TABLE IX

FRAMEWORK CHARGES[a]

Type	I	II	III	IV	V	VI
C–H equatorial (C6)	−0.48	−0.44	0.38	0.30	0.08	0.02
C–H apical (C1)	−0.58	−0.57	0.32	0.28	0.01	0.00
B–H bonded to both C's (B2, B5)	0.35	0.34	0.01	0.01	0.15	0.13
B–H bonded to 1 C (B3, B4)	0.12	0.11	−0.07	−0.07	0.00	−0.01
B–H bonded to 1 C (B7, B9)	0.10	0.10	−0.10	−0.09	−0.05	−0.02
B–H bonded to 1 C, apical (B10)	0.03	0.02	−0.13	−0.08	−0.05	−0.01
B–H bonded to no C's (B8)	−0.09	−0.10	−0.23	−0.19	−0.25	−0.19

[a] Defined as the sum of the atomic charges for a B–H or C–H unit.

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The Chlorination of 2,4-Dicarba-*closo*-heptaborane(7)

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The *closo*-carborane, $C_2B_5H_7$, reacts rapidly with Cl_2 in the presence of $AlCl_3$ to form HCl and 5-$ClC_2B_5H_6$. The reaction without $AlCl_3$ is accelerated by light forming, in addition to the 5 isomer, 1-$ClC_2B_5H_6$ and 3-$ClC_2B_5H_6$. The identity and structure of the new compounds are indicated by their mass spectra and ^{11}B nmr spectra. A trans effect is observed in the ^{11}B nmr of the 1-chloro derivative and reciprocal effects are observed in all compounds.

Introduction

Recent studies have shown that chlorine and bromine can be substituted for boron-bonded hydrogen on $C_2B_4H_8$[1] and B_5H_9[2] by treating the compound with molecular halogen. In the case of B_5H_9, both apex and base substitutions occur when no aluminum halide catalyst is used. If aluminum halide is present, substitution takes place at only the apex position. In $C_2B_4H_8$ substitution occurs at the base position adjacent to a carbon atom. In both compounds, the aluminum halide catalyzed substitutions are directed toward the boron atom with the most negative or least positive charge.

The charge distribution of 2,4-dicarba-*closo*-heptaborane(7)[3] has also been calculated[4] and the 5,6-boron atoms have the highest negative charge: −0.179 *vs.* 0.031 and 0.334 for the 3 and 1,7 positions, respectively. Therefore, it is expected that electrophilic substitution will occur at the 5 position in the presence of aluminum halide. This investigation reports the synthesis and properties of 5-$ClC_2B_5H_6$ by such a reaction. In addition, the other two boron-substituted isomers are also produced from a similar reaction in which no $AlCl_3$ is added.

Experimental Section

Standard high-vacuum equipment was used for the manipulation of all volatile components. 2,4-Dicarba-*closo*-heptaborane(7), $C_2B_5H_7$, was synthesized by the pyrolysis of $C_2H_4H_8$.[5] It was purified by glpc. *Chlorine* was distilled to remove hydrogen chloride and water; it was measured as a gas using a mercury manometer which was protected by silicone oil.

Gas chromatography equipment (glpc) consisted of a 20-ft glass coil, of $^5/_{16}$-in. inside diameter, packed with 20% Apiezon L on Chromosorb P. This column packing proved to be much better for separating the compounds involved here than the Kel-F on firebrick used in previous studies. Infrared spectra were recorded from 2 to 15 μ by a Perkin-Elmer 137 or Beckman IR-5 instrument. Gas-phase spectra at 10–20 Torr were obtained in 10-cm cells. The nmr spectra were run on Varian instruments at 220 and 100 MHz for ^1H and 32.1 MHz for ^{11}B. External tetramethylsilane and boron trifluoride diethyl etherate were used for respective standards. Mass spectra were obtained from West Coast Technical Service, San Gabriel, Calif.

Chlorine and $C_2B_5H_7$ in the Presence of Aluminum Chloride.—About 0.3 g of $AlCl_3$ was introduced into a 1 l. bulb which was then evacuated. The $AlCl_3$ was sublimed onto the walls of the flask by flaming gently. Chlorine gas, 1.5 mmol, and $C_2B_5H_7$, 3.0 mmol, were condensed into the bulb at −196° which was

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* To whom correspondence should be addressed.

(1) J. R. Spielman, G. B. Dunks, and R. Warren, *Inorg. Chem.*, **8**, 2172 (1969).

(2) D. F. Gaines and J. A. Martens, *ibid.*, **7**, 704 (1968).

(3) The numbering system for this compound is not clear from the nomenclature article in *Inorg. Chem.*, **7**, 1945 (1968). Using, 3,6 rather than 2,4 for the placement of the carbon atoms is more consistent with the symmetry rules; however, the rules governing carbon replacement of boron do not exclude the use of 2,4. In a discussion with R. Adams of the nomenclature committee it was decided to use the 2,4 rather than the 3,6 numbering of carbon atoms.

(4) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963, pp 93–100.

(5) J. F. Ditter, *Inorg. Chem.*, **7**, 1748 (1968). The authors are indebted to Dr. J. F. Ditter and Dr. R. E. Williams of Chemical Systems Co., for a generous supply of this material.

then sealed. On warming to room temperature, the color of the Cl_2 disappeared rapidly. The volatile components recovered were $C_2B_5H_7$ (*ca.* 1.5 mmol), HCl (1.7 mmol), and 5-$ClC_2B_5H_6$ (0.78 mmol). No H_2 was detected and the only other volatile material found was a possible $Cl_2C_2B_5H_5$ which is still under investigation. In subsequent experiments it was found that the reaction vessel could be conveniently closed with a Teflon needle valve. The 5-$ClC_2B_5H_6$ was identified by its mass spectrum, elemental analysis, and nmr spectrum (Figures 1 and 2) which are discussed below. The analysis was performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. *Anal.* Calcd for $ClC_2B_5H_6$: Cl, 29.65; C, 20.09; B, 45.20; H, 5.06. Found: Cl, 29.40; C, 20.01; B, 45.52; H, 5.13. The mass spectrum (Table I) cut off at a maximum of *m/e* 122 corresponding to $^{37}Cl-{}^{12}C_2{}^{11}B_5{}^1H_6$. Infrared spectrum ($cm^{-1}$): 3310 b, m, 3080 w, 2800 b, w, 2630 s, 1232 s, 1123 s, 1052 ms, 1010 m, 969 mw, 877 ms, 847 m, 807 m, 711 m. The vapor pressures at 0 and 23.5° were 5.4 and 21.7 Torr, respectively.

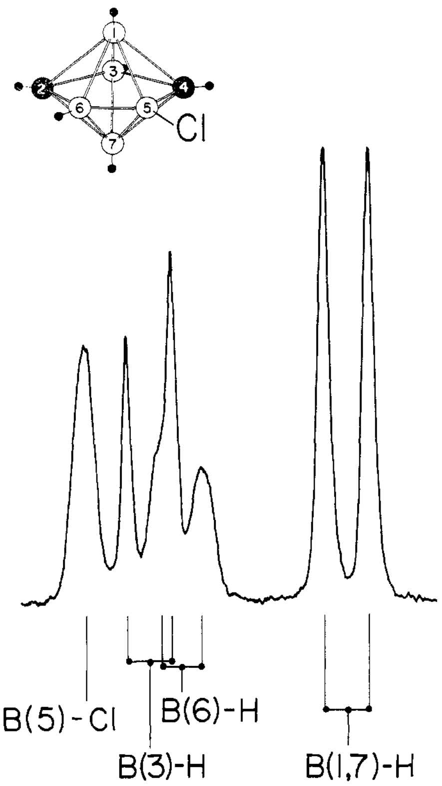

Figure 1.—^{11}B nmr spectrum (32.1 MHz) of 5-Cl-2,4-$C_2B_5H_6$.

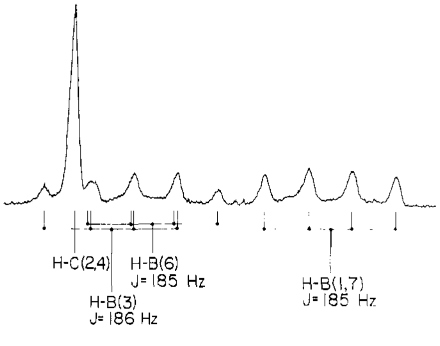

Figure 2.—^1H nmr spectrum (220 MHz) of 5-Cl-2,4-$C_2B_5H_6$.

TABLE I

PARENT PEAK ENVELOPE IN THE POLYISOTOPIC MASS SPECTRUM OF 5-$ClC_2B_5H_6$

m/e	Normalized intens	*m/e*	Normalized intens	*m/e*	Normalized intens
123	0.49	118	76.3	113	3.98
122	16.89	117	42.0	112	1.49
121	29.38	116	19.8	111	0.54
120	75.2	115	11.4	110	0.27
119	100.0	114	7.47		

Chlorine and $C_2B_5H_7$ without Aluminum Chloride.—A mixture of Cl_2 (2.5 mmol) and $C_2B_5H_7$ (5.0 mmol) were sealed in a 1-l. bulb. No immediate reaction was apparent on warming to room temperature; however, when the gas mixture was exposed to diffuse sunlight, a white cloud of droplets rapidly formed as the color of the Cl_2 disappeared. After preliminary distillation to remove HCl (2.5 mmol), the volatile mixture was passed through the glpc apparatus. The peaks corresponding to 5-$ClC_2B_5H_6$, 1-$ClC_2B_5H_6$, and 3-$ClC_2B_5H_6$ were found in addition to recovered $C_2B_5H_7$. Although it was not possible to separate the latter two chloro isomers completely, the identity of the 3-$ClC_2B_5H_6$ is apparent from the ^{11}B nmr shown in Figure 3. Subtracting these resonances from the ^{11}B nmr of the impure 1-$ClC_2B_5H_6$ allowed for the structural assignment of the latter compound. The mass spectra of three $ClC_2B_5H_7$ isomers were nearly identical, showing cutoffs at *m/e* 122. The approximate yields were estimated from the glpc peak intensities and are given along with the relative retention times in Table II. When a medium-pressure, mercury-arc quartz lamp was used for a light source, the mixture exploded inside the bulb leaving a black solid on the walls of the container and very little volatile material other than HCl.

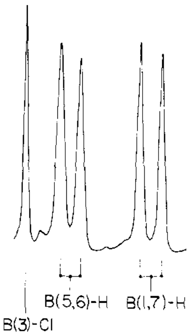

Figure 3.—The ^{11}B nmr spectrum (32.1 MHz) of 3-Cl-2,4-$C_2B_5H_6$.

TABLE II

	Yield, %	% yield based on $C_2B_5H_7$ consumed	Rel retention time
$C_2B_5H_7$	0.75 (recovered)	...	1.0
5-$ClC_2B_5H_6$	6.8	27.2	3.59
3-$ClC_2B_5H_6$	1.6	6.4	2.64
1-$ClC_2B_5H_6$	1.6	6.4	2.72

Results and Discussion

The structure of the single isomer formed in the reaction between chlorine and 2,4-$C_2B_5H_7$ and catalyzed by $AlCl_3$ is indicated by the ^{11}B nmr shown in Figure 1 and summarized in Table III. The doublet found at δ −2 ppm in $C_2B_5H_7$ has been assigned to the 5,6 position.[6] This doublet decreases in intensity and a new singlet appears at −12.4 ppm corresponding to the B–Cl. Further support of this structure is found in the ^1H nmr

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(6) T. Onak, G. B. Dunks, R. A. Beaudet, and R. L. Poynter, *J. Amer. Chem. Soc.*, **88**, 4622 (1966).

TABLE III

^{11}B NMR CHEMICAL SHIFTS

	δ ($BF_3\cdot(C_2H_5)O$ = 0); J, Hz		
	B(1) B(7)	B(3)	B(5) B(6)
$C_2B_5H_7$	+23.5, 178	−5.0, 187	−2.0, 170
5-$ClC_2C_5H_6$	+21.1, 181	−4.1, 185	−12.4 (Cl) −0.15, 184
3-$ClC_2B_5H_6$	+18.7, 177	−15.1 (Cl)	−3.0, 172
1-$ClC_2B_5H_6$	+13.7 (Cl) +31.0, 184	−9.6, 179	−4.2, 160

spectrum at 220 MHz shown in Figure 2. It is apparent that there are three quartets due to three different B–H groups in the area ratio of about 1:1:2 as well as a single resonance for the C–H protons. The middle quartet assigned to the H–B(6) is only half the intensity of the H–B(5,6) resonance in the parent compound.

As in the similar reactions of B_5H_9[2] and $C_2B_4H_8$,[1] substitution occurs at the boron atom with the highest negative charge.[4]

Two other isomers, 1-Cl and 3-Cl, are formed in addition to 5-$ClC_2B_5H_6$ when no aluminum chloride is used. It has not been possible to prepare these two compounds in large amounts nor has it been possible to obtain them completely pure. However the ^{11}B nmr spectra obtained from the samples are clearly compatible with the assigned structures. Figure 3 shows the ^{11}B nmr spectrum of 3-$ClC_2B_5H_6$ and the assignments are obvious by comparison to the ^{11}B nmr parent compound. Although not much is known about the mechanism for the type of reaction that led to these products, the rapid acceleration by light indicates that it is a chain reaction initiated by atomic chlorine.

Some useful comparisons can be made between the ^{11}B nmr of these compounds and ClB_5H_8.[2,7,8] When a chlorine is placed in the 2 position (basal) of pentaborane, the effect is to shift the 4 position upfield about 10 ppm. The effect on the immediately attached boron is an expected downfield shift of about 12 ppm. Boron atoms not in either of these two categories are not appreciably affected. For chloro derivatives of 2,4-$C_2B_5H_7$ it is interesting to note a pattern vaguely similar to the chloropentaboranes. The most noticeable trans effect is observed in the 1-chloro derivatives where an upfield shift of 7–8 ppm is noted for the trans 7 position. It is curious that no substantial upfield "trans" shifts are observed for the 3- and 5-chloro derivatives. However, only in the 1-chloro derivative is there a trans boron in the sense that there is a boron of identical but mirror image environment (7 position of the parent compound). This boron is situated directionally opposite the substituted boron if one were to draw a line through the center of the cage. It is possible that resonance features in the $C_2B_5H_7$ structure which are similar to the sort of delocalization effects found for the pentaborane derivatives[7,8] would account for this observation. Other effects found for these chloro derivatives of $C_2B_5H_7$ are as follows: (a) a boron immediately attached to the chlorine is shifted downfield 10 ppm regardless of the position of substitution; (b) an effect which we have chosen to call a "reciprocal" effect is also observed. That is, substitution on the 3-boron shifts the 1-boron downfield 5 ppm and substitution on the 1-boron shifts the 3-boron downfield 5 ppm. Another reciprocal effect is found when substitution in the 5 position shifts the 1-boron downfield 2+ ppm and substitution in the 1 position shifts the 5-boron downfield +2 ppm. These reciprocal effects, along with the trans effect, tend to support an electronic structure for the molecule which is rather delocalized and sensitive to electronic perturbations in the cage electrons as a result of substitution.

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(7) T. Onak and G. B. Dunks, *Inorg. Chem.*, **3**, 1060 (1964).

(8) A. B. Burg, *J. Amer. Chem. Soc.*, **90**, 1407 (1968).