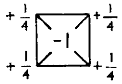
82. *Boron Hydride Derivatives. Part III.* Electrophilic Substitution in Pentaborane and Decaborane.*

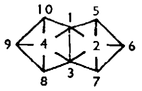
By N. J. Blay, I. Dunstan, and R. L. Williams.

Friedel–Crafts ethylation of pentaborane-9 (B_5H_9) and decaborane ($B_{10}H_{14}$) has been studied and the structures of some of the products have been determined by nuclear magnetic resonance spectroscopy. Substitution takes place mainly at the apical position, where the charge density is highest.

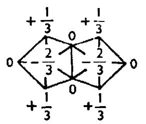
The structures of the simple boron hydrides have been described by Lipscomb,[1] and their charge distribution has been predicted theoretically by Eberhardt, Crawford, and Lipscomb.[2] In the case of pentaborane-9 (B_5H_9), which has a tetragonal pyramid of boron atoms, the apical boron carries a charge of $-e$, while the basal borons each possess $+\frac{1}{4}e$ charge (cf. I). Decaborane consists of two pentagonal pyramids sharing a common edge with the numbering of atoms [3] as shown (cf. II); the predicted charge distribution is as in (III).



(I)



(II)



(III)

Electrophilic substitution would be expected [4] to take place at the regions of high electron density, *viz.*, the apical positions in both molecules, and this view has been confirmed by structural determinations of the monobromo- and monoiodo-derivatives of pentaborane and decaborane by nuclear magnetic resonance spectroscopy [5] and of di-iododecaborane by *X*-ray crystallography.[6]

In the present investigation, the examination of substitution in boranes by electrophilic reagents has been extended to Friedel–Crafts ethylation of pentaborane and decaborane.

Ethylpentaborane was obtained by reaction between pentaborane and ethylene in a sealed flask in the presence of aluminium chloride. As expected, substitution occurred at the apex of the molecule [7] and there was little evidence to suggest that the other monosubstituted isomer had been formed.

Relative retention volumes of Friedel–Crafts ethyldecaboranes $B_{10}H_{14-n}Et_n$ *with hydrogen carrier on an Apiezon L stationary phase with C22 firebrick support* (185°) *or Embacel support* (167°) (V_R *naphthalene* = 1).

n:	0	1	2	2	3	3	3
V_R, at 185°:	0·77	1·58	2·86	3·38	5·56	6·76	7·33
at 167°:	0·77	1·68	3·28	3·88	6·65	8·22	8·98

The reaction between decaborane and ethyl bromide in the presence of aluminium chloride in boiling carbon disulphide gave mixtures of ethylated decaboranes, the degree of ethylation varying with the conditions. Vapour-phase chromatograms of these products invariably gave four or five well-spaced peaks, the first two of which were singlets and the remainder doublets. The retention volume of the first peak showed that it arose from decaborane and it was observed that $\log_{10}$ (Retention volume) of the peaks could be plotted

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* Part II, preceding paper.

[1] Lipscomb, *J. Chem. Phys.*, 1954, **22**, 985.

[2] Eberhardt, Crawford, and Lipscomb, *ibid.*, 1954, **22**, 989.

[3] Shapiro, Lustig, and Williams, *J. Amer. Chem. Soc.*, 1959, **81**, 838.

[4] Lipscomb, *J. Chim. phys.*, 1956, **53**, 515.

[5] Schaeffer, Shoolery, and Jones, *J. Amer. Chem. Soc.*, 1958, **80**, 2670.

[6] Schaeffer, *ibid.*, 1957, **79**, 2726.

[7] Figgis and Williams, *Spectrochim. Acta*, 1959, 331.

linearly against the integers, $n = 0$—3 (Fig. 1), indicating that a series of compounds $B_{10}H_{14-n}Et_n$ was present. This behaviour is similar to that of the polyethylated decaboranes described in Part II. However, the retention volumes of the Friedel–Crafts products (see Table) are all slightly less than those of the corresponding compounds in the latter series, implying that substitution isomers are being produced. This was confirmed by an examination of the infrared spectra and the ^{11}B nuclear magnetic resonance spectra of ethyl- and the two diethyl-decaboranes isolated from the Friedel–Crafts product by chromatography on a preparative scale.

The ^{11}B nuclear magnetic resonance spectrum of decaborane (Fig. 2) consists of a low-field triplet of relative intensities 2, 4, 2 and a high-field doublet of intensities 1, 1. It has been shown [8,9] that the doublet arises from the apical 2,4-boron atoms while the triplet consists of two overlapping doublets, the lower-field component of which results from boron atoms 1, 3, 6, and 9 and the higher-field component from atoms 5, 7, 8, and 10.

The corresponding spectrum of ethyldecaborane shows several changes relative to that of decaborane. The high-field doublet, peaks 4*b* and 5, shows a reduction in intensity, compared with decaborane, coupled with the growth of a new peak, 4*a*, just on the low-field side of the doublet, which results from the collapse of the doublet on substitution of the hydrogen in positions 2 and 4. If all the substituting ethyl groups had entered these positions, the ratio of peak 5 to the composite peak 4 would have been 1 : 3. However, the mean value from four spectra was 0·57, which corresponds to a concentration of at least 55% of 2-ethyldecaborane in the mixture.

FIG. 1. *Plot of* $\log_{10} V_R$ *against number of ethyl groups for the Friedel–Crafts products* $B_{10}H_{14-n}Et_n$. *A*, 185°; *B*, 167°. *The ordinate for line B is that given; for line A add* 0·2 *units. Points are for isomeric forms.*

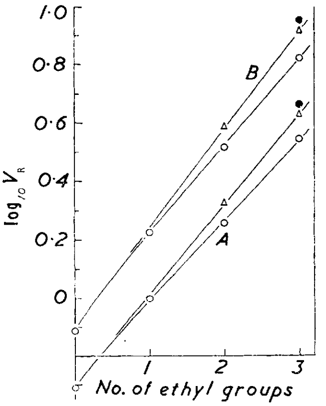
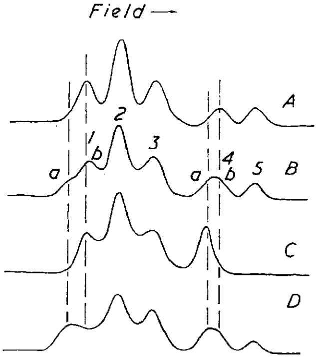


FIG. 2. ^{11}B *nuclear magnetic resonance spectra of*: *A*, $B_{10}H_{14}$; *B*, $B_{10}H_{13}Et$; *C*, $B_{10}H_{12}Et_2$, *first isomer*; *D*, $B_{10}H_{12}Et_2$, *second isomer.*



The reduction in areas of peaks 1*b* and 2, together with the growth of a new peak 1*a*, on the low-field side of these peaks, shows that the remainder of the mixture is either 1- and/or 6-ethyldecaborane. There is no direct evidence as to which of these points has been substituted. However, the reaction of decaborane with acetonitrile at the 6,9-positions,[10] and the preferential deuteration of these points with deuterium oxide,[3] both imply that 6,9-positions are the most electropositive in the molecule and would therefore be unlikely to be attacked by an electrophilic reagent. This view is in agreement with the suggestion

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[8] Schaeffer, Shoolery, and Jones, *J. Amer. Chem. Soc.*, 1957, **79**, 4606.
[9] Williams and Shapiro, *J. Chem. Phys.*, 1958, **29**, 677.
[10] Reddy and Lipscomb, *J. Amer. Chem. Soc.*, 1959, **81**, 754.

by Williams and Shapiro[9] that the charge distribution calculated by Eberhardt *et al.*[2] for positions 1, 5, and 6 in decaborane is in error. It therefore appears probable that the second isomer of ethyldecaborane is the 1-ethyl form.

Since the 2,4-positions and to a smaller extent the 1,3-positions are the most reactive, further ethylation of the mixture of 2- and 1-ethyldecaboranes would be expected to yield 2,4- and 1,2-diethyldecaborane. This is confirmed by the ^{11}B nuclear magnetic resonance spectra for the two peaks corresponding to diethyldecaborane in the vapour-phase chromatogram.

In the spectrum of the first isomer of diethyldecaborane emerging from the column the high-field doublet has collapsed to a single peak of double the intensity, while the low-field triplet is largely unaltered from that of decaborane. Both ethyl groups are therefore in the apical 2,4-positions.

In the spectrum of the second diethyldecaborane isomer, there has been only a partial collapse of the high-field doublet, the area of peak 4*a*,*b* to peak 5 being 2·8, in satisfactory agreement with the required value of 3 for one apical ethyl group. The reduction in height of peak 2 and the partial replacement of peak 1*b* by a new one at 1*a* show that the second group is in the 1-position and that the substance is the 1,2-diethyl compound.

The relative areas of the two diethyldecaborane peaks on the chromatogram show that about 40% of the diethyldecaborane is the 2,4-isomer, the remainder being the 1,2-isomer. This mixture corresponds to ethylation of 70% of all apical positions and proves that this is the chief point of attack in Friedel–Crafts ethylation.

EXPERIMENTAL

Ethylpentaborane.—Finely powdered aluminium chloride (0·93 g., 0·00697 mole) was placed in a 150 c.c. seal-off reaction flask and this was attached to a vacuum-line and evacuated. Pentaborane (0·44 g., 0·00698 mole, measured as gas) and ethylene (600 c.c. at N.T.P.; 0·0268 mole) were distilled into the flask, which was then sealed off. After the mixture had been heated at 60° for 5 hr. the vessel was cooled in liquid nitrogen and opened on the line. A small amount of permanent gas was removed by pumping; the mixture was then held at $-78·5°$ while unchanged ethylene (15·8 c.c. at N.T.P.) was distilled into a trap cooled in liquid nitrogen. The reaction flask was allowed to warm to room temperature and the product, a colourless liquid (0·6 c.c.), was collected by distillation into a trap cooled in liquid nitrogen.

The product, which was spontaneously inflammable in air, was shown by vapour-phase chromatography to consist of pentaborane (57%) and ethylpentaborane (43%). A sample of ethylpentaborane (Found: B, 58·5; C, 26·4; H, 13·3. Calc. for $C_2H_5B_5H_8$: B, 59·3; C, 26·3; H, 14·4%) obtained by preparative-scale vapour-phase chromatography had a vapour pressure of 29 mm. at 19·5°, b. p. 104°, and m. p. $-85°$. The infrared and nuclear magnetic resonance spectra have already been discussed.[7]

Ethylation of Decaborane.—Decaborane (4·14 g., 0·0339 mole) was dissolved in carbon disulphide (50 c.c.) in a 3-necked 250 c.c. round-bottomed flask fitted with mercury-sealed stirrer, gas inlet and reflux condenser. A slightly positive pressure of hydrogen chloride gas was maintained in the apparatus throughout the experiment. Powdered aluminium chloride (4·53 g., 0·0339 mole) and ethyl bromide (1·68 c.c., 0·022 mole) were added and the mixture was heated under reflux for 5 hr. Further ethyl bromide (1·68 c.c., 0·022 mole) was added and heating continued for a further 8 hr. The mixture was filtered and the solution evaporated, to yield a mixture of ethylated decaboranes as a red liquid (4·64 g.), and unchanged decaborane as a yellow solid (0·36 g., 8·7%). The crude product, distilled in a molecular still ($150°/10^{-3}$ mm.), gave fractions F_1 (0·96 g.) and F_2 (1·93 g.) which were shown by vapour-phase chromatography to have the composition: F_1, decaborane 0·4, ethyldecaborane 32·8, diethyldecaborane 49·5, triethyldecaborane 17·4. (Found: B, 62·4; C, 24·0. Calc. for this mixture: B, 63·1; C, 24·7%); F_2, decaborane 10·9, ethyldecaborane 38·0, diethyldecaborane 36·3, triethyldecaborane 7·5% (Found: B, 65·0; C, 21·2. Calc. for this mixture: B, 66·7; C, 21·1%).

Separation by preparative-scale vapour-phase chromatography gave *ethyldecaborane* as a colourless liquid, vapour pressure <1 mm. at 25°; when the b. p. was determined by Siwoloboff's method the sample began to darken at 175° and decomposed rapidly at 217°. It melted at −25° (Found: B, 70·9; C, 15·7. $C_2H_5B_{10}H_{13}$ requires B, 72·0; C, 16·0%). The infrared spectrum was consistent with that expected for an ethyldecaborane.

A fraction corresponding to the combined diethyldecaborane peaks was similarly obtained as a colourless viscous liquid (Found: B, 59·4; C, 26·0. $C_4H_{10}B_{10}H_{12}$ requires B, 60·0; C, 26·9%). The infrared spectrum was similar to that of ethyldecaborane, but with relatively more intense alkyl absorptions in the regions 3, 6·8, and 7·2 μ.

Analytical vapour-phase chromatograms were measured with a Griffin and George Mark II apparatus, at a range of temperatures around 170°. Columns, 2 m. long and 0·6 cm. in diameter, were packed with Apiezon L grease (20%) on Embacel (80%). Carefully dried hydrogen was used as carrier. The preparative chromatographic apparatus is described in Part II. For diethyldecaborane, though there were two peaks on the analytical chromatogram, only one broad one was observed with the preparative column. However, it was possible to resolve this peak by dividing it into three fractions. When the first and last fraction were examined on the analytical column they corresponded respectively to the first and the second peak of diethyldecaborane in the reaction product. The preparative process was then repeated with the middle fraction until sufficient material was obtained for nuclear magnetic resonance examination.

Nuclear magnetic resonance spectra were measured with a Varian Associates V.4310C high-resolution spectrometer. The ^{11}B spectra were obtained at 12 Mc./sec. Specimens from the chromatographic column were sealed *in vacuo* in tubes of 0·3 cm. diameter.

Infrared spectra were measured in carbon disulphide and carbon tetrachloride solutions with a Grubb-Parsons GS2 double-beam grating spectrometer.

We thank Dr. B. N. Figgis for his co-operation in obtaining the nuclear magnetic resonance spectra and Mr. J. V. Griffiths for analysing the samples.

Explosives Research and Development Establishment,
Ministry of Supply, Waltham Abbey, Essex.

[*Received, August* 15*th*, 1959.]