Studies on Cyclic Organotetraborane Derivatives

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Several derivatives of dimethylenetetraborane are prepared from olefins and B_4H_8CO, as well as from B_4H_{10}. Proton magnetic resonance properties of these cage compounds suggest angle strain at B(2,4) and at the bridging carbons. A method of preparing B_4H_8CO directly from B_2H_6 and CO is described.

A REACTION between ethylene and tetraborane(10) has been reported to give 2,4-dimethylenetetraborane in good yield.[1] The cyclic bridge structure in which the carbons are bonded to B(2) and B(4) (see Figure) is proposed for this compound on the basis of infrared evidence; this assignment is supported by n.m.r. studies.[2] Consistent with this structural assignment, oxidative hydrolysis and methanolysis of 2,4-dimethylenetetraborane produces ethylene glycol and 1,2-bis(dimethoxy)boraethane, respectively.[1] In all probability the formation of dimethylenetetraborane from tetraborane and ethylene occurs without hydrogen transfer[3] according to the scheme:

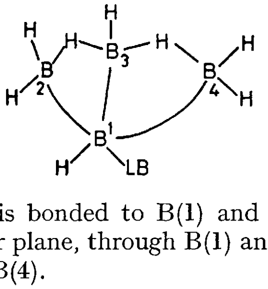
$$B_4H_{10} \xrightarrow{-H_2} [B_4H_8] \xrightarrow{C_2H_4} (CH_2)_2B_4H_8$$

Tetraborane carbonyl, B_4H_8CO, was the first B_4H_8 containing compound to be isolated[4] and can be prepared by the action of carbon monoxide on either B_4H_{10}[5,6] or B_5H_{11}.[4,5]

$$B_4H_{10} + CO \xrightarrow{100^\circ} B_4H_8CO + H_2$$

$$B_5H_{11} + 2CO \longrightarrow B_4H_8CO + BH_3CO$$

In both reactions there is strong reason to believe that the unstable B_4H_8 species is an important intermediate, as it is in the above described formation of dimethylenetetraborane. B_4H_8CO is believed to be structurally related to $B_4H_8PF_2NMe_2$ into which it can be converted by CO displacement with Me_2NPF_2.[7] The structure of the B_4H_8 group in this complex[8] is that of a B_4H_{10} molecule with two bridge hydrogens missing on the same long side of the molecule:

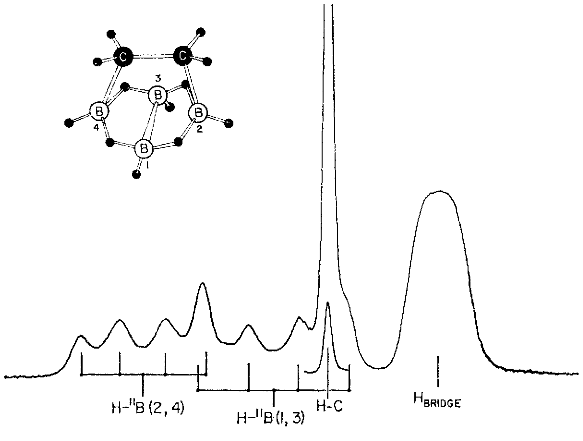


The Lewis base is bonded to B(1) and lies in the perpendicular mirror plane, through B(1) and B(3) bisecting the line B(2) to B(4).

In the present study we have found that B_4H_8CO and ethylene can be irreversibly converted into $(CH_2)_2B_4H_8$. During the progress of this investigation an easy synthetic route to B_4H_8CO from B_2H_6 and CO was discovered; also, several unusual n.m.r. features of $(CH_2)_2B_4H_8$ and some *C*-methyl derivatives are discussed.

EXPERIMENTAL

Materials.—Tetraborane was prepared by the reaction of polyphosphoric acid with tetramethylammonium triborohydride[9] and tetraborane carbonyl was obtained from both the reaction of pentaborane (11) with carbon monoxide[5] and by the method described below. All chemical manipulations were carried out in a standard high-vacuum apparatus. Purification of both starting materials and products was effected by the use of either a 30% Kel-F on firebrick g.l.p.c. column, or a low-temperature, high-vacuum distillation column. All chemicals were manipulated using standard high-vacuum techniques. Infrared spectra were recorded on a Beckman IR-5 and Perkin-Elmer 137 spectrophotometers and the absorption bands for dimethylenetetraborane, *C*-methyldimethylenetetraborane, and *C,C'*-dimethyldimethylenetetraborane are given in Table 1.



220 MHz ^1H n.m.r. of $(CH_2)_2B_4H_8$

N.m.r.—Proton spectra were recorded on Varian A-60, HA-100, and HR-200 spectrometers † (a sample spectrum

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† The Varian HA-100 at California State University, Los Angeles, Calif., was obtained through a grant from the National Science Foundation and the HR-220 n.m.r. spectrometer at California Institute of Technology was available through a National Science Foundation Grant.

[1] B. C. Harrison, I. J. Solomon, R. D. Hites, and M. J. Klein, *J. Inorg. Nuclear Chem.*, 1960, **14**, 195.

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is shown in the Figure). The boron-11 spectra were obtained at 32·1 MHz using the Varian HA-100 instrument (see Table 1). Decoupled proton spectra at 100 MHz were observed during irradiation at 32·1 MHz using the Nuclear Magnetic Resonance Specialties model HD-60 spin decoupler modified for use with the HA-100 and Hewlett–Packard model 200 CD wide-range audio oscillators. Conversely, decoupled ^{11}B spectra at 32·1 MHz were observed during irradiation with the heteronuclear decoupling apparatus equipped with 100-MHz modules.

The chemical-shift data for the protons were obtained with tetramethylsilane (τ 10·00) as an internal standard. The chemical-shift data for boron-11 were obtained with boron trichloride, δ −46·8 relative to boron trifluoride–diethyl ether, as an external secondary standard.

The chemical-shift data obtained from the ^{11}B n.m.r. spectra were used to predict the relative double-irradiation frequencies used in obtaining boron-11 decoupled proton n.m.r. spectra. The frequency band used for the decoupling experiments was broad enough with the available equipment to cause the collapse of the ^{1}H n.m.r. multiplets into reasonably sharp singlets. Each kind of boron could be separately irradiated with an acceptable minimum effect on neighbouring boron resonances as long as there was at least 5-p.p.m. separation between such resonances.

TABLE 1

I.r. and n.m.r. data

Compound	λ_{max}/cm^{-1}	Group	^{1}H τ, TMS, (*J*), rel. area	^{11}B δ, BF_3, Et_2O, (*J*), rel. area
B_4H_{10}		H_T-B(1,3)	8·66 (155), 2	+41·1 (160), 2
		H_T-B(2,4a or 2,4e)	7·74 (134), 2	+5·16 (132), 2
		H_T-B(2,4e or 2,4a)	7·54 (125,) 2	
		Hμ	11·38, 4	
$CH_2 \cdot CH_2 \cdot B_4H_8$	2900m (CH str); 2550s and 2510s (B-H str); 2150ms (BHB), 1490w, 1420m, 1360m, 1270mw, 1050s, 965mw, 880ms, 815w, and 720m	CH_2	9·44, 4	
		H_T-B (1,3)	8·61 (150—5), 2	+40·0 ± 0·5 (146), 2
		H_T-B(2,4)	6·72 (130), 2	−3·0 ± 0·3 (139), 2
		Hμ	11·0, 4	
$MeCH \cdot CH_2 \cdot B_4H_8$	2900ms (CH str); 2550s and 2510(s) (BH str); 2160ms (BHB str), 1600w, 1480w, 1410-mw, 1370wm, 1060s, 970mw, 890m, 825w, 770w, and 720mw	CH_3	9·05 ± 0·02, } 5	
		CH_2	9·05 + 0·06,	
		CH	10·02, 1	
		H_T-B(1,3)	8·64 (153), 2	+39·6 (153), 2
		H_T-B (2 or 4)	6·85 (136), } 2	−5·3 (127), 1
		H_T-B(4 or 2)	6·85 (136),	−2·3 (125), 1
		Hμ	10·98, 4	
$MeCH \cdot CHMeB_4H_8$	2950ms and 2800ms (CH str); 2580s and 2530s (BH str); 2154m (BHB str), 1550w, 1480-m, 1380m, 1340m, 1250mw, 1080ms, 1050ms, 1005w, 960m, 875m, 820w, 770w, and 730mw	CH_3	9·07, 6	
		CH	9·64, 2	
		H_T-B(1,3)	8·83 (150—5), 2	+40·1 (147), 2
		H_T-B(2,4)	6·90 (133), 2	−4·0 (130—5), 2
		Hμ	11·1, 4	

TABLE 2

Reaction conditions and yields of products from the reaction of tetraborane with alkenes

Starting materials mmol		Reactor temp. °C		Time min	Products mmol
B_4H_{10}	Alkene	Hot tube	Cold tube		
5·0	Ethylene 5·0	100	0	75	$(CH_2)_2B_4H_8$ (3·7)
5·1	Propene 5·1	100	0	90	$CH_3CH \cdot CH_2 \cdot B_4H_8$ (3·0) B_5H_9 (0·1)
10	*trans*-But-2-ene 10	100	0	90	$(CH_3CH)_2B_4H_8$ (7·1) B_2H_6 (1·1)
1·0	*cis*-But-2-ene 1·0	100	0	75	$(CH_3CH)_2B_4H_8$ (0·2) B_2H_6 (0·13) B_5H_9, B_5H_{11} (0·11) Alkane (trace)
2·0	$CH_2=C=CH_2$ 2·0	100	0	90	$CH_3CH \cdot CH_2 \cdot B_4H_8$ (0·15) B_5H_9 (0·1)

Preparation of Dimethylenetetraborane and C-*Methyl Derivatives from Tetraborane and Alkenes.*—Following the hot/cold tube procedure outlined earlier [1] the parent dimethylenetetraborane and the new derivatives; *C*-(methyl)-dimethylenetetraborane and *CC′*-(dimethyl)dimethylenetetraborane, were prepared. The reaction conditions and yields are given in Table 2.

At room-temperature liquid $(CH_2)_2B_4H_8$ slowly becomes a transluscent glossy material. Both the boron-11 and proton n.m.r. strongly indicate that most of the basic structural unit of monomer is still intact (*i.e.* CH_2CH_2 and B_4H_8 groups); however, the multiplets in these spectra are beginning to collapse. This is an indication of partial quadrupole relaxation [10,11] and is to be associated with a less-mobile liquid. It is proposed that polymer units such as $(CH_2CH_2{-}B_4H_8)_n$ could well account for the observations. The polymerization does not appear to be reversible, as it is with $(CH_2)_3B_2H_4$ [10] since a sample when heated *in vacuo* from 30 to 150° gave only decomposition products, B_2H_6 and B_4H_{10}, a considerable quantity of the solid material remaining behind.

Preparation of B_4H_8CO *from Diborane and Carbon Monoxide.*—Diborane and carbon monoxide were allowed to react in a hot/cold reactor. In the initial studies equimolar amounts of diborane and CO were used. The amount of diborane and the conditions for several reactions are given:

Temp./°C		Initial B_2H_6	Yield of condensable volatiles *
Hot portion of tube	Cold portion	mmol	mmol
100—115	−70 to −78	7·5	0·08
140—180	−70 to −78	5·0	1·55
180—245	−70 to −78	5·0	1·4

* Not including unchanged B_2H_6 nor CO.

The volatiles consisted primarily of B_4H_8CO and B_5H_{11} and small amounts of B_5H_9 (*ca.* 2%) trimethylboroxine (*ca.* 5%) and BH_3CO. By placing the entire mixture in excess of CO all the B_5H_{11} could be converted into B_4H_8CO. Higher pressures of CO initially in a stainless-steel reactor gave higher $B_4H_8CO : B_5H_{11}$ ratios. The highest yield of B_4H_8CO was found to be *ca.* 60% of theoretical yield for the equation $2B_2H_6 + CO \longrightarrow B_4H_8CO + 2H_2$.

Conversion of Tetraborane Carbonyl into Dimethylenetetraborane.—Under hot/cold reactor conditions of 75 : 0 °C a reaction of B_4H_8CO (1·0 mmol) with ethylene (1·0 mmol) during a 90 min period yielded dimethylenetetraborane (0·54 mmol), B_5H_9 (0·1 mmol), B_2H_6 (0·05 mmol), and non-condensables (CO, H_2) (0·8 mmol). Although the yield of desired product was reasonable, it was thought that the reaction conditions might have been too drastic and therefore a rate study was conducted at room temperature.

After 2·5 h at room temperature a mixture of B_4H_8CO (0·10 mmol) and ethylene (0·10 mmol) showed no further change in the i.r. region. An analysis of the products, dimethylenetetraborane (0·095 mmol) by i.r. and n.m.r. spectroscopy and CO (0·098 mmol) by combustion to CO_2, indicated that the reaction proceeded nearly quantitatively according to the equation $B_4H_8CO + H_2C{=}CH_2 \longrightarrow (CH_2)_2B_4H_8 + CO$. In this reaction only a small amount of H_2 (0·01 mmol) and a trace of B_5H_9 was formed.

Reaction of B_4H_8CO *with trans-But-2-ene.*—Using a hot/cold reactor, at 75 : 0 °C, a mixture of B_4H_8CO (1·0 mmol) and *trans*-but-2-ene (1·0 mmol) was allowed to react for 80 min. The products consisted of the dimethyl derivative of dimethylenetetraborane $(MeCH)_2B_4H_8$ (*ca.* 0·59 mmol), B_5H_9 (0·15 mmol), B_2H_6 (0·11 mmol), B_4H_{10} (trace), and uncharged *trans*-but-2-ene (trace).

Attempt to prepare the Carbonyl of Dimethylenetetraborane (8).—Under hot/cold reactor conditions of either 100 : 0 °C or 150 : 0 °C the reaction of $C_2H_4B_4H_8$ with CO appears to give mainly decomposition products at a rate roughly the same as that when $C_2H_4B_4H_8$ is heated alone. No evidence of a $(CH_2)_2B_4H_6CO$ product nor any substantial amount of B_4H_8CO was found. At carbon monoxide : alkyl borane ratios of 2 : 1 and 3 : 1 the starting material $(C_2H_4B_4H_8)$ is recovered in yields of *ca.* 85—95%. The volatile products isolated are B_2H_6, 1,1-$Et_2B_2H_4$, and BH_3CO.

DISCUSSION

B_4H_8CO *from* B_2H_6 *and* CO.—A convenient one-step preparation of B_4H_8CO from diborane and carbon monoxide has been effected using a hot/cold reactor. This method eliminates the need for the separate preparation of either B_4H_{10} or B_5H_{11} both of which have been previously used [4-6] for obtaining B_4H_8CO. The one-step procedure we have developed does suffer from B_5H_{11} and small B_5H_9 impurities but the B_5H_{11} can be easily removed by fractional condensation techniques. If the B_4H_8CO is to be used for further chemical preparative work this may not necessarily be an important problem.

Dimethylenetetraborane and C-*Methyl Derivatives.*—The formation of dimethylenetetraborane from B_4H_8CO and ethylene appears to take place under milder conditions than when B_4H_{10} is used instead of the carbonyl. This is readily understood in terms of the relative ease with which the unstable intermediate $[B_4H_8]$ can be obtained from either of the two boron containing reactants.

$$B_4H_8CO \longrightarrow [B_4H_8] + CO \qquad (1a)$$

$$B_4H_{10} \longrightarrow [B_4H_8] + H_2 \qquad (1b)$$

$$[B_4H_8] + C_2H_4 \longrightarrow (CH_2)_2B_4H_8 \qquad (2)$$

The activation energy of equation (1a) is undoubtedly less than (1b) [4,5,7] and should equation (1) be the rate-limiting step the milder conditions observed when using B_4H_8CO is understandable. Of course this assumes that the high-energy intermediate $[B_4H_8]$ produced from the carbonyl has essentially the same structure and properties as does the intermediate from B_4H_{10}. In this regard it should be noted that the carbons of the entering olefin become attached to the same borons (2,4) which lose hydrogen when B_4H_{10} is used, whereas the carbonyl compound appears to lose CO from another boron, B-1 (see Scheme).

The *C*-methyl and *CC'*-dimethyl derivatives of dimethylenetetraborane can be prepared from either tetraborane(10) or the carbonyl and the appropriate olefin. An unsuccessful attempt was made to synthesize a *C*-chloro-derivative from chloroethylene.

N.m.r.—The ^{11}B n.m.r. of the *C*-methyl and *CC'*-dimethyl derivatives of dimethylenetetraborane (Table 1) agree well with the spectra obtained for the parent compound.[2] The small dissymmetry caused by the monomethyl compound is sufficient to produce two distinctly observed doublets at low field. In all the dimethylene compounds the B(2,4) is shifted to lower field (7—10 p.p.m.) than those in B_4H_{10}. This is roughly as expected when shifts caused by alkyl substitution in

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[10] H. H. Lindner and T. Onak, *J. Amer. Chem. Soc.*, 1966, **88**, 1886.

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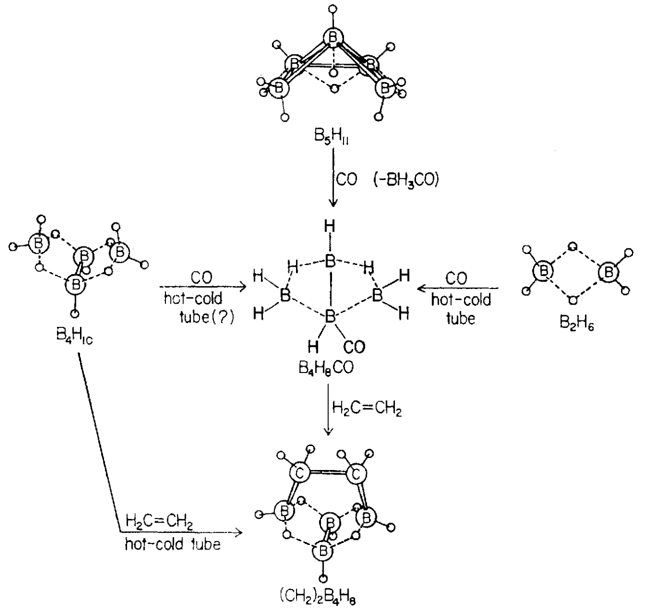
other boron hydride systems[12-14] as well as for tetraborane itself[15] are considered. Also, an expected[12-14] downfield shift (*ca.* 0·4 p.p.m.) is observed for the bridge hydrogens in the proton n.m.r. spectrum (Table 1).

It is surprising, however, to find that both *H*-B(2,4) and the cage *H*-C protons significantly shifted from standard positions. The methylene protons in $(CH_2)_2$-B_4H_8 are found at τ 9·44 which is *ca.* 0·7—0·9 p.p.m. upfield from methylene protons in simple alkanes[16] and *ca.* 0·3—0·4 p.p.m. upfield from such protons in saturated C–CH_2–B systems (where the boron is attached to R or H).[11] Similarly, the methyne hydrogen of $(CH_3CH)_2$-B_4H_8 is shifted upfield by *ca.* 1·2 p.p.m. when compared to simple tertiary hydrogens in alkanes[16] and 0·5 p.p.m. when compared to ·C·CH(C·)B· environment of alkyldiboranes.[11] The hydrogens attached to B(2,4) are shifted downfield by 0·6—1·0 p.p.m. when compared to the parent B_4H_{10}. Up to 0·4 p.p.m. of this shift is expected when one of the two terminal hydrogens of the tetraborane BH_2 group is replaced with an alkyl group;[14] however, the remainder must be due to (an)other effect(s).



SCHEME

We suggest that cage strain may be playing an important role as regards the observed anomalous proton shifts. If it is assumed that the tetraborane cage in the dimethylene derivatives prefer the same boron skeletal geometry as the parent[17,18] compound then the angle of the axial bond to the plane of B(1)–B(2)–B(3) drops from 122° in B_4H_{10} to 97: in the dimethylene derivative. The C–C–B bond is stretched from a tetrahedral position to 114°. It is tempting to believe that not all of the strain is concentrated in these two regions; but, because the n.m.r. shifts of B(1,3), H_T(1,3), and the bridge hydrogens are found about where they might normally be expected, it would appear that this region of the molecule is relatively undisturbed. It is to be noted that the methyl hydrogens in the *C*-methyl derivatives are not directly involved in unusual bond-angle deviations and are also found in a normal methyl proton region. That downfield shifts should occur with angle constraint and upfield shifts with an increase in bond angle appears to be consistent with the trend found in the cycloalkanes[22] (bond angle ⩾90°). Base cleavage of $(CH_2)_2B_4H_8$ with tetrahydrofuran, to give what is anticipated to be $LB \longrightarrow H_3B\text{–}CH_2\text{–}CH_2\text{–}B_3H_7 \longleftarrow LB$,[23] shifts the methylene hydrogens from τ 9·44 to 9·14. The latter value is considered more normal for boron-attached methylene protons[11] in situations that do not involve bond angle strain.

The nearly normal CH_2 proton shift and the very abnormally high CH shift in the *C*-monomethyl derivative of $(CH_2)_2B_4H_8$ may indicate that a greater portion of the bridge strain is accommodated on the tertiary carbon. The presumably nearly eclipsed CH_2–CH_2 interaction in the parent compound will probably adjust to a slightly staggered conformation upon methyl substitution. Since it is unlikely the bridge C–C bond length will accommodate this effect, an enlargement of one or more B–C–C bond angles must occur. It is a little surprising to expect the tertiary carbon to assume most of the strain; however, molecular models are not found to be decisive in predicting which of the two carbons should take on the added bond angle expansion due to a twist of the C–C bridge. Obviously, in the more symmetrical compounds, $(CH_2)_2B_4H_8$, and its *CC'*-dimethyl derivative, the strain is equally distributed amongst the two bridging carbons.

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* The C–C bond and the C–B bond lengths are assumed to be consistent with *X*-ray studies on other organoboranes.[19-21]

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