in part, under Contract AF33(616)-5874 with the U. S. Air Force, the sponsoring agency being the Aeronautical Research Laboratory of Wright Air Development Center, Air Research and Development Command. Such support is gratefully acknowledged. The authors also wish to express their sincere appreciation to the Chrysler Corporation for the heterodyne beat apparatus used in this work.

Contribution from Chemistry Hall,
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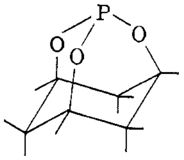
Phosphorus Complexes of Group III Acids. III. Boron Acids and 2,8,9-Trioxa-1-phospha-adamantane

By J. G. Verkade and C. W. Heitsch

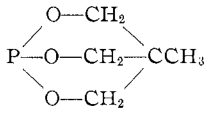
Received October 6, 1962

One to one complexes of the bicyclic phosphite 2,8,9-trioxa-1-phospha-adamantane, $C_6H_9O_3P$, have been prepared with the acids BH_3, B_3H_7, $B(CH_3)_3$, and BF_3. The adduct $C_6H_9O_3PBH_3$ has a melting point of 247–251° dec. and a measured dipole moment of 8.82 ± 0.05 D. The higher moment of this compound compared to $CH_3C(CH_2O)_3PBH_3$ (8.60 ± 0.05 D.) is expected in view of the higher moment of the ligand, $C_6H_9O_3P$, which was more accurately determined in this work to be 4.51 ± 0.05 D. ΔH for the process: $C_6H_9O_3P(s) + B(CH_3)_3(g) = C_6H_9O_3PB(CH_3)_3(s)$ from pressure–temperature data was estimated to be -15.9 ± 0.1 kcal./mole. The foregoing dipole moment data and the value for ΔH as well as the displacement of $(CH_3)_3N$ from $(CH_3)_3NBH_3$ indicate that $C_6H_9O_3P$ is a better ligand than $CH_3C(CH_2O)_3P$ toward BH_3 and $B(CH_3)_3$.

The synthesis in 20% yield of the phosphite ester 2,8,9-trioxa-1-phospha-adamantane ($C_6H_9O_3P$) was first reported by Stetter and Steinacker.[1] Brown, Verkade, and Piper recently reported an improved synthesis (70% yield)[2] by a *trans*-esterification procedure. The synthesis and properties of adducts of



boron Lewis acids and a phosphite having the caged structure



have been investigated previously.[3] It was decided, however, that a comparison of the ligand properties of the adamantane system toward some boron reference acids such as BH_3 and $B(CH_3)_3$ would be of interest. Since the change in steric requirements between the two phosphite ligands upon adduct formation will be quite small, any change in ligand properties will be more purely a function of the lone-pair electron availability on the phosphorus which in turn is determined largely by any change in O–P–O bond angle and inductive effects due to the variation in carbon skeletons.

Experimental

Preparation of $C_6H_9O_3P$.—The phosphite, $C_6H_9O_3P$, was prepared by a method described previously.[2] Although $C_6H_9O_3P$ is more stable to moisture than is $CH_3C(CH_2O)_3P$, a small amount of ether-insoluble material is formed on prolonged storage of the pure ester *in vacuo* over $CaCl_2$ with intermittent exposure to the atmosphere for use. Final purification, therefore, was necessary before use in a reaction and this was effected by filtering a solution of $C_6H_9O_3P$ in dry ether under an inert atmosphere.[3]

Preparations and Analytical Data.—The experimental procedures used to obtain diborane, tetraborane, boron trifluoride, boron trimethyl, trimethylamine, trimethylamineborane, the adducts formed with the boron acids, and the pure solvents used in this research, as well as the physical properties of the adducts discussed, are described elsewhere except where indicated.[3]

The method of purifying $B(CH_3)_3$ reported by Brown was found to be tedious and wasteful since a significant portion of the $B(CH_3)_3$ could not be recovered from the triethylamine complex.[4] Moreover, other workers have found this product to be impure.[5] The following improved purification procedure was developed, which proved to be markedly simpler than that previously reported.[5]

Approximately 15 g. of $CH_3C(CH_2O)_3P$ was dissolved in 100 ml. of anhydrous ether and filtered to remove insoluble impurities. When attached to the vacuum line, about 2 l. (1 atm., 25°) of crude $B(CH_3)_3$ gas was condensed into the solution and stirred. The $CH_3C(CH_2O)_3PB(CH_3)_3$ complex formed as a precipitate. The volatile components of this system were removed at −23° and the pure $B(CH_3)_3$ removed at 25° and passed through a trap at −78° to condense traces of $CH_3C(CH_2O)_3P$. The product so prepared was quite pure as shown by its infrared spectrum.[6] The residue of $CH_3C(CH_2O)_3P$ then could be used repeatedly. This solid was found to absorb $B(CH_3)_3$ rapidly so that in subsequent cycles the step involving ether solution could be eliminated.

The BH_3 adduct of $C_6H_9O_3P$ decomposed with melting from 247–251°.

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[1] H. Stetter and K. Steinacker, *Ber.*, **85**, 451 (1952).

[2] T. L. Brown, J. G. Verkade, and T. S. Piper, *J. Phys. Chem.*, **65**, 2051 (1961).

[3] C. W. Heitsch and J. G. Verkade, *Inorg. Chem.*, **1**, 392 (1962).

[4] H. C. Brown, *J. Am. Chem. Soc.*, **67**, 374 (1945).

[5] G. S. Ross, D. Enagonio, C. A. Hewitt, and A. R. Glascow, *J. Res. Natl. Bur. Std.*, **66A**, 59 (1962).

[6] C. W. Heitsch, to be published.

TABLE I

DIPOLE MOMENT DATA AND INDICES OF REFRACTION OF SOLUTIONS OF $C_6H_9O_3P$ AND $C_6H_9O_3PBH_3$ IN 1,4-DIOXANE AT 25°

$C_6H_9O_3P$ X (mole fraction)	ε	$C_6H_9O_3PBH_3$ X (mole fraction)	ε
0.0102	2.524	0.00547	2.710
.00692	2.430	.00344	2.497
.00450	2.359	.00242	2.430
.00404	2.346	.00124	2.319
.00231	2.295	.000659	2.267
.00000	2.228	.000302	2.233
		.000000	2.210

$\frac{\partial \epsilon}{\partial X} = 29.18$ $\qquad$ $\frac{\partial \epsilon}{\partial X} = 90.15$

$\frac{\partial n_D}{\partial X} = 0.17$ $\qquad$ $\frac{\partial n_D}{\partial X} = 0.19$

$\mu = 4.51 \pm 0.05$ D. $\qquad$ $\mu = 8.82 \pm 0.05$ D.

Anal. Calcd. for $BPO_3C_6H_{12}$: B, 6.22; C, 41.42; H (total), 6.95; H (hydridic), 1.72. Found: B, 6.24; C, 41.67; H (total), 6.91; H (hydridic), 1.72.

The B_3H_7 adduct of $C_6H_9O_3P$ decomposed without melting at about 270°.

Anal. Calcd. for $B_3PO_3C_6H_{16}$: B, 16.30; C, 36.10; H (total), 8.03; H (hydridic), 3.55. Found: B, 15.60; C, 37.89; H (total), 8.09; H (hydridic), 3.53.

The hydridic hydrogen was measured by hydrolyzing a weighed sample of the adduct with 5 *M* HCl in a sealed tube and measuring the evolved hydrogen volumetrically. That the $B(CH_3)_3$ and BF_3 compounds are 1:1 adducts is shown by the stoichiometry data summarized in Fig. 1.

Dielectric constant data and indices of refraction for solutions of $C_6H_9O_3P$ and $C_6H_9O_3PBH_3$ are presented in Table I. Dielectric constant *vs.* concentration data are represented in Fig. 2.

The *d* values and relative intensities from the Debye–Scherrer X-ray powder patterns for the ligand and the BH_3 and B_3H_7 adducts are given in Table II.

TABLE II

INTERPLANAR SPACINGS AND INTENSITIES

$C_6H_9O_3P$ *d*, Å.	I^a	$C_6H_9O_3PBH_3$ *d*, Å.	I^a	$C_6H_9O_3PB_3H_7$ *d*, Å.	I^a
6.30	1/2	7.22	1	7.06	1
5.73	1	6.79	10	6.36	10
5.54	10	6.00	4	5.42	1
4.48	8	5.38	10	4.88	10
3.91	4	4.96	9	4.18	5
3.47	2	4.39	6	3.88	5
3.21	1	4.28	1	3.18	2
3.10	3	4.12	1	3.05	3
3.03	2	3.99	1	2.67	7
2.69	7	3.92	1	2.45	1
2.61	1/2	3.68	1	2.31	2
2.56	2	3.58	2	2.28	1
2.51	2	3.40	1/2	2.12	1
2.35	1	3.26	5	1.88	2
2.31	1	3.16	2	1.79	2

[a] Larger numbers represent greater relative intensities.

Pressure–temperature data for the vapor tension of $B(CH_3)_3$ over $C_6H_9O_3P$ are presented in Table III. Equilibrium conditions for this system could not be attained rapidly as previously described for the $CH_3C(CH_2O)_3P$–$B(CH_3)_3$ system.[3] Therefore the adduct was first prepared by the reaction of $C_6H_9O_3P$ in ether with an excess of $B(CH_3)_3$ with subsequent removal of ether and $B(CH_3)_3$ between −45° and room temperature. The $C_6H_9O_3P$ crystals prepared in this fashion rapidly absorbed $B(CH_3)_3$ to reach equilibrium.

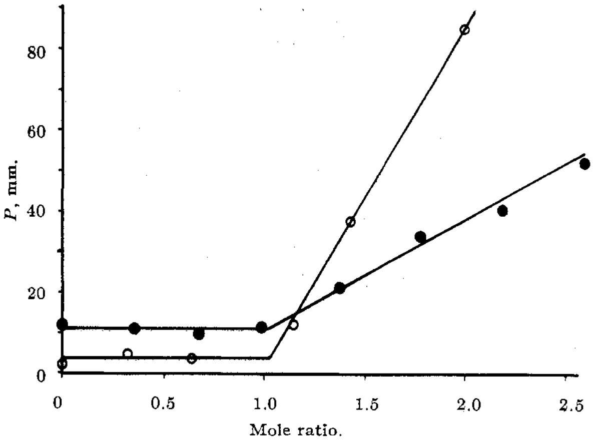

Fig. 1.—*P* (mm.) *vs.* mole ratio of $B(CH_3)_3$–$C_6H_9O_3P$ (●) at −45° in $CHCl_3$ and BF_3–$C_6H_9O_3P$ (○) at −78° in $CHCl_3$.

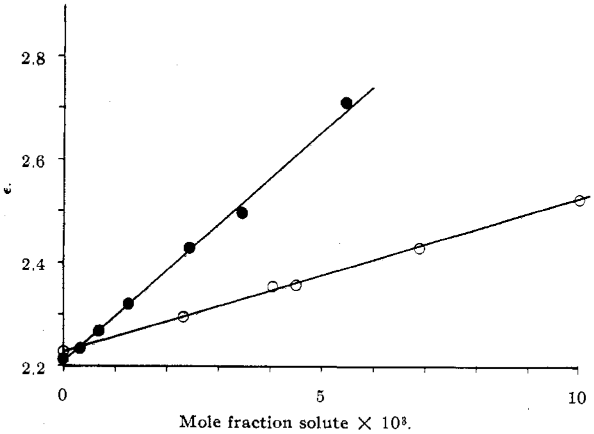

Fig. 2.—Dielectric behavior of solutions of $C_6H_9O_3P$ (○) and $C_6H_9O_3PBH_3$ (●) in 1,4-dioxane.

Displacement Reactions.—A sealed tube of approximately 60-cc. volume with a break-off tip, containing 1.42 mmoles of $C_6H_9O_3P$ and 2.87 mmoles of $(CH_3)_3NBH_3$, was heated in an oven to 110°. A single liquid phase existed in the tube under these conditions.

After 72 hr. at 110°, the components which were volatile at 0° were removed and found to contain a trace of non-condensable gas and 0.58 mmole of $N(CH_3)_3$ as determined by a standard Kjehldahl procedure and identified by its gas-phase infrared spectrum. The infrared spectrum of the non-volatile residue from the reaction was recorded in $CHCl_3$ solution. With the

TABLE III

PRESSURE–TEMPERATURE DATA FOR $C_6H_9O_3PB(CH_3)_3$

Temp., °K.	Pressure obsd., mm.	Pressure calcd.,^{a} mm.
318.19	53.2	51.6
321.21	65.4	65.4
323.98	80.0	80.9
326.33	95.9	96.7
328.73	117	116
329.01	117	118
330.38	128	131
332.05	148	148
335.00	184	182
335.95	195	197
337.90	218	224
341.26	278	283
344.48	354	352
345.18	380	369
347.79	445	440

[a] $\log P$ (mm.) $= 12.6430 - 3477.94/T$.

exception of a medium intensity band at 855 cm.$^{-1}$, this spectrum resembled a combination of the spectra of $(CH_3)_3NBH_3$[7] and $C_6H_9O_3P$.[8] An examination of the spectra of these two materials and of $C_6H_9O_3PBH_3$ reveals that the only band unique to the latter is the 855 cm.$^{-1}$ peak, assigned to the B–P stretching mode.[8] On this basis, the presence of $C_6H_9O_3PBH_3$ in the reaction residue was assumed. These facts imply the equilibrium

$$(CH_3)_3NBH_3 + C_6H_9O_3P = (CH_3)_3N + C_6H_9O_3PBH_3$$

The reverse of the above reaction was observed in tetrahydrofuran (THF) solution. A fresh sample of $C_6H_9O_3PBH_3$ (0.84 mmole) and 1.76 mmoles of $N(CH_3)_3$ were contained in a tube similar to that described above along with approximately 15 cc. of THF. After 72 hr. at room temperature (25–30°), the tube was opened and the components which were volatile at −23° removed. These contained a trace of non-condensable gas, the THF solvent, and excess $N(CH_3)_3$. The THF–$N(CH_3)_3$ mixture was treated with an excess of anhydrous HCl in the vacuum line, removed to the atmosphere, dissolved in water, and analyzed for nitrogen by the Kjehldahl method. A total of 1.12 mmoles of $N(CH_3)_3$ was found in the mixture, implying the consumption of 0.64 mmole in the reaction. The infrared spectrum of the nonvolatile residue in $CHCl_3$ was similar to that for the residue recovered from the forward (fusion) reaction.

Discussion

On the basis of scale models, $C_6H_9O_3P$ and $CH_3C(CH_2O)_3P$ are rigid but essentially strainless caged structures. Because of the similarity of the structures of the two phosphites, very little difference in their donor abilities should arise from differences in steric hindrance to coördination or from skeletal differences *per se*[9] if anomalous solvent effects with one of the ligands in complex formation can be excluded. The variation in donor properties of these ligands should arise primarily from the change in electronic environment around the phosphorus atoms in the two donor molecules and the moments of the ligands. That the electronic environments around the phosphorus atom in $CH_3C(CH_2O)_3P$ and $C_6H_9O_3P$ are different is substantiated by P^{31} nuclear magnetic resonance studies.[10] F^{19}, H^1, P^{31}, and B^{11} nuclear magnetic resonance studies are in progress on the adducts to further determine the nature of the bonding in these compounds.

In this work, three sources of experimental data have been investigated, where feasible, which elucidate the difference in ligand properties of $CH_3C(CH_2O)_3P$ and $C_6H_9O_3P$. The dipole moments of the two ligands and their BH_3 adducts are compared as well as the heats of association of their $B(CH_3)_3$ adducts. Finally, the abilities of $CH_3C(CH_2O)_3P$ and $C_6H_9O_3P$ to displace $N(CH_3)_3$ from $(CH_3)_3NBH_3$ are contrasted.

Because of crystal lattice effects in the solid ligands and their BH_3 and $B(CH_3)_3$ adducts, a satisfactory comparison of the analogous solid addition compounds is precluded. However, some knowledge of the relative magnitudes of these effects can be gained from melting points and dielectric constant data taken in solution if dipole–dipole interactions are predominant in these molecular solids compared to local moment effects. Comparisons of the displacement reaction equilibria and heats of association also yield qualitative information on the lattice energies of the ligands.

Table IV

Comparison of Dipole Moments of $C_6H_9O_3P$ and $CH_3C(CH_2O)_3P$ and their BH_3 Adducts in 1,4-Dioxane at 25°

Compound	μ, D.	Δμ, D.
$CH_3C(CH_2O)_3P$	4.15[2]	0.36
$C_6H_9O_3P$	4.51	
$CH_3C(CH_2O)_3PBH_3$	8.60	0.22
$C_6H_9O_3PBH_3$	8.82	

Dipole Moments.—A summary of the dipole moment values to be discussed appears in Table IV. Although the value for the dipole moment of $C_6H_9O_3P$ was reported to be 4.7 D., an uncertainty of 0.2 D. was indicated[2] due to suspected partial oxidation. For the purpose of this work, the dielectric constant measurements were repeated under rigorously anaerobic conditions. The quality of the present data indicates a value of 4.51 ± 0.05 D. for the dipole moment of $C_6H_9O_3P$; a value substantially higher than that for $CH_3C(CH_2O)_3P$ (4.15 ± 0.05 D.)[2] measured in the same solvent, 1,4-dioxane.

If dipole–dipole interactions can be considered as the main contribution to the lattice energy of these molecules, evidence for the higher lattice energy of $C_6H_9O_3P$ arises from the dielectric constant data for two ligands. It is possible that the main contribution to the larger moment in $C_6H_9O_3P$ stems from the presence of more electron induction from the additional carbon groups. Although the effect of small O–P–O bond angle changes from one ligand to the other cannot be ruled out, crude calculations on the basis of P^{31} nuclear magnetic resonance data indicate a bond angle difference of less than 1°.[10] X-Ray measurements are in progress to elucidate this point.

The higher melting point of $C_6H_9O_3P$ (208–209°)[2] compared to $CH_3C(CH_2O)_3P$ (97–98°)[11] indicates that $C_6H_9O_3P$ has the higher lattice energy since the molecular weights are reasonably similar (mol. wt.: $C_6H_9O_3P$, 160; $CH_3C(CH_2O)_3P$, 148). This is further substantiated by the lower solubility of $C_6H_9O_3P$ in non-polar solvents such as hydrocarbons or slightly polar solvents such as chloroform and ether.

The relatively high melting point with decomposition of $C_6H_9O_3PBH_3$ (247–251°) compared to the melting point of $CH_3C(CH_2O)_3PBH_3$ (199°)[3] implies a larger lattice energy for the $C_6H_9O_3P$ complex. It is interesting to note the large difference in the melting points of the ligands (109°) compared to that of the adducts (61°). Undoubtedly the lattice energy difference in the adducts is not as great as that in the ligands. If the lattice energies in these compounds are largely due to dipole–dipole interactions, then a similar conclusion can be derived from the polarization data. The larger difference in the dipole moments of the

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(7) B. Rice, R. V. Galiano, and W. J. Lehman, *J. Phys. Chem.*, **61**, 1222 (1957).

(8) C. W. Heitsch and J. G. Verkade, *Inorg. Chem.*, **1**, 863 (1962).

(9) It is interesting to speculate at this point how various atoms or groups in place of the oxygen atoms in the ligand molecules would affect their donor properties. Work involving the synthesis of such ligands with atoms or groups of different electronegativity adjacent to the phosphorus is now in progress.

(10) J. G. Verkade and R. W. King, *Inorg. Chem.*, **1**, 948 (1962).

(11) J. G. Verkade and L. T. Reynolds, *J. Org. Chem.*, **25**, 663 (1960).

ligands (0.35 D.) compared to that of the adducts (0.22 D.) again suggests that there should be a larger lattice energy difference for the ligands.

Heats of Association.—In the temperature range indicated in Table III, the vapor pressures of $C_6H_9O_3P$ and the $B(CH_3)_3$ complex are less than 1 mm. Hence, it was assumed that the pressure was due to pure $B(CH_3)_3$. The data in Table III afforded a value of $\Delta H_{\text{assoc}} = -15.9 \pm 0.1$ kcal./mole for the reaction

$$B(CH_3)_3(g) + C_6H_9O_3P(s) = C_6H_9O_3PB(CH_3)_3(s)$$

It can be concluded, therefore, that $C_6H_9O_3P$ is a better donor toward $B(CH_3)_3$ than is $CH_3C(CH_2O)_3P$ since $\Delta H_{\text{assoc}} = -14.4 \pm 0.5$ kcal./mole for the reaction

$$B(CH_3)_3(g) + CH_3C(CH_2O)_3P(s) = CH_3C(CH_2O)_3PB(CH_3)_3(s)^3$$

However, $C_6H_9O_3P$ is still a weaker base toward $B(CH_3)_3$ than is $N(CH_3)_3$ in the reaction

$$N(CH_3)_3(s) + B(CH_3)_3(g) = (CH_3)_3NB(CH_3)_3(s)$$

where $\Delta H_{\text{assoc}} = -25.1$ kcal./mole.[3] It is probable that a comparison of $C_6H_9O_3P$ and $(CH_3)_3N$ in the gas phase would show them to be much more similar. The comparison made here in the solid phase reflects the differences in lattice energies; an effect which must enhance the apparent stability of the trimethylamine adduct.

Displacement Reactions.—Under the conditions employed in a previous investigation,[3] $CH_3C(CH_2O)_3P$ would not displace $N(CH_3)_3$ in the reaction

$$CH_3C(CH_2O)_3P + (CH_3)_3NBH_3 = CH_3C(CH_2O)_3PBH_3 + N(CH_3)_3$$

whereas the reverse reaction could be brought to completion. In contrast, $C_6H_9O_3P$ will substantially displace $N(CH_3)_3$ in the reaction

$$C_6H_9O_3P + (CH_3)_3NBH_3 = C_6H_9O_3PBH_3 + N(CH_3)_3$$

but the reaction is only partially reversed under the same conditions. Hence, $C_6H_9O_3P$ is a stronger base than $CH_3C(CH_2O)_3P$ with respect to BH_3 also.

If steric effects can be neglected in the comparison of $C_6H_9O_3P$ and $N(CH_3)_3$, then the use of either $B(CH_3)_3$ or BH_3 as reference acids should give similar results. Yet relative to $B(CH_3)_3$, solid $N(CH_3)_3$ is the stronger of the two bases by 9.2 kcal., while the liquid phase displacement reactions show that, relative to BH_3, the two ligands are much more comparable. This variation probably is due to lattice energy effects. The energies in these systems can be represented in a cyclic fashion

$$\begin{tikzcd}
L(s) + B(CH_3)_3(g) \arrow[r, "-\Delta H"] \arrow[d, "+\Delta H_v"] & LB(CH_3)_3(s) \\
L(g) + B(CH_3)_3(g) \arrow[r, "\Delta H'"] & LB(CH_3)_3(g) \arrow[u, "-\Delta H_v'"']
\end{tikzcd}$$

where $L = N(CH_3)_3$ or $C_6H_9O_3P$. $\Delta H = \Delta H' + (\Delta H_v' - \Delta H_v)$.

The equilibria observed in the liquid phase displacement reactions indicate that the enthalpies of formation of the adducts are similar under these conditions. To a rough approximation the same should be true of the gas phase. Thus $\Delta H'$ for the $C_6H_9O_3P$–$B(CH_3)_3$ system is probably very close to that for the $N(CH_3)_3$–$B(CH_3)_3$ system. The differences in ΔH must be due to the difference in the quantities $(\Delta H_v' - \Delta H_v)$ for both systems. This difference in turn probably is due mainly to differences in ΔH_v, another manifestation of the high lattice energy of $C_6H_9O_3P$.

Acknowledgments.—We wish to thank Mr. T. J. Huttemann for some of the dielectric constant measurements. J. G. V. also wishes to thank the National Science Foundation for a grant in support of this work. The contribution of the sample of $(CH_3)_3NBH_3$ by the Callery Chemical Company is greatly appreciated.

CONTRIBUTION FROM THE GORGAS LABORATORY, ROHM AND HAAS COMPANY,
REDSTONE ARSENAL RESEARCH DIVISION, HUNTSVILLE, ALABAMA

The Amine Complexes of Aluminum Hydride. V.[1] Hydrido Aluminum Borohydride Derivatives

BY JOHN K. RUFF

Received December 17, 1962

A series of compounds $H_{3-x}Al(BH_4)_x \cdot N(CH_3)_3$ (x = 1, 2, and 3) and $H_{2-x}Al(BH_4)_xN(CH_3)_2$ (x = 1 and 2) were prepared by a metathetical reaction between $LiBH_4$ and the corresponding chloro derivatives. Their properties and reactions with trimethylamine and mercuric chloride are discussed.

Aluminum borohydride was first prepared by the interaction of aluminum trimethyl and diborane.[2] The subsequent availability of lithium borohydride resulted in the development of a better preparative method[3]

$$3LiBH_4 + AlCl_3 \longrightarrow 3LiCl + Al(BH_4)_3$$

and this reaction has been extended to the preparation

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(1) This work was performed under Contract No. DA-01-021 ORD 5135.

(2) H. I. Schlesinger, R. T. Sanderson, and A. B. Burg, *J. Am. Chem. Soc.*, **62**, 3421 (1940).

(3) H. I. Schlesinger, H. C. Brown, and E. K. Hyde, *ibid.*, **75**, 209 (1953).