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Further Studies of the Tetraborane Carbonyl B_4H_8CO

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Tetraborane-8 carbonyl (B_4H_8CO) is made by the action of CO on either B_4H_{10} or B_5H_{11}, suggesting the processes $B_4H_{10} \rightarrow B_4H_8 + H_2$ and $B_5H_{11} \rightarrow B_4H_8 + BH_3$. The reversal of these (significant for polyborane interconversion mechanisms) is shown by the high yields of B_4H_{10} and B_5H_{11} obtained when H_2 or B_2H_6 reacts with B_4H_8CO. Basic reagents attack B_4H_8CO to form nonvolatiles without liberation of any CO; dimethyl ether and water behave so, and trimethylamine forms some $(CH_3)_3NBH_3$. Ethylene also fixes the CO, in a slightly volatile unstable compound, $(C_2H_4)_4B_4H_8CO$ (structure uncertain), whereas $BH_3CO + 3C_2H_4 \rightarrow (C_2H_5)_3B + CO$ is quantitative. With excess PF_3, B_5H_{11} forms BH_3PF_3 and $B_4H_8PF_3$, from the latter of which CO reversibly displaces PF_3; in these reactions CO is not irreversibly fixed. In support of structural elucidation of B_4H_8CO by infrared and nuclear magnetic resonance spectra, B_4D_{10}, B_5D_{11}, and B_4D_8CO were made in nearly pure form. The structure of B_4H_8CO remains uncertain but the possibilities are limited. There may be a tautomeric equilibrium such that at least one H atom alternates between two B–H–B bridgings and a terminal B–H situation—much like the tautomerism of B_5H_{11}.

Tetraborane-8 carbonyl (B_4H_8CO)[1] undergoes chemical reactions suggesting two different initial dissociations: $B_4H_8CO \rightarrow B_4H_8 + CO$ and possibly $B_4H_8CO \rightarrow BH_3 + B_3H_5CO$. Thus the room-temperature decomposition gives yields of B_5H_{11} near 30%, as expected from the secondary process $B_4H_8 + BH_3 \rightarrow B_5H_{11}$. The yield of B_5H_{11} is still higher if much B_2H_6 is present during the decomposition, and the availability of B_4H_8 is still further indicated when B_4H_8CO decomposes in the presence of much H_2 to give high yields of B_4H_{10}, suggesting the reaction $B_4H_8 + H_2 \rightarrow B_4H_{10}$. The direct reverse of this reaction is indicated by the formation of B_4H_8CO from B_4H_{10} and CO,[2] at CO-independent rates.[3] Thus the easily reversible reactions $B_4H_{10} \rightarrow B_4H_8 + H_2$ and $B_4H_8 + {}^1/_2B_2H_6 \rightarrow B_5H_{11}$ (already suggested by arguments from rate data)[4] gain more direct support, contributing toward a full understanding of the long-known reversible interconversions involving H_2, B_2H_6, B_4H_{10}, and B_5H_{11}.[5] The B_4H_8 group again plays an obvious role in the nearly quantitative formation of the new compound $B_4H_8PF_3$ from B_5H_{11} and PF_3 and in the reversible displacement of PF_3 to make B_4H_8CO.

The initial formation of the B_3H_5CO unit (whether by the action of B_4H_8 to remove BH_3 from B_4H_8CO or by a direct dissociation) would account for much of the 34% yield of CO-containing brown solids (formed during the decomposition of B_4H_8CO), for one would expect B_3H_5CO to condense very quickly to polymeric boron hydride material with permanent incorporation of the CO; in fact a strong heating of the brown solids *in vacuo* yields only very little CO.

The CO also is permanently incorporated in the products of the reactions of B_4H_8CO with substances having a surplus of electrons available for bonding, such as amine or oxygen bases or ethylene. The extreme contrast to the corresponding reactions of BH_3CO may be illustrated by the following examples, of which (1) and (2) are quoted from an earlier paper.[6]

$$BH_3CO + (CH_3)_3N \longrightarrow (CH_3)_3NBH_3 + CO \qquad (1)$$

$$BH_3CO + 3H_2O \longrightarrow B(OH)_3 + 3H_2 + CO \qquad (2)$$

$$BH_3CO + 3C_2H_4 \longrightarrow (C_2H_5)_3B + CO \qquad (3)$$

$$B_4H_8CO + 1.03(CH_3)_3N \longrightarrow [(CH_3)_3N]_{1.03}B_{3.87}H_{7.61}(CO)_{0.96} + 0.04BH_3CO + 0.045B_2H_6 \qquad (4a)$$

$$+ 1.47(CH_3)_3N \longrightarrow [(CH_3)_3N]_{1.76}B_{3.13}H_{5.4}(CO)_{0.94} + 0.74(CH_3)_3NBH_3 \qquad (4b)$$

$$B_4H_8CO + xH_2O \longrightarrow 8.8H_2 + yB(OH)_3 + \text{residue} + 0.035CO \qquad (5)$$

$$B_4H_8CO + (CH_3)_2O \longrightarrow \text{“}(CH_3)_2OB_4H_8CO\text{”} \qquad (6)$$

$$B_4H_8CO + 4C_2H_4 \longrightarrow (C_2H_5)_4B_4H_4CO \qquad (7)$$

Reaction 4a occurred during 6 days at −78° with no excess amine; 4b during a further 3 months at −78° with excess amine acting upon the residue of 4a. It is not known whether some $(CH_3)_3NBH_3$ formed early in the process or exclusively at later stages. The hydrolysis (5) also lacks quantitative neatness, since $10H_2$ would be expected from each B_4H_8 group. The H_2 deficiency could be explained partly by the transfer of one H from B to C and partly by the retention of some B–B bonds, but there is no direct evidence whereby to judge the relative importance of these effects. The dimethyl ether reaction (6), occurring during 40 hr. at −78°, seemed neater; however the main product was nonvolatile and uncertain as to content of $(CH_3)_2O$, nearly all of which could be removed in no specific steps as the mixture warmed slowly to room temperature. Traces of unidentified polyboranes also were evolved (leaving a resinous product very different from the original B_4H_8CO), but under no conditions was there any such main formation of polyboranes as in the B_5H_{11}–$(CH_3)_2O$ reaction.[7]

The ethylene reaction (7) seemed much like the corresponding BH_3CO–C_2H_4 reaction (3) except for the retention of CO in stable combination. The slightly volatile liquid product, of molecular formula as written,

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[1] A. B. Burg and J. R. Spielman, *J. Am. Chem. Soc.*, **81**, 3479 (1959).

[2] A. B. Burg, Eighth Annual Technical Report to the Office of Naval Research, Nov., 1954, p. 12.

[3] R. Schaeffer, ARL Technical Report 60-334, Contract No. 33(616)-5827 (1960), p. 15.

[4] J. A. Dupont and R. Schaeffer, *J. Inorg. Nucl. Chem.*, **15**, 310 (1960).

[5] A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, **55**, 4009 (1933).

[6] A. B. Burg and H. I. Schlesinger, *ibid.*, **59**, 780 (1937).

[7] J. L. Boone and A. B. Burg, *ibid.*, **81**, 1766 (1959).

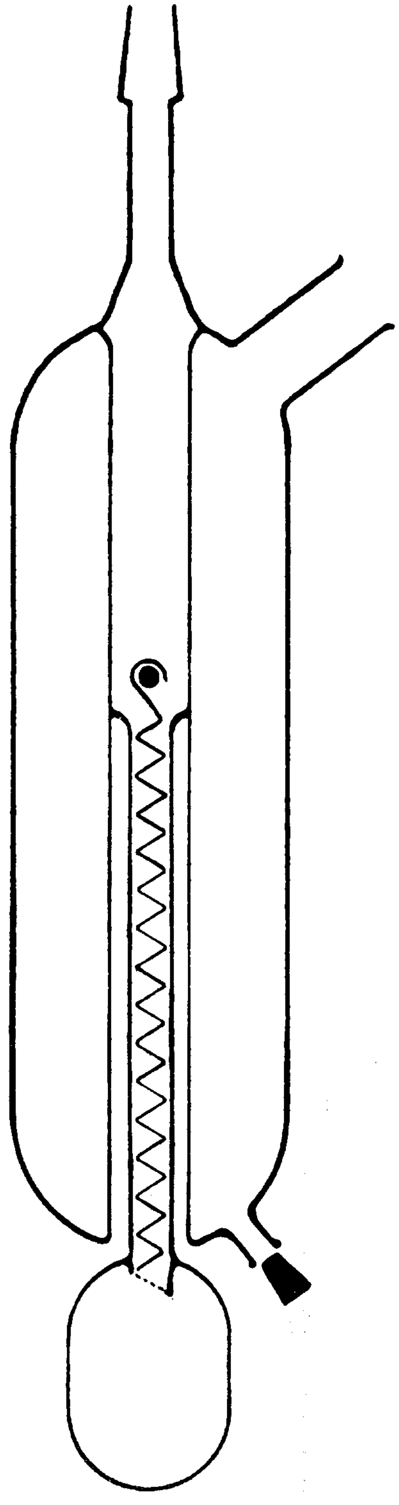

Fig. 1.—Column for removal of B_5H_9 from B_5H_{11}. A nearly total reflux under high vacuum is maintained by Dry Ice (in isohexanes) in the large outer chamber, from which the inner chamber is air-gap insulated to aid development of a thermal gradient favoring separation. External insulation is by glass wool. For temperatures down to −100° a pump connects to the upper right opening.

proved to be unstable in the sense of forming hydrogen and a nonvolatile oil, but no carbon monoxide.

The permanent capture of the CO unit in such reactions prevented the use of B_4H_8CO for further attempts to make polyboranes such as B_5H_9, B_6H_{10}, or $B_{10}H_{14}$ by the action of basic reagents.[8] Indeed, no simply connected adduct of B_4H_8 with a base lacking the electron acceptor character of PF_3 or CO seems yet to have been clearly demonstrated. On the other hand, base adducts of B_3H_7 seem stable enough,[9] whereas our best attempts failed to demonstrate any B_3H_7CO as a by-product of the synthesis of B_4H_8CO from either B_4H_{10} or B_5H_{11}. Two distinctly different approaches by Schaeffer also failed to produce any B_3H_7CO.[3] It is suggested that the dissociation $B_4H_{10} \rightarrow B_3H_7 + BH_3$ makes good progress only in the presence of a base which can combine firmly with the very strong Lewis acid B_3H_7; otherwise the reaction $B_4H_{10} \rightarrow B_4H_8 + H_2$ is more probable.[4] Indeed, we find that B_4H_{10} has no appreciable influence on the decomposition of B_4H_8CO, showing that BH_3 is not nearly so readily available from B_4H_{10} as from B_2H_6.

Speculations concerning the molecular structure of B_4H_8CO are aided by its chemical behavior. For example, the easy loss of CO in some reactions, such as the cleanly reversible $B_4H_8CO + PF_3 \rightleftarrows B_4H_8PF_3 + CO$ (for the forward reaction, see reference 3, pp. 21–22), argues strongly against any B–C–O–B pattern like the B–C–C–B bonding in $B_4H_8C_2H_4$.[10] It is reasonable to suggest that both CO and PF_3 act as σ-bond donors to boron and as π-acceptors for electrons in the B_4H_8 unit. Such a system of weak π-bonds, wherein B_4H_8 electrons interact with C_{2p} and P_{3d} orbitals, would be like the π-bonding which we assume to occur in BH_3CO and BH_3PF_3, accounting for their low polarity and high volatility.

The infrared spectra of B_4H_8CO and B_4D_8CO include a C═O stretching band closely similar to that in BH_3CO, suggesting a very similar kind of B–C–O bonding. The B^{11} nuclear magnetic resonance spectrum is even more indicative of structure, suggesting a three-way proton-shift tautomerism like that found in B_5H_{11}.[11] However, a reliable determination of the dominant structure remains a problem for the future.

Syntheses

The Reaction of Pentaborane-11 with CO.—The quantitative reaction $B_5H_{11} + 2CO \rightarrow B_4H_8CO + BH_3CO$ has been mentioned briefly[1] but requires fuller description. To make pure B_4H_8CO (free of B_5H_9) by this method, one must begin with pure B_5H_{11}. This was obtained from a flow-process product[12] by the use of the small and relatively simple fractionating column shown in Fig. 1. Designed for work at the lowest possible pressures, this column used a wire-spiral packing and operated under a high reflux ratio, with Dry Ice in hexane (−78°) in the reflux head. The B_5H_9 impurity slowly escaped to a high-vacuum trap at −196°, behaving as the more volatile component of the liquid even though solid B_5H_9 probably is less volatile than liquid B_5H_{11} at −78°. Our purest B_5H_{11} melted at −122.0 ± 0.1° (earlier value, −123.3°)[5]; vapor tensions 52.8 mm. at 0°, 103.1 mm. at

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(8) J. L. Boone and A. B. Burg, *J. Am. Chem. Soc.*, **80**, 1519 (1958).

(9) (a) W. V. Hough, M. D. Ford, G. T. Hefferan, and L. J. Edwards, U. S. Atomic Energy Comm. Rept. CCC-1024-TR-274 (1957); (b) G. Kodama, R. W. Parry, and J. D. Carter, *J. Am. Chem. Soc.*, **81**, 3534 (1959).

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

(11) R. E. Williams, *ibid.*, **20**, 198 (1961).

(12) A. B. Burg and F. G. A. Stone, *J. Am. Chem. Soc.*, **75**, 228 (1953).

13.5°, and 116.1 mm. at 16.1°. Its B^{11} n.m.r. spectrum showed no trace of the spurious peak attributed to B_5H_9 impurity.[13]

The conversion of B_5H_{11} to B_4H_8CO required a great excess of dry, oxygen-free carbon monoxide. This was made by warming a mixture of formic and sulfuric acids in an evacuated flask attached directly to the high-vacuum system, wherein it could be condensed and redistilled. For such distillations the evaporation was from traps immersed in liquid nitrogen (−196°) and the receiving traps were cooled by pumped liquid nitrogen which had attained temperatures as low as −210°. After being measured as a gas, the CO could be condensed almost completely in the reaction tube at −210°, and that which remained in the apparatus after the seal-off could be collected by an automatic Sprengel pump for measurement over mercury. Then, after the bomb-tube reaction, the CO could be distilled out of the reaction tube (opened *in vacuo*) and measured back by the same methods, for a rough estimate of the consumed CO. In one experiment a top fraction of the CO was collected by means of the Sprengel pump, and CuO combustion showed less than 0.01 H_2 per B_5H_{11} originally present.

The stoichiometry of two such quantitative experiments has been presented.[1] Times no longer than 2.5 hr. at room temperature were sufficient for complete reaction. Longer times led to lower yields because the decomposition of B_4H_8CO to nonvolatile solids is not reversible, nor entirely inhibited by carbon monoxide. This method of making B_4H_8CO is fast and it virtually proved the formula B_4H_8CO (confirmed by analysis),[1] but the tedium of making pure B_5H_{11} for such use might lead to a preference for the B_4H_{10} method.

The Reaction of Tetraborane-10 with CO.—For the reaction $B_4H_{10} + CO \rightarrow H_2 + B_4H_8CO$, pure B_4H_{10} was made from B_5H_{11}[5,12] and measured as a gas. The sample was condensed from the high-vacuum system into a 230-ml. stainless-steel pressure cylinder (having a Teflon-seated safety valve); then a much larger measured sample of CO was condensed into the cylinder by means of pumped-down liquid nitrogen. In most experiments relatively high CO pressures were used in order to minimize the decomposition of B_4H_8CO during the relatively long times which were required for extensive reaction.

The conditions and results of our most informative experiments are presented in Table I. The reaction ran at mean temperatures in the range 20–30°, with rates varying accordingly. In expt. 9 the formation of H_2 was roughly 2 mmoles, exceeding that required by the formation of B_4H_8CO according to the ideal equation $B_4H_{10} + CO \rightarrow H_2 + B_4H_8CO$; the difference is attributable to a parallel decomposition of B_4H_{10}. Experiments 8 and 9 began with 1.17 and 2.70 mmoles of BH_3CO, respectively, resulting in an indication that this component is moderately consumed if present at the start, while other experiments show that some BH_3CO is formed if not initially present. In each case the per cent yield is based upon the consumed B_4H_{10}.

TABLE I
THE REACTION OF B_4H_{10} WITH CO

Expt. no.	B_4H_{10}, mmoles	P_{CO}, atm.	Time, hr.	Volatiles recovered, mmoles			% yield	10^4k, min.$^{-1}$
				B_4H_{10}	BH_3CO	B_4H_8CO		
1	2.68	10	55	2.01	0.02	0.27	40	0.87
2	3.62	9	23	2.68	.09	.36	38	2.17
3	5.75	89	23	5.04	.45	.36	51	0.96
4	5.45	59	62	3.79	.07	.71	43	.97
5	3.62	56	75	2.72	.09	.67	74	.63
6	2.59	53	222	1.21	.24	1.12	81	.57
7	1.21	50	261	0.49	.17	0.49	68	.57
8	4.53	67	235	0.56	1.06	1.44	27	1.49
9	4.97	71	66	2.35	2.00	1.40	54	1.91

Although these experiments (of which 1–7 were performed in the years 1951–1954) were not planned as accurate rate and mechanism studies, the values here found for 10^4k, based upon the equation $-d(B_4H_{10})/dt = k(B_4H_{10})$ (independent of CO pressure), are quite reasonably consistent with Schaeffer's flow-process rate studies at 80–110°, with CO pressures around 0.5 atm.[3] From his results 10^4k can be estimated as 0.55 at 20° and 2.21 at 30°, in close agreement with our results in this temperature range. Thus it is confirmed that the rate is independent of extreme variation of pressure of carbon monoxide, and it is evident that Schaeffer's results are dependable for long-range extrapolation.

Synthesis of Deuterioboron Compounds.—For infrared spectroscopic comparisons it was important to have samples of B_2D_6, B_4D_{10}, B_5D_{11}, and B_4D_8CO. Accordingly, a 15.3-mmole sample of B_2D_6 was made from LiD and BF_3.[14] Its initial D-content was estimated as 98% by the intensity of the infrared band at 2585 cm.$^{-1}$ in relation to that of the 2705 cm.$^{-1}$ band, using published data[15] for calibration. Then the D content was raised above 99% by two equilibrations (sealed bulbs, 20 hr. at 65°) with 99.5+% D_2. The vacuum-fractionated sample showed a 238.0-mm. vapor tension at −111.9°, in agreement with an earlier estimate.[16]

This B_2D_6 sample was employed in a miniature vapor-flow apparatus to produce 0.42 mmole of B_4D_{10} and 1.50 mmoles of B_5D_{11}. Treatment of 0.964 mmole of this B_5D_{11} with high-pressure CO gave 0.965 mmole of BD_3CO (57 mm. at −102°; calcd., 55 mm.)[16] and B_4D_8CO presumably in similar yield.

Physical Properties.—The volatility of B_4H_8CO is well described by the original vapor-tension equation.[1] Each of the deuterioboron compounds is slightly more volatile than its protium counterpart, as shown by the comparisons in Table II.

TABLE II
INCREASED VOLATILITY OF DEUTERIUM COMPOUNDS

t, °C.	Vapor tension values, P_{mm}, corr.					
	B_4H_{10}	B_4D_{10}	B_5H_{11}	B_5D_{11}	B_4H_8CO	B_4D_8CO
0.0	387	423	52.8	56.7	71.3	74.2
−40.1	49.0	59.3	...	...	...	...
−78.5	3.2	3.8	...	...	...	...

Five new observations of the melting point of B_4H_8CO gave readings ranging from −110.3 to −113.2°. The highest result was for B_4H_8CO which had been freshly made from B_5H_{11} + 2CO; older samples probably had formed some B_5H_{11}, which could be removed only by reaction with CO at high pressures. The melting points of two of the deuterium compounds were observed as slightly lower than for the protium compounds: B_4D_8CO, −112.2° (*vs.* −110.3°); B_5D_{11}, −122.9° (*vs.* −122.0°). However, a trace of B_5D_9 impurity might have affected both results.

Chemistry Involving the Tetraborane-8 Group

The New Trifluorophosphine Adduct.—The reaction of B_2H_6 with PF_3 to give BH_3PF_3[17] is so like the synthesis of borine carbonyl as to suggest the analogous reaction of B_5H_{11} with PF_3 to make BH_3PF_3 and $B_4H_8PF_3$. In fact, this reaction proved to be quite easy and straightforward.

Phosphorus trifluoride was purified through the formation and dissociation of the adduct $(CH_3)_3NPF_3$,[18] and after high-vacuum distillation from a trap at −160° its vapor tension at −112° was 372 mm. Two experiments on its reaction with pure B_5H_{11} are summarized in Table III (quantities in mmoles). In each experiment the reaction occurred in a sealed 25-ml. tube, so that the partial pressure of PF_3 was near 10 atm. The BH_3PF_3 and unused PF_3 were isolated by high-vacuum fractional condensation, with identification of the former by its 77.9-mm. vapor ten-

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[13] R. E. Williams, S. G. Gibbins, and I. Shapiro, *J. Chem. Phys.*, **30**, 320 (1959). We are grateful to Dr. Williams for obtaining this spectrum for our sample.

[14] H. I. Schlesinger, H. C. Brown, J. R. Gilbreath, and J. J. Katz, *J. Am. Chem. Soc.*, **75**, 195 (1953).

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

[16] A. B. Burg, *J. Am. Chem. Soc.*, **74**, 1340 (1952).

[17] R. W. Parry and T. C. Bissot, *ibid.*, **78**, 1524 (1956).

[18] J. E. Griffiths and A. B. Burg, *ibid.*, **82**, 1507 (1960).

TABLE III

SYNTHESIS OF $B_4H_8PF_3$

Reactants		Temp., °C.	Time, hr.	Products		PF_3 used
B_5H_{11}	PF_3			BH_3PF_3	$B_4H_8PF_3$	
0.465	9.85	32	4.0	0.437	0.424	0.87
0.651	9.95	29	2.0	0.642	0.623	1.20

sion at −97.6° (known, 77.6 mm.)[17] and its molecular weight (100.6; calcd., 101.8).

The fraction which passed a high-vacuum trap at −78° and condensed at −97° seemed uniform, for three successive fractions showed respective vapor tensions of 6.0, 6.2, and 6.1 mm. at −47.7°. Two vapor-phase molecular weight results (corrected for dissociation) were 136 and 141; calcd. for $B_4H_8PF_3$, 139.3.

The molecular formula $B_4H_8PF_3$, strongly indicated by the nearly quantitative syntheses and the molecular weight results, was confirmed by a quantitative conversion to B_4H_8CO. A $B_4H_8PF_3$ sample measured as 0.215 mmole, standing in a mixture with CO at a partial pressure of 18 atm. during 1 hr. at 28°, yielded 0.216 mmole of PF_3 (377 mm. at −112°) and 0.220 mmole of B_4H_8CO, identified by its 70.5-mm. vapor tension at 0° and by its infrared spectrum. The reverse reaction, $B_4H_8CO + PF_3 \rightarrow CO + B_4H_8PF_3$, also can be made nearly quantitative (ref. 3, p. 22).

The decomposition of $B_4H_8PF_3$ is somewhat faster than that of B_4H_8CO and is not quite analogous, for less PF_3 than CO is permanently trapped in the condensing solids. Thus 0.42 mmole of $B_4H_8PF_3$, left for 3 days at room temperature, produced a slightly volatile white solid, 0.126 mmole of H_2, 0.044 mmole of B_5H_9, and a mixture equivalent to 0.060 mmole of B_2H_6 and 0.387 mmole of PF_3. This 92% recovery of the PF_3 indicated that PF_3 is not much concerned with the further conversion of the B_4H_8 moiety, and presumably the dissociation produces no polymerizable fragment containing PF_3. Also of interest is the complete displacement of PF_3 from $B_4H_8PF_3$ by trimethylamine,[3] in contrast to the total retention of CO when B_4H_8CO reacts with this amine. Thus it appears that $B_4H_8PF_3$ is the better source of B_4H_8 for most chemical purposes.

Reactions Related to Polyborane Conversions.—The thermal decomposition of B_4H_8CO yields H_2, B_2H_6, BH_3CO, B_4H_{10}, B_5H_{11}, and nonvolatile solid material containing CO. The yield of B_4H_{10} is strongly increased by a large excess of H_2, while an abundance of B_2H_6 leads to far higher yields of B_5H_{11}, but B_4H_{10} seems not to affect the course of the reaction very much. Since CO inhibits the dissociation $B_4H_8CO \rightarrow B_4H_8 + CO$, its frequent removal is necessary if the process is to go forward faster than the decomposition of such unstable products as B_4H_{10} or B_5H_{11}. Accordingly, experiments 1, 3, and 4 of Table IV were interrupted at 5-min. intervals for removal of CO and H_2 through a −196° trap by means of an automatic Sprengel pump. At some of these intervals and at the end there was a complete resolution of the products: the CO and H_2 were collected for measurement over mercury and analyzed by CuO combustion, and the other volatile components were separated into three main fractions by high-vacuum fractional condensation. The B_2H_6–BH_3CO fraction was analyzed by allowing the BH_3CO to dissociate to B_2H_6 and CO. Tetraborane was isolated directly. The B_5H_{11}–B_4H_8CO fraction was analyzed by exposure to water during 90 sec. at 0°, whereby each B_5H_{11} formed one B_4H_{10}[8]; in the meantime the hydrolysis of B_4H_8CO yielded no volatiles except H_2 and a trace of CO, and any B_5H_9 would have been observed as such, but could not be found.

The experiments described by Table IV employed a 130-ml. Pyrex tube with a stopcock protected by mercury to avoid the otherwise quite noticeable reaction between Apiezon L grease and B_4H_8CO. After each interval the mixture was warmed rapidly (within 30 sec.) from −196° to room temperature and rapidly quenched at −196° at the end of the interval.

TABLE IV

B_4H_8CO DISSOCIATION REACTIONS

Experiment no.	1	2	3	4
B_4H_8CO, mmoles	0.354	0.236	0.407	0.673
Added reagent, per B_4H_8CO	None	$41H_2$	$14B_2H_6$	$13B_4H_{10}$
Time, total min.	23	16	30	27
Av. temp., °C.	25	26	26	26
Per cent B_4H_8CO consumed	78	39	94	86
Yields of prod. per $100B_4H_8CO$ consumed:				
CO	63	85	57	59
H_2	39	-89^a	7	15
B_2H_6	17	18	-34^a	19
BH_3CO	4	Nil	10	2
B_4H_{10}	21	67	4	-1^a
B_5H_{11}	28	Nil	75	28

[a] Material consumed.

In expt. 2 it is evident that the large proportion of H_2 caused an almost complete conversion of B_4H_8 to B_4H_{10}, if we allow for some decomposition of this product during the process. In contrast, expt. 3 afforded little H_2 for the conversion to B_4H_{10}; instead, the large proportion of B_2H_6 caused almost a complete conversion to B_5H_{11}, some of which must have decomposed. In expt. 4 the slight loss of B_4H_{10} would be ascribed to the decomposition of slightly more of it than was formed.

Additions of B_4H_8CO to Electron-Rich Reactants

In its reactions with basic reagents (or even ethylene) B_4H_8CO never liberates more than a trace of CO. Apparently there is a direct attack at a rate far faster than the dissociation $B_4H_8CO \rightarrow B_4H_8 + CO$. Hence we suppose that the first step is the formation of an adduct of B_4H_8CO, and then it can be argued that the resulting increase of electron density in the B_4H_8 part would increase the hydridic activity of some B–H bonds enough for a rapid attack upon the CO part. Such an enhancement of hydridic activity through complex formation is well known for BH_3 complexes,[19] and it would seem that just such a more effective hydridic tendency would explain why the methyldiboranes react with CO not to form a methylated borine carbonyl, but to destroy all B–H bonds and capture the CO,[20] probably forming $(\text{-B-C-O-})_2$ rings.

The Trimethylamine Reaction.—A 0.790-mmole sample of B_4H_8CO absorbed all of a 0.817-mmole sample of $(CH_3)_3N$ during 6 days at −78° (in a 30-ml. tube with a stopcock attached to the vacuum system), with an apparently accidental liberation of 0.036 mmole of B_2H_6 and 0.031 mmole of BH_3CO and formation of a slightly yellow solid. A further 1.750-mmole sample of $(CH_3)_3N$ was partially absorbed as shown in Table V. The only volatile product now was 0.581 mmole of $(CH_3)_3NBH_3$, which was isolated by sublimation from the nonvolatile glassy residue. Its formation from this CO-containing polyborane is reminiscent of

TABLE V

ABSORPTION OF $(CH_3)_3N$ BY 0.790 MMOLE OF B_4H_8CO

Time interval, hr.	Interim temp., °C.	Total amine absorbed, mmoles	Ratio $(CH_3)_3N/B_4H_8CO$
144	−78	0.817	1.034
511	−78	1.553	1.96
479	−78	1.703	2.16
25	Warming to 0°	1.903	2.41
15	25	1.930	2.44
930	25	1.969	2.49

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[19] A. B. Burg, *Angew. Chem.*, **72**, 185 (1960); XVIth International Congress of Pure and Applied Chemistry, Butterworths, London, 1960, p. 44.

[20] F. L. McKennon, Ph.D. Dissertation, University of Chicago Libraries, 1937.

the $(CH_3)_3N$–B_5H_9 reaction, which forms $2(CH_3)_3NBH_3$ per B_5H_9; but this does not necessarily mean that a BH_3 pattern is to be found in the structure of B_4H_8CO.

The Hydrolysis.—Measured samples of B_4H_8CO were allowed to warm to room temperature with vacuum-degassed pure water, in stopcock tubes attached to the high-vacuum system. The evolved H_2 and CO were collected for measurement and analyzed by CuO combustion, with the results shown in Table VI. The only other volatile component was water. The white solid residue was dried *in vacuo* at 110° and mulled with hexachlorobutadiene, for an infrared spectrum which showed only the bands of the mull liquid and of boric acid.[21] One of the three residues was heated for 1 hr. with aqueous HCl at 90°, giving only negligible further evolution of hydrogen.

TABLE VI
THE HYDROLYSIS OF B_4H_8CO

Expt. no.	B_4H_8CO, mmoles	CO, mmoles	H_2, mmoles	Ratio H_2/B_4H_8CO
1	0.13	0.008	1.14	8.8
2	0.318	0.012	2.80	8.7
3	0.426	0.015	3.73	8.8

The Dimethyl Ether Reaction.—An initial experiment used 0.266 mmole of B_4H_8CO with 1.33 mmoles of $(CH_3)_2O$, reacting during 4 days in a 15-ml. tube at −78°. Slow warming to −26° permitted recovery of 1.15 mmoles of the ether and a trace of an unidentified boron hydride, leaving a yellow nonvolatile solid. A fresh measured sample of $(CH_3)_2O$ was added and withdrawn in stages at −78°, in an attempt to recognize a definite etherate, but as the ether content diminished the pressure at −78° only decreased smoothly, except for a fairly sharp drop from 12.9 to 5.8 mm. as the ratio of the ether to B_4H_8CO dropped from 0.86 to 0.78. It appeared that the B_4H_8CO had been converted to a nonvolatile solid which combined only very weakly and indefinitely with the dimethyl ether.

In a second experiment, B_4H_8CO was treated with $(CH_3)_2O$ in an apparatus designed to measure the molecular weight of the solid product by the vapor tension lowering method.[22] With dimethyl ether as the solvent at −26° the results at mole fractions 0.064 and 0.032 were 192 and 189, respectively, indicating an average molecular weight about 2.4 times that of B_4H_8CO.

The Ethylene Reaction.—In a typical experiment, 0.528 mmole of B_4H_8CO, stabilized by 2.08 mmoles of CO, was allowed to react at room temperature with 9.47 mmoles of C_2H_4 in a 24-ml. sealed tube (C_2H_4 pressure nearly 10 atm.) for 2 hr. Then the mixture was resolved into 0.014 mmole of H_2, 2.13 mmoles of CO (1% liberation from B_4H_8CO), 7.62 mmoles of C_2H_4 (consumed, 1.85 mmoles), 0.142 mmole of $(C_2H_5)_3B$, and approximately 0.25 mmole of a new volatile compound, the molecular formula of which proved to be $(C_2H_4)_4B_4H_8CO$. The low yield of this (not quite 50%) could be explained by its instability, for on standing at room temperature it forms a nonvolatile oil, such as was observed in major proportion. A purified sample of the new compound had 0.5 mm. vapor tension at 25°; values at higher temperatures were not sought because the decomposition was too rapid. Indeed, its tendency to form more volatile material was such that it could be distilled quantitatively only by pumping continually beyond the receiving trap. On exposure to the open air, it demonstrated an aromatic or fruity odor, very different from the typical boron hydride odor.

The formula $(C_2H_4)_4B_4H_8CO$ was confirmed by analysis, using the "wet combustion" method: oxidation by nitric acid in a sealed soda-lime glass tube at 270°. The resulting CO_2 was passed over hot copper to reduce the oxides of nitrogen and through a trap at −78° to remove water, but the infrared spectrum showed the presence of some N_2O. For separation, the CO_2 was absorbed in a slight excess of 0.2 *N* $Ba(OH)_2$, so that the N_2O could be isolated and measured, and then the CO_2 was liberated by aqueous HCl and measured, for a recheck of the result obtained by subtracting the N_2O from the measured volume of the mixture. The boric acid remaining in the original reaction tube was titrated, using the usual mannitol method. Of the results shown in Table VII, those from the largest sample (15.4 mg.) are regarded as the most dependable.

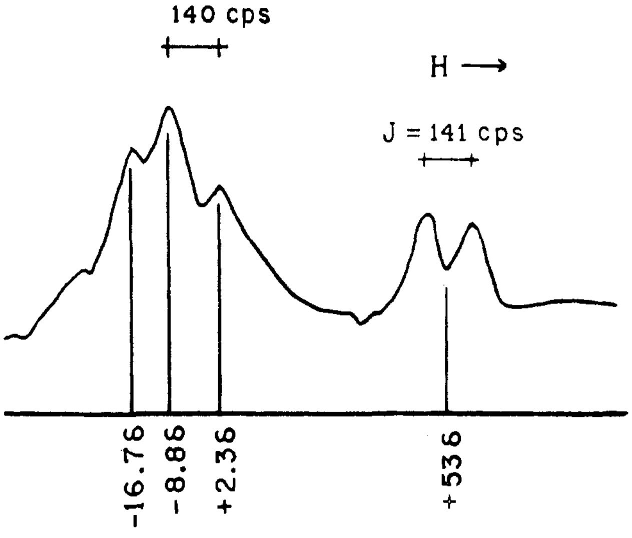

Fig. 2.—The B^{11} magnetic resonance spectrum of $(C_2H_4)_4B_4H_8CO$.

TABLE VII
ANALYSIS OF $(C_2H_4)_4B_4H_8CO$

Sample weight, mg.		...	7.1	15.4
mmoles of CO_2	found	0.234	0.334	0.724
	calcd.	...	.334	.724
mmoles of $B(OH)_3$	found	0.102	.176	.330
		...	.148	.322
Ratio C:B	found	2.29	1.90	2.19
	calcd.	2.25	2.25	2.25

The molecular weight determination was attempted by the vapor-tension lowering method, using as the solvent very pure *n*-butane which had been made by the Grignard method (vapor tension 781 mm. at 0°); however, the result was low (159 *vs.* calcd. 191) because of traces (estimated less than 11 mole %) of more volatile material which developed during the measurements at 0°.

The infrared spectrum of $(C_2H_4)_4B_4H_8CO$ in solution in cyclohexane showed a strong band at 2121 cm.$^{-1}$. This might represent the C=O stretching frequency (2150 cm.$^{-1}$ in B_4H_8CO), but it cannot be distinguished from a possible symmetric in-phase B–H–B bridge frequency; a more complete spectrum is needed, but cannot be obtained dependably except by special low-temperature methods. B–H stretching was observed at 2480 cm.$^{-1}$ and C–H bending at 1370 cm.$^{-1}$.

The B^{11} n.m.r. spectrum of pure liquid $(C_2H_4)_4B_4H_8CO$ (run at 12.83 Mc.) is shown in Fig. 2, wherein the chemical shifts relate to boron trifluoride diethyl etherate as a reference zero. The doublet centered at $+53\delta$ represents apical B–H. The peaks at -8.8δ and $+2.3\delta$ might represent a doublet (J = 140 c.p.s.) with one peak raised by overlap with the -16.7δ peak, or two singlets. Any conclusion concerning structure would be premature. For example, the ethylene might go in to become a C_2H_5 group (in good analogy to the BH_3CO reaction with ethylene) or at least some of it might form B–C_2H_4–B connections.

Borine Carbonyl with Ethylene.—The reaction of BH_3CO with C_2H_4 is a typical hydroboration,[23] almost quantitatively forming $(C_2H_5)_3B$ and CO. The numerical data of three such experiments are given by Table VIII. All of these occurred near room temperature. Direct observation in the case of expt. 3 showed a

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(21) R. R. Servos and H. M. Clark, *J. Chem. Phys.*, **26**, 1175 (1957).

(22) A. B. Burg, *J. Am. Chem. Soc.*, **65**, 1630 (1943).

(23) H. C. Brown and B. C. Subba Rao, *ibid.*, **81**, 6423 (1959).

TABLE VIII

THE REACTION OF BORINE CARBONYL WITH ETHYLENE

Expt. no.	1	2	3
Container volume, ml.	24	115	50
BH_3CO, mmoles	0.407[a]	0.750	0.544
C_2H_4, mmoles	9.07	3.79	1.71
Time, min.	120	30	5
C_2H_4 consumed, mmoles	1.23	1.99	1.47
Products, mmoles			
$(C_2H_5)_3B$	0.399	0.390	0.359
CO	0.383	0.526	0.535
H_2	Nil	0.310	0.190

[a] Corrected for 0.039 mmole of B_2H_6 impurity, as demonstrated by subsequent treatment of the ethylene fraction with $(CH_3)_3N$; by this method no B_2H_6 was found after expt. 2 and 3.

fairly sudden precipitation of white droplets 2.5 min. after the tube was warmed to 25°. Table VIII does not include unidentified volatile products resulting from expt. 2 and 3, wherein the relatively low pressure of C_2H_4 (near 1 atm., *vs.* 9 atm. in expt. 1) permitted extensive side reactions correlated with the formation of H_2. One volatile product showed 50 mm. vapor tension at 0° (mol. wt. 89); another, 0.9 mm. at 25°. Nonvolatile products also were observed in these experiments.

The product triethylboron was recognized by its vapor tension (12.5 mm. at 0°)[24] and mol. wt. (98.4; calcd., 98.0); also its nearly quantitative formation in expt. 1 left no doubt.

Instrumental Approaches to Structure

Infrared Spectra.—The infrared spectra of ordinary and completely deuterated B_4H_{10}, B_4H_{11}, and B_4H_8CO were recorded in the sodium chloride range by a Perkin Elmer Infracord spectrophotometer, whereby complete scans occurred fast enough to avoid appreciable effects of decomposition. The path length was 10 cm. and the pressures approximately 20 mm. Calibration by polystyrene film reduced the probable error to 1%.

The spectra of the six samples are compared in Table IX, with suggested assignments based upon correlations reported in the literature.[25,26] The frequency ratios *R* show which bands represent BH and BD modes. Although some assignments remain uncertain, the spectra do give structural information.

TABLE IX

COMPARISONS OF INFRARED SPECTRA OF POLYBORANE COMPOUNDS[a,b]

B_4H_{10}	B_4D_{10}	*R*	B_5H_{11}	B_5D_{11}	*R*	B_4H_8CO	B_4D_8CO	*R*	Suggested assignments
2600 vs	1950 vs	1.33	2600 vs	1960 vs	1.33	2570 vs	1940 vs	1.32	B—H asymm. stretch
2510 vs	1830 vs	1.37	2500 vs	1840 vs	1.36	2490 vs	1830 vs	1.36	B—H symm. stretch
2280 w	1730 w	1.32	2330 w	. . .	. . .	2320 w	1750 w	1.33	2 × BH_2 scissors
. . .	. . .	. . .	. . .	. . .	. . .	2150 vvs	2150 vvs	1.00	C═O stretching
2160 s	1580 s	1.37	2050 s	1515 m	1.35	1940 s	1440 s	1.35	Hydrogen bridge modes
1870 w	. . .	. . .	1910 w	1400 w,sh	1.36	1810 w,sh	. . .	. . .	
1710 w	. . .	. . .	. . .	. . .	. . .	. . .	. . . .	. . .	
1580 w	1360 w	1.36	. . .	. . .	. . .	1510 s	1110 s,sh	1.36	
1400 m	1040 m	1.35	1440 s,b	1090 s,b	1.32	1440 m	1080 s	1.34	
1260 w	960 w	1.31	. . .	. . .	. . .	. . .	. . .	. . .	
1155 s	854 s	1.35	1170 vs	850 s	1.38	1160 s	880 m	1.32	BH_2 scissors bend
1140 s	844 s	1.35	. . .	. . .	. . .	1056 vs	815 vs	1.30	B—H bending
1080 m	805 s	1.34	. . .	. . .	. . .				
. . .	. . .	. . .	1050 s	1030 m,sh	1.02	1080 sh	975 m	1.10	B—B stretching
977 s	725 m	1.34	960 s	760 m,b	1.26	944 w	700 mw	1.34	BH_2 wagging
863 ms	(Off-scale)		905 s,vb	690 w,vb	1.31	899 ms	(Off-scale)		BH_2 in-plane rocking?
850 ms	(Off-scale)		. . .	. . .	. . .	804 m	(Off-scale)		Uncertain

[a] Frequencies in cm. [b] v, very; s, strong; m, medium; w, weak; b, broad; sh, shoulder.

The two B–H stretching bands and the scissors-bending frequency (1160 cm.$^{-1}$) show that B_4H_8CO has at least one BH_2 group. The very strong band at 2150 cm.$^{-1}$, unchanged by deuteration, compares directly with the known C–O stretching frequencies of CO (2143 cm.$^{-1}$) and BH_3CO (2165 cm.$^{-1}$).[27] It is reasonable that the B–C–O bonding in BH_3CO and B_4H_8CO is nearly the same, with carbon bonded only to one boron atom. Another mode not much affected by deuteration is the B–B stretching, indicated by the shoulder at 1080 cm.$^{-1}$ for B_4H_8CO and 975 cm.$^{-1}$ for B_4D_8CO. The comparison seems analogous to the B_5H_9–B_5D_9 case, for which B–B stretching has been recognized at 1126 and 960 cm.$^{-1}$.[28] Less certain are the assignments for the 899 and 804 cm.$^{-1}$ bands for B_4H_8CO. The absence of similar bands for B_4D_8CO probably means that these would have been found if the scan could have gone below 670 cm.$^{-1}$ and then would have been assigned to a BH_2 in-plane rocking mode. On the whole, it appears that the B_4H_8 unit suffered no extreme structural change on conversion from its environment in B_5H_{11} to that in B_4H_8CO.

Nuclear Magnetic Resonance.—The B^{11} n.m.r. spectra of "neat" liquid B_4H_8CO and B_4D_8CO were obtained by means of a Varian V-4300 high-resolution spectrometer operating at 12.83 Mc., through the courtesy of National Engineering Science Co., with the operation directed by Dr. R. E. Williams. The chemical shift and spin coupling values were measured by reference to triethylboron and boron trichloride as secondary standards, in turn referred to boron trifluoride etherate as zero. The first traces were made as quickly as possible, with the samples at temperatures just high enough for a stable spectrum. However,

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(24) A. Stock and F. Zeidler, *Ber.*, **54**, 531 (1921).

(25) L. J. Bellamy, W. Gerrard, M. F. Lappert, and R. L. Williams, *J. Chem. Soc.*, 2412 (1958).

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

(27) G. W. Bethke and M. K. Wilson, *J. Chem. Phys.*, **26**, 1118 (1957).

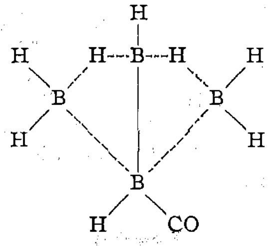
(28) H. J. Hrostowsky and G. C. Pimentel, *J. Am. Chem. Soc.*, **76**, 998 (1954).

partial decomposition at higher temperatures did not appreciably change the spectra.

The n.m.r. record for B_4H_8CO (Fig. 3) consists of a low-field triplet, the slight asymmetry of which was repeatedly confirmed, and a high-field doublet (of area one-third as great) typically representing the apical B–H group found in most polyboranes. The pattern for B_4D_8CO is simpler because the spin coupling constant for B–D is only about 17% as large as for B–H, so that multiplets are not resolved. Thus the B_4H_8CO low-field triplet becomes for B_4D_8CO only a single peak centered at 2.3δ, and the high-field doublet is similarly collapsed to a singlet.

The asymmetry of the B_4H_8CO low-field triplet must be due to some kind of composite character. Its components cannot be either a pair of doublets, two closely adjacent peaks forming the central peak, or a doublet nearly coincident with two peaks of a triplet, for in such cases the low-field pattern of B_4D_8CO would have been a doublet instead of a singlet. However the components could be either (1) a triplet and a doublet having nearly the same chemical shift, with the doublet so broadened as to show only as a distortion of the triplet, or (2) a triplet and a singlet having nearly the same chemical shift. Present evidence does not support any decision between these two cases.

If case 1 is correct, the most probable structure is one derived from that proposed for the B_4H_8 intermediate in the decomposition of B_4H_{10},[4] namely



However, if case 2 is correct, we may consider a three-way tautomerism in which an apical B–H forms a bridge to either of two other boron atoms. This situation would be like the apical *vs.* bridging effect of the unique hydrogen atom in B_5H_{11},[11] which is shown for comparison with the three B_4H_8CO patterns in Fig. 4.

The three views of B_5H_{11} with apex-to-base bridge bonding are shown with dotted lines indicating prospective shifts of bonds, such as to form the suggested tautomers of B_4H_8CO with minimal reorganization. It can be argued that the easiest point of attack by CO upon B_5H_{11} would be at one of the upper-corner boron atoms, either of which must be especially electron-deficient because of participation in three three-center bonds. As BH_3 is removed (as shown by the dotted line slicing if off), the central (apical) boron atom would become a good place to attach the second CO. Such a mechanism would be consistent with the hydrolysis of B_5H_{11} to give mole-for-mole yields of B_4H_{10}[8]; in that case, however, a BH unit would be hydrolyzed off at the sensitive upper corner, leaving the B_4H_{10} pattern with scarcely the motion of even one atom.

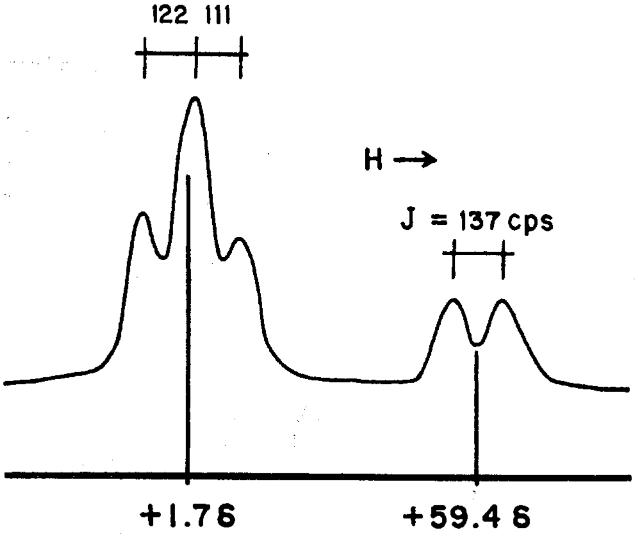


Fig. 3.—B^{11} magnetic resonance spectrum of B_4H_8CO.

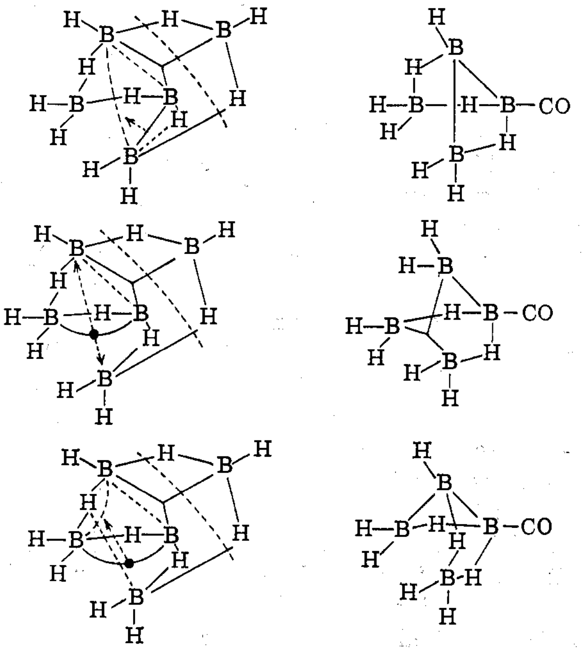


Figure 4.

Although it seems more difficult to find any way whereby B_5H_{11} could go so directly to the case 1 structure for B_4H_8CO, it still can be argued that the conversion from any of the tautomeric patterns to the case 1 structure is not very difficult, involving only minor redirection of B–H–B bridge *vs.* B–B and B–H terminal bonding. Hence no speculative discussion of possible easy mechanisms for the formation of B_4H_8CO from either B_5H_{11} or B_4H_{10} can aid in the selection of the most appropriate structural pattern.

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