

947. The Gas-phase Reaction of Decaborane and Ethyl Bromide.

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The kinetics of the gas-phase reaction of decaborane and ethyl bromide have been investigated for a static system in the temperature range 210–230° and at decaborane pressures between 60 and 800 mm. and ethyl bromide pressures between 60 and 1200 mm. A reaction mechanism is suggested.

Three reactions are involved in the initial stage of the process, leading to the formation of 2-ethyldecaborane, brominated products, and non-volatile solid hydrides. In the later stages side reactions occur involving the products and the original reactants. Decaborane reacts with the ethylated decaboranes and brominated products to give non-volatile solid hydrides. Similarly, ethyl bromide reacts with 2-ethyldecaborane to give 1,2- and 2,4-diethyldecaborane. The presence of an ethyl group has a significant effect on the electron distribution in the decaborane molecule. Analysis of the results has shown that the yield of 2-ethyldecaborane that can be obtained by the above process is limited. At 210°, the maximum conversion of the initial decaborane into 2-ethyldecaborane is 22%.

Aluminium chloride catalyses the process.

ETHYLATED derivatives of decaborane may be obtained by a Friedel-Crafts reaction of decaborane with ethyl bromide in carbon disulphide at 70° with aluminium chloride and hydrogen chloride as catalysts. Under these conditions, the yields of product, based on the decaborane converted, are 2-ethyldecaborane 24%, diethyldecaboranes 23%, and triethyldecaboranes 7%.¹ Separation of the products may be achieved by gas chromatography.

It has, however, been shown that, in the temperature range 210–230°, the reaction can proceed in the gas phase in the absence of solvents and catalysts. The isolated products then consist mainly of 2-ethyldecaborane and non-volatile solid hydrides.² The kinetics of this high-temperature reaction have therefore been studied with a view to obtaining high conversions of decaborane into 2-ethyldecaborane without the isolation of polyethylated decaboranes.

Since side reactions occur simultaneously with the main reaction of decaborane and ethyl bromide, attention has been paid to the factors that limit the yield of 2-ethyldecaborane; for example, the reactions of 2-ethyldecaborane have been briefly investigated. Other ethyl halides have been used as ethylating agents, and the catalytic effects of aluminium chloride and boron tribromide have been examined.

EXPERIMENTAL

Reactants.—Decaborane, 2-ethyldecaborane, and the diethyldecaboranes were purified by methods already described.^{1,2} Ethyl bromide was dried, distilled, and stored in the absence of light. Hydrogen bromide was prepared from tetrahydronaphthalene and bromine.³ Before use, the ethyl bromide, hydrogen bromide, and boron tribromide were separately distilled under a vacuum and stored in traps maintained at liquid nitrogen temperature.

Aluminium chloride from a general-purpose reagent bottle, was crushed and the surface discarded, only the inner crystals being used.

Apparatus.—The apparatus and procedure were described previously.² Experiments were carried out in the temperature range 210–230°. In the experiments concerned with the reaction of decaborane and ethyl bromide, the initial decaborane pressures were varied between 60 and 800 mm., and the initial ethyl bromide pressures between 60 and 1200 mm. Most of the other reactions were examined at initial reactant pressures of 300 mm.

Analysis.—The products of the decaborane-ethyl bromide reaction were identified as 2-ethyldecaborane, 1,2- and 2,4-diethyldecaboranes, non-volatile solid hydrides, ethylated

¹ N. J. Blay, I. Dunstan, and R. L. Williams, *J.*, 1960, 430.

² A. J. Owen, *J.*, 1961, 5438.

³ A. I. Vogel, "Practical Organic Chemistry," Longmans, London, 1961, 3rd edn., p. 182.

non-volatile solid hydrides, hydrogen, hydrogen bromide, methane, and a little ethane. A brominated boron hydride is believed also to be formed, but so far it has not proved possible to isolate and characterise it.

The products were analysed as follows: The reaction vessel was immersed in liquid nitrogen for 10 min. before being opened. Hydrogen was estimated by pressure measurement after expansion of the non-condensable gases in the reaction vessel into a known volume. At -196° the vapour pressure of methane is 9 mm.; this value was subtracted from the "hydrogen" pressure in the later stages of the reaction. The stage at which there was insufficient methane to satisfy the vapour-pressure requirements was determined graphically. From the beginning of the reaction to this point it was assumed that the methane pressure was linearly related to the reaction time. The reaction vessel was then allowed to warm to the temperature of carbon dioxide-acetone, and the combined volume of methane and hydrogen bromide was determined. These gases were condensed and isolated in a flask containing a known volume of 0.1N-silver nitrate; after the flask and its contents had come to room temperature, the hydrogen bromide was determined by back-titration of the unused silver nitrate. In some experiments, the gases remaining after removal of the hydrogen bromide were examined in the mass spectrometer. The results confirmed the ratio of the hydrogen and methane in the gas mixture. They also showed that the hydrocarbon gases contained $\sim 95\%$ of methane and 5% of ethane. Finally, the unchanged ethyl bromide was estimated by a pressure measurement after the reaction vessel had come to room temperature.

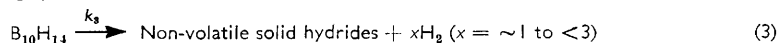
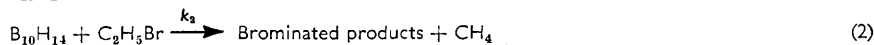
The solid and the liquid products were extracted with dry benzene, and the composition of the benzene extract quantitatively determined by gas chromatography.⁴ Solids remaining after extraction with benzene were oxidised to boric acid and titrated with barium hydroxide.⁵ In the early stages of the reaction, at least 96% (by analysis) of the initial boron was recovered in the product mixture, but in the later stages, the recovery was sometimes as low as 75%. Oxidation of the benzene-soluble extract to boric acid subsequently showed that some of the boron-containing products in the solution were retained in the chromatographic column. Similarly, not all the bromine from the decomposed ethyl bromide was recovered as hydrogen bromide. This unrecovered bromine was found by the Carius method to be distributed quantitatively between the liquid extract and the insoluble products, approximately half being soluble in benzene. In Fig. 1, methane is shown to be formed at almost the same rate as hydrogen bromide. It is therefore probable that the unrecovered boron compound has an empirical formula $B_{10}CH_{15}Br$; it could be either B- or C-brominated methyldecaborane. Since bromopentaborane is not recovered from a similar chromatographic column,⁶ it is likely that these brominated decaboranes would also be retained on the column. Evidence that such compounds are present among the products has been obtained from their infrared spectra. A peak is observed at 555 cm.^{-1} , the frequency at which the B-Br and C-Br stretching absorption occurs. Efforts to isolate the derivative were unsuccessful.

The results reported below do not show analyses for the brominated decaborane products, although reactions leading to their formation are used to explain the kinetic results.

RESULTS AND DISCUSSION

The Course of the Reaction.—The fate of the reactants and products during the reaction is illustrated in Fig. 1 by the results obtained at 230° and initial pressures of decaborane and ethyl bromide of 800 and 300 mm., respectively.

In the initial stages, three reactions are occurring simultaneously, namely, the reactions of decaborane and ethyl bromide to form ethyldecaborane and the bromo-derivative and the thermal decomposition of decaborane:



⁴ N. J. Blay, J. Williams, and R. L. Williams, *J.*, 1960, 424.

⁵ I. Dunstan and J. V. Griffiths, *Analyt. Chem.*, 1961, **33**, 1598.

⁶ N. J. Blay, personal communication.

Reaction (3), the thermal decomposition of decaborane, has been studied previously.² It was shown that the initial step produces one molecule of hydrogen for every molecule of decaborane decomposed; in the later stages, hydrogen is also formed by the decomposition of the non-volatile solid hydrides. Reaction (3) accounts for the fact that the rate of reaction of decaborane is faster than that of ethyl bromide.

In the later stages of the reaction, both the decaborane and ethyl bromide curve show a much faster rate than would be predicted by a simple bimolecular reaction. When the initial pressures of the reactants are equal, the ethyl bromide curve exhibits a sigmoid

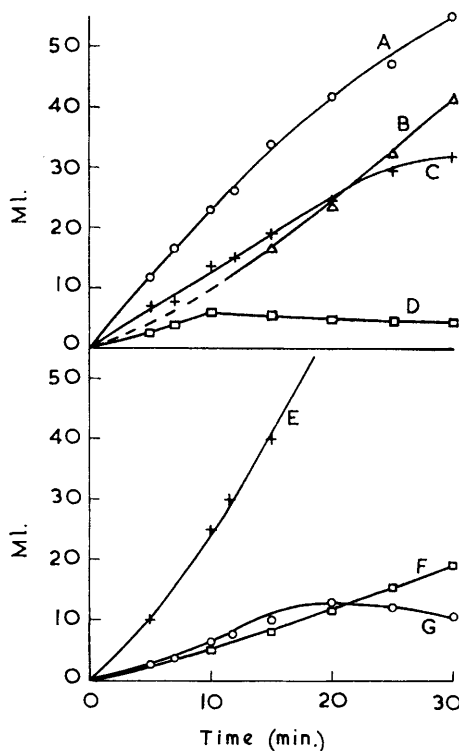
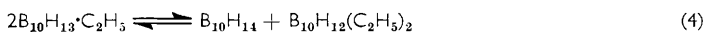


FIG. 1. The course of the reaction when $T^\circ = 230^\circ$, p° (decaborane) = 800 mm., and p° (ethyl bromide) = 300 mm. [A, $B_{10}H_{14}$ used; B, non-volatile solid hydrides; C, EtBr bromide used; D, $B_{10}H_{13}C_2H_5$; E, H_2 ; F, $CH_4(+C_2H_6)$; G, HBr.]

character, *i.e.*, the rate of reaction of ethyl bromide increases with the reaction time. Clearly, both decaborane and ethyl bromide undergo reaction with the products. The same conclusion is also reached by a consideration of the maximum exhibited by the 2-ethyldecaborane curve. It can be shown that the thermal decomposition of 2-ethyldecaborane alone,



which has been the subject of a separate investigation,⁷ does not occur to a significant extent under the present conditions. Secondary reactions of 2-ethyldecaborane with ethyl bromide and decaborane are more significant; these reactions have therefore been examined more closely.

The reaction of ethyl bromide with 2-ethyldecaborane is analogous to the present system; its rate of reaction is ~ 2.5 times faster. The main products are 1,2-diethyldecaborane, 2,4-diethyldecaborane, decaborane, hydrogen, and methane. Decaborane was present in relatively low concentrations, and probably resulted from thermal decomposition of 2-ethyldecaborane (reaction 4). The principal products were 1,2- and 2,4-diethyldecaborane, in a 2 : 1 ratio. In the reaction of ethyl bromide and decaborane, they were seldom present

⁷ F. W. Emery, P. L. Harold, and A. J. Owen, *J.*, 1963, 426.

in sufficient quantity to be identified, but, when they were, the ratio was again 2 : 1. No other volatile polyethylated derivatives were present in sufficient concentration to allow of estimation by gas chromatography. These results show that the electron distribution in the decaborane molecules is substantially perturbed by the presence of one substituent ethyl group.⁷ Since 2-ethyldecaborane is ethylated more rapidly than decaborane, the presence of a 2-ethyl group activates positions 1 and 3 so that they rival the reactivity of position 4 to electrophilic attack. The increased reactivity of 2-ethyldecaborane over that of decaborane is not surprising in view of the electron-deficient nature of the decaborane structure.

The high rate of reaction maintained by the ethyl bromide throughout the process is therefore due to reaction with the more active ethylated decaborane derivatives. It is not due to thermal decomposition of ethyl bromide⁸ according to the equation

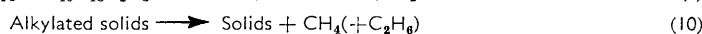
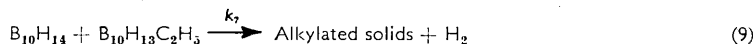
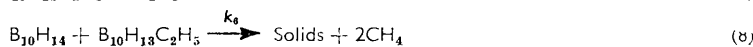
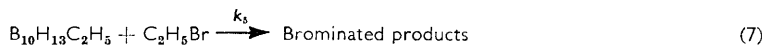
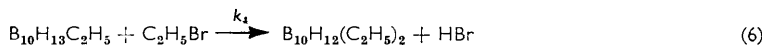
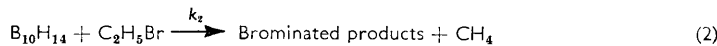
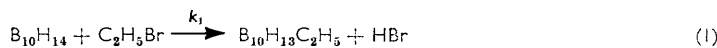


since ethylene has not been found among the products of the reaction. Experiments have shown that ethylene is not polymerised by decaborane.

It has previously been shown⁷ that decaborane reacts with ethylated decaborane to yield non-volatile solid hydrides. Reactions of this type must be responsible for maintaining the high rate of reaction of decaborane in the later stages of the present reaction.

Hydrogen, hydrogen bromide, methane, and ethane are formed during the initial stages of the reaction according to equations (1), (2), and (3). They are formed more rapidly as the reaction proceeds, though secondary reactions and the decomposition of products. The curve for production of hydrogen bromide exhibits a maximum, indicating a secondary reaction. At 220° hydrogen bromide reacts with the non-volatile solid hydrides: it does not react with decaborane.

Reaction Mechanism.—The reaction mechanism may therefore be represented by the following equations:



The rate of reaction of decaborane is given by the expression

$$-d(\text{B}_{10}\text{H}_{14})/dt = (\text{B}_{10}\text{H}_{14})[(k_1 + k_2)(\text{C}_2\text{H}_5\text{Br}) + (k_6 + k_7)(\text{B}_{10}\text{H}_{13}\text{C}_2\text{H}_5) + k_3] \quad (11)$$

In the early stages of the reaction the concentration of $\text{B}_{10}\text{H}_{13}\text{C}_2\text{H}_5$ is small and equation (11) then approximates to

$$-d(\text{B}_{10}\text{H}_{14})/dt = (\text{B}_{10}\text{H}_{14})[(k_1 + k_2)(\text{C}_2\text{H}_5\text{Br}) + k_3] \quad (12)$$

Fig. 2 shows a plot of the initial rate of reaction of decaborane against the initial pressure of decaborane at a fixed initial pressure of ethyl bromide of 300 mm. The slopes of the lines at the three temperatures 210, 220, and 230° are given by the expression $s = (k_1 + k_2)[\text{C}_2\text{H}_5\text{Br}] + k_3$. Similarly, the initial rate of reaction of decaborane against the initial pressure of ethyl bromide at a fixed initial pressure of decaborane of 300 mm. is

⁸ P. J. Thomas, *J.*, 1959, 1192.

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plotted in Fig. 3, when the slope $s = (k_1 + k_2)[B_{10}H_{14}]$ and the intercept $i = k_3[B_{10}H_{14}]$. Fig. 4 shows similar plots of the initial rate of reaction of ethyl bromide against the initial pressure of decaborane. Values of k_3 are known from previous work,² and the values of $(k_1 + k_2)$ were obtained from Figs. 2–4. It appears from a comparison of the

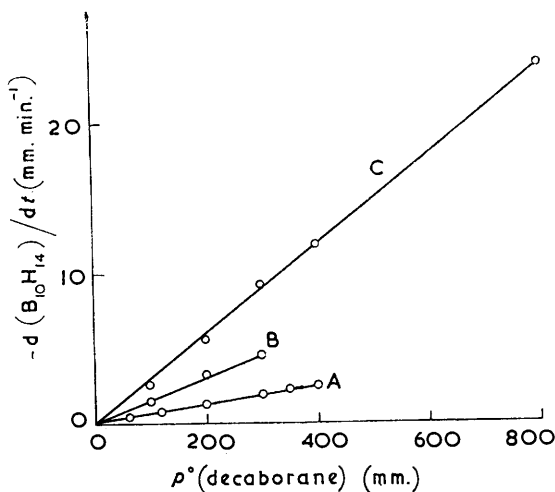


FIG. 2.

FIG. 2. Variation of the rate of reaction of decaborane with the initial pressure of decaborane; p° (ethyl bromide) = 300 mm.

A, at 210° , $s = 6.05 \times 10^{-3}$; B, at 220° , $s = 1.53 \times 10^{-2}$; C, at 230° , $s = 3.03 \times 10^{-2}$.

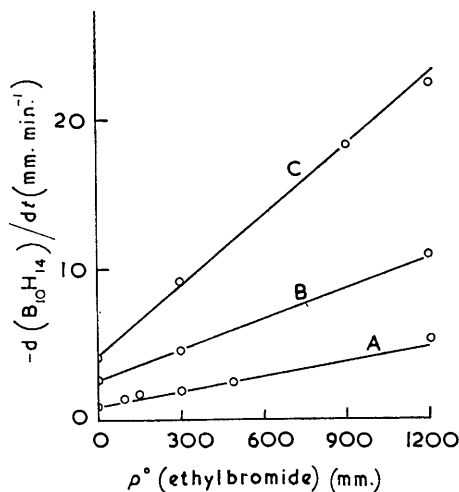


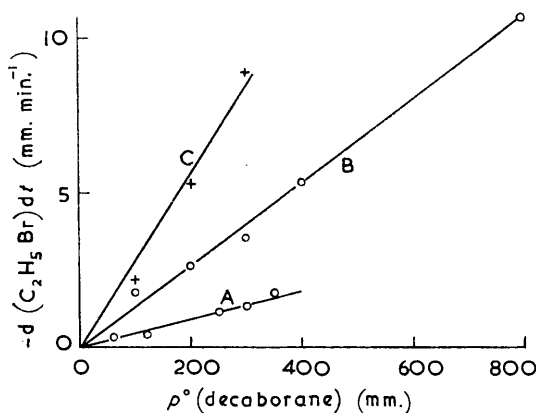
FIG. 3.

FIG. 3. Variation of the rate of reaction of decaborane with the initial pressure of ethyl bromide at different temperatures; p° (decaborane) = 300 mm.

A, at 210° , $s = 3.32 \times 10^{-2}$; B, at 220° , $s = 6.86 \times 10^{-2}$; C, at 230° , $s = 1.605 \times 10^{-2}$.

FIG. 4. Variation of the initial rate of reaction of ethyl bromide with the initial pressure of decaborane.

A, at 210° , $s = 4.57 \times 10^{-3}$ } $p^\circ(\text{EtBr}) =$
 B, at 230° , $s = 1.40 \times 10^{-2}$ } 300 mm.
 C, at 220° , $s = 2.87 \times 10^{-2}$, $p^\circ(\text{EtBr}) =$
 1200 mm.



initial rate of reaction of ethyl bromide with the rate of formation of 2-ethyldecaborane that $k_1 \approx k_2$.

The initial stages of the reaction mechanism have been further substantiated by calculating the rate of formation of hydrogen and hydrogen bromide from the appropriate rate expressions and comparing the values so obtained with the experimental figures. The agreement is shown in Table I to be satisfactory. At 230° , the experimental hydrogen values tend to be higher than the predicted value; this is almost certainly due to side reactions occurring before the first measurement was made.

TABLE I.

Comparison of the predicted and experimental values of the rates of formation of hydrogen and hydrogen bromide.

Temp.	p° ($B_{10}H_{14}$) (mm.)	p° (C_2H_5Br) (mm.)	$d(H_2)/dt$ (ml. min. ⁻¹)		$d(HBr)/dt$ (ml. min. ⁻¹)	
			Pred.	Expt.	Pred.	Expt.
210°	60	300	0.02	0.03	0.01	—
	120	300	0.04	0.04	0.02	—
	200	300	0.07	0.04	0.04	—
	300	300	0.10	0.08	0.05	0.05
	350	300	0.12	0.08	0.06	0.02
	300	490	0.10	0.08	0.08	—
	300	1200	0.10	0.08	0.22	—
220°	100	300	0.09	0.10	0.04	0.03
	200	300	0.18	—	0.08	0.09
	300	300	0.27	0.10	0.11	0.10
	100	1200	0.09	0.10	0.15	0.05
	200	1200	0.18	0.40	0.30	0.40
	300	1200	0.27	0.50	0.45	—
230°	100	300	0.15	0.23	0.09	0.08
	200	300	0.30	0.50	0.18	0.15
	300	300	0.45	1.00	0.27	—
	400	300	0.60	1.20	0.36	0.50
	800	300	1.20	1.80	0.72	0.60
	300	900	0.45	0.70	0.81	0.80
	300	1200	0.45	1.00	1.08	1.60

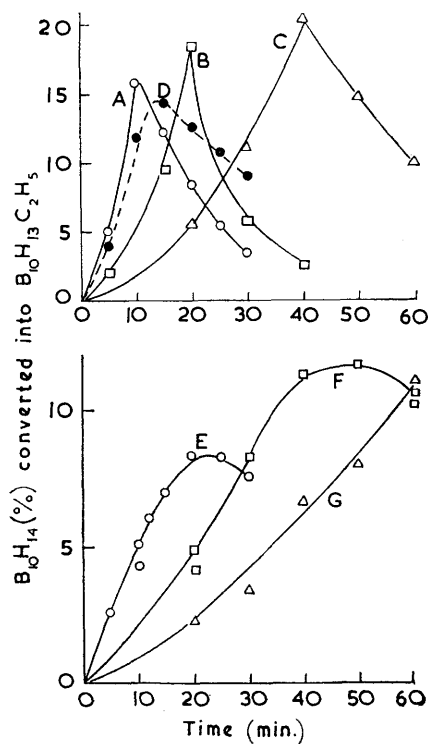


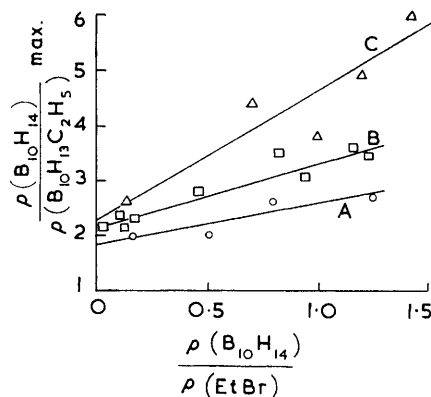
FIG. 5. The fate of ethyldecaborane (a) Curves A, B, and C are for $p^\circ(\text{EtBr}) = 1200$ mm., $p^\circ(B_{10}H_{14}) = 300$ mm., and 230, 220, and 210°, respectively. Curve D is for $p^\circ(\text{EtBr}) = 900$ mm., $p^\circ(B_{10}H_{14}) = 300$ mm. and 230°. (b) Curves E, F, and G are for $p^\circ(\text{EtBr}) = 300$ mm., $p^\circ(B_{10}H_{14}) = 300$ mm., and 230, 220, and 210°, respectively.

The proposed mechanism is also consistent with the observation that, during the reaction, the yield of 2-ethyldecaborane reaches a maximum. A number of curves of this

$$\frac{(B_{10}H_{14})}{(B_{10}H_{13}C_2H_5)} = \left(\frac{k_4 + k_5}{k_1}\right) + \left(\frac{k_6 + k_7}{k_1}\right) \frac{(B_{10}H_{14})}{(C_2H_5Br)} \quad (13)$$

type, obtained under different initial conditions, are illustrated in Fig. 5(a) and (b). At a given temperature, the ratio of pressures of decaborane to 2-ethyldecaborane plotted against the ratio of the pressures of decaborane to ethyl bromide, all pressures referring to those that exist at a reaction time when the 2-ethyldecaborane reaches the maximum, should lead to a straight line whose slope and intercept are the rate-constant expressions $(k_6 + k_7)/k_1$ and $(k_4 + k_5)/k_1$, respectively. The results of over 150 experiments have been summarised in Fig. 6 and straight lines drawn through the points at temperatures of 210, 220, and 230°. The large scatter of the points around the lines is mainly due to the difficulty in determining the value of the maximum yield of 2-ethyldecaborane and the interpolation of the reaction time at which it occurs. Errors in the determination of the reaction time are also reflected by errors in the decaborane and ethyl bromide values. Numerical values of the rate-constant ratios, more particularly of $(k_6 + k_7)/k_1$, may

FIG. 6. The rate-constants ratios $(k_4 + k_5)/k_1$ and $k_6 + k_7/k_1$. Curves A, B, C are for 210°, 220°, and 230°, and have slopes, $s = 0.8, 1.2, \text{ and } 2.3$, respectively.



therefore be subject to quite large errors. Nevertheless, the results clearly show that there is a limit to the yield of 2-ethyldecaborane that can be obtained at a given temperature. The highest yield would be obtained at low ratios of decaborane to ethyl bromide, and at the lowest temperatures. Extrapolating in Fig. 6 at 210°, shows that by using a ratio of decaborane to ethyl bromide of less than 0.05, the maximum yield of 2-ethyldecaborane obtainable would be 37% based on the decaborane converted, or ~22% based on the initial decaborane. Lower temperatures are impracticable if the reaction is to be carried out in the gas phase, since the boiling point of decaborane is 213°.

In practice, the best yield was obtained at 210° by using a decaborane pressure of 300 mm., an ethyl bromide pressure of 1200 mm., and a reaction time of 40 min.; 43% of decaborane is then recovered unchanged, and 20.2% is converted into 2-ethyldecaborane and 2% into diethyldecaboranes. The yield of 2-ethyldecaborane is comparable with the 24% obtained at 70° by the Friedel-Crafts reaction,¹ but in that experiment a 30% yield of polyethylated decaboranes was also isolated.

The Effect of Catalysts.—Experiments have been made on the effect of aluminium chloride and boron tribromide on the reaction of decaborane and ethyl bromide. Aluminium chloride was such an efficient catalyst that, under most conditions quoted earlier in this Paper, the ethyl bromide was completely removed from the system within 5 minutes. The results indicated that aluminium chloride catalyses, to approximately the same extent, all the reactions postulated previously, with the exception of the thermal decomposition of

decaborane. For example, at 210° when decaborane and ethyl bromide pressures of 300 mm. each, 0·01 g. of aluminium chloride, and a reaction time of 5 minutes were used, 50% of the decaborane was recovered unchanged while 29% had been converted to 2-ethyldecaborane. This was the highest yield obtained in a catalysed reaction.

Boron tribromide was not catalytic.

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