tetrachloride gave 2.45 g. (20%) of white needles, m.p. 201–203°.

*Anal.* Calcd. for $C_4H_{14}B_{10}O_2$: C, 23.73; H, 6.97; B, 53.48; neut. equiv., 202.3. Found: C, 23.63; H, 6.93; B, 53.82; neut. equiv., 209.5.

**Methylation of Neocarborane.**—*n*-Butyllithium (0.05 mole) was slowly added to 0.05 mole of neocarborane in 100 ml. of anhydrous ethyl ether at 0–5° over a 30-min. period. After the addition was completed, 0.05 mole of methyl iodide in 20 ml. of ether was added. The reaction mixture was refluxed for 2 hr. and then hydrolyzed by pouring over a mixture of cracked ice and hydrochloric acid. The ether layer was separated, washed with aqueous sodium thiosulfate, and dried. After filtration, the solvent was removed under vacuum. Sublimation of the crude residue gave 3.06 g. (38.7%) of C-methylneocarborane, m.p. 208–210° (sealed tube). The infrared spectrum of the product was identical with that of the thermal isomerization product with slight, but discernible contamination by neocarborane.

**Hydrazine Hydrate Degradation of C-Methylneocarborane.**[14]—Methylneocarborane (0.010 mole) was added to 20 ml. of hydrazine hydrate and the mixture was refluxed for 3.5 hr. under a cold finger condenser. Solids that sublimed during this time were determined to be unreacted methylneocarborane (80% recovery). The gas, 220 ml. (corrected to N.T.P.), evolved during the reaction was found to be pure hydrogen by mass spectrum and represented 4.9 moles of hydrogen per mole of reacted methylneocarborane.

The solvent was removed by evaporation under reduced pressure, leaving a semisolid residue which has not been characterized further.

**Neocarborane and Sodium in Ammonia.**—Ammonia was condensed in a three-necked, round-bottom flask equipped with a Teflon stirring bar, Dry Ice condenser, thermometer, and gas inlet tube. The apparatus had previously been flamed out and continuously flushed with argon to prevent the return of moisture into the system. When 250 ml. of ammonia had been condensed, 0.0083 mole of spectrally and chromatographically pure neocarborane was added to the ammonia while the system was flushed with argon. Then sodium, cut in small pieces, was added, with almost instantaneous bleaching of the incipient blue color. The addition of sodium was stopped when the blue color persisted for 15 min. (0.0078 mole had been added). Evaporation of the ammonia left a gray-white hygroscopic solid from which the last trace of ammonia was removed under vacuum. The solid was then washed several times with sodium-dried benzene while an argon atmosphere was maintained over the mixture. Nothing was obtained from the benzene solution. When the solid was treated with 3 *N* aqueous hydrochloric acid, gas was evolved which contained over 50% hydrogen and lesser amounts of ammonia, methane, and ethane. A water-insoluble residue remained which was taken up in ethyl ether, and the ether solution was dried over calcium sulfate. A pink solid was obtained after the ether solution was removed at reduced pressure. Sublimation gave a white sublimate (0.20 g.) which was pure carborane (by its infrared spectrum) free of neocarborane. The residue from sublimation decomposed at 205°.

On treating the hydrochloric acid solution with tetramethylammonium hydroxide, 2.4 g. of a white solid precipitated which melted above 320° after being crystallized from methanol.

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[14] Reaction run by Mr. Harry F. Smith.

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# The Reaction of Ethylene with Pentaborane-11

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Ethylpentaborane-11 was found to be the major product in the reaction of ethylene with pentaborane-11. Also found were diborane, ethyldiboranes, diethylpentaborane-11, tetraborane, and dimethylenetetraborane. The amounts of these various products can be controlled by variations in the reaction conditions. A mechanism accounting for all the products is proposed. Decomposition of ethylpentaborane-11 resulted in a complex mixture of products. The mechanism postulated for this decomposition is supported by other studies.

As an interesting extension to the previously reported work on the reactions of ethylene with diborane,[1,2] tetraborane,[3] and pentaborane-9,[4] a study of the reaction of ethylene with pentaborane-11 was undertaken.

The major product of the reaction was identified as ethylpentaborane-11, $C_2H_5B_5H_{10}$. First, vapor density measurements showed a molecular weight of 94.5, compared with the calculated value of 93.6 for $C_2H_5B_5H_{10}$. Second, oxidative hydrolysis followed by titration of the boric acid gave 4.8 boron atoms and 9.7 active hydrogens per molecule, which indicated that the product was a pentaborane derivative. However, since the active hydrogen analysis was not accurate enough to distinguish between the derivatives of $B_5H_9$ and $B_5H_{11}$, infrared spectra were used for this purpose.

The infrared spectra of $B_5H_9$ and $B_5H_{11}$ are quite dif-

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[1] D. T. Hurd, *J. Am. Chem. Soc.*, **70**, 2053 (1948).

[2] A. T. Whatley and R. N. Pease, *ibid.*, **76**, 835 (1954).

[3] B. C. Harrison, I. J. Solomon, R. D. Hites, and M. J. Klein, *J. Inorg. Nucl. Chem.*, **14**, 195 (1960).

[4] B. Figgis and R. L. Williams, *Spectrochim. Acta*, 331 (1959).

ferent in that $BH_2$ groups are present in $B_5H_{11}$ whereas only B–H and B–H–B groups are present in $B_5H_9$.[5] As shown in Table I, comparison of the peak values for $B_5H_9$ and $B_5H_{11}$ with those for the product gave supporting evidence that the product was $C_2H_5B_5H_{10}$.

The side products which were separated and identified in a typical run are shown in Table II. An unidentified fraction which exerted a vapor pressure of 0.5 mm. at 0° was also observed, but because of its low volatility it could not be measured accurately as a gas. Its infrared spectrum was similar to that of ethylpentaborane-11, but with an increase in the intensity of the C–H bands. The boron and hydrogen analyses corresponded closely to the values expected for diethylpentaborane-11.

TABLE I

INFRARED SPECTRA OF PENTABORANES[a]

| $B_5H_9$ | $B_5H_{11}$ | $C_2H_5B_5H_{10}$ |
|---|---|---|
| | | 3.38 (s) |
| 3.80 (s) | 3.9–4.1 (doublet s) | 3.38–3.99 (doublet s) |
| | 4.9 (m) | 4.80 (m) |
| | | 5.20 (w) |
| 5.50 (m) | | |
| 7.0 (s) | 7.0 (m) | 6.86 (s) |
| | 8.6 (s) | 8.6 (s) |
| 9.6 (w) | 9.6 (m) | 9.6 (m) |
| 11.3 (s) | 11.2 (m) | 11.23 (m) |

[a] Peak values in microns; s, strong; m, medium; w, weak.

TABLE II

PRODUCTS FROM THE REACTION OF ETHYLENE WITH PENTABORANE-11[a]

| Product | Amount, mmoles |
|---|---|
| $H_2$ | 0.64 |
| $C_2H_5B_5H_{10}$ | 3.30 |
| *sym*-$(C_2H_5)_2B_2H_4$ | 0.03 |
| $B_4H_{10} + C_2H_5B_2H_5$[b] | 0.16 |
| $B_2H_6$ | [c] |
| $C_2H_4B_4H_8$ | 0.77 |

[a] 25°, 500 mm., 60 min. [b] Not separated because of similar volatilities. [c] Present in $C_2H_4$ fraction but not measured.

The formation of dimethylenetetraborane, $C_2H_4B_4H_8$, was surprising. This material was identical with the product of the reaction of ethylene with tetraborane.[3] As will be shown later, dimethylenetetraborane is not a decomposition product of ethylpentaborane-11. Therefore, it appears to have been formed in a simultaneous reaction.

A possible mechanism for the formation of all of the product can be surmised from the cleavage of pentaborane-11,[6] as illustrated in eq. 1.

$$B_5H_{11} \rightleftharpoons B_4H_8 + BH_3 \qquad (1)$$

Other investigators have also obtained evidence for the existence of $B_4H_8$.[3,7] Thus, the reaction of ethylene with $B_4H_8$ would yield the dimethylenetetraborane, and the reaction of the $BH_3$ fragment with ethylene would yield the alkylated borane[2] (eq. 2), which in turn would react with $B_4H_8$ to form $C_2H_5B_5H_{10}$ (eq. 3).

$$C_2H_4 + BH_3 \longrightarrow C_2H_5BH_2 \qquad (2)$$

$$C_2H_5BH_2 + B_4H_8 \longrightarrow C_2H_5B_5H_{10} \qquad (3)$$

The presence of mono- and diethyldiboranes can then be explained on the basis of the reactions shown in eq. 4 and 5.[8]

$$C_2H_5BH_2 + BH_3 \rightleftharpoons C_2H_5B_2H_5 \qquad (4)$$

$$2C_2H_5BH_2 \rightleftharpoons sym\text{-}(C_2H_5)_2B_2H_4 \qquad (5)$$

The decomposition of ethylpentaborane-11 was studied in both liquid and gaseous phases and in the presence of other boron hydrides, in the hope that the mode of decomposition could be determined by this procedure. However, the large number of products and their complex interactions precluded any definite conclusions. The effects of time on the decomposition are shown in Table III. In almost all cases the amount of a specific product increased with time. The obvious exception is diethyldiborane. In some of the larger runs, infrared analysis of the nonvolatile residue indicated that decaborane or ethyl derivatives of decaborane were present.

The data from the decomposition runs with ethylpentaborane-11 in the liquid phase, both alone and in the presence of other boron hydrides, are shown in Table IV. It can be seen that the decomposition of ethylpentaborane-11 decreased in the presence of pentaborane-9. However, since only a small amount of pentaborane-9 decomposed, evidently it merely acted as a diluent to slow the decomposition of the ethylpentaborane-11.

No pentaborane-11 was found from the decomposition of ethylpentaborane-11 in the liquid phase, and the amount of ethyldiborane found was small. In the presence of diborane, some pentaborane-11 and a larger amount of ethyldiborane were found, which suggested the reaction illustrated in eq. 6.

$$C_2H_5B_5H_{10} + B_2H_6 \rightleftharpoons C_2H_5B_2H_5 + B_5H_{11} \qquad (6)$$

From the decomposition of ethylpentaborane-11 in the presence of tetraborane, pentaborane-11 and ethyldiborane were found in amounts similar to those obtained in the presence of diborane. This can be understood, since tetraborane decomposes to yield diborane. If eq. 6 is considered to be reversible, the data from the decomposition in the presence of pentaborane-11 are also consistent with the postulated reaction. The smaller amount of ethyldiborane could be accounted for by a subsequent reaction of ethyldiborane with pentaborane-11 to form ethylpentaborane-11. Formation of the latter product would account for the lower net loss of ethylpentaborane-11.

These postulations led to a further study of the reactions of ethyldiboranes and pentaborane-11. It was subsequently learned that the reversible reaction given by eq. 6 is a reality, and this study will be completely described in a separate publication. Thus, some of the

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[5] L. V. McCarty, G. C. Smith, and R. S. McDonald, *Anal. Chem.*, **26**, 1027 (1954).

[6] R. W. Parry and L. J. Edwards, *J. Am. Chem. Soc.*, **81**, 3554 (1959).

[7] A. B. Burg and J. R. Spielman, *ibid.*, **80**, 3419 (1958).

[8] I. J. Solomon, M. J. Klein, and K. Hattori, *ibid.*, **80**, 4520 (1958).

TABLE III

LIQUID PHASE DECOMPOSITION OF ETHYLPENTABORANE-11[a]

| Time, hr. | Products, mmoles | | | | | | | | | Decomp., % |
|---|---|---|---|---|---|---|---|---|---|---|
| | $H_2$ | $B_2H_6$ | $C_2H_5B_2H_5$ | $B_4H_{10}$ | $(C_2H_5)_2B_2H_4$ | $(C_2H_5)_2B_5H_9$ | $C_2H_5B_{10}H_{13}$ | $B_5H_{11}$ | $C_2H_5B_5H_{10}$ | |
| 0.5 | 0.027 | 0.009 | 0.013 | 0.009 | 0.116 | 0.005 | .. | 0.0 | 0.442 | 50.5 |
| 1.0 | .040 | .022 | .027 | .009 | .197 | .009 | .. | .0 | .389 | 65.5 |
| 2.0 | .058 | .067 | .045 | .018 | .174 | .027 | + | .013 | .273 | 69.5 |
| 3.0 | .121 | .112 | .049 | .049 | .179 | .018 | + | .0 | .232 | 74 |
| 6.0 | .143 | .156 | .112 | .040 | .049 | .005 | + | .089 | .196 | 78 |

[a] Sample size, 0.900 ± 0.002 mmole; bulb vol., 13 ± 0.5 cc.; reaction temp., 25°.

TABLE IV

LIQUID PHASE DECOMPOSITION OF ETHYLPENTABORANE-11 WITH OTHER BORON HYDRIDES[a]

| Reactants | | Products, mmoles | | | | | | | | | | Decomposition, % | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | Amount, mmoles | $H_2$ | $B_2H_6$ | $B_4H_{10}$ | $C_2H_5$-$B_2H_5$ | $(C_2H_5)_2$-$B_2H_4$ | $B_5H_{11}$ | $C_2H_5$-$B_5H_{10}$ | $(C_2H_5)_2$-$B_5H_9$ | $B_5H_9$ | $C_2H_5$-$B_{10}H_{13}$ | $C_2H_5$-$B_5H_{10}$ | Second component |
| $C_2H_5B_5H_{10}$ | 0.907 | 0.080 | 0.125 | 0.054 | 0.063 | 0.183 | 0 | 0.228 | 0.004 | 0 | + | 75 | .. |
| $C_2H_5B_5H_{10}$ | .928 | .071 | .750 | .085 | .174 | .121 | 0.103 | .232 | Trace | 0 | + | 75 | 19 |
| $B_2H_6$ | .928 | | | | | | | | | | | | |
| $C_2H_5B_5H_{10}$ | .906 | .107 | .134 | .780 | .089 | .058 | .134 | .241 | 0.004 | 0 | + | 73 | 11 |
| $B_4H_{10}$ | .902 | | | | | | | | | | | | |
| $C_2H_5B_5H_{10}$ | .848 | .080 | .130 | .013 | .018 | .058 | .691 | .334 | .004 | 0 | + | 60 | 18 |
| $B_5H_{11}$ | .848 | | | | | | | | | | | | |
| $C_2H_5B_5H_{10}$ | .898 | .022 | .018 | .013 | .018 | .022 | 0 | .437 | Trace | 0.955 | .. | 51 | 2 |
| $B_5H_9$ | .974 | | | | | | | | | | | | |
| $C_2H_5B_5H_{10}$ | .907 | .027 | .027 | .009 | .027 | .036 | 0 | .411 | 0.004 | 0.889 | .. | 54 | 6 |
| $B_5H_9$ | .943 | | | | | | | | | | | | |

[a] Reaction time, 3 hr.; temp., 25°; bulb vol., 20 cc.

reactions of ethylpentaborane-11 are understood but others are complicated by the interactions of the other boron hydrides.

The decomposition of ethylpentaborane-11 was also carried out in the gas phase for various periods of time. It was found that the reaction is slower, but the products are approximately the same. A decomposition range of 10.3 to 85% was obtained in 4.5 to 19 hr. under these conditions.

## Experimental

For this study the majority of the reactions between ethylene and pentaborane-11 were carried out at 25° and approximately 500 mm. pressure. However, in a few brief experiments, the effects of time and temperature were examined in an effort to determine the optimum conditions for the production of a maximum amount of ethylpentaborane-11. The results, although not conclusive, indicated that the reaction is much slower but that fewer side products are formed and the relative yield of ethylpentaborane-11 is higher at 0°. No dimethylenetetraborane was detected in the products of the 0° reactions. Below 0° very little reaction occurs.

The effect of time was observed in a series of reactions carried out with 2 mmoles of pentaborane-11 and 10 mmoles of ethylene in a 350-cc. reactor at 25°. The yield of ethylpentaborane-11 was found to decrease with time. The optimum time appeared to be 30 min. Under these conditions a 96% yield ($C_2H_5B_5H_{10}$ formed/$B_5H_{11}$ consumed) and an 18% conversion ($B_5H_{11}$ consumed/$B_5H_{11}$ charged) were obtained.

The diborane (obtained from Callery Chemical Co.) was purified by repeated passages through a −138° trap.

The tetraborane and the pentaborane-11 were prepared and purified by previously described methods.[9]

The pentaborane-9 and the decaborane were obtained from Callery Chemical Co. The decaborane was purified by vacuum sublimation. Since infrared analysis of the pentaborane-9 indicated the presence of small amounts of pentaborane-11, the pentaborane-9 was passed repeatedly through a hot tube at 180°, and the final traces of pentaborane-11 were removed by reaction with trimethylamine.

The molecular weight determinations and the hydrolysis and infrared techniques were the same as those previously described.[3] The separation of the components from the various mixtures was different in each case, depending on the contents of the original mixture. The fractionation procedures were those generally used in high vacuum techniques. All materials were purified to tensiometric homogeneity.

The vapor pressures of the various compounds are: $B_2H_6$, 69 mm. at −126°; $B_4H_{10}$, 388 mm. at 0°; $B_5H_9$, 69 mm. at 0°; $B_5H_{11}$, 52.5 mm. at 0°; $C_2H_4B_4H_{10}$, 14.5 mm. at 0°; $C_2H_5B_5H_{10}$, 5 mm. at 0°; $(C_2H_5)_2B_5H_9$, 0.5 mm. at 0°; $C_2H_5B_2H_5$, 7 mm. at −78°; *sym*-$(C_2H_5)_2B_2H_4$, 36 mm. at 0°.

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(9) M. J. Klein, B. C. Harrison, and I. J. Solomon, *J. Am. Chem. Soc.*, **80**, 8149 (1958).