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Preparation and Some Reactions of Unsymmetrically-Substituted Borazines[1]

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The reaction of borazine with mercury(II) chloride in ether or *n*-pentane at room temperature gave a mixture of 2-chloro- and 2,4-dichloroborazine in good yields. The mixture was easily separated into pure components, which were identified by mass spectral and analytical analyses. The synthesis of unsymmetrically-substituted borazines by this method was shown to be applicable also to 1,3,5-trimethylborazine. The reaction of borazine with a number of other metal chlorides was tried. Tin(IV) chloride gave unsymmetrically-substituted borazines. Iron(III) chloride reacted but no unsymmetrical borazines were obtained. Copper(II), lead(II), and silver chlorides did not react. The reaction of 1,3,5-trimethylborazine with thionyl chloride was shown to yield 2-chloro-1,3,5-trimethylborazine. Samples of 2-chloro- and 2,4-dichloroborazine reacted with dimethylamine to form 2-dimethylamino- and 2,4-bis(dimethylamino)borazine, respectively. Thermal stability studies of 2,4-bis(dimethylamino)borazine and 2-chloro- and 2,4-dichloroborazine indicated that the latter two compounds are more stable than previously believed. Possible mechanisms for the partial chlorination of borazine by mercury(II) chloride are discussed.

Introduction

The unsymmetrically-substituted borazines, 2-chloroborazine ($ClH_2B_3N_3H_3$) and 2,4-dichloroborazine ($Cl_2HB_3N_3H_3$), were first prepared by the reaction of borazine with boron trichloride.[3] This method required long reaction times and only low yields were obtained. In attempts to prepare unsymmetrically-substituted borazines in larger amounts, various haloborazines have been treated with deficient amounts of Grignard-type reagents, but this procedure gives mixtures of products which are difficult to purify.[4-6] The compounds, such as 2-chloro-1,3,4,5,6-pentamethylborazine, prepared by this latter method generally have only one type reactive center, a boron–halogen bond, remaining on the borazine ring and, therefore, are not the most advantageous compounds for solving synthetic problems. Compounds like 2-chloroborazine have reactive boron–hydrogen, boron–halogen, and nitrogen–hydrogen centers and are much more useful derivatives for synthetic work. The purpose of this investigation was to find a convenient method for the preparation of unsymmetrically-substituted haloborazines.

Mercury(II) chloride had previously been reported to react with $H_3Al{-}N(CH_3)_3$ to give $H_{3-n}Cl_nAl{-}N(CH_3)_3$ ($n = 1, 2, 3$), hydrogen, and metallic mercury.[7] It therefore appeared likely that mercury(II) chloride might also react with borazine to form chloroborazines.

Very recently chlorinating agents such as $SOCl_2$ and $COCl_2$ have been shown to react with B-hydroborazines to yield B-unsymmetrically-chlorinated borazines.[8,9] We have further investigated this reaction as a general method for the specific preparation of unsymmetrically-substituted borazines.

Experimental Section

Materials.—Borazine was prepared by the reduction of 2,4,6-trichloroborazine with sodium hydroborate.[10] 1,3,5-Trimethylborazine was made from methylamine hydrochloride and sodium hydroborate.[11] All solvents used were dried by conventional means. Reagent grade mercury(II) chloride, tin(IV) chloride, lead(II) chloride, thionyl chloride, and silver chloride were used without further purification. Commercial hydrated forms of iron(II) chloride and copper(II) chloride were dehydrated by refluxing with thionyl chloride, which was then removed by vacuum distillation.[12]

Analytical Methods.—Boron was determined by standard mannitol pH titrations. Nitrogen determinations were obtained by a standard Kjeldahl method. Chloride was determined by a potentiometric titration using a silver chloride reference electrode. Hydrolyzable hydrogen values were obtained by basic hydrolysis of the samples and measurement of the hydrogen evolved with a Toepler system.

Reaction of Borazine with Mercury(II) Chloride.—In these experiments, examples of which are given in Table I, the stated amount of borazine and 25 ml of solvent were condensed onto a known amount of mercury(II) chloride contained in a flask attached to a vacuum line. The mixtures were warmed to the desired temperature and were stirred for the time specified. The products were then fractionated by vacuum distillation using trap temperatures of −10, −46, −78, and −196°, which separated the compounds 2,4,6-trichloroborazine, 2,4-dichloroborazine, 2-chloroborazine, and borazine plus solvent, respectively. No free hydrogen or hydrogen chloride gas was observed. The nonvolatile reaction residues were shown to contain mercury(I) chloride and the hydrogen chloride addition compound of borazine, $H_3B_3N_3H_3 \cdot 3HCl$, by their X-ray powder pattern[13] and infrared spectrum,[14] respectively. When *n*-pentane was used as solvent, mercury metal was also found in the reaction residue. The presence of mercury metal was shown by a black coloration of the residue, droplets of mercury metal, and the formation of a

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Table I

Reaction of Borazine with Mercury(II) Chloride

Reactants: H_3B_3-N_3H_3, mmoles	Reactants: Mole ratio, $H_3B_3N_3H_3$/$HgCl_2$	Temp, °C	Solvent	$H_3B_3N_3H_3$ recovered, mmoles	Mole $\%_3$ $H_3B_3N_3H$ converted to ClH_2B_3-N_3H_3	Mole $\%_3$ $H_3B_3N_3H$ converted to Cl_2HB_3-N_3H_3
9.3^a	2.5	22	Pentane	7.5	22	18
82^b	1.7	22	Pentane	55	23	21
21^b	1.4	0	Ether	5.0	4.7	6.2
16^b	1.4	22	Ether	8.8	32	8.5
8.4^b	0.71	36	Ether	0.0	10	12
55^b	0.62	22	Pentane	13	15	31
58^b	0.42	22	Pentane	5.0	18	24
45^b	1.0	22	Ether	13	14	15
13^b	1.0	22	Pentane	9.3	19	26
6.5^a	1.0	22	Tetraglyme	6.5	0	0

^{a} Reaction time 24 hr. ^{b} Reaction time 3 hr.

silver-like mirror when the residue was rubbed on a piece of copper metal.

The unsymmetrically-substituted borazine compounds were characterized by mass spectral analysis (see latter section), analytical data, and their vapor pressures.[3]

Anal. Calcd for $Cl_2HB_3N_3H_3$: Cl, 47.4; N, 28.1; hydrogen on hydrolysis, 0.67. Found: Cl, 46.9; N, 27.6; hydrogen on hydrolysis, 0.69. Calcd for $ClH_2B_3N_3H_3$: Cl, 30.8; N, 36.5; B, 28.2. Found: Cl, 28.1; N, 35.8; B, 27.9. Vapor pressure of $Cl_2HB_3N_3H_3$: lit.,[3] 6 mm at 20°; found, 5. Vapor pressure of $ClH_2B_3N_3H_3$: lit.,[3] 33 mm at 25°; found, 32.

2,4,6-Trichloroborazine, which was identified by its mass spectrum,[15] was formed only when the amount of mercury(II) chloride used was in excess of the amount needed to convert all the borazine to 2,4-dichloroborazine.

The following idealized equations account for the products isolated when the reactions were carried out using ether as solvent.

$$4H_3B_3N_3H_3 + 6HgCl_2 \longrightarrow 3ClH_2B_3N_3H_3 + 3Hg_2Cl_2 + H_3B_3N_3H_3{\cdot}3HCl \quad (1)$$

$$5H_3B_3N_3H_3 + 12HgCl_2 \longrightarrow 3Cl_2HB_3N_3H_3 + 6Hg_2Cl_2 + 2H_3B_3N_3H_3{\cdot}3HCl \quad (2)$$

$$2H_3B_3N_3H_3 + 6HgCl_2 \longrightarrow Cl_3B_3N_3H_3 + 3Hg_2Cl_2 + H_3B_3N_3H_3{\cdot}3HCl \quad (3)$$

The best conditions for obtaining large yields of unsymmetrically-substituted borazines were found to be room temperature, 3 hr reaction time, and a borazine to mercury(II) chloride mole ratio of approximately 1:2. Pentane was chosen as the solvent because its removal from the borazines by fractionation through a −78° trap was easier than for ether.

Reaction of 2-Chloroborazine with Mercury(II) Chloride.—In order to determine whether 2,4-dichloroborazine is formed from the reaction of 2-chloroborazine with mercury(II) chloride, 2.29 mmoles of 2-chloroborazine and 1.95 mmoles of mercury(II) chloride were allowed to react for 18 hr using pentane as solvent. Upon fractionation, 0.55 mmole of 2,4-dichloroborazine and 0.59 mmole of 2-chloroborazine were recovered. The nonvolatile residue was white, indicating that no mercury metal was formed, unlike the case of borazine in pentane. An infrared spectrum of the residue was very similar to the one obtained for the residue from the reaction of borazine and mercury(II) chloride, indicating the probable formation of $ClH_2B_3N_3H_3{\cdot}3HCl$. The residue from this reaction gave only the X-ray powder pattern for mercury(I) chloride.[13] Thus, the idealized equation for this reaction can be written as

$$4ClH_2B_3N_3H_3 + 6HgCl_2 \longrightarrow 3Hg_2Cl_2 + 3Cl_2HB_3N_3H_3 + ClH_2B_3N_3H_3{\cdot}3HCl \quad (4)$$

In this reaction 32% of the 2-chloroborazine was converted to 2,4-dichloroborazine.

Reaction of Borazine and Other Metal Chlorides.—Borazine and the metal chlorides listed below were mixed according to the previous procedure. Lead(II), copper(II), and silver chlorides did not react with borazine. Iron(III) chloride reacted with borazine in ether solution. Hydrogen and a very small amount of 2,4,6-trichloroborazine were identified as products by mass spectral analysis. The state of iron in the nonvolatile residue was shown to be entirely Fe^{2+} by qualitative analysis. However, unsymmetrically-substituted borazines were not obtained.

Tin(IV) chloride in pentane solution reacted to give 2-chloro- and 2,4-dichloroborazine. A very volatile tin-containing species formed during this reaction made separation of the products very difficult. Therefore, this reaction does not appear to be a very useful method for the preparation of unsymmetrically-substituted borazines.

Reaction of Mercury(II) Chloride with 1,3,5-Trimethylborazine.—In a typical experiment, 4.4 g (35.8 mmoles) of 1,3,5-trimethylborazine and 25 ml of pentane solvent were condensed onto 9.1 g (33.6 mmoles) of mercury(II) chloride in a flask connected to a vacuum line. After stirring the reaction for 18 hr at room temperature, the mixture was filtered and the residue was washed with pentane several times to remove any borazine species present. Then the filtrate was fractionated by vacuum distillation using traps at −15, −23, −78, and −196°. After 25 hr of fractionating, solvent was shown to be present in the −196° trap and 22.4 mmoles of unreacted 1,3,5-trimethylborazine was recovered in the −78° trap. Small amounts of 1,3,5-trimethylborazine and 2-chloro-1,3,5-trimethylborazine, $ClH_2B_3N_3(CH_3)_3$, were collected in the −23° trap, and 2,4-dichloro-1,3,5-trimethylborazine, $Cl_2HB_3N_3(CH_3)_3$, was found in the −15° trap. The borazine compounds were identified by mass spectral analysis (see latter section).

The analytical data and the melting point of the material from the −15° trap indicated that the sample was $Cl_2HB_3N_3(CH_3)_3$, mp 99.0–99.5°, although 2-chloro-1,3,5-trimethylborazine was shown still to be present by mass spectral analysis.

Anal. Calcd for $Cl_2HB_3N_3(CH_3)_3$: Cl, 37.2; N, 21.9; hydrogen on hydrolysis, 0.52. Found: Cl, 38.1; N, 21.5; hydrogen on hydrolysis, 0.52.

The nonvolatile residue obtained upon fractionation was white, indicating that no mercury metal was obtained as in the reaction of borazine and mercury(II) chloride in pentane. Mercury(I) chloride was shown to be present in the residue by its X-ray powder pattern.

The yield of $Cl_2HB_3N_3(CH_3)_3$, 1.2 g (6.1 mmoles), was 45% of the 1,3,5-trimethylborazine which reacted. An idealized equation similar to eq 2 may be written for this reaction. The amount of impure $ClH_2B_3N_3(CH_3)_3$ obtained was very small.

Reaction of Thionyl Chloride with 1,3,5-Trimethylborazine.—A solution of 15 mmoles of 1,3,5-trimethylborazine and 9.8 mmoles of $SOCl_2$ in 35 ml of *n*-heptane was refluxed for 12 hr. The gas given off during reflux was collected by displacement of paraffin oil. The reaction flask and container holding the gas were then connected to the vacuum line, and all species volatile at room temperature were separated by vacuum fractionation using traps at −23, −78, −112, and −196°. After 12 hr of fractionation, 6.1 mmoles of pure 2-chloro-1,3,5-trimethylborazine was shown to be present in the −23° trap by analytical data and mass spectral analysis (see latter section), mp 40.5–41.0°.

Anal. Calcd for $ClH_2B_3N_3(CH_3)_3$: N, 26.8; Cl, 22.6; hydrogen on hydrolysis, 1.27. Found: N, 26.9; Cl, 22.9; hydrogen on hydrolysis, 1.23.

Unreacted 1,3,5-trimethylborazine and solvent collected in the −78° trap. Sulfur dioxide was obtained in the −196° trap and was identified by mass spectral analysis. The infrared spectrum of the reddish brown nonvolatile residue was identical with that of the nonvolatile residue obtained during the reaction of 1,3,5-trimethylborazine with mercury(II) chloride; thus,

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the formation of a hydrogen chloride addition compound of 1,3,5-trimethylborazine is postulated for both reactions. The presence of free sulfur in the nonvolatile residue was indicated by chemical and physical means. Thus, the reaction of 1,3,5-trimethylborazine with thionyl chloride to form 2-chloro-1,3,5-trimethylborazine may be written according to the idealized equation

$$8H_3B_3N_3(CH_3)_3 + 6SOCl_2 \longrightarrow 3S^0 + 3SO_2 + 6ClH_2B_3N_3(CH_3)_3 + 2H_3B_3N_3(CH_3)_3\cdot 3HCl \quad (5)$$

Under the conditions used for this reaction, 40% of the 1,3,5-trimethylborazine was recovered as pure 2-chloro-1,3,5-trimethylborazine.

Reaction of 2-Chloroborazine with Dimethylamine.—Dimethylamine, 8.79 mmoles, and 4.01 mmoles of 2-chloroborazine were allowed to react in *n*-pentane according to a previously described procedure.[16] Reaction appeared completed after 0.5 hr at $-78°$. The mixture was fractionated by vacuum distillation using traps at -78 and $-196°$ which separated 2.88 mmoles of pure liquid 2-dimethylaminoborazine, $(CH_3)_2NH_2B_3N_3H_3$, mp 3.0–4.0°, and 0.72 mmole of unreacted dimethylamine, respectively. The 2-dimethylaminoborazine was identified by mass spectral analysis (see latter section) and analytical data.

Anal. Calcd for $(CH_3)_2NH_2B_3N_3H_3$: N, 45.6; hydrogen on hydrolysis, 1.63. Found: N, 46.4; hydrogen on hydrolysis, 1.67.

A small amount of nonvolatile material remained in the $-78°$ trap after removal of the 2-dimethylaminoborazine and accounts for the low yield of the same. A quantitative yield of dimethylamine hydrochloride, 4.15 mmoles, was obtained and identified by chemical means.

Reaction of 2,4-Dichloroborazine with Dimethylamine.—2,4-Dichloroborazine, 3.03 mmoles, and dimethylamine, 12.8 mmoles, were allowed to react as described above. The reaction mixture was filtered to remove dimethylamine hydrochloride and then pentane was removed by vacuum distillation while the filtrate was held at $-20°$ so that the slightly volatile, solid 2,4-bis(dimethylamino)borazine, $((CH_3)_2N)_2HB_3N_3H_3$, was not lost. Pure 2,4-bis(dimethylamino)borazine, 2.46 mmoles, mp 45.0–45.5°, was obtained by sublimation onto a $-78°$ cold finger and identified by mass spectral analysis (see latter section).

Anal. Calcd for $((CH_3)_2N)_2HB_3N_3H_3$: N, 42.2; hydrogen on hydrolysis, 0.60. Found: N, 41.8; hydrogen on hydrolysis, 0.63.

Mass Spectra of Unsymmetrically-Substituted Borazines.—The mass spectra were recorded on a Consolidated Corp. Model 21-103 mass spectrometer using a sweep scan technique and a slow scan rate. The spectra all have the correct *m/e* cut-off values expected for the unsymmetrically-substituted borazines. They also agree very closely with spectra calculated for the compounds considering only boron and chlorine isotopes and using a simple theorem of probability.[15,17] The following paragraph lists the *m/e* values and the relative intensities found for the highest set of *m/e* values for each of the unsymmetrically-substituted borazines.

$ClH_2B_3N_3H_3$.—117, 13; 116, 32; 115, 59; 114, 100; 113, 58; 112, 18; 111, 6; 110, 2. **$Cl_2HB_3N_3H_3$.**—153, 5; 152, 10; 151, 37; 150, 62; 149, 82; 148, 100; 147, 51; 146, 11; 145, 1. **$ClH_2B_3N_3(CH_3)_3$.**—159, 9; 158, 31; 157, 44; 156, 100; 155, 62; 154, 14; 153, 2. **$Cl_2HB_3N_3(CH_3)_3$.**—195, 2; 194, 9; 193, 23; 192, 61; 191, 65; 190, 100; 189, 60; 188, 16; 187, 2. **$(CH_3)_2NH_2B_3N_3H_3$.**—125, 1; 124, 31; 123, 100; 122, 80; 121, 27; 120, 5; 119, 3. **$((CH_3)_2N)_2HB_3N_3H_3$.**–168, 3; 167, 35; 166, 100; 165, 60; 164, 15; 163, 1.

Infrared Spectra.—The infrared spectra of the unsymmetrically-substituted borazines were recorded in the range 4000–400 cm^{-1} with a Perkin-Elmer Model 337 grating spectrophotometer. The spectra of 2-chloro-, 2,4-dichloro-, and 2-dimethylaminoborazine were taken on samples in the gas phase at equilibrium vapor pressures. The spectra of 2,4-dichloro-1,3,5-trimethylborazine were taken as potassium bromide pellets and those of 2,4-bis(dimethylamino)- and 2-chloro-1,3,5-trimethylborazine were taken as mulls in Nujol and hexachlorobutadiene. The following paragraph lists the infrared frequencies (cm^{-1}) for each of the unsymmetrically-substituted borazines.

$ClH_2B_3N_3H_3$.—3465, s; 2593, w; 2531, s; 2414, w; 1454, vs; 1430, m sh; 1418, m sh; 1380, w; 1368, w; 1310, w sh; 1084 m; 1072, s; 1067, s; 1061, s; 1033, s; 1028, s sh; 1022, s sh; 988, w; 924, s; 911, s; 905, s sh; 793, w; 724, s sh; 715, s; 630, s; 611, m. **$Cl_2HB_3N_3H_3$.**—3455, m; 2581, w sh; 2537, m; 2481, w sh; 1460, vs; 1400, w; 1369, w; 1335, w; 1269, w; 1222, w; 1107, w sh; 1095, w sh; 1080, w sh; 1061, m; 990, m; 923, w sh; 918, w sh; 911, m. 743, w; 720, m sh; 712, s; 670, vw; 641, w sh; 634, w; 628, w sh. **$Cl_2HB_3N_3(CH_3)_3$.**—2932, s br; 2845, m sh; 2812, m sh; 2745, w sh; 2551, m sh; 2500, m sh; 2474, m; 1440–1490, vs br; 1378–1410, vs br; 1295, s; 1267, m sh; 1198, w; 1145, w; 1081, s; 1068, s sh; 1034, m; 960–970, s br; 940 m sh; 891, m; 877, s; 678, w sh; 671, w sh; 661, m; 633, m; 615, w sh; 590, w. **$ClH_2B_3N_3(CH_3)_3$.**—2933, m; 2894, m sh; 2855, w sh; 2810, w; 2486, s; 1483, s sh; 1465, vs; 1415, vs; 1303, m; 1290, w sh; 1207, vw; 1095, m; 1070, s; 1018, w sh; 1000, s; 966, vw; 937, m; 926, w; 898, w; 879, s; 643, w; 621, m; 590, w. **$(CH_3)_2NH_2B_3N_3H_3$.**—3470, w; 2972, w sh; 2919, w sh; 2883, w; 2802, w; 2506, m; 2444, w sh; 1539, s; 1467, s sh; 1455, s sh; 1450, s; 1417, w sh; 1353, w; 1261, w; 1162, w sh; 1139, w; 952, w; 919, w; 912, w; 747, m; 680, w sh; 673, m. **$((CH_3)_2N)_2HB_3N_3H_3$.**—3448, s; 2963, m; 2908, m sh, 2862, s; 2791, s; 2626, w; 2490, s; 2430, m sh; 2351, w; 2323, w sh; 2290, w; 2145, w; 1607, m; 1530, vs; 1463, vs; 1430, vs; 1403, vs sh; 1325, s; 1278, m; 1255, w sh; 1186, m; 1148, m; 1096, vs; 1068, m; 1044, w; 1026, w; 947, m; 913 m sh; 899 s; 745, w; 692, s; 677, s; 670, m; 656, s; 642, s; 568, w.

These spectra clearly indicate the N–H, C–H, and B–H stretching vibrations in the ranges 3470–3448, 2972–2745, and 2593–2414 cm^{-1}, respectively. The symmetrical B–N ring vibrations, the strongest bands in the spectra, can be assigned to the absorptions at 1460, 1454, 1378–1410, 1415, 1450, 1430 cm^{-1} for $Cl_2HB_3N_3H_3$, $ClH_2B_3N_3H_3$, $Cl_2HB_3N_3(CH_3)_3$, $ClH_2B_3N_3(CH_3)_3$, $((CH_3)_2N)_2HB_3N_3H_3$, and $(CH_3)_2NH_2B_3N_3H_3$, respectively. The out-of-plane B–N ring vibrations might be assigned to the absorptions at 712, 715, 661, and 621 cm^{-1} for $Cl_2HB_3N_3H_3$, $ClH_2B_3N_3H_3$, $Cl_2HB_3N_3(CH_3)_3$, and $ClH_2B_3N_3(CH_3)_3$, respectively. The only other significant assignment which can be made is the $B-N(CH_3)_2$ deformation at 1530 and 1539 cm^{-1} for $((CH_3)_2N)_2HB_3N_3H_3$ and $(CH_3)_2NH_2B_3N_3H_3$, respectively. The other deformation modes and B–Cl stretching modes could not be assigned due to the complexity of the spectra in the low-frequency region.

Thermal Stability of 2-Chloro-, 2,4-Dichloro-, and 2,4-Bis(dimethylamino)borazine.—Samples of 2-chloro- and 2,4-dichloroborazine were pyrolyzed in sealed tubes at three different temperatures for 10 hr. The product mixtures were separated by vacuum distillation using traps at -10, -46, -78, and $-196°$. Listed in Table II are the conditions for the decompositions and the results obtained. A possible error in these experiments was due to weighing, as the products sometimes weighed less than 10 mg even when 0.1-g samples were used. A small amount of hydrogen gas was formed at 100 and 145° with both compounds; but none was observed at 50° for either compound.

From the data given in Table II it appears that both 2-chloro- and 2,4-dichloroborazine are less stable at 100° than they are at 145°. When the pyrolysis tubes were in the oven, a liquid was observed in both tubes at 100°, while at 145° all the constants appeared to be in the gas phase. Thus, like borazine,[18] the unsymmetrically-chlorinated borazines seem to decompose more rapidly in the liquid phase than they do in the gas phase. On the other hand, liquid 2-chloro- and solid 2,4-dichloroborazine have been stored at room temperature for several days with only a small

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[18] R. Schaeffer, M. Steindler, L. F. Hohnstedt, H. S. Smith, Jr., L. B. Eddy, and H. I. Schlesinger, *ibid.*, **76**, 3303 (1954).

TABLE II

THERMAL STABILITY OF 2-CHLORO- AND 2,4-DICHLOROBORAZINE

			Wt % of starting material isolated as				
Starting compd	Temp, °C	Sample wt, g	ClH_2-B_3N_3-H_3	Cl_2-HB_3-N_3H_3	Cl_3B_3-N_3H_3	H_3B_3-N_3H_3	Nonvol residue by diff
$Cl_2HB_3N_3H_3$	50	0.1489	2	82	None	None	16
$Cl_2HB_3N_3H_3$	100	0.1090	8	2	None	None	90
$Cl_2HB_3N_3H_3$	145	0.0729	23	30	6	2	39
$ClH_2B_3N_3H_3$	50	0.0879	54	3	None	None	43
$ClH_2B_3N_3H_3$	100	0.0991	22	9	None	None	69
$ClH_2B_3N_3H_3$	145	0.0708	60	3	None	4	33

amount of decomposition. In comparison there has been no observed decomposition of $ClH_2B_3N_3(CH_3)_3$ and $Cl_2HB_3N_3(CH_3)_3$ at 25°.

When pure 2,4-bis(dimethylamino)borazine was allowed to stand at room temperature it decomposed completely in 4 days. Mass spectral analysis of all the volatile material remaining when small samples were stored in sealed tubes for this length of time indicated that the main volatile product of the decomposition was dimethylamine. A nonvolatile viscous liquid, probably a polynucleated borazine, remained in the tubes.

Discussion

The mechanism of the reaction of borazine with mercury(II) chloride to form unsymmetrically-substituted borazines must be rather complicated. When *n*-pentane was used as solvent, mercury metal, as well as mercury(I) chloride, was formed; while in diethyl ether the only mercury species obtained was mercury(I) chloride. These results might be explained by the exchange of chloride ion (Cl^-) for a hydride ion (H^-), eq 6, followed by further reaction of the mercury(II) chlorohydride to give either mercury(I) chloride and hydrogen chloride or mercury metal and hydrogen chloride depending on the reactants and the conditions.

$$nHgCl_2 + H_3B_3N_3R_3 \longrightarrow nClHgH + Cl_nH_{3-n}B_3N_3R_3 \quad (6)$$

$$ClHgH + HgCl_2 \longrightarrow Hg_2Cl_2 + HCl \quad (7)$$

$$ClHgH \longrightarrow HCl + Hg^0 \quad (8)$$

The mercury(II) chlorohydride probably undergoes these reactions while still associated with a borazine molecule, because the mercury species formed depends on the solvent and the borazine reagent. This exchange mechanism is similar to the mechanism proposed by Ruff[7] for the reaction of mercury(II) chloride with the amine alanes.

The reactivity of borazine with the different metal chlorides[19] indicates that the reaction is probably controlled by the covalent character and/or the solubility of the metal chloride in organic solvents. This is apparent since, of the easily reducible metal chlorides used, only the three with considerable covalent character and some solubility in organic solvents, mercury(II) chloride, iron(III) chloride, and tin(IV) chloride, reacted.

The thermal stability data on the unsymmetrically-substituted borazines prepared in this investigation suggest the following order. $Cl_3B_3N_3H_3 \sim Cl_2HB_3N_3(CH_3)_3 \sim ClH_2B_3N_3(CH_3)_3 > Cl_2HB_3N_3H_3 > ClH_2B_3N_3H_3 \sim H_3B_3N_3H_3 > [(CH_3)_2N]_2HB_3N_3H_3 \sim (CH_3)_2NH_2B_3N_3H_3$. This order is probably related to the strength of the boron–nitrogen bonds, but kinetic factors might also be significant. The stability of the B-chloro-N-methylborazines is probably due to the combination of the inductive effect of the methyl group and the high electronegativity of the chlorine atoms, which increase the strength of the boron–nitrogen bond. The inductive effect of the methyl group is apparently the more important factor because the B-chloro-N-methylborazines are more stable than the corresponding B-chloroborazines. However, the B-chloro-N-methylborazines might only exhibit stability because they might not undergo a condensation reaction with the elimination of methyl chloride or even methane, whereas the B-chloroborazines could decompose by forming HCl or H_2. Similarly, the instability of the dimethylaminoborazines might be related to an electron-releasing effect of the $(CH_3)_2N$ group. However, the ease with which these compounds eliminate $(CH_3)_2NH$ could also explain their instability. Therefore, it is difficult to relate thermal stabilities and strengths of boron–nitrogen bonds if the compounds under consideration have different types of substituent groups.

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(19) NOTE ADDED IN PROOF.—G. A. Anderson and J. J. Lagowski, *Chem. Commun.*, 649 (1966), have recently reported their work on the preparation of unsymmetrically substituted haloborazines from the reactions of stannic halides and mercury(II) chloride with 1,3,5-trimethylborazine. Our results are similar. The discrepancies between the tin products and the temperature needed for reaction of $HgCl_2$ might be related to different solvent conditions.