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SYNTHESIS AND CHARACTERIZATION OF THE METHYLETHYLBORANES

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Summary

The compounds $(CH_3)_2BC_2H_5$ and $CH_3B(C_2H_5)_2$ were prepared by reaction of $(CH_3)_4B_2H_2$ and C_2H_4. The compounds were readily isolable in the pure state. A thorough characterization of these compounds is presented. Conclusions relevant to bonding in the analogous unsaturated methylvinylboranes are discussed in the light of the results of this investigation.

Introduction

Conflicting reports concerning the existence and stability of the molecules $(CH_3)_2BC_2H_5$ and $CH_3B(C_2H_5)_2$ can be found in the literature. In one instance [1,2], it was reported that these molecules are unstable and rapidly disproportionate at temperatures above —10° C. In this study, dimethylbromoborane was allowed to react with diethylzinc at room temperature and the product was collected at —80° C by fractionation. The fraction retained at —80° C was presumably $(CH_3)_2BC_2H_5$, but the only evidence presented was that the vapor pressure of this material below —9° C obeyed the Clausius—Clapeyron equation.

More recent evidence indicates that the mixed methylethylboranes can indeed be prepared and isolated. Haszeldine et al. [3] reported the preparation of these compounds via the hydroboration of ethylene with tetramethyldiborane-(6). Alternatively, Köster et al. [4] reported the preparation of the mixed methylethylboranes by pyrolysis of symmetrical trialkylboranes in an autoclave at high temperatures. Although both groups reported the preparation, no thorough characterization of the compounds has ever been reported.

The question of the preparation of the methylethylboranes in itself is an interesting one; however, a more fundamental question concerns their stability

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* Taken in part from the Ph.D. thesis of E.J. Stampf submitted to the Department of Chemistry, August 1976.

towards disproportionation. Parsons and Ritter have investigated the mixed methylvinylboranes and have contrasted the stability of these molecules with the saturated methylethylboranes [1]. Since they were unable to isolate the methylethylboranes, they suggested that the stability of the methylvinylboranes arises from a boron—carbon π-interaction which imposes a degree of planarity on the unsaturated molecules. Since a simple group redistribution would most likely involve a dimeric complex with approximately tetrahedral geometry around each boron atom, this process would be energetically less favorable in the unsaturated methylvinylboranes than in the saturated methylethylboranes.

Because of our interest in the nature of the boron—carbon bond in organoboranes bearing electron rich substituents [5,6], we felt it was necessary to also fully characterize the saturated methylethylboranes if indeed they were stable towards disproportionation. The existence (or non-existence) of these compounds would shed light on the argument previously presented which attributed the stability of the methylvinylboranes to a π-delocalization mechanism.

Experimental

Tetramethyldiborane(6) was prepared in good yield by reaction of 11.7 mmoles $(CH_3)_3B$ with 2.8 mmoles B_2H_6. This mixture was held for five days at room temperature in an all glass, high pressure reaction vessel having a volume of ca. 60 ml [7]. The contents of the reaction vessel were fractionated through traps held at —95, —160 and —196° C. Unreacted B_2H_6 (0.02 mmol) condensed at —196° C. The product $(CH_3)_4B_2H_2$ solidified at —95° C and further purification was achieved on a low temperature vacuum fractionation column [8]. The vapor pressure of the compound (54 Torr at 0° C, lit. value [9], 47 Torr at 0° C) was found to rise over a period of time, indicating that disproportionation occurs. An ^{11}B NMR spectrum of the compound * confirmed the presence of $(CH_3)_4B_2H_2$ ($\delta = +24.3$ ppm deshielded from external $BF_3 \cdot O(C_2H_5)_2$, $J(BH_b) = 42.7$ Hz; lit. value [10], $\delta = +24.8$ ppm, $J(BH_b) = 39.7$ Hz) as well as a small amount of $(CH_3)_3B$ ($\delta = +85.9$ ppm; lit. value [10], $+86.0 \pm 0.2$ ppm). No other resonances were observed in the region expected for other possible disproportionation products.

Hydroboration of C_2H_4 with $(CH_3)_4B_2H_2$.

(A) Gas phase hydroborations. Reaction of 3.69 mmol of $(CH_3)_4B_2H_2$ with 60.3 mmol of C_2H_4 [3] in an all glass reaction vessel of ca. 500 ml volume for 10.5 h at room temperature resulted in the consumption of 7.5 mmol of C_2H_4 (calcd. consumption based on the starting quantity of $(CH_3)_4B_2H_2$, 7.5 mmol) with the formation of 2.06 mmol of $B(CH_3)_3$, 3.14 mmol of $(CH_3)_2BC_2H_5$, 1.64 mmol of $CH_3B(C_2H_5)_2$ and 0.27 mmol of $B(C_2H_5)_3$ which were readily separated on the low temperature vacuum fractionation column.

In a second experiment, 1.15 mmol of $(CH_3)_4B_2H_2$ was allowed to react with 10.25 mmol of C_2H_4 for 17.5 h at room temperature in an all glass reaction

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* In accord with the general opinion expressed at the IMEBORON III meeting, (Munich, Germany, July 5—9, 1976) please note that the sign convention for expressing ^{11}B chemical shifts is reversed. Resonances deshielded with respect to $BF_3 \cdot O(C_2H_5)_2$ are assigned a positive chemical shift. All chemical shifts reported in this paper (^1H, ^{13}C, ^{11}B) employ the convention that a positive sign denotes a deshielded resonance with respect to the appropriate reference compound.

vessel of ca. 40 ml volume. In this experiment, 2.25 mmol of C_2H_4 was consumed (calcd. consumption 2.30 mmol) with the formation of 0.65 mmol of $B(CH_3)_3$, 0.90 mmol of $(CH_3)_2BC_2H_5$, 0.52 mmol of $CH_3B(C_2H_5)_2$, and 0.10 mmol of $B(C_2H_5)_3$.

(B) Solution hydroborations. Bis(2-methoxyethyl)ether (diglyme) was freshly distilled from $LiAlH_4$ under a N_2 atmosphere (b.p. 161°; lit. b.p. 162°C [9]) prior to use. In one experiment, 5 ml of diglyme was syringed into a 500 ml round-bottomed flask containing a magnetic stirring bar and fitted with a stopcock adapter in order to isolate the reaction vessel from the vacuum line. The diglyme was freeze-thaw degassed several times prior to the introduction of 5.0 mmol of $(CH_3)_4B_2H_2$. Enough C_2H_4 (20.5 mmol) was condensed into the reaction vessel to produce ca. one atmosphere of ethylene in the gas phase at room temperature. After isolating the reaction vessel from the vacuum line, the vessel was warmed from —196 to 0° C and the reaction mixture was stirred at 0° C for 30 min. The volatile products were fractionated through two —160° C slush baths (isopentane/liquid N_2) to recover unreacted C_2H_4 which condensed at —196° C. A non-condensable gas was produced which was not observed in the gas phase reactions. Of the starting quantity of C_2H_4, 10.5 mmol was consumed (calcd. consumption, 10.0 mmol) producing 3.25 mmol of $B(CH_3)_3$, 4.0 mmol of $(CH_3)_2BC_2H_5$, 2.36 mmol of $CH_3B(C_2H_5)_2$, and 0.48 mmol of $B(C_2H_5)_3$.

In a second experiment, 3.56 mmol of $(CH_3)_4B_2H_2$ in 5 ml of diglyme was treated with 20.46 mmol of C_2H_4 for 5 min at —20° C. Only 1.54 mmol (21.6% consumption) of ethylene reacted. The resulting mixture of products was very complex. Unreacted $(CH_3)_4B_2H_2$ and $B(CH_3)_3$ were identified and four components exhibiting a single terminal B—H stretching frequency as well as a BHB bridge hydrogen stretching frequency were detected. No $(CH_3)_2BC_2H_5$, $CH_3B(C_2H_5)_2$ or $B(C_2H_5)_3$ were observed in the product mixture at this point.

Vapor pressures were measured in the range —57 to +8.5° C for $(CH_3)_2BC_2H_5$. The vapor pressure data was subjected to a least squares analysis and the following expression is derived for the vapor pressure equation:

$$\log p_{\mathrm{Torr}} = 7.170 - 1281/T$$

The observed and calculated (in parenthesis) vapor pressures are: +8.5°, 432 Torr (416); +4.0°, 353 Torr (351); 0.0°, 306 Torr (300); —5.0°, 248 Torr (246); —9.0°, 205 Torr (208); —24.0°, 104 Torr (106); —40.0°, 46 Torr (47); —57.0° C, 18 Torr (17). From the vapor pressure data the following constants are obtained: extrapolated boiling point, 25.5° C; ΔH_{vap}, 5.86 kcal/mol; Trouton constant, 19.6 cal/deg.-mol. The melting point (Stock plunger technique) is below —160° C.

Some difficulty was encountered in obtaining vapor pressure data for $CH_3B(C_2H_5)_2$. At any fixed temperature, the pressure was found to slowly rise over a period of several minutes. This problem was minimized by repurifying the compound after several measurements. The observed vapor pressure data for $CH_3B(C_2H_5)_2$ (+ 19.0°, 152 Torr (151); +14.0°, 120 Torr (120); +6.5°, 83 Torr (84); 0.0°, 61 Torr (61); —5.0°, 49 Torr (47); —10.0°, 37 Torr (36); —16.0°, 26 Torr (26); —19.0° C, 21 Torr (22)) is expressed by the equation:

$$\log p_{\mathrm{Torr}} = 7.818 - 1647/T$$

For $CH_3B(C_2H_5)_2$, the vapor pressure data yields the following parameters: extrapolated boiling point, 61°C; ΔH_{vap}, 7.54 kcal/mol; Trouton constant, 22.6 cal/deg-mol. The melting point (Stock plunger technique) is −135.5°C.

Spectroscopic studies

Infrared spectra were recorded in the gas phase in a 10 cm cell equipped with KBr optics using a Perkin—Elmer 337 spectrophotometer. The spectra were calibrated against polystyrene film and are considered accurate to ±5 cm^{-1}. The observed gas phase frequencies are: $(CH_3)_3B$ at 10 Torr: 2990m, 2920m, 1290s, 1180s, 1150s, 1138s, 980w, 963w; $(CH_3)_2BC_2H_5$ at 10 Torr: 2960s, 2920m, 2880m(sh), 1470w, 1290s, 1140m, 1121m, 1112m(sh), 1004w, 960w, 870w; $CH_3B(C_2H_5)_2$ at 10 Torr: 2960s, 2920s, 2880s, 1463m, 1385w, 1295s, 1107m, 1010w, 953m(sh), 944m, 825w; $B(C_2H_5)_3$ at 6 Torr: 2965s, 2925m, 2885m, 1460m, 1380m, 1100m, 1015w, 920m, 789w.

Nuclear magnetic resonance spectra were obtained in the FT mode on Varian Associates XL-100-15 (^1H, 100.1 MHz; ^{11}B, 32.1 MHz) and CFT-20 (^{13}C, 20.0 MHz) spectrometers. The ^{11}B chemical shifts for $(CH_3)_2BC_2H_5$ and $CH_3B(C_2H_5)_2$ are +86.1 and +86.2 ppm with respect to external $BF_3 \cdot O(C_2H_5)_2$, respectively. The ^{13}C NMR spectrum of $(CH_3)_2BC_2H_5$ (Fig. 1) consists of three resonances

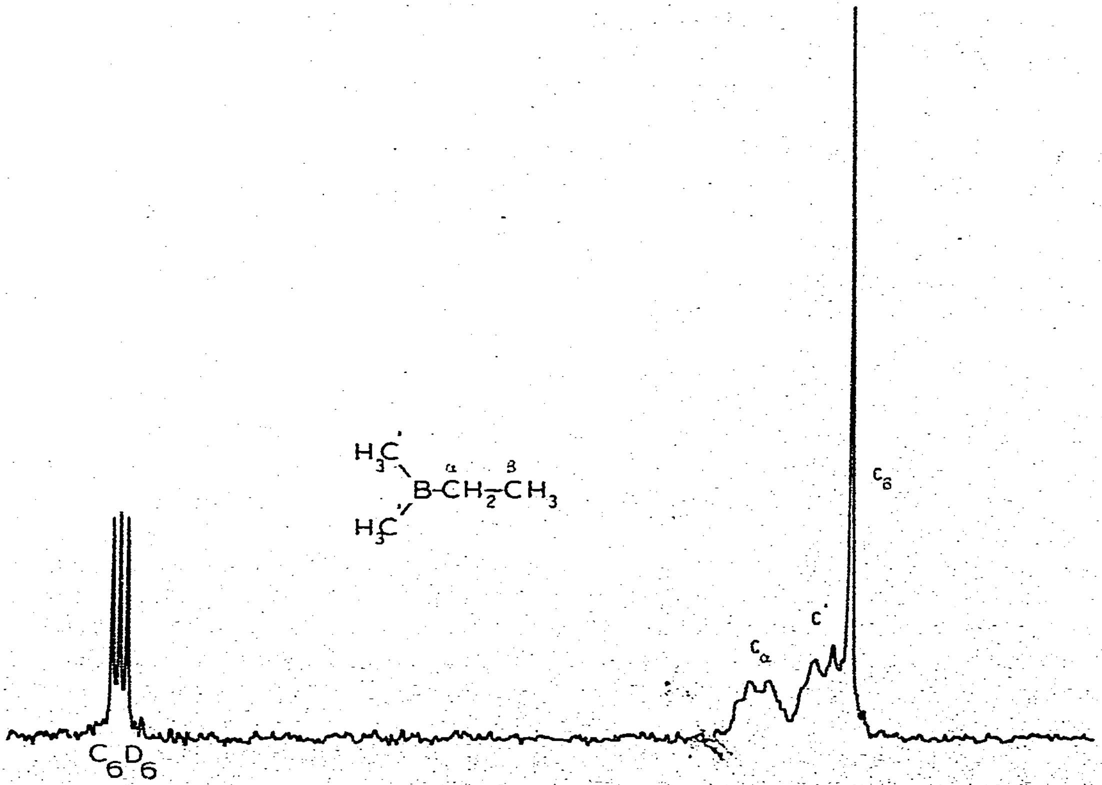

Fig. 1. The 20 MHz ^{13}C NMR spectrum of a C_6D_6 solution of $(CH_3)_2BC_2H_5$ under conditions of complete ^1H decoupling. The assignment of resonances can be found in the Spectroscopic Studies section. This spectrum resulted from the accumulation of 29,000 transients with an acquisition time of 0.4 sec., a pulse delay of 0.6 sec. and a flip angle of 30°.

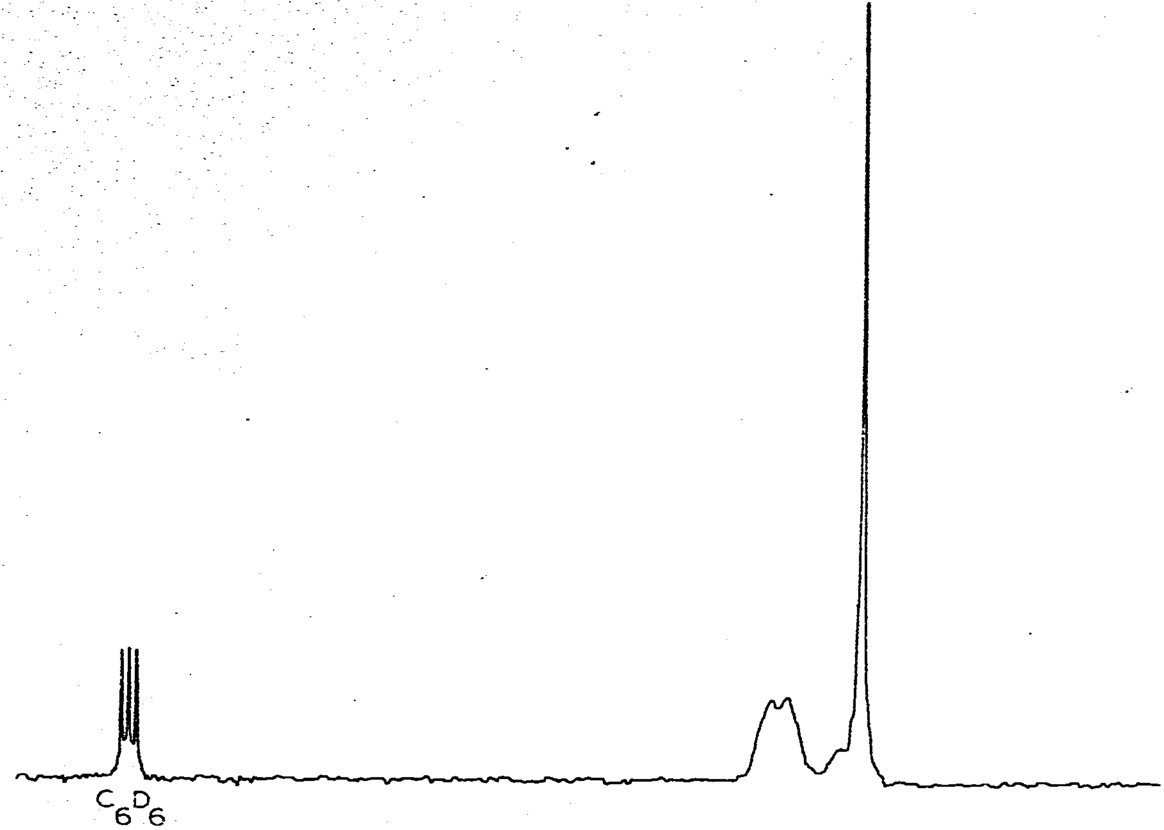

Fig. 2. The 20 MHz ^{13}C NMR spectrum of a C_6D_6 solution of $CH_3B(C_2H_5)_2$ obtained under conditions of complete proton decoupling. The assignment of resonances can be found in the Spectroscopic Studies section. This spectrum resulted from accumulation of 38,000 transients with an acquisition time of 0.8 sec., a pulse delay of 0.6 sec. and a 30° flip angle.

all deshielded with respect to external TMS. The resonances are assigned as follows: (1) $\delta = +6.1$ ppm, C_β of the ethyl group; (2) $\delta = +11.3$ ppm, $J(BC) \leqslant 58$ Hz, the directly bonded methyl carbons; (3) $\delta = +21.6$ ppm, $J(BC) \leqslant 64$ Hz, C_α of ethyl group. The ^{13}C NMR spectrum of $CH_3B(C_2H_5)_2$ (Fig. 2) also consists of three resonances; however, the resonance of the directly bonded methyl carbon is partially obscured as a result of overlap with the ethyl C_β resonances. The three resonances are: (1) $\delta = +6.1$ ppm, C_β of ethyl groups; (2) $\delta = +7.7$ ppm, directly bonded methyl carbon; (3) $\delta = +19.7$ ppm, $J(BC) \leqslant 47$ Hz, C_α of ethyl groups. The ^{1}H NMR spectra yielded little useful information. The spectra consist of broad, overlapping resonances and even under conditions of ^{11}B decoupling are not readily interpretable. The ^{1}H spectrum of $(CH_3)_2BC_2H_5$ consists of two broad resonances centered at 0.0 and +0.25 ppm with respect to external TMS. The ^{1}H NMR spectrum of $CH_3B(C_2H_5)_2$ consists of a broad resonance at +0.1 and a very complex, unsymmetrical envelope of resonances centered at +0.34 ppm.

Mass spectral data were obtained on a Perkin—Elmer RMU-6 at 70 eV (Table 1). Molecular ions were observed for $(CH_3)_2BC_2H_5$ at $m/e = 70$, and for $CH_3B(C_2H_5)_2$ at $m/e = 84$. Exact mass measurements were obtained on an AEI MS

TABLE 1

MASS SPECTRAL DATA[a] FOR THE SERIES $(CH_3)_NB(C_2H_5)_{3-N}$ FOR $N = 0, 1, 2, 3$[b]

m/e	$(CH_3)_3B$	$(CH_3)_2BC_2H_5$	$CH_3B(C_2H_5)_2$	$B(C_2H_5)_3$	Assignment
15		11.9			CH_3^+
25			6.9	13.2	$^{10}BCH_3^+$
26	5.9	27.1	29.2	28.9	$^{11}BCH_3^+$
27	11.8	55.9	87.5	13.2	
28		13.6	15.3	7.9	$C_2H_4^+$
36	5.9	8.5			
37	14.7	18.6	12.5	13.2	
38	5.9	10.2	6.9	10.5	
39	17.6	28.8	18.1	28.9	$^{10}BC_2H_5^+$
40	26.5	33.9	12.5	31.6	$^{11}BC_2H_5^+$, $(CH_3)_2{}^{10}B^+$
41	100.0	100.0	25.0	100.0	$(CH_3)_2{}^{11}B^+$
43		42.4			
50		6.8	6.9		
51		6.8	6.9		
53		8.5	12.5	7.9	
54		13.6	30.6		$CH_3{}^{10}BC_2H_5^+$
55		40.7	100.0		$CH_3{}^{11}BC_2H_5^+$
56*	2.9				$(CH_3)_3{}^{11}B^+$
57		6.8		7.9	
58					
68				13.2	$^{10}B(C_2H_5)_2^+$
69				47.4	$^{11}B(C_2H_5)_2^+$
70*					$(CH_3)_2{}^{11}BC_2H_5^+$
84*		6.8	6.9		$CH_3{}^{11}B(C_2H_5)_2^+$
98*				5.3	$^{11}B(C_2H_5)_3^+$

[a] Obtained at 70 eV. Relative intensities are tabulated for each molecule as well as tentative assignments for pertinent ions. [b] See also Ref. 15.

902 with the following results: $^{11}B^{12}C_4{}^1H_{11}$, exptl. 70.0950, calcd. 70.0954; $^{11}B^{12}C_5{}^1H_{13}$, exptl. 84.1114, calcd. 84.1110.

Discussion

In an earlier study, Haszeldine et al. reported the preparation of the methylethylboranes [3]. In this study, characterization of the compounds was limited to boiling points only. For $(CH_3)_2BC_2H_5$ and $CH_3B(C_2H_5)_2$, they reported boiling points of 22 and 58° C, respectively. Our extrapolated normal boiling points of 25.5 and 61° C compare favorably.

An important question which arises at this point is the origin of the "unexpected" by-products $B(CH_3)_3$, $CH_3B(C_2H_5)_2$ and $B(C_2H_5)_3$. These products could arise from a dissociation-redistribution of the starting material $(CH_3)_4B_2H_2$ to produce intermediates which then react with ethylene.

$$R_2BH_2BR_2 \rightleftharpoons 2\ R_2BH \rightleftharpoons R_3B + RBH_2\text{, etc.}$$

Support of this mechanism as the origin of intermediates giving rise to by-products of the hydroboration is based on evidence presented by Lehmann et al. [11] which indicates rapid disproportionation of $(CH_3)_4B_2H_2$ into $B(CH_3)_3$ and $(CH_3)_3B_2H_3$.

Alternatively, the formation of a mixture of trialkylboranes in the hydroboration of ethylene could arise from a redistribution reaction involving the products. The expected product of the $(CH_3)_4B_2H_2/C_2H_4$ reaction is $(CH_3)_2BC_2H_5$. The presence of any B—H species could catalyze a redistribution reaction of $(CH_3)_2BC_2H_5$ to generate the other observed trialkylboranes [12].

It is beyond the scope of this investigation to determine which of these mechanisms gives rise to the mixture of products, but based on our results of the solution hydroborations, it appears likely that it is disproportionation of the starting material $(CH_3)_4B_2H_2$ [3] which results in formation of the mixture of trialkylboranes. This is best exemplified by the observation of intermediates which exhibit terminal and bridge hydrogen stretching modes in the infrared. This suggests that although the reaction had progressed to only 22% completion in 5 min, the starting material had already undergone significant disproportionation. Since the same distribution of products was observed in both the gas phase and solution hydroborations, the gas phase reaction is a simpler route to products in this instance.

Prior to this investigation, the ^{11}B chemical shifts of the methylethylboranes had not been reported. Recently, Spielvogel [13] has utilized an empirical relationship to predict these ^{11}B chemical shifts. The chemical shifts were calculated from pairwise additivity parameters which have previously been shown by Malinowski [14] to reproduce the ^{11}B chemical shifts for haloboranes of the type BXYZ. The chemical shift is calculated by summing all pairwise interactions. Using this technique, ^{11}B chemical shifts were calculated to be +85.1 and +85.5 ppm for $(CH_3)_2BC_2H_5$ and $CH_3B(C_2H_5)_2$ and are in excellent agreement with our experimental values of +86.1 and 86.2 ppm, respectively.

The proton NMR spectra of the methylethylboranes are very complex and not interpretable by first-order principles. This is not unexpected since the chemical shift range of all the protons within each molecule is very small. In systems where the chemical shift difference ($\Delta\nu$) between coupled spins is comparable to the spin coupling constant ($J(AB)$), complex, non-first order spectra are observed. For $CH_3B(C_2H_5)_2$, there can also be long range spin coupling between chemically equivalent protons on the two different ethyl groups. In a similar manner, the ^{19}F NMR spectrum of $CH_3B(C_2F_3)_2$ [6] exhibited a non-first order spectrum which was rationalized on the basis of long range spin coupling between chemically equivalent but magnetically non-equivalent fluorines. Thus, the appearance of the ^1H NMR spectra of the methylethylboranes is predictably complex.

Several interesting features observed in the mass spectra of the molecules $(CH_3)_NB(C_2H_5)_{3-N}$ ($N = 0, 1, 2, 3$) deserve mention. The fragments $CH_3{}^{10}BC_2H_5{}^+$ (m/e 54) and $CH_3{}^{11}BC_2H_5{}^+$ (m/e 55) are observed in the spectra of $(CH_3)_2BC_2H_5$ and $CH_3B(C_2H_5)_2$ and are absent in the spectra of $(CH_3)_3B$ and $B(C_2H_5)_3$. However, the fragment $(CH_3)_2{}^{11}B^+$ (m/e 41) is the most intense ion in the spectra of $(CH_3)_3B$, $(CH_3)_2BC_2H_5$ and $B(C_2H_5)_3$ and is also intense in the spectrum of $CH_3B(C_2H_5)_2$. It is obvious that rearrangement is a facile process for these molecules. Molecular ions are observed in the low resolution spectra of all four molecules.

The primary purpose of this investigation was to determine whether or not the mixed methylethylboranes exist and to characterize these molecules if they are stable. The data presented in this paper clearly establishes that these molecules are stable and can be isolated in the pure state with little difficulty. Therefore, the hypothesis that the methylvinylboranes are stabilized by resonance delocalization of the vinyl π-electron density now requires some clarification. Delocalization of vinyl π-electron density has been demonstrated in other vinylboranes [5] and most likely occurs in the mixed methylvinylboranes also. However, the original implication that the stability of the methylvinylboranes arises primarily from the mesomeric interaction is invalid since the elusive methylethylboranes have now been fully characterized. Although no thorough studies of thermal stability were undertaken, samples of the mixed alkylboranes were found to disproportionate over a period of several days into all possible rearrangement products. Thus, the saturated and unsaturated mixed alkylboranes behave similarly [1], although the relative rates of disproportionation are not known at this time.

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