extreme narrowing region ($T_1 = T_2$), the effects are seen in the line width as well. The presence of a quadrupolar nucleus (e.g., Br) bound to boron is known to broaden the ^{11}B resonance lines.

(25) In view of the complexity of the spin systems, calculations were performed to determine if nonzero $^2J_{PP}$ or $^3J_{BP}$ would introduce enough second-order character into the patterns so that J_{PB} could not be straightforwardly measured. Values of $|^2J_{PP}|$ and $|^3J_{BP}|$ were allowed to vary from 10 to 20 Hz and the simulations indicated that as long as a triplet pattern appeared J_{BP} could be measured directly from the spectrum. When $^1J_{BP}$ could not be measured directly, the pattern had deviated enough from

a triplet pattern so that at least partial resolution of a nontriplet pattern would be experimentally feasible.

(26) A. H. Cowley and M. C. Damasco, *J. Am. Chem. Soc.*, **93**, 6815 (1971).
(27) R. W. Rudolph and C. W. Schultz, *J. Am. Chem. Soc.*, **93**, 6821 (1971).
(28) F. A. L. Anet and R. Anet in "Dynamic Nuclear Magnetic Resonance Spectroscopy", L. M. Jackson and F. A. Cotton, Ed., Academic Press, New York, N.Y., 1975, p 543.
(29) E. Carberry and R. West, *J. Am. Chem. Soc.*, **91**, 5440 (1969).
(30) H. Friebolin, H. G. Schmid, S. Kabuss, and W. Faisst, *Org. Magn. Reson.*, **1**, 67 (1969).

Synthesis and Characterization of Some Partially B-Halogenated 1,2,3,4,5,6-Hexahydrocyclotriboraphosphanes[2,3]

MARVIN H. GOODROW*[4] and ROSS I. WAGNER

Using stoichiometrically controlled halogenation of $[(CH_3)_2PBH_2]_3$ (I) with a variety of reagents, a series of partially B-halogen-substituted derivatives of I was prepared. N-Halosuccinimides proved to be the most selective of the halogenating agents studied particularly for preparation of individual lower B-halo-substituted I with selectivity increasing with increasing atomic number of the halogen. Two isomers each were isolated for the dibromo-, diiodo-, trichloro-, and tetrachlorocyclotriborophosphane derivatives. From infrared and NMR spectra, the di- and trihalogenated compounds were assigned structures with nongeminal halogens and the tetrahalogenated I was assigned a structure having one geminal and two nongeminal halogen-substituted borons. Halogenation apparently is sterically controlled and proceeds in a stepwise manner whereby nongeminal substitution occurs preferentially.

Introduction

Over the last 20 years, a considerable amount of research has been directed toward the synthesis of novel inorganic polymers with the objective of discovering systems having extreme chemical and thermal stability. One such metalloid system attaining limited sucess is the polyboraphosphanes containing a P-B backbone structure. The lower member, cyclic polymers show unusual resistance to thermal decomposition and to oxidative and hydrolytic attack.[5]

Attempts to synthesize high molecular weight polymers having desirable physical and chemical properties produced instead only new four-, six-, or eight-membered cyclic structures[5b,6,7,8] when substituents on the monomer unit R_2PBR_2 were altered. Excess Lewis base as end blocking groups aided synthesis of moderate molecular weight linear polymers[5c,9,10] which depolymerized thermally to the cyclic structures. Clearly another approach to stable high molecular weight polymers was required. Condensation polymerization of the stable cyclic structures appeared to be a promising approach to stable high polymers. To this end it was necessary to develop a method for selective placement of two (or more) reactive substituents on a preformed cyclic unit.

Of the many reactions attempted[5] on cyclotriboraphosphanes, only halogen substitution of the hydrogens on boron has proved consistently successful.[5c-e,11,12] 1,1,3,3,5,5-Hexahydrocyclotriboraphosphanes, $(R_2PBH_2)_3$ (where R = methyl, ethyl, or phenyl), have been halogenated with a variety of reagents, namely, haloalkanes, aluminum halide catalyzed haloalkanes, halogens, mixed halogens, hydrogen halides, or N-halosuccinimides using a variety of techniques and reaction conditions. In most cases the completely B-hexahalogenated compounds, $(R_2PBX_2)_3$, were explicitly sought. The halogens in these geminally substituted derivatives of I, however, proved to be inert in attempted substitution reactions. It was anticipated that in cyclotriboraphosphane compounds containing three, or fewer, nongeminal >BHX functions the halogens
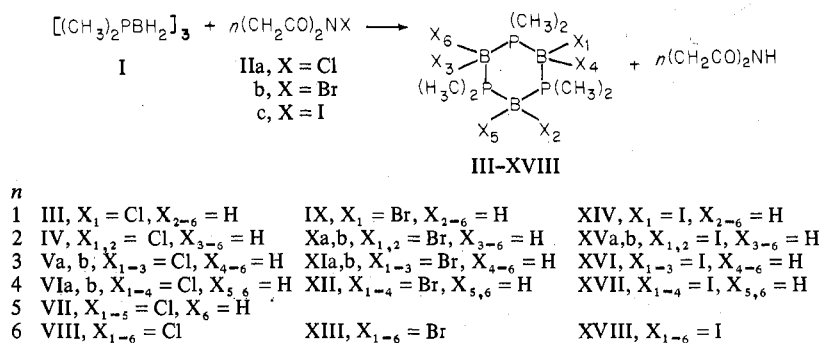
would be more reactive. Indeed, these partially halogenated compounds subsequently proved to possess readily replaceable halogens.[13]

Initially, partially halogenated trimeric species were found as products of ring halogenation with mole ratios of Br$_2$:I ≤ 3[12] and subsequently as inadvertent by-products of incomplete halogenation of $[(C_6H_5)_2PBH_2]_3$.[11] In the presence of excess chlorinating agent, the latter was reported to produce in addition to the expected B-hexachloro derivative some tetra- and pentachlorinated trimers as well. Slow reaction of $[(C_6H_5)_2PBH_2]_3$ with excess iodine in boiling carbon tetrachloride or 1-iodobutane (conditions comparable to total hexahalogenation when chlorine or bromine were used) gave only the triiodide $(C_6H_5)_6P_3B_3H_3I_3$; further substitution did not occur, even on prolonged heating.[5f] Likewise, we have previously observed[5e] a similar reluctance of $[(CH_3)_2PBH_2]_3$ (I) to undergo complete iodination. Whereas chlorination and bromination of I proceeded rapidly at room temperature to give $[(CH_3)_2PBX_2]_3$, iodination required an extensive time at a higher temperature (50 °C). Furthermore, I was readily hexahalogenated with N-chloro- or N-bromosuccinimides while only partially B-iodinated species were isolable when N-iodosuccinimide was used. In sum, one observes that partially substituted species are favored by an increase in steric requirements of the halogen and/or the substituents on phosphorus.

Results

Our initial attempts to obtain specific partially B-halogenated cyclotriboraphosphanes utilized stoichiometric quantities of bromine and I in dibromomethane.[12] A 1:1 ratio of reactants produced a multicomponent mixture of partially B-brominated species. After tedious fractional crystallizations and sublimations, only a small yield of the B,B'-dibromo isomer Xa, mp 129–130 °C, was isolated and characterized. Employing a 3:1 bromine:I ratio in glacial acetic acid, a 75% yield of a mixture of tribrominated isomers of I was obtained.

Scheme I

$$[(CH_3)_2PBH_2]_3 + n(CH_2CO)_2NX \longrightarrow$$

III–XVIII

$$+ n(CH_2CO)_2NH$$

I	IIa, X = Cl
	b, X = Br
	c, X = I

n			
1	III, $X_1 = Cl, X_{2-6} = H$	IX, $X_1 = Br, X_{2-6} = H$	XIV, $X_1 = I, X_{2-6} = H$
2	IV, $X_{1,2} = Cl, X_{3-6} = H$	Xa,b, $X_{1,2} = Br, X_{3-6} = H$	XVa,b, $X_{1,2} = I, X_{3-6} = H$
3	Va,b, $X_{1-3} = Cl, X_{4-6} = H$	XIa,b, $X_{1-3} = Br, X_{4-6} = H$	XVI, $X_{1-3} = I, X_{4-6} = H$
4	VIa,b, $X_{1-4} = Cl, X_{5,6} = H$	XII, $X_{1-4} = Br, X_{5,6} = H$	XVII, $X_{1-4} = I, X_{5,6} = H$
5	VII, $X_{1-5} = Cl, X_6 = H$		
6	VIII, $X_{1-6} = Cl$	XIII, $X_{1-6} = Br$	XVIII, $X_{1-6} = I$

The analytical data (Table I), the broad melting range (109–115 °C), and the barely discernible infrared absorption bands assigned[14] to BH$_2$ rocking (1003–994 cm^{-1}) and scissoring (1112–1104 cm^{-1}) suggested that the mixture consisted mainly of *cis*- and *trans*-2,4,6-tribromo-1,2,3,4,-5,6-hexahydro-1,1,3,3,5,5-hexamethylcyclotriboraphosphanes (XIa and b). Employing a 6:1 bromine:I ratio in glacial acetic acid followed by immediate quenching of the reaction produced a multicomponent mixture from which a small quantity of a single *B*-tetrabromo isomer was isolated. The absence of typical BH$_2$ bands in the infrared spectrum established the structure as a 2,2,4,6-tetrabromo isomer (XII). Also investigated was the possibility of obtaining partially halogenated materials by interrupting a very slow reaction before completion. Earlier, we reported[5e] the reaction of carbon tetrachloride with I that required 113 h at 130 °C to produce a 97.7% yield of the *B*-hexachloro trimer (VIII). If the reaction is stopped short of this time, partially halogenated components are found, but only as complex mixtures. One such experiment produced a mixture consisting of tri-, tetra-, penta-, and hexachloro trimers from which the 2,2,4,4,6-pentachloro trimer, VII, was easily isolated because of its (and VIII's) unique insolubility in aliphatic hydrocarbon solvents and its higher solubility (than that of VIII) in benzene. In a similar manner, treatment of [(CH$_3$)(C$_2$H$_5$)PBH$_2$]$_3$ with carbon tetrachloride for a lesser time resulted in a partial chlorination to give a mixture of 12.9% tri-, 57.7% tetra-, and 28.2% pentachloro products as deduced by comparison of GLC (gas–liquid chromatography) retention times with the known *B*-hexachlorinated compound[5e] and the partially chlorinated trimers from I. Since the search for the higher halogenated species was not the primary objective of the investigation, isolation and definitive characterization of these compounds were not pursued.

Faced with the multicomponent mixtures and the obviously difficult isomer resolution problems presented by the poor selectivity encountered in these early experiments, we directed our attention toward utilizing the slower, more selective and easily handled halogenating agents the *N*-halosuccinimides (IIa, b, c).[15] These we had used successfully for the hexahalogenation of I to form [(CH$_3$)$_2$PBCl$_2$]$_3$ (VIII), [(CH$_3$)$_2$PBBr$_2$]$_3$ (XIII), and mixtures of partially B-iodinated species.[5e] When used in stoichiometric ratios[16] with I they produced nearly quantitative yields of succinimide and as the major product the partially B-halogenated species indicated by Scheme I admixed with both more and less highly halogenated trimers.

Thus the cyclotriboraphosphane I and *N*-chlorosuccinimide (IIa), the least selective *N*-halosuccinimide, in a 1:1 ratio afforded a mixture consisting of 15.2% I, 61.4% 2-chlorocyclotriboraphosphane III, and 17.8% dichlorocyclotriboraphosphane isomers. Such mixtures could only be partially purified by fractional crystallization but were readily resolved by preparative-scale GLC. The 2-chloro compound could then

be obtained in 99.9% purity for analyses (Table I). The *B*-dichloro fraction was obtained in 97.5% purity; the broad melting range suggested the presence of more than one isomer (cis, trans, and, of less probability, geminal isomers). One of the dichloro isomers, IV, readily crystallized from solution. 2-Bromo-1,2,3,4,5,6-hexahydro- (IX), and 1,2,3,4,5,6-hexahydro-2-iodo-1,1,3,3,5,5-hexamethylcyclotriboraphosphane (XIV) were also prepared from I and the respective *N*-halosuccinimides using 1:1 ratios of reactants and provided crude yields of about 95%. Two recrystallizations sufficed to obtain products assaying 98–99% with 1–2% I as impurity. Treatment of I with 2 equiv of IIb followed by repeated fractional crystallization gave the 2,4-dibromocyclotriboraphosphane isomer Xa in 58% yield. Using preparative-scale GLC, a similar reaction mixture was conveniently resolved into its components, each in high-purity and high-recovery yields. In this manner, IX was obtained in 11% yield assaying 98.4%; the isomeric dibromo mixture was obtained in 75.8% yield, assaying 99.9%, and was definitively characterized by analyses (Table I). From this mixture the more abundant isomer Xa was easily crystallized in high purity. A very small quantity of the second 2,4-dibromo isomer Xb was eventually obtained in pure form from the Xa filtrates only after a slow crystallization procedure. The isomeric tribromo GLC fraction represented 6% of the reaction product and provided only one of the 2,4,6-tribromocyclotriboraphosphane isomers, XIa. The infrared spectrum of the residues from this isolation suggested that the second nongeminal isomer, XIb, was present, but it could not be isolated in pure form. Treatment of the more abundant 2,4-dibromo trimer, Xa, with 1 mol of IIb produced a complex mixture of polybrominated materials. The GLC showed that the second, and more mobile (by GLC), tribromo isomer, XIb, was indeed the more abundant, the ratio of formation being about 9:1. Experiments using 2:1 *N*-iodosuccinimide:I ratios proved less satisfactory than experiments with IIb. The reaction was considerably slower and produced undesirable brown byproducts which necessitated tedious and difficult workup techniques. The more abundant and less soluble 2,4-diiodocyclotriboraphosphane isomer XVa was easily obtained by fractional crystallization. A second diiodo isomer, XVb, was obtained in concentrated form (76.5%) from the above residues by preparative-scale GLC and then fractionally crystallized to provide the pure isomer. This was the only dihalocyclotriboraphosphane whose isomers were separable by GLC techniques under the conditions used.

Two trichloro- (Va and Vb), and two tetrachloro- (VIa and VIb) cyclotriboraphosphanes were isolated from a reaction mixture using a IIa:I ratio of 3.76:1 and consisting of 71.7% trichloro-, 26.5% tetrachloro-, and 0.5% pentachlorocyclotriboraphosphanes. Resolution by preparative-scale GLC followed by slow fractional crystallization of the two major GLC fractions afforded isomers Va and Vb (both having the 2,4,6-trichloro structure) and isomers VIa and VIb (both

Table I. Preparation, Isolation and Analyses of Some B-Halogenated 1,2,3,4,5,6-Hexahydro-1,1,3,3,5,5-hexamethylcyclotriboraphosphanes

Expt no.	Reactants (amt in mmol)	Solvent (amt in ml)	Reaction conditions		Product		Compd
			Time, h	Temp, °C	Wt, g	Compn, % (by GLC)	
1	20.45 I + 20.86 IIa	60 CCl$_4$	8	25	5.138	15.2 I, 61.4 III, 17.8 IV, 5.6 unk	III IV
2	0.881 I + 0.896 PCl$_5$	1 C$_5$H$_5$N	2	75	0.171	28.2 I, 68.6 III, 0.4 IV, 2.8 unk	III
3	45.11 I + 169.8 IIa	60 CCl$_4$	48	25	13.354	71.7 V, 26.5 IV, 0.5 VII	Va Vb VIa VIb
4	5.51 I	10 CCl$_4$	10 months	25		18.5 VI, 76.3 VII, 5.2 VIII	VII
5	1.97 [C$_2$H$_5$(CH$_3$)PBH$_2$]$_3$	7.4 CCl$_4$ 4.8 CCl$_4$	14.5 25	120 130		12.9 tri, 57.7 tetra, 28.2 penta	
6	1.733 I + 1.74 IIb	25 C$_6$H$_6$	2 0.17	25 80	0.518		IX
7	7.25 I + 14.55 IIb	150 C$_6$H$_6$	0.083	80	2.72		Xa
8	45.16 I + 95.67 IIb	50 C$_6$H$_6$	0.083	80	17.165	11 IX, 76 X, 6 XI, 7 unk	Xa Xb XIa
9	90.84 I + 273 Br$_2$	550 CH$_3$COOH	0.2	20			XIa, b
10	2.92 I + 11.74 IIb	50 C$_6$H$_6$	3	80	1.467		XII
11	4.042 I + 24.24 Br$_2$	35 CH$_3$COOH	0.17	25			XII
12	11.44 I + 11.58 IIc	25 C$_6$H$_6$	16	25	3.308		XIV
13	6.79 I + 14.26 IIc	60 C$_6$H$_6$	16 1	25 80			XVa XVb
14	6.78 I + 44.7 I$_2$	20 C$_2$H$_5$I	8	72			XVI
							XVII

[a] Key: C, crystallization; EV, evaporation at ambient temperature; EX, extraction; FC, fractional crystallization; FS, fractional

having the 2,2,4,6-tetrachloro structure). Only one isomeric 2,2,4,6-tetrabromocyclotriboraphosphane isomer, XII, could be isolated after extensive fractional crystallization of the crude product from reaction of IIb and I (4:1 ratio). The low yield of only 4% clearly demonstrates the desirability of initial separation by preparative GLC prior to isomer resolution by fractional crystallization.

To test the possibility of reaction of N-halosuccinimides with a C–H bond of the methyl group of phosphorus (or boron), [(CH$_3$)$_2$PB(CH$_3$)$_2$]$_3$ was refluxed with N-bromosuccinimide in benzene for several hours. No succinimide was found; a black residue and 76% (after one crystallization) of starting trimer were recovered. No halogenated product could be found, but this does not rule out the possibility of the formation of an unstable species leading to the black residue encountered.

Discussion

In addition to providing the desired partially B-substituted cyclotriboraphosphanes for polymerization studies, other interesting aspects were revealed—the apparent successive manner in which halogenation of I proceeds and the positions of the halogens in the products isolated. Although all isomers in each series were not isolated in pure form, it was possible to ascertain some structural features based on infrared and NMR[17] spectra and the known structure of the hexa-

hydrocyclotriboraphosphane ring.[18,19] Infrared studies[13,15] were initially utilized for establishing the structures and some of these have now been confirmed by ^{1}H, ^{11}B, and ^{31}P NMR investigations.[17] Of particular use was information about the >BH$_2$ group available from four regions of the infrared spectrum: 2425–2345 cm^{-1} (BH and BH$_2$ asymmetric and symmetric stretching); 1112–1097 cm^{-1} (BH$_2$ scissoring); 1004–989 cm^{-1} (BH$_2$ rocking); 814–807 cm^{-1} (BH$_2$ wagging).[20,21] All of the B-monohalogenated compounds, III, IX, and XIV, displayed diminished intensities of these bands compared to the corresponding bands in the spectrum of I. Further diminishing of the BH$_2$ bands is observed in the spectra of the five dihalogenated compounds, IV, Xa, Xb, XVa, and XVb, and is evidence that the halogen substitution is 2,4, rather than geminal 2,2. Using an infrared spectrophotometer[22] with better resolution than employed for other spectra cited herein and expanding the B–H stretching region, the KBr spectrum of Xa clearly showed three bands at 2427, 2418, and 2410 cm^{-1} while the spectrum of Xb contained only a single nearly symmetrical band at 2412 cm^{-1}. A possible interpretation of these data is that the simpler spectrum might arise from the cis structure (Xb) in which each of the BH hydrogens occupies an axial position while the halogens occupy the more sterically favorable equatorial positions. However, without additional data such as solution

Isolation sequence[a]	Mp, °C	Empirical formula	% C Calcd	% C Found	% H Calcd	% H Found	% X Calcd	% X Found	Mol wt Calcd	Mol wt Found
GLC, FS	72.5–74.0	$C_6H_{23}B_3ClP_3$	28.14	28.37	9.05	9.10	13.85		256.1	261
GLC, FS, C (3 times from 4:1 ethanol–water) T (water), S	117–118	$C_6H_{22}B_3Cl_2P_3$	24.80	25.27	7.63	7.81	24.41		290.1	
GLC, FS, C (hexane), S	138.5–139.5	$C_6H_{21}B_3Cl_3P_3$	22.18	22.04	6.51	6.62	32.73	32.5	324.9	335
EV (filtrate from Va), C, MS (Va, Vb), C (hexane), S	130.5–132.0			22.21		6.78				325
GLC, FS, C (hexane), S	178–179	$C_6H_{20}B_3Cl_4P_3$	20.05	20.12	5.61	5.63	39.46	39.3	359.4	360
EV (filtrate from VIa), C, MS (VIa, VIb, V), C (hexane)	155–156			19.86		5.89				360
EV, T (hexane), EV, C (benzene)	297–304	$C_6H_{19}B_3Cl_5P_3$								
EV, hot EX (isohexane), EV, C (isohexane or pentane)	77–78	$C_6H_{23}B_3BrP_3$	23.98	24.43	7.71	7.84	26.58	26.4	300.6	296
EV, hot EX (isohexane), EV, C (isohexane)	129–130	$C_6H_{22}B_3Br_2P_3$	19.01		5.84		42.12		379.5	
GLC, S, EV, C (20:1 methanol-water), C (hexane), S	129–130			19.06		5.81			42.5		372
EV (filtrate from Xa) C, MS (Xa, Xb), C (hexane)	74–76			19.40		5.64					378
GLC, S, EV, C (methanol), C (hexane)	163–164	$C_6H_{21}B_3Br_3P_3$	15.72	16.17	4.62	4.75	52.30	52.8	458.4	466
P (water), C (methanol)	109–115			15.64		4.72			52.2	
Soln EX (water), EV, C (cyclohexane)	208–209	$C_6H_{20}B_3Br_4P_3$	13.41	13.15	3.75	3.60	59.49	59.3	537.3	550
P (water), FC (methanol, methanol–benzene)	208–210			13.82		4.12			59.0	
EV, T (dil aq $Na_2S_2O_3$), FS, C (4:1 ethanol–water), S	82.5–84.0	$C_6H_{23}B_3IP_3$	20.73	20.57	6.67	6.76	36.52		347.6	349
EV, EX (isohexane), EV, T (dil aq $Na_2S_2O_3$), S, FC (5:1 ethanol–water), C (hexane)	118.5–119.5	$C_6H_{22}B_3I_2P_3$	15.22	15.25	4.68	4.72	53.61		473.5	477
EV (filtrate from XVa), GLC, S, EV, C (methanol), MS (XVa, XVb), C (hexane)	131–132			15.46		4.70					481
EV, FS, C (ethanol), EV, C (hexane), MS (XVI, XVII), EV, EX (methanol), EV, C (methanol), MS (XVI, XVII), C (2 times from methanol, 1 time from hexane)	185–186	$C_6H_{21}B_3I_3P_3$	12.02	11.97	3.53	3.43	63.52		599.4	625
C (hexane)	205–206	$C_6H_{20}B_3I_4P_3$	9.94	10.33	2.78	2.80	70.00		725.3	745

sublimation; GLC, gas-liquid chromatography; MS, mechanical separation; P, precipitation; S, sublimation; T, trituration.

spectra to assess possible crystal field effects, a definitive structural assignment is precluded. Chemical[12,15] and NMR[17] evidence has unequivocally confirmed the assignment of nongeminal structures to these compounds. The ^{11}B NMR spectrum of Xa shows a quartet at 37.3 ppm, characteristic of the

$$\begin{matrix} P \\ \diagdown \\ \diagup \\ P \end{matrix} BHBr$$

group, and a distorted quintet at 51.1 ppm, characteristic of the

$$\begin{matrix} P \\ \diagdown \\ \diagup \\ P \end{matrix} BH_2$$

group,[17] upfield from trimethyl borate as external standard with relative intensities of 2:1. The spectrum of Xb was similar and contained a quartet at 37.9 ppm and a quintet at 51.4 ppm also with relative intensities of 2:1.[23]

All of the trihalides isolated, Va, Vb, XIa, and XVI, and the isomeric XI a, b mixture lacked bands in the BH_2 scissoring, rocking, and wagging regions. These data firmly establish the nongeminal 2,4,6-trihalo structures. Like the 2,4-dihalides, these nongeminal trihalogenated compounds undergo displacement with ease,[13] quite contrary to obser-

vations for structures containing $>BCl_2$ groups, e.g., VIII, which are noted for their chemical stability.[5e,f] Similar nongeminal assignments have also been made for a number of di- and trihalogenated species derived from $[(C_6H_5)_2P$-$BH_2]_3$.[5f,16] The tetrahalogenated cyclotriboraphosphanes VIa, VIb, XII, and XVII also lacked $>BH_2$ absorption bands and thus can be assigned the 2,2,4,6-tetrahalo structure (one $>BCl_2$ and two $>BHCl$ groups).

In each of the three series of partially halogenated I, the individual members which have been isolated clearly indicate that halogenation proceeds in a stepwise manner with $>BH_2$ groups reacting in preference to $>BHX$ groups. Such a stepwise reaction sequence would be expected if one considers the polarity of the ring, $[(CH_3)_2P^{\delta+}B^{\delta-}H_2]_3$, where boron bears the negative charge. An electronegative halogen on one boron would reduce the negative character of that boron, making electrophilic attack (if this is the mechanism) at the remaining $>BH_2$ groups more favorable. Geminal halogen substitution would then be less likely to occur until each of the three borons had been monosubstituted. This same reaction sequence would be expected considering the greater steric hindrance which would be found on introducing a second halogen on a boron relative to introducing the first. A further consquence of the steric requirement is illustrated by the preponderance of one isomer of the 2,4-dihalo-substituted I; e.g., monoiodination of

Table II. Infrared Frequencies (cm⁻¹) of Some B-Halogenated 1,2,3,4,5,6-Hexahydro-1,1,3,3,5,5-hexamethylcyclotriboraphosphanes in KBr[a]

I: 2980 m, 2920 m, 2820 w, 2375 vs, 2345 vs, 2215 m, 1425 s, 1414 s, 1294 m, 1284 s, 1112 s, 1104 s, 1003 m, 994 s, 945 s, 934 vs, 894 vw, 853 s, 810 m, 750 s, 743 m, 720 vs, 665 s

III: 2985 m, 2920 m, 2800 w, 2395 vs, 2355 vs, 2205 m, 2020 w, 1428 s, 1414 s, 1305 s, 1290 s, 1112 s, 1107 s, 1003 m, 991 s, 981 s, 946 s, sh, 928 vs, 886 w, 870 w, 853 s, 821 vw, 807 m, 754 s, 745 w, 734 m, 722 s, 697 w, 674 m

IV: 2990 w, 2925 w, 2810 vw, 2405 vs, 2370 s, 2205 w, 2025 vw, 1428 s, 1408 s, 1302 m, 1291 s, 1112 m, 1004 w, 989 s, 983 s, 946 s, 926 vs, 891 w, 877 w, 856 m, 826 w, 814 w, 770 w, 757 s, 743 w, 730 s, 698 w, 686 m, 671 w

Va: 3000 w, 2940 w, 2825 vw, 2410 s, 2375 m, sh, 2225 vw, 2030 vw, 1418 s, 1306 m, 1289 s, 983 s, 944 s, 912 vs, 868 m, 853 m, 823 m, 768 w, sh, 757 s, 745 m, 732 w, 703 m, sh, 692 s, 668 w, sh

Vb: 3000 w, 2930 w, 2410 s, 2365 m, sh, 2230 vw, 2030 vw, 1418 s, 1302 m, sh, 1289 m, 984 s, 944 s, 913 vs, 867 m, 853 m, 823 m, 768 w, sh, 757 m, 746 m, 732 w, 704 m, sh, 692 s, 669 w, sh

VIa: 3000 w, 2930 w, 2425 m, 2350 w, sh, 2225 vw, 2040 vw, 1418 m, sh, 1413 m, 1303 m, sh, 1296 m, sh, 1288 m, 984 s, 947 s, 916 vs, 886 vw, 870 m, 854 m, 825 m, 768 w, sh, 759 m, 747 m, 730 m, sh, 718 s, 698 s, 675 w, sh

VIb: 3000 w, 2940 w, 2410 s, 2370 w, sh, 2230 vw, 2035 vw, 1420 m, 1412 m, sh, 1298 m, 1288 m, 1004 s, 949 s, 921 vs, 887 vw, 873 m, 848 m, 838 m, 825 m, 757 s, 753 m, sh, 736 m, 720 s, sh, 704 s, 699 s, sh, 679 w, sh

VIII: 2985 vw, 2915 vw, 1411 s, 1387 s, 1305 m, 1300 w, 1286 m, 949 s, 931 vs, 843 w, 795 w, 779 m, 767 m, 760 s, 755 s, 742 s, 730 vs, 715 s, 689 s

IX: 3000 m, 2930 m, 2820 vw, 2415 vs, 2350 vs, 2205 m, 2025 vw, 1429 s, 1416 s, 1305 s, 1290 s, 1112 s, 1108 s, 1002 m, 991 s, 959 w, 945 s, sh, 922 vs, 885 w, 870 w, 853 s, 823 vw, 808 m, 753 s, 737 m, 722 s, 698 w, 673 m

Xa:[22] 2985 m, 2915 m, 2805 vw, 2427 s, sh, 2418 vs, 2410 s, sh, 2371 m, 2360 m, sh, 2205 w, 1427 m, sh, 1418 s, sh, 1411 s, 1300 m, 1287 s, 1280 m, 1108 m, 998 w, 984 m, 961 m, 941 s, 935 m, 921 vs, 915 vs, 888 s, 875 m, 859 m, 851 s, 822 m, 811 m, 771 w, 755 s, 748 m, 741 m, 729 s, 708 w, 634 w, 610 m, sh, 604 m, 580 vw, 564 m, 538 vw, 526 w, 507 m, 340 m

Xb:[22] 2980 m, 2915 m, 2805 vw, 2412 vs, 2360 m, 2340 m, sh, 2200 vw, 2020 vw, 1418 s, sh, 1410 s, 1295 m, sh, 1285 s, 1104 m, 990 w, sh, 980 m, sh, 970 m, 937 vs, 921 vs, sh, 913 vs, 886 m, 874 w, 866 m, 847 m, 837 w, sh, 822 w, 810 m, 753 s, 746 m, 734 s, 707 w, 610 m, 604 m, sh, 569 w, 563 w, 532 w, 521 m, 505 w, 340 m

XIa: 2995 w, 2930 w, 2425 s, 2305 w, sh, 1422 m, sh, 1409 s, 1300 m, sh, 1286 m, 963 m, 953 w, 927 vs, 919 s, 901 m, 883 m, 867 m, 854 m, 818 w, 766 w, sh, 755 m, 744 m, 730 m, 667 w

XII: 2980 w, 2900 w, 2440 s, 2325 w, 1416 s, 1406 s, 1302 m, 1294 s, 1286 s, 960 m, 942 s, 912 vs, 904 vs, 868 s, 854 s, 823 m, 769 w, 757 m, 745 w, 723 w

XIV: 2995 m, 2925 m, 2810 vw, 2410 vs, 2360 vs, 2190 m, 2020 vw, 1420 s, sh, 1410 s, 1300 m, 1289 s, 1100 s, 1097 s, 1004 m, 993 s, 945 s, sh, 928 vs, 904 s, 882 m, 867 m, 845 s, 808 m, 752 s, 738 m, 723 s, 701 w, 671 m

XVa: 3000 w, 2925 w, 2815 vw, 2425 s, 2370 m, 2210 vw, 2020 vw, 1416 s, 1303 m, 1291 s, 1112 m, 997 vw, 983 w, 951 w, sh, 932 vs, 903 vs, 885 m, 876 w, 852 vs, 823 vw, 812 w, 774 w, 756 m, 744 w, 732 m, 708 w, 676 vw

XVb: 3000 w, 2930 w, 2815 vw, 2405 s, 2360 s, 2200 w, 2025 vw, 1418 s, sh, 1410 s, 1300 m, sh, 1288 m, 1103 m, 1100 m, 1001 w, 991 m, 948 m, sh, 929 vs, 868 w, 852 w, 807 w, 749 m, 716 s, 673 vw, 663 w

XVI: 3000 w, 2930 w, 2445 s, 2335 w, sh, 2240 vw, 2025 vw, 1420 m, 1298 m, 1289 m, 953 m, 932 s, 911 w, 890 vs, 858 vs, 848 w, sh, 823 w, 770 w, 757 m, 745 m, 725 vw, 668 vw

XVII: 3000 w, 2920 w, 2450 s, 2340 w, 1415 s, 1401 m, sh, 1301 m, 1294 s, 1287 s, 946 s, 933 s, 926 s, 901 vs, 890 vs, 865 s, 849 s, 822 m, 765 w, 753 m, 743 w, 723 w, 675 w

[a] Abbreviations used: v, very; s, strong; m, medium; w, weak; sh, shoulder.

XIV formed XVa and XVb in an approximate 30:1 ratio.

Experimental Section

All melting points were determined in sealed capillary tubes under dry nitrogen and are uncorrected. Molecular weights were determined in ca. 0.05 M benzene solution by the vapor pressure osmometric method.[24] Elemental analyses were performed in this laboratory. Infrared spectra (KBr disks) were determined using a Perkin-Elmer Model 21 spectrophotometer with sodium chloride optics. Analytical gas–liquid chromatographic (GLC) analyses were done employing a Perkin-Elmer 154B vapor fractometer with a 2-m silicone oil–Celite column; preparative-scale GLC separations utilized a Beckman Megachrom instrument equipped with a 2-m silicone oil–Celite column.[25] Boron-11 NMR spectra were obtained in benzene solutions at 32.1 MHz using a Varian HA-100 instrument and trimethyl borate as external standard. Experiments described in detail are typical of the procedures used for syntheses and isolation of partially B-halogenated derivatives of I. Table I summarizes the remainder of the preparations.

2,4-Dibromo-1,2,3,4,5,6-hexahydro-1,1,3,3,5,5-hexamethylcyclotriboraphosphane (Xa) Using Bromine. A 7.297-g quantity (45.65 mmol) of bromine in 25 ml of dibromomethane was added dropwise (ca. 10 min) to 10.051 g (45.68 mmol) of I in 100 ml of dibromomethane at room temperature. A white 14.09-g solid residue was obtained on removal of the solvent under reduced pressure. Recrystallization and progressive concentration of light petroleum mother liquors furnished several fractions, totaling 7.873 g and melting

within the range of 55–90 °C, and one fraction, 3.684 g, mp 85–100 °C, presumed to be polybrominated material. Fractional sublimation of the latter under high vacuum yielded two distinct fractions: (a) 1.119 g, mp 103–115 °C (subliming at 60–80 °C), and (b) 2.001 g, mp 95–120 °C. Repeated crystallization of the former from isohexane finally gave 0.385 g of Xa, mp 129.5–130.0 °C. Anal. Calcd for $C_6H_{22}B_3Br_2P_3$: C, 18.99; H, 5.97; mol wt 379.5. Found: C, 18.65; H, 5.84; mol wt 374.4. Repeated crystallizations of the latter fraction failed to yield a sharp melting material; fractional sublimation and solution chromatography on alumina also failed to effect separation of a pure product.

2,4-Dibromo-1,2,3,4,5,6-hexahydro-1,1,3,3,5,5-hexamethylcyclotriboraphosphane (Xa) and N-Bromosuccinimide. To 0.8500 g (2.240 mmol) of Xa, mp 129–130 °C, in 75 ml of benzene was added 0.4067 g (2.285 mmol) of N-bromosuccinimide. After 5-h reflux, the solvent was removed at reduced pressure and the residual solid was extracted twice with 40-ml portions of hexane. The 0.2204-g (2.224-mmol) white residue, mp 115–121 °C, represented a 97.3% yield of succinimide. Evaporation of the hexane extracts left a yellow residue which on high-vacuum sublimation at 50–125 °C gave 1.0257 g (99.9% of theoretical tribrominated I) of a white solid, mp 90–130 °C. GLC analysis showed it was a complex mixture of (in order of increasing retention time) 3.8% I (probably present in the starting material), 0.1% unknown, 24.2% Xa, 0.5% unknown, 58.7% tribromo isomer XIb, 6.4% tribromo isomer XIa, and 6.3% tetrabromo isomers. The less mobile tribromocyclotriboraphosphane was identified as the isomer, mp 163–164 °C, by a comparison of retention times under

identical chromatographic conditions; the more mobile isomer had the same retention time as the major component of the residue from which the 163–164 °C melting isomer was originally obtained (cf. Table I).

1,2,3,4,5,6-Hexahydro-1,1,2,2,3,3,4,4,5,5,6,6-dodecamethyl-cyclotriboraphosphane and N-Bromosuccinimide. [(CH$_3$)$_2$PB(CH$_3$)$_2$]$_3$, 0.311 g (1.02 mmol), and 1.084 g (6.09 mmol) of N-bromosuccinimide in 15 ml of benzene were heated under reflux for 4 h as the solution gradually turned dark red and finally black. Unlike the normal reaction, no succinimide was observed suspended in the mixture; however, a black residue adhered to the sides of the flask. The filtered solution was evaporated in a stream of nitrogen and the residue crystallized from methanol–water (3:1) to recover 0.235 g (76%) of starting material (characterized by mp 333–337 °C, undepressed mixture melting point, and infrared spectrum).

1,2,3,4,5,6-Hexahydro-2-iodo-1,1,3,3,5,5-hexamethylcyclo-triboraphosphane (XIV) and N-Iodosuccinimide. A heterogeneous mixture of 0.1130 g (0.325 mmol) of XIV assaying 99.7% by GLC and 0.0768 g (0.341 mmol) of N-iodosuccinimide in 20 ml of benzene was heated under reflux for 6 h. The benzene was removed at reduced pressure leaving a brown residue which was extracted twice with 20-ml portions of hexane. Sublimation of the residue under vacuum at 30–90 °C, after removal of the hexane, provided a white solid, 0.1373 g. GLC analysis established the composition of the product as a mixture consisting of (in order of increasing retention time) 34.7% XIV, 1.5% unknown, 4.1% diiodocyclotriboraphosphane isomer (XVb) plus degradation products (XVb was estimated to be less than half of this peak, or about 2%), and 65.3% diiodocyclotriboraphosphane isomer (XVa).

Registry No. I, 3706-54-5; IIa, 128-09-6; IIb, 128-08-5; IIc, 516-12-1; III, 59830-68-1; IV, 59830-69-2; Va, 59830-70-5; Vb, 59872-27-4; VIa, 59830-71-6; VIb, 59830-72-7; VII, 59830-73-8; VIII, 59830-74-9; IX, 59830-75-0; Xa, 59830-76-1; Xb, 59830-77-2; XIa, 59830-78-3; XIb, 59872-28-5; XII, 59830-79-4; XIV, 59830-80-7; XVa, 59830-81-8; XVb, 59830-82-9; XVI, 59830-83-0; XVII, 59830-84-1.

References and Notes

(1) Now a part of Kerr-McGee Corp., Oklahoma City, Okla.
(2) This work was supported in part by the U.S. Air Force under Contracts AF 33(616)-3506, -5435, -6913, and -7810 monitored by the Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio.
(3) The nomenclature used in this report is that proposed by the International Union of Pure and Applied Chemistry Commission on Nomenclature of Inorganic and Organic Chemistry ("Information Bulletin—Appendices on Tentative Nomenclature, Symbols, Units, and Standards", No. 31, Section D, Aug 1973).
(4) To whom correspondence should be addressed at Modesto Junior College, Modesto, Calif. 95350.
(5) (a) A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, **75**, 3872 (1953); (b) A. B. Burg and G. Brendel, *ibid.*, **80**, 3198 (1958); (c) R. I. Wagner, F. F. Caserio, Jr., L. D. Freeman, and R. D. Stewart, Abstracts, 135th National Meeting of the American Chemical Society, Boston, Mass., April 1959, p 49-O; (d) R. H. Biddulph, M. P. Brown, R. C. Cass, R. Long, and H. B. Silver, *J. Chem. Soc.*, 1822 (1961); (e) M. H. Goodrow, R. I. Wagner, and R. D. Stewart, *Inorg. Chem.*, **3**, 1212 (1964); (f) W. Gee, J. B. Holden, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.*, 3171 (1965).
(6) W. Gee, R. A. Shaw, B. C. Smith, and G. J. Bullen, *Proc. Chem. Soc., London*, 432 (1961).
(7) W. Gee, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.*, 4180 (1964).
(8) H. Nöth and W. Schragle, *Chem. Ber.*, **98**, 352 (1965); *Angew. Chem., Int. Ed. Engl.*, **1**, 457 (1962); *Z. Naturforsch., B*, **16**, 473 (1961).
(9) A. B. Burg, *J. Inorg. Nucl. Chem.*, **11**, 258 (1959).
(10) R. I. Wagner and F. F. Caserio, Jr., *J. Inorg. Nucl. Chem.*, **11**, 259 (1959).
(11) E. Hofmann, British Patent 928 350 (1963); *Chem. Abstr.*, **59**, 12 843 (1963).
(12) R. I. Wagner et al., WADC Technical Report 57-126, Part I, Wright Air Development Center, Air Research and Development Command, Wright-Patterson Air Force Base, Ohio, March 1957 (AD 142028, Available from National Technical Information Service, Alexandria, Va., 22151).
(13) M. H. Goodrow and R. I. Wagner, *Inorg. Chem.*, following paper in this issue; other manuscripts are in preparation.
(14) A. C. Chapman, *Trans. Faraday Soc.*, **59**, 806 (1963).
(15) R. I. Wagner et al., WADC Technical Report 57-126, Part V, Wright Air Development Division, Air Research and Development Command, Wright-Patterson Air Force Base, Ohio, Jan 1961 (AD 458476, available from National Technical Information Service, Alexandria, Va., 22151).
(16) W. Gee, J. B. Holden, R. A. Shaw, and B. C. Smith, *J. Chem. Soc.*, 1545 (1967), have also used N-bromosuccinimide as a selective brominating agents. A series of (C$_6$H$_5$)$_6$P$_3$B$_3$H$_{6-n}$Br$_n$ (n = 1–4) products were prepared from [(C$_6$H$_5$)$_2$PBH$_2$]$_3$ and stoichiometric quantities of IIb in boiling carbon tetrachloride.
(17) M. A. Sens, J. D. Odom, and M. H. Goodrow, *Inorg. Chem.*, preceding paper in this issue.
(18) W. C. Hamilton, *Acta Crystallogr.*, **8**, 199 (1955).
(19) G. J. Bullen and P. R. Mallinson, *J. Chem. Soc.*, 1295 (1973).
(20) A. B. Burg, *Acc. Chem. Res.*, **2**, 353 (1969).
(21) In a private communication, Professor A. B. Burg indicated his assignments of bands associated with the BH$_2$ deduced from the appropriate shifts of bands in the spectra of I and [(CH$_3$)$_2$PBD$_2$]$_3$. We have presented here, in agreement with his assignment of the 810-cm^{-1} band in the spectrum of I to the BH$_2$ wagging mode, seven similar compounds, III, IV, IX, Xa, XIV, XVa, and XVb, all containing >BH$_2$ groups and displaying absorption bands in this region (see Table II). The eight new, more highly halogenated compounds do not absorb in this region indicating the absence of the >BH$_2$ function.
(22) Perkin-Elmer Model 325 infrared spectrophotometer.
(23) The ^{11}B NMR spectrum of the B-monobromo compound (IX) displayed a quartet at 36.5 ppm (>BHBr) and a distorted quintet at 50.6 ppm (>BH$_2$) in a ratio of 1:2, while the unsubstituted trimer (I) shows only a distorted quintet for the >BH$_2$ group centered at 50.5 ppm.
(24) J. J. Neumayer, *Anal. Chim. Acta*, **20**, 519 (1959).
(25) It should be noted that cyclotriboraphosphanes containing a B–H bond should be free of halogen-containing solvent before injection on the column as we suspect further halogenation of the borons occurs when catalyzed by the hot aluminum injection block. Usually solid samples were dissolved in benzene for injection; when solubility problems were encountered, dimethylacetamide was used.