mixture was warmed to room temperature and stirred overnight in a shielded metal bomb. After 18 h, the reaction mixture was light beige in color. Volatile materials were fractionated through traps at −78, −111, and −196 °C; 6.0 mmol of C_2H_2 was recovered in the −196 °C trap. $(C_2H_5)_2O$ stopped in the −111 °C trap. The −78 °C trap contained 162 mg of *nido*-5,6-$C_2B_8H_{12}$ (9% based on B_5H_9 starting material), which was identified by its ^{11}B NMR[36] and mass spectra.

8. Conversion of B_5H_9 to *n*-$B_{18}H_{22}$. $Na[B_9H_{14}]$ was prepared from 8.30 mmol of NaH (199.3 mg) and 15.0 mmol of B_5H_9 reacting in 10 mL of dry glyme in a 500-mL reaction vessel according to the procedure described in section 1(b). By the use of a procedure reported by Dobson, Keller, and Schaeffer,[7] the $Na[B_9H_{14}]$ was first converted to $B_9H_{13}\cdot O(C_4H_9)_2$, which was then pyrolyzed to form *n*-$B_{18}H_{22}$; 316 mg of *n*-$B_{18}H_{22}$ (35% based on B_5H_9) was isolated.

9. Improved Preparation of $B_{10}H_{14}$ from B_5H_9. This preparation is similar to that reported earlier[1] except that the mole ratio of reactants is 1.8:1:1 B_5H_9:NaH:$[(CH_3)_4N]Cl$ (instead of 2:1:1) and glyme is used as the solvent. In this example, 372.4 mg of NaH (95% active, 14.74 mmol) and 26.3 mmol of B_5H_9 were used as starting material.

Isolation of the product can be achieved either by sublimation (method A) or extraction with *n*-butyl ether (method B).

Method A. The reaction flask was immersed in an oil bath heater, and the U-trap was cooled to 0 °C in an ice bath. While the reaction was pumped under dynamic vacuum (10^{-3} torr), the temperature of the oil bath was slowly raised to 45 °C and maintained there for 3 h. Most of the product sublimed in this step. The temperature was then raised to 110 °C over a period of 3 h. After cooling, the vessel was disassembled and the 938 mg (7.68 mmol) of slightly yellow decaborane(14) was scraped out. This represents a 58.4% conversion from B_5H_9.

Method B. If this method is used it is not necessary to attach the U-trap to the reaction vessel. After H_2 has been pumped away following reaction with BCl_3, 40 mL of dry *n*-butyl ether was added in the drybox. The vessel was again attached to the vacuum line, and the solvent was degassed. The flask was heated to 110 °C over a period of 3–4-h with an oil bath heater. The light yellow solution was filtered. A product yield of approximately 50% was estimated by comparison with ^{11}B NMR samples of standard concentrations.

Acknowledgment. We thank the Army Research Office for support of this work through Grant DAAG29-82-K-0112.

Registry No. B_5H_9, 19624-22-7; $[Me_4N][B_9H_{14}]$, 12545-93-6; $K[B_9H_{14}]$, 39296-28-1; $Na[B_9H_{14}]$, 70865-40-6; $[Me_4N][B_{11}H_{14}]$, 52619-67-7; $B_9H_{13}\cdot O(C_5H_5)_2$, 12545-41-4; $(CH_3)_2S\cdot B_9H_{13}$, 32357-02-1; $(C_5H_5)_2S\cdot B_9H_{13}$, 32356-99-3; $(t\text{-}C_4H_9)_2S\cdot B_9H_{13}$, 99686-00-7; $B_9H_{13}\cdot S(C_6H_5)_2$, 99666-93-0; $B_9H_{13}\cdot P(C_6H_5)_3$, 32235-80-6; $(n\text{-}C_4H_9)_2S\cdot B_9H_{13}$, 99666-94-1; 5,6-$(CH_3)_2$-5,6-$C_2B_8H_{10}$, 31566-09-3; $B_{10}H_{14}$, 17702-41-9; *nido*-5,6-$C_2B_8H_{12}$, 41655-26-9; *n*-$B_{18}H_{22}$, 21107-56-2.

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Methylpentaborane(11): A Mixture of Isomers

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Use of high-field-strength NMR, 500.1 MHz for ^1H and 160.4 MHz for ^{11}B, has shown that preparations previously considered to be $2\text{-}CH_3B_5H_{10}$ and $3\text{-}CH_3B_5H_{10}$ are identical equilibrium mixtures of the two isomers. Through assessment of relative values for areas under the ^1H(C–H) resonance curves, temperature-dependent equilibrium constants and the related thermochemical values have been determined for the isomerization process.

Two preparations have been reported for methylpentaborane(11), $CH_3B_5H_{10}$. The product from the exchange of pentaborane(11) and methyldiboranes was called the 2-methyl derivative[1] (I), and the product from the NH_3/H^+ process applied to methylhexaborane(12) was considered to be the 3-methyl isomer[2] (II). We can now show that the two preparations are very probably identical equilibrium mixtures of isomers having substituent locations at front corners (2 or 5) or back corners (3 or 4) of the trapezoidal-pyramidal base. This conclusion was not reached earlier because prior work[1-3] was handicapped by the necessity of using NMR spectrometers unequal to the task of fully resolving the spectra. In this work, it has been possible to measure spectra at 500.1 MHz for ^1H NMR and at 160.4 MHz for ^{11}B NMR with ^1H decoupling. Consequently the ^{11}B NMR spectra are found dispersed to the point of zero overlap, and the ^1H NMR spectra, though still displaying overlap, can be interpreted with much more certainty than before.

Results and Discussion

Preparations I and II were recognized to be identical when the two were found to have the same ^{11}B NMR spectra at 64 MHz. This is a remarkable result as one would scarcely expect that preparative pathways so different would yield the same product. One proceeds through a gas/liquid-phase molecular exchange reaction and the other via ionic intermediates. Confirmation that samples identical with the original preparation of II were being dealt with can be seen by comparison with ^{11}B NMR spectra taken at 32.1 MHz[2,2b] and at 160.4 MHz as seen in Table I. Even though the field strength is so much reduced, of the eight resonances seen at 160 MHz, six are seen almost identically at 32 MHz.

Table I. ^{11}B Magnetic Resonance Spectra of Methylpentaborane(11) Mixtures

this work[a]			ref 2a[b]		assignts[c] (this work)	
δ	*J*, Hz	rel area	δ	*J*, Hz	2-Me	3-Me
21.0	130	1	20.4		B(2) (d)	
19.4		2				B(3) (s)
8.5	125	3	8.78	122	B(5) (t)	B(5) (t)
1.8	126	2	0.9	103		B(2) (t)
−1.7	126	1			B(4) (d)	
−2.4	126	1	−2.4	127	B(3) (d)	
−8.7	166	2	−7.8	179		B(4) (d)
−52.3	149	3	−52.0	142	B(1) (d)	B(1) (d)

[a] At 160.4 MHz, −35 °C. [b] At 32 MHz. [c] Key: (d) doublet; (s) singlet; (t) triplet.

The ^{11}B NMR spectrum taken at 164.4 MHz shows the nature of the situation as can be seen in Figure 1 and Table I. It is apparent that the preparations are mixtures of 3-methylpentaborane(11) and 2-methylpentaborane(11). At −35 °C the proportions seen in the ^1H-decoupled spectrum are 2:1.

Ten resonances might be expected from a mixture of the two isomers, but since only eight can be seen in Figure 1, two peaks must be common to both. It is unlikely that atoms in different environments in the two isomers would have chemical shifts that are not resolved at the field strength employed; therefore, the common peaks must arise from similarly located boron atoms. The two peaks with relative area 3, a triplet at 8.5 ppm and a doublet at −52.3 ppm, are the ones shared. These have been

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

(2) (a) Jaworiwsky, I. S.; Long, J. R.; Barton, L.; Shore, S. G. *Inorg. Chem.* **1979**, *18*, 56. (b) Jaworiwsky, I. S. Ph.D. Dissertation, Ohio State University, 1975; *Diss. Abstr. Int., B* **1975**, *36* (3) 1209.

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0020-1669/86/1325-0372$01.50/0

Table II. Proton NMR of $CH_3B_5H_{10}$ Isomers[a]

ref 2	$2\text{-}CH_3B_5H_{10}$	$3\text{-}CH_3B_5H_{10}$	B_5H_{11}
	4.06 (126) —	axial 2	3.66 (126) $H(2)_{ax}$, $H(5)_{ax}$
3.35	3.49 (118)	3.49 (118) — axial 5	
		axial 2	3.43 (159) H(3), H(4)
		3.36 (127)	
		4	3.31 (136) $H(2)_{eq}$, $H(5)_{eq}$
3.13	3.13 (150) —	3	
	3.06 (120)	3.06 (120) — equat 5	
		equat 2	
2.76	2.96 (157) —	2.91 (133)	
		2.89 (155)	
		μ1′	2.00 (46) Hμ(1′)
1.87	1.75 (52) —	1.65 (52) — μ1′	
0.73		0.70	C-H
0.39	0.38		C-H
−0.03	~0.0	~0.0 — μ1	−0.21 (151) H(1)
		−0.30 (146) — 1	−0.30 (49) Hμ(1), Hμ(3)
−0.44	−0.38 (148) — 1	μ3	
	−0.51 (42)	−0.51 (42)	
−1.32		−1.44 — μ2	−1.76 (37) Hμ(2)
−1.85	−1.91 (28) —	μ2	

[a] In units of ppm.

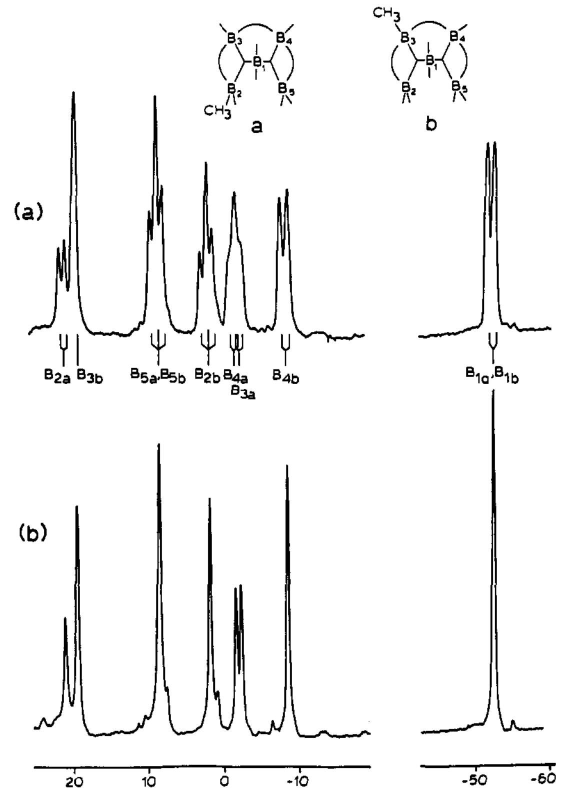

Figure 1. ^{11}B NMR spectra of $CH_3B_5H_{10}$ at −35 °C and 160.4 MHz: (a) full spectrum; (b) ^1H-decoupled spectrum.

assigned to B(5) and B(1), respectively. Methylation is known to cause resonance of the substituted boron atom to be shifted downfield from that of the unsubstituted atom.[4] Therefore the two lowest field resonances, a doublet at 21.0 ppm and a singlet at 19.4 ppm, must arise, respectively, from B(2) of $BHCH_3$ in $2\text{-}CH_3B_5H_{10}$ and B(3) of BCH_3 in $3\text{-}CH_3B_5H_{10}$ with a relative area ratio of 1:2. The triplet at 1.8 ppm and the doublet at −8.7 ppm have been assigned respectively to B(2) of $B(2)H_2$ and B(4) of B(4)H in $3\text{-}CH_3B_5H_{10}$ on the basis of their relative integrated areas being equal to 2. What appears to be a poorly resolved triplet in the proton-coupled spectrum is seen by comparison with the decoupled spectrum to be two closely spaced doublets at −1.7 and −2.4 ppm resulting from B(4)H and B(3)H, respectively, in the 2-methyl isomer, for which the relative areas are each 1.

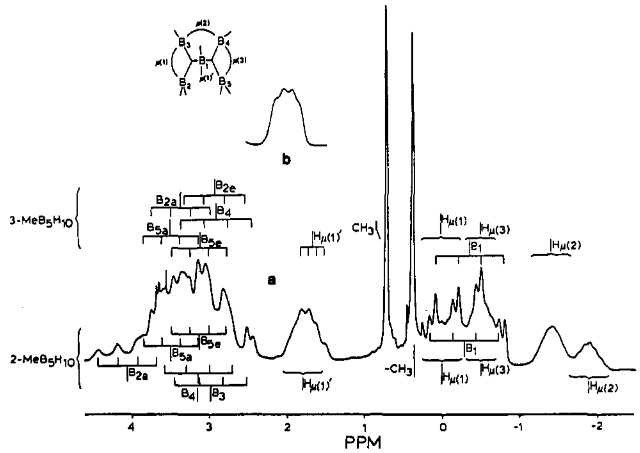

Figure 2. (a) ^1H NMR spectrum of $CH_3B_5H_{10}$ at 15 °C and 500.1 MHz: a = axial; e = equatorial. (b) ^1H NMR resonance from Hμ(1′) of B_5H_{11} at 500.1 MHz.

The ^1H NMR spectrum at 15 °C with field strength at ~500 MHz is to be seen in Figure 2, and the data are to be found in Table II.

No boron decoupling of the ^1H NMR spectrum was possible at 500 MHz because the necessary instrumentation was not available. Without such assistance other logic was required to interpret the spectrum, in which some features stand out separately but others exhibit considerable overlap of adjacently positioned resonances. Where it is possible to apply them, four guidelines

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(4) Lindner, Hans Hasso; Onak, Thomas. *J. Am. Chem. Soc.* **1966**, *88*, 1890. Deever, W. R.; Ritter, D. M. *Inorg. Chem.* **1969**, *8*, 2461.

were used in the analysis of the proton spectrum: (1) relative area ratios should match those found for ^{11}B; (2) coupling constants should be close to those found for ^{11}B and to those of the parent B_5H_{11}; (3) changes in chemical shift caused by methylation should be roughly parallel with those for ^{11}B, and the sequence of resonances along the chemical shift scale should reflect the ordering found in the more clearly delineated ^{11}B NMR spectrum; (4) the assignments should be self-consistent; i.e. for requirements 1–3 to be met, every feature in the spectrum should be accounted for to the optimum extent.

As is true in B_5H_{11}, the proton resonances of $CH_3B_5H_{10}$ are divisible into four groups. Beginning upfield, the septets assigned to $H\mu(2)$ are found at −1.44 and −1.91 ppm.

The pair exhibits the already established isomer ratio at 15 °C. The upfield member belonging to 2-$CH_3B_5H_{10}$ is the more structured one because the J values coupling $H\mu(2)$ to B(3) and B(4) are identical, while in 3-$CH_3B_5H_{10}$ the J value to B(3) differs from that to B(4) owing to the methyl substituent on B(3). The next downfield peaks ~0.0 to −0.51 ppm are quartets ascribed to protons on B(1) and septets arising from $H\mu(1)$ and $H\mu(3)$. Each peak in the quartets can be seen as a clearly distinguishable maximum. The quartets have coupling constants, 146 and 148 Hz, close to the value for B_5H_{11}, 151 Hz. The septets are so heavily overlapped as to defy complete analysis. $H\mu(3)$, the upfield bridge proton resonance, shows enough structure to be located and to reveal a J value, but location of the downfield resonance from $H\mu(1)$ is very tentative, but near 0.0 ppm. $H\mu(3)$ is likely the same for both isomers from which arises the larger upfield intensity. The lower downfield intensity distribution indicates that $H\mu(1)$ resonances have different chemical shifts.

Still farther downfield is the pair of peaks with no analogue in pentaborane(11). These are the resonances arising from H–C. They are more narrow and thus taller than the boron peaks, and they have intensities that reflect the isomer ratio.

The resonances from $H\mu(1')$, in pentaborane(11) often called the unique proton, are found at 1.65 and 1.75 ppm, just downfield from the H–C peaks. The chemical shifts for the two isomers differ by very little, estimated at ~0.10 ppm. The dissymmetry in the band is believed to arise from the close overlap of two members of unequal intensity, the more intense member being the one downfield. The shape of the band on the upfield side resembles that of the unequally membered quartet in pentaborane(11), vide infra.

The group of peaks farthest downfield are members of eight quartets belonging to the resonances attributable to the five terminal protons linked to the basal boron atoms. In principle there might be ten, but two of the possible ten are considered to be identical in each isomer. These come from the protons on B(5) atoms, oriented equatorial and axial, which like the $H\mu(3)$ atoms are most remote from the site of methylation and thus almost equally affected. Many quartets could be related to four maxima; a few had some members at maxima while othe members fell along broad, slightly inflected edges, clearly the result of closely spaced maxima. No member of a quartet was permitted to fall at a minimum. Within the region 0.24 to −1.0 ppm there are four unassigned peaks or inflections at 0.24, 0, −0.36 and −0.56 ppm which are identical with peaks found in B_5H_{11}, arising from the slight disproportionation of $CH_3B_5H_{10}$.

Examination of the data in Table II shows that each of the resonances in the pentaborane(11) spectrum have become methyl derivative resonances with coupling constants not identical with, but very nearly those, in the spectrum of the parent substance. What small changes are found are mostly dimunitions, the larger the more remote from the site of substitution. Only at B(1)–$H\mu(1')$ do J values increase, and at B(2)–H_{ax} there is no change. Farther along the reason will be given for the particular choice of stereo configuration, axial or equatorial, in the methylderivatives and in B_5H_{11}.

The NMR spectra of pentaborane(11) were redetermined at 160.4 MHz and 500.1 MHz for ^{11}B and ^{1}H, respectively, because this substance is the comparison standard for its methyl derivatives. The newest determinations found the values for chemical shifts and coupling constants almost the same as those previously determined;[5] however, the individual resonances became better defined, especially that assigned to $H\mu(1')$ as determined previously.[5b] At 220 MHz this feature appeared on the upfield edge of the group of downfield resonances by which it was partially enveloped.[5b] Seen at 500 MHz it stands alone. Had the coupling been one to a single boron atom, the members of the quartet would have had equal intensities. Instead the signal observed, as seen in Figure 2b, had members in approximately an 0.8:1:1:0.8 ratio. Thus, there appears to be a perturbation of the normal quartet presumably ascribable to atoms B(2) and B(5) as previously thought possible.[5b] The nature of this multiplet has added importance since it occurs in the spectra of the $CH_3B_5H_{10}$ isomers.

It is apparent from Tables I and II that introduction of a methyl group into pentaborane(11) causes change in the local magnetic field around each boron atom. The changes are reflected in altered chemical shifts as found in Table III. The symbol $\Delta\sigma$ identifies such an alteration, positive for downfield change and negative for change upfield. The $\Delta\delta$ values are also chemical shifts referenced to pentaborane(11), as toluene and alkanes are referenced to the parent hydrocarbons.

The general conclusions are these:

(1) Concerning ^{11}B NMR the modest electron-attracting capacity of the methyl group deshields the boron atom bearing the substituent. This appears to be a universal phenomenon[5] observed also with ^{13}C NMR.[6,8] The deshielding effect is greater for 3-methylpentaborane(11) than for 2-methylpentaborane(11).

(2) In response to the depletion of electron density at the substituted boron atom, small readjustments of electron density are seen at the others. Atoms B(1) and B(5) are slightly deshielded to an identical extent in each isomer. The remaining atoms in the trapezoidal plane become somewhat more shielded. In 2-methylpentaborane(11) B(3), the only boron atom adjacent to B(2), has increased shielding just slightly more than the remote B(4). In 3-methylpentaborane(11) both the adjacent atoms, B(2) and B(4), exhibit increased shielding, larger than that seen for the other isomer. It is interesting to note that these inductive effects are propagated along pathways and to relative extents consistent with the patterns of electron density found by the SCF computations.[9]

(3) In both isomers those ^{1}H nucleii adjacent to the substituted atom are deshielded. All other ^{1}H nucleii show increased shielding.

(4) Overall, using $\sum|\Delta\delta|$ as the index, the changes in chemical shift occasioned by substituting methyl groups for hydrogen atoms are seen to be larger for 3-methylpentaborane(11) than for its isomer with respect to both ^{11}B and ^{1}H nucleii.

In Table III are found data on ^{13}C and ^{1}H NMR for toluene and for the alkanes. In comparison with the pentaborane(11) derivatives, toluene appears more of an analogue than do the methylated alkanes, possibly testimony to electron delocalization and aromatic character. The focus here is on the extent to which deshielding of the substituted atoms alters shielding in the other atoms.

The proportion between the isomers is reversibly temperature dependent. The values of ln K conform to the Antoine equation where the slope is $-\Delta H/R$ and the intercept is $\Delta S/R$. The reversibility and the close linearity of the relation ln K vs. $1/T$ are taken to indicate that equilibrium is maintained over the temperature range 173–293 K. The observed and calculated values of K are given in Table IV, and the equations with the associated

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(5) (a) Leach, J. B.; Onak, T.; Spielman, J.; Rietz, R. R.; Schaeffer, R. R.; Sneddon, L. G. *Inorg. Chem.* **1970**, *9*, 2170. (b) Onak, T.; Leach, J. B. *J. Am. Chem. Soc.* **1970**, *92*, 3513. (c) Rietz, R. R.; Schaeffer, R. R.; Sneddon, L. G. *Ibid.* **1970**, *92*, 3514.

(6) Silverstein, Robert M.; Bassler, G. Clayton; Morrill, Terence C. "Spectrometric Identification of Organic Compounds", 4th ed.; Wiley: New York, 1981; p 265.

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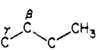
(9) Switkes, Eugene; Epstein, Irving R.; Tossell, John A.; Stevens, Richard M.; Lipcomb, William N. *J. Am. Chem. Soc.* **1970**, *92*, 3837.

Table III. NMR Data[a]

	2-$CH_3B_5H_{10}$		3-$CH_3B_5H_{10}$			$CH_3C_6H_5$[b]	
atom	$\Delta\delta(^{11}B)$	$\Delta\delta(^{1}H)$	$\Delta\delta(^{11}B)$	$\Delta\delta(^{1}H)$	atom	$\Delta\delta(^{13}C)$[c]	$\Delta\delta(^{1}H)$[d]
B(1)	2.6		2.6		C(1)	8.9	
H(1)		−0.17		−0.09	C(2)	0.7	−0.19
$H\mu(1')$		−0.25		−0.35	C(3)	−0.1	−0.07
$H\mu(1)$		0.30		0.30	C(4)	−2.9	−0.15
B(2)	13.6		−5.6		^{13}C alkane carbons[e]		
$H(2)_{ax}$		0.40		−0.30			
$H(2)_{eq}$				−0.40			
$H\mu(2)$		−0.15		−0.32	α	9[f]	6[g]
B(3)	−3.1		18.7		β	10[f]	8[g]
H(3)		−0.30			γ	−2[f]	−2[g]
$H\mu(3)$		−0.21		−0.21			
B(4)	−2.4		−9.4				
H(4)		−0.47		−0.54			
B(5)	1.1		1.1				
$H(5)_{ax}$		−0.17		−0.17			
$H(5)_{eq}$		−0.25		−0.25			
$\sum\|\Delta\delta\|$	22.8	2.67	37.4	2.93			

[a] In units of ppm. [b] Referenced to benzene; ref 6. [c] Reference 7. [d] Reference 7. [e] Reference 8. [f] Alkane structure: 

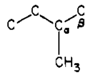
[g] Alkane structure: 

Table IV. Equilibrium Constants for 3-$CH_3B_5H_{10}(l) \rightleftarrows$ 2-$CH_3B_5H_{10}(l)$

	K_{obsd}		K_{calcd}[c]	
T, K	A[a]	B[b]	A	B
298			0.97	0.97
293	0.96		0.96	
288		0.96		0.88
273	0.93	0.82	0.92	0.85
253		0.75		0.79
248	0.89		0.87	
233		0.71		0.73
218	0.79		0.80	
213		0.72		0.68
193	0.73		0.73	
173	0.67		0.67	

[a] Neat samples. [b] 4 mol % in $CDCl_3$. [c] Calculated by using equations in Table V.

Table V. Antoine Equations[a] and Thermodynamic Quantities

process system A[b]	3-$CH_3B_5H_{10}(l) \rightleftarrows$ 2-$CH_3B_5H_{10}(l)$ $\ln K = (-155 \pm 15)/T + 0.49 \pm 0.07$ $r = -0.99712$ $\Delta H° = 300 \pm 30$ cal mol^{-1}; $\Delta S° = 1.0 \pm 0.1$ eu $\Delta G°_{298}{}^{d} = 18 \pm 2$ cal mol^{-1}
process system B[c]	3-$CH_3B_5H_{10} \rightleftarrows$ 2-$CH_3B_5H_{10}$ (in $CHCl_3$) $\ln k = (-217 \pm 23)/T + 0.63 \pm 0.22$ $r = -0.85765$ $\Delta H = 430 \pm 40$ cal mol^{-1}; $\Delta S = 1.3 \pm 0.4$ eu $\Delta G_{298}{}^{e} = 43 \pm 11$ cal mol^{-1}

[a] The uncertainties are standard deviations. [b] Neat sample, 60 MHz. [c] 4 mol % in $CDCl_3$; 500 MHz. [d] From $-\Delta G° = RT \ln K$. [e] From $\Delta G = \Delta H - T\Delta S$.

thermodynamic quantities are given in Table V. The thermochemical differences between the isomers in the two media, neat and in chloroform, are really very small. The entropies are, within the uncertainties, identical. The enthalpies differ by only 2 standard deviations and the free energies by 3. These barely significant differences probably arise from dissimilar enthalpies of solution in chloroform.

The value of *K* for a neat sample of $CH_3B_5D_{10}$ at 263 K is 0.69 compared with 0.90 for $CH_3B_5H_{10}$. This represents an 11% enrichment of the 3-methyl isomer in the mixture of deuterated molecules.

The structure of pentaborane(11) reveals the clue to the process of isomerization. The terminal hydrogen atoms on B(3) and B(4) and the equatorial hydrogen atoms on B(2) and B(5) all have approximately the same orientation to their attached boron atoms and to the center of the basal plane. The three bridging hydrogen atoms lie below the basal plane as do the axial hydrogen atoms on B(2) and B(5) with the latter hydrogen atoms twisted toward bridging positions along the open edge and face of the trapezoidal pyramid. When a methyl group is substituted equatorially at B(2), a "pseudorotation" rocks the apical boron atom B(1) and its terminal hydrogen atom toward the back of the molecule. With a slight twist at B(5), two of the three bridge and both axial hydrogen atoms rearrange to form a molecule that has the methyl group on B(3). The proposed rotation is illustrated in Figure 3. In viewing the figure it should be noted that in all respects save optical activity locations 2, 5 and 3, 4 are indistinguishable pairs. The isomerization makes resolution of optical isomers unachievable. Were the methyl group to be substituted axially on B(2), the facile rearrangement would be blocked, and the transfer of a methyl group would occur through the slower steps of methyl transfer from boron to boron[10] or by insertion. Upon this proposed mechanism in relation to the proton NMR of pentaborane(11) and the methylpentaboranes(11) rests the assignment of particular

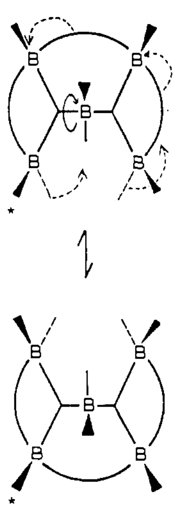


Figure 3. Isomerization mechanism. Asterisks denote sites of substitution.

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proton resonances to hydrogen nucleii in atoms substituted equatorially or axially at boron atoms B(2) and B(5).

Experimental Section

Preparations. I and II were obtained by methods cited previously.[1,2] Alternatively, preparation (II) was made by a sequence of reactions starting with B_5H_9 instead of $CH_3B_5H_8$, then using $(BH_2CH_3)_2$ instead of diborane(6).[11] Extraordinary care is required to purify these rather unstable substances. The preferred process is fractional codistillation[12] followed by passage through a short (0.5-cm diameter × 6 cm long) column packed with 20% mineral oil on firebrick. This column was scrupulously dried by several hours conditioning with diborane. The function of the column was to "smooth out" the dissymmetrically distributed output from fractional codistillation.[11]

The isomeric methylpentaboranes(9),[13] diborane(6),[14] monomethyldiborane(6),[10a,14] 1,2-dimethyldiborane(6),[15] pentaborane(11),[16] and perdeuteriopentaborane(11)[3] were prepared as described in the references.

NMR. Unless otherwise stated all isotopic species were at natural abundance. Early observations of ^{11}B NMR on preparation I were made at 80 MHz on a spectrometer built at the University of California, Los Angeles. ^1H NMR spectra of the hydrogen nucleii in the methyl groups of preparation I were determined at 60 MHz by using a Varian HA-60 spectrometer with a V4343 temperature-control attachment. All measurements were made on neat samples.

Other NMR measurements were made at 64.2 MHz for ^{11}B and 200.1 MHz for ^1H on a Bruker CXP 200 and on a Bruker WM-500 spectrometer set at 160.437 MHz for ^{11}B and at 500.137 MHz for ^1H. For these measurements the samples were dissolved in deuteriochloroform, which had been treated with 4A molecular sieves. The concentrations were approximately 0.04 mole fraction. Temperatures were maintained from −60 °C to 15 °C with standard Bruker controllers. Boron trifluoride diethyl etherate in $DCCl_3$ was used as the external standard for ^{11}B, and the residual protons in $DCCl_3$ were used as the internal reference for ^1H with $\delta(Me_4Si) = 0$. Values of chemical shift upfield from the references are given the negative sign; downfield values are positive.

Data Processing. Chemical shifts and coupling constants were determined graphically from the analog charts recorded by the NMR spectrometers. Curves produced by the Bruker-WM500 were integrated by the device incorporated in the machine. Members of the pseudodoublets arising from the methyl group as observed at 60 MHz and at 500 MHz were compared by using the Dupont curve resolver. The ratios of area were considered to be the equilibrium constants. The inductive effects of substituting a methyl group for a hydrogen atom on the boron atom framework were calculated from

$$\Delta\delta(A(S)) = \delta(A(S))_i - \delta(A(S))_0$$

where S is the location of atom A (B or H), i is a methylated species, 2-methyl or 3-methyl, and the zero subscript denotes the corresponding value for pentaborane(11).

The data in Table IV were fitted to linear relation by using least-squares computation[17] to give the equations in Table V.

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Registry No. $2\text{-}CH_3B_5H_{10}$, 88574-97-4; $3\text{-}CH_3B_5H_{10}$, 68051-06-9.

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Synthesis and Reactions of Substituted Alkyl Trifluoromethyl Ethers

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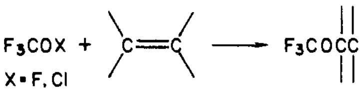
Trifluoromethyl hypochlorite has been reacted with $RCH{=}CH_2$ ($R = SO_2CH{=}CH_2$, $(CH_3O)_3Si$, Cl_3Si, $(CH_3)_3Si$) to form isomeric mixtures of the trifluoromethyl ethers. With SbF_3, $CF_3OCH_2CH(SiCl_3)Cl$ gave $CF_3OCH_2CH(SiF_3)Cl$, and when $CF_3OCH[Si(CH_3)_3]CH_2Cl$ was thermolyzed, the vinyl ether $CF_3OCH{=}CH_2$ resulted. The addition product of CF_3OCl with $Cl_2C{=}CHCl$ was dehydrochlorinated to $CF_3OCCl{=}CCl_2$, which when chlorinated gave $CF_3OCCl_2CCl_3$. The latter could not be obtained by direct reaction of CF_3OCl with tetrachloroethylene. Dechlorination of the $CF_3OCl/Cl_2C{=}CF_2$ addition products (**6a**) gave $CF_3OCCl{=}CF_2$, which formed a bis(trifluoromethyl) ether (**6c**/**d**) with CF_3OCl. The latter when dechlorinated gave $(CF_3O)_2C{=}CF_2$ (**6e**). 1,1,1-Trifluoropropene with CF_3OCl gave a 60% yield of the Markovnikov-type addition **8a**, which when reacted with KOH formed *cis*-$CF_3CH{=}CClH$ as a result of the loss of $[CF_3OH]$. The former with CF_3OCl produced $CF_3OCH(CF_3)CHCl_2$. The yields of trifluoromethyl ethers formed by reaction of $CH_3OC(O)CH{=}CH_2$, $CH_3C(O)CH{=}CH_2$, and $HC(O)CH{=}CH_2$ with CF_3OCl decreased from 65 to 5%.

Introduction

Fluoroalkyl ethers have high synthetic value as monomers for polymerizations as well as for their useful physical properties.[1] However, the preparation of alkyl trifluoromethyl ethers is difficult, and only a few synthetic routes are known. The standard method, the addition of alcohols to olefins, fails because of CF_3OH is unstable except at low temperature, and the yields and variety of compounds generated by electrochemical fluorination or halogen-exchange reactions are very small.[2,3] Aldrich and Sheppard prepared alkyl trifluoromethyl ethers by treating fluoroformates with sulfur tetrafluoride but their method is limited only to stabilized starting material.[4]

A more extensive approach is the addition of trifluoromethyl hypohalites to olefins[5]



Recently DesMarteau and Johri have shown that the CF_3OF

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