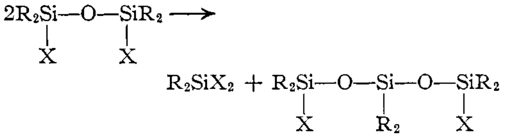
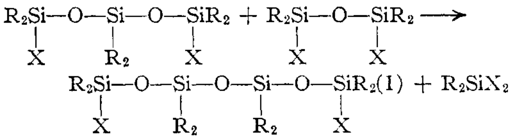
of disproportionation. If the relative thermodynamic stabilities of the reactants and products are different for the fluorine compounds than for the chlorine compounds, the disproportionation reaction may be reversible with different equilibrium points for fluorine than for chlorine compounds. The temperature 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]

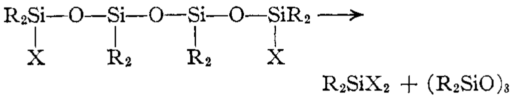
The formation of trimeric cyclosiloxane only in the disproportionation of *sym*-tetraalkyldifluorodisiloxanes parallels the result observed for the corresponding chlorine compounds. The exclusive formation of trimer in this reaction might be anticipated if a bimolecular reaction, as proposed above, were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



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



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



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

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.

[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).

TABLE I

AMINODICHLOROBORANES[a]

Name	Structural formula	Physical data	Yield, %		Analyses					
					Mol. wt.	Boron	Nitrogen	Carbon	Hydrogen	Chlorine
Dichloro-(ethylphenylamino)-borane (3)	$\begin{smallmatrix}C_6H_5\\ C_2H_5\end{smallmatrix}>N-B<\begin{smallmatrix}Cl\\ Cl\end{smallmatrix}$	B.p. 67° (3 mm.)	89	Calcd.	201.9	5.4	6.9	47.6	5.0	35.2
				Found	204	5.2	6.9	47.5	5.0	35.1
Dichloro-(methylphenylamino)-borane (3)	$\begin{smallmatrix}C_6H_5\\ CH_3\end{smallmatrix}>N-B<\begin{smallmatrix}Cl\\ Cl\end{smallmatrix}$	B.p. 94–98° (7 mm.)	83	Calcd.	187.9	5.7	7.4	44.7	4.3	37.8
				Found	192	5.2	7.4	44.3	4.3	37.3
Dichloro-(methylnaphthylamino)-borane (4)	$\begin{smallmatrix}C_{10}H_7\\ CH_3\end{smallmatrix}>N-B<\begin{smallmatrix}Cl\\ Cl\end{smallmatrix}$	B.p. 124° (4 mm.) M.p. 70°[b]	73	Calcd.	237.9	4.5	5.9	55.4	4.2	29.2
				Found	239	4.7	5.9	55.5	3.7	29.5
Dichloro(-dicyclohexylamino)-borane (4)	$\begin{smallmatrix}C_6H_{11}\\ C_6H_{11}\end{smallmatrix}>N-B<\begin{smallmatrix}Cl\\ Cl\end{smallmatrix}$	B.p. 114–116° (4 mm.) M.p. 71°	81	Calcd.	262.0	4.1	5.3	54.2	8.5	27.1
				Found	262	4.4	5.4	54.3	8.8	26.9
Dichloro-(di-*sec*-butylamino)-borane (4)	$\begin{smallmatrix}\textit{sec}\text{-}C_4H_9\\ \textit{sec}\text{-}C_4H_9\end{smallmatrix}>N-B<\begin{smallmatrix}Cl\\ Cl\end{smallmatrix}$	B.p. 62° (6 mm.)	92	Calcd.	210.0	5.2	6.7	45.8	8.6	33.8
				Found	211	5.2	6.6	45.9	8.9	33.6

[a] The number appended to the names of the compounds refers to the preparative technique presented in the cited literature. [b] The m.p. of the freshly distilled compound was near 70°. A short time after the distillation a sharp m.p. could no longer be obtained; this may indicate the initiation of dimerization.

TABLE II

AMINOBORANES

Name	Structural formula	Physical data	Yield, %		Analyses				
					Mol. wt.	Boron	Nitrogen	Carbon	Hydrogen
(Di-*sec*-butylamino)-diethylborane	$\begin{smallmatrix}\textit{sec}\text{-}C_4H_9\\ \textit{sec}\text{-}C_4H_9\end{smallmatrix}>N-B<\begin{smallmatrix}C_2H_5\\ C_2H_5\end{smallmatrix}$	B.p. 212–214°	87	Calcd.	197.2	5.5	7.1	73.0	14.3
				Found	193	5.6	7.2	72.7	14.5
(Dicyclohexylamino)-dimethylborane	$\begin{smallmatrix}C_6H_{11}\\ C_6H_{11}\end{smallmatrix}>N-B<\begin{smallmatrix}CH_3\\ CH_3\end{smallmatrix}$	B.p. 259°	75	Calcd.	221.2	4.9	6.3	75.9	12.7
				Found	223	4.7	6.5	76.1	12.5
(Ethylphenylamino)-diethylborane	$\begin{smallmatrix}C_2H_5\\ C_6H_5\end{smallmatrix}>N-B<\begin{smallmatrix}C_2H_5\\ C_2H_5\end{smallmatrix}$	B.p. 68° (6 mm.)	79	Calcd.	189.1	5.7	7.4	76.2	10.7
				Found	188	5.5	7.6	76.3	10.6
(Ethylphenylamino)-diphenylborane	$\begin{smallmatrix}C_2H_5\\ C_6H_5\end{smallmatrix}>N-B<\begin{smallmatrix}C_6H_5\\ C_6H_5\end{smallmatrix}$	B.p. 158–165° (5–6 mm.) M.p. 27°	86	Calcd.	285.2	3.8	4.9	84.2	7.0
				Found	278	3.7	4.7	84.3	7.2
(Methylphenylamino)-dimethylborane	$\begin{smallmatrix}CH_3\\ C_6H_5\end{smallmatrix}>N-B<\begin{smallmatrix}CH_3\\ CH_3\end{smallmatrix}$	B.p. 51° (4 mm.)	83	Calcd.	147.0	7.3	9.5	73.4	9.5
				Found	146	7.1	9.3	73.0	9.5
(Methylnaphthylamino)-dimethylborane	$\begin{smallmatrix}CH_3\\ C_{10}H_7\end{smallmatrix}>N-B<\begin{smallmatrix}CH_3\\ CH_3\end{smallmatrix}$	B.p. 89° (3 mm.)	67	Calcd.	197.1	5.5	7.1	79.1	8.2
				Found	194	5.3	7.1	79.3	8.2
(Ethylphenylamino)-di-*p*-tolylborane	$\begin{smallmatrix}C_2H_5\\ C_6H_5\end{smallmatrix}>N-B<\begin{smallmatrix}C_7H_7\\ C_7H_7\end{smallmatrix}$	M.p.[a] 169°	59	Calcd.	313.2	3.5	4.5	84.3	7.7
				Found	311	3.5	4.7	81.2	7.8

[a] M.p. after distillation (fraction collected, b.p. 160–180° (3 mm.)) and recrystallization from *n*-heptane.

boranes. (Ethylphenylamino)-diethylborane (Typical Reaction).—A solution of 40.4 g. (0.2 mole) of dichloro-(ethylphenylamino)-borane in 300 cc. of dry benzene was added to a solution of 81.1 g. (0.45 mole) of ethylmagnesium iodide in 300 cc. of dry ether with rapid stirring. The initially exothermic reaction was completed by refluxing the mixture for several hours. After filtration, two-thirds of the solvent was stripped off. The concentrate was filtered free of precipitated magnesium salts and the remaining solvent evaporated. The residue was distilled under reduced pressure and the resultant aminoborane finally purified by redistillation *in vacuo*, affording 20.9 g. (79%) of a colorless liquid b.p. 68° (6 mm.).

Table II shows the aminoboranes which were prepared, using the molar ratios and the techniques described above.

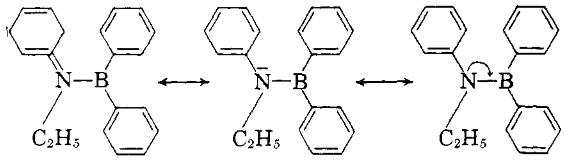
Aminoboranes substituted with one or more phenyl groups have a very unpleasant and tenacious smell. The odor of (methylnaphthylamino)-dimethylborane is reminiscent of hydrogen sulfide.

Discussion

The infrared spectra of all the described aminoboranes afford a means of determining the B–N bond absorption. Evidence of such absorption usually appears as one of the strongest bands of the spectra between 6.6 and 7.6 μ. This unusually wide range apparently is due to the different substituents which appear to produce a more or less double bond character between the boron and the nitrogen.

The position of the B–N bond absorption of various substituted aminoboranes are presented in Table III. Table III clearly demonstrates the change in character of the B–N bond. There appears to be a relationship to the B-aminoborazines,[1] wherein the B–N bond of the borazine ring with its more evident double bond character shows an infrared absorption at about 1500 cm.$^{-1}$, while the B–N side chain bond absorption, which appears to indicate a greater single bond character, was found near 1350 cm.$^{-1}$. Thus the influence of the substituents on the B–N grouping of aminoboranes is quite evident. For example, the π-electrons of the ethylanilino-grouping of (ethylphenylamino)-diphenylborane (I) are in resonance with the free pair of electrons of the nitrogen.

However, the phenyl substituents on the boron seem to have a lessened attraction for the pair, as indicated by the structures



The B–N double bond character of I, therefore, is somewhat stronger than in (ethylphenylamino)-diethylborane (II), where the boron-attached alkyl groups do not produce such a degree of electron delocalization on the B–N bond. Further weakening of the double bond character appears in dichloro-(diphenylamino)-borane (III), though the difference between II and III is not as great as expected. Presumably the N-attached phenyl rings in the latter case are not both coplanar with the rest of the molecule,[6] otherwise two of the *o*-hydrogens of the phenyl groups would constitute steric hindrance. The planarity is likely to be distorted thus affording a decrease of resonance which demonstrates why the second phenyl group on the nitrogen does not produce as much weakening of the B–N double bond character as one might expect.

TABLE III

INFRARED ABSORPTION OF THE B–N BOND OF SOME AMINOBORANES

Compound	Absorption, cm.$^{-1}$
(Monophenylamino)-dimethylborane[6]	1330
Dimethyl-(pyrrolo)-borane[6]	1343
(Methylnaphthylamino)-dimethylborane	1370
Dichloro-(diphenylamino)-borane[6]	1378
(Ethylphenylamino)-diethylborane	1408
(Ethylphenylamino)-diphenylborane	1424
(Di-*sec*-butylamino)-diethylborane	1459
Dichloro-(diethylamino)-borane[1]	1505
(Amino)-dimethylborane[8]	1515
Dichloro-(dimethylamino)-borane[9]	1526
(Dimethylamino)-dimethylborane[8]	1530

The influence of substituents on the stability and bond characteristics of the B–N linkage of aminoboranes is under further investigation; the findings will be published later.

Acknowledgment is accorded to the Schwarzkopf Microanalytical Laboratory, Woodside 77, New York, for analyses reported herein.

(8) H. J. Becher and J. Goubeau, *Z. anorg. allgem. Chem.*, **268**, 133 (1952).

(9) J. Goubeau, M. Rahtz and H. J. Becher, *ibid.*, **275**, 161 (1954).

DURHAM, NORTH CAROLINA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

Infrared and Visible Spectra of Gaseous B_2S_3 at High Temperatures[1]

BY FRANK T. GREENE AND JOHN L. MARGRAVE

RECEIVED JUNE 1, 1959

Infrared emission and absorption spectra of gaseous B_2S_3 have been observed for the normal isotopic mixture and for a sample prepared with B^{10}. Examination of the isotope shifts with the aid of the Redlich–Teller product rule gives support to a twisted zigzag model for B_2S_3 with C_2 symmetry. Electronic absorption spectra were observed in the regions 5400–7200 Å., 3900–4200 Å., and 3100–3500 Å.

During the past few years considerable attention has been given to the determination of the fundamental properties of B_2O_3.[2] Its sulfur analog, B_2S_3, has, however, been neglected almost entirely.

Infrared Studies of Gaseous B_2S_3.—An infrared spectroscopic investigation of gaseous B_2S_3 has been made over the range 600–1000°. For this work, B_2S_3 was prepared by passing dried H_2S through amorphous boron at 700° and collecting the vaporized product on a cold finger. The resulting product contains HBS_2, B_2S_3 and some sulfur and boric acid impurity. Single crystals, apparently of HBS_2, have been prepared and are being studied. This mixture was introduced directly into a 1-inch quartz or Vycor tube to which suitable windows were attached and heated *in vacuo* at 300 and 600° for several hours until degassed and all H_2S removed. At the higher temperatures there was considerable condensation of vaporized material as a white smoke in cool portions of the tube and usually about 100 mm. of dry argon was introduced to prevent boiling and retard diffusion just before the temperature was raised to that of a run.

The spectrum of the gas over B_2S_3 was examined in emission and absorption in the region 10,000 to 400 cm.$^{-1}$ with a Beckman Model IR 2 spectrometer. The source housing was separated about 1 meter from the entrance optics and a 12-inch nichrome furnace containing a quartz or Vycor tube with KBr windows was inserted. For emission studies with this instrument, an external chopper which could be synchronized with the synchronous rectifier was mounted in front of the entrance optics. For the longer wave length region, a Perkin-Elmer Model 112 double pass spectrometer with a CsBr prism was used in emission out to 300 cm.$^{-1}$. For emission work, a series of diaphragms was used to mask out wall radiation. Several tracings were made for each spectral region studied at a variety of temperatures and with a number of different samples.

Five bands were observed both in emission and absorption. Their maxima were at 1322, 990, 919, 859 and 602 cm.$^{-1}$. When boron containing 95% B^{10} was substituted for the normal isotopic mixture, the bands were observed to shift to 1389, 1040, 952, 906 and 605 cm.$^{-1}$. This isotope shift is probably too small as a result of the overlapping of B^{10}–B^{11} bands with B^{11}–B^{11} bands; correction for this effect indicates net isotope shifts of 71, 54, 37, 51 and 6 cm.$^{-1}$, respectively.

There are several chemically plausible models for B_2S_3: a linear molecule ($D_{\infty h}$), a bipyramid (D_{3h}), a plane V or W-shaped molecule (C_{2v}) or a twisted zigzag (C_2). An upper limit for the isotope shift permitted for a given model can be calculated

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(1) Presented before the 135th Meeting, American Chemical Society, Boston, April, 1959.

(2) (a) D. A. Dows and R. F. Porter, THIS JOURNAL, **78**, 5165 (1956); (b) D. White, P. N. Walsh and D. E. Mann, *J. Chem. Phys.*, **28**, 508 (1958); (c) E. N. Lotkova, V. V. Obukhov-Denisov, N. N. Sobolev and V. P. Cheremicinov, *Optics and Spectroscopy (Russian)*, **1**, 772 (1956); **3**, 560 (1957); (d) W. Taylor, *J. Chem. Phys.*, **28**, 625 (1958).