

assumption for the structure of II would be $[(\text{C}_6\text{H}_5)_2\text{P}(\text{Cl})\text{NHP}(\text{NH}_2)(\text{C}_6\text{H}_5)_2]\text{Cl}_2$.

It is interesting to note that the virtually quantitative formation of the compound $[(\text{C}_6\text{H}_5)_2\text{P}(\text{NH}_2)\text{Cl}]\text{Cl}$ by the direct reaction of chloramine with $(\text{C}_6\text{H}_5)_2\text{PCl}$ in the absence of any base stronger than $(\text{C}_6\text{H}_5)_2\text{PCl}$ or diethyl ether is further evidence against the necessity for assuming the existence of the NHCl^- species as an intermediate in the chloramination process.⁹

It is interesting to note that the work reported herein,

(9) G. Yagil and M. Anbar, *J. Am. Chem. Soc.*, **84**, 1797 (1962).

along with that previously reported in this laboratory,¹ has established three related procedures for converting $(\text{C}_6\text{H}_5)_2\text{PCl}$ to $[(\text{C}_6\text{H}_5)_2\text{PN}]_3$ and $[(\text{C}_6\text{H}_5)_2\text{PN}]_4$.

In each case an intermediate was isolated, each one bearing an interesting relationship to the others, as the reactions shown in Scheme II indicate.

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CONTRIBUTION FROM SHIONOGI RESEARCH LABORATORY,
SHIONOGI & CO., LTD. FUKUSHIMA-KU, OSAKA, JAPAN

Steric Effects in Tris(N-boryl-2-pyridylamino)borane and Its Derivatives

By K. NAGASAWA, T. YOSHIZAKI, AND H. WATANABE

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The presence of three B←N coordinate bonds in tris(N-boryl-2-pyridylamino)boranes was confirmed by the chemical shift of the ¹¹B nuclear magnetic resonance spectrum as well as by the B-H stretching frequency of tris(N-boryl-2-pyridylamino)borane itself. The reactions between boron trichloride and some ring-substituted 2-aminopyridines were examined to appraise the importance of the coordinate bonds in the formation of this series of compounds. The reactions indicated that the substituent on the 3-position of pyridine prevented the formation of the B←N coordinate bonds and of the framework, and that the coordinate bonds are indispensable.

In an earlier paper¹ dealing with the reaction between boron trichloride and 2-aminopyridine followed by an appropriate Grignard reaction, it was shown that the reaction afforded a new type of compounds as shown in

Figure 1. The three coordinate bonds between ring nitrogen and boryl boron atoms were deduced from the electronegativity of boron and steric requirements. The present paper has aimed first, at confirming the presence of the three boron-nitrogen coordinate bonds and second, at evaluating the importance of the B←N coordinate bond in formation of this series of compounds.

(1) H. Watanabe, K. Nagasawa, T. Totani, T. Yoshizaki, and T. Nakagawa, "Boron-Nitrogen Chemistry," *Advances in Chemistry Series*, No. 42, American Chemical Society, Washington, D. C., 1964, p. 116.

TABLE I
 STRETCHING FREQUENCIES AND HYBRIDIZATION

Compound	B(sp ²)-H frequencies, cm. ⁻¹	Average ^a	Compound	B(sp ³)-H frequencies, cm. ⁻¹	Average ^a
B ₃ H ₃ N ₃ H ₃ ^{b,c}	2530		(CH ₃) ₂ NBH ₃ ^e	2270	
B ₃ H ₃ N ₃ (CH ₃) ₃ ^d	2483		H ₃ NBH ₃ ^f	2330	2310
B ₃ H ₃ N ₃ (C ₆ H ₅) ₃ ^d	2556		H ₆ B ₃ N ₃ H ₃ (CH ₃) ₃ (I) ^f	2285	
(CH ₃ O) ₂ BH ^f	2504	2539	H ₆ B ₃ N ₃ H ₃ (CH ₃) ₃ (II) ^f	2316	2306
(C ₂ H ₅ O) ₂ BH ^g	2513		C ₆ H ₅ NBH ₃ ^h	2279	~2326
(i-C ₃ H ₇ O) ₂ BH ^h	2505		(CH ₃) ₂ OBH ₃ ⁱ	2367	~2326
	2490			2290	2338
				2401	2364

^a W. J. Lehmann, *J. Mol. Spectry.*, **7**, 1, 261 (1961). ^b H. Watanabe, M. Narisada, T. Nakagawa, and M. Kubo, *Spectrochim. Acta*, **16**, 78 (1960). ^c B. L. Crawford, Jr., and J. T. Edsall, *J. Chem. Phys.*, **7**, 223 (1939); W. C. Price, R. D. B. Fraser, T. S. Robinson, and H. C. Longuet-Higgins, *Discussions Faraday Soc.*, **9**, 131 (1950). ^d H. Watanabe, Y. Kuroda, and M. Kubo, *Spectrochim. Acta*, **17**, 454 (1961). ^e H. J. Becher and S. Frick, *Z. anorg. allgem. Chem.*, **295**, 83 (1958). ^f W. J. Lehmann, T. P. Onak, and I. Shapiro, *J. Chem. Phys.*, **30**, 1215 (1959). ^g W. J. Lehmann, H. G. Weiss, and I. Shapiro, *ibid.*, **30**, 1222 (1959). ^h W. J. Lehmann, H. G. Weiss, and I. Shapiro, *ibid.*, **30**, 1226 (1959). ⁱ R. C. Taylor, "Boron-Nitrogen Chemistry," *Advances in Chemistry Series*, No. 42, American Chemical Society, Washington, D. C., 1964, p. 59; B. Rice, R. J. Galiano, and W. J. Lehmann, *J. Phys. Chem.*, **61**, 1222 (1957). ^j D. F. Gaines and R. Schaeffer, *J. Am. Chem. Soc.*, **85**, 395 (1963). ^k W. J. Lehmann, Ph.D. Dissertation, Saint Louis University, 1954. ^l B. Rice and H. S. Uchida, *J. Phys. Chem.*, **59**, 650 (1955).

Excellent evidence for three B←N coordinate bonds in tris(N-boryl-2-pyridylamino)boranes may be derived from ¹¹B n.m.r. chemical shifts which provide information on the electron density around the boron nucleus.² Tris(N-diethylboryl-2-pyridylamino)borane

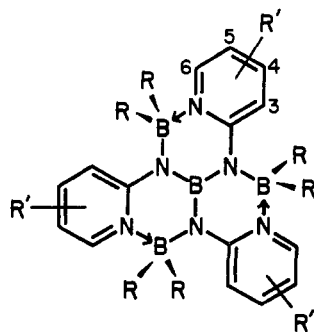


Figure 1.—Structure.

showed two peaks at -7.2 and $+16.8$ p.p.m. as referred to trimethyl borate, the intensity of the latter peak being three times as great as that of the former, to indicate that the peak at $+16.8$ p.p.m. is attributable to the three surrounding boron atoms and that at -7.2 p.p.m. to the central boron. On comparison of these chemical shifts with those of various other boron-containing compounds reported by Phillips, *et al.*,³ the value of $+16.8$ p.p.m. turns out to be much the same value as that for the N,N-dimethylaminoborane dimer, $+14.5$ p.p.m., indicating the bonding hybrid of the three boron atoms to be sp³ as a result of coordination.

Additional evidence is afforded by the B-H stretching frequency in the infrared spectrum of tris(N-boryl-2-pyridylamino)borane (I) itself. For the C-H stretching vibrations,⁴ it is well established and employed in

(2) This was suggested by R. Schaeffer.

(3) W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959).

(4) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 43; C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press, New York, N. Y., 1963, pp. 150, 155.

some quantitative studies⁵ that the normal C-H vibrations of saturated structures occur at frequencies below 3000 cm.⁻¹, whereas the olefinic hydrogen stretching vibrations occur in the range 3100 to 3000 cm.⁻¹ and the C-H stretching vibrations of aromatic rings occur near 3030 cm.⁻¹. If this difference is mainly due to hybridization of carbon, a similar relationship must hold between the B-H stretching vibration and the hybridization of boron, and B-H stretching frequencies can be classified into two groups in accordance with hybridization of boron. Table I gives some instances in which the hybridizations of borons are simple and unambiguous, all the data of boron hydrides being omitted for their abnormal valence states. Further studies are in progress on this relation. On the basis of these data, it seemed reasonable to assume that tris(N-boryl-2-pyridylamino)borane involves B←N coordinate bonds to give rise to B-H stretching vibrations with frequencies as low as 2330 and 2270 cm.⁻¹.

Thus, the above-mentioned evidence, *i.e.*, the electronegativity of boron, ¹¹B chemical shift, and the B-H stretching frequency, indicates the existence of B←N coordinate bonds in this series of molecules, and we are now in a position to discuss the steric requirements in the formation of this series of molecules.

Some substituted 2-aminopyridines and 3- and 4-aminopyridine were subjected to reactions identical with that employed for the preparation of tris(N-dialkylboryl-2-pyridylamino)boranes from 2-aminopyridine¹ in order to see whether these amines afford similar frameworks in spite of steric hindrance which bear upon the inability to form the B←N coordinate bonds. Processing 3- and 4-aminopyridine according to the procedure gave a sticky mixture instead of tris(N-dialkylboryl-3(or 4)-pyridylamino)borane in which the surrounding borons would be situated apart from their partner nitrogen to prevent the coordinate bond forma-

(5) E. L. Saier and N. D. Coggeshall, *Anal. Chem.*, **20**, 812 (1948).

tion. In the case of 2-amino-3-methylpyridine, the reaction gave tris(3-methyl-2-pyridylamino)borane (VI) in 34.8% yield rather than the expected tris(N-dialkylboryl-3-methyl-2-pyridylamino)borane. Although the possibility that the reaction mixture might involve the desired product cannot be excluded, the failure to isolate it by a similar method indicates the instability of tris(N-dialkylboryl-3-methyl-2-pyridylamino)borane owing to the steric hindrance of the methyl groups on 3-positions in pyridyl groups, which prevent the pyridyl group from achieving coplanarity and from formation of a B←N coordinate bond.

Substituents attached at positions other than 3 would exert no steric hindrance to the formation of a B←N coordinate bond and allow the extraction of stable products from the reaction mixtures. The ring-substituted derivatives obtained are listed in Table II,

compounds I to V in Table II can be ascribed to the stabilization due to the B←N coordinate bonds. A question may be raised as to the low yield of the pyrimidyl derivative (V), for which it is not unreasonable to expect a steric hindrance larger than for the others. The conceivable main factor leading to the low yield is the steric hindrance of the hydrogen chloride or boron trichloride molecule coordinated onto a ring nitrogen simulating the above-mentioned 3-methyl group in the course of preparation. The arguments presented above constitute an imposing body of evidence in favor of the B←N coordinate bond and its stabilizing function.

The ultraviolet spectra are shown in Figures 2 and 3 along with the curves of tris(N-dimethylboryl-2-pyridylamino)borane for comparison. The spectra of the 4-methylpyridyl and 5-chloropyridyl derivatives closely resemble those of the unsubstituted pyridyl derivatives

TABLE II

No.	R	R'	Yield, %	M.p., °C.	Mol. wt.		C, %		H, %		N, %		B, %	
					Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
I	H	H	14.0 ^a	240 dec.	323	326	55.22	55.32	5.95	5.57	25.68	25.81	12.35	13.29
II	CH ₃	4-CH ₃	39.0	198-199	455	452	64.61	64.73	8.31	8.02	18.29	18.58	9.33	9.58
III	<i>n</i> -C ₄ H ₉	4-C ₄ H ₉	34.6	166-167	693	704	71.43	71.61	10.42	10.30	11.74	11.93	6.09	6.16
IV	C ₂ H ₅	5-Cl	35.2	168-169	626	597	54.52	54.29	6.64	6.58	13.54	14.07	7.02	7.25
V	<i>n</i> -C ₄ H ₉	Pyrimidyl	0.7	105-106			64.50	64.99	9.75	9.54	19.30	18.95		
VI	(3-CH ₃ -py-NH) ₃ B		34.8	92-96			64.45	65.07	6.46	6.37	24.94	25.29	3.10	3.28

^a For the reduction process.

together with their yields, melting points, molecular weights, and analytical data. The structure determination of each molecule listed here rests on analytical data, molecular weight data, and some physicochemical investigations, such as ultraviolet spectra, infrared spectra, and nuclear magnetic resonance spectra, which will be discussed later. The stability of

to suggest the analogous structure of the conjugate system. Although the spectrum of the pyrimidyl derivative differs to some extent in the intensity of its 350 mμ band, it would be due to the electronegativity difference between sp² carbon and ring nitrogen, but not due to dissimilarity in molecular configuration.

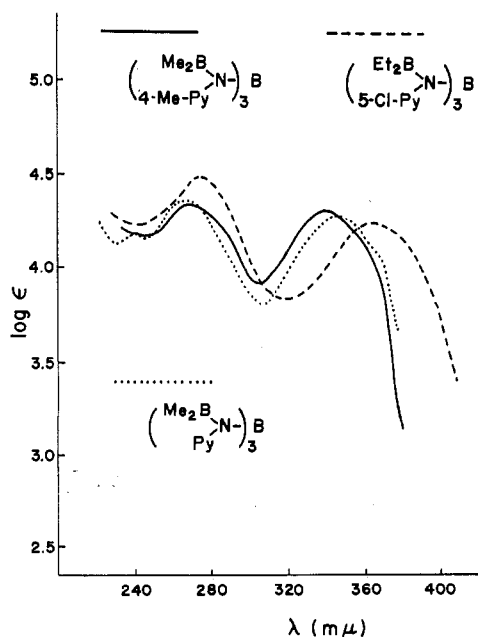


Figure 2.—Ultraviolet spectra of some tris(N-dialkylboryl-2-pyridylamino)boranes.

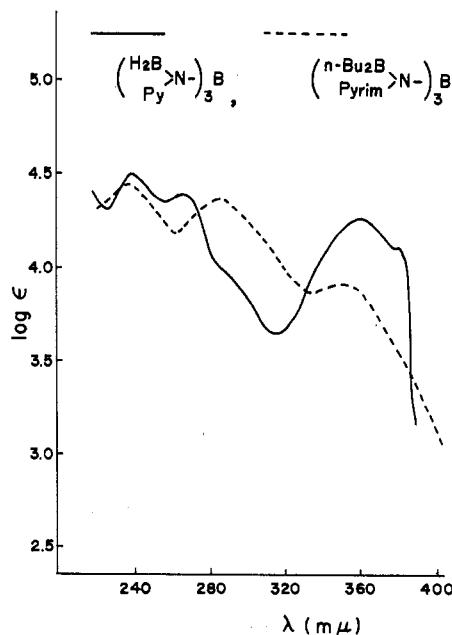


Figure 3.—Ultraviolet spectra of tris(N-boryl-2-pyridylamino)borane and tris(N-di-*n*-butylboryl-2-pyrimidylamino)borane.

TABLE III
 INFRARED ABSORPTION BANDS (CM.⁻¹) OF TRIS(N-BORYL-2-PYRIDYLAMINO)BORANE AND ITS DERIVATIVES

Substituent on ring Substituent on B Assignment	None H	4-CH ₃ CH ₃	4-CH ₃ <i>n</i> -C ₄ H ₉	5-Cl C ₂ H ₅	Pyrim. CH ₃	Pyrim. <i>n</i> -C ₄ H ₉
BH	2405 w, sh 2310 w 2270 w					
Pyridine or pyrimidine ring	1631 m 1567 m	1642 s 1565 w, sh 1550 m 1543 m, sh 1503 s	1643 s 1565 w, sh 1555 s 1545 s, sh 1502 s	1621 s 1554 m 1545 m, sh 1503 m, sh 1495 vs, sh 1488 vs	1615 s 1553 ms 1543 m, sh 1512 w 1472 vs 1430 m	1631 ms 1554 ms 1543 m, sh 1510 w 1471 s, sh 1465 vs, sh 1460 vs
CH ₂ , CH ₃ asym. def.		1466 s, sh 1453 vs 1430 s, sh	1464 s, sh 1453 vs 1425 s, sh	1478 s, sh 1460 w 1403 vs	Masked Masked	Masked Masked
Pyrim. ring	1448 s	Masked	Masked		Masked	1448 vs
C-CH ₃ sym. def.		1380 m, sh	1383 m, sh	1394 vs		1372 s
ν ¹⁰ B-N	1393 m, sh	1364 s	1369 s, sh	1364 s, sh	1315 s, sh	1320 s
ν ¹¹ B-N (central)	1381 vs	1352 vs	1355 vs	1352 s	1304 s	1309 s
ν N-C (ring)	1333 s	1307 s	1320 s	1312 s	1382 s	1372 s
B-CH ₃ sym. def.		1324 s 1311 vs			1338 w 1321 s	
Ring	1294 w 1281 w, sh	1282 m 1264 w, sh 1193 m	1286 w 1272 w 1187 w	1282 w 1255 w 1149 w	1258 m 1251 m 1140 w	1248 m 1134 w
Alkyl group		1064 w, sh 1049 m, s 1032 m 978 m 878 w	1098 m 1042 m 980 w 937 w 870 w	1047 m 897 m 863 m 853 m 830 m	1051 m 1040 m 1032 m 973 w 941 w 835 vw	1092 mw 1031 m 932 w 834 vw
Pyrim. pyrid. ring CH out-of- plane	776	797	797 m	775 w, sh 762 m	786 m	788 m

Comparing the infrared spectra of these derivatives with those of the corresponding alkyl derivatives having unsubstituted pyridyl groups,¹ one can easily recognize a close similarity between them and assent to the resemblance in molecular structure with each other. Tentative assignments of some of the absorption bands on the basis of this structure are indicated in Table III. Although Table III involves the data for tris(N-dimethylboryl-2-pyrimidylamino)borane prepared by the same method as for the butyl derivatives (V), the low yield prevented its being submitted for other measurements. The B-H stretching and ring vibrations can be unambiguously assigned to the bands of the 2300 and 1500 cm.⁻¹ regions, respectively, except for some of the ring vibrations at about 1450 cm.⁻¹ where methyl and methylene bending vibrations occur to leave some ambiguity in their assignments.

Each of the five derivatives exhibits the characteristic B-N stretching vibration¹ in the 1350 cm.⁻¹ region with a satellite of less intensity due to ¹⁰B-N stretching. The pyrimidyl derivatives have absorption bands at the normal position, 1382, 1338, 1321, 1315, 1304 (pyrimidyl CH₃), 1372, 1320, and 1309 cm.⁻¹ (pyrimidyl C₄H₉), of which the choice of 1304 and 1309 cm.⁻¹ appears to be more reasonable. This is because (a) there are no ¹⁰B-N stretching bands neighboring to 1372 and 1382 cm.⁻¹, although the degenerate ¹⁰B-N₃ vibration should show a considerable shift from the

corresponding ¹¹B-N₃ vibration, and (b) because the bands observed at 1321 and 1338 cm.⁻¹ for the methyl derivative completely disappear for the butyl derivative, showing that these bands are attributable to B-CH₃ symmetric deformation,⁶ a similar relation being observed for the 4-methylpyridyl derivatives. On the other hand, the bands at 1309 and 1304 cm.⁻¹ have slightly weaker bands at 1320 and 1315 cm.⁻¹ as shoulders, respectively.

The low-frequency shift of the B-N stretching band observed in going from the 2-pyridyl derivatives to the 2-pyrimidyl derivatives may be attributable to the replacement of an electronegative nitrogen atom for a ring CH group, *i.e.*, the additional ring nitrogens withdraw π -electrons on three *exo* nitrogens to decrease the bond orders and the force constants of the central three B-N bonds. This explanation seems to fit in the high-frequency shifts of the N(*exo*)-C(ring) stretching bands.

The spectrum is relatively flat in the region of 850 to 1150 cm.⁻¹ for the boryl derivative itself (I), whereas the dialkylboryl derivatives show many intense peaks which are attributable to R₂-B stretching vibrations coupled with rocking, wagging, and twisting vibrations of methyl and methylene groups. In the lower frequency region are observed several CH out-of-plane

(6) Cf. references in Table I and W. J. Lehmann, C. O. Wilson, Jr., and I. Shapiro, *J. Chem. Phys.*, **28**, 777 (1958).

TABLE IV
 CHEMICAL SHIFTS AND COUPLING CONSTANTS (RELATIVE INTENSITIES IN PARENTHESES)^a

Compd.	Chemical shift τ value					Coupling constant, c.p.s.				
	3	4	5	6	R ₂ on B	J_{34}	J_{35}	J_{45}	J_{46}	J_{56}
I	2.2-2.8 (2.0)		3.32 (1.0)	2.07 (1.0)	...		1.5	6.7		6.7
II	2.95 (1.0)	[7.74 (2.9)]	3.57 (1.0)	2.16 (1.0)	9.84 (6.1)		1.2			6.2
III	2.88 (1.1)	[7.71 (2.8)]	3.59 (1.1)	2.25 (1.1)	8.3-9.8 (17.9)		1.1			6.5
IV	2.4-2.8 (2.1)		...	2.11 (1.0)	8.7-9.8 (10.0)				1.7	
V	...	1.47 (0.9)	3.28 (0.9)	1.75 (0.9)	8.5-9.9 (18.4)			4.1	2.3	6.1
VI	[7.64]	2.72	3.40	1.96	NH 5.55			7.2	1.6	5.0
4-CH ₃ -py	3.75	[7.83]	3.57	2.10	NH 5.42	[~0.6]	1.2	[~0.6]		5.3
5-Cl-py	3.58	2.66	...	2.02	NH 5.50	8.5			2.5	
3-CH ₃ -py	[7.96]	2.80	3.46	2.09	NH 5.40			7.2	1.4	5.0
Pyrimidine	...	1.77	3.46	1.77	NH 4.22			4.8		4.8

^a The values in brackets are concerned with methyl groups on the rings. The values in parentheses represent relative intensities.

vibrations characteristic of the number of adjacent hydrogen atoms.⁷

The proton magnetic resonance spectra of these compounds are summarized in Table IV along with those of starting materials (amines) for comparison. Substituents on the rings make the ring proton signals simple, thus making possible the assignments of the signals which could not be assigned in the previous paper.¹ The signal features and the relative integrated intensities of alkyl proton signals as compared with those of ring proton signals confirm the molecular structures of compounds, I, II, III, IV, and V to be as shown in Figure 1. On the other hand, compound VI gives rise to a single unresolved broad peak centered at τ 5.55 due to protons directly bonded to nitrogens which indicates the absence of dialkylboryl groups and tris(3-methyl-2-pyridylamino)borane structure.

Mention should be made here of the assignment of some ring proton signals in conjunction with the B \leftarrow N coordinate bond formation. The proton chemical shifts, τ 2.16 and 2.25, of the ring protons adjacent to the ring nitrogens (6 position) in compounds II and III are greater than that in the starting amine, 2-amino-4-methylpyridine, τ 2.10, whereas the τ values of H₃ in compounds II and III are much smaller than that in the amine. These shifts can be explained in terms of the diamagnetic anisotropy of the lone pair on the ring nitrogen and its disappearance due to the B \leftarrow N coordinate bond formation which will exert an inductive effect on the ring proton chemical shift. It has been reported⁸ that the anisotropy of a pyridine nitrogen affects an *ortho* ring proton in a way to lower its chemical shift and the coordinate bond formation causes the anisotropy effect to vanish, leading to a high-field shift of the *ortho* proton signal. The coordinate bond formation, the B \leftarrow N bond in the present case, leads to an increase in electronegativity of the nitrogen atom, which results in shifting the ring proton signals downfield. These two effects cancel at the *ortho* (6 position) proton while the inductive effect remains at the *meta* (3 position) proton.

A similar relation holds between the proton chemical shifts of compound III and its starting amine. Keep-

ing this relation in mind and comparing the chemical shifts of compound V with its starting material, one can reasonably assign the peak at τ 1.75 to the proton adjacent to the B \leftarrow N coordinate bond. The appearance of three separate ring proton signals lends some support to the B \leftarrow N coordinate bond formation.

Experimental

Tris(N-boryl-2-pyridylamino)borane (I).—The mixture obtained by the procedure described before¹ from 24.5 g. (0.209 mole) of boron trichloride and 9.8 g. (0.105 mole) of 2-aminopyridine was filtered under nitrogen and the residue was suspended in 150 ml. of diglyme. This solution was added dropwise to 19.5 g. (0.52 mole) of sodium borohydride in 150 ml. of diglyme over a period of 1 hr. to reduce the BCl₂ groups. The mixture was heated for 1 hr. and filtered under nitrogen. The filtrate was evaporated to dryness under reduced pressure and the residue recrystallized from chloroform-hexane mixed solvent to give colorless needles.

Tris(N-dialkylboryl-4-methyl-2-pyridylamino)boranes (II and III) and Tris(N-dialkylboryl-5-chloro-2-pyridylamino)borane (IV).—These compounds were prepared according to the method described before.¹

Tris(N-di-n-butylboryl-2-pyrimidylamino)borane (V).—Processing 2-aminopyrimidine in the same manner did not furnish the compound V and some modification was necessary. A solution of 15 g. (0.16 mole) of 2-aminopyrimidine in 1000 ml. of dry toluene was added over a period of 1 hr. to 70 g. (0.59 mole) of boron trichloride in 300 ml. of dry toluene under cooling in an ice bath. Heating of the reaction mixture brought about precipitation of yellow crystals which turned to white in 10 min. The reaction mixture was then refluxed for 20 hr. under a nitrogen atmosphere. After removal of the solvent, the residue was suspended in 150 ml. of ether and then added in small portions to *n*-butylmagnesium bromide solution prepared in the usual manner from 7.6 g. (0.316 g.-atom) of magnesium and 43 g. (0.31 mole) of *n*-butyl bromide. The reaction mixture was stirred for 3 hr. at room temperature and then refluxed for 1 hr. The precipitate was removed by filtration and the filtrate was concentrated to dryness under reduced pressure. The residue was then extracted with petroleum ether and recrystallized from the same solvent several times.

Tris(3-methyl-2-pyridylamino)borane (VI).—Though the same molar ratios and the same technique as cited above¹ were employed in the reaction between 3-methyl-2-aminopyridine and boron trichloride, treatment with appropriate Grignard reagent afforded no crystalline product but tris(3-methyl-2-pyridylamino)borane (VI) in a very low yield. All attempts to prepare the object matter by modification in the stoichiometry ended in failure. The best yield of VI was obtained when six times as much amine as boron trichloride was used.

Analysis and Physicochemical Measurements.—Molecular weights were determined by a Mechrolab, Inc., Model 301A vapor pressure osmometer. The usual micro-Dumas method

(7) H. Shindo and N. Ikekawa, *Pharm. Bull. (Tokyo)*, **4**, 192 (1956); H. Shindo, *ibid.*, **5**, 472 (1957); J. K. Wilmhurst and H. J. Bernstein, *Can. J. Chem.*, **35**, 1183 (1957); H. E. Podall, *Anal. Chem.*, **29**, 1423 (1957).

(8) C. Smith and W. G. Schneider, *Can. J. Chem.*, **39**, 1158 (1961).

was used for the determination of nitrogen without any particular precautions, whereas carbon and hydrogen were determined by a modification⁹ of the usual microdetermination method which was improved to prevent low carbon analyses.¹⁰ Boron was determined by a flame spectrophotometric method¹¹ which had been developed for determining boron in boron-nitrogen compounds.

The proton magnetic resonance spectra were obtained at room temperature with a Varian A-60 high resolution n.m.r. spectrometer operating at 60 Mc. In these experiments, 10% carbon tetrachloride solutions were used with tetramethylsilane as an internal reference except for compound I and for amines,

(9) S. Mizukami and T. Ieki, *Microchem. J.*, **7**, 485 (1963).

(10) W. Gerrard, H. R. Hudson, and E. F. Mooney, *J. Chem. Soc.*, 113 (1962).

(11) T. Yoshizaki, *Anal. Chem.*, **35**, 2177 (1963).

CONTRIBUTION NO. 1023 FROM THE CENTRAL RESEARCH DEPARTMENT,
EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY, WILMINGTON 98, DELAWARE

Chemistry of Boranes. XXIII.¹ $B_{10}H_9S(CH_3)_2^-$ and $B_{10}H_8[S(CH_3)_2]_2$

By W. H. KNOTH, W. R. HERTLER, AND E. L. MUETTERTIES

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The reaction of $B_{10}H_{10}^{2-}$ with dimethyl sulfoxide and hydrogen chloride has given $B_{10}H_9S(CH_3)_2^-$ [(dimethyl sulfide)nonahydrodecaborate(1-)] and $B_{10}H_8[S(CH_3)_2]_2$ [bis(dimethyl sulfide)decaborane(8)]. Although apical (1,10—see Figure 1) substitution predominates in this reaction, significant amounts of equatorial isomers are also formed. The carbon-sulfur bond in $B_{10}H_8[S(CH_3)_2]_2$ is kinetically more labile than the boron-sulfur bond as shown by reaction with tributylphosphine to give $(CH_3)_2SB_{10}H_8SCH_3^-$. Thermal rearrangement of 1,10- $B_{10}H_8[S(CH_3)_2]_2$ to 2,7(8)- $B_{10}H_8[S(CH_3)_2]_2$ has been observed at 230°. Halogenated derivatives of $B_{10}H_8[S(CH_3)_2]_2$ and $B_{10}H_9S(CH_3)_2^-$ have been prepared as well as diazonium, deuterio, hydroxy, benzoyl, and amine derivatives of the latter.

The polyhedral borane anions $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ are atypical boron hydride species as documented in previous publications.¹⁻⁸ The basic cage structure is kinetically very stable. However, the hydrogen atoms are susceptible to replacement by other atoms or groups. This has led to the development of a vast derivative chemistry which includes such varied substituents as halogen,⁴ carboxyl,⁵ azide,⁵ isocyanate,⁵ nitrile,⁵ acyl,⁷ hydroxy,⁷ and nitrogen.⁵ The subject of this paper is the chemistry of the two inner sulfonium salts, $B_{10}H_9S(CH_3)_2^-$ and $B_{10}H_8[S(CH_3)_2]_2$.²

Results

Dimethyl sulfoxide and $B_{10}H_{10}^{2-}$ react readily under acidic conditions to give good yields of $B_{10}H_9S(CH_3)_2^-$ and $B_{10}H_8[S(CH_3)_2]_2$ at 40–60°. With excess dimethyl sulfoxide as solvent, the ratio of these products

for which saturated chloroform-*d*₃ solutions were employed. The ¹¹B n.m.r. spectrum of the ethyl derivative was recorded by Varian Associates, Palo Alto, Calif., using a Model HR-100 with the substitution of a 32.1 Mc. radiofrequency unit for the 100-Mc. unit.

The ultraviolet spectra were recorded in ether solution over a region of 220 to 500 mμ, using a Hitachi Model EPS-2 recording spectrophotometer.

The infrared spectra were recorded over a rock-salt region on a Type DS-201B spectrophotometer from the Optical Research Institute, Tokyo Kyoiku University. Polystyrene was the calibration standard. The spectra were taken in solutions, using both carbon disulfide and carbon tetrachloride as solvent. In Table III are listed the wave numbers in carbon disulfide, except in regions where the solvent showed its own absorptions. In these regions, the data in carbon tetrachloride solutions are given.

is dependent on reaction time; with acetic acid as solvent, preferential formation of $B_{10}H_8[S(CH_3)_2]_2$ occurs regardless of stoichiometry or reaction time.⁹ The stereochemistry of $B_{10}H_8[S(CH_3)_2]_2$ was initially reported² as bis-apical (1,10—see Figure 1) on the basis of 10-Mc. n.m.r. data. More sensitive spectral probes have since shown that significant, though minor, amounts of equatorially-substituted isomers are also formed. Crude $CsB_{10}H_9S(CH_3)_2$ prepared in excess dimethyl sulfoxide was found to contain 77% of the apical isomer; separation of this from the equatorial isomer was readily accompanied by recrystallization from water. Apical substitution predominates to about the same extent in the second substitution with dimethyl sulfoxide, since crude $B_{10}H_8[S(CH_3)_2]_2$ formed in excess dimethyl sulfoxide was found to contain 56% of the 1,10- isomer [(0.77)² = 0.59]. Virtually all of the remaining $B_{10}H_8[S(CH_3)_2]_2$ is the 1,6- isomer. The two isomers can be separated by chromatography. Heating 1,10- $B_{10}H_8[S(CH_3)_2]_2$ to 230° for 45 min. in Dowtherm A resulted in partial rearrangement to 2,7(8)- $B_{10}H_8[S(CH_3)_2]_2$.

The chemical stabilities of $B_{10}H_9S(CH_3)_2^-$ and $B_{10}H_8[S(CH_3)_2]_2$ are comparable to that of $B_{10}H_{10}^{2-}$. Neither of the sulfonium salts is oxidized by silver nitrate. Oxi-

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