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B-Alkyl and *B*-Aryl Derivatives of 1,2,3,4,5,6-Hexahydro-1,1,3,3,5,5-hexamethylcyclotriboraphosphane[2,3]

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A new synthetic method for *B*-organo-substituted 1,2,3,4,5,6-hexahydrocyclotriboraphosphane derivatives has been developed based on the replacement of *B*-halogen substituents using organometallic reagents. Reported herein are the limitations of the method, with regard to competing degradation, reduction, and halogenation reactions, which influence product yield, degree of alkylation, and isomerization.

Introduction

All reported syntheses of *B*-alkyl-substituted boraphosphane oligomers or polymers have utilized precursors already containing the *B*-alkyl group. The first examples were reported by Burg and Wagner[5] who dehydrobrominated phosphine dimethylbromoborane with triethylamine to obtain an initially monomeric product which polymerized in solution giving rise to $[H_2PB(CH_3)_2]_n$, considered to have a linear structure. The monomer $H_2PB(n\text{-}C_4H_9)_2$, similarly prepared,[6] appeared to polymerize more slowly but like the *B,B*-dimethyl polymer was reactive with oxygen and probably had a linear structure. Attempted pyrolytic dehydrogenation of dimethylphosphine–dimethylborane, $(CH_3)_2PH\cdot BH(CH_3)_2$, was preceded by disproportionation so that the principal product was not a polymeric $(CH_3)_2PB(CH_3)_2$ species but an inhomogeneous material assumed to consist principally of $(CH_3)_2PBHCH_3$ units with lesser amounts of $(CH_3)_2PBH_2$ and $(CH_3)_2PB(CH_3)_2$ units.[5] The volatility of the mixture suggested that

Table I. Preparation of 1,2,3,4,5,6-Hexahydro-2,2,4,4,6,6-hexaorgano-1,1,3,3,5,5-hexamethylcyclotriboraphosphanes

$[(CH_3)_2PBX_2]_3$		Organometallic reagent		Reaction temp, °C	Time, h	$[(CH_3)_2$-$PBR_2]_3$, % yield
X	mmol	Reagent	mmol			
F (I)	0.328	$Al(CH_3)_3$	10.4	100	2	55
	0.327	$Al(CH_3)_3$	7.30	100	6	55
	0.365	$B(CH_3)_3$	21.0	100	144	87
	0.359	$Zn(CH_3)_2$	7.2	100	15	0[a]
	0.303	$Zn(CH_3)_2$	7.2	75	15	0[b]
	0.322	$Zn(CH_3)_2$	7.2	50	12	0[c]
	0.361	$Sn(CH_3)_4$	7.22	100	6	0[d]
	0.553	$LiCH_3$	4.05	25–30	72	0[e]
	0.361	$B(C_2H_5)_3$	7.1	125	12	0[f]
	0.332	$B(C_2H_5)_3$	7.07	125	86	20
	0.288	$Al(C_6H_5)_3$	0.605	100	15	0[f]
	0.313	$Sn(C_6H_5)_4$	2.212	125	17	0[f]
Cl (II)	0.236	$Al(CH_3)_3$	31.2	125	16	95
	0.286	$Zn(CH_3)_2$	7.2	125	16	92
	0.258	$Hg(CH_3)_2$	6.4	145–160	15	0[g]
	2.25	CH_3MgBr	30	142	3	0[h]
	0.350	$Al(C_2H_5)_3$	6.0	125	18	0
	0.284	$Zn(C_2H_5)_2$	~2[i]	125	24	0
	0.287	$B(C_2H_5)_3$	7.07	150	12	
				200	192	0
Br (III)	0.313	$Al(CH_3)_3$	9.43	125	20	95
	0.212	CH_3MgBr	3	25	17	0[h]
I (IV)	0.245	$Al(CH_3)_3$	10.4	150	72	76
H (XIII)	0.508	$Al(CH_3)_3$	6.25	200	18	0[j]
	0.738	$Al(CH_3)_3$	10.4	125	12	0[k]

[a] Complete decomposition of I. [b] Recovered I, 50%. [c] Recovered I, 88%. [d] Recovered I, 11%. [e] Recovered I, trace; plus 29.7 cm^3 of methane. [f] IR spectra indicated partial alkylation (or arylation), but no pure components were isolated. [g] Recovered II, 97%. [h] Recovered II or III, nearly quantitative. [i] As a 25% solution in heptane. [j] Recovered XIII, 87%; 98% at 100 °C. [k] Reaction mixture also contained 0.048 mmol of I_2; recovered XIII, 95% containing 2.7% *B*-mono- and 1.0% *B*-dimethyl derivatives.

cyclotriboraphosphane compounds predominated, but no further characterization was undertaken. Preparation of the fully B-methylated derivative, $[(CH_3)_2PB(CH_3)]_3$, was achieved by treatment of dimethylphosphine dimethylbromoborane with triethylamine in ethereal solution.[5] The only other reported *B*-alkylcyclotriboraphosphane, $[(CH_3)_2PB(n\text{-}C_3H_7)_2]_3$, was obtained on pyrolysis of the adduct $(CH_3)_3Si(CH_3)_2P{\cdot}B(n\text{-}C_3H_7)_2Cl$.[7]

Results

Each of the *B*-hexahalocyclotriboraphosphanes (I–IV[8]) was found to react with one or more methylmetallic reagents as outlined in eq 1, but B-ethylated yields and the amount of

$$[(CH_3)_2PBX_2]_3 + (6/y)MR_y \rightarrow [(CH_3)_2PBR_2]_3 + (6/y)MX_y \qquad (1)$$

I, X = F V, R = CH_3
II, X = Cl VI, R = C_2H_5
III, X = Br VII, R = C_6H_5
IV, X = I

starting material recovered varied considerably, depending on the organometallic reagent employed and on the thermal stability of the *B*-hexahalocyclotriboraphosphane (see Table I). The best yield of V from the fluorinated trimer was obtained using trimethylborane. With trimethylaluminum, I gave a moderate yield of V in a few hours but was accompanied by significant degradation of the starting material, as evidenced by the strong odor of phosphine on workup of the reaction mixture. The methyl derivatives of zinc, tin, and lithium, as well as tetravinyltin, completely degraded I rather than alkylating it. The arylmetallics, tetraphenyltin and triphenylaluminum, although decomposing most of the *B*-hexafluoro compound, did provide detectable quantities of crude partially arylated products, as indicated by infrared spectra which displayed bands characteristic of the cyclotriboraphosphane[9] and phenyl rings. In marked contrast to the *B*-hexafluoro derivative, the *B*-hexachloro- (II), *B*-hexabromo- (III), and *B*-hexaiodocyclotriboraphosphanes (IV) gave high yields of V on reaction with both trimethylaluminum and dimethylzinc.

Unlike the smooth alkylation reaction and well-defined product obtained with certain methylmetallic reagents, the analogous ethylmetallic derivatives produced mixtures of partially B-ethylated cyclotriboraphosphanes as a result of only partial replacement of halogen accompanied by some reduction. Only with *B*-hexafluorocyclotriboraphosphane (I) and triethylborane at 125 °C was complete ethylation attained, and then only in low yield. Application of the organometallic alkylation reaction to partially *B*-halogenated cyclotriboraphosphanes[10] produced mixtures of partially *B*-alkylated cyclotriboraphosphanes as the result of several competing reactions, alkylation, halogenation, and reduction. The data summarized in Table II show the distribution, as determined by gas–liquid chromatography (GLC) of the partially B-alkylated products derived from 2-iodo- (VIII), 2-bromo- (IX), 2,4-dibromo- (X), and 2,4,6-tribromo-1,2,3,4,5,6-hexahydro-1,1,3,3,5,5-hexamethylcyclotriboraphosphanes (XI) and various organometallic reagents. Product analysis in each case established that alkylation (or arylation) was nonspecific and failed to follow the simple stoichiometry illustrated in eq 2

$$\begin{aligned}&[(CH_3)_2PBH_2]_{3-n}[(CH_3)_2PBHX]_n + n(CH_3)_3Al \rightarrow \\ &\quad [(CH_3)_2PBH_2]_{3-n}[(CH_3)_2PBHCH_3]_n + n(CH_3)_2AlX\end{aligned} \qquad (2)$$

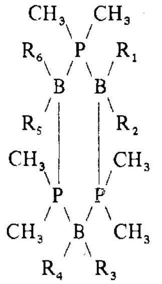
using trimethylaluminum. 2-Iodocyclotriboraphosphane (VIII) produced the greatest distribution of products with trimethylaluminum, as only one-third of the anticipated 2-methyl derivative (XIIa, Figure 1) was formed, while the major component was the mixture of *B*-dimethyl isomers, accompanied by an appreciable amount of $[(CH_3)_2PBH_2]_3$ (XIII, Figure 1). Lesser, but still appreciable, quantities of byproducts were observed when either dimethylzinc, dimethylcadmium, or dimethylmercury was used as the alkylating agent.

A cursory study of the *B*-bromo derivatives of XIII and trimethylaluminum (Table II) confirmed the nonspecificity of the alkylation reaction. Thus, the 2,4-dibromo trimer X (stereoisomer mp 129–130 °C)[10] and trimethylaluminum gave by GLC an isomeric mixture of *B*-dimethyl derivatives of XIII

Table II. Reactions of Some Partially B-Halogenated 1,2,3,4,5,6-Hexahydro-1,1,3,3,5,5-hexamethylcyclotriboraphosphanes with Organometallic Reagents

Cyclotriboraphosphane derivatives	g	mmol	Organometallic reagent: Reagent	Organometallic reagent: mmol	Time, h	Temperature, °C	Product weight, g	% distribution of $(CH_3)_6P_3B_3H_{6-n}R_n$ for values of n: 0	1	2	3	4
2-Iodo (VIII)	0.3192	0.918	$Al(CH_3)_3$	10.43	9	100	0.1592	11.1	33.8	54.7	0.3	0.1
	0.3198	0.920	$Zn(CH_3)_2$	10.21	9	100	0.1745	6.6	74.4	18.7	0.3	
	0.3345	0.962	$Cd(CH_3)_2$	13.9	9	130	0.1944	2.2	78.9	16.4	2.5	
	1.0388	2.99	$Cd(CH_3)_2$	13.9	9	125	0.6160	8.8	71.9	18.2	1.1	
	0.3172	0.913	$Hg(CH_3)_2$	7.68	9	125	0.3145[a]					
	0.1803	0.519	$Hg(CH_3)_2$	7.68	8	175–250	0.0033[b]	30.0	9.4	58.2	2.4	
	0.2013	0.579	$Sn(CH_3)_4$	7.22	9	175	0.1910[c]					
	1.5256	0.439	$Zn(C_2H_5)_2$	14.3	10	100	0.9611[d]	53.4	44.9	1.5	0.2	
	0.0974	0.280	$Mg(C_6H_5)_2$[e]	1.62	20	125	0.0964[f]					
	0.1544	0.444	$BrMgC_6H_5$	3.0	15	125	0.1337[g]					
2-Bromo (IX)	0.1045	0.348	$Zn(C_6H_5)_2$	1.273	17	125	0.0837[h]					
2,4-Dibromo[i] (X)	0.2003	0.527	$Al(CH_3)_3$	15.1	18	140	0.1007	0.9	7.2	80.2	10.0	1.7
2,4,6-Tribromo[j] (XI)	0.1217	0.265	$Al(CH_3)_3$	11.5	18	125	0.0595	0.1	0.3	2.6	93.0	4.0

[a] No methylated products detected; recovered VIII, 0.3145 g (99.1%), assaying 100% by GLC. [b] Also 47.4 cm^3 of methane and elemental mercury. [c] No methylated products detected; recovered 62.3% VIII with remainder unidentifiable. [d] Contained 12.4% VIII by GLC; other assignments were based on relative volatilities obtained from GLC data and should be regarded as tentative only. [e] Halogen free in benzene; W. Strohmeier, *Chem. Ber.*, 88, 1218 (1955). [f] Contained biphenyl, XIII, VIII, and XIIg,h (0.0350 g, 34% yield isolated by sublimation and crystallization from 1:1 ethanol/water). [g] Contained biphenyl, VIII, and XIIf,g,h (0.0145 g, 8.7% yield isolated by sublimation and crystallization from 10:1 ethanol/water). [h] Contained 0.0590 g of XIIf (57% yield isolated by sublimation). [i] Stereoisomer mp 129–130 °C (GLC assay, 99.4%). [j] Stereoisomeric mixture, mp 112–115 °C (IR assay, ~95%).



XIIa, $R_1 = CH_3$; $R_{2-6} = H$
b, $R_{1-2} = CH_3$; $R_{3-6} = H$
c, $R_{1-3} = CH_3$; $R_{4-6} = H$
d, $R_{1-4} = CH_3$; $R_{5-6} = H$
e, $R_1 = C_2H_5$; $R_{2-6} = H$
f, $R_1 = C_6H_5$; $R_{2-6} = H$
g, $R_{1-2} = C_6H_5$; $R_{3-6} = H$
h, $R_{1,3} = C_6H_5$; $R_{2,4-6} = H$
XIII, $R_{1-6} = H$

Figure 1.

as the major product (80.2%), accompanied by lesser quantities of the parent trimer XIII and the *B*-monomethyl, *B*-trimethyl, and *B*-tetramethyl derivatives. Similarly, 2,4,6-tribromocyclotriboraphosphane (XI) and trimethylaluminum yielded the *B*-trimethyl isomers as the major product (90.1%), containing lesser amounts of the unsubstituted, *B*-mono-, *B*-di-, and B-tetramethylated cyclotriboraphosphanes. In order to confirm the assignment of the peaks, larger quantities of B-methylated derivatives were separated by preparative-scale GLC, and one isomer from each isomeric mixture was isolated by fractional crystallization and definitively characterized.

An attempt to methylate XIII with trimethylaluminum was made in order to determine whether the organometallic compound was reacting with a BH_2 group. No reaction was observed either at 100 °C during 8 h (98% recovery of XIII) or under more drastic conditions, 18 h at 200 °C, where the trimethylaluminum was completely decomposed while 97% of XIII was recovered unchanged. When a small quantity of iodine was added to the mixture of these reagents, formation of *B*-monomethyl and *B*-dimethyl derivatives was observed.

Ethylation of a partially B-halogenated cyclotriboraphosphane (VIII) with diethylzinc resulted in extensive reduction with concomitant decreased yield of the expected product, XIIe of Figure 1 (see Table II).

B-Iodocyclotriboraphosphane (VIII) and ethereal phenylmagnesium bromide failed to give aryl substitution at reflux but in a sealed tube at 125 °C produced biphenyl, *B*-phenylcyclotriboraphosphane (XIIf), and *B*-diphenyl-substituted cyclotriboraphosphanes, from which only a single *B*-diphenylcyclotriboraphosphane isomer (XIIg,h) could be recovered in low yield. Diphenylmagnesium gave similar results. In contrast to the organomagnesium compounds, diphenylzinc and VIII gave the expected *B*-phenylcyclotriboraphosphane in 57% yield.

Discussion

The data summarized in Table I for the syntheses of V are alone sufficient to conclude that the hexatomic ring of *B*-hexafluorocyclotriboraphosphane (I) is considerably less thermodynamically stable than in the chloro, bromo, and iodo analogues. Corroboratory evidence is found in the relative ease of hydrolysis and air oxidation of the hexafluoro derivative.[8] Clearly the most valuable organometallic reagent for methylation of *B*-hexahalocyclotriboraphosphanes is $Al(CH_3)_3$ because of the relatively high yields and short reaction times.

Complete ethylation of *B*-hexahalocyclotriboraphosphanes is considerably more difficult presumably as a result of the lesser stability of the ethylmetallic reagents compared with methylmetallic compounds. For example, thermal decomposition of triethylaluminum (eq 3) to a species, possibly

$$Al(C_2H_5)_3 \rightarrow HAl(C_2H_5)_2 + CH_2{=}CH_2 \tag{3}$$

diethylaluminum hydride, capable of reducing B–Cl to B–H (eq 4) apparently does occur since B–H absorption is quite

$$>\!B{-}Cl + HAl(C_2H_5)_2 \rightarrow\ >\!B{-}H + Al(C_2H_5)_2Cl \tag{4}$$

pronounced in the infrared spectrum and thus accounts for the multicomponent mixtures derived whenever ethylmetallic reagents were employed. That no ethene was observed is not unexpected since under these Ziegler-type polymerization conditions it would be converted to higher alkyl groups which would be difficult to detect by infrared spectroscopy in the alkylated product mixtures.

When partially B-halogenated cyclotriboraphosphanes were alkylated with methylmetallic reagents, appreciable quantities of methylated products which contained either a greater or lesser number of *B*-methyl groups than the original number of *B*-halo substituents in the starting material were observed. These products could not arise solely by simple redistribution of an initial alkylation product since in all experiments the more highly B-methylated by-products predominated. The data in Table II indicate that the methylation reaction proceeds under approximately comparable conditions with decreasing amounts of reduction (cf. eq 4) with increasing atomic number of the metal, as would be expected from the decreasing thermal stabilities of the respective binary metal hydrides.[11] Since $(CH_3)_3Al$ failed to react with $>BH_2$ groups in the absence of halogen compounds, methylation of *B*-halo-substituted cyclotriboraphosphanes, in excess of the initial number of halo substituents, is presumably preceded by halogenation (eq 5, forward reaction) by the organometallic halides arising from

$$[(CH_3)_2PBH_2]_{3-n}[(CH_3)_2PBHCH_3]_n + (m+n)(CH_3)_2AlX \rightleftarrows [(CH_3)_2PBH_2]_{3-n-m}[(CH_3)_2PBXCH_3]_n[(CH_3)_2PBHX]_m + (m+n)(CH_3)_2AlH \tag{5}$$

the alkylation reaction (eq 2). However, the possibility that $(CH_3)_3Al$, $(CH_3)_2AlX$, or $(CH_3)_2AlH$ might directly exchange a methyl group for the hydridic hydrogen in a $>BHCH_3$ group is not ruled out. The co-product organometallic hydride produced during ring halogenation presumably could reduce any halogenated species and would give rise to the observed unsubstituted cyclotriboraphosphane XIII or its *B*-methyl derivatives with fewer $\geqslant B–CH_3$ groups than original $\geqslant B–X$ groups (eq 5, reverse reaction). Similar boron–halogen reductions have been observed from reactions of lithium aluminum hydride and $[(C_2H_5)_2PBCl_2]_3$ at 100 °C, leading to $[(C_2H_5)_2PBH_2]_3$.[12] Our studies have shown that the *B*-bromo trimer (IX) is slowly reduced to XIII with lithium aluminum hydride in refluxing ether.

The infrared spectra of partially B-methylated XIII listed in Table III provide supporting evidence for certain of the band assignments made by Chapman[9] and are the basis for structural assignments of the single isolated isomers of these compounds. The $>BH_2$ in-plane (near 1110 cm^{-1}) and out-of-plane (near 1000 cm^{-1}) deformation bands and the $>BH_2$ in-plane (near 660 cm^{-1}) and out-of-plane (near 805 cm^{-1}) rocking modes found in XIII[13] persist in the series of *B*-mono-, *B*-di-, *B*-tri-, and *B*-tetramethyl compounds and are absent in the fully B-methylated compound (V). The presence of the $>BH_2$ group in both *B*-tri- and *B*-tetramethyl-substituted compounds establishes their structures as 1,1,2,2,3,3,4,5,5-nonamethylcyclotriboraphosphane (XIIc) and 1,1,2,2,3,3,4,4,5,5-decamethylcyclotriboraphosphane (XIId). Further supporting evidence for these structures is found in the $>B–C_2$ antisymmetrical stretching bands observed at 974 (in-phase) and 1012 cm^{-1} (degenerate) in dodecamethylcyclotriboraphosphane. The $>B–C_2$ antisymmetrical stretching bands are observed not only in the *B*-tetra- and *B*-trimethyl derivatives but in the *B*-dimethyl compound as well. The structure of the latter compound was unequivocally established as 1,1,2,2,3,3,5,5-octamethylcyclotriboraphosphane (XIIb) by ^{11}B NMR.[14,15] It is noteworthy that a prominent band of medium intensity appears near 1057 cm^{-1} in the *B*-mono- and *B*-trimethyl derivatives only and is possibly associated with the in-plane B–H deformation of the $>BHCH_3$ group.

The structures of the most readily isolated *B*-di-, *B*-tri-, and *B*-tetramethyl isomers of XIII are most interesting in that they do not correspond to the structures of the most abundant isomers of the *B*-di-, *B*-tri-, and *B*-tetrachloro compounds[10] from which they were prepared. This observation suggests firstly that the $>BHCH_3$ group is more readily halogenated than is the $>BH_2$ group (eq 5, forward reaction) and secondly that either the $>BClCH_3$ is more readily methylated than is the $>BHCl$ (eq 5, reverse reaction) or that preferential reduction of $>BHCl$ groups relative to $>BClCH_3$ occurs.

Table III. Infrared Frequencies (cm^{-1}) of Some *B*-Organo Derivatives of 1,2,3,4,5,6-Hexahydro-1,1,3,3,5,5-hexamethylcyclotriboraphosphane in KBr[a]

XIII	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.
XIIa	2995 m, 2930 s, 2850 w, 2385 vs, 2350 vs, 2210 w, 1423 s, 1416 s, 1297 s, 1285 s, 1108 s, 1056 m, 1005 m, 995 s, 930 vs, 882 vw, 864 vw, 852 s, 807 m, 746 s, 717 vs, 658 m
XIIb	3000 m, 2940 s, 2850 m, 2385 vs, 2350 vs, 2210 w, 1427 s, 1413 s, 1294 s, 1282 m, 1109 m, 1103 m, 1018 w, 1005 w, 987 m, 928 vs, 887 w, 867 w, 844 m, 822 vw, 805 w, 746 s, 717 vs, 668 vw
XIIc	2995 s, 2930 vs, 2850 s, 2380 vs, 2340 vs, 2210 w, 1445 m, 1423 s, 1418 s, 1295 vs, 1282 m, 1108 m, 1058 m, 1017 w, 1005 w, 992 s, 924 vs, 885 w, 860 w, 845 m, 823 vw, 807 m, 743 vs, 716 vs, 654 vw
XIId	3000 s, 2940 vs, 2850 s, 2375 s, 2350 vs, 2210 w, 1430 s, 1417 s, 1295 vs, 1280 m, 1110 m, 1040 w, 1017 s, 1004 w, 980 s, 943 s, 920 vs, 886 w, 874 vw, 846 m, 823 vw, 804 w, 744 vs, 713 vw, 658 w
V	2900 vs, 2825 s, 1412 s, 1383 m, 1297 s, 1276 m, 1012 s, 974 s, 928 vs, 908 vs, 863 w, 837 m, 820 w, 770 w, 738 s, 702 s
XIIe	2945 m, 2915 s, 2860 m, 2815 w, 2370 vs, 2335 vs, 2200 w, 1458 w, 1424 s, 1413 s, 1370 vw, 1301 m, 1286 m, 1253 vw, 1110 m, 1106 m, 1068 w, 1003 w, 994 m, 934 vs, 922 vs, 888 vw, 869 w, 846 m, 816 w, 807 w, 746 s, 740 m, 718 s, 712 s, 672 w, 661 w
XIIf	3060 w, 2985 w, 2905 w, 2810 vw, 2385 vs, 2345 vs, 2205 w, 2005 vw, 1952 vw, 1882 vw, 1822 vw, 1588 vw, 1562 vw, 1490 w, 1430 s, 1417 s, 1302 m, 1287 m, 1261 vw, 1162 w, 1107 m, 1068 w, 1033 w, 1006 m, 995 m, 945 s, sh, 926 vs, 892 w, 869 w, 851 m, 822 vw, sh, 807 m, 762 vs, 749 vs, 742 s, sh, 719 vs, 705 vs, 672 w
XIIg	3020 w, 2970 w, 2900 w, 2800 vw, 2380 vs, 2335 vs, 2200 vw, 1600 w, 1484 m, 1427 m, 1412 m, 1390 vw, 1299 m, 1281 m, 1248 vw, 1157 vw, 1107 m, 1002 m, 990 m, 943 s, sh, 928 vs, 904 vw, 870 vw, 851 m, 835 m, 815 m, 807 m, 761 vs, 748 s, 744 s, 718 vs, 686 m, 674 w

[a] vw, very weak; w, weak; m, medium; s, strong; vs, very strong; sh, shoulder.

The *B*-monoethyl derivative was separated and purified by preparative GLC and definitively characterized by elemental analyses, molecular weight, and infrared spectrum, which also showed a band at 1068 cm^{-1}, presumably associated with the in-plane B–H deformation in the $BHCH_2CH_3$ grouping (Table III).

The infrared spectra (Table III) of the $>B$-aryl derivatives, as expected, were more complex than those of the alkyl analogues and in the case of the *B*-diphenyl compound did not provide conclusive evidence permitting a definitive choice between the possible isomers, 2,2-diphenyl- (XIIg) and *cis*- or *trans*-2,4-diphenylcyclotriboraphosphane (XIIh).

Experimental Section

All melting points, taken in sealed capillary tubes under a nitrogen atmosphere, are uncorrected. Molecular weights were determined by the vapor pressure osmometric method[16] using ca. 0.05 M benzene solutions. Infrared spectra were obtained on KBr disks using a Perkin-Elmer Model 21 spectrophotometer with sodium chloride optics. Gas–liquid chromatographic (GLC) separations were effected utilizing a Beckman Megachrom instrument equipped with a 2-m silicone–Celite column; analytical data were obtained on the same type column with a Perkin-Elmer Fractometer 54B.

2,2,4,4,6,6-Hexahalo-1,2,3,4,5,6-hexahydro-1,1,3,3,5,5-hexamethylcyclotriboraphosphanes and Organometallic Reagents. The following example typifies the experimental operations used to treat the *B*-hexahalocyclotriboraphosphanes with organometallic reagents. The exceptions were methyllithium in ether and methyl Grignard reagent in *n*-butyl ether, which were added to a solution of the cyclotriboraphosphane in the same solvent under nitrogen.

Table IV. Analysis and Physical Properties of Some *B*-Organo Derivatives of 1,2,3,4,5,6-Hexahydro-1,1,3,3,5,5-hexamethylcyclotriboraphosphane

Compound	Melting point, °C	Form	Empirical formula	% C		% H		Mol wt	
				Calcd	Found	Calcd	Found	Calcd	Found
XIIa	34.5–35.0	Needles (subl.)	$C_7H_{26}B_3P_3$	35.68	35.45	11.12	10.94	235.7	248
XIIb	77.0–78.0	Needles (CH_3OH)	$C_8H_{28}B_3P_3$	38.48	38.57	11.30	11.11	249.7	247
XIIc	57.0–58.5	Needles (CH_3OH)	$C_9H_{30}B_3P_3$	40.99	40.87	11.47	11.41	263.7	252
XIId	172.5–175.0	Needles (CH_3OH)	$C_{10}H_{32}B_3P_3$	43.25	43.11	11.61	11.63	277.7	270
XIIe	36.5–37.0	(subl.)	$C_8H_{28}B_3P_3$	38.48	38.35	11.30	11.16	249.7	252
B-Hexaethyl derivative of XIII	195–202	Needles (CH_3OH)	$C_{18}H_{48}B_3P_3$	55.39		12.40		390.3	
XIIf	101.0–101.5	Needles (1:1 C_2H_5OH/H_2O)	$C_{12}H_{28}B_3P_3$	48.41	48.41	9.48	9,72	297.7	305.9
XIIg	163–164	Fine needles (10:1 C_2H_5OH/H_2O)	$C_{18}H_{32}B_3P_3$	57.83	57.76	8.63	8.89	373.8	379

2,2,4,4,6,6-Hexachloro-1,2,3,4,5,6-hexahydro-1,1,3,3,5,5-hexamethylcyclotriboraphosphane (0.1012 g, 0.236 mmol) was weighed into a heavy wall Pyrex tube of 6-mL capacity. Under high vacuum, 3.0 mL (2.25 g, 31.2 mmol) of trimethylaluminum was condensed into the tube at −196 °C. The tube was sealed, allowed to warm to ambient temperature, and then heated at 125 °C for 16 h. A trace of noncondensable gas, presumably methane, was observed on opening the tube at −196 °C on the vacuum line. The excess organometallic reagent was distilled from the tube at ambient temperature. (An alternate procedure was to destroy excess organometallic reagent by cautious hydrolysis or methanolysis.) The residual white solid was sublimed under high vacuum at a bath temperature of 90–100 °C from the reaction tube through an all-glass system to an air-cooled condenser to obtain 0.0688 g (0.225 mmol, 95.3%) of dodecamethylcyclotriboraphosphane (V), mp 336–338 °C. The product was definitively identified by an undepressed mixture melting point (336–337.5 °C) with authentic material[5] and direct comparison of infrared spectra.

Partially B-Halogenated 1,2,3,4,5,6-Hexahydro-1,1,3,3,5,5-hexamethylcyclotriboraphosphanes and Methylmetallic Reagents. Experimental techniques for the series of reactions listed in Table II were essentially identical with those given for the reactions of the B-hexahalogenated compounds. One preparation and typical isolation procedure is given below.

To 14.7 g of a mixture of partially B-chlorinated derivatives[10] of XIII (GLC assay, 0.3% XIII, 18.7% *B*-chloro, 33.0% *B*-dichloro, 23.0% *B*-trichloro, 19.4% *B*-tetrachloro, 3.6% *B*-pentachloro, and 2.0% II) was added 32.4 g (280 mmol) of dimethylzinc. After heating at 110 °C for 9 h, the reaction tube was opened under vacuum and the excess dimethylzinc, 19.4 g (168 mmol), was recovered. The residue, heated slowly to 125 °C under high vacuum, gave 5.9877 g of sublimate trapped at −78 °C. The sublimate was dissolved in benzene and analyzed by GLC on a 2-m silicone grease–Celite column at 250 °C with helium carrier gas at 45 mL/min and 20 psig. Under these conditions, the approximate peak retention times (min) for the following *B*-methyl derivatives of XIII were: XIII, 3.0; *B*-monomethyl (XIIa), 4.0; *B*-dimethyl isomers, 5.1; *B*-trimethyl isomers, 6.9; *B*-tetramethyl isomers, 9.1; *B*-pentamethyl, 12.5; *B*-hexamethyl (V), 16.2. Peak assignments were confirmed by comparison of retention times with those of the subsequently obtained pure compounds, XIII, XIIa–d, and V, each of which passed through the column without redistribution of the *B*-methyl groups (see Table IV). The major components, containing 1–4 *B*-methyl groups, were then separated on a preparative scale GLC apparatus.

The *B*-monomethyl compound (XIIa) was separated by preparative scale GLC and sublimed at ambient temperatures to give analytically pure white needles.

The *B*-dimethyl fraction (GLC assay, 99.3%) was fractionally sublimed at 25 °C under vacuum to obtain 1.2000 g of crystalline material (mp 66.0–74.0 °C, softened at 59 °C), which after three recrystallizations from methanol gave needles. High vacuum resublimation at 25–35 °C gave 0.4660 g of a single isomer, XIIb.

The *B*-trimethyl fraction (GLC assay, 96.5%) was fractionally sublimed under vacuum at 25 °C to give 0.9712 g of opaque crystals (mp 55.0–57.0 °C, softened at 50 °C). Several fractional crystallizations from methanol followed by sublimation under vacuum at 25 °C provided XIIc.

Fractional sublimation of the *B*-tetramethyl fraction (GLC assay, 95.5%) under high vacuum at 60-85 °C provided 1.0503 g of a white solid (mp 140.5–149.0 °C, softened at 126 °C). Several recrystallizations from methanol followed by high vacuum sublimation at 35–55 °C provided XIId.

Reduction of 2-Bromo-1,2,3,4,5,6-hexahydro-1,1,3,3,5,5-hexamethylcyclotriboraphosphane (IX). A mixture of 0.1660 g (0.553 mmol) of the *B*-bromo trimer and 0.0295 g (0.778 mmol) of lithium aluminum hydride in 10 mL of ether was heated under reflux for 7 h and decomposed by the addition of water. After extraction with 10 mL of ether and evaporation of the ether extract, the residue was sublimed. The 0.1622-g sublimate, mp 70–75 °C, was found to contain 14.2% XIII and 85.8% *B*-bromo trimer by GLC. Since the starting material contained 1.0% XIII determined under identical GLC conditions, the reduction reaction occurred to the extent of about 13%.

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References and Notes

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(2) This work was supported in part by the United States Air Force under Contracts AF 33(616)-6913 and -7810, monitored by the Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio.
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Phosphoranes. 7. Chemistry and Stereochemistry of Monofunctionally Substituted Tetraalkylphosphoranes, $(CH_3)_2(CF_3)_2PY$ [Y = F, Cl, OCH_3, SCH_3, and $N(CH_3)_2$], Including a Second Example of Individual Nonequivalence of Fluorine Atoms in a Trifluoromethyl Group Attached to Phosphorus[1]

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Methylation of $(CF_3)_2PCl_3$ with excess $(CH_3)_4Pb$ leads to dimethylated molecular phosphoranes, $(CF_3)_2P(CH_3)_2Cl$, which can be fluorinated (with SbF_3) to $(CF_3)_2P(CH_3)_2F$, converted to the derivatives $(CF_3)_2(CH_3)_2PECH_3$ (E = O and S) by means of the silyl reagent $(CH_3)_3SiECH_3$, and converted to $(CF_3)_2(CH_3)_2PN(CH_3)_2$ with $(CH_3)_2NH$. NMR spectroscopic studies strongly suggest molecular phosphorane structures in which halogens (X = F and probably Cl) and CF_3 groups occupy axial positions in the trigonal bipyramid. Alkaline hydrolysis of all compounds results in the formation of 2 mol of CF_3H and the $(CH_3)_2PO_2^-$ ion, whereas neutral hydrolysis yields 1 mol of CF_3H and $CF_3(CH_3)_2PO$. The very low temperature (−110 °C) ^{19}F NMR spectrum of $(CH_3)_2(CF_3)_2PSCH_3$ consists of an $[AB_2]_2P$ spectral pattern with $^2J_{PF_A} = 19.4$, $^2J_{PF_B} = 9.5$, and $^2J_{F_AF_B} = 108$ Hz, showing that F atom equivalence within both CF_3 groups has been destroyed, presumably as the result of steric interactions with the SCH_3 group.

Introduction

Extension of methylation reactions to bis(trifluoromethyl)halogenophosphoranes leads to a series of tetraalkylphosphoranes with two methyl and two trifluoromethyl substituents which are complementary to the monomethylated tetraalkylphosphoranes[1] reported earlier. In these and related[2-5] systems, we have found that temperature-dependent ^{19}F (and also ^1H, ^{31}P, and ^{13}C) NMR spectroscopy appears to indicate the position of the substituent in the five-coordinate molecular framework. This and related work have led to an empirical axial preference series.[6] Herein we describe the preparation, characterization, and substitutional preferences in the series $(CH_3)_2(CF_3)_2PY$, where Y = F, Cl, OCH_3, SCH_3, and $N(CH_3)_2$, and an interesting case of magnetic nonequivalence of the F atoms in the (axial) CF_3 NMR of $(CH_3)_2(CF_3)_2PSCH_3$ at very low temperatures.

Results and Discussion

Synthesis. The action of $(CH_3)_4Pb$ on $(CF_3)_2PCl_3$ leads to $(CH_3)_2(CF_3)_2PCl$ or $CH_3(CF_3)_2PCl_2$[3] according to the reaction conditions (eq 1 and 2). Reaction 1 therefore provides an

$$(CF_3)_2PCl_3 + (CH_3)_4Pb \rightarrow CH_3(CF_3)_2PCl_2 + (CH_3)_3PbCl \qquad (1)$$

$$(CF_3)_2PCl_3 + 2(CH_3)_4Pb \rightarrow (CH_3)_2(CF_3)_2PCl + 2(CH_3)_3PbCl \qquad (2)$$

alternative route to the latter compound first synthesized by direct oxidative chlorination of $CH_3(CF_3)_2P$.[3] Fluorination of the chlorophosphorane was smoothly effected by SbF_3 at ordinary temperatures (eq 3),

$$(CH_3)_2(CF_3)_2PCl \xrightarrow{SbF_3} (CH_3)_2(CF_3)_2PF \qquad (3)$$

and the silyl reagents $(CH_3)_3SiOCH_3$ and $(CH_3)_3SiSCH_3$ converted the chloro- or fluorophosphorane to the methoxy or methylthio derivative in good yields (eq 4). Both of the resultant derivatives appear

$$(CH_3)_2(CF_3)_2PX + (CH_3)_3SiECH_3 \rightarrow (CH_3)_2(CF_3)_2PECH_3 + (CH_3)_3SiX \qquad (4)$$

X = F or Cl; E = O or S

to be stable at ordinary temperatures, in contrast to the dimethylamino derivative, $(CH_3)_2(CF_3)_2PN(CH_3)_2$, prepared by direct dimethylaminolysis (eq 5), which appeared to de-

$$(CH_3)_2(CF_3)_2PCl + 2(CH_3)_2NH \rightarrow (CH_3)_2(CF_3)_2PN(CH_3)_2 + (CH_3)_2NH_2Cl \qquad (5)$$

compose readily in the vacuum system whenever transfer was attempted. Because of this unexpected instability, only NMR spectral characterization of the aminophosphorane was achieved.

Neutral hydrolysis of all of the stable phosphoranes yielded 1 molar equiv of CF_3H, leaving $CF_3(CH_3)_2PO$ in solution (eq 6). The phosphine oxide, $CF_3(CH_3)_2PO$,[7] a volatile crystalline

$$(CF_3)_2(CH_3)_2PX + H_2O \rightarrow CF_3H + CF_3(CH_3)_2PO + HX \qquad (6)$$

solid, was synthesized independently from $CF_3(CH_3)_2PCl_2$ and H_2O and from $CF_3(CH_3)_2PCl_2$ and $[(CH_3)_3Si]_2O$.

Alkaline hydrolysis of the phosphoranes yielded 2 molar equiv of CF_3H, with the $(CH_3)_2PO_2^-$ ion remaining in solution (eq 7).

$$(CF_3)_2(CH_3)_2PX + 2H_2O \xrightarrow{OH^-} 2CF_3H + (CH_3)_2PO_2^- + H^+ + HX \qquad (7)$$

Mass Spectroscopy. In keeping with the typical behavior of pentacoordinate fluorophosphoranes[8] and trifluoromethylphosphoranes,[1,3-5] parent molecular ions were not observed in the mass spectra of any of these tetraalkyl-

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