SECTION A

Inorganic, Physical, and Theoretical Chemistry

Boron and Phosphorus Chemistry. Part I. Simple, High-yield Syntheses of Pure Chlorodiorganoboranes ‡

By **Leo F. Hohnstedt, James P. Brennan, and Kennard A. Reynard,***† Department of Chemistry, St. Louis University, St. Louis, Missouri 63103, U.S.A.

The reaction of R_2BNH_2(R = Bu^n or Pr^n) with phosphorus pentachloride and with hydrogen chloride gave chlorodiorganoboranes in high yields. Diethylaminodi-n-butylborane and phosphorus pentachloride produced chlorodi-n-butylborane. Separate experiments demonstrated that reaction of trialkylboranes to form $R^1{}_2BSR^2$ and then $R^1{}_2BNH_2$ followed by reaction with phosphorus pentachloride or hydrogen chloride produced $R^1{}_2BCl$ without the necessity for isolation of intermediates.

THE chemistry of aminodiorganoboranes (R_2BNH_2) has received only limited study to date. The literature contains reports on the pyrolysis [1,2] of these compounds and on their reactions with hydrogen chloride,[1,3] boron trifluoride,[4] amines,[5,6] carbon dioxide,[7] and carbon disulphide.[7]

Recently Mikhailov published [5,8] a simple two-step reaction scheme which produced aminodialkylboranes in 88—96% yield from readily available starting materials. This reaction scheme is shown in equation (1).

$$\begin{gathered} R^1{}_3B + R^2SH \longrightarrow R^1{}_2BSR^2 + R^1H \\ R^1{}_2BSR^2 + NH_3 \longrightarrow R^1{}_2BNH_2 + R^2SH \qquad (1) \\ R^1 = \text{Alkyl, allyl} \end{gathered}$$

By this convenient synthetic method, further chemical characterization of aminodialkylboranes was undertaken. The reactions of R_2BNH_2 and of one *N*-disubstituted derivative, $R^1{}_2BNR^2{}_2$, with phosphorus pentachloride and with hydrogen chloride are reported.

Preparation of Chlorodialkylboranes.—Until recently chlorodiorganoboranes were prepared by prolonged and tedious methods which often involved multiple separations and purifications,[9] and pure products were often obtained in poor yields. Recently, two reports [10,11] appeared which detailed methods for the preparation of chlorodiorganoboranes in high yield as shown in equations (2) and (3). Reaction (2) gave products which are

$$2BX_3 + R_4Sn \longrightarrow 2R_2BX + SnX_4 \qquad (2)$$

$$BX_3 + R_3B \xrightarrow{MBH_4} R_2BX + RBX_2 \qquad (3)$$

separated easily by distillation.

Our investigations of aminodiorganoboranes have led to a method, outlined by equations (1) and (4), which provides a simple preparation of pure chlorodialkylboranes in high yields from readily available starting materials.

$$R_2BNH_2 + PCl_5 \xrightarrow{CCl_4} R_2BCl + [PCl_4NH_2] \qquad (4)$$

In the cases studied, reaction began immediately when the phosphorus pentachloride and the aminoborane were mixed and was accompanied by the formation of a white powder, which for the aminodialkyl derivatives, was found to have the approximate empirical formula PCl_4NH_2. The chlorodiorganoboranes were obtained in yields approaching 100% conversion.

The reaction of diethylaminodi-n-butylborane with phosphorus pentachloride proceeds smoothly and rapidly even though there are no labile hydrogens attached to nitrogen. Thus, phosphorus pentachloride directly chlorinates the B–N bond since *in situ* generation of hydrogen chloride is ruled out. In the case of R_2BNH_2, hydrogen chloride generation cannot be ruled out, but is considered unlikely.

As shown in equation (5), pure chlorodimethylborane

$$Me_2BNH_2 + HCl \longrightarrow [ClMe_2BNH_3] \xrightarrow[100\%]{+HCl} Me_2BCl + NH_4Cl \qquad (5)$$

was obtained in yields approaching 100% by earlier workers.[1] We found that the higher homologues were produced with yields of 80% or less under the conditions used in this study for the reaction of hydrogen chloride and R_2BNH_2.

Yields were lowered by 5—10% when the borane

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† *Present address:* Horizons, Inc., 23800 Mercantile Rd., Beachwood, Ohio 44122.

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intermediates were not isolated before the addition of hydrogen chloride or phosphorus pentachloride [equation (6)].

$$R^1_3B \xrightarrow[-R^1H]{+R^2SH} R^1_2BSR^2 \xrightarrow[-R^2SH]{+NH_3} R^1_2BNH_2 \xrightarrow{+HCl\ or\ PCl_5} R^1_2BCl + \text{byproduct(s)} \quad (6)$$

$$R = \text{alkyl}$$

Provided substituent groups on R^1 or R^2 are not effected, the procedures outlined are proposed as fast, simple, and general methods to produce pure chlorodiorganoboranes.

Preparation of Chlorodiphenylborane.—This procedure involves the first preparation of an aminodiarylborane from a triarylborane without proceeding through chlorodiarylborane. The method developed by Mikhailov for the general preparation of aminodiallyl-[12] and aminodialkyl-boranes[8] [equation (1)] was not extended to include aryl derivatives. Alkanethiols were generally employed for these reactions. As shown in equation (7), Mikhailov[13] employed chlorodiphenylborane for the preparation of aminodiphenylborane.

$$Ph_2BCl + Bu^nSH \xrightarrow{-HCl} Ph_2BSBu^n \xrightarrow{+NH_3} Ph_2BNH_2 + Bu^nSH \quad (7)$$

We found that α-toluenethiol rather than an alkanethiol was required for reaction with triphenylborane to produce an intermediate which gave aminodiphenylborane. The success of this reaction may be related either to the difference in boiling points or acidities of the two thiols. The postulated intermediate is the diarylthioborinic acid ester, Ph_2BSCH_2Ph.

TABLE 1

Analysis, melting point or boiling point for amino- and chloro-diorganoboranes

Compound	Analysis (%) [a] C	H	B	N	Cl	M.p. or b.p.[d]	Ref.
Ph_2BNH_2	79·55 (79·57)	6·91 (6·68)	6·14 (5·98)	7·18 (7·74)		141—142° (141—142, 129—130°)	*e*
Ph_3BNH_3	82·35 (83·40)	6·99 (7·00)	4·01 (4·17)	5·48 (5·41)		221—223° (216—217°)	*f*
$Bu^n_2BNEt_2$	73·10 (73·07)	14·33 (14·34)	5·75 (5·49)	7·35 (7·10)		97—98°/10 mm.	
Bu^n_2BCl [b,c]	59·81 (59·86)	11·31 (11·31)	6·88 (6·74)		22·10 (22·09)	54—55°/10 mm. (54/10)	*g*
Pr^n_2BCl [b,c]			8·55 (8·17)			126—127°/760 mm. (127)	*h*
Ph_2BCl [b]	69·74 (71·87)	5·07 (5·03)	5·43 (5·40)				*i*

[a] Required values in parentheses. [b] I.r. spectra confirmation. [c] Chemical reaction confirmation. [d] Lit. values in parentheses. [e] Ref. 13; G. Coates and J. Livingstone, *J. Chem. Soc.*, 1961, 1000. [f] B. Mikhailov and N. Fedotov, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1960, 1590 (*Chem. Abs.*, 1955, 9353d). [g] V. Buls, O. Davis, and R. Thomas, *J. Amer. Chem. Soc.*, 1957, **79**, 337. [h] D. Dollimore and L. Long, *J. Chem. Soc.*, 1953, 3906. [i] L. Bellamy, W. Gerrard, M. F. Lappert, and R. Williams, *J. Chem. Soc.*, 1958, **2412**.

The Material $[PCl_4NH_2]$.—When $[PCl_4NH_2]$, the solid byproduct from the reaction of R_2BNH_2 and phosphorus pentachloride, was heated, either as a solid or slurry, hexachlorophosphazene was produced. Yields were found to be dependent on experimental conditions, but $(NPCl_2)_3$ was produced in somewhat better yield than had previously been obtained[14-16] from the reaction between phosphorus pentachloride and ammonium chloride.

On the basis of solubility studies which led to the isolation of several different solids, $[PCl_4NH_2]$ is believed to be a mixture. Therefore, we do not consider the aforementioned decomposition to give $(NPCl_2)_3$ a validation of the reaction scheme shown in equation (8),

$$PCl_5 + NH_4Cl \longrightarrow PCl_4NH_2 + 2HCl \longrightarrow PCl_3NH + HCl \longrightarrow (NPCl_2)_x + xHCl \quad (8)$$

which often has been postulated[16-19] for the formation of halogenophosphazenes.

EXPERIMENTAL

Materials.—All manipulations and reactions were carried out either in a dry nitrogen atmosphere or in a vacuum line. Tri-n-butyl- and tri-n-propyl-borane were prepared and purified by standard procedures.[20,21] A commercial sample of triphenylborane was purified by sublimation followed by vacuum distillation. The distillate was sublimed once more and gave a white crystalline material, m.p. 137—142° (lit., 136°[22] and 151°[23]). Analytical and i.r. spectral data are reported in Tables 1 and 2.

Preparation of Aminodialkylboranes.[8]—Excess of ethanethiol was condensed in a flask containing trialkylborane. The contents of the flask were stirred and reacted below room temperature. When evolution of gas ceased, the mixture was heated under reflux for 15—30 min. The mixture was cooled to room temperature and excess of ammonia was passed through or over the solution. Passage of ammonia was maintained while the reaction mixture was refluxed for *ca.* 30 min. The resulting mixtures were separated and purified by vacuum distillation ($Bu^n_2BNH_2$, b.p. 62—64°/13 mm.; $Pr^n_2BNH_2$, b.p. 65—66°/110 mm.).

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TABLE 2

I.r. spectra of aminodiphenyl-, aminodi-n-propyl- and aminodi-n-butyl-borane (fluorolube and Nujol mulls)

I.r. absorption frequencies (cm.$^{-1}$) [a]

Ph_2BNH_2	$Pr^n{}_2BNH_2$	$Bu^n{}_2BNH_2$
708s		
721m		
747s		
845m		
895m		895w,br
905w,sh	905w,br	
935vw		
958w		
980w		
	1000s	
1007vw		1005s
1030m		
1060s		
1078w,sh		
	1090s	
	1138s,sh	
1155s		
1228w		
		1230m,br
	1249s,sh	
1270w		1320s,br
	1340s,sh	
1414s		1455s
	1458s	
1550s		1550w,br
	1555w	
		1610s
	1615s	
	2905s	2905s
2980vw		
3285vw		
	3380m	
		3435m
	3450m	
		3510m

[a] s, Strong; m, moderate; w, weak; v, very; b, broad; sh, shoulder.

Contrary to reports[8] no solid ammonia adduct was observed in the reactions. When less than a stoicheiometric quantity of ethanethiol was used, the yield appeared to be dependent on the amount of thiol, in contrast to the report that only a catalytic amount of thiol need be present.[5]

Preparation of Aminodiphenylborane.—Triphenylborane (1·7 g., 7·2 mmoles) and α-toluenethiol (2 ml., 17 mmoles) were heated under reflux for 1 hr. Upon cooling to room temperature, a cloudy solution was obtained. Passage of ammonia over the solution caused heating and the reaction mixture solidified. The solid was recrystallized from benzene (very soluble) to give white needles which were soluble in ether and insoluble in carbon tetrachloride.

Triphenylborane–Ammonia Adduct.—In an unsuccessful attempt to prepare aminodiphenylborane, triphenylborane and excess of butanethiol were heated under reflux overnight. Ammonia was passed over the solution for several hours and volatiles were removed from the reaction mixture *in vacuo*. Sublimation of the residue gave Ph_3BNH_3 rather than Ph_2BNH_2.

Preparation of Diethylaminodi-n-butylborane.—Excess of diethylamine dissolved in carbon tetrachloride reacted exothermically with chlorodi-n-butylborane in carbon tetrachloride to form a white precipitate after a brief induction period. The reaction mixture was cooled, filtered, and solvent was removed at atmospheric pressure. Vacuum distillation gave a colourless liquid (76% yield).

The product was obtained in 86% yield from tri-n-butylborane by successive addition and refluxing of a 10% excess of ethanethiol and of diethylamine.

Reaction of Aminodialkylboranes or Diethylaminodi-n-butylborane with Phosphorus Pentachloride.—Phosphorus pentachloride and carbon tetrachloride were slurried and aminodialkylborane or diethylaminodi-n-butylborane in carbon tetrachloride was added dropwise. In the case of R_2BNH_2 equimolar quantities of starting materials were necessary to avoid side reactions of $[PCl_4NH_2]$. Slight heating and immediate formation of a white precipitate were observed. There was no indication of hydrogen chloride evolution. The mixture was filtered and the solid was washed several times with carbon tetrachloride followed by anhydrous ether. The combined filtrate upon distillation yielded chlorodialkylboranes in *ca.* 100% conversion. The identity of the products was confirmed by elemental analysis, i.r. spectral comparisons with authentic samples, and/or chemical characterization. Substitution of dry ether or hexane for carbon tetrachloride gave excellent yields of borane product but the solid byproduct changed to a tacky mass after several hours.

Preparation of Chlorodiphenylborane.—Crystalline aminodiphenylborane was added in excess to a stirred carbon tetrachloride slurry containing phosphorus pentachloride. A change in the mixture gradually took place with phosphorus pentachloride disappearing and the aminodiphenylborane appearing to transform into a white powder. Chlorodiphenylborane was obtained by filtration and distillation. Residual solid was found to have the same i.r. spectrum as the white solid (empirical formula PCl_4NH_2) formed in similar reactions employing alkyl derivatives, except for the superimposition of some bands also present in aminodiphenylborane. Attempts to clean the solid product by washing with benzene were unsuccessful because the product oiled. This impure product was probably caused by the method of preparation which employed a double slurry.

Reaction of Aminodialkylboranes and Hydrogen Chloride.—Gaseous hydrogen chloride was passed over or through an ether solution of aminodialkylborane which was stirred and cooled to 0°. The exothermic reaction gave a white solid immediately. Direct distillation from the reaction mixture gave chlorodialkylboranes. Filtration of the reaction mixtures was difficult due to the small particle size of solid byproduct. This problem was obviated by use of benzene as reaction medium and reflux of the mixture before filtration. The white solid formed in the reactions was believed to be predominately ammonium chloride.

Preparation of Chlorodialkylboranes from Trialkylboranes.—The isolation of the intermediates was shown to be unnecessary in the preparation of chlorodialkylboranes. After refluxing and cooling the ethanethiol and trialkylborane (n-butyl or n-propyl) mixture, excess of ammonia was passed through the solution which was again refluxed. The solution was cooled and the thiol was removed *in vacuo*. The reaction mixture was diluted with anhydrous carbon tetrachloride and either was added dropwise to a phosphorus pentachloride slurry or hydrogen chloride was passed through the solution. Pure chlorodialkylboranes were isolated by the methods already discussed, but yields were slightly less (70—80%).

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