[CONTRIBUTION FROM THE CHEMISTRY AND CHEMICAL ENGINEERING RESEARCH DEPARTMENT, ARMOUR RESEARCH FOUNDATION, ILLINOIS INSTITUTE OF TECHNOLOGY]

Preparation and Reactions of Mono- and Diethyldiboranes[1]

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Ethyldiborane and the isomeric symmetrical and unsymmetrical diethyldiboranes have been prepared and their reactions studied. The reaction of ethyldiborane alone is a rapid and reversible disproportionation to form diborane and *sym*-diethyldiborane. An equilibrium constant of 0.039 ± 0.006 has been measured for the reaction and a reaction mechanism has been postulated. Contrary to the predictions from other work, *sym*-diethyldiborane has been found to be a stable compound. A method has been developed to prepare pure *unsym*-diethyldiborane.

Schlesinger and his co-workers[2] prepared four of the five theoretically possible ethyldiboranes by equilibration of diborane with triethylboron. The isomer not obtained in this study was *sym*-diethyldiborane. In similar studies with the corresponding methyl compounds[3,4] all the possible derivatives were prepared. The mono-substituted derivatives were found to be unstable and readily decomposed when allowed to warm to room temperature. It was observed that *sym*-dimethyldiborane was unstable and apparently formed the unsymmetrical isomer on standing. By analogy, it was expected that the corresponding ethyl compound would also be unstable.

Disproportionation of Ethyldiborane: Preparation of *sym*-Diethyldiborane.—It had been observed by others, as well as in our laboratories, that monoethyldiborane was quite unstable and decomposed readily. Therefore, the isolation and study of the reactions of this compound were undertaken in order to learn more about the nature of its instability and the course of its reactions. It was found that in 1 hr. at 25° equal amounts of diborane and diethyldiborane had been formed, and a corresponding amount of ethyldiborane had been consumed. Therefore, the reaction of ethyldiborane may be illustrated as in eq. 1.[5]

$$2C_2H_5B_2H_5 \longrightarrow B_2H_6 + (C_2H_5)_2B_2H_4 \qquad (1)$$

The reaction proceeded with practically no degradation, as evidenced by the fact that there were no measurable amounts of hydrogen or polymeric solids. This is rather unique in reactions of boron hydrides. Thus, the self-reaction of ethyldiborane was actually a disproportionation to diethyldiborane and diborane. The extent of disproportionation depended on whether the reaction took place in the liquid or gas phase. Typical data from three runs are shown in Table I.

Only very small amounts (<0.1 cc.) of less volatile material were found in addition to the products shown in Table I. The fractions were too small to analyze and were assumed to be higher ethyl derivatives of diborane.

The diethyldiborane from the reaction was studied in greater detail in order to determine whether it was the unsymmetrical or the symmetrical isomer. Their difference in structure was used to develop a rapid infrared method for their analysis. From the infrared spectra for the known boron hydrides[6] and for the derivatives prepared in this Laboratory, it had been observed empirically that the two strong, sharp peaks near 3.9 and 4.1 μ and another peak near 8.6 μ were characteristic of the BH_2 group as present in the unsymmetrical isomer. The spectra of compounds which contain BH groups, as the symmetrical isomer does, only show one peak near 3.9 μ, and the 8.6 μ peak is absent. The diethyldiborane prepared from the disproportionation of ethyldiborane had only the BH peak in its infrared spectrum, and it was thus shown to be the symmetrical isomer. These features can be seen in the spectra of the diethyldiboranes shown in Fig. 1 and 2.

TABLE I

DISPROPORTIONATION OF ETHYLDIBORANE[a]

Phase	Vol., cc.	C_2H_5-B_2H_5, cc.	Products, cc. B_2H_6	$(C_2H_5)_2$-B_2H_4	C_2H_5-B_2H_5	C_2H_5-B_2H_5, % Disproportionation
Gas	330	50.3	7.1	7.0	36.4	27.6
Mixed	10	20.5	4.5	4.1	11.4	44.4
Liquid	1	33.2	7.7	7.2	18.1	45.3

[a] 25°, 1 hr.

The only diethyldiborane previously reported in the literature[2] was the unsymmetrical isomer. The new *sym*-diethyldiborane is analogous to the corresponding methyl derivative previously reported.[4]

The isomeric *unsym*-diethyldiborane was isolated and found to have chemical and physical properties which were quite different from the symmetrical derivative. Corroborating evidence for the structural assignment of these isomers was obtained at Callery Chemical Company by analysis of the hydrolysis products from the two compounds.[7] As expected, the unsymmetrical isomer yielded one mole of boric acid and one mole of diethylboronic acid, whereas the symmetrical isomer yielded two moles of ethylboronic acid and no boric acid.

It is interesting to note that theoretically there are two geometrical isomers of *sym*-diethyldiborane, a *cis* and a *trans* form, depending on whether the

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(1) Presented at the 133rd Meeting of the American Chemical Society, San Francisco, Calif., April 13–18, 1958.

(2) H. I. Schlesinger, L. Horvitz and A. B. Burg, THIS JOURNAL, **58**, 407 (1936).

(3) H. I. Schlesinger and A. O. Walker, *ibid.*, **57**, 621 (1935).

(4) H. I. Schlesinger, N. W. Flodin and A. B. Burg, *ibid.*, **61**, 1078 (1939).

(5) When the disproportionation reaction was run in an infrared cell, a different product distribution was obtained. This may have been caused by grease from the stopcock.

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

(7) R. K. Pearson, R. J. Shreve and L. J. Edwards, Callery Chemical Company, private communication.

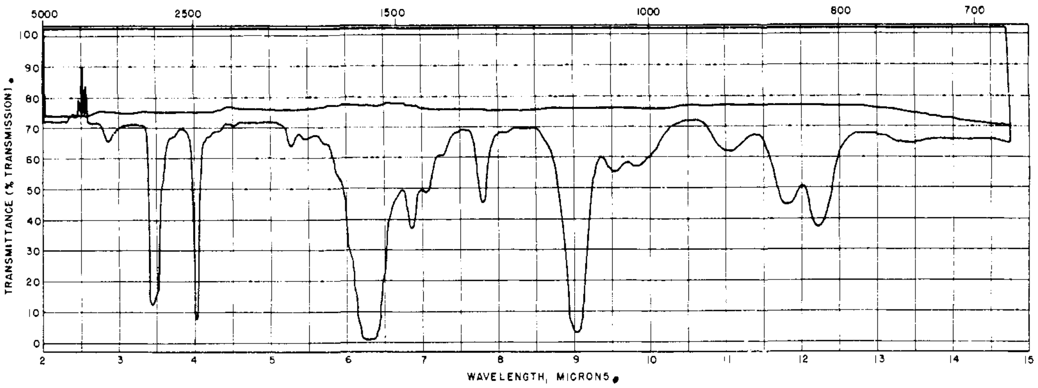

Fig. 1.—Infrared spectrum of *sym*-diethyldiborane.

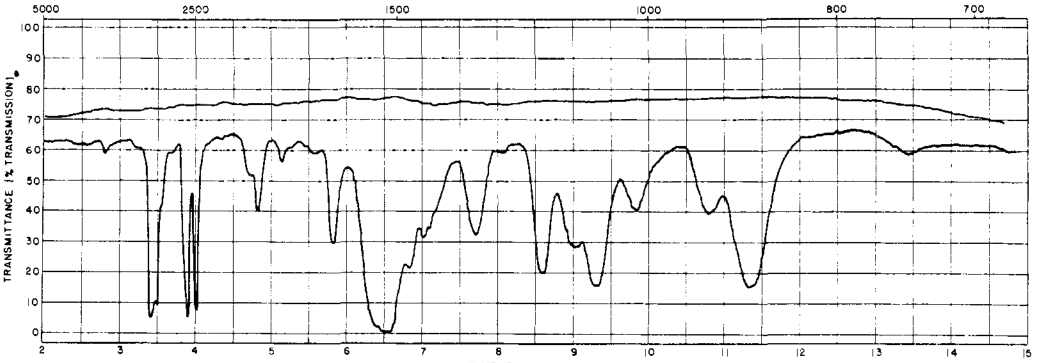

Fig. 2.—Infrared spectrum of *unsym*-diethyldiborane.

two ethyl groups are on the same or opposite sides of the BHB; however, it is not known which form is actually present.

An indication that the reaction is reversible was obtained from the reaction of ethyldiborane in the presence of equal amounts of diborane, which is a product of the disproportionation. In this experiment only 7% of the ethyldiborane was consumed, compared to 28% when it is reacting alone. Final proof for the reversibility of the reaction was obtained from a reaction of diborane and *sym*-diethyldiborane which gave the same products in approximately the same amounts as the reaction of ethyldiborane alone. Thus, since the equilibrium was approached from both sides, the reversibility of the reaction was proved. Therefore, eq. 1 is more nearly correctly shown as eq. 2.

$$2C_2H_5B_2H_5 \rightleftharpoons B_2H_6 + sym\text{-}(C_2H_5)_2B_2H_4 \qquad (2)$$

The data for these two experiments are shown in Table II.

After it had been established that the self-reaction of ethyldiborane was a reversible equilibrium, a series of reactions were conducted at varied lengths of time to determine the approximate rate and equilibrium constant. The data are shown in Table III.

The results show that equilibrium is reached rapidly (1–5 min.) and, using eq. 2, an equilibrium constant of $K_p = 0.039 \pm 0.006$ can be calculated from the four runs which varied in length from 5 min. to 6 hr. It should be noted that these calculations are for the gas phase reaction. The equilibrium constant for the liquid phase reaction, calculated from the data in Table I, is 0.169.

TABLE II

FORMATION OF ETHYLDIBORANES

Run	Reactants	Vol., cc.	Products	Vol., cc.
1[a]	$C_2H_5B_2H_5$	56.3	$C_2H_5B_2H_5$	52.5
	B_2H_6	60.9	B_2H_6	63.0
			sym-$(C_2H_5)_2B_2H_4$	1.0
2[b]	*sym*-$(C_2H_5)_2B_2H_4$	27.6	$C_2H_5B_2H_5$	37.5
	B_2H_6	27.6	B_2H_6	9.2
			sym-$(C_2H_5)_2B_2H_4$	9.2

[a] 1-hr. reaction at 25° in a 330-cc. bulb. [b] 15-min. reaction at 25° in 80-cc. bulb.

TABLE III

RATE OF DISPROPORTIONATION OF ETHYLDIBORANE[a]

Run	C_2H_5-B_2H_5, cc.	Reaction time, min.	Products, cc. C_2H_5-B_2H_5	B_2H_6	$(C_2H_5)_2$-B_2H_4	Disproportionation, %	K_p
1	57.0	360	39.8	8.5	8.5	30.0	0.045
2	50.3	60	36.4	7.0	7.0	27.5	.037
3	56.1	15	41.5	7.6	7.7	26.1	.034
4	57.1	5	40.5	8.3	7.9	28.6	.039
5	57.0	1	49.4	3.6	3.9	13.5	...

[a] 25 ± 0.5°, approximately 120 mm. pressure.

Many of the reactions of diborane chemistry are best explained in terms of borane, its dissociation product. For example, diborane is prepared by reduction of boron halides to borane followed by association, and diborane generally reacts with Lewis bases to form borane complexes. Since diborane and only the symmetrically substituted diethyldiborane (*i.e.*, not the unsymmetrical derivative) are formed from ethyldiborane by a rapid and reversible reaction, the mechanism of the disproportionation is best explained by reversible dissociation and association of the diboranes as illustrated in eq. 3

$$\begin{tikzcd}
2C_2H_5B_2H_5 \arrow[r, shift left] & 2C_2H_5BH_2 \arrow[l, shift left] \arrow[d, shift right] & + & 2BH_3 \arrow[d, shift left] \\
& \textit{sym}\text{-}(C_2H_5)_2B_2H_4 \arrow[u, shift right] & & B_2H_6 \arrow[u, shift left]
\end{tikzcd} \tag{3}$$

The mechanism indicates that at equilibrium all possible products from the combination of ethylborane and borane will be formed, and their relative amounts will depend on the constants for the various equilibria involved. It was shown that all those, and only those, products predicted by the mechanism were actually found. If it can be assumed that the dissociation of a B–C bond requires much greater energy than the dissociation of diboranes to boranes, the mechanism predicts that neither *unsym*-diethylborane nor the tri- or tetra-substituted diboranes would be formed, since these cannot be formed from association of ethylborane and/or borane. The mechanism also predicts that *sym*-diethyldiborane would be relatively stable since its dissociation product cannot associate to any other products.

The mechanism could be proven by the use of diborane prepared with isotopic boron-10. Equilibration of this material with *sym*-diethyldiborane of normal isotope content would yield ethyldiborane, which, on hydrolysis, should yield ethylboronic acid with normal isotope content and boric acid with boron-10. Also disproportionation of the ethyldiborane should yield *sym*-diethyldiborane with normal isotope content and diborane containing boron-10.

Preparation of *unsym*-Diethyldiborane.—The usual preparation of *unsym*-diethyldiborane yields a product which contains a small amount of the symmetrical isomer. Separation of the two isomers by the conventional distillation-condensation techniques is not possible; therefore, a means was sought to obtain pure *unsym*-diethyldiborane in order to determine its chemical and physical properties and to compare it with the *sym*-diethyldiborane.

It was shown that *sym*-diethyldiborane reacted rapidly with diborane to form ethyldiborane, but according to the mechanism proposed for this reaction, it was not expected that *unsym*-diethyldiborane would react readily with diborane. Thus, a sample of mixed diethyldiboranes, whose infrared spectrum showed that it contained a small amount of the symmetrical isomer, was treated with diborane. After equilibration, the excess diborane and the ethyldiborane formed were removed by fractional distillation. The recovered diborane then reacted again with the diethyldiborane. These steps were repeated until all the *sym*-diethyldiborane had been removed, as evidenced by the very low yields of ethyldiborane formed from the diborane equilibration. The data are shown in Table IV.

Table IV

Reaction of Diborane with Mixed Isomeric Diethyldiboranes

	Reactants, cc.		Products, cc.			Reactants consumed, cc.	
Run[a]	B_2H_6	$(C_2H_5)_2$-B_2H_4	B_2H_6	$(C_2H_5)_2$-B_2H_4	C_2H_5-B_2H_5	B_2H_6	$(C_2H_5)_2$-B_2H_4
1	546	51.1	536	42.4	24.3	10	8.7
2	536	42.4	528	36.8	15.5	8	5.6
3	528	36.8	526	34.1	4.2	2	2.7
4	526	34.1	525.5	32.1	0.9	0.5	2.0
5	525.5	32.1	525.5	31.7	.3	0	0.4
6	525.5	31.7	525.5	31.5	.3	0	0.2
7	525.5	31.5	520	24.7	9.9	5.5	6.8

[a] Run 1–6 carried out for 20 min. at 25° in 5-liter flasks. Run 7 carried out for 16 hr. at 25° in 5-liter flask.

The amount of ethyldiborane obtained after each run decreased sharply, as shown in the table, which indicated that the *sym*-diethyldiborane was rapidly consumed. The diethyldiborane obtained after run 4 no longer showed the presence of the symmetrical isomer in its infrared spectrum, and its vapor pressure increased from an initial 41 to 46 mm. at 0° (*sym*-diethyldiborane has a v.p. of 36 mm. at 0°).

Run 5 was carried out for 16 hr., rather than 20 min., in order to confirm that a slow reaction continued to occur after apparently all the *sym*-diethyldiborane had been removed. Later studies showed that it was probably due to a slow decomposition of the *unsym*-diethyldiborane.

Stability of Diethyldiboranes.—It was believed by some investigators that *sym*-diethyldiborane was a rather labile compound which readily disproportionated to *unsym*-diethyldiborane, probably because of the reported instability of the corresponding *sym*-dimethyldiborane.[4] This conception was shown to be untrue by an experiment in which a sample of *sym*-diethyldiborane was stored in the gas phase at 25° for 24 hr. Within experimental measurements, all the sample was recovered and was shown to be the symmetrical isomer by its infrared spectrum. It had previously been determined in a separate experiment that the presence of 5% of the unsymmetrical isomer readily can be detected in the infrared spectrum of a synthetic mixture of both isomers. Therefore, *sym*-diethyldiborane is a rather stable compound which exhibits little tendency to disproportionate or react in any other manner by itself.[8]

Samples of the purified *unsym*-diethyldiborane also were studied for their thermal stability. In 0.5 hr. at 25°, 4.5% of the *unsym*-diethyldiborane decomposed; and in 16 hr., 29.4% of the compound decomposed. Diborane and all the ethyldiboranes, except *sym*-diethyldiborane, were found in the decomposition products.

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(8) After completion of the disproportionation and stability studies it was learned that Burg had reinvestigated the methyldiboranes and had obtained corresponding results.

The triethyldiborane and tetraethyldiborane were not analyzed to prove their identities; however, their vapor pressures agree with those reported by Schlesinger[2] and they are expected decomposition products. Their infrared spectra contained the BHB bridge peak of diboranes. The triethyldiborane spectrum contains a BH peak at 3.9 μ, and the tetraethyldiborane spectrum has no BH peak, as would be expected from their structures.

This self-decomposition of *unsym*-diethyldiborane accounts for the continued formation of small amounts of ethyldiborane reported during the preparation of *unsym*-diethyldiborane. The stability study shows that the unsymmetrical diethyl derivative is significantly less stable than the symmetrical isomer which underwent no measurable amount of decomposition in 24 hr. It is interesting that very little, if any, of the *unsym*-diethyldiborane underwent a disproportionation to diborane and tetraethyldiborane analogous to the ethyldiborane reaction.

Experimental

The fractionation procedures were those generally used in high vacuum techniques (10^{-5} mm.) and were used for samples of approximately 100 cc. (gaseous) or less.

The diborane and ethyldiborane were obtained by fractionation of a mixture of ethyldiboranes supplied by the Callery Chemical Company.

Pure *unsym*-diethyldiborane was obtained from a mixture of diethyldiboranes by repeated expansion with diborane to remove the symmetrical isomer (see text), followed by the fractionation. The resulting diethyldiborane was the pure unsymmetrical isomer with a vapor pressure of 46 mm. at 0°. Previous literature[2] reported 42 mm. at 0°.

The *sym*-diethyldiborane was prepared by the disproportionation of ethyldiborane for 15–20 min. followed by separation of the diborane, ethyldiborane and *sym*-diethyldiborane. Disproportionation of the recovered ethyldiborane was repeated until sufficient product had been obtained. The diethyldiborane produced in this manner is the pure symmetrical isomer with a vapor pressure of 36 mm. at 0°. Other characterization data included a molecular weight measurement of 86.3 (calcd. 83.8) and an active hydrogen determination of 148 cc. (calcd. 132 cc.). on a 33-cc. sample. The compound did not decompose in 24 hr. at 25°. The infrared spectra were taken on a Perkin-Elmer Model 21 spectrometer with a 10-cm. gas cell. Sample sizes which resulted in approximately 35 mm. pressure were found to give the best results.

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CHICAGO, ILL.

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DEPARTMENT, U. S. NAVAL POWDER FACTORY]

Decaborane Grignard Reagents

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Inorganic Grignard reagents are formed when decaborane reacts with methylmagnesium iodide. Either $B_{10}H_{13}MgI$ or $B_{10}H_{12}(MgI)_2$ can be prepared. Upon hydrolysis of $B_{10}H_{13}MgI$, decaborane and MgIOH are formed. That a substituted decaborane could be formed by a Grignard condensation reaction was demonstrated by preparing benzyldecaborane, $B_{10}H_{13}CH_2C_6H_5$. In the latter, the benzyl group was shown to be bonded to a basal boron atom.

Introduction

Very few substituted decaboranes are known.[1] Because of the versatility of Grignard reactions it seemed that such reactions could be used to prepare substituted decaboranes if the decaboryl analog of the organic RMgX could be prepared. In attempts to prepare such a compound by treating iododecaborane with magnesium in various ether solutions, it was found that high temperatures were required for magnesium to be consumed; no reaction was observed at 68° and only a very slow reaction at 140°.[2] To avoid complicating side reactions at high temperatures a milder method for preparing a decaborane Grignard reagent was sought.

Although Wiberg[3] recently showed that diborane reacts with ethylmagnesium halides to form triethylboron and HMgX, we found that methane was formed when decaborane was treated with methylmagnesium iodide. Since this indicated that a decaborane Grignard reagent probably had been formed, a study of this reaction was initiated.

Experimental

Decaborane-monomagnesium Iodide ($B_{10}H_{13}MgI$).—In a typical preparation, 0.057 mole of methylmagnesium iodide (free of methyl iodide) in dried diethyl ether solution was added rapidly to 0.075 mole of decaborane (purified by vacuum sublimation) also in dried diethyl ether solution. This was carried out in a conventional vacuum apparatus; the solutions were prepared in a dry box or under dry nitrogen. The solutions generally were added between 0–20°. An immediate reaction, liberating a gas, ensued. This reaction was completed in a few minutes. The gas was identified as methane by its infrared spectrum and by its vapor pressure of 10 mm. at −195°. The quantity of methane was determined by the usual *PVT* relationship and corresponded to 0.055 mole. After distilling the solvent, the unreacted decaborane was recovered by vacuum sublimation at 25–50°; it corresponded to 0.016 mole. After evacuation in a high vacuum apparatus for several days the residue was a viscous yellow liquid that had no detectable vapor pressure on a U-tube manometer. *Anal.* Calcd. for $C_4H_{23}OB_{10}IMg$: C, 13.9; H, 6.6; B, 31.2; I, 36.7; Mg, 7.2. Found: C, 16.3; H, 6.6; B, 30.3; I, 37.0; Mg, 6.8.[4]

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(1) Stock prepared $B_{10}H_{12}I_2$ and $B_{10}H_{12}Br_2$: A. Stock, "Hydrides of Boron and Silicon," Cornell Univ. Press, Ithaca, N. Y., 1933. Recently Schaeffer found that decaborane condensed with two molecules of acetonitrile; R. Schaeffer, THIS JOURNAL, **79**, 1006 (1957).

(2) Unpublished results of the present authors and J. T. MacQueen.

(3) E. Wiberg and P. Strebel, *Ann.*, **607**, 9 (1957).

(4) The carbon values are slightly higher than theoretical for monoetherates and could be represented as 1.1–1.2 etherates, but considering how strongly ether is retained by these reagents and the viscosity of the preparations, calculating for a monoethereate is logical; the other analyses could fit a slightly higher fractional value.