969. *Boron Hydride Derivatives. Part IV.*[1] *Friedel–Crafts Methylation of Decaborane.*

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Friedel–Crafts methylation of decaborane has been shown to yield a series of methylated compounds which have been separated by gas chromatography, and their structures determined by nuclear magnetic resonance spectroscopy. Compounds which have been identified include the 2-methyl, 2,4- and 1,2-dimethyl, 1,2,3- and 1,2,4-trimethyl, and 1,2,3,4-tetramethyl derivatives. The structure of decaborane is discussed in relation to these substances.

In Part III,[1] the Friedel–Crafts ethylation of decaborane, $B_{10}H_{14}$, in carbon disulphide with ethyl bromide and aluminium chloride was shown to give a number of substitution

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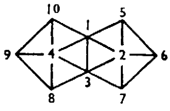
[1] Part III, Blay, Dunstan, and R. L. Williams, *J.*, 1960, 430.

products from which a monoethyl- and two isomeric diethyl-decaboranes could be separated by preparative gas chromatography. The structures of these compounds, which were determined by ^{11}B nuclear magnetic resonance spectroscopy, indicated that the 2,4- and, to a smaller extent, the 1,3-positions were the most reactive in decaborane (I) in this type of reaction.



(I)

Derivatives with more than two ethyl groups were also formed in the reaction, but these could not be purified by gas chromatography because their large retention volumes led to excessive thermal decomposition at the column temperature. However, the products from the corresponding Friedel–Crafts methylation have much smaller retention volumes and it is possible, therefore, to isolate polymethyl-decaboranes and determine their structures. The results of such an investigation are presented below.

EXPERIMENTAL

Methylation of Decaborane.—Decaborane (1·22 g., 0·01 mole; recrystallised from n-hexane), finely powdered aluminium chloride (1·33 g., 0·01 mole), and carbon disulphide (20 c.c.) were placed in a 150 c.c. seal-off tube. The tube was attached to the vacuum-line, cooled, and evacuated. Methyl bromide (2·85 g., 0·03 mole; measured as gas) and hydrogen chloride (20 c.c.) were distilled into the tube, which was then sealed. The mixture was heated at 70° for 36 hr., then cooled in liquid nitrogen, attached to the line, and opened. Material readily volatile at room temperature was distilled off, leaving a red, oily residue to which isopentane (20 c.c.) was added by distillation. Filtration gave a yellow solution which was evaporated, a mixture of methylated decaboranes being obtained as a non-volatile, mobile, yellow liquid (0·84 g.). The product was purified and rendered suitable for gas chromatography by distillation in an evaporative still. The analytical gas chromatogram of the distillate gave a series of peaks, the logarithm of whose retention volumes could be plotted against number of methyl substituents to give a smooth, nearly linear, plot in a similar manner to that found previously for the ethylated decaboranes [1,2] (Fig. 1). However, the points corresponding to 2,4-substituted compounds lay below the curve, while that corresponding to a 5-substituted substance lay above the line. Similar changes in retention volume have been observed for other alkyl-decaboranes substituted in these positions.[3] In a typical experiment, the product was shown by this method to consist of decaborane (20·5%), monomethyldecaborane (55·8%), two dimethyldecaboranes (16·0%), two trimethyldecaboranes (6·6%), tetramethyldecaborane

FIG. 1. *Plot of* $\log_{10} V_R$ *against number of methyl groups for* $B_{10}H_{14-n}Me_n$ *at 140°, relative to* V_R *(naphthalene) = 1. Symbols* ○, △, *and* ▽ *refer to isomers.*

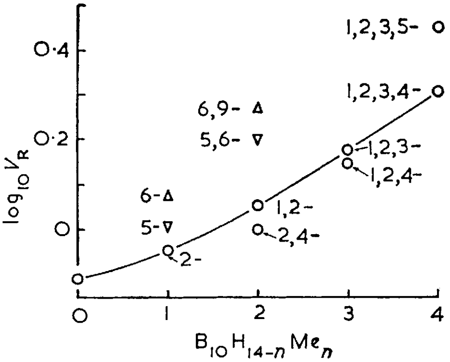
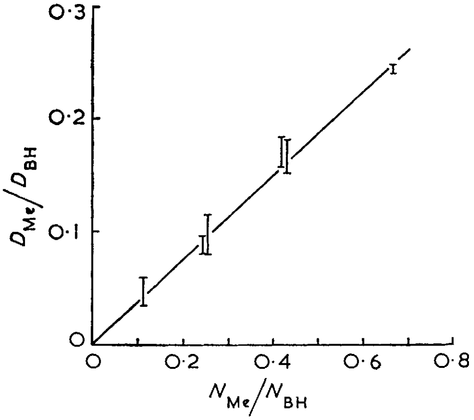


FIG. 2. *Plot of (peak optical density of* 3·5 μ Me *band)/(peak optical density* 4·0 μ BH *band) against (number of* Me *groups)/(number of terminal* BH *bonds).*



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[2] Part II, Blay, J. Williams, and R. L. Williams, *J.*, 1960, 424.

[3] Part V, following paper.

(1·0%), and a derivative (1·0%) of long retention volume which was later shown to be also a tetramethyldecaborane.

The experiment was repeated on a larger scale in a 750 c.c. glass-lined, stainless-steel autoclave to provide sufficient material for preparative gas chromatography. Decaborane (7·32 g., 0·06 mole), aluminium chloride (8 g., 0·06 mole), carbon disulphide (100 c.c.), and methyl bromide (22·8 g., 0·24 mole) were heated at 80° for 6 hr. The distilled product (4·1 g.) was separated on the column and gave decaborane (6·3%), 2-methyl- (18·9%), 1,2- and 2,4-dimethyl- (18·0 and 11·5%), 1,2,3- and 1,2,4-trimethyl- (4·8 and 16·2%), 1,2,3,4-tetramethyl- (20·1%), and 1,2,3,5(or 8)-tetramethyl-decaborane (3·5%). The components were characterised by their gas-chromatographic retention volumes (Fig. 1), elemental analysis, and infrared spectra. The spectra were consistent with those expected for substituted decaboranes: in particular, the plot of the ratio (peak optical density of the 3·5 μ Me band)/(peak optical density of the 4·0 μ BH band) against the ratio (number of Me groups)/(number of terminal BH bonds) gave a satisfactorily smooth plot in a similar fashion to that found with the ethyldecaboranes [2] (Fig. 2).

The methyldecaboranes behave as weak acids, and an additional check on the identity of a derivative is its equivalent weight. This was determined for a number of the compounds by potentiometric titration of their acetonitrile solutions with aqueous alkali.[3,4]

Structures were assigned from the ^{11}B nuclear magnetic resonance spectra of the compounds.

Compounds examined.—Retention volumes at 140° are relative to V_R (naphthalene) = 1 and V_R (decaborane) = 0·78. With 2,4-dimethyl-, 1,2,3-trimethyl-, and 1,2,3,5(or 8)-tetramethyldecaboranes, the observed equivalents are only approximate because of the small amounts of material available for titration.

2-*Methyldecaborane*, m. p. 4—6°, b. p. 223°, v. p. <1 mm. Hg at 20° (Found: B, 77·0; C, 8·9%; equiv., 137·4. $B_{10}H_{13}CH_3$ requires B, 79·4; C, 8·8%; equiv., 136·3), retention volume 0·90.

1,2-*Dimethyldecaborane*, liquid, giving a glass at −40° [Found: H, 11·9; C, 16·0%; equiv., 149·3. $B_{10}H_{12}(CH_3)_2$ requires H, 12·1; C, 16·0%; equiv., 150·4], retention volume 1·13.

2,4-*Dimethyldecaborane*, m. p. 43·5—44·5° [Found: H, 11·7; C, 16·4%; equiv., 150. $B_{10}H_{12}(CH_3)_2$ requires H, 12·1; C, 16·0%; equiv., 150·4], retention volume 1·00.

1,2,3-*Trimethyldecaborane*, m. p. 161—163° [Found: H, 11·9; C, 21·6%; equiv., 167. $B_{10}H_{11}(CH_3)_3$ requires H, 12·3; C, 21·9%; equiv., 164·4], retention volume 1·54.

1,2,4-*Trimethyldecaborane*, m. p. 12—13° [Found: H, 12·0; C, 22·3%; equiv., 165·0. $B_{10}H_{11}(CH_3)_3$ requires H, 12·3; C, 21·9%; equiv., 164·4], retention volume 1·44.

1,2,3,4-*Tetramethyldecaborane*, m. p. 178—179° [Found: B, 60·3; H, 12·5; C, 26·7%; equiv., 178·2. $B_{10}H_{10}(CH_3)_4$ requires B, 60·6; H, 12·4; C, 26·9%; equiv., 178·4], retention volume 2·13.

1,2,3,5(or 8)-Tetramethyldecaborane, m. p. 70—71° [Found: equiv., 171. Calc. for $B_{10}H_{10}(CH_3)_4$: equiv., 178·4], retention volume 3·08. Since only a very small amount of material was recovered after nuclear magnetic resonance examination, no satisfactory analysis could be made.

Methods.—The analytical gas chromatograms were measured with a Griffin and George mark II apparatus at $\sim$140°. Two-metre columns packed with Apiezon L grease (20%) on Embacel support (80%) were used with dry hydrogen as carrier. Preparative separations were carried out with a newly constructed apparatus which was fitted with a 12 ft. column, 1″ in diameter, packed as above. Efficiencies of about 1100 theoretical plates were obtained under normal operating conditions with this apparatus.

Infrared spectra were measured with a Grubb–Parsons S3A double-beam spectrometer fitted with a sodium chloride prism. Solutions of the compounds in carbon disulphide and carbon tetrachloride were used.

The ^{11}B nuclear magnetic resonance spectra were obtained with a Varian Associates V 4310 C spectrometer at 12 Mc./sec. Liquid samples were sealed *in vacuo* in tubes of 5 mm. diameter, and solutions in carbon disulphide were used for the solid samples. The spectra of the samples were run consecutively so that instrumental conditions were the same for all of them. In order to obtain reliable measurements of area the spectra were recorded through a linear auxiliary amplifier with a Sunvic recorder. Areas are believed to be accurate to about 10%.

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[4] Atteberry, *J. Phys. Chem.*, 1958, **62**, 1458; Griffiths and R. L. Williams, *Chem. and Ind.*, 1959, 655.

Nuclear Magnetic Resonance Spectra.—The ^{11}B spectra, including that of decaborane, are shown in Fig. 3; band areas, obtained by graphical separation, are recorded in the Table.

FIG. 3. ^{11}B *nuclear magnetic resonance spectra of*: *A*, $B_{10}H_{14}$; *B*, 2-$B_{10}H_{13}Me$; *C*, 2,4-$B_{10}H_{12}Me_2$; *D*, 1,2-$B_{10}H_{12}Me_2$; *E*, 1,2,4-$B_{10}H_{11}Me_3$; *F*, 1,2,3-$B_{10}H_{11}Me_3$; *G*, 1,2,3,4-$B_{10}H_{10}Me_4$; *H*, 1,2,3,5 (or 8)-$B_{10}H_{10}Me_4$.

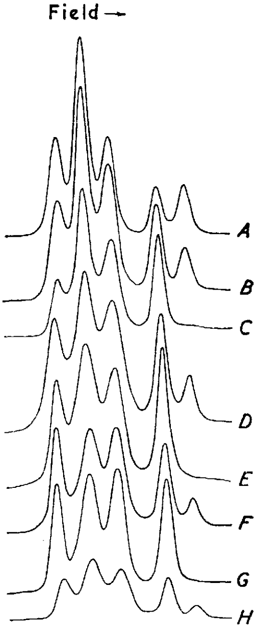
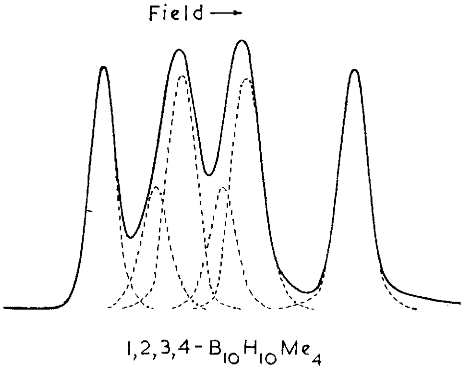


FIG. 4. ^{11}B *nuclear magnetic resonance spectrum of* 1,2,3,4-$B_{10}H_{10}Me_4$ *showing graphical resolution into component peaks.*



Relative peak areas in the ^{11}B *nuclear magnetic resonance spectra of compounds* $B_{10}H_{14-n}Me_n$. (*Spectra have been normalised to a total area of* 20 *units.*)

				High-field doublet					Triplet/
		Low-field triplet		Sum	*A*	*B*	*A*/*B*	Sum	Doublet
$B_{10}H_{14}$ (theor.)	4·0	8·0	4·0	16·0	2·0	2·0	1·00	4·0	4·00
$B_{10}H_{13}Me$	3·55	7·26	5·22	16·02	2·70	1·27	2·14	3·98	4·03
2,4-$B_{10}H_{12}Me_2$	2·30	7·64	5·94	15·88	4·12	0		4·12	3·86
1,2-$B_{10}H_{12}Me_2$	3·8	7·2	4·9	15·9	3·0	1·1	2·7	4·1	3·8
1,2,4-$B_{10}H_{11}Me_3$	3·42	6·98	5·37	15·76	4·24	0		4·24	3·72
1,2,3-$B_{10}H_{11}Me_3$	4·08	5·63	5·90	15·61	3·30	1·09	3·02	4·39	3·56
1,2,3,4-$B_{10}H_{10}Me_4$	3·66	5·97	6·18	15·81	4·19	0		4·19	3·77
1,2,3,5(or 8)-$B_{10}H_{10}Me_4$	3·30	2·04, 3·93 7·07	2·02, 4·16 5·55	15·91	3·11	0·97	3·20	4·08	3·90

DISCUSSION

Interpretation of Spectra.—The spectrum of decaborane consists of a low-field triplet of relative intensities 4, 8, 4 and a high-field doublet of strengths 2, 2. It has been shown [5] that the latter originates with boron atoms 2 and 4. The triplet is made up of two doublets of strengths 4, 4 and 4, 4, the high-field pair of which is due to equivalent atoms 5, 7, 8, and 10, and the low-field pair to the geometrically non-equivalent pairs of atoms 1,3 and 6,9.[5,6] The splitting into doublets is the result of the interaction of the spin of the ^{11}B

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[5] Schaeffer, Shoolery, and Jones, *J. Amer. Chem. Soc.*, 1957, **79**, 4606.

[6] R. E. Williams and Shapiro, *J. Chem. Phys.*, 1958, **29**, 677.

nucleus with that of its attached proton, and when the latter is replaced by a zero-spin nucleus the doublet collapses to a single peak of double the intensity.[7]

With methyldecaborane, there has been a partial collapse of the high-field doublet, with the new peak superimposed on the low-field member of the original doublet. Complete substitution in the 2-position would require the ratio of the area of the low-field member to that of the high-field component to be 3 : 1. However, the observed ratio is about 2·2 : 1, which implies that the substance is a mixture of 2-methyldecaborane and a small amount of an isomer. By analogy to the ethyldecaboranes [1] and from the considerations below, this is 1-methyldecaborane. Accordingly, the presence of the latter should be reflected by changes in the low-field triplet. If it is assumed that methyl-substitution always produces a collapsed peak superimposed on the low-field member of the original doublet, then the intensities of the triplet in 1-methyldecaborane should be 5 : 7 : 4 compared with 4 : 8 : 4 in 2-methyldecaborane. The observed ratios are 3·5 : 7·3 : 5·2, where the intensity of the lowest member is lower than the predicted intensities for both isomers. The discrepancy can be explained by a shift of the 6,9-doublet to higher field, whenever 2,4-substitution takes place. This assumption adequately explains the spectra of the polymethylated compounds and there is also evidence that substitution at the 6,9-positions similarly affects the 2,4-doublet.[3] On this basis, the theoretical intensity ratio for 2-methyldecaborane is 2 : 8 : 6, and the observed spectrum is therefore in qualitative agreement with that required for a mixture of 1- and 2-methyldecaborane.

In the spectrum of the first dimethyldecaborane isomer to be separated by chromatography, the high-field doublet has collapsed completely to a single peak, thereby showing that both methyl groups are in the apices of the molecule and that the substance is 2,4-dimethyldecaborane. The lowest component of the low-field triplet shows a pronounced reduction in strength. The relative peak areas are 2·3 : 7·6 : 5·9. If it is assumed that 2,4-substitution has shifted the 6,9-doublet towards higher field, the theoretical ratio is 2 : 8 : 6.

The second dimethyldecaborane isomer shows a high-field doublet whose areas are in the ratio 2·7 : 1; this is sufficiently close to the required value of 3 : 1 to indicate one methyl group in the 2(4)-position. The low-field triplet has an area ratio 3·8 : 7·2 : 4·9. Partial collapse of the 1,3-doublet together with a shift of the 6,9-doublet to higher field would require a theoretical ratio of 3 : 7 : 6, hence the substance is 1,2-dimethyldecaborane.

The first trimethyldecaborane compound has a very similar spectrum to that of 2,4-dimethyldecaborane. There has been a complete collapse of the high-field doublet, showing that both apical positions are substituted. The low-field triplet has an area ratio of 3·4 : 7 : 5·4. With the assumptions made above on the shift of the 6,9-doublet, the theoretical ratio for one methyl in the 1(3)-position is 3 : 7 : 6. The compound is therefore 1,2,4-trimethyldecaborane.

In a similar fashion, it can be shown that the second trimethyl isomer is 1,2,3-trimethyldecaborane. The high-field doublet has a ratio 3·0 : 1, indicating one methyl in the 2(4)-position. The low-field triplet has an area ratio of 4·1 : 5·6 : 5·9, compared with a required ratio of 4 : 6 : 6 for 1,3-disubstitution.

The main tetramethyl isomer has a spectrum with a low-field triplet identical with that of 1,2,3-trimethyldecaborane and a singlet in place of the high-field doublet. The compound is therefore 1,2,3,4-tetramethyldecaborane. Since the substance was obtained in a good state of purity, particular care was taken to obtain a noise-free spectrum, and then this was subjected to a very careful graphical analysis, as opposed to the approximate ones made above. The result is shown in Fig. 4, where the shift of the 6,9-doublet to near-coincidence with the higher-field 5,7,8,10-doublet is clearly shown.

The spectrum of the last substance to be isolated from the column shows that it is not a pentamethyldecaborane, as was at first indicated by its retention volume. The high-

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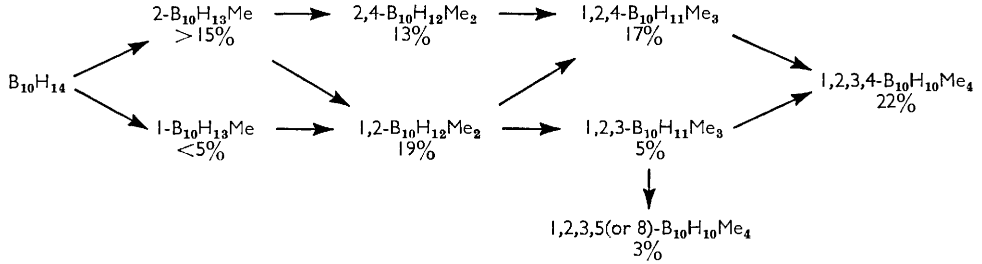
[7] Schaeffer, Shoolery, and Jones, *J. Amer. Chem. Soc.*, 1958, **80**, 2670; Figgis and R. L. Williams, *Spectrochim. Acta*, 1959, 331.

field doublet shows only a partial collapse, giving an area ratio of 3·2 : 1, and there is accordingly only one methyl group in the 2(4)-position. However, the retention volume shows that the substance must be at least a tetramethyldecaborane. Two alternatives are available: 1,2,3,6- and 1,2,3,5(or 8)-tetramethyldecaborane. Both of these would require a low-field triplet of ratio 4 : 7 : 5. The observed value of 3·3 : 7·1 : 5·6 compares favourably with this. However, it will be shown in Part V that 6-substitution results in a splitting of the high-field 2,4-doublet into four peaks. Hence the only possibility remaining is 1,2,3,5(or 8)-tetramethyldecaborane. These would have the same spectra, so that no further identification can be made.

In all the foregoing compounds, when 2,4-substitution has taken place, it has been necessary to postulate a shift of the 6,9-doublet. This shift, of about 10 p.p.m., is of the same order as those observed in other boron compounds, which have been attributed to inductive effects,[8] and also to that which occurs when a doublet collapses on methyl-substitution, *viz.*, 6 p.p.m. It is probable therefore that this shift is due to a similar cause. Moreover, in a theoretical treatment of decaborane, Eberhardt *et al.*[9] postulated that the 2,4- and the 6,9-positions are joined by single bonds whereas all other linkages are 3-centred. Consequently, electrical effects would be more effectively relayed between these points than any others in the molecule.

Charge Distribution in Decaborane.—The Friedel–Crafts reaction proceeds by an electrophilic mechanism with the attacking alkyl group carrying a positive charge. Substitutions would therefore be expected at points of maximum electron density. The main products in the ethylation of decaborane show that the 2,4-positions are most reactive, and this result is amply confirmed by the sequence of products in the methylation, as shown in the Chart: the major products are those with 2,4-substitutions. The predominance of 2,4-substituted products also implies that methyl substitution does not greatly alter the charge distribution in these compounds. The second most electronegative positions follow from the nature of the minor products, though it is not possible to determine directly from their nuclear magnetic resonance spectra whether these are 1,3- or 6,9-substituted except that the presence of two monomethyl, two dimethyl, two trimethyl, and one tetramethyl derivative shows conclusively that it is either the 1(3)- or the 6(9)-position, but not both, which is attacked. However, none of these materials shows a splitting of the 2,4-doublet into a quadruplet, whereas the products from the reaction of methyl-lithium and decaborane do.[3] The latter are 6(9)-substituted, hence the 1(3)-position is that attacked in the Friedel–Crafts reaction.



The presence of a small amount of 5-substitution in a tetramethyl derivative indicates that this position is probably less electropositive than the 6-position so that the order of decreasing negative charge in decaborane is 2- > 1- > 5- > 6-. A number of other reactions show similar characteristics to the Friedel–Crafts reactions. For example, the structures of a number of halogen derivatives [7,10] of decaborane have been determined.

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[8] Onak, Landesman, R. E. Williams, and Shapiro, *J. Phys. Chem.*, 1959, **63**, 1533; Phillips, Miller, and Muetterties, *J. Amer. Chem. Soc.*, 1959, **81**, 4496.

[9] Eberhardt, Crawford, and Lipscomb, *J. Chem. Phys.*, 1954, **22**, 989.

[10] Schaeffer, *J. Amer. Chem. Soc.*, 1957, **79**, 2726.

These substances were prepared by the action of bromine, iodine, or iodine chloride on decaborane, with or without the addition of aluminium chloride. The principal products in each case are found, as would be expected, to be either 2-bromo-, 2-iodo-, or 2,4-di-iododecaborane. However, an isomeric iodo-compound, *viz.*, 5-iododecaborane, has also been isolated from such a reaction.[11] We repeated this preparation using iodine chloride and found the yield of this substance to be very low (~5%; remainder 2-iododecaborane). It is possible that this substance may arise from reaction of the neutral atom or molecule with decaborane and hence the electronegativity order will not apply to it.

Deuteration of decaborane with deuterium chloride in carbon disulphide solution in the presence of aluminium chloride [12] also shows some similarity to the reactions above in that two of the six protons which undergo exchange are in the 2,4-positions. The remaining protons are, however, those in the 5,7,8,10-positions. Here, again, there are probably two exchange mechanisms: first, one involving $DAlCl_4$, which is analogous to the Friedel–Crafts reaction, and secondly, one involving exchange of deuterium with a bridge proton, which then moves in the presence of aluminium chloride, to the 5,7,8,10-positions. The latter possibility is now being investigated.

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[11] Hillman, Abs. 135th Amer. Chem. Soc. Meeting, Boston, 1959.
[12] Dupont and Hawthorne, *J. Amer. Chem. Soc.*, 1959, **81**, 4998.