81. *Boron Hydride Derivatives. Part II.* The Separation and Identification of Some Ethylated Pentaboranes and Decaboranes.*

By N. J. BLAY, J. WILLIAMS, and R. L. WILLIAMS.

The complex product obtained by reaction of ethylene with diborane has been shown by vapour-phase chromatography to contain, *inter alia*, two homologous series, namely, ethylpentaboranes-9 (from B_5H_9) and ethyldecaboranes (from $B_{10}H_{14}$). Some members of the series have been isolated and characterized by their nuclear magnetic resonance spectra, infrared spectra, and retention volumes.

DIBORANE and ethylene at ~100° have been found by Hurd[1] to produce triethylboron. However, it is well known[2] that diborane, when heated, decomposes to give higher boron hydrides, and since triethyl boron is an ethylating agent for these compounds[3] it might be expected that under suitable conditions diborane and ethylene would give ethyl derivatives of the higher boron hydrides.

The product from the reaction

$$C_2H_4 + B_2H_6 \longrightarrow \text{Ethyldiboranes and triethylboron} \xrightarrow[\text{heat}]{B_2H_6} \text{Product}$$

has now been studied and shown to contain such compounds.

---

* Part I, Figgis and R. L. Williams, *Spectrochim. Acta*, 1959, **331**.

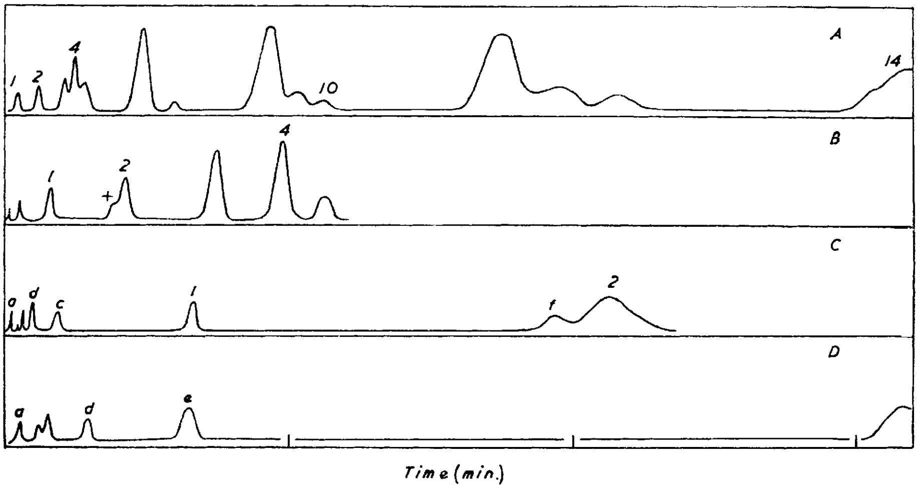
[1] Hurd, *J. Amer. Chem. Soc.*, 1948, **70**, 2053.

[2] Bell and Emeléus, *Quart. Rev.*, 1948, **2**, 132; Stone, *ibid.*, 1955, **9**, 174.

[3] Schlesinger, Horvitz, and Burg, *J. Amer. Chem. Soc.*, 1936, **58**, 407.

A vapour-phase chromatogram of the product on an Apiezon L column at 180° is shown in Fig. 1, and relative retention volumes are given in Table 1. At this temperature, fourteen peaks are observed. At lower temperatures, however, the peaks of smaller retention volume are found to be composite and six more peaks are resolved. If decaborane ($B_{10}H_{14}$) is added to the reaction product and the chromatogram repeated, it is found that peak **3** is considerably increased, thereby identifying this peak.

FIG. 1. *Vapour-phase chromatogram of pyrolysis–ethylation product of diborane.* *A*, 185°; *B*, 148°; *C*, 100°; *D*, 56°.



(*In curve C* the peak *e* is incorrectly labelled *c*)

The identity of some of the other peaks follows from a consideration of their retention volumes. James and Martin[4] showed that for normal and iso-alkanoic acids, a plot of the logarithm of the retention volume against the number of carbon atoms yielded an almost straight line, and the relation has since been extended to other classes of compound.[5] If this is now applied to our chromatogram two straight lines of similar slope are obtained,

TABLE 1. *Relative retention volumes* (V_R) *of ethylated boron hydrides with hydrogen carrier on an Apiezon L stationary phase and C22 firebrick support.*

	$B_5H_{9-n}Et_n$		$B_{10}H_{14-n}Et_n$			$B_5H_{9-n}Et_n$		$B_{10}H_{14-n}Et_n$	
Temp.	n	V_R	n	V_R	Temp.	n	V_R	n	V_R
185° [a]	2	0·16	0	0·77	148° [a]	2	0·16	0	0·78
	3	0·43	1	1·72		3	0·40	1	1·92
	4	0·91	2	3·38		4	0·94	2	4·42
	4	1·04	2	3·72		4	1·04	2	5·07
	5	2·13	2	3·98		5	2·38	3	8·96
			3	6·27				3	10·00
			3	7·06				3	10·85
			3	7·78	100 [b]	0	0·83		
			4	11·72		1	3·47		
			4	13·07		2	12·41		
			4	14·73		3	36·29		
						3	40·29		
					56	0	0·747		
						1	4·05		
						2	20·6		

[a] V_R naphthalene = 1. [b] V_R n-hexane = 1.

---

[4] James and Martin, *Biochem. J.*, 1952, **50**, 679.

[5] Ray, *J. Appl. Chem.*, 1954, **4**, 21.

as shown in Fig. 2. The two series are: peaks **3**, **6**, **8**–**9**–**10**, **11**–**12**–**13**, and **14**: and 1, 2, 4–5, and 7, and at lower temperatures, *b* and *e*.

Since peak **3** is identified as due to decaborane, the first series is that of the compounds $B_{10}H_{14-n}Et_n$ ($n = 0$—4), the groups of peaks around each retention volume being due to substitution isomers. This was confirmed by separating most of the components by preparative vapour-phase chromatography. The substances were analysed in some cases, and their infrared spectra measured (see p. 428).

The nature of the second series was indicated by the infrared spectra of the components. Under standard spectrometer conditions for the infrared spectra of ethyldecaboranes, the ratio, R (peak optical density for the 3·5 μ alkyl band)/(peak optical density for the 4μ BH band), could be fitted to the empirical equation $R = (n_{\text{Et}}/n_{\text{B}}) + 0{\cdot}8$, where n_{Et} and n_{B} are the numbers of ethyl groups and B–H links in the molecule. When applied to the second series this relation afforded $n_{\text{Et}}/n_{\text{B}}$ 0·43, 1·0, 1·54, and 2·58 for peaks *e*, 1, 2, and 4—5 respectively. These results in combination with an approximate carbon figure of 51·8% for peaks 4—5 are shown in Table 2, compared with the theoretical values for possible ethylated boron hydrides: best agreement is obtained with the pentaborane-9 series.

TABLE 2. $n_{\text{Et}}/n_{\text{B}}$ *for the second series of products.*

		Homologous series based on:				
Peak	Obs.	B_2H_6	B_4H_{10}	B_5H_9	B_5H_{11}	
e *	0·25	0·33 Et	0·20 Et	0·25 Et	0·33 Et_2 or	0·60 Et_3
1	0·8	1·00 Et_2	0·50 Et_2	0·67 Et_2	0·60 Et_3	1·00 Et_4
2	1·36	3·00 Et_3	1·00 Et_3	1·50 Et_3	1·00 Et_4	1·67 Et_5
4—5	2·40	∞ Et_4	2·00 Et_4	4·00 Et_4	1·67 Et_5	3·00 Et_6
C (%) in highest homologue......	51·8	64·4 Et_3	58·0 Et_4	54·8 Et_4	58·5 Et_5	61·7 Et_6

* Incorrectly labelled *c* in Fig. 1*c*.

Subsequently, it was observed that on distilling a small quantity of pure pentaborane-9 into the pyrolysis product and then repeating the chromatogram peak *b* was considerably increased. This satisfactorily establishes the second series as ethylated pentaboranes, $B_5H_{9-n}Et_n$, where $n = 0$—5, especially when taken in conjunction with the analyses in the Experimental section and the nuclear magnetic resonance spectra given below.

Three components of the product, *viz.*, peaks *a*, *c*, and *d*, remain unidentified. They form part of another homologous series, since their retention volumes are logarithmically related in the same way as the series discussed above.

^{11}B *Nuclear Magnetic Resonance Spectra.*—The ^{11}B resonance spectra of pentaborane-9 and decaborane have been measured and interpreted in terms of their structures [6] by Schaeffer, Shoolery, and Jones.[7] For pentaborane, the boron atoms are arranged as a tetragonal pyramid and so can be divided into four boron atoms around the base of the pyramid and one at the apex. The spectrum consists of two doublets: one at low field, of intensity 4, due to the basal borons, and one at high field, of intensity 1, due to the apical boron. The splitting into doublets is due to interaction with the nuclear spin of the attached protons. When one of these is replaced by a nucleus having no spin the doublet collapses to a single peak of double the intensity.[2,8]

With triethylpentaborane, there are three possible isomers (I)—(III).

The ^{11}B spectrum of isomer (I) should consist of a low-field triplet of relative strengths 1, 6, 1 and a doublet of strengths 1, 1 on the higher-field side. The spectra of isomers (II) and (III) should be identical (to a first approximation), consisting of a low-field triplet of strengths 2, 4, 2 and a high-field single peak of strength 2.

The presence of six peaks in the observed spectrum (Fig. 3) shows that all three isomers are present. It is possible to estimate the proportion of form (I) from the ratio of the

---

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

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

[8] Figgis and R. L. Williams, *Spectrochim. Acta*, 1959, **331**.

areas under the two highest-field peaks. The observed ratio is 1·043, from which it follows that form (I) constitutes about 50% of the mixture.

Similar considerations apply to tetraethylpentaboranes (IV) and (V). Isomer (IV) should have a single peak at low field, and a high-field doublet of intensities 8, 1, 1, while form (V) should possess a low-field triplet and a high-field singlet of relative strengths 1, 6, 1, 2. The observed spectrum shows that both isomers are present (Fig. 3). The ratio of the highest-field peak to its neighbour is 0·33, from which it follows that about 40% of the material is isomer (IV).

FIG. 2. *Plot of* $\log_{10}$ *(Retention volume) against number of ethyl groups. A, Series* $B_{10}H_{14-n}Et_n$. *B, series* $B_5H_{9-n}Et_n$. *The symbols* ○, ●, ▽ *refer to isomeric forms.*

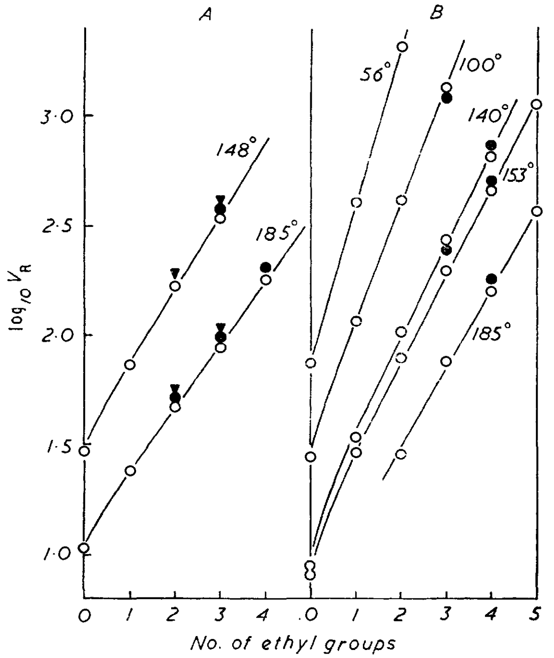
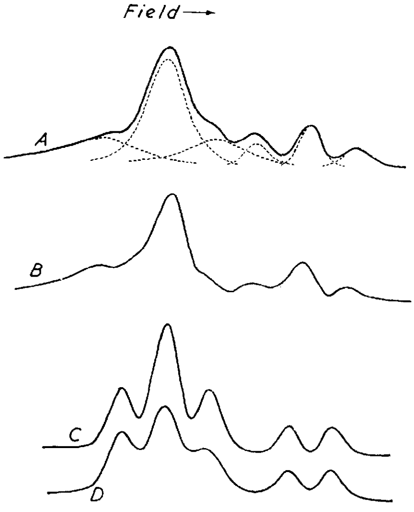
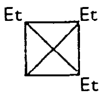


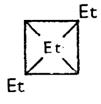
FIG. 3. ^{11}B *nuclear magnetic resonance spectra of:* A, $B_5H_6Et_3$; *B*, $B_5H_5Et_4$; *C*, $B_{10}H_{14}$; *D*, $B_{10}H_{13}Et$.



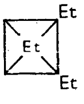
Decaborane consists of two pentagonal pyramids of B atoms, sharing a common edge, and numbered [9] as in (VI). The ^{11}B spectrum consists of a high-field doublet of strengths 2, 2, and a low-field triplet of strengths 2, 4, 2. Schaeffer *et al.*[7] showed that the doublet originated with the apical atoms 2, 4, and that the low-field triplet was the result of the accidental coincidence of two doublets. Williams and Shapiro [10] subsequently showed that the lower-field doublet of this pair arose from atoms 1, 3 : 6, 9 and the higher field doublet from atoms 5, 7, 8, 10.



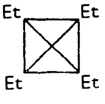
(I)



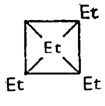
(II)



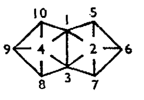
(III)



(IV)



(V)



(VI)

The spectrum of ethyldecaborane is shown in Fig. 4. The high-field doublet has two

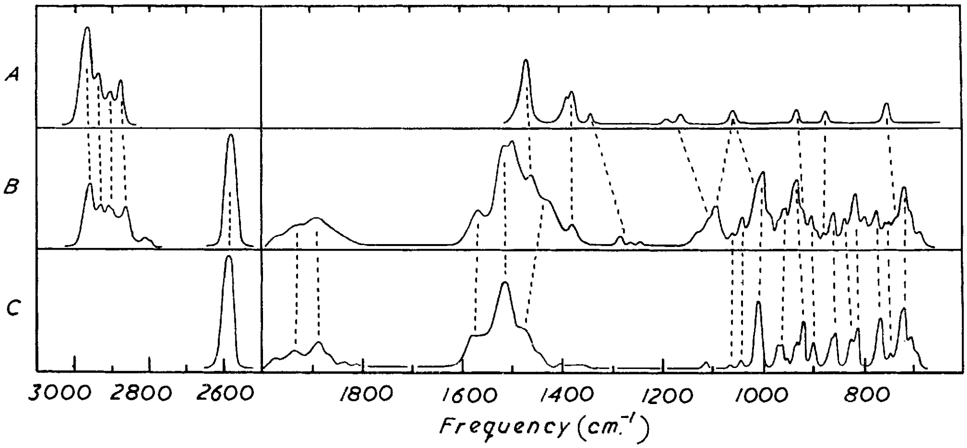
---

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

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

equal peaks, showing that within experimental error no substitution has taken place in the 2,4-positions. With the low field triplet, however, only the lowest-field member is unchanged relative to that of decaborane, the other two being lower in intensity and with their resolution reduced by broadening. This shows that the doublet arising from atoms 5, 7, 8, 10 has been affected and that the substance is therefore very largely (±)-5-ethyldecaborane.

FIG. 4. *Infrared spectra of*: *A*, $CH_3-C_2H_5$; *B*, $B_{10}H_{13}-C_2H_5$; *C*, $B_{10}H_{13}-H$. *Solutions in carbon tetrachloride, except for the region* 825—725 *cm.*$^{-1}$ *where carbon disulphide was used.*



EXPERIMENTAL

Methods.—Infrared spectra were measured with a Grubb–Parsons S3A double-beam spectrometer fitted with a rock-salt prism. Solutions of the materials in carbon disulphide and in carbon tetrachloride were examined in 0·1 mm. thick cells. A few of the pentaboranes were spontaneously inflammable in air, and their solutions were prepared *in vacuo* but could thereafter be handled safely in air.

Nuclear magnetic resonance spectra were measured with a Varian Associates V4310C high-resolution spectrometer. ^{11}B spectra were obtained at 12 Mc./sec. and proton spectra at 40 Mc./sec., in the usual manner with a spinning sample.

Specimens, separated on the preparative vapour-phase chromatographic column, were transferred to sample tubes of 0·3 cm. diameter and, where necessary, the depth of liquid was made up to 3 cm. by the addition of carbon disulphide. The tubes were then frozen, evacuated, and sealed.

Vapour-phase chromatograms were measured with a Griffin and George Mark II apparatus, at a range of temperatures from 40—210°. The columns were 200 cm. long and 0·6 cm. in diameter and were packed with Apiezon L grease (20%) on Johns-Manville C22 firebrick (80%) of 72—85 B.S. mesh. Columns packed with silicone MS.550 and silicone high-vacuum grease gave similar results. Carefully dried hydrogen was used as carrier gas.

In preparative work, a column 200 cm. × 1·5 cm. diameter, which accommodated about 1 g. of material, was mounted in a electrically heated air-bath equipped with a circulating fan. A platinum-in-glass katharometer was used and the substances were condensed from the carrier gas in traps similar to those described by Whitham.[11]

Components from the pyrolysis–ethylation were separated and were examined by infrared spectroscopy. Some elemental analyses carried out by wet oxidation with Van Slyke combustion fluid gave satisfactory results for carbon, but boron values were always low because of the difficulty of working up the acid solution for boric acid.

Summarised Results.—Decaborane series. Peak 3. The infrared spectrum of this component

---

[11] Whitham in Desty's " Vapour Phase Chromatography," Butterworths, London, 1957, p. 197.

was identical with that of decaborane. The extinction coefficient of the red colour given with a 5% solution of quinoline in benzene was also the same as that found with decaborane.[12]

Peak 6. Two samples were isolated from different vapour-phase chromatographic preparations. Both were colourless liquids; they had identical infrared spectra. The extinction coefficients of the coloured reaction products with quinoline in benzene were also the same, indicating that reproducible separations were obtained by chromatography. The infrared spectrum (Fig. 4) is approximately the sum of that of decaborane and propane, the latter being roughly equivalent to a $B\cdot CH_2\cdot CH_3$ unit. Analysis indicated a *monoethyldecaborane* (Found: C, 16·3; B, 68·7. $C_2H_5\cdot B_{10}H_{13}$ requires C, 16·0; B, 72·0%).

Peaks 8, 9, and 10. These peaks could not be separated completely in the column, but fractions were obtained which were predominantly peak 8 or peak 10. The former was a colourless liquid, while the latter was crystalline but mixed with some liquid. The infrared spectra of both fractions had alkyl bands at 3·5, 6·8, and 7·2 μ, of the same intensity relative to the BH stretching band at 4 μ; the general outlines of the rest of the spectra were also very similar, but differed in relative intensities of many peaks. Analysis of the first fraction gave B, 57·3%, and of the second fraction *B*, 56·9%. These values, in conjunction with the similar retention volumes and infrared spectra, indicate that the substances are isomers. Elemental analyses indicate diethyldecaboranes (Found, for combined fractions 8, 9, and 10: C, 26·8; B, 58·0. Calc. for $C_4H_{10}B_{10}H_{12}$: C, 26·9; B, 60·6%).

Peaks 11, 12, and 13. Complete separation was not attained. The infrared spectrum was similar to that of the previous fractions but with relatively stronger bands due to alkyl vibrations at 3·5, 6·8, and 7·2 μ. A sample recovered from solution after its spectrum had been measured was analysed (Found: C, 36·7; B, 46·6. Calc. for $C_6H_{15}B_{10}H_{11}$: C, 34·9; B, 52·4%).

Peak 14. Only a small quantity of this material was isolated (Found: C, 41·4. Calc. for $C_8H_{20}B_{10}H_{10}$: C, 41·0%).

*Pentaborane-*9 *series.* Peak *e*. Less than 1% of the substance was present in the original mixture, and only sufficient material was isolated to give a weak infrared spectrum, which was similar to that of pentaborane and apically substituted ethylpentaborane.[8] As with the latter, there were alkyl absorptions of the same intensity at 3·5, 6·8, and 7·2 μ and strong bands at 7, 11·9, and 15·7 μ, but the spectrum between 7 and 11 μ contained many more relatively weak bands. The retention volumes in vapour-phase chromatography at 56° and 100° relative to n-hexane were 4·37 and 3·51; the corresponding values of apical ethylpentaborane are 3·72 and 2·90. These results are consistent with the material's being ethylpentaborane, with the ethyl group substituted in the base of the molecule.

Peak 1. This was isolated only in a very small amount. Its infrared spectrum was similar to that of peaks 2 and 4, but with less intense alkyl absorptions at 3·5, 6·8, and 7·2 μ.

Peaks 2 and 4—5. The substances constitute about 3% and 5% respectively of the product. Only a partial separation of peaks 4 and 5 could be made, but peak 2 and the two fractions from 4—5 showed similar infrared spectra except that the alkyl absorptions of peak 2 were less than those of either of the peaks 4—5 fractions. These had alkyl bands of approximately the same strength. Steam-distillation of the original pyrolysis–ethylation product yielded an oil whose chromatogram showed it to consist largely of peaks 4—5, with a small amount of peak 2. The carbon content is consistent with peaks 4—5 being isomers of $B_5H_5Et_4$ (Found: C, 51·8. Calc.: C, 54·8%), and peak 2 is therefore $B_5H_6Et_3$. The results are supported by approximate boron analysis from direct combustion of peaks 2 and 4—5 of (B, 33·7 and 30·7%; required 36·7 and 30·9% respectively). The ^{11}B nuclear magnetic resonance spectra of the substances are consistent with their being pentaborane derivatives.

Peak 7. This was inseparable from peak 6, ethyldecaborane. However, since the peak persists in the chromatogram of the steam-distillate mentioned above, even though the ethyldecaborane has disappeared, it cannot be an isomeric ethyl decaborane. Its retention volume identifies it as pentaethylpentaborane.

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, May* 12*th,* 1959.]

[12] Hill and Johnston, *Analyt. Chem.*, 1955, **27**, 1300.