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Tetradecaborane(18). Preparation and Structure

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Controlled hydrolysis of $B_{16}H_{20}$ forms the new borane $B_{14}H_{18}$. Deuterolysis of $B_{16}H_{20}$ generates $B_{14}H_{18-x}D_x$. On the basis of the method of synthesis and the 70.6-MHz ^{11}B NMR and the 33.7-MHz ^2H NMR spectra of these compounds, a structure for $B_{14}H_{18}$ is proposed. This structure involves an edge fusion of decaborane and hexaborane frameworks which is similar to the structure of *i*-$B_{18}H_{22}$.

Introduction

At present approximately 20 neutral boranes (i.e., B_2H_6,[2] B_4H_{10},[2a,3] B_5H_9,[2a,4] B_5H_{11},[2a,5] B_6H_{10},[2a,6] B_6H_{12},[7] B_8H_{12},[8] B_8H_{18},[9] *n*-B_9H_{15},[10] $B_{10}H_{14}$,[2a,11] 1,1'-$B_{10}H_{16}$,[12] 1,2'-$B_{10}H_{16}$,[13] 2,2'-$B_{10}H_{16}$,[13] $B_{13}H_{19}$,[14] $B_{14}H_{20}$,[15] $B_{15}H_{23}$,[16] $B_{16}H_{20}$,[17] *n*-$B_{18}H_{22}$,[18,19] *i*-$B_{18}H_{22}$,[20] and $B_{20}H_{16}$[21]) have been isolated and their structures fairly well determined. In addition there are ten or more boranes which have been mentioned in the literature that are of low stability and unknown structure.

This paper deals with detailed information about another borane, $B_{14}H_{18}$ (I), which we have already described in a preliminary report.[22]

Experimental Section

The ^{11}B NMR spectra were obtained on equipment consisting of a pulsed NMR apparatus (built at Indiana University) operating at 70.6 MHz, a Varian 51.7-kG superconducting magnet, and a 20 K Nicolet 1080 series computer. The spectra were measured in CS_2 and externally referenced to $BF_3{\cdot}O(C_2H_5)_2$. The ^2H spectra were measured at 33.7 MHz on the same equipment. The mass spectra were recorded with a LKB 9000 instrument at 70 eV and inlet temperature of 50°. Infrared spectra were measured with a Beckman IR 20A instrument. The ultraviolet spectra were obtained in cyclohexane on a Beckman DK 1 spectrometer. Gas-phase chromatographic analyses were carried out with a Chrom-3 laboratory chromatograph employing a 2400-mm column (6-mm diameter) and hydrogen as carrier gas.

All preparations were carried out in a nitrogen atmosphere. Hexadecaborane(20) was prepared according to the method of Plesek et al.[17]

Hydrolysis of $B_{16}H_{20}$ to $B_{14}H_{18}$ in Hexane. To a solution of 1.0 g of $B_{16}H_{20}$ in 50 ml of hexane was added 25 ml of H_2O under nitrogen. The mixture was maintained at 60° with vigorous stirring for 8 hr. During this time 630 cm^3 of hydrogen gas was evolved. After cooling to room temperature, the hexane layer was separated and the solvent was removed by evaporation in vacuo. The residue was kept for another 2 hr at 10^{-2} Torr to remove the last traces of water. The mixture of reaction products was then separated by gradual heating in vacuo at 10^{-4} Torr with the aid of an adapter having a collar as illustrated in Figure 1. The by-product $B_{10}H_{14}$ (30–35 mg) sublimed at room temperature and was collected in the upper part of the tube over the collar by cooling the walls with Dry Ice. When no further $B_{10}H_{14}$ sublimed, the temperature was raised to 50° and the slowly distilling $B_{14}H_{18}$ (130–150 mg, 30% yield based on $B_{16}H_{20}$ consumed) was collected in the collar by cooling its wall locally with Dry Ice. By raising the temperature to 80–90° the unreacted $B_{16}H_{20}$ (0.45–0.5 g) sublimed and was collected as crystals by cooling the lower part of the tube under the collar. The tetradecaborane(18), a very viscous and slightly yellowish liquid was transferred by suction under nitrogen into a glass bulb and purified by repeated distillation at 50° and 10^{-4} Torr. The mass spectrum of $B_{14}H_{18}$ is given in Figure 2. The infrared spectrum of the neat liquid includes absorptions at 332 sh, 343 sh, 355 sh, 379 mw, 392 mw, 431 sh, 439 ms, 465 w, 478 w, 511 w, 534 w, 563 w, 590 w, 615 s, 653 sh, 669 s, 681 s, 710 s, 717 sh, 743 w, 756 sh, 774 ms, 794 ms, 813 ms, 825 s, 851 ms, 869 w, 882 ms, 903 sh, 913 sh, 924 ms, 940 sh, 946 ms, 964 ms, 981 vs, 1000 ms, 1020 ms, 1039 ms, 1063 w, 1079 ms, 1108 w, 1300 sh, 1376 sh, 1388 s, 1442 sh, 1469 sh, 1505 s, 1553 ms, 1830 sh, 1900 sh, 1952 ms, 1990 sh, 2580 vs, 2606 cm^{-1} sh. The ultraviolet spectrum shows absorptions in cyclohexane at λ_{max} (ϵ) 213 nm (5420), 246 nm (4020), and 321 nm (1260).

Deuterolysis of $B_{16}H_{20}$ to $B_{14}H_{18-x}D_x$. To a solution of 0.50 g of $B_{16}H_{20}$ in 25 ml of hexane was added 10 ml of D_2O (99.5% isotopic purity). The solvolysis as well as the separation of products was performed in the same manner as described above. By repeated distillation 50 mg of $B_{14}H_{18-x}D_x$ was obtained. The infrared spectrum of the neat liquid contained absorptions at 379 sh, 392 sh, 418 mw, 426 sh, 441 mw, 507 w, 524 w, 545 mw, 562 w, 582 mw, 616 w, 637 ms, 653 vw, 670 vw, 713 s, 726 sh, 738 sh, 750 ms, 771 ms, 797 ms, 809 sh, 827 w, 860 mw, 895 ms, 906 sh, 919 w, 920 sh, 953 s, 964 sh, 981 ms, 999 ms, 1017 ms, 1050 ms, 1062 sh, 1103 sh, 1115 ms, 1156 ms, 1168 sh, 1341 ms, 1380 sh, 1388 ms, 1413 ms, 1425 sh, 1460 sh, 1502 ms, 1534 ms, 1900 sh, 1944 ms, 2591 vs, 2604 sh cm^{-1}.

Degradation of $B_{16}H_{20}$ to $B_{14}H_{18}$ by the Theoretical Amount of H_2O in Diethyl Ether. To a solution of 0.5 g of $B_{16}H_{20}$ in 30 ml of dry diethyl ether was added 0.14 g of H_2O under nitrogen and the reaction mixture was stirred for 1 hr at room temperature. During this period 0.35 l. (theory 0.235 l.) of hydrogen was evolved. By a separation procedure similar to that described above tetradecaborane(18) (22 mg), decaborane(14) (45 mg), and 365 mg of a sublimable, highly air-sensitive mixture of unidentified compounds was obtained.

Results and Discussion

The discovery of the borane $B_{16}H_{20}$[17] which represents the combination of a decaborane and octaborane skeleton has clearly demonstrated that higher boranes, in which two different borane fragments are fused by a common edge, can exist. It seems quite possible then that other boranes of this general type such as $B_{14}H_{18}$ and $B_{13}H_{17}$ (i.e., the combinations of decaborane with hexaborane or pentaborane, respectively) might also exist.

Employing the knowledge that hydrolytic degradation of octaborane(12) yields hexaborane(10),[23] we studied a similar solvolysis of hexadecaborane(20) (II). This reaction gave the expected tetradecaborane(18) according to the equation

$$B_{16}H_{20} + 6H_2O \rightarrow B_{14}H_{18} + 2H_3BO_3 + 4H_2$$

The best yields of borane I (15–30%) were obtained in the absence of oxygen and in hexane as a reaction medium. In ethers, the selective hydrolysis to $B_{14}H_{18}$ was accompanied by a much more extensive degradation. In acetonitrile solution, hydrolysis was even less selective and only traces of I were found. This study suggested that the rate of the undesired degradation rises with the increasing solubility of the water in the Lewis base solvent (cf. ref 24). In a heterogeneous hexane–water mixture the hydrolysis of $B_{16}H_{20}$ proceeds stepwise with $B_{14}H_{18}$ being an initial product. The concentration of I at first rises and then falls, and the maximum is dependent on time, temperature, agitation, and hexane:water ratio. In the reaction mixture there was always present unreacted $B_{16}H_{20}$, $B_{14}H_{18}$, and $B_{10}H_{14}$ and these were separated by a combination of sublimation and distillation, under vacuum, with a very slow rise in temperature. The purification process had to be repeated several times.

Tetradecaborane(18) is a colorless, viscous liquid which

Table I. ^{11}B NMR Chemical Shift Assignments for $B_{10}H_{14}$, B_6H_{10}, and $B_{14}H_{18}$

$B_{10}H_{14}$		B_6H_{10}		$B_{14}H_{18}$	
$\delta(^{11}B)^a$	Assignment	$\delta(^{11}B)$	Assignment	$\delta(^{11}B)$	Proposed assignment
				−23.9	B(6,6′)
				−19.9	B(3′) or B(9)
−12.6	B(1), B(3)	−14.1	B(2)–B(6)	−14.1	B(1) or B(3)
				−9.0	B(3) or B(1)
−10.4	B(6), B(9)			−7.1	B(9) or B(3′)
				−4.4	B(7), B(8), or B(10)
				−3.1	B(7), B(8), or B(10)
				−2.1	B(5,5′)
−1.0	B(5), B(7), B(8), B(10)			−0.4	B(7), B(8), or B(10)
				+8.4	B(4′)
				+18.8	B(2′)
35.5	B(2), B(4)			+36.7	B(2) or B(4)
				+39.8	B(4) or B(2)
		+51.8	B(1)	+46.4	B(1′)

[a] In ppm relative to external $BF_3{\cdot}OEt_2$.

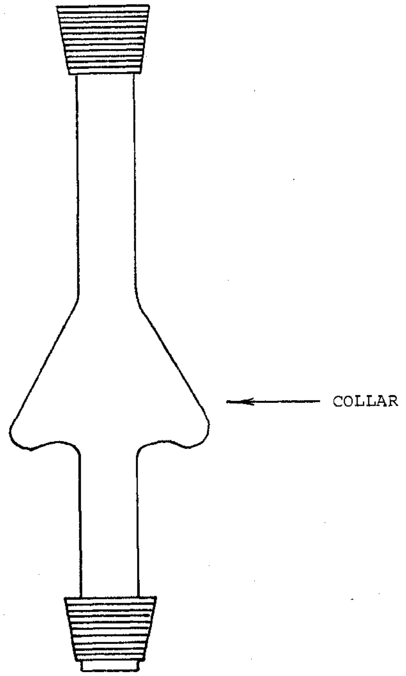


Figure 1. Adapter used for separation of $B_{14}H_{18}$.

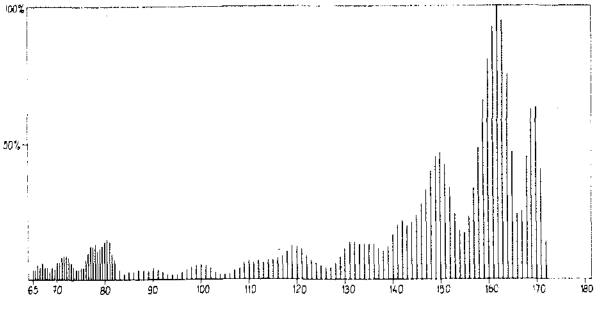
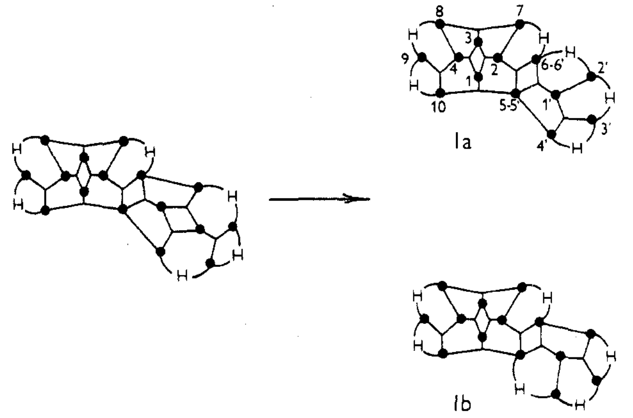


Figure 2. Mass spectrum of $B_{14}H_{18}$ at 70 eV.

shows no tendency to crystallize even at low temperature at which point it changes only to a glassy mass. It is heat sensitive and starts to decompose above 100°. When sealed under nitrogen it is stable for at least 1 year at ambient temperature. Despite its heat sensitivity, borane I can be identified by gas–liquid chromatography on Chromosorb W, impregnated by 20% fluorosilicon polymer QF 1. Under these conditions at 152.5°, $B_{14}H_{18}$ has a retention time of 506 sec and $B_{10}H_{14}$ has a retention time of 93 sec.

The mass spectrum of $B_{14}H_{18}$ (Figure 2) at 70 eV shows the cutoff at *m/e* 172, corresponding to the $^{11}B_{14}{}^1H_{18}{}^+$ cation.

Scheme I



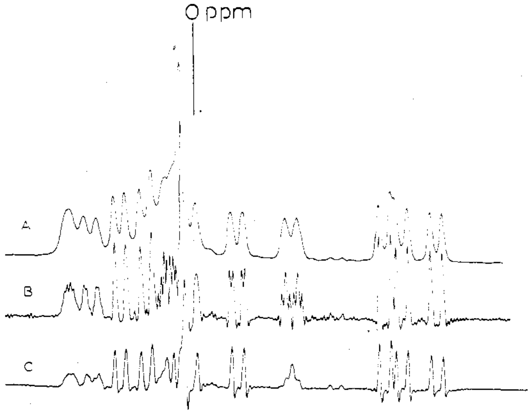


Figure 3. (A) The 70.6-MHz ^{11}B NMR spectrum of $B_{14}H_{18}$ in CS_2 solution. (B) The line-narrowed ^{11}B NMR spectrum of $B_{14}H_{18}$. (C) The line-narrowed ^{11}B NMR spectrum of $B_{14}H_{18-x}D_x$.

The fragmentation is typical for nido compounds, having a deep valley at the $(M - 6)^+$ mass. The infrared spectrum exhibits strong BH_t absorption vibrations at 2580 and 2606 cm^{-1}, B–H–B vibrations in the regions of 1540–1600 and 1830–1990 cm^{-1}, and a great deal of skeletal absorptions below 1100 cm^{-1} which indicates the low symmetry of the $B_{14}H_{18}$ molecule.

Structure of $B_{14}H_{18}$. The method of synthesis of $B_{14}H_{18}$ by hydrolytic removal of two boron atoms from $B_{16}H_{20}$ strongly suggests that the product will have one of the two structures presented in Scheme I. Structures Ia and Ib are similar to the known structures of *i*-$B_{18}H_{22}$[18] and *n*-$B_{18}H_{22}$,[18] respectively.

In Figure 3A and 3B are given the normal and line-narrowed 70.6-MHz ^{11}B NMR spectra of $B_{14}B_{18}$, respectively. Although only 13 resonances can be seen in the spectrum, peak area

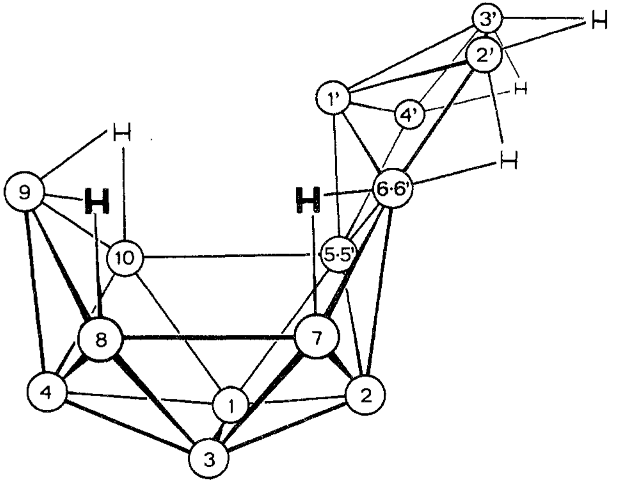


Figure 4. Proposed structure of $B_{14}H_{18}$.

integration indicates that 14 boron atom resonances are present with the 14th resonance hidden in the −4-ppm region. To a large extent, the ^{11}B NMR spectrum of $B_{14}H_{18}$ appears to be a composite of the signals expected for both $B_{10}H_{14}$ and B_6H_{10}. A comparison of the chemical shift data of these three molecules is given in Table I. The two singlet resonances at −23.9 and −2.1 ppm in Figure 3A can be assigned to the two junction boron atoms which are common to both the hexaborane and decaborane parts of the structure. The resonance at −23.9 ppm exhibits additional spin–spin coupling in the line-narrowed spectrum. The coupling pattern can be due to contributions from bridge hydrogen coupling as well as ^{11}B–^{11}B coupling of the type observed recently for B(6) and B(9) of $B_{10}H_{14}$.[25] Therefore considering its chemical shift (−23.9 ppm) and coupling pattern we propose that this signal is due to B(6,6') [see numbering on structure Ia]. The other singlet at −2.1 ppm shows no observable spin coupling and lies in the chemical shift region of atoms B(5), B(7), B(8), and B(10) of $B_{10}H_{14}$. On this basis we propose that this signal is due to B(5,5') and that the isomer we have prepared corresponds to structure Ia. In the proposed structure (Figure 4) B(5,5') has six near-neighbor boron atoms and no bridge hydrogens. In the line-narrowed spectrum of $B_{14}H_{18}$ five doublets show no observable additional coupling. The highest field resonance at 46.4 ppm can be assigned to the B(1') atom of the hexaborane fragment of $B_{14}H_{18}$. The resonance of the B(1) atom of B_6H_{10} is found at 51.8 ppm. The two closely spaced doublets at 39.8 and 36.7 ppm occur in the region expected for the B(2) and B(4) atoms of $B_{10}H_{14}$ (i.e., 35.5 ppm). The two lower field doublets at −14.1 and −9.0 ppm have the appropriate shieldings expected for the B(1) and B(3) atoms of the decaborane fragment. The two doublets at 8.4 and 18.8 ppm occur outside the normal shift region for $B_{10}H_{14}$. The former signal, with line narrowing, appears as a doublet of doublets which suggests coupling with one bridge hydrogen and can be assigned to B(4') of the hexaborane fragment. The resonance at 18.8 ppm appears to have spin coupling to two bridge hydrogens and can be assigned to either B(2') or B(3'). A narrow-band proton decoupling irradiation was applied at various frequencies in the bridge proton region while the ^{11}B NMR spectrum of $B_{14}H_{18}$ was recorded. The bridge hydrogen coupling on the 8.4-ppm resonance could be removed without affecting the bridge hydrogen coupling on the 18.8-ppm signal. This indicates that these two boron resonances are not due to adjacent boron atoms which share a bridge proton and suggests that the signal at +18.8 ppm is due to B(2').

$B_{14}H_{18-x}D_x$. Formation of I by degradation of $B_{16}H_{20}$ with deuterium oxide gives a product which is partly deuterated. The infrared spectrum of this product contains a new relatively intense band at 1944 cm^{-1} which is due to ν_{BD_t}. The Fourier transform ^2H NMR spectrum at 33.7 MHz of $B_{14}H_{18-x}D_x$ is given in Figure 5. In the line-narrowed spectrum six resonances are observed at high field in the region expected for bridge deuterium atoms. In addition there is a broad multiplet at lower field of approximate relative area 4 which can be attributed to deuterium atoms in terminal positions. Exchange of all six of the bridge hydrogens with deuterium leads to a simplified ^{11}B NMR spectrum which is presented in Figure 3C. This spectrum reveals three resonances at −7.1, −4.4, and −3.1 ppm which could not be seen in the line-narrowed ^{11}B NMR spectrum of $B_{14}H_{18}$ due to bridge hydrogen coupling. In addition the presence of terminal deuteriums is apparent in the signals at −19.9 and +18.8 ppm. Analysis of the available NMR data is consistent with the proposal that this $B_{14}H_{18}$ isomer has a structure consisting of edge fusion of decaborane and hexaborane frameworks which is similar to the structure of *i*-$B_{18}H_{22}$.

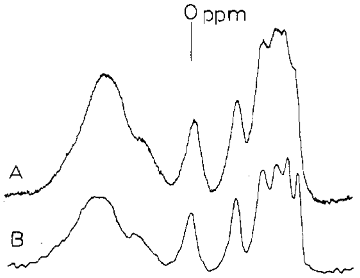


Figure 5. (A) The 33.7-MHz ^2H NMR spectrum of $B_{14}H_{18-x}D_x$ in CS_2 solution (external tetramethylsilane-d_{12} = 0 ppm). (B) The line-narrowed ^2H NMR spectrum of $B_{14}H_{18-x}D_x$.

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Registry No. $B_{16}H_{20}$, 28265-11-4; $B_{14}H_{18}$, 55606-55-8.

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Reaction of Silyl Radical and Silylene with Acetylene and Application of Orbital Symmetry to the Pyrolysis of Silane and Disilane

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The thermal decomposition of SiH_4 and Si_2H_6 was examined in the presence of C_2H_2. The product from reaction of SiH_2 (generated from Si_2H_6) with C_2H_2 was found to be $H_3SiC{\equiv}CH$. The absence of this product, near zero reaction time, in the SiH_4–C_2H_2 pyrolysis system suggests that SiH_2 is not the dominant radical species in the SiH_4 pyrolysis. The products in the SiH_4–C_2H_2 pyrolysis system were consistent with silyl radicals as the dominant silicon radical species. The thermal decomposition of SiH_4 to SiH_2 and H_2 was examined by orbital symmetry considerations. The least motion path must generate a high-energy $^1SiH_2$ to be allowed, while another path yielding ground state $^1SiH_2$ adds a strain energy to the activation energy. These results are consistent with the apparent absence of SiH_2 from the thermolysis of SiH_4.

Introduction

Examinations of the pyrolysis of SiH_4 and related studies have recently been carried out by various groups.[1-3] At this time, no concensus exists concerning the mechanism of the pyrolysis of SiH_4. A detailed kinetic study of the thermal decomposition of SiH_4 was carried out by Purnell and Walsh.[1] The decomposition rate was found to be independent of the surface to volume ratio over a silicon mirror (result confirmed in our laboratory). Purnell and Walsh determined that the initial silane decomposition could be represented by

$$\text{rate} = 10^{(15.2-(55.9/2.3RT))}(\text{SiH}_4)^{3/2}\ \text{mol/(l. sec)} \tag{1}$$

Purnell and Walsh[1] proposed the following two mechanisms which would be consistent with their results: mechanism A, molecular hydrogen elimination

$$SiH_4 \rightarrow SiH_2 + H_2 \tag{2}$$

$$SiH_2 + SiH_4 \rightarrow Si_2H_6 \tag{3}$$

mechanism B, homolytic Si–H bond rupture

$$SiH_4 \rightarrow SiH_3 + H \tag{4}$$

$$H + SiH_4 \rightarrow SiH_3 + H_2 \tag{5}$$

$$SiH_3 + SiH_4 \rightarrow Si_2H_6 + H \tag{6}$$

$$2SiH_3 \rightarrow Si_2H_6 \tag{7}$$

Purnell and Walsh favored mechanism A but could not rule out mechanism B. In an attempt to demonstrate that only mechanism A was operative, the pyrolyses of equimolar SiH_4–SiD_4 mixtures were examined in a recirculating flow system with a cold trap which removed the product disilanes from the stream.[2] If SiH_4 decomposed solely by mechanism A, the hydrogen fraction produced from such an experiment should have consisted of only H_2 and D_2. The hydrogen fraction contained 31% HD which suggested that mechanism B was also important.

Assuming mechanism B to be predominant, one calculates that the *A* factor for the SiH_4 pyrolysis should be between 10^{12} and 10^{13} which does not agree with the $10^{15.2}$ experimental value.

Recently, John and Purnell have obtained equilibrium constants for reactions of SiH_3 radicals[3] (eq 8, 9). These authors have suggested that the equilibrium data argue in favor of reaction 2 as the primary decomposition mode of SiH_4 and in favor of the SiH_2 diradical as the dominant radical species in SiH_4 decompositions.

$$SiH_3 + H \rightleftarrows SiH_2 + H_2 \quad K_8 = 10^{15.9} \tag{8}$$

$$2SiH_3 \rightleftarrows SiH_2 + SiH_4 \quad K_9 = 10^{11.3} \tag{9}$$

The thermal reaction of SiH_4 and acetylene has been examined by White and Rochow.[4] This pyrolysis was carried out in a flow system at 450–510° with a –78° cold trap. The major product was ethynyldivinylsilane with lighter unidentified products containing ethynyl and vinyl groups. These authors were unable to account for the presence of ethynyl groups bonded to silicon.

At this time, two important questions concerning the monosilane pyrolysis remain unanswered. First, what is the dominant reactive intermediate (SiH_3 radical, SiH_2, or both), and second, what is the overall homogeneous mechanism?

In this paper we report our results on the decompositions of SiH_4 and of Si_2H_6 in the presence of C_2H_2. These investigations should allow us to determine the product from reaction of SiH_2 (generated from Si_2H_6) with C_2H_2 and, if this product is absent in the SiH_4–C_2H_2 thermolysis, to eliminate SiH_2 as the dominant radical species in the SiH_4 decomposition.

The reaction of silylenes with acetylenes has been examined in some detail but continues to be of interest in organosilicon chemistry.[5]

Results

I. Application of Orbital Symmetry to the Pyrolysis of Silane and Disilane. Recently, Pearson has discussed the application of orbital symmetry rules to unimolecular reactions.[6] It was concluded that there are no orbital symmetry barriers to reactions of molecules decomposing into a radical and an atom such as the decomposition of SiH_4 into SiH_3 radicals and H atoms (eq 4). However, reactions in which bonds are broken and made in a concerted process (eq 2) can be restricted by