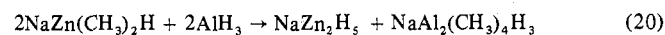


The reaction of $\text{NaZn}_2(\text{CH}_3)_4\text{H}$ with NaAlH_4 also yielded NaZnH_3 . The X-ray powder diffraction pattern of NaZnH_3 prepared by this route is given in Table III. The mechanism by which NaZnH_3 was formed in this reaction is not understood at present.

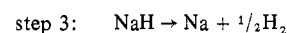
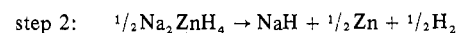
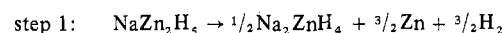
NaZn_2H_5 . In a manner similar to the reaction of $\text{KZn}(\text{CH}_3)_2\text{H}$ with AlH_3 which formed KZn_2H_5 , AlH_3 was also found to react with $\text{NaZn}(\text{CH}_3)_2\text{H}$ to form NaZn_2H_5 (eq 20). The X-ray powder pattern of NaZn_2H_5 (Table III)



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 $\text{NaAlMe}_2\text{H}_2$.

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 endothermic. This endotherm is believed to be due to dis-

proportionation 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 endothermic. 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.



Acknowledgment. We are indebted to the Office of Naval Research (Contract No. N000 14-67-A-0159-0005 and Contract Authority No. NR-93-050/12-5-67-429) for support of this work.

Registry No. LiH , 7580-67-8; (*sec*- C_4H_9) $_2\text{Zn}$, 7446-94-8; LiAlH_4 , 16853-85-3; Li_2ZnH_4 , 38829-84-4; $(\text{CH}_3)_2\text{Zn}$, 544-97-8; CH_3Li , 917-54-4; LiZnH_3 , 38829-83-3; Li_3ZnH_5 , 38887-62-6; KH , 7693-26-7; $\text{KZn}(\text{CH}_3)_2\text{H}$, 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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Received February 20, 1973

A series of unsymmetrical B-disubstituted borazine derivatives, $\text{H}(\text{Cl})(\text{OCN})\text{B}_3\text{N}_3\text{H}_3$, $\text{H}(\text{Cl})(\text{CN})\text{B}_3\text{N}_3\text{H}_3$, $\text{H}(\text{CN})(\text{OCN})\text{B}_3\text{N}_3\text{H}_3$, $\text{H}(\text{OCN})_2\text{B}_3\text{N}_3\text{H}_3$, and $\text{H}(\text{CN})_2\text{B}_3\text{N}_3\text{H}_3$, 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-disubstituted borazine was unreactive to silver(I) salts for the conditions used in our experiments. Our previous work has shown that $\text{H}_3\text{B}_3\text{N}_3\text{H}_3$ 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 compounds²⁻⁴ or from disproportionation reactions² 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 substituent effects. Previous experiments have demon-

(1) O. T. Beachley, Jr., *J. Amer. Chem. Soc.*, **93**, 5066 (1971).
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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(CH₃)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 P₄O₁₀ and distilled prior to use. The silver salts were dried *in vacuo* and then used without further purification. The 2,4,6-trichloroborazine⁶ was prepared by allowing BCl₃ to react with NH₄Cl in a tube at 200°. The borazines, H₂CIB₃N₃H₃ and HCl₂B₃N₃H₃, were prepared by the lithium borohydride reduction³ of a pyridine complex of Cl₃B₃N₃H₃. The preparations of H₂[N(CH₃)₂]₂B₃N₃H₃,⁴ H[(N(CH₃)₂)₂B₃N₃H₃],⁴ H₂FB₃N₃H₃,² HF₂B₃N₃H₃,² H₂BrB₃N₃H₃,² and HBr₂B₃N₃H₃² have been previously described.

Preparation of H₂(CN)B₃N₃H₃ and H₂(OCN)B₃N₃H₃. The compounds, H₂(CN)B₃N₃H₃ and H₂(OCN)B₃N₃H₃, were prepared by allowing H₂CIB₃N₃H₃ to react with appropriate silver(I) salts. In a typical reaction, 0.5720 g (4.95 mmol) H₂CIB₃N₃H₃ 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, H₂(OCN)B₃N₃H₃ (0.4160 g, 3.40 mmol) and H₂CIB₃N₃H₃ (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, H₂(OCN)B₃N₃H₃, was identified by its melting point [37-39° (lit. 37-38°)] and infrared spectrum.¹ The yield of H₂(OCN)B₃N₃H₃ was 76.8% based on the amount of H₂CIB₃N₃H₃ which reacted.

The compound, H₂(CN)B₃N₃H₃, was prepared in a manner identical with that described for H₂(OCN)B₃N₃H₃. The reagents, 0.4690 g (4.06 mmol) of H₂CIB₃N₃H₃ 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 H₂CIB₃N₃H₃, 0.365 g (3.48 mmol) of H₂(CN)B₃N₃H₃, and 0.120 mmol of noncondensable gas were isolated. The H₂(CN)B₃N₃H₃ was sublimed at 35° to a cold finger. The yield of H₂(CN)B₃N₃H₃ [mp 111-112° (lit.¹ 111-112°)] was 94.0%, based on the amount of H₂CIB₃N₃H₃ consumed.

Attempted Reactions of H₂(OCN)B₃N₃H₃, H₂(CN)B₃N₃H₃, and AgCN. Previous work¹ has shown that H₃B₃N₃H₃ 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 H₂(OCN)B₃N₃H₃ and H₂(CN)B₃N₃H₃ were attempted using CH₃CN as solvent. In the case of H₂(OCN)B₃N₃H₃, 2.05 mmol was combined with 2.16 mmol of AgCN for 5 hr in 20 ml of CH₃CN at 25°. Only 0.0378 mmol of H₂ was formed and 1.80 mmol (0.2200 g) of H₂(OCN)B₃N₃H₃ was recovered unchanged. If the solvent was refluxed for 3 hr, only 24.8% of the H₂(OCN)B₃N₃H₃ could be recovered. No material corresponding to the desired product, H(CN)(OCN)B₃N₃H₃, was observed. Apparently, the H₂(OCN)B₃N₃H₃ decomposes at the reflux temperature of CH₃CN. Similar observations were made in experiments using H₂(CN)B₃N₃H₃ as the potential reactant; 88%

Table I. Reactions of HCl₂B₃N₃H₃ with Silver(I) Salts

X	HCl ₂ B ₃ N ₃ H ₃		Reaction medium	H(Cl)(X)-B ₃ N ₃ H ₃		H(X) ₂ B ₃ N ₃ H ₃	
	AgX, mmol	N ₃ H ₃ , mmol ^a		% ^b	T, °C ^c	% ^b	T, °C ^c
OCN	1.76	1.27	CH ₃ CN	9.3	-15	29.8	35
OCN	5.60	1.86	C ₅ H ₁₂	16.1	-15	23.0	35
OCN ^d	5.18	2.18	C ₅ H ₁₂	26.3	-15	7.43	35
CN	3.17	3.17	CH ₃ CN	25.5	25	37.2	60
CN	2.07	0.79	C ₅ H ₁₂	38.8	25	0	
CN	3.75	1.70	CH ₃ CN	0		88.8	60

^a Millimoles of HCl₂B₃N₃H₃ consumed during reaction. In most experiments, some HCl₂B₃N₃H₃ was recovered. ^b Per cent yield based on millimoles of HCl₂B₃N₃H₃ consumed. ^c Temperature required for isolation of product. ^d AgOCN was added slowly over a period of 4 hr.

H₂(CN)B₃N₃H₃ could be recovered. When the CH₃CN was refluxed, the starting material decomposed. Thus, it becomes obvious why the reaction of H₃B₃N₃H₃ 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 H₃B₃N₃H₃.

Reactions of HCl₂B₃N₃H₃ with AgX. All of the reactions of HCl₂B₃N₃H₃ with silver(I) salts were run in a manner similar to that previously described for the preparation of H₂(CN)B₃N₃H₃ and H₂(OCN)B₃N₃H₃. The quantities of reagents, reaction medium, percentage yields of products based on HCl₂B₃N₃H₃ 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 CCl₄ and C₅H₁₂ but soluble in CH₃CN.

H(Cl)(CN)B₃N₃H₃. *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)₂B₃N₃H₃. *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)B₃N₃H₃. *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)₂B₃N₃H₃. *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)B₃N₃H₃. The compound, H(CN)(OCN)B₃N₃H₃, was prepared by allowing H(Cl)(CN)B₃N₃H₃ to react with AgOCN or by allowing H(Cl)(OCN)B₃N₃H₃ 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 CH₃CN solution of H(Cl)(OCN)B₃N₃H₃ (0.145 g, 0.898 mmol). The mixture was stirred for 3 hr and then the CH₃CN was removed by vacuum distillation. The product, H(CN)(OCN)B₃N₃H₃ [0.0700 g, 0.477 mmol, 53.2% yield based on H(Cl)(OCN)B₃N₃H₃], was sublimed from the reaction flask at 50° to a -78° cold finger. There was no sublimation at 25°. The compound, H(CN)(OCN)B₃N₃H₃, was identified by its elemental analysis and infrared, nmr, and mass spectra. When H(Cl)(CN)B₃N₃H₃ was allowed to react with AgOCN, an identical product was obtained in 47.3% yield based on H(Cl)(CN)B₃N₃H₃.

H(CN)(OCN)B₃N₃H₃. *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)₂B₃N₃H₃ and H(OCN)₂B₃N₃H₃. 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 KBr mulls.

The following gives the spectral frequencies in reciprocal centimeters. Band intensities are reported according to the method of Durkin, DeHayes, and Gloré⁷ (intensity, vs = very strong, s = strong,

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(7) T. R. Durkin, L. DeHayes, and J. Gloré, *J. Chem. Educ.*, **48**, 452 (1971).

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

H(Cl)(CN)B₃N₃H₃: 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 (m), 725 (m), 705 (m), 648 (m), 625 (w), 581 (w).

H(CN)₂B₃N₃H₃: 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)B₃N₃H₃: 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).

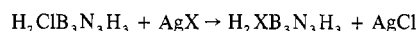
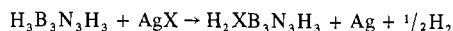
H(OCN)₂B₃N₃H₃: 3438 (s), 3422 (s), 2610 (w), 2600 (w), 2580 (w), 2562 (m), 2290 (vs), 1520 (vs), 1460–1430 (vs), 1378 (s), 1362 (s), 1280 (m), 1115 (w), 1100 (m), 1068 (m), 1002 (m), 932 (m), 908 (s), 765 (m), 722 (s), 691 (m), 642 (m), 605 (s), 590 (m).

H(CN)(OCN)B₃N₃H₃: 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 CH₃CN. 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.

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 H₃B₃N₃H₃¹ or H₂ClB₃N₃H₃. The following equations describe these reactions (X = CN, OCN, SCN, O₂CCH₃, OSO₂CH₃)



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 H₂ClB₃N₃H₃ 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 HXClB₃N₃H₃ have not been observed as products from these preparative reactions. It had been previously observed that AgCl did not react with H₃B₃N₃H₃.⁴

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)₂B₃N₃H₃, H(CN)₂B₃N₃H₃, H(CN)(OCN)B₃N₃H₃, H(Cl)(OCN)B₃N₃H₃, and H(Cl)(CN)B₃N₃H₃, 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 HCl₂B₃N₃H₃ is allowed to react with 1 mol of silver salt, both H(Cl)(X)B₃N₃H₃ and HX₂B₃N₃H₃ are formed. The percentage yield of H(Cl)(X)B₃N₃H₃ 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)B₃N₃H₃ than when acetonitrile is used. The compounds, H(Cl)(X)B₃N₃H₃, are insoluble in the nonpolar solvent, pentane, but soluble in CH₃CN. This solubility difference possibly accounts for the difference in activity. The slow addition of the silver salt to the pentane

Table II. ¹H Nuclear Magnetic Resonance Data^a

Compound	Chemical shift ^b (NH), ppm
H ₃ B ₃ N ₃ H ₃	-5.97 (T, <i>J</i> = 55 Hz)
H ₂ ClB ₃ N ₃ H ₃	-5.88 (T, <i>J</i> = 55 Hz)
HCl ₂ B ₃ N ₃ H ₃	-5.96 (T, unresolved)
Cl ₂ B ₃ N ₃ H ₃	-6.05 (S)
H(Cl)(CN)B ₃ N ₃ H ₃	-6.54 (T, <i>J</i> = 56 Hz)
H(CN) ₂ B ₃ N ₃ H ₃	-6.96 (T, unresolved)
H ₂ (CN)B ₃ N ₃ H ₃	-6.48 (T, <i>J</i> = 55 Hz)
H(Cl)(OCN)B ₃ N ₃ H ₃	-5.84 (T, unresolved)
H(OCN) ₂ B ₃ N ₃ H ₃	-5.64 (S)
H ₂ (OCN)B ₃ N ₃ H ₃	-5.80 (T, <i>J</i> = 56 Hz)
H(CN)(OCN)B ₃ N ₃ H ₃	-6.30 (S)

^a Solvent, CH₃CN; 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	$\delta_{\text{NH}}(\text{calcd})^c$	$\delta_{\text{NH}}(\text{obsd})$
H(CN) ₂ B ₃ N ₃ H ₃	-0.51	-6.97	-6.96
H(OCN) ₂ B ₃ N ₃ H ₃	+0.17	-5.63	-5.64
H(CN)(OCN)B ₃ N ₃ H ₃	-0.51, +0.17	-6.31	-6.30
H(Cl)(CN)B ₃ N ₃ H ₃	-0.03, ^d -0.51	-6.51	-6.52
H(Cl)(OCN)B ₃ N ₃ H ₃	-0.03, ^d +0.17	-5.83	-5.84
H(Cl) ₂ B ₃ N ₃ H ₃	-0.03 ^d	-6.03	-5.96
H(Br) ₂ B ₃ N ₃ H ₃	-0.07	-6.11	-6.08
H(F) ₂ B ₃ N ₃ H ₃	+0.24 (para NH)	-4.37 (2 ortho)	
	+0.80 (ortho NH)	-4.93 (ortho, para)	-5.14
		-4.49 (2 para)	
H(N(CH ₃) ₂)B ₃ N ₃ H ₃	+0.69 (para NH)	-3.53 (2 ortho)	
	+1.17 (ortho NH)	-4.11 (ortho, para)	-4.30
		-4.59 (2 para)	

^a Solvent, CH₃CN. ^b $\delta_{\text{NH}}(\text{H}_3\text{B}_3\text{N}_3\text{H}_3) - \delta_{\text{NH}}(\text{H}_2\text{XB}_3\text{N}_3\text{H}_3)$ (see Table II) (-, downfield; +, upfield from H₃B₃N₃H₃). ^c $\delta_{\text{NH}}(\text{calcd}) = \delta_{\text{NH}}(\text{H}_3\text{B}_3\text{N}_3\text{H}_3) + \text{relative } \delta/\text{sub.}$ (for each substituent). ^d The value of -0.03 ppm is $\delta_{\text{NH}}(\text{H}_3\text{B}_3\text{N}_3\text{H}_3) - \delta_{\text{NH}}(\text{Cl}_2\text{B}_3\text{N}_3\text{H}_3)/3$. See text.

mixture also leads to larger yields of H(Cl)(X)B₃N₃H₃. It is tempting to try to relate the percentage yields of H(Cl)(X)B₃N₃H₃ and HX₂B₃N₃H₃ 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, H₂(CN)B₃N₃H₃ and H₂(OCN)B₃N₃H₃, were unreactive toward either AgCN or AgOCN at 25° under the conditions of our experiments. In comparison H₃B₃N₃H₃ 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 substituents, CN and OCN, provide good examples of the additivity effect (Table III). The chemical shift of an NH proton in $\text{H}(\text{CN})_2\text{B}_3\text{N}_3\text{H}_3$ and $\text{H}(\text{OCN})_2\text{B}_3\text{N}_3\text{H}_3$ is twice that observed for $\text{H}_2(\text{CN})\text{B}_3\text{N}_3\text{H}_3$ and $\text{H}_2(\text{OCN})\text{B}_3\text{N}_3\text{H}_3$, respectively. An even more interesting example involves the compound, $\text{H}(\text{CN})(\text{OCN})\text{B}_3\text{N}_3\text{H}_3$, which has both electron-withdrawing and electron-donating substituents. The observed chemical shift of the NH protons in $\text{H}(\text{CN})(\text{OCN})\text{B}_3\text{N}_3\text{H}_3$ 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 $\text{H}_2\text{ClB}_3\text{N}_3\text{H}_3$, $\text{HCl}_2\text{B}_3\text{N}_3\text{H}_3$, and $\text{Cl}_3\text{B}_3\text{N}_3\text{H}_3$ are compared. However, if one uses one-third of the relative chemical shift of $\text{Cl}_3\text{B}_3\text{N}_3\text{H}_3$, -0.03 ppm, as the effect of one chlorine on the nmr shift, a reasonable correlation is obtained for the shift in $\text{H}(\text{Cl})(\text{OCN})\text{B}_3\text{N}_3\text{H}_3$ and $\text{H}(\text{Cl})(\text{CN})\text{B}_3\text{N}_3\text{H}_3$ (Table III). It is interesting to note that with respect to the NH shift of $\text{H}_3\text{B}_3\text{N}_3\text{H}_3$, $\text{Cl}_3\text{B}_3\text{N}_3\text{H}_3$ exhibits a downfield shift,

$\text{HCl}_2\text{B}_3\text{N}_3\text{H}_3$ is essentially unchanged, and $\text{H}_2\text{ClB}_3\text{N}_3\text{H}_3$ 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 $\text{N}(\text{CH}_3)_2$, 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 $(\text{OCN})_3\text{B}_3\text{N}_3\text{H}_3$ and $(\text{CN})_3\text{B}_3\text{N}_3\text{H}_3$ but the compounds are not sufficiently soluble to obtain good spectra.

Acknowledgments. We wish to thank the National Science Foundation, Grant No. GP-20200, for financial support of this research.

Registry No. $\text{H}_2\text{ClB}_3\text{N}_3\text{H}_3$, 15061-65-1; AgNCO , 3315-16-0; AgCN , 506-64-9; $\text{H}(\text{Cl})_2\text{B}_3\text{N}_3\text{H}_3$, 15259-40-2; $\text{H}(\text{Cl})(\text{CN})\text{B}_3\text{N}_3\text{H}_3$, 41380-16-9; $\text{H}(\text{CN})_2\text{B}_3\text{N}_3\text{H}_3$, 41380-17-0; $\text{H}(\text{Cl})(\text{OCN})\text{B}_3\text{N}_3\text{H}_3$, 41380-18-1; $\text{H}(\text{OCN})_2\text{B}_3\text{N}_3\text{H}_3$, 41380-19-2; $\text{H}(\text{CN})(\text{OCN})\text{B}_3\text{N}_3\text{H}_3$, 41380-20-5; $\text{H}_3\text{B}_3\text{N}_3\text{H}_3$, 6569-51-3; $\text{Cl}_3\text{B}_3\text{N}_3\text{H}_3$, 933-18-6; $\text{H}(\text{Br})_2\text{B}_3\text{N}_3\text{H}_3$, 41380-21-6; $\text{H}(\text{F})_2\text{B}_3\text{N}_3\text{H}_3$, 41380-22-7; $\text{H}[\text{N}(\text{CH}_3)_2]_2\text{B}_3\text{N}_3\text{H}_3$, 15599-21-0.

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Oxidation of 1,1-Dimethyldiborane. Gas-Phase Peroxide Intermediates¹

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Received April 19, 1973

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, $(\text{CH}_3)_2\text{B}_2\text{O}_3$. 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, $(\text{CH}_3)_2\text{BOOH}$, which either rearranges intermolecularly to form dimethoxyborane or condenses, with the elimination of methanol and methane, to form $(\text{CH}_3)_2\text{B}_2\text{O}_3$. 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 $\text{H}_2\text{B}_2\text{O}_3$ 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 Miller⁸ have reported that 1,1- $(\text{CH}_3)_2\text{B}_2\text{H}_4$, $(\text{CH}_3)_4\text{B}_2\text{H}_2$, and B_2H_6 are not susceptible to oxidation in solution at low temperatures. Bauer, Wiberley, and Sandvik¹⁰ observed an intermediate in the oxidation of 1,2- $(\text{C}_2\text{H}_5)_2\text{B}_2\text{H}_4$ 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, $(\text{CH}_3)_2\text{BOOH}$, which rearranges or

(1) (a) Work supported by NSF Grant GP 11211. (b) Presented at the 165th National Meeting of the American Chemical Society, Dallas, Tex., April 1973.

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