step 1: $2NaZnH_3 \rightarrow Na_2ZnH_4 + ZnH_2$

step 2: $ZnH_2 \rightarrow Zn + H_2$

step 3: $Na_2ZnH_4 \rightarrow 2NaH + Zn + H_2$

step 4: $2NaH \rightarrow 2Na + H_2$

The reaction of $NaZn_2(CH_3)_4H$ with $NaAlH_4$ also yielded $NaZnH_3$. The X-ray powder diffraction pattern of $NaZnH_3$ prepared by this route is given in Table III. The mechanism by which $NaZnH_3$ was formed in this reaction is not understood at present.

$NaZn_2H_5$. In a manner similar to the reaction of $KZn(CH_3)_2H$ with AlH_3 which formed KZn_2H_5, AlH_3 was also found to react with $NaZn(CH_3)_2H$ to form $NaZn_2H_5$ (eq 20). The X-ray powder pattern of $NaZn_2H_5$ (Table III)

$$2NaZn(CH_3)_2H + 2AlH_3 \rightarrow NaZn_2H_5 + NaAl_2(CH_3)_4H_3 \qquad (20)$$

contained no lines due to NaH, ZnH_2, Na_2ZnH_4, or $NaZnH_3$. The infrared spectrum of the filtrate remaining after filtration of the solid $NaZn_2H_5$ showed a very broad band in the Al-H stretching region centered at 1610 cm^{-1}. In view of this spectrum and elemental analysis of the filtrate, the product in solution is believed to be a complex between Me_2AlH and $NaAlMe_2H_2$.

The vacuum dta-tga of $NaZn_2H_5$ is shown in Figure 9. Large evolutions of noncondensable gas occurred at 123, 210, and 315°. The ratio of the weight loss during the first gas evolution to that during the second and third ones was 3:1:1. The thermal effect for the first gas evolution was endothermal. This endotherm is believed to be due to disproportionation of $NaZn_2H_5$ to Na_2ZnH_4 and ZnH_2 with simultaneous decomposition of the ZnH_2. The thermal effects for the second and third gas evolutions were also endothermal. The second gas evolution is due to decomposition of Na_2ZnH_4 to NaH and ZnH_2 with simultaneous decomposition of ZnH_2. The third gas evolution is due to decomposition of NaH. The mechanism of decomposition, shown in the three steps below, is supported by X-ray powder diffraction data, taken after the first two stages of gas evolution. The X-ray powder pattern taken after the first step showed lines for Na_2ZnH_4 and Zn metal only. The X-ray powder pattern taken after the second step showed lines for NaH and Zn metal. More evidence is provided by the fact that the ratio of the weight losses in the three steps should be 3:1:1, which is what was observed.

step 1: $NaZn_2H_5 \rightarrow {}^1/_2Na_2ZnH_4 + {}^3/_2Zn + {}^3/_2H_2$

step 2: ${}^1/_2Na_2ZnH_4 \rightarrow NaH + {}^1/_2Zn + {}^1/_2H_2$

step 3: $NaH \rightarrow Na + {}^1/_2H_2$

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Registry No. LiH, 7580-67-8; (*sec*-$C_4H_9)_2Zn$, 7446-94-8; $LiAlH_4$, 16853-85-3; Li_2ZnH_4, 38829-84-4; $(CH_3)_2Zn$, 544-97-8; CH_3Li, 917-54-4; $LiZnH_3$, 38829-83-3; Li_3ZnH_5, 38887-62-6; KH, 7693-26-7; $KZn(CH_3)_2H$, 41202-98-6; AlH_3, 7784-21-6; KZn_2H_5, 37276-96-3; NaH, 7646-69-7; $NaAlH_4$, 13770-96-2; $NaZnH_3$, 34397-46-1; $NaZn_2H_5$, 39356-34-8.

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Syntheses and Properties of Unsymmetrical Boron-Disubstituted Borazine Derivatives

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A series of unsymmetrical B-disubstituted borazine derivatives, $H(Cl)(OCN)B_3N_3H_3$, $H(Cl)(CN)B_3N_3H_3$, $H(CN)(OCN)B_3N_3H_3$, $H(OCN)_2B_3N_3H_3$, and $H(CN)_2B_3N_3H_3$, has been prepared and characterized. The synthetic reactions and the nature of the resulting compounds have been investigated in order to more fully elucidate the effects of substituents on the chemical and physical properties of the borazine ring. The substituents in these new compounds represent unique combinations of electron-withdrawing and electron-donating groups. These B-disubstituted borazine compounds were synthesized from an appropriate *B*-chloroborazine and silver(I) salt by reaction at only a B-Cl bond. The compounds could not be prepared from the B-monosubstituted borazine by reaction with a silver(I) salt. A hydrogen bound to boron in the B-substituted borazine was unreactive to silver(I) salts for the conditions used in our experiments. Our previous work has shown that $H_3B_3N_3H_3$ readily reacts with silver(I) salts. Therefore, our new reactivity data represent the first clear example of a substituent effect in borazine chemistry. The ^1H nmr data for the B-disubstituted borazine derivatives indicate that there is an additivity relationship for the effects of substituents on the chemical shift of the NH protons. However, the additivity relationship is only observed for those substituents for which the ortho and para NH protons are magnetically equivalent in the B-monosubstituted derivative.

One of the most intriguing problems in synthetic inorganic chemistry involves the preparation of unsymmetrically substituted borazine derivatives. Significant advancements have been made in the syntheses of B-monosubstituted borazines. There are many reactions which can be used to prepare only specific B-monosubstituted compounds.[1,2] However, there are no routes designed for the B-disubstituted compounds. All of the simple B-disubstituted borazine derivatives have been previously obtained as products from reactions designed to prepare B-monosubstituted compounds[2-4] or from disproportionation reactions[2] of monosubstituted compounds. Therefore, a knowledge of synthetic reactions for B-disubstituted borazine derivatives would be significant and could provide interesting data on the nature of substitutent effects. Previous experiments have demon-

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strated that substituents affect the properties of the borazine ring,[1,2] and the ring influences the chemical properties of a substituent.[5] The verification of these substituent effects in synthetic chemistry could prove useful for extending our knowledge of the nature of the borazine ring.

In this paper, we report the synthesis and characterization of a series of B-disubstituted borazine derivatives. During the course of this research, we investigated the effects of substituents on the reactivities of the borazine ring to further substitution. The effects of both electron-releasing and electron-withdrawing substituents were compared. Furthermore, the effects of the two substituents in the B-disubstituted derivatives on the nmr chemical shifts of the NH protons were studied in detail in order to ascertain if there was an additivity effect for substituents. The substituents which have been studied include F, Cl, Br, $N(CH_3)_2$, CN, and NCO.

Experimental Section

Materials. All compounds described in this investigation were manipulated in a vacuum system or a purified nitrogen atmosphere. Common solvents and reagents were purified by conventional means. Acetonitrile was dried over P_4O_{10} and distilled prior to use. The silver salts were dried *in vacuo* and then used without further purification. The 2,4,6-trichloroborazine[6] was prepared by allowing BCl_3 to react with NH_4Cl in a tube at 200°. The borazines, $H_2ClB_3N_3H_3$ and $HCl_2B_3N_3H_3$, were prepared by the lithium borohydride reduction[3] of a pyridine complex of $Cl_3B_3N_3H_3$. The preparations of $H_2[N(CH_3)_2]B_3N_3H_3$,[4] $H[N(CH_3)_2]_2B_3N_3H_3$,[4] $H_2FB_3N_3H_3$,[2] $HF_2B_3N_3H_3$,[2] $H_2BrB_3N_3H_3$,[2] and $HBr_2B_3N_3H_3$[2] have been previously described.

Preparation of $H_2(CN)B_3N_3H_3$ and $H_2(OCN)B_3N_3H_3$. The compounds, $H_2(CN)B_3N_3H_3$ and $H_2(OCN)B_3N_3H_3$, were prepared by allowing $H_2ClB_3N_3H_3$ to react with appropriate silver(I) salts. In a typical reaction, 0.5720 g (4.95 mmol) $H_2ClB_3N_3H_3$ was allowed to react with 0.7860 g (5.25 mmol) of AgNCO in 10 ml of pentane at room temperature. After the mixture was stirred for 1 hr, the volatile components were fractionated using −46, −78, and −196° traps. The compounds, $H_2(OCN)B_3N_3H_3$ (0.4160 g, 3.40 mmol) and $H_2ClB_3N_3H_3$ (0.0610 g, 0.527 mmol), were isolated in the −46 and −78° traps, respectively. The solvent, pentane, was recovered from the −196° trap. The residue remaining in the reaction flask was a purple solid, indicative of AgCl. It should be noted that only a trace of noncondensable gas was observed to be formed during the reaction. The product, $H_2(OCN)B_3N_3H_3$, was identified by its melting point [37–39° (lit. 37–38°)] and infrared spectrum.[1] The yield of $H_2(OCN)B_3N_3H_3$ was 76.8% based on the amount of $H_2ClB_3N_3H_3$ which reacted.

The compound, $H_2(CN)B_3N_3H_3$, was prepared in a manner identical with that described for $H_2(OCN)B_3N_3H_3$. The reagents, 0.4690 g (4.06 mmol) of $H_2ClB_3N_3H_3$ and 0.5520 g (4.12 mmol) of AgCN, were allowed to react in pentane at room temperature. After reaction, 0.0420 g (0.363 mmol) of $H_2ClB_3N_3H_3$, 0.365 g (3.48 mmol) of $H_2(CN)B_3N_3H_3$, and 0.120 mmol of noncondensable gas were isolated. The $H_2(CN)B_3N_3H_3$ was sublimed at 35° to a cold finger. The yield of $H_2(CN)B_3N_3H_3$ [mp 111–112° (lit.[1] 111–112°)] was 94.0%, based on the amount of $H_2ClB_3N_3H_3$ consumed.

Attempted Reactions of $H_2(OCN)B_3N_3H_3$, $H_2(CN)B_3N_3H_3$, and AgCN. Previous work[1] has shown that $H_3B_3N_3H_3$ reacts rapidly and completely with silver(I) salts to form B-monosubstituted borazines. Therefore, it was felt that the reaction of a B-monosubstituted borazine with a silver(I) salt would be an ideal preparative route for B-disubstituted borazines. Reactions of AgCN and $H_2(OCN)B_3N_3H_3$ and $H_2(CN)B_3N_3H_3$ were attempted using CH_3CN as solvent. In the case of $H_2(OCN)B_3N_3H_3$, 2.05 mmol was combined with 2.16 mmol of AgCN for 5 hr in 20 ml of CH_3CN at 25°. Only 0.0378 mmol of H_2 was formed and 1.80 mmol (0.2200 g) of $H_2(OCN)B_3N_3H_3$ was recovered unchanged. If the solvent was refluxed for 3 hr, only 24.8% of the $H_2(OCN)B_3N_3H_3$ could be recovered. No material corresponding to the desired product, $H(CN)(OCN)B_3N_3H_3$, was observed. Apparently, the $H_2(OCN)B_3N_3H_3$ decomposes at the reflux temperature of CH_3CN. Similar observations were made in experiments using $H_2(CN)B_3N_3H_3$ as the potential reactant; 88% $H_2(CN)B_3N_3H_3$ could be recovered. When the CH_3CN was refluxed, the starting material decomposed. Thus, it becomes obvious why the reaction of $H_3B_3N_3H_3$ with silver(I) salts is such an ideal preparative route for B-monosubstituted borazines. The product is much less reactive toward silver(I) salts under the conditions of the experiment than is $H_3B_3N_3H_3$.

Table I. Reactions of $HCl_2B_3N_3H_3$ with Silver(I) Salts

X	AgX, mmol	HCl_2B_3-N_3H_3, mmol[a]	Reaction medium	$H(Cl)(X)$-$B_3N_3H_3$		$H(X)_2B_3N_3H_3$	
				%[b]	T,[c] °C	%[b]	T,[c] °C
OCN	1.76	1.27	CH_3CN	9.3	−15	29.8	35
OCN	5.60	1.86	C_5H_{12}	16.1	−15	23.0	35
OCN[d]	5.18	2.18	C_5H_{12}	26.3	−15	7.43	35
CN	3.17	3.17	CH_3CN	25.5	25	37.2	60
CN	2.07	0.79	C_5H_{12}	38.8	25	0	
CN	3.75	1.70	CH_3CN	0		88.8	60

[a] Millimoles of $HCl_2B_3N_3H_3$ consumed during reaction. In most experiments, some $HCl_2B_3N_3H_3$ was recovered. [b] Per cent yield based on millimoles of $HCl_2B_3N_3H_3$ consumed. [c] Temperature required for isolation of product. [d] AgOCN was added slowly over a period of 4 hr.

Reactions of $HCl_2B_3N_3H_3$ with AgX. All of the reactions of $HCl_2B_3N_3H_3$ with silver(I) salts were run in a manner similar to that previously described for the preparation of $H_2(CN)B_3N_3H_3$ and $H_2(OCN)B_3N_3H_3$. The quantities of reagents, reaction medium, percentage yields of products based on $HCl_2B_3N_3H_3$ consumed, and temperature required for isolation of product are given in Table I.

The following lists the analyses and melting points of the new B-disubstituted borazines. It should be noted that these compounds are insoluble in nonpolar solvents such as CCl_4 and C_5H_{12} but soluble in CH_3CN.

$H(Cl)(CN)B_3N_3H_3$. *Anal.* Calcd: N, 29.8; hydrolyzable H, 0.713. Found: N, 29.2; hydrolyzable H, 0.713. The compound softens at 84° and then turns yellow and decomposes at 108°.

$H(CN)_2B_3N_3H_3$. *Anal.* Calcd: N, 32.1; hydrolyzable H, 0.764. Found: N, 32.1; hydrolyzable H, 0.764. The compound turns yellow and decomposes at 126–130°.

$H(Cl)(OCN)B_3N_3H_3$. *Anal.* Calcd: N, 36.8; Cl, 22.7; hydrolyzable H, 0.639. Found: N, 36.8, Cl, 23.5; hydrolyzable H, 0.624. The melting point of the compound is 38–40°. It exhibits a vapor pressure of 0.4 mm at 27°.

$H(OCN)_2B_3N_3H_3$. *Anal.* Calcd: N, 42.9; hydrolyzable H, 0.613. Found: N, 42.9; hydrolyzable H, 0.610. The compound melts at 97–98°.

Preparation of $H(CN)(OCN)B_3N_3H_3$. The compound, $H(CN)(OCN)B_3N_3H_3$, was prepared by allowing $H(Cl)(CN)B_3N_3H_3$ to react with AgOCN or by allowing $H(Cl)(OCN)B_3N_3H_3$ to react with AgCN. Identical products were obtained from both reactions. In a typical experiment, 0.2350 g (1.75 mmol) of AgCN was added to 10 ml of a CH_3CN solution of $H(Cl)(OCN)B_3N_3H_3$ (0.145 g, 0.898 mmol). The mixture was stirred for 3 hr and then the CH_3CN was removed by vacuum distillation. The product, $H(CN)(OCN)B_3N_3H_3$ [0.0700 g, 0.477 mmol, 53.2% yield based on $H(Cl)(OCN)B_3N_3H_3$], was sublimed from the reaction flask at 50° to a −78° cold finger. There was no sublimation at 25°. The compound, $H(CN)(OCN)B_3N_3H_3$, was identified by its elemental analysis and infrared, nmr, and mass spectra. When $H(Cl)(CN)B_3N_3H_3$ was allowed to react with AgOCN, an identical product was obtained in 47.3% yield based on $H(Cl)(CN)B_3N_3H_3$.

$H(CN)(OCN)B_3N_3H_3$. *Anal.* Calcd: N, 38.0; hydrolyzable H, 0.680. Found: N, 37.9; hydrolyzable H, 0.686. The compound softens at 80° and melts with decomposition at 103–108°. It should be noted that this compound appears to decompose upon standing. Mass spectral data indicated the presence of the disproportionation products $H(CN)_2B_3N_3H_3$ and $H(OCN)_2B_3N_3H_3$. These products were not present in a freshly prepared sample.

Infrared Spectra. The infrared spectra were recorded in the range 4000–400 cm^{-1} by means of a Perkin-Elmer 457 spectrometer. The spectra of gases were observed in a 10-cm cell equipped with KBr optics. The spectra of solids were taken on samples as Nujol and Kel-F mulls.

The following gives the spectral frequencies in reciprocal centimeters. Band intensities are reported according to the method of Durkin, DeHayes, and Glore[7] (intensity, vs = very strong, s = strong,

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m = medium, w = weak, vw = very weak, sh = shoulder).

$H(Cl)(CN)B_3N_3H_3$: 3438 (m), 3422 (sh), 3385 (m), 2612 (w), 2582 (w), 2565 (m), 2235 (w), 1470–1450 (vs), 1380 (s), 1370 (s), 1278 (m), 1082 (sh), 1068 (m), 1002 (m), 987 (m), 925 (m), 910 (m), 788 (w), 725 (m), 705 (m), 648 (m), 625 (w), 581 (w).

$H(CN)_2B_3N_3H_3$: 3440 (s), 3422 (sh), 3380 (s), 2620 (m), 2608 (m), 2585 (m), 2238 (m), 1470 (vs), 1405 (m), 1392 (m), 1378 (s), 1368 (sh), 1285 (m), 1100 (m), 1020 (w), 1012 (w), 931 (m), 921 (m), 770 (m), 763 (sh), 718 (m), 660 (w).

$H(Cl)(OCN)B_3N_3H_3$: 3495 (s), 2598 (w), 2540 (m), 2300 (vs), 1525 (vs), 1460–1430 (vs), 1285 (w), 1092 (m), 1070 (m), 1037 (m), 995 (m), 916 (m), 912 (m), 743 (m), 655 (w), 610 (w).

$H(OCN)_2B_3N_3H_3$: 3438 (s), 3422 (s), 2610 (w), 2600 (w), 2580 (w), 2562 (m), 2290 (vs), 1520 (vs), 1460–1430 (vs), 1378 (s), 1362 (s), 1280 (m), 1115 (w), 1100 (m), 1068 (m), 1002 (m), 932 (m), 908 (s), 765 (m), 722 (s), 691 (m), 642 (m), 605 (s), 590 (m).

$H(CN)(OCN)B_3N_3H_3$: 3432 (s), 3415 (s), 3390 (s), 2600 (w), 2580 (m), 2560 (m), 2535 (w), 2320 (vs), 2230 (m), 1535 (s), 1470–1440 (vs), 1378 (s), 1353 (s), 1260 (w), 1125 (w), 1088 (m), 1070 (sh), 1005 (m), 925 (sh), 910 (s), 755 (m), 720 (sh), 675 (sh), 660 (m), 620 (sh), 610 (sh), 600 (m).

Nuclear Magnetic Resonance Spectra. The ^1H nmr spectra were recorded at 100 MHz by means of a Jeolco Model MH-100 spectrometer. In all cases the solvent was CH_3CN. Concentration does not influence the chemical shifts. Tetramethylsilane was used as the internal reference. The chemical shifts of the unsymmetrically substituted borazines are given in Table II.

Table II. ^1H Nuclear Magnetic Resonance Data[a]

Compound	Chemical shift[b] (NH), ppm
$H_3B_3N_3H_3$	−5.97 (T, J = 55 Hz)
$H_2ClB_3N_3H_3$	−5.88 (T, J = 55 Hz)
$HCl_2B_3N_3H_3$	−5.96 (T, unresolved)
$Cl_3B_3N_3H_3$	−6.05 (S)
$H(Cl)(CN)B_3N_3H_3$	−6.54 (T, J = 56 Hz)
$H(CN)_2B_3N_3H_3$	−6.96 (T, unresolved)
$H_2(CN)B_3N_3H_3$	−6.48 (T, J = 55 Hz)
$H(Cl)(OCN)B_3N_3H_3$	−5.84 (T, unresolved)
$H(OCN)_2B_3N_3H_3$	−5.64 (S)
$H_2(OCN)B_3N_3H_3$	−5.80 (T, J = 56 Hz)
$H(CN)(OCN)B_3N_3H_3$	−6.30 (S)

[a] Solvent, CH_3CN; reference, TMS. [b] T, triplet; S, singlet; the BH protons were generally not observed.

Table III. Additivity Effects in ^1H Nmr Data[a]

Compound	Relative δ/sub.[b]	$\delta_{NH(calcd)}$[c]	$\delta_{NH(obsd)}$
$H(CN)_2B_3N_3H_3$	−0.51	−6.97	−6.96
$H(OCN)_2B_3N_3H_3$	+0.17	−5.63	−5.64
$H(CN)(OCN)B_3N_3H_3$	−0.51, +0.17	−6.31	−6.30
$H(Cl)(CN)B_3N_3H_3$	−0.03,[d] −0.51	−6.51	−6.52
$H(Cl)(OCN)B_3N_3H_3$	−0.03,[d] +0.17	−5.83	−5.84
$H(Cl)_2B_3N_3H_3$	−0.03[d]	−6.03	−5.96
$H(Br)_2B_3N_3H_3$	−0.07	−6.11	−6.08
$H(F)_2B_3N_3H_3$	+0.24 (para NH) +0.80 (ortho NH)	−4.37 (2 ortho) −4.93 (ortho, para) −4.49 (2 para)	−5.14
$H(N(CH_3)_2)B_3N_3H_3$	+0.69 (para NH) +1.17 (ortho NH)	−3.53 (2 ortho) −4.11 (ortho, para) −4.59 (2 para)	−4.30

[a] Solvent, CH_3CN. [b] $\delta_{NH}(H_3B_3N_3H_3) - \delta_{NH}(H_2XB_3N_3H_3)$ (see Table II) (−, downfield; +, upfield from $H_3B_3N_3H_3$). [c] $\delta_{NH(calcd)} = \delta_{NH}(H_3B_3N_3H_3)$ + relative δ/sub. (for each substituent). [d] The value of −0.03 ppm is $\delta_{NH}(H_3B_3N_3H_3) - \delta_{NH}(Cl_3B_3N_3H_3)/3$. See text.

Results and Discussion

There are two major routes for the synthesis of a great variety of B-monosubstituted borazine derivatives, the reactions of silver(I) salts with either $H_3B_3N_3H_3$[1] or $H_2ClB_3N_3H_3$. The following equations describe these reactions (X = CN, OCN, SCN, O_2CCH_3, OSO_2CH_3)

$$H_3B_3N_3H_3 + AgX \rightarrow H_2XB_3N_3H_3 + Ag + {}^1/_2H_2$$

$$H_2ClB_3N_3H_3 + AgX \rightarrow H_2XB_3N_3H_3 + AgCl$$

Both of these reactions are synthetically attractive. The reactions occur very readily at room temperature. The B-monosubstituted borazine is easily isolated from the reaction mixture and is obtained in very high yield. It is significant that the chlorine in $H_2ClB_3N_3H_3$ is more reactive than the hydrogens bound to boron. Furthermore, the AgCl formed in the reaction does not react with the hydrogens bound to boron. Compounds of the type $HXClB_3N_3H_3$ have not been observed as products from these preparative reactions. It had been previously observed that AgCl did not react with $H_3B_3N_3H_3$.[4]

The variety of reactions of silver(I) salts with borazines suggests several possible ways to prepare some interesting B-disubstituted borazine derivatives. However, there is only one type of reaction which appears useful. The compounds, $H(OCN)_2B_3N_3H_3$, $H(CN)_2B_3N_3H_3$, $H(CN)(OCN)B_3N_3H_3$, $H(Cl)(OCN)B_3N_3H_3$, and $H(Cl)(CN)B_3N_3H_3$, have only been synthesized by allowing a *B*-chloroborazine to react with a silver(I) salt. A chlorine is the only site which reacts with silver(I) salts to yield B-disubstituted borazine derivatives. The hydrogens bound to boron in B-monosubstituted borazine derivatives are unreactive toward the silver(I) salts for the combinations of reagents and conditions we studied. When 1 mol of $HCl_2B_3N_3H_3$ is allowed to react with 1 mol of silver salt, both $H(Cl)(X)B_3N_3H_3$ and $HX_2B_3N_3H_3$ are formed. The percentage yield of $H(Cl)(X)B_3N_3H_3$ depends on the reaction medium, the rate of addition of silver salt, and possibly on the nature of the ring substituent, X (Table I). The use of *n*-pentane as a reaction medium leads to larger yields of $H(Cl)(X)B_3N_3H_3$ than when acetonitrile is used. The compounds, $H(Cl)(X)B_3N_3H_3$, are insoluble in the nonpolar solvent, pentane, but soluble in CH_3CN. This solubility difference possibly accounts for the difference in activity. The slow addition of the silver salt to the pentane mixture also leads to larger yields of $H(Cl)(X)B_3N_3H_3$. It is tempting to try to relate the percentage yields of $H(Cl)(X)B_3N_3H_3$ and $HX_2B_3N_3H_3$ to an effect of the substituent, X. However, considering all the differences in conditions, solubilities, and reactivities of silver(I) salts, definite conclusions should probably not be made. Further work is necessary.

The B-monosubstituted borazines, $H_2(CN)B_3N_3H_3$ and $H_2(OCN)B_3N_3H_3$, were unreactive toward either AgCN or AgOCN at 25° under the conditions of our experiments. In comparison $H_3B_3N_3H_3$ reacts very readily with AgCN and AgOCN under the same conditions. These reactions are essentially complete in minutes at 25°. The decreased reactivity of these B-monosubstituted borazines toward these silver salts is probably related to a substituent effect generated by the single substituent bound to boron. The nature of this substituent effect is unusual. The effect of electron-donating and electron-withdrawing substituents on the reactivity is similar. It is very difficult to account for the origin of this effect. The substituent might cause a significant change in the nature of the ring. The substituents might alter the polarity of the ring atoms and subsequently increase the extent of delocalization of the π electrons in the ring. In addition, the charge on the atoms bound to the ring could change. The hydrogens bound to boron might have less hydridic character and less reactivity toward silver salts. There is no doubt that the substituents, CN and OCN, have a profound influence on the electronic properties of the borazine ring.

A comparison of the ^1H nmr data for a variety of B-mono- and B-disubstituted borazine derivatives suggests that there is an additivity effect per substituent on the ^1H chemical shift of the NH protons for those compounds in which the ortho and para NH protons are magnetically equivalent. Compounds which have the substitutents, CN and OCN, provide good examples of the additivity effect (Table III). The chemical shift of an NH proton in $H(CN)_2B_3N_3H_3$ and $H(OCN)_2B_3N_3H_3$ is twice that observed for $H_2(CN)B_3N_3H_3$ and $H_2(OCN)B_3N_3H_3$, respectively. An even more interesting example involves the compound, $H(CN)(OCN)B_3N_3H_3$, which has both electron-withdrawing and electron-donating substituents. The observed chemical shift of the NH protons in $H(CN)(OCN)B_3N_3H_3$ is obtained from the algebraic sum of shifts for the CN and OCN groups. The data for compounds containing a chlorine are less clear. There does not appear to be an additivity effect for the substituent, chlorine, when the data for $H_2ClB_3N_3H_3$, $HCl_2B_3N_3H_3$, and $Cl_3B_3N_3H_3$ are compared. However, if one uses one-third of the relative chemical shift of $Cl_3B_3N_3H_3$, -0.03 ppm, as the effect of one chlorine on the nmr shift, a reasonable correlation is obtained for the shift in $H(Cl)(OCN)B_3N_3H_3$ and $H(Cl)(CN)B_3N_3H_3$ (Table III). It is interesting to note that with respect to the NH shift of $H_3B_3N_3H_3$, $Cl_3B_3N_3H_3$ exhibits a downfield shift, $HCl_2B_3N_3H_3$ is essentially unchanged, and $H_2ClB_3N_3H_3$ is shifted upfield. The existence of an additivity effect for the bromine is also unclear. However, an additivity effect is clearly not observed for those substituents, F and $N(CH_3)_2$, in which the ortho and para protons do not have the same chemical shifts. Additional work is necessary to establish the extent of this additivity effect. We attempted to look at $(OCN)_3B_3N_3H_3$ and $(CN)_3B_3N_3H_3$ but the compounds are not sufficiently soluble to obtain good spectra.

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Registry No. $H_2ClB_3N_3H_3$, 15061-65-1; AgNCO, 3315-16-0; AgCN, 506-64-9; $H(Cl)_2B_3N_3H_3$, 15259-40-2; $H(Cl)(CN)B_3N_3H_3$, 41380-16-9; $H(CN)_2B_3N_3H_3$, 41380-17-0; $H(Cl)(OCN)B_3N_3H_3$, 41380-18-1; $H(OCN)_2B_3N_3H_3$, 41380-19-2; $H(CN)(OCN)B_3N_3H_3$, 41380-20-5; $H_3B_3N_3H_3$, 6569-51-3; $Cl_3B_3N_3H_3$, 933-18-6; $H(Br)_2B_3N_3H_3$, 41380-21-6; $H(F)_2B_3N_3H_3$, 41380-22-7; $H[N(CH_3)_2]_2B_3N_3H_3$, 15599-21-0.

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Oxidation of 1,1-Dimethyldiborane. Gas-Phase Peroxide Intermediates[1]

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The reaction between 1,1-dimethyldiborane and oxygen at 80° in the gas phase is described in which the major final stable product is 2,5-dimethyl-1,3,4-trioxadiborolane, $(CH_3)_2B_2O_3$. Mass spectrometric–molecular leak techniques indicate that the reaction proceeds *via* the formation of an unstable intermediate. The intermediate has been identified as dimethylboryl hydroperoxide, $(CH_3)_2BOOH$, which either rearranges intermolecularly to form dimethoxyborane or condenses, with the elimination of methanol and methane, to form $(CH_3)_2B_2O_3$. Evidence for this rearrangement is obtained from isotope substitution experiments in the mass spectral study. Evidence for the hydroperoxide is obtained from mass spectral and infrared spectrophotometric data and from chemical data.

Introduction

It is well established that the autoxidation of trisubstituted boranes proceeds by the formation of peroxides.[2] Samples of relatively stable mono-, di-, and triperoxyboranes have been prepared in autoxidation studies of various tributylboranes. It has been demonstrated recently that these reactions proceed *via* autocatalytic radical chain mechanisms.[3,4] However, in the case of the lower alkyl and unsubstituted boranes, the intermediate peroxides are less stable and much of the evidence for them is indirect. Studies of the autoxidation of triethylborane establish that peroxides are formed although these intermediate peroxides have not been characterized conclusively.[5,6] A well-characterized process is the oxidation of trimethylborane in which the initially formed dimethylboryl methyl peroxide slowly rearranges to dimethoxy(methyl)borane.[7,8] The oxidation of BH_3CO[9] and BH_3PF_3 to form $H_2B_2O_3$ has been shown to proceed *via* an intermediate which forms without the scission of the O–O bond in oxygen but the intermediates formed are too short-lived to have been observed by the techniques used.

Mechanistic information on the oxidation of partially substituted diboranes is lacking and the nature of any unstable intermediates in these processes is unknown. Indeed Parts and Miller[8] have reported that 1,1-$(CH_3)_2B_2H_4$, $(CH_3)_4B_2H_2$, and B_2H_6 are not susceptible to oxidation in solution at low temperatures. Bauer, Wiberley, and Sandvik[10] observed an intermediate in the oxidation of 1,2-$(C_2H_5)_2B_2H_4$ which appeared to be diperoxide.

This report describes mechanistic studies of the oxidation of 1,1-dimethyldiborane in the gas phase at temperatures up to 100°. Evidence shows that one intermediate is dimethylboryl hydroperoxide, $(CH_3)_2BOOH$, which rearranges or

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[2] For reviews of peroxide formation in the autoxidation of boranes see A. G. Davies, *Progr. Boron Chem.*, 1, 265 (1964); T. G. Brilkina and V. A. Shushunov, "Reactions of Organometallic Compounds with Oxygen and Peroxides," Iliffe Books Ltd., London, 1969.

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