TABLE VI

DISTRIBUTION OF TETRAALKYLTETRAZENES AS A FUNCTION OF THE MOLE RATIO OF 1,1-DIMETHYLHYDRAZINE AND 1,1-DIETHYLHYDRAZINE

	Reactants		Found			Calculated		
No.	DMH	DEH	TMT	DED-MT	TET	TMT	DED-MT	TET
1	1.00	1.00	0.95	1.94	1.11	1.00	2.00	1.00
			0.97	1.92	1.10			
2	2.00	1.00	3.88	3.95	1.17	4.00	4.00	1.00
3	1.00	2.00	0.95	3.89	4.16	1.00	4.00	4.00
4	1.00	1.00	0.97	2.06	0.96	1.00	2.00	1.00
5[a]	1.00	1.00	1.06	1.99	0.96	1.00	2.00	1.00
6	3.00	1.00	8.66	6.06	1.28	9.00	6.00	1.00
7	1.00	3.00	0.98	5.95	9.07	1.00	6.00	9.00
9[b]	1.00	1.00	0.98	2.06	0.98	1.00	2.00	1.00
10[c]	1.00	1.00	0.95	1.97	1.03	1.00	2.00	1.00

[a] In this experiment the 1,1-dialkylhydrazines were oxidized separately, the solutions mixed and then neutralized to form the tetraalkyltetrazenes. [b] Three reactants in equal mole ratio, 1,1-dimethyl-, 1,1-diethyl- and 1,1-di-*n*-propylhydrazine. [c] Four reactants in equal mole ratio, all in *b* and in addition 1,1-di-*n*-butylhydrazine.

TABLE VII

TETRAALKYLTETRAZENES FORMED IN MULTIPLE COMPONENT SYSTEMS

		Mole ratios		
		Found		Calcd.
Tetrazene	Elution time, min.	9	10	9 and 10
Tetramethyl-	3.3	0.92	0.95	1.00
1,1-Diethyl-4,4-dimethyl-	6.3	1.97	1.97	2.00
Tetraethyl-, 1,1-dimethyl-4,4-di-*n*-propyl-	12.3			
Tetraethyl-	12.3	0.93	1.03	1.00
1,1-Dimethyl-4,4-di-*n*-propyl-	13.5	1.89	2.06	2.00
1,1-Diethyl-4,4-di-*n*-propyl-, 1,1-di-*n*-butyl-4,4-dimethyl-	24.9			
1,1-Diethyl-4,4-di-*n*-propyl-	25.5	2.12		2.00
1,1-Di-*n*-butyl-4,4-diethyl-	40.6			
Tetra-*n*-propyl-	48.2	1.17		1.00
1,1-Di-*n*-butyl-4,4-di-*n*-propyl-	74.0			
Tetra-*n*-butyl-	143.0			

methyltetrazene and tetraethyltetrazene from equal molar solutions of 1,1-dimethylhydrazine and 1,1-diethylhydrazine oxidized separately, mixed and coupled through careful neutralization of the resultant solution was given in Table III. Calculations for the distribution of these tetraalkyltetrazenes as a function of mole ratios of 1,1-dimethylhydrazine and 1,1-diethylhydrazine are listed in Table VI. The distribution of tetraalkyltetrazenes formed in the oxidation of multiple component systems with three and four 1,1-dialkylhydrazines is given in Tables VI and VII. All data, within experimental error, conform to a random distribution of products corresponding to the multinomial expansion, $(r + s + \ldots + z)^n$ for n equal to two. The oxidation of the 1,1-dialkylhydrazines for two, three and four component mixtures resulted in the formation of three, six and ten component mixtures of tetraalkyltetrazenes.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Reactions of Haloboranes with Organocyclosiloxanes. II. Boron Fluoride with Methyl and Ethyl Trimer and Tetramer[1-3]

BY PATRICK A. McCUSKER AND THOMAS OSTDICK, O.S.B.

RECEIVED FEBRUARY 18, 1959

The reactions of boron fluoride with the cyclosiloxanes, $(R_2SiO)_3$ and $(R_2SiO)_4$, where R is methyl or ethyl, give the products: $(R_2SiO)_n \cdot nBF_3$, $(R_2SiFO)BF_2$, $(R_2SiFO)_3B$, $(R_2SiF)_2O$, R_2SiF_2 $(R_2SiO)_3$, by a series of disproportionation reactions. With the exception of the coördination complexes, the intermediate fluorine compounds disproportionate much more readily than the corresponding chlorine compounds. *sym*-Tetramethyldifluorodisiloxane disproportionates slowly but completely at room temperature with the evolution of gaseous dimethyldifluorosilane and the formation of hexamethylcyclotrisiloxane. A reaction sequence which accounts for the exclusive formation of trimeric cyclosiloxane from the disproportionation of *sym*-tetraalkyldihalodisiloxanes is proposed. Steric factors involving the size of the boron halide molecule as well as the availability of the oxygens of the siloxanes strongly influence the rate of the initial reaction between boron halides and organocycloiloxanes.

The reactions of boron chloride with hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, hexaethylcyclotrisiloxane and octaethylcyclotetrasiloxane[4] were described in a previous paper from these Laboratories.[1] Through a series of disproportionations these reactions were found to produce, in sequence, dialkylchlorosiloxydichloroboranes, $(R_2SiClO)BCl_2$; tris-(dialkylchlorosiloxy)-boranes, $(R_2SiClO)_3B$; *sym*-tetraalkyldichloridisiloxanes, $(R_2SiCl)_2O$; dialkyldichlorosilanes and hexaalkylcyclotrisiloxanes.

The analogous reactions of boron fluoride with these alkylcyclosiloxanes and the relative disproportionation tendencies of the intermediate fluorine and chlorine compounds have now been studied and the results are reported in the present paper.

Experimental

Reagents and Procedures.—Most of the reagents used, the reaction apparatus and the methods of purification and characterization used have been described previously.[1] Boron fluoride, technical grade from the Matheson Company was passed through sulfuric acid saturated with boric oxide.

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[1] Previous paper, THIS JOURNAL, **80**, 1103 (1958).

[2] Abstracted from portions of the June 1958 doctoral dissertation of Rev. Thomas Ostdick, O.S.B. Presented in part at the New York Meeting of the American Chemical Society, September, 1957.

[3] Contribution from the Radiation Project operated by the University of Notre Dame and supported in part under Atomic Energy Commission Contract AT-(11-1)-38.

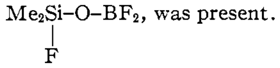
[4] The four cyclic compounds will be referred to as methyl trimer, methyl tetramer, ethyl trimer and ethyl tetramer.

Analyses for fluorine were made by titration of aqueous suspensions with standard base in the presence of excess calcium chloride, using methyl orange as indicator. Intermittent titration and refluxing were carried out until complete hydrolysis was effected. A value of 2.00 for the boron–fluorine bond refraction was calculated as $^1/_3$ of the molar refraction of boron fluoride reported by Klemm and Henkel.[5]

Detection of Coördination Complexes.—Boron fluoride (10.3 g., 0.152 mole) was added at −50° to 11.3 g. (0.051 mole) of methyl trimer to give a 3:1 molar ratio. To a weighed quantity of benzene, cooled to about 6°, was added a portion of the cold (−50°) reaction product. The mixture was weighed rapidly to determine its composition and held below 5°. The first freezing point of the mixture was determined within five minutes of the time of sample preparation, and a number of freezing point determinations were made during the next half-hour. The molecular weights so obtained varied from 400 to 443 (calcd. for 1 trimer:3 boron fluoride, 426). Repeated measurements indicated a decrease in molecular weight noticeable after the first half-hour. After a total of 1 hr. from the time of sample preparation the observed molecular weight was 319.

In a similar manner the molecular weight of 4:1 boron fluoride–methyl tetramer mixture formed at −50° was measured over a period of time. Again during the first half hour the apparent molecular weight varied from 597 to 578 (calcd. for 1 methyl tetramer:4 boron fluoride, 564). The observed values of molecular weight decreased steadily during the next half hour until a value of 167 was observed.

Molecular weight determinations under the same conditions on a 3:1 mixture of boron fluoride and ethyl trimer, formed at −35°, gave initially a value of 521 (calcd. for 1 ethyl trimer:3 boron fluoride, 510). A 4:1 molar mixture of boron fluoride and ethyl tetramer, formed at liquid nitrogen temperature, gave under the same conditions of determination an initial molecular weight of 689 (calcd. for 1 ethyl tetramer:4 boron fluoride, 680). The apparent molecular weight of this mixture decreased during 50 minutes at 5° in benzene solution to 490.

Preparation of Tris-(dimethylfluorosiloxy)-borane.—Boron fluoride was passed over solid methyl trimer (17.1 g., 0.077 mole) at −20°. After 1.5 hr. the reaction mixture was completely liquid and had the composition: 1 trimer:3 boron fluoride. The liquid mixture evolved no gas when held at −20°. At this temperature the composition, 1 trimer:3 boron fluoride, remained constant indicating that either the coördination complex or the cleavage product,  $\mathrm{Me_2}\underset{\mathrm{F}}{\underset{|}{\mathrm{Si}}}\mathrm{{-}O{-}BF_2}$, was present. On warming to room temperature, however, gas was evolved steadily. The evolved gas was collected in a liquid nitrogen trap and was identified as boron fluoride by passing into water and titrating the resulting solution. The weight of the residual liquid corresponded to the retention of $^1/_3$ of the boron fluoride originally added. As soon as the evolution of gas had ceased, the properties of the residual liquid were measured, as listed in Table I, and it was thereby identified as tris-(dimethylfluorosiloxy)-borane.

Using approximately the same weight of methyl tetramer the above procedure was repeated. Four moles of boron fluoride was absorbed per mole of tetramer and on warming to room temperature $^2/_3$ of the boron fluoride was evolved. The properties of the liquid remaining were measured as soon as evolution of boron fluoride ceased and were found to be identical with those of the tris-(dimethylfluorosiloxy)-borane obtained from methyl trimer.

Preparation of Tris-(diethylfluorosiloxy)-borane.—Boron fluoride was passed over 23.8 g. (0.077 mole) of ethyl trimer frozen at −38°. A total of 4 hr. was required to cause complete liquefaction and to give a boron fluoride to ethyl trimer ratio of 3:1. On allowing the liquid to warm to room temperature $^2/_3$ of the boron fluoride was evolved. As soon as evolution of gas ceased, the properties of the residual liquid were measured, as listed in Table I, and led to its identification as tris-(diethylfluorosiloxy)-borane.

To 24.9 g. of ethyl tetramer, held at −35°, was added boron fluoride over a period of 30 hr. during which time only 3.6 g. of boron fluoride was absorbed. The mixture was then cooled to liquid nitrogen temperature. The rate of absorption of boron fluoride increased and after 2 hr. the molar ratio of boron fluoride to tetramer was 4:1. On warming to room temperature $^2/_3$ of the absorbed boron fluoride was evolved and the properties of the remaining liquid were found to be identical with those of the product of the reaction of boron fluoride with ethyl trimer.

Disproportionation of Tris-(dimethylfluorosiloxy)-borane.—A sample of tris-(dimethylfluorosiloxy)-borane (15.4 g., 0.053 mole), which had been stored below room temperature, was placed under a Vigreux column at 2 mm. pressure. On warming the liquid became cloudy due to the separation of boric oxide. No condensation occurred in the water-cooled condenser, but 12.2 g. of a clear liquid was collected in the solid carbon dioxide–acetone trap. The liquid was identified as *sym*-tetramethyldifluorodisiloxane (yield 90%) by fluorine analysis and physical properties, as listed in Table I. A solid residue in the distilling flask was extracted with ether and found to consist of 1.7 g. of boric oxide (89% yield) and 0.6 g. of methyl trimer. A few drops of a fuming low boiling liquid, identified as dimethyldifluorosilane, were found in the liquid nitrogen trap.

Disproportionation of Tris-(diethylfluorosiloxy)-borane.—Under a Vigreux column, 10.9 g. of tris-(diethylfluorosiloxy)-borane, which had been stored below room temperature, was warmed at 1.5 mm. A liquid (9.6 g.) distilled at 35° and was redistilled at 1.5 mm. with the same boiling point. Analysis for fluorine and physical constants, as listed in Table I, enabled the liquid to be identified as *sym*-tetraethyldifluorodisiloxane (yield 96%). Boric oxide (1.0 g., 95% yield) remained as a residue.

Distillation and Disproportionation of *sym*-Tetramethyldifluorodisiloxane.—A rapid distillation, using an ordinary distilling flask, of 19.1 g. of *sym*-tetramethyldifluorodisiloxane at 751 mm. gave 12.8 g. (67% recovery) of liquid distilling at 71–72°. The physical constants for this product, listed in Table I, were found to be the same as those of the product from the disproportionation of tris-(dimethylfluorosiloxy)-borane described above. Another sample of *sym*-tetramethyldifluorodisiloxane (4.2 g., 0.025 mole) showed no change in properties on standing overnight at −70°. On standing at room temperature for 40 minutes, however, 2.4 g. (96% yield) of dimethyldifluorosilane, b.p. 2°, passed off and was condensed in a solid carbon dioxide–acetone trap. Methyl trimer (1.8 g., 96% yield) remained as a residue.

Disproportionation of *sym*-Tetraethyldifluorodisiloxane.—In a simple distillation set up, 7.0 g. of *sym*-tetraethyldifluorodisiloxane was heated to 165° at atmospheric pressure. A 3.3-g. fraction was collected at 71–72° and identified by its constants as diethyldifluorosilane (87% yield). The pressure was decreased and a second fraction was collected at 97–98° at 2 mm. The latter fraction was identified by its constants as ethyl trimer (2.6 g., 84% yield).

Discussion

The same sequence of reactions, shown in the following equations for the trimer, occurs with organocyclosiloxanes and boron fluoride as was previously observed with boron chloride.[1]

$$(\mathrm{R_2SiO})_3 + 3\mathrm{BF_3} \longrightarrow (\mathrm{R_2SiO})_3\cdot 3\mathrm{BF_3} \qquad (1)$$

$$(\mathrm{R_2SiO})_3\cdot 3\mathrm{BF_3} \longrightarrow [3\mathrm{R_2SiFOBF_2}] \qquad (2)$$

$$[3\mathrm{R_2SiFOBF_2}] \longrightarrow (\mathrm{R_2SiFO})_3\mathrm{B} + 2\mathrm{BF_3} \qquad (3)$$

$$2(\mathrm{R_2SiFO})_3\mathrm{B} \longrightarrow \mathrm{B_2O_3} + 3(\mathrm{R_2SiF})_2\mathrm{O} \qquad (4)$$

$$3(\mathrm{R_2SiF})_2\mathrm{O} \longrightarrow 3\mathrm{R_2SiF_2} + (\mathrm{R_2SiO})_3 \qquad (5)$$

The identification of the compounds is based on molecular weights, molar refraction and composition. The composition was determined, in the cases of the coördination complexes and the tris-(dialkylfluorosiloxy)-boranes, from the proportions of reagents added; in the case of the distillable compounds by analysis for fluorine. The identification of the non-distillable fluorine compounds is supported by the more complete identification of the analogous distillable chlorine compounds.[1]

The rate of the initial reaction of boron halides with organocyclosiloxanes is affected by steric factors involving the availability of the oxygens of

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(5) W. Klemm and P. Henkel, *Z. anorg. Chem.*, **213**, 115 (1933).

TABLE I

PROPERTIES OF COMPOUNDS

	B.p.° (mm.)	$n^{20}\mathrm{D}$	d^{20}	$MR\mathrm{D}$ Calcd.	Obsd.	Mol. wt. Calcd.	Obsd.	% Fluorine Calcd.	Obsd.
$(\mathrm{Me_2}\underset{\mathrm{F}}{\underset{\vert}{\mathrm{Si}}}\mathrm{O})_3\mathrm{B}$	....	1.3649	1.0797	60.18	59.99	290	279	...	...
$(\mathrm{Et_2}\underset{\mathrm{F}}{\underset{\vert}{\mathrm{Si}}}\mathrm{O})_3\mathrm{B}$	....	1.4019	1.0419	87.96	87.33	374	364	...	...
$(\mathrm{Me_2}\underset{\mathrm{F}}{\underset{\vert}{\mathrm{Si}}})_2\mathrm{O}$	71–72 (751)	1.3360	0.9605	36.78	36.78	170	178	22.35	22.32
$(\mathrm{Et_2}\underset{\mathrm{F}}{\underset{\vert}{\mathrm{Si}}})_2\mathrm{O}^a$	35 (1.5)	1.3850	0.9583	55.30	55.35	226	219	17.22	17.20
$\mathrm{Et_2SiF_2}^a$	60.9 (755)	1.3385	0.9375	27.40	27.66	124	128	30.40	30.50

[a] Previously reported; further characterized.

the siloxane and the size of the boron halide molecule. In the cyclosiloxane with the least accessible oxygen atoms, ethyl tetramer, only partial reaction was observed with boron chloride. With the smaller boron fluoride molecule, reaction was made to go to completion, but it was necessary to use liquid nitrogen temperatures to obtain a sufficiently high concentration of boron fluoride. All the remaining cyclosiloxanes reacted readily with boron fluoride at temperatures just below room temperature.

The coördination complexes of organocyclosiloxanes with boron fluoride have a lesser tendency to undergo the cleavage reaction 2 than do the corresponding chlorine complexes. This is consistent with the greater stability of ether–boron fluoride complexes than of ether–boron chloride complexes toward cleavage reactions. At 5° the boron fluoride complexes of organocyclosiloxanes have sufficient stability to be detected by molecular weight determinations. In contrast the boron chloride complexes, whose formation was assumed in the boron chloride reaction, could not be detected even at low temperatures. The conclusion that the first step in the reaction sequence is the formation of a coördination complex was arrived at indirectly in the case of the boron chloride reactions. This conclusion is supported by the results obtained with boron fluoride.

The presumed cleavage product, dialkylfluorosiloxydifluoroborane, which would be formed according to reaction 2 is evidently much less stable to disproportionation than the corresponding chlorine compound. The presence of dialkylfluorosiloxydifluoroboranes could not be experimentally established in the reaction products even at low temperature. If these compounds are formed during the reaction they are very short lived and rapidly lose boron fluoride according to reaction 3.

The difference in the relative stabilities of tris-(dialkylchlorosiloxy)-boranes and the corresponding fluorine compounds at the same temperature is also very marked. Whereas the tris-(dialkylchlorosiloxy)-boranes can be subjected to slow, repeated fractional distillation in packed columns at temperatures up to 100° and obtained in high purity with no indication of disproportionation, the corresponding fluorine compounds disproportionate rapidly at room temperature according to reaction 4. For example tris-(diethylfluorosiloxy)-borane on standing at room temperature for 15 minutes becomes cloudy due to the separation of boric oxide.

Similarly the *sym*-tetraalkyldifluorodisiloxanes undergo disproportionation according to reaction 5 much more readily than do the corresponding chlorine compounds. Whereas the chlorine compounds could be distilled slowly at temperatures up to 130° without any indication of disproportionation and require very slow fractional distillation in a packed column above 170° to effect quantitative disproportionation, the corresponding fluorine compounds undergo slow disproportionation even at room temperature. In the case of the methyl compound the disproportionation proceeds to completion at room temperature. The disproportionation of *sym*-tetraalkyldifluorodisiloxanes was found to give, as in the case of the corresponding chlorine compounds, only cyclic trimer with no trace of higher cyclic or linear siloxanes. *sym*-Tetraethyldifluorodisiloxane has been reported[6] previously as the product of the fluorination of *sym*-tetraethyldichlorodisiloxane, but its disproportionation apparently was not observed.

The more facile disproportionation of compounds having silicon–fluorine bonds than of those with silicon–chlorine bonds is apparently a general phenomenon since it has been observed also with other types of compounds.[7] A mechanism, proposed by MacDiarmid, to explain the more facile disproportionation of silyl fluoride than of silyl chloride appears to provide a satisfactory explanation for the differences in the disproportionation tendencies of the compounds studied in the present work. This mechanism involves a bimolecular reaction in which a halogen on one molecule forms a pi bond with a silicon atom of a second molecule to form the activated complex. The ease of formation of such a pi bond complex would be greater for fluorine compounds than for chlorine compounds and would thus result in a faster rate of reaction. While the above mechanism provides for a more rapid rate of disproportionation of silicon–fluorine compounds than for silicon–chlorine compounds it enables no prediction to be made concerning the ultimate extent

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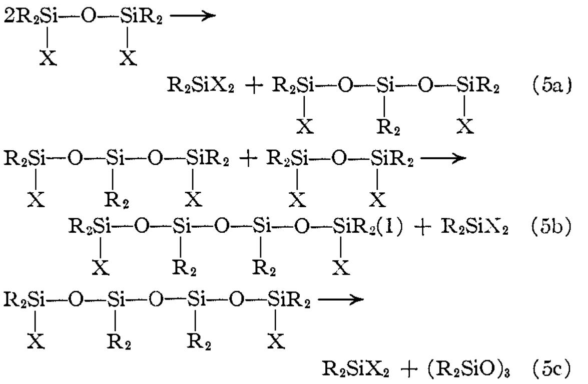
(6) D. S. Payne, *J. Chem. Soc.*, 2143 (1954).

(7) A. G. MacDiarmid, *Quart. Revs.*, **10**, 222 (1956); H. J. Emeleus and A. G. Maddock, *J. Chem. Soc.*, 293 (1944); A. Stock and C. Somieski, *Ber.*, **52**, 695 (1919).

of disproportionation. If the relative thermodynamic stabilities of the reactants and products are different for the fluorine compounds than for the chlorine compounds, the disproportionation reaction may be reversible with different equilibrium points for fluorine than for chlorine compounds. The temperature dependence of such an equilibrium may also vary. In the cases reported here and in the first paper of the series the products of the disproportionation reaction were removed as fast as formed. For this reason the reactions would be made to go to completion even if an equilibrium were involved.[8]

The formation of trimeric cyclosiloxane only in the disproportionation of *sym*-tetraalkyldifluorodisiloxanes parallels the result observed for the corresponding chlorine compounds. The exclusive formation of trimer in this reaction might be anticipated if a bimolecular reaction, as proposed above, were to be involved and if the following sequence of reactions were to occur



$$2\underset{X}{R_2Si}-O-\underset{X}{SiR_2} \longrightarrow R_2SiX_2 + \underset{X}{R_2Si}-O-\underset{R_2}{Si}-O-\underset{X}{SiR_2} \quad (5a)$$

$$\underset{X}{R_2Si}-O-\underset{R_2}{Si}-O-\underset{X}{SiR_2} + \underset{X}{R_2Si}-O-\underset{X}{SiR_2} \longrightarrow \underset{X}{R_2Si}-O-\underset{R_2}{Si}-O-\underset{R_2}{Si}-O-\underset{X}{SiR_2}(I) + R_2SiX_2 \quad (5b)$$

$$\underset{X}{R_2Si}-O-\underset{R_2}{Si}-O-\underset{R_2}{Si}-O-\underset{X}{SiR_2} \longrightarrow R_2SiX_2 + (R_2SiO)_3 \quad (5c)$$

In the tetrasiloxane (I) the geometry of the molecule is such that a halogen atom on one terminal silicon could approach quite closely to the other terminal silicon atom. A shift of the halogen atom and a splitting off of a molecule of dialkyldihalosilane would then leave a residue of three siloxane units in a favorable position to close the ring.

NOTRE DAME, IND.

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[8] Preliminary work in these Laboratories indicates that the disproportionation of *sym*-tetraalkyldihalodisiloxanes is indeed reversible and that the equilibrium point for the fluorine compounds is farther to the right than for the chlorine compounds at temperatures above room temperature.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Boron–Nitrogen Compounds. II.[1,2] Aminoboranes, Part 1: The Preparation of Organic Substituted Aminoboranes through a Grignard Reaction

BY KURT NIEDENZU AND JOHN W. DAWSON

RECEIVED APRIL 23, 1959

The reaction of various Grignard compounds with N-disubstituted aminodichloroboranes, R_2N-BCl_2, provides a method for the preparation of organic substituted aminoboranes. Experimental details are presented and some aminoboranes are described.

Aminoboranes have the basic structure =N—B=, where hydrogen and/or organic groups are attached to the nitrogen and to the boron. Heretofore, the aminoboranes have usually been prepared by the thermal decomposition of amine-boranes[3] as illustrated by the equation

$$(CH_3)_2NH\cdot B(CH_3)_3 \longrightarrow (CH_3)_2N-B(CH_3)_2 + CH_4$$

or by the interaction of diborane with the appropriate anhydrous amine in sealed tubes, employing high vacuum techniques.[4] The experimental difficulties inherent in this type of reaction have made the resultant aminoboranes available only in small quantities.

A considerable improvement in the preparation of aminoboranes was achieved through the reaction between metalloborohydrides and ammonium halides[5]

$$R_2NH_2Cl + LiBH_4 \longrightarrow 2H_2 + LiCl + R_2N-BH_2$$

It now has been found that the addition of N-disubstituted aminodichloroboranes, R_2N-BCl_2, to an excess of various Grignard compounds results in the formation of organic substituted aminoboranes in good yield. The general equation may be expressed as

$$2RMgX + Cl_2B-NR'R'' \longrightarrow R_2B-NR'R'' + MgX_2 + MgCl_2$$

The reaction, however, seems to be more complex as is indicated by the formation of small amounts of unidentified volatile boron compounds which may ignite spontaneously or explode. Since aminodichloroboranes are easy to prepare, the reaction permits great variation of synthesis.

Experimental

The N-disubstituted aminodichloroboranes were prepared through the reaction of addition compounds of boron trichloride with secondary amines. These addition compounds were converted into the respective aminodichloroboranes through the evolution of hydrogen chloride at elevated temperatures[6] or by treatment with the stoichiometric amount of a tertiary amine.[7] The resultant aminodichloroboranes are illustrated in Table I.

Preparation of Organic Substituted Aminoboranes through the Reaction of Grignard Compounds with Aminodichloro-

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[1] Boron-Nitrogen Compounds. I. THIS JOURNAL, **81**, 3561 (1959).

[2] Supported by the Office of Ordnance Research, U. S. Army.

[3] "Gmelins Handbuch der anorganischen Chemie," "Bor" Ergaenzungsband, p. 238.

[4] E. Wiberg, A. Bolz and P. Buchheit, *Z. anorg. allgem. Chem.*, **256**, 285 (1948).

[5] G. W. Schaeffer and E. R. Anderson, THIS JOURNAL, **71**, 2143 (1949).

[6] H. J. Becher, *Z. anorg. allgem. Chem.*, **289**, 262 (1957).

[7] J. F. Brown, THIS JOURNAL, **74**, 1219 (1952).