deever, E. R. Lory, and D. M. Ritter, *Inorg. Chem.*, **8**, 1263 (1969).

[10] G. R. Seely, J. P. Oliver, and D. M. Ritter, *Anal. Chem.*, **31**, 1993 (1959).

[11] I. Shapiro, C. O. Wilson, J. F. Ditter, and W. J. Lehmann, "Borax to Boranes," Advances in Chemistry Series, No. 32, American Chemical Society, Washington, D. C., 1961, p 127.

TABLE II
PARTIAL MONOISOTOPIC MASS SPECTRA OF DIMETHYLTETRABORANES

Mass no.	Rel abundances		
m/e	2,4	1,2	2,2
82	0.5	0.1	0.7
81	0.2	0.0	0.1
80	4.6	5.6	6.9
79	9.3	2.0	5.0
78	100.0	100.0	100.0
77	0.0 (−0.4)	5.9	4.6
76	8.6	35.2	14.2
75	0.2	6.2	3.3
74	3.0	36.7	10.4
73	1.1	11.6	4.9
72	0.6	17.8	4.0
71	0.8	9.2	3.2
70	0.2	5.1	1.0
69	1.3	4.3	1.1
68	0.0 (−0.4)	1.2	0.0 (−0.2)
R	0.004	0.005	0.002

TABLE III
ABUNDANCE OF HIGH-RESOLUTION MASSES

	Substituent location in $B_4H_8(CH_3)_2$		
Ions	1,2	2,4	2,2
$^{11}BH_3$	0.11	0.03	0.12
$^{10}BCH_4$	6.4		
$^{11}BCH_4$	25.1		
$^{11}BCH_5$	0.49	3.3	
$^{10}BC_2H_6$			12.2
$^{11}BC_2H_6$	0.00	0.00	49.3
$^{11}B_2H_4$	3.3	4.2	18.9
$^{11}B_2CH_7$			12.1
$^{11}B_3H_6$			3.4
$^{11}B_3C_2H_7$	9.4	3.2	
$^{11}B_3C_2H_8$	0.74	0.28	

from the latter with doubled terminal $BHCH_3$ the ion BCH_5^+ should be more abundantly obtainable than from the former with a single terminal $BHCH_3$. The second $B-CH_3$ in the 1,2 isomer would be available only by rearrangement while breaking a B–B bond in addition to two BHB bonds. In neither substance is there a direct source of a BC_2H_n configuration, and none was found, as exemplified by absence of $BC_2H_6^+$ from both spectra. Finally on grounds of adjacency of methyl groups the ions $B_3C_2H_7^+$ and $B_3C_2H_8^+$ should arise in greater abundance from 1,2-dimethyltetraborane than from 2,4-dimethyltetraborane. Concerning the third isomeric dimethyltetraborane, a source of BH_3^+ equally as available as in the 1,2 isomer, and most particularly the almost spectacular abundance of $BC_2H_6^+$, introduced a bias toward selecting the 2,2 substitution as the correct one for the isomer having those features. The ion $BC_2H_6^+$ should be no more available from 1,3-dimethyltetraborane than from the 1,2 and 2,4 isomers. The large abundance of $B_2H_4^+$ found for the candidate isomer, while not predictable for it as larger than the abundance for the 2,4 isomer, is scarcely expected to be characteristic of a parent molecule substituted in the 1,3 positions. Thus some ion populations seem to support a 2,2 assignment and others appear to exclude a 1,3 configuration.

The infrared spectra recorded in Table IV and Figure 1 show that altogether the substitution of methyl groups into tetraborane(10) produces numerous small alterations. Whatever may be the assignments a practical empirical application to identification seems possible. The bands in the 2140-cm^{-1} region furnish unique patterns each characteristic of a particular molecule. The symmetrical tetraborane(10) molecules, the parent and the 2,4 isomer, have essentially a single peak; the peak for the 2-methyl derivative is unequally bifurcated and that for the 1,2-dimethyl derivative is trifurcated. On this basis a 1,3-methyl derivative should have a single peak. Accordingly the bifurcated peak has been ascribed to 2,2-dimethyltetraborane(10). A more detailed interpretation can be attempted with the aid of assignments made for tetraborane by Dahl[12] and for the methyldiboranes by Lehmann and his coworkers.[13] The high frequencies from the stretching modes of the methyl vibrational system vary slightly over the same range, 2834–2961 cm^{-1}, found for the methyldiboranes.[13] Similarly, the intermediate methyl-related frequencies, though laced through or near borane bridge frequencies of similar value, remain separate at 2020–2058, 1425 ± 5, and 1323 ± 4 cm^{-1}. At lower frequencies, however, there appears to be accidental degeneracy between methyl wagging and rocking modes and borane modes of similar description. Unfortunately there has disappeared in this way the BC_2 system seen in the 1,1-dimethyl-, trimethyl-, and tetramethyldiboranes,[13] which would be of prime value in the identification of 2,2-dimethyltetraborane. In tetraborane(10) the band at 2142 cm^{-1} has been assigned to the three modes ν_{13}, ν_{21}, and ν_{30} (dissymmetric bridge vibrations), and 55 cm^{-1} lower lies ν_4, the corresponding ir-inactive totally symmetric bridge vibration.[12] Systematically in this region of the spectra from the 2, 1,2, and 2,2 derivatives, which are of lower symmetry than tetraborane and the 2,4 isomer, there are found the band pairs 2175 and 2114, 2186 and 2104, and 2184 and 2150 cm^{-1}, respectively, with separations averaging 58 cm^{-1}. The lower frequency of each pair may be ν_4 of tetraborane.

Using ^{11}B nmr structures were determined unambiguously for all of the presently known methylated tetraboranes except the one believed on other less certain grounds to be 2,2-dimethyltetraborane(10). Data in Table V disclose that substitution of methyl for hydrogen produces a net reinforcement of the local field at the substituted atom which results in downfield translation of the resonance frequency, and the chemical shift values show that remote effects are produced at other boron atoms. The particular monomethyltetraborane(10) at hand has a spectrum in which roughly half the intensity of the downfield triplet found in the parent molecule has been transferred to a downfield adjacent doublet, thus confirming the placement of the substituent on the 2-boron atom. There is a cor-

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(12) A. J. Dahl, Dissertation, University of Michigan, 1963; *Dissertation Abstr.*, **25**, 2252 (1964).

(13) W. J. Lehmann, C. O. Wilson, and I. Shapiro, *J. Chem. Phys.*, **32**, 1088 (1960); **33**, 590 (1960); **34**, 476, 783 (1961).

TABLE IV
INFRARED FREQUENCIES OF METHYLTETRABORANES (CM^{-1})

Assignments	B_4H_{10}	2-$B_4H_9CH_3$	2,4 $B_4H_8(CH_3)_2$	1,2 $B_4H_8(CH_3)_2$	2,2-$B_4H_8(CH_3)_2$
	4200 w	4200 w	4195 w		
				4060 w	
		3494 w			
	3333 w				
			3090 w, sh		
		3060 w, sh		3066 w, sh	
CH_3 str			2961 ms		
		2950 m		2944 ms	2943 ms
	2920 w				
	2856				
CH_3 str			2857 w, sh	2850 w, sh	2855 w, sh
		2834 w			
BH and BH_2 str	2561 s		2562 s		2559 s
		2551 s		2548 s	
BH_2 str					2494 s
				2467 s	
	2478 s		2481 s		
		2471 s		2467 s	
	2400 w	2380 w	2387 w	2356 w	2355 w
	2256 w	2256 w	2250 w, sh	2262 w, sh	2250 w, sh
				2186 m	2184 s
		2175 s			
			2160 s		
					2150 s
	2142 s				
Bridge str		2114 m, sh			
				2104 s	
CH_3			2075 w, sh		
					2058 w, sh
				2049 m	
		2030 w, sh			
				2020 m, sh	
	1995 w				
BH_2 wag + BH_2 rock	1850 w				
			1830 vw		
Bridge str	1457 w			1486 m	
					1430 m, sh
		1428 m	1420 m	1424 ms	
	1385 s				
CH_3 asym def			1380 w, sh	1379 m	
					1376 ms
		1370 m, sh			
CH_3 sym def		1327 s	1324 s	1319 s	1322 s
BH def	1245 w				
	1190 m, sh	1195 w, sh	1200 vw, b	1185 w, sh	
Skeleton	1155 m, sh	1152 m, sh	1165 vw	1143 m, sh	1143 m, sh, b
BH wag	1140 s				
Ring bend	1116 m, sh				
		1102 s	1093 vs	1094 vs	1088 vs
BH_2 sciss	1070 m	1062 m, b			
				1048 m	
BH_2 wag		990 s	993 s		990 m, b
CH_3 rock				979 s	
	970 s				
BH_2 rock	915 m				
	899 m	895 m, sh	885 m, b, sh	887 m	909 w
BH_2 twist				871 m	
					862 m, b
	848 m	852 s	850 s		
Bridge def	772 w, b	780 w, b		770 w, b	780 w, b

responding dimethyl derivative for which the downfield triplet resonance is replaced by a doublet. This leads to the 2,4 location assignment. In the spectrum of the isomer designated as being 1,2 substituted a singlet resonance appears slightly downfield from the upfield doublet indicating occupation of one of the 1,3-BH locations by methyl while the other remains unsubstituted. The triplet frequency is found to have been transformed in the same manner as in the spectrum of 2-methyltetraborane.

When the remote effects of substitution were treated as neighboring atom contributions according to the

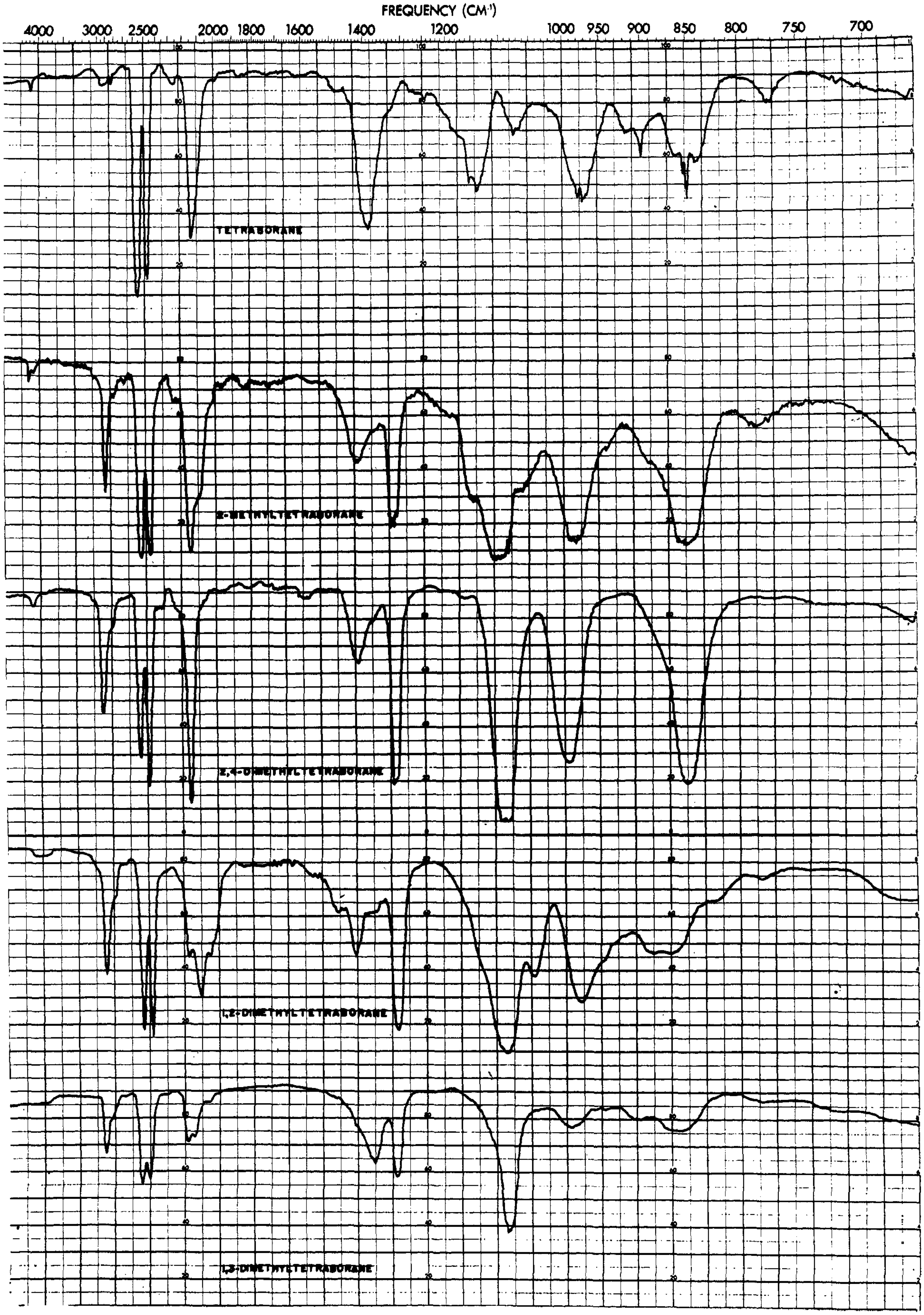

Figure 1.—Infrared spectra of methyltetraboranes.

TABLE V
^{11}B CHEMICAL SHIFTS AND H–^{11}B COUPLING CONSTANTS FOR METHYLTETRABORANES(10)[a]

		Resonance multiplicities				
		t	t′	d_t	d_o	s_d
Substances		BH_2	BH_2'	BHR	BH	BR
B_4H_{10}	δ	6.9			42.0	
	J	131	29		154	
$B_4H_9CH_3$	δ	9.0		−5.5	38.2	
	J	122	30	126	143	
2,4-$B_4H_8(CH_3)_2$	δ			−3.5	34.9	
	J			116	132	
1,2-$B_4H_8(CH_3)_2$	δ	8.6		−6.5	37.9	28.5
	J	122	27	121	159	−(18)

[a] δ in ppm relative to $BF_3 \cdot (C_2H_5)_2O$; J in Hz. t = triplet; d = doublet; s = singlet. H′ represents bridge hydrogen. Subscripts t, d, and o show origins of the resonance frequencies, meaning triplet, doublet, and original, respectively.

formalism deduced by Pople[14] and by McConnell,[15] these were found amplified over the theoretically reasonable values even as was found in the case of ^{13}C chemical shifts in the alkanes.[16] An elaboration of the observations will be the subject of a subsequent publication.

Experimental Section

Standard methods of high-vacuum manipulation were used for transport, separation, and measurement of volatile materials. The glpc columns[17] contained 38 wt % no. 3 white oil on acid-washed, Silaclad-treated[18] firebrick.[19] The columns were conditioned by exposure to chemicals of the type to be separated. The fractional codistillation column was a coiled 122-cm length of 8-mm i.d. Pyrex glass tubing. It was packed with 40 mesh pentane-washed magnesium powder.[20] The trapping and detection systems have been described in ref 17.

Preparations.—Diborane(6) was made by dropping sodium hydroborate into polyphosphoric acid[21] using a screw-feed dispenser.[17] The yields averaged 71%.

Boron trifluoride was purified by formation of the adduct with *p*-chlorobenzonitrile at −30°, where all volatile components were removed; the adduct was decomposed during sublimation at room temperature.[22]

Trimethylborane was prepared from boron trifluoride–diethyl ether adduct and methylmagnesium bromide[23] with special precautions taken to exclude moisture from the system and the reagents to avoid formation of methane. The only impurities, <0.5% diethyl ether and a trace of unidentifiable material, were removed by glpc.

Tetraborane(10) was prepared in the hot–cold reactor[24] and by the reaction of tetramethylammonium trihydroborate(8) and polyphosphoric acid[25] at 40° in the apparatus used for preparing diborane(6). The product was purified during preparation by fractional condensation through a trap cooled to −80° and later by glpc using a preparative column of 3-cm i.d. and 244-cm length.

Monomethyldiborane(6) was prepared in a series of steps beginning with the reaction of diborane(6) and trimethylborane[26] in equimolar proportions (~50 mmol) for 5 days at room temperature in a 5-l. vessel. Monomethyldiborane(6) and trimethyldiborane(6) (3.0 and 9.1 mmol, respectively) were separated on the preparative glpc column (3.0-cm i.d. and 244-cm length) operated at ambient temperature.[10] The remainder of the batch was returned to the preparation flask to reestablish equilibrium. To continue the process equimolar amounts of diborane(6) and trimethyldiborane(6) (9 mmol) were mixed at room temperature for 3 hr. The components were separated by glpc to give (in millimoles) diborane (3.7), monomethyldiborane (3.9), 1,1-dimethyldiborane (8.4), 1,2-dimethyldiborane (0.5), trimethyldiborane (1.4), and trimethylborane (0.2). The monomethyldiborane (6.9 mmol) was purified by glpc at 0° on a column of 1.2-cm i.d. and 122-cm length.

1,2-Dimethyldiborane (0.5 mmol) was found in the original reaction mixture, but separation at that point was inconvenient. Collection of the 0.5 mmol obtained from trimethyldiborane was routine. The bulk of the product was made by a modification of the original dimethyl ether adduct conversion of monomethyldiborane.[27] The base adopted was tetraethylene glycol dimethyl ether (tetraglyme), purified by distillation from lithium hydroaluminate at 114° (1 mm) and then stored under nitrogen and transferred by syringe. The tetraglyme was applied in acetone solvent to Chromosorb P, treated as described for use as a glpc support, to give a coating comprising 40% by weight. The packing was dried in a heated rotary evaporator. The reaction column, with a 1.2-cm i.d. and 200-cm length, was conditioned with diborane using helium as the carrier gas. Monomethyldiborane was vaporized in the chromatograph injection system. It was transported through the base-loaded column at 25° by helium carrier gas at a flow rate of 40–50 ml/min while the course of reaction was monitored by the glpc detector system. The elution curve resembled one obtained in normal glpc. The retention times in minutes were: diborane, 2.2; monomethyldiborane, 4.0; 1,2-dimethyldiborane, 12.0 min. In the interval 9.0–14.5 min almost pure 1,2-dimethyldiborane emerged. The trace of monomethyldiborane and 1,2-dimethyldiborane was removed by glpc.

Formation of Methyltetraboranes.—Mono- and dimethyltetraboranes were prepared from (dimethyl ether)–triborane(7).[8] This was made in a 15-ml Pyrex reaction tube in which 1,2-dimethyldiborane (1.880 mmol) was condensed on the adduct (0.451 mmol) at −196°. The mixture was warmed to −13°. After 30 min the solid adduct disappeared and a clear liquid remained. After 3–6 hr the mixture was separated by glpc on a column 30 cm long and 0.8 cm in diameter into monomethyltetraborane(10) (0.195 mmol, 43.3%), dimethyltetraborane(10) (0.164 mmol, 36.4%), tetraborane (0.045 mmol, 10.4%), diborane, 1,2-dimethyldiborane, and dimethyl ether. Because the isomeric dimethyl derivatives could not be completely separated during a single pass through the gas chromatograph, the composition of the eluent was estimated by comparison of areas on the recording potentiometer trace using a five-channel Du Pont curve analyzer.[28] The isomeric dimethyltetraboranes were separated by repeated passes (15–20) through a glpc column 390 cm long and 0.8 cm in diameter at a helium carrier gas flow rate of 55 ml/min. The retention times were 2.95, 3.20, and 3.45 hr for the 2,4, 1,2, and 2,2, isomers, respectively. The elution curve for 1,2-dimethyltetraborane was a shoulder on the curve for the 2,4 isomer, and the curve for the 2,2-dimethyl derivative was a shoulder on the curve for 1,2-dimethyltetraborane. The composition of the dimethyltetraborane fraction was: 2,4, 63.3%; 1,2, 27.9%; 2,2, 8.7%.

Monomethyltetraborane was prepared exclusively, but in not much greater yield, by conducting the previously described re-

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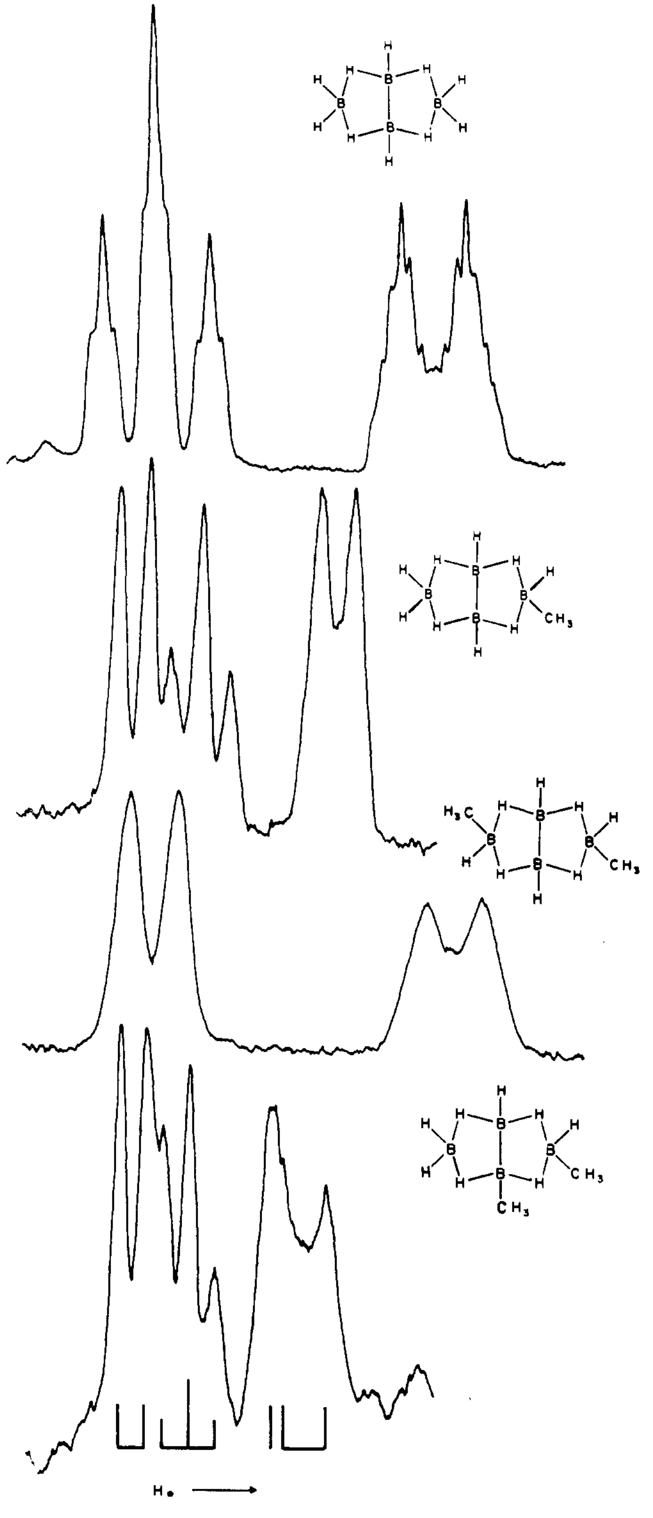

Figure 2. Boron-11 nmr spectra of methyltetraboranes, from top to bottom: tetraborane, 2-methyltetraborane, 2,4-dimethyl-, tetraborane, 1,2-dimethyltetraborane, 1,3-dimethyltetraborane.

action in the presence of born trifluoride. The adduct (0.397 mmol), 1,2-dimethyldiborane (1.603 mmol), and boron trifluoride (0.659 mmol) were kept in a reaction tube (11 ml) at −16° for 4 hr. Without changing the temperature the volatile materials were removed for separation by glpc to give in millimoles tetraborane(10) (0.323) and 2-methyltetraborane (0.212). The yields varied between this 53 and 45%.

Characterization of Methyltetraboranes(10).—**Melting points** were determined by the ring-dropping plunger method.[29] Values obtained for 2-methyltetraborane(10) were −126.1 and −126.0° with reference to the vapor pressure of ethylene. A sample of 2,4-dimethyltetraborane(10) was divided into approximate halves during glpc. Melting points for the first half were −92.7 and −92.5° and for the second half were −92.3 and −92.8° with reference to the vapor pressure of propylene. 1,2-Dimethyltetraborane(10) congealed to a low-melting glass.

Mass spectra were obtained on an AEI Model MS-9 double-focusing spectrometer[30] employing a cooled source (110–140°) and using a carbide-conditioned tungsten filament operated at an ionizing potential of 24 V. Polyisotopic spectra were observed using a low resolving power (1 part in 200) to ensure complete integration of all peaks belonging to a single mass number. The results of the measurements at low resolution are given in Tables I and II. For obtaining the monoisotopic spectrum the $^{11}B:^{10}B$ ratio of 4.00 was used as is customary.[31] A ^{13}C content of 1.108% was assumed. The residual R is a statistic useful in judging the success of the reduction to the monoisotopic representation. $R = \Sigma(N_i^2)^{1/2}/\Sigma I_i$, where N_i is the residual for the ith mass and I_i is the intensity of each peak in the monoisotopic spectrum. Peak assignments for the narrow-scan high-resolution spectra (1 part in 15,000) were made by the mass ratio technique using perfluorotributylamine as the standard. The individual ion abundances were obtained from the peak heights on the recorder trace. The components were normalized to the total abundance for the low-resolution m/e value on a scale where the most abundant low-resolution peak corresponds to a value of 100.

As an additional check for the mass ratio assignment both ^{10}B and ^{11}B ions were surveyed in two cases. They were found to be present in the expected abundance ratio. The results of the measurements are given in Table III.

Boron-11 nmr measurements were made on a Varian Model 4311 high-resolution spectrometer operated at a resonance frequency of 19.25 MHz. The usual side-band technique was used to calibrate the magnetic field scale. Chemical shifts were determined relative to diethyl ether–boron trifluoride observed as an external standard. Some spectra were observed on samples as small as 2 mmol. On such occasions sample tubes were used in which the bottom 5 mm was solid glass. This confined the sample volume to that portion of the tube within the receiver coil region. A sample depth 0.5–1.0 cm gave an excellent spectrum. The ^{11}B spectra for three of the four known methyltetraboranes are shown in Figure 2 and the chemical shifts and coupling constants are collected in Table V. Insufficient material was available for examination of 2,2-dimethyltetraborane.

Infrared spectra were recorded using a Perkin-Elmer Model 21 spectrometer with sodium chloride optics for the range 3000–650 cm^{-1}. The light path length was 5 cm. The frequency scale was calibrated by observing the spectrum of polystyrene film. The uncertainty was estimated at ±5 cm^{-1}. The results for the methyltetraboranes are listed in Table IV, and they are illustrated in Figure 1. Above 1200 cm^{-1} the frequencies for tetraborane recorded on this spectrometer were lower than those recorded by Dahl[12] by about 10 cm^{-1}, twice the estimated uncertainty. Below 1200 cm^{-1} there was agreement within the uncertainty.

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