Heat of Vaporization.—The molar heat of vaporization at the normal boiling point, calculated from the Clausius–Clapeyron equation, is 5684 cal./mole. Trouton's constant is 21.1 cal./deg. mole, a value consistent with those usually obtained for unassociated compounds.

Chemical Properties. Stability.—Essentially no decomposition of $B_3C_2H_5$ has been observed, even on prolonged storage at room temperature.

Reactivity.—$B_3C_2H_5$ has been in contact with acetone, trimethylamine, carbon dioxide, air and water at room temperature without noticeable reaction.

An exchange reaction occurs with deuteriodiborane in which the three hydrogens attached to boron are replaced by deuterium atoms (half-time at room temperature *ca.* 7 hours).

Discussion

The combination of information derived from mass spectra and n.m.r. spectra of the product described here dictates a molecular structure consisting of three identical B–H units and two identical C–H units. Although the infrared spectra show no absorption frequencies which can be assigned to a C–H stretching mode, the evidence is strongly in favor of the existence of two C–H units.

The mass spectral fragmentation pattern of $B_3C_2H_5$ indicates that most fragments result from a loss of hydrogens rather than a breaking of the boron-carbon skeleton and, as such, is more akin to aromatics, *e.g.*, benzene, rather than to aliphatics, *e.g.*, hexane or even cyclohexane. This stability may be attributed to resonance.

Based on the above considerations, the most probable structure for the $B_3C_2H_5$ molecule is a trigonal bipyramid in which the three boron and associated hydrogen atoms lie in one plane with the two carbons and their hydrogen atoms lying along the axis perpendicular to the equilateral triangle formed by the boron atoms, and occupying apical position, *i.e.*, the carbon atoms lie on opposite sides of the boron plane. This structure is compatible with the small number of fundamental bands observed in the infrared spectrum.

$B_3C_2H_5$ has been formed as one of the reaction products of acetylene and pentaborane. No doubt the mechanism of such reaction is complex; however, the hydrogens originally attached to the borons and carbons are primarily retained in the new structure.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, OLIN MATHIESON CHEMICAL CORPORATION, PASADENA, CALIF.]

Cyclic Organodiboranes: 1,2-Tetramethylenediborane and 1,2-(1′-Methyltrimethylene)-diborane

BY H. G. WEISS,[1a] W. J. LEHMANN[1b] AND I. SHAPIRO[1c]

RECEIVED JULY 2, 1962

Two compounds having the empirical formula $B_2C_4H_{12}$ were prepared by the reaction of butadiene and diborane. These compounds have been characterized as the cyclic organodiboranes: 1,2-tetramethylenediborane and 1,2-(1′-methyltrimethylene)-diborane by means of their mass, infrared and n.m r. spectra and by analysis of their oxidation products.

Introduction

The reaction between diborane and 1,3-butadiene has been reported by Köster[2,3] and also by Zweifel, Nagase and Brown,[4] and a possible conflict[4] has arisen regarding products of the reaction.[2,3] Köster has reported the isolation of 1,1′-tetramethylene-bis-borolene, $B_2(C_4H_8)_3$, and bis-borocyclopentene, $C_4H_8BH_2BC_4H_8$, as products of the reaction. All reported compounds have boron attached at the 1,4-positions in butadiene. Brown and co-workers, on the other hand, report the reaction product to be polymeric, having average molecular weights of 320 to 365. Interestingly, oxidation of this product was reported to yield substantial amounts of the 1,3-diols, thus indicating like substitution in the original borane polymer. The reaction conditions reported in the separate papers are different, however, Köster having used trialkylamineboranes with butadiene at 0° to 25°, while Brown's group utilized tetrahydrofuran solutions of diborane at room temperature. In both cases a borane adduct was used as one of the reactants.

In our laboratory, the reactions between diborane and 1,3-butadiene were studied under still other conditions, *i.e.*, in the vapor phase at 100° with only hydrogen as a diluent. Under these conditions the product contained, in addition to polymeric materials, an appreciable amount of the 1:1 butadiene–diborane addition product. Analysis of the product revealed it to be primarily 1,2-tetramethylenediborane, containing also small amounts of 1,2-(1′-methyltrimethylene)-diborane. The compounds are unique in that they incorporate the double-hydrogen bridge of the diborane molecule into a single cyclic organoborane compound. Assuming the reported work of the previous authors[2,3,4] to be correct, it appears that the

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[1] (a) Dynamic Science Corp., South Pasadena, Calif. (b) Aerospace Corp., Los Angeles 45, Calif. (c) Universal Chemical Systems, Inc., Culver City, Calif.

[2] R. Köster, *Angew. Chem.*, **71**, 520 (1959).

[3] R. Köster, *ibid.*, **72**, 626 (1960).

[4] G. Zweifel, K. Nagase and H. C. Brown, *J. Am. Chem. Soc.*, **84**, 183 (1962).

reaction conditions are the principal factors in determining the final products of the reaction between 1,3-butadiene and diborane.

Experimental

Reagents. Diborane.—Diborane was prepared by the reaction of sodium borohydride (obtained from Metal Hydrides, Inc., Beverly, Mass.) with methanesulfonic acid.[5]

1,3-Butadiene.—C.P. 1,3-butadiene, prepared by the Matheson Company, was used without further purification.

Hydrogen.—Prepurified hydrogen was obtained from the Matheson Company.

Deuterium.—Deuterium gas, having a purity greater than 99.5% deuterium, was obtained from Stuart Oxygen Co.

Procedure.—The following procedure was found satisfactory for the reaction and was derived from several preliminary experiments in which temperature and the diborane–1,3-butadiene–hydrogen ratios were varied. In a typical experiment, diborane, butadiene and hydrogen in the mole ratio of 5:1:2 were transferred into a 100-cc. reactor by high vacuum techniques. The gases were warmed to room temperature and mixed for 15–20 minutes by shaking the reactor containing glass beads. The reactor then was placed in a bath at 100°, at which temperature the calculated total pressure in the reactor was one atmosphere. After a few minutes of heating, liquid droplets appeared in the reactor and the heating was stopped. The volatile material was fractionated through a trap at −150° into liquid nitrogen. A quantity of non-volatile material remained in the reactor. (In the absence of hydrogen a vigorous reaction occurred at temperature above about 100°, and solid products were formed.)

The volatile products of the reaction (−150° fraction) constituted on the average a yield of 40% based upon butadiene; small amounts of unreacted diborane were recovered in the liquid nitrogen fraction. The reaction products could be separated into two distinct compounds by further fractionation. The more volatile component was removed by repeated fractionation through a trap at −80°, the 1,2-tetramethylenediborane (I) being retained. The other compound, 1,2-(1′-methyltrimethylene)-diborane (II), was obtained by slow fractionation from −80°, through −90° to −95°, and into liquid nitrogen, with continuous pumping. The liquid nitrogen fraction was retained and refractionated through a −95° trap to remove the last traces of I. Vapor pressures of the pure compounds at 0° are 26.3 ± 1.0 mm. for I and 39.2 ± 1.0 mm. for II.

Exchange experiments between B_2D_6 and I were carried out at room temperature by repeatedly exposing I to freshly prepared B_2D_6. Each exchange reaction was found to approach equilibrium after about 30 minutes. Compound I was then separated from the diborane by fractionation through a trap at −150°; an infrared spectrum was taken after each exchange experiment. The used diborane was deuterium-enriched by heating for 1 hour at 100° in the presence of excess deuterium gas and was then fractionated through a −150° bath to remove any possible pyrolysis products before being reexposed to I.

Compound I was hydrolyzed and oxidized (alkaline hydrogen peroxide) to the corresponding glycol. Comparison of the infrared and H^1–n.m.r. spectra of the oxidation product with spectra taken of known glycols showed the oxidation product of I to be 1,4-butanediol. Oxidative analysis of II was not carried out because of the small quantity of this material obtained.

Results and Discussion

Compound I is the predominant volatile compound formed in the reaction and is the more stable of the two compounds. Pure I decomposes only slightly at room temperature (liquid phase) over a period of two or three days, with the formation of diborane. Decomposition at a more rapid rate is observed in the gas phase at temperatures of about 100°. Compound II decomposes to diborane and other unidentified (non-volatile) products at a moderate rate at room temperature. At elevated temperatures the rate of decomposition is fast. Hence, purification of I contaminated with small amounts of II can be accomplished by heating to about 50° (vapor phase) without significant loss of I. Neither I nor II was transformed into the other by heating, as indicated by their infrared spectra, as might be expected from the work of Brown and Zweifel.[6] This may indicate that the solvent plays a part in the reported transfer of borane to the terminal carbon.

The polyisotopic mass spectra of the two compounds are given in Table I. Both compounds

TABLE I

POLYISOTOPIC MASS SPECTRA[a] OF 1,2-TETRAMETHYLENEDIBORANE (I) AND 1,2-(1′-METHYLTRIMETHYLENE)-DIBORANE (II)

Average sensitivities: (I) 15.0 div./μ for *m/e* 40 and (II) 12.6 div./μ for *m/e* 68, both values adjusted to butane sensitivity of 50 for *m/e* 43

I				II			
M/e	Rel. peak hts.	*M/e*	Rel. peak hts.	*M/e*	Rel. peak hts.	*M/e*	Rel. peak hts.
12	8.7	50	37.8	12	9.5	50	24.6
13	23.5	51	63.5	13	21.6	51	38.3
14	0.8	52	43.7	14	2.8	52	25.6
15	6.2	53	98.0	15	9.6	53	63.8
16	0.2	54	41.5	16	1.9	54	26.9
22	0.3	55	3.3	22	0.7	55	7.1
23	1.1	56	1.4	23	2.2	56	5.3
24	2.8	57	1.0	24	1.4	57	3.0
25	7.9	58	0.5	25	8.8	58	5.1
26	32.5	59	1.0	26	35.7	59	3.0
27	56.6	60	2.3	27	77.9	60	3.9
28	6.0	61	4.1	28	23.6	61	4.5
29	3.6	62	2.7	29	21.1	62	3.0
30	0.3	63	7.6	30	1.1	63	4.8
31	.3	64	23.9	31		64	8.5
32	.1	65	42.5	32	2.2	65	14.1
33	.2	66	13.2	33	0.4	66	4.7
34	.7	67	24.2	34	1.4	67	28.8
35	3.4	68	68.6	35	4.4	68	100
36	20.3	69	3.3	36	18.5	69	10.7
37	53.7	70	0.4	37	47.6	70	.8
38	24.7	71	0.8	38	25.8	71	.6
39	79.7	72	1.4	39	19.6	72	.9
40	100	73	1.6	40	74.2	73	.9
41	39.7	74	1.5	41	56.8	74	.7
42	4.4	75	2.3	42	11.0	75	1.0
43	1.1	76	3.8	43	33.0	76	2.2
44	1.5	77	7.6	44	13.5	77	2.5
45	0.3	78	10.7	45	1.8	78	2.7
46	1.0	79	19.6	46	2.5	79	3.9
47	4.8	80	21.7	47	5.6	80	3.0
48	13.8	81	20.2	48	11.4	81	5.8
49	24.7	82	36.6	49	17.6	82	10.5
		83	1.7			83	0.7
		84	0.1				

[a] Consolidated model 21-103 mass spectrometer operated at an ionizing potential of 70 volts.

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(5) H. G. Weiss and I. Shapiro, *J. Am. Chem. Soc.*, **81**, 6167 (1959).

(6) H. C. Brown and G. Zweifel, *ibid.*, **82**, 1504 (1960).

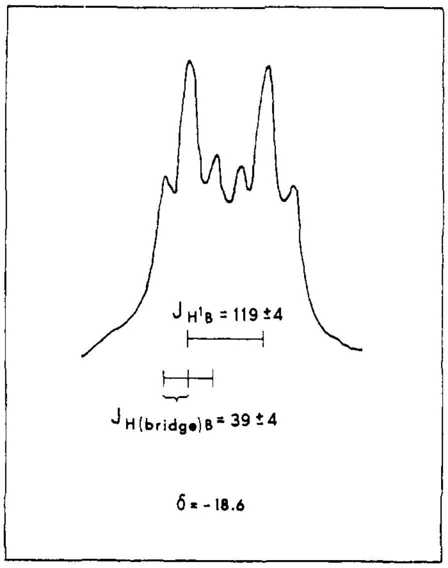
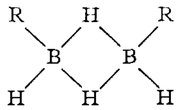


Fig. 1.—B^{11}-n.m.r. spectrum of compound I.

have parent peaks at m/e 82. (The small peaks at m/e 83 are attributed to C^{13}-isotope.) The molecular weights of both compounds are therefore indicated as 82.

The compounds were also prepared with B^{10}-enriched diborane as one reactant. The shift of the parent peaks to m/e 80 signifies that the compounds contain two boron atoms. The empirical formula for both I and II is therefore $B_2C_4H_{12}$, a formula which corresponds to a 1:1 adduct of diborane and butadiene, in agreement with other reactions involving diborane addition to the double bond. After exchange with deuteriodiborane, the parent peak of I appeared at m/e 86, indicating that only four of the hydrogen atoms in I participated in the exchange. This technique of H–D exchange to ascertain the number of hydrogen atoms attached to boron in the presence of carbon–hydrogen bonds has proved useful after it was established that C–H do not exchange with B–D.

The B^{11}- and H^1-n.m.r. spectra[7] of I are shown in Figs. 1 and 2, respectively. The B^{11}-spectrum consists basically of a doublet, each member of which is a partially resolved triplet. The J_{H^1B} value of 119 ± 4 c./s. corresponds closely to the value (128 ± 4 c./s.) given for diborane,[8] and the $J_{H^1(\text{Bridge})B}$ value of 39 ± 4 c./s. falls within the range of values reported for diborane as well as other boron hydrides.[9,10] These values eliminate all but a structure of the type



for the borane portion of the molecule. The value obtained for δ, −18.6 as compared to −16.6 for diborane, is consistent with the shift to lower field observed for alkyl substitution of terminal hydrogens in the diborane molecule.[10,11]

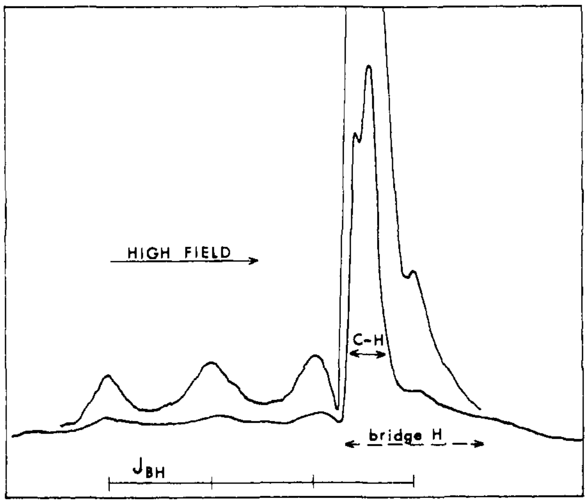


Fig. 2.—H^1-n.m.r. spectra of compound I.

The H^1-n.m.r. spectrum shown in Fig. 2 is a composite of two separate recordings. The upper recording shows the quartet resulting from the boron acting on hydrogen. The lower attenuated curve shows the detail of the carbon–hydrogen peaks. These, plus the high-field B–H peak, are complicated somewhat by the bridge protons, as indicated by the trailing-off at the high field (right) end.

The B^{11}-spectrum obtained of B_2D_6-exchanged compound (I_d) is a singlet, thus indicating that all boron–hydrogens have been replaced by deuterium. The B^{11}-spectrum of II was determined to be essentially the same as that of I and is therefore not included.

Table II lists the infrared spectra for I, I_d and II. Single sharp peaks near 2500 cm.$^{-1}$ in the spectra of both I and II verify the presence of single terminal hydrogens attached to boron atoms; *i.e.*, R–B–H rather than BH_2 groups as in diborane.[12,13] A shift of this absorption to *ca.* 1900 cm.$^{-1}$ in the partly deuterated compound I_d proves that all the boron–protiums have been replaced by deuterium. That no carbon–hydrogens have exchanged is shown by the fact that the absorptions at 2800–2900 cm.$^{-1}$ remained unchanged.

Very strong absorptions near 1600 cm.$^{-1}$ for both I and II (and 1200 cm.$^{-1}$ for I_d) substantiate the presence of double-hydrogen (or deuterium) bridges, *i.e.*, the same kind of bridging as in diborane itself.[14,15] In this connection, it was observed during the deuterium exchange reaction that two bands at 1640 and 1230 cm.$^{-1}$ appeared

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(7) A Varian Associates high resolution nuclear magnetic resonance spectrometer operating at 12.8 and 40 mc., respectively, was used.

(8) T. P. Onak, H. Landesman, R. E. Williams and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959).

(9) R. E. Williams, S. G. Gibbins and I. Shapiro, *J. Am. Chem. Soc.*, **81**, 6164 (1959).

(10) R. E. Williams, H. D. Fisher and C. O. Wilson, *J. Phys. Chem.*, **64**, 1583 (1960).

(11) Boron trifluoride is used as the zero reference for δ.

(12) I. Shapiro, C. O. Wilson and W. J. Lehmann, *J. Chem. Phys.*, **29**, 237 (1958).

(13) W. J. Lehmann and I. Shapiro, *Spectrochim. Acta*, **17**, 396 (1961).

(14) W. J. Lehmann, J. F. Ditter and I. Shapiro, *J. Chem. Phys.*, **29**, 1248 (1958).

(15) W. J. Lehmann and J. F. Ditter, *ibid.*, **31**, 549 (1959).

at the beginning of the exchange reaction, reached a maximum in intensity and then diminished as deuteration neared completion. The two bands are assigned as the asymmetric B–H′$_{\text{single}}$ and B–D′$_{\text{single}}$ vibrations of a partially deuterated bridge supporting previous assignments[12–14] for such partially deuterated bridges.

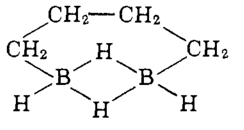
TABLE II

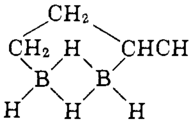
INFRARED SPECTRA[a] OF 1,2-TETRAMETHYLENEDIBORANE (I), PARTIALLY DEUTERATED 1,2-TETRAMETHYLENEDIBORANE (I$_d$) AND 1,2-(1′-METHYLTRIMETHYLENE)-DIBORANE (II)

Compound		
I	I$_d$	II
		2950s
2930s	2930s	
2890sh	2890sh	2900
2840w	2840w	
2510s	2510mw	2530s
	1890s	
	1640m	
1580vs	1580w	1510vs
1460w	1460m	1470sh
1420m	1410m	1430sh
	1350m	
1300mw	1300m	
		1260m
	1230mw	
	1170vs	
1120s		1130ms
		1060s
	1090m	
	1030ms	
	930m	
870m		
	830m	

[a] Perkin–Elmer model 21 double-beam spectrophotometer equipped with sodium chloride optics.

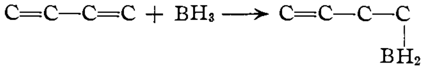
In view of other additions of diborane across double bonds, two structures involving no carbon–carbon rupture came into consideration

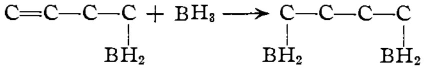

I


II

Strain considerations militate against organodiboranes with only two carbons in the ring. The total combined spectral evidence along with the previously mentioned hydrolysis and oxidation of I to 1,4-butanediol established I as the compound with the B_2C_4 ring. The B_2C_3 ring structure shown above is therefore assigned to represent compound II. Consideration of bond angles and interatomic distances decrees *cis*-type structures (*i.e.*, the BH groups are *cis* to each other). Therefore, the five-membered ring would be expected to be planar with some strain involved, while the six-membered ring would be non-planar and involve little or no strain.

These results show that definite compounds are formed, in addition to polymeric materials, in the reaction between diborane and butadiene in the gas phase. The addition of diborane is primarily to the 1,4-positions of 1,3-butadiene, but a small amount of addition to the 1,3-positions also takes place. The reaction most likely occurs as addition of BH_3, *viz.*


$$C{=}C{-}C{=}C + BH_3 \longrightarrow C{=}C{-}C{-}\underset{BH_2}{\underset{|}{C}} \qquad (1)$$


$$C{=}C{-}C{-}\underset{BH_2}{\underset{|}{C}} + BH_3 \longrightarrow \underset{BH_2}{\underset{|}{C}}{-}C{-}C{-}\underset{BH_2}{\underset{|}{C}} \qquad (2)$$

The intermediate product may then cyclize to give the more stable form of 1,2-tetramethylenediborane.

Acknowledgment.—The authors wish to thank Dr. R. E. Williams for assistance with the n.m.r. spectra.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE SPECTROSCOPY LABORATORY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASS.]

Hydration of Deoxyribonucleic Acid. I. A Gravimetric Study[1]

BY MICHAEL FALK,[2] KARL A. HARTMAN, JR., AND R. C. LORD

RECEIVED JUNE 8, 1962

The weight of water adsorbed by solid sodium and lithium deoxyribonucleate was determined as a function of relative humidity at 21°. An equation of the BET type fits the data between 0 and 80% relative humidity. From the values of the BET constants it is concluded that two molecules of water are strongly bound to each phosphate group, with an energy about 2 kcal. higher than that for the adsorption of further water molecules. The disappearance of adsorption hysteresis, negative deviation from the BET equation, and the sharp onset of swelling, all of which occur above 80% relative humidity, indicate that at about this point water fills completely the void spaces in the DNA structure.

Introduction

The structure of deoxyribonucleic acid has been found to be highly sensitive to the humidity of the surrounding atmosphere.[3] Wilkins and co-workers[4–6] have reported at least four different types of X-ray diffraction patterns from DNA fibers

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(2) Atlantic Regional Laboratory, National Research Council, Halifax, Canada.

(3) R. E. Franklin and R. G. Gosling, *Acta Cryst.*, **6**, 673 (1953).

(4) M. Feughelman, R. Langridge, W. E. Seeds, A. R. Stokes, H. R. Wilson, C. W. Hooper, M. H. F. Wilkins, R. K. Barclay and L. D. Hamilton, *Nature*, **175**, 834 (1955).

(5) R. Langridge, H. R. Wilson, C. W. Hooper, M. H. F. Wilkins and L. D. Hamilton, *J. Mol. Biol.*, **2**, 19 (1960).

(6) D. A. Marvin, M. Spencer, M. H. F. Wilkins and L. D. Hamilton, *ibid.*, **3**, 547 (1961).