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Synthesis of Mono-, Di-, and Triaminoborazines: Pyrolysis of Triaminoborazines

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The B-triamino-, B-tris-(methylamino)-, and B-tris-(dimethylamino)- derivatives of N-trimethyl- and N-triphenylborazine have been prepared and characterized. The compounds were pyrolyzed at temperatures to 400° and the volatile products examined. Ring opening decomposition and "normal" deamination were observed. B-Tris-(methylamino)-N-triphenylborazine underwent an irreversible transformation, without change in composition, at its melting point. This phenomenon may be due to isomerism. B-Chloro-B-dimethyl- and B-dichloro-B-methyl-N-trimethylborazine have been prepared by alkylation of B-trichloro-N-trimethylborazine with methylmagnesium bromide in ether solution. Treatment of the chloro compounds with ammonia, methylamine, or dimethylamine gave the corresponding B-aminoborazines. The B-aminoborazines were converted back to the chloro compounds by reaction with phosphorus trichloride. The infrared spectra and X-ray diffraction patterns of the aminoborazines are recorded.

Introduction

Methods for the synthesis of B-triaminoborazines have been reported in a patent by Gould[1] and in papers by Niedenzu and Dawson[2] and Aubrey and Lappert.[3] Three distinct methods have been described: (1) reaction of a B-trichloroborazine[4] with an excess of amine[1,2]

$$Cl_3[BN]_3R_3 + 6NHR'R'' \longrightarrow (R''R'N)_3[BN]_3R_3 + 3NH_2R'R''Cl \quad (1)$$

(2) reaction of an aminodichloroborane with an excess of ammonia or primary amine[2]

$$3R_2NBCl_2 + 9NH_2R' \longrightarrow (R_2N)_3[BN]_3R_3' + 6NH_3R'Cl \quad (2)$$

and (3) pyrolysis of a triaminoborane[3]

$$3(RNH)_3B \longrightarrow (RNH)_3[BN]_3R_3 + 3NH_2R \quad (3)$$

Practical considerations exclude the applicability of the second and third methods for certain types of compounds. For example, neither method can be employed in the synthesis of the B-triaminoborazines $(H_2N)_3[BN]_3(R_3)$, while many primary amino derivatives, $(RHN)_3[BN]_3R'_3$, with different R and R′ substituents, will be inaccessible through routes 2 and 3. The first method, however, is not subjected to these limitations. With a wide variety of B-trichloroborazines available,[5] method 1 provides a convenient route to B-triaminoborazines.

The reactions of B-trichloroborazines with excess ammonia, methylamine, and dimethylamine have been employed in the preparation of the B-triamino-, B-tris-(methylamino)-, and B-tris-(dimethylamino)-derivatives of N-trimethyl- and N-triphenylborazine. The synthesis of these compounds and the results of preliminary pyrolysis studies are reported here.

Grignard reagents have commonly been employed in the conversion of B-trichloroborazines to B-trialkyl- or B-triarylborazines.[6,7] Ryschkewitsch, *et al.*,[7] utilized a deficiency of Grignard reagent to butylate partially B-trichloro-N-trimethylborazine. They obtained B-dichloro-B-*n*-butyl-N-trimethylborazine, B-chloro-B-di-*n*-butyl-N-trimethylborazine, and B-tri-*n*-butyl-N-trimethylborazine. Their results indicated that, with respect to the Grignard reaction, the reactivity of each boron atom of the borazine ring was unaffected by substitution at the remaining boron positions. Hence, a more or less statistical distribution of products was obtained. Similar results were obtained with the corresponding B-ethyl-B-chloro derivatives, although no pure compounds were isolated.

It has now been found that the reaction of one mole of B-trichloro-N-trimethylborazine with one or two moles of methylmagnesium bromide in diethyl ether solution gives either B-chloro-B-dimethyl-N-trimethylborazine or B-dichloro-B-methyl-N-trimethylborazine, depending upon the amount of Grignard reagent employed. These results do suggest that methyl substitution on boron atoms alters the electronic environment about the other boron atoms in the borazine structure. Amination of the unsymmetrical chloroborazine with

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[1] J. R. Gould, U. S. Patent 2,754,177 (July 10, 1956).

[2] K. Niedenzu and J. W. Dawson, *J. Am. Chem. Soc.*, **81**, 356 (1959).

[3] D. W. Aubrey and M. F. Lappert, *J. Chem. Soc.*, 2927 (1959).

[4] The notation $[BN]_3$ to designate the borazine ring was suggested by R. Didchenko. Where no structural isomerism is possible, this notation is convenient and descriptive.

[5] L. F. Hohnstedt and D. T. Haworth, *J. Am. Chem. Soc.*, **82**, 89 (1960).

[6] (a) S. J. Groszos and S. F. Stafiej, *ibid.*, **80**, 1357 (1958); (b) D. T. Haworth and L. F. Hohnstedt, *ibid.*, **82**, 3860 (1960).

[7] G. E. Ryschkewitsch, J. J. Harris, and H. H. Sisler, *ibid.*, **80**, 4515 (1958).

TABLE I

ANALYTICAL DATA FOR B-AMINOBORAZINES

Compound	M.p./b.p. (mm.) °C.	% yield	Calculated				Found			
			B	N	C	H	B	N	C	H
$(H_2N)_3[BN]_3(C_6H_5)_3$	255	70	9.17	23.8	61.1	5.98	9.62	23.8	61.7	6.20
$(CH_3NH)_3[BN]_3(C_6H_5)_3$	165	87	8.20	21.2	63.7	6.87	8.31	21.5	63.6	6.93
$[(CH_3)_2N]_3[BN]_3(C_6H_5)_3$	199	44	7.41	19.2	65.8	7.60	7.72	19.1	66.0	7.72
$(H_2N)_3[BN]_3(CH_3)_3$	89	83	19.4	50.1	21.5	9.02	19.6	49.8	21.7	9.03
$(CH_3NH)_3[BN]_3(CH_3)_3$	131 (1.7)	95	15.5	40.1	34.4	10.1	15.4	39.9	34.6	9.97
$[(CH_3)_2N]_3[BN]_3(CH_3)_3$	64	85	12.9	33.4	42.2	10.8	12.7	32.9	..	...
$(H_2N)_2CH_3[BN]_3(CH_3)_3$	90	61	19.5	42.0	28.9	9.68	19.3	40.6	28.6	9.61
$(CH_3NH)_2CH_3[BN]_3(CH_3)_3$	72 (0.17)	30	16.6	36.0	37.0	10.3	16.6	35.9	37.6	10.7
$[(CH_3)_2N]_2CH_3[BN]_3(CH_3)_3$	102 (1.3)	51	14.6	31.6	43.2	10.8	14.2	31.9	43.3	10.9
$(H_2N)(CH_3)_2[BN]_3(CH_3)_3$	87	63	19.6	33.8	36.3	10.3	19.7	33.7	37.2	10.9
$(CH_3NH)(CH_3)_2[BN]_3(CH_3)_3$	48 (0.15)	48	18.3	31.1	40.0	10.6	18.2	31.1	40.1	10.7
$(CH_3)_2N(CH_3)_2[BN]_3(CH_3)_3$	72 (1.0)	43	16.7	28.9	43.4	10.9	17.1	29.2	43.1	11.1

ammonia, methylamine, and dimethylamine gave the corresponding B-aminoborazines in good yields.

Results

Synthesis and Pyrolysis of B-Triaminoborazines.—The triaminoborazines were prepared by slowly adding a solution of a B-trichloroborazine to an excess of amine dissolved in toluene at −78°. When this procedure was employed, the yield of aminoborazine usually was high and the coproduct amine hydrochloride was obtained in near quantitative yield. The yields of aminoborazines generally were lower when the reactions were carried out at room temperature. Lower yields also were obtained when the mixing process was reversed, *i.e.*, when the amine was added to the borazine solution. Yields, melting points, and analytical data are presented in Table I. Infrared spectra and X-ray diffraction patterns were determined and are recorded in Tables II and III.

The B-triaminoborazines were pyrolyzed either in sealed evacuated tubes under autogenous pressure or on the vacuum line with continuous removal of volatile products. B-Triamino-N-triphenylborazine evolved aniline above 260°. Upon heating to 300° for 18 hr. on the vacuum line, the decomposition was nearly quantitative according to the equation

$$(H_2N)_3[BN]_3(C_6H_5)_3 \longrightarrow 3BN + 3H_2NC_6H_5 \qquad (4)$$

However, in a sealed tube at 400°, B-triamino-N-triphenylborazine evolved in 2 hr. only one-half the amount of aniline required by eq. 4; further heating at 300° for 1 hr. under vacuum gave no additional volatile products. B-Tris-(methylamino)-N-triphenylborazine behaved similarly, evolving aniline above 170°. B-Tris-(dimethylamino)-N-triphenylborazine was stable at 350° under vacuum.

Pyrolysis of B-triamino-N-trimethylborazine above 120° gave ammonia and methylamine in approximately 1:2 molar ratio. B-Tris-(methylamino)-N-trimethylborazine evolved methylamine above 150°. B-Tris-(dimethylamino)-N-trimethylborazine produced a small quantity of unidentified gas at 400°.

B-Tris(-methylamino)-N-triphenylborazine underwent an irreversible transformation at its melting point. The pure compound melted sharply at 165° and then the melt solidified at about 50°. Remelting occurred at 60–70°, and no further change in the melting point was observed after repeated fusion and cooling of the sample. The transformed substance has the same composition as the original borazine. It may be molecularly distilled or precipitated from solution without change in composition or melting point. It is amorphous and tends to solidify as a glass which may be readily ground to a fine powder. Molecular weight measurements indicated an average molecular weight of 350, showing that the transformed substance was of about the same molecular size as the aminoborazine (395). Similar transformations were not observed on melting the other aminoborazines. In particular, repeated fusion and crystallization of B-triamino-N-triphenylborazine failed to lower the melting point significantly.

Synthesis and Amination of B-Chloro-B-dimethyl- and B-Dichloro-B-methyl-N-trimethylborazine.—B-Chloro-B-dimethyl- and B-dichloro-B-methyl-N-trimethylborazine were prepared by slowly adding the stoichiometric quantity of methylmagnesium bromide to an ether solution of B-trichloro-N-trimethylborazine.

The syntheses have been carried out on a 25–100 g. scale and generally yields have ranged from 70–90%. The reaction may be carried out at 0° or with gentle reflux of the solvent. Satisfactory results have been obtained at solution concentrations of 5 g./100 ml. and 20 g./100 ml. of the trichloroborazine in diethyl ether. The Grignard reagent (*ca.* 3.5–4.0 *M* in diethyl ether) must be added slowly, a rate of addition of about 0.5 mole/hr. being satisfactory.

The two chloro-methyl borazines are crystalline solids and have been purified by vacuum sublimation or recrystallization. They are soluble in, and may be recrystallized from, a variety of organic solvents, among which acetonitrile has been most useful. In some instances the crude products were contaminated with yellow impurities which were difficult to eliminate by sublimation or recrystallization. When such impurities are present they may be removed by extracting a petroleum ether solution of the borazine with successive small portions of dimethylformamide.

Characterization of B-chloro-B-dimethyl- and B-dichloro-B-dimethyl-N-trimethylborazine as pure sub-

TABLE II

INFRARED SPECTRA OF B-AMINOBORAZINES[a]

$(H_2N)_3[BN]_3(C_6H_5)_3$	$(CH_3NH)_3[BN]_3(C_6H_5)_3$	$[(CH_3)_2N]_3[BN]_3(C_6H_5)_3$	$(H_2N)_3[BN]_3(CH_3)_3$	$(CH_3NH)_3[BN]_3$-$(CH_3)_3$	$[(CH_3)_2N]_3[BN]_3[CH_3)_3$
3540, w	3470, w		3540, w	3500, w	
3450, w			3470, w		
3050, w	3050, w	3020, w	2900, w	2930, m	2980, m
	2970, w	2930, m	2830, w	2850, m	2900, m
		2860, m			2860, m
		2800, m			2810, m
1590, m	1600, w	1600, m	1608, m	1600, vw	1753, w
1483, m	1495, m	1495, s		1492, s	1497, s
			1475, m		1473, s
	1450, m	1460, m	1450, s	1457, s	1454, s
			1420, vs	1440, m	1418, m
1410, s	1403, s	1402, s		1390, s	1380, s
			1357, w, sh	1368, s	1351, m, sh
	1310, vw	1288, s, b		1300, vw	
	1286, vw				
1219, vw	1222, vw	1221, m		1195, m	1192, m
		1147, m	1152, m	1118, w	1147, w
					1102, m
1069, vw		1063, w	1065, w	1077, w	1069, w
1027, w		1031, w			1042, w
					953, vw
697, m	697, m	696, m	693, w	702, w	704, vw

$(H_2N)_2CH_3[BN]_3$-$(CH_3)_3$	$(H_2N)(CH_3)_2[BN]_3$-$(CH_3)_3$	$(CH_3NH)_2CH_3[BN]_3$-$(CH_3)_3$	$(CH_3NH)(CH_3)_2[BN]_3$-$(CH_3)_3$	$[(CH_3)_2N]_2CH_3[BN]_3$-$(CH_3)_3$	$(CH_3)_2N(CH_3)_2[BN]_3$-$(CH_3)_3$
3550, w	3550, w				
3480, w	3480, w	3450, w	3480, vw		
2970, m, sh					
2920, m	2920, m	2930, m, sh	2950, m	2980, m	2970, m
2835, m	2835, m	2890, m	2840, w	2910, m	2900, m
		2835, m		2860, m	2840, m
				2800, m	2780, m
1610, s	1608, s	1600, w, vb	1580, vw, b		
1485, s, sh	1483, s, sh	1489, s	1480, s, sh	1501, s	1480, s, sh
1455, s	1450, s	1453, s	1459, s	1478, s	1450, s
1418, vs	1409, vs	1408, s, sh	1414, vs	1452, s	1409, s, sh
		1392, s	1383, s	1418, s, sh	1381, vs
				1391, vs	
1355, vw	1340, w	1338, vw			
1330, vw	1320, vw	1303, w	1321, w	1320, w	1321, m
1282, vw	1285, w	1271, vw	1281, w	1270, m	1275, m
	1223, w	1242, w	1253, vw, b		1243, w. b
		1190, m	1200, vw	1190, m	1191, w
1154, m	1152, w	1156, vw		1147, w	1143, vw
1109, m	1114, m	1109, m	1110, m	1111, m, sh	1120, m, sh
		1075, w	1075, vw	1098, m	1098, m
1052, w	1040, m	1039, w	1045, w	1071, m	1071, w
		1018, vw	1020, vw	1047, m	1040, m
		957, m	960, w	1018, w	1010, w, b
880, w, b	881, w	880, w	881, w	881, w	881, w
		704, vw			
696, w, b	692, vw	692, m	679, w	700, w, b	687, w
684, m	682, w			671, vw	673, w

[a] Wave lengths in cm.$^{-1}$; s, strong; m, medium; w, weak; vw, very weak; b, broad; sh, shoulder; spectra of compounds in CCl_4 solution.

stances was at first not unambiguous because no method was available for detecting one component in the presence of the other. Impurities due to hexamethylborazine and unreacted B-trichloroborazine also might be present. As isolated from the Grignard reaction, however, the substances were sharp melting solids which gave analyses corresponding closely to the calculated compositions and hence appeared to be in a high state of purity.

Amination of the mono- and dichloro compounds with ammonia, methylamine, and dimethylamine gave the corresponding B-aminoborazines in 40–80% yields. B-Amino-B-dimethyl-, B-methylamino-B-dimethyl-, B-dimethylamino-B-dimethyl-, B-diamino-B-methyl-, B-

TABLE III

X-RAY DIFFRACTION PATTERNS OF B-AMINOBORAZINES[a]

$(H_2N)_3[BN]_3(C_6H_5)_3$		$(CH_3NH)_3[BN]_3(C_6H_5)_3$		$[(CH_3)_2N]_3[BN]_3(C_6H_5)_3$		$(H_2N)_3[BN]_3(CH_3)_3$		$[(CH_3)_2N]_3[BN]_3(CH_3)_3$		$(H_2N)_2CH_3[BN]_3(CH_3)_3$		$(H_2N)(CH_3)_2[BN]_3(CH_3)_3$	
d, Å.	*I*	*d*, Å.	*I*	*d*, Å.	*I*	*d*, Å.	*I*	*d*, Å.	*I*	*d*, Å.	*I*	*d*, Å.	*I*
9.60	vs	9.11	m	9.50	vs	8.50	vw	8.75	m	6.86	w	7.96	vs
8.70	m	8.84	w	8.60	s	7.69	vs	8.58	m	6.52	w	6.46	m
7.49	m	8.50	vw	8.40	s	6.30	vw	7.37	w	6.45	w	5.66	w
5.71	m	7.89	vw	7.65	m	5.98	s	7.25	s	4.93	m	4.95	vs
5.47	s	7.33	w	6.55	vs	5.47	vw	6.60	vw	4.08	vw	4.53	vw
5.27	vs	6.88	w	6.19	vw	5.34	w	6.15	s	3.92	m	3.97	m
4.93	w	6.23	m	5.37	s	5.22	m	5.35	m	3.85	s	3.91	vs
4.69	vs	5.92	vw	5.22	vw	5.03	w	5.01	m	3.70	vs	3.70	m
4.60	vs	5.80	w	4.68	m	4.92	vw	4.69	w	2.81	s	3.22	w
4.48	s	5.60	vw	4.40	vs	4.77	vw	4.39	w	2.49	vw	3.19	m
4.35	vs	5.37	s	4.06	w	4.44	w	4.33	m	2.34	vw	3.08	w
3.97	w	4.95	vs	3.86	m	4.27	vw	4.04	w	2.19	vw	3.06	w
3.83	w	4.74	vw	3.74	vw	4.19	vw	3.90	w	1.98	m	2.96	vw
3.77	m	4.55	w	3.67	w	4.00	m	3.77	m	1.82	vw	2.87	vw
3.74	s	4.35	vw	3.25	w	3.98	w	3.59	s	1.72	vw	2.79	vw
3.70	s	4.29	w	3.12	w	3.93	w	3.25	w				
3.64	s	3.86	s	2.98	w	3.87	w	3.20	w				
3.59	vs	3.70	w	2.85	w	3.80	s	3.08	vw				

[a] vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

bis-(methylamino)-B-methyl-, and B-bis-(dimethylamino)-B-methyl-N-trimethylborazine were prepared in this way. Of these compounds all but B-amino-B-dimethyl- and B-diamino-B-methyl-N-trimethylborazine are liquids and were purified by fractional distillation. The B-amino- and B-diamino derivatives are solids and were purified by vacuum sublimation. Sharp melting points and elemental analysis indicated a high state of purity for these two compounds. Analytical data, infrared spectra, and X-ray diffraction patterns of these aminoborazines are shown in Tables I, II, and III, respectively.

Final confirmation that the compounds isolated from the Grignard reaction were pure substances was obtained by converting B-dimethylamino-B-dimethyl-N-trimethylborazine to B-chloro-B-dimethyl-N-trimethylborazine and B-bis-(dimethylamino)-B-methyl-N-trimethylborazine to B-dichloro-B-methyl-N-trimethylborazine by reaction with phosphorus trichloride. The chloro compounds thus obtained gave melting points identical with those previously determined for the products of the Grignard reaction.

Experimental

The amines used in this investigation were commercial products (Matheson Company). They were dried by passing the gas through a sodium hydroxide tower. All solvents were dried with calcium hydride or lithium aluminum hydride and were freshly distilled before use.

Commercially available[8] methylmagnesium bromide in diethyl ether was used for the Grignard reactions. As obtained from the supplier the solutions were in the 3.5–4.0 *M* concentration range. The Grignard solutions were assayed before use and the quantities used for the experiments were measured in calibrated addition funnels.

Preparation of B-Trichloroborazines.—B-Trichloro-N-trimethylborazine and B-trichloro-N-triphenylborazine were prepared by the reaction of boron trichloride with methylamine hydrochloride or aniline hydrochloride in chlorobenzene at reflux temperatures.[4,7,9]

Preparation of B-Triaminoborazines.—The synthesis of a B-triaminoborazine is illustrated by the following example. A 500-ml. 3-necked flask, equipped with stirrer, dropping funnel, and Dry Ice condenser, was thoroughly flushed with dry nitrogen. Fifty ml. of toluene was added to the flask, which was cooled to −78° in a Dry Ice–isopropyl alcohol bath. Ammonia was then admitted to the Dry Ice condenser until 9 ml. had dropped into the flask. While rapidly stirring the toluene–ammonia mixture, a solution of 10.0 g. of $Cl_3[BN]_3(CH_3)_3$ in 300 ml. of toluene was added dropwise over a period of 40 min. A white precipitate formed with addition of the first drop of $Cl_3[BN]_3(CH_3)_3$ solution. The reaction mixture then was stirred for 90 min. and allowed to warm overnight to room temperature.

When the flocculent white precipitate had settled, the mixture was filtered and the insoluble residue was extracted once with 250 ml. of toluene. The combined filtrates were evaporated to dryness and the product was vacuum-dried. The crude product (6.1 g., 82% yield) was a white solid, m.p. 50–80°. One recrystallization from petroleum ether gave the analytical sample, m.p. 87–89°.

Other hydrocarbon solvents with low freezing points also may be used for the reaction medium. The N-phenylborazines were recrystallized from hot *n*-heptane and B-triamino- and B-tris-(dimethylamino)-N-trimethylborazine were recrystallized from petroleum ether at −78°. The crude B-tris-(monomethylamino)-N-trimethylborazine[3] was purified by vacuum distillation. It appeared to decompose slowly during distillation, leaving an orange residue in the still pot.

Preparation of B-Dichloro-B-methyl-N-trimethylborazine.—Fifty g. (0.22 mole) of B-trichloro-N-trimethylborazine and 250 ml. of dry diethyl ether were placed in a 500-ml. flask equipped with stirrer, reflux condenser, and addition funnel. The borazine solution was stirred rapidly and to it was added dropwise 54.0 ml. of a 4.1 *M* solution of methylmagnesium bromide in diethyl ether (0.22 mole of CH_3MgBr). The rate of addition was such that a gentle reflux was maintained (total time for addition about 20 min.). The mixture was stirred for an additional 2 hr. and set aside for 18 hr. The solution then was filtered through glass wool and the clear, yellow filtrate was evaporated to dryness to give 25.1 g. of crude product, m.p. 141–145°. The residue from the filtration was washed with 200 ml. of diethyl ether; evaporation of this filtrate gave an additional 16.7 g. of yellowish product, m.p. 137–144°. Both crops were combined and recrystallized from hot 1,2-dimethoxy-

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[8] Obtained from the Anderson Chemical Company, Weston, Michigan.

[9] C. A. Brown and A. W. Laubengayer, *J. Am. Chem. Soc.*, **77**, 3699 (1955).

ethane to give 37 g. of white needles, m.p. 143.5–145.0°; yield 82%. *Anal.* Calcd. for $Cl_2(CH_3)[BN]_3(CH_3)_3$: B, 15.8; N, 20.4; Cl, 34.5; C, 23.4; H, 5.90; mol. wt., 206. Found: B, 15.9; N, 19.8; Cl, 34.6; C, 23.3; H, 6.00; mol. wt., 202.

Preparation of B-Chloro-B-dimethyl-N-trimethylborazine.—A solution of 56.5 g. (0.25 mole) of B-trichloro-N-trimethylborazine in 750 ml. of diethyl ether was treated with 0.50 mole (122 ml. of 4.1 *M* solution) of methylmagnesium bromide in diethyl ether. Gentle reflux was maintained by dropwise addition of Grignard reagent and then the mixture was stirred for 2 hr. and set aside overnight. The solution was filtered through glass wool and the insolubles washed with one 600-ml. portion of diethyl ether. The combined extracts were evaporated to dryness and the crude product was recrystallized from petroleum ether to give 35.1 g. (76% yield) of white needles, m.p. 124–126°. Recrystallization from hot *n*-heptane raised the melting point to 127–129°. *Anal.* Calcd. for $Cl(CH_3)_2[BN]_3(CH_3)_3$: B, 17.5; N, 21.6; Cl, 19.2; C, 32.4; H, 8.18; mol. wt., 185. Found: B, 17.2; N, 21.0; Cl, 19.2; C, 30.6; H, 7.88; mol. wt., 186.

Preparation of B-Amino-B-dimethyl-N-trimethylborazine.—Ammonia was metered into a solution of 5.0 g. of $Cl(CH_3)_2[BN]_3(CH_3)_3$ in 125 ml. of tetrahydrofuran at a rate of 200 cc./min. The exothermic reaction warmed the mixture to *ca.* 45° and when the solution began to cool the reaction was deemed complete. The mixture then was refluxed for 1 hr. and set aside until the insolubles had settled. The insolubles were filtered off and the filtrate evaporated to dryness to yield a pasty yellow mass. The crude product was sublimed at 50–60° and 0.05 mm. to give 2.8 g. (63% yield) of white crystalline product, m.p. 85.5–87.5°.

Preparation of B-Diamino-B-methyl-N-trimethylborazine.—A 1-l. flask containing 500 ml. of diethyl ether was cooled to −78° and 4 g. (0.24 mole) of ammonia was condensed into the flask. While stirring the solution, 10.0 g. (0.049 mole) of $Cl_2(CH_3)[BN]_3(CH_3)_3$ in 300 ml. of diethyl ether was added over a 30-min. period. The mixture was stirred an additional hour at −78° and set aside to warm to room temperature. When the solids had settled the mixture was filtered through glass wool and the filtrate evaporated to dryness. The sticky white mass which remained was heated to 40–50° at 0.05 mm. and a white crystalline sublimate was collected on a water-cooled cold finger. The sublimed product weighed 5.0 g. (61% yield) and melted at 89.5–90.5°.

Preparation of B-Methylamino-B-dimethyl-N-trimethylborazine.—A 250-ml. flask was charged with 5.5 g. of $Cl(CH_3)_2[BN]_3(CH_3)_3$ and 100 ml. of petroleum ether. The flask was cooled to −78° and approximately 2 g. of methylamine was dropped into the solution from a cold finger cooled to −78°. The mixture was stirred an additional 4 hr. and set aside to warm to room temperature. After filtration and evaporation in the usual manner a yellow liquid was obtained. This was distilled at 0.15 mm. and 48–49° to give 2.5 g. of colorless product.

Preparation of B-Bis-(methylamino)-B-methyl-N-trimethylborazine.—Ten g. of $Cl_2(CH_3)[BN]_3(CH_3)_3$ in 100 ml. of petroleum ether at 0° was treated with 6.5 g. of methylamine dropped into the solution from a cold finger at −78°. After the usual work-up 2.8 g. (30% yield) of pure product was obtained, b.p. 71–73° at 0.17 mm.

Preparation of B-Dimethylamino-B-dimethyl-N-trimethylborazine.–A 3-l. flask was charged with 1.5 l. of diethyl ether and 29.8 g. of $Cl(CH_3)_2[BN]_3(CH_3)_3$. While stirring the solution, dimethylamine was bubbled through the mixture at a rate of 200 cc./min. for a 1-hr. period. The reaction was mildly exothermic and caused very gentle reflux of the solvent. After the solids had settled the mixture was filtered and the filtrate evaporated at 3 mm. to give a pale yellow liquid. This was distilled to give 13.4 g. (43% yield) of the aminoborazine, b.p. 72–73° at 1.0 mm.

Preparation of B-Bis-(dimethylamino)-B-methyl-N-trimethylborazine.—Twenty-five g. of $Cl_2(CH_3)[BN]_3(CH_3)_3$ in 500 ml. of *n*-heptane was added to a stirred solution of 23 g. of $HN(CH_3)_2$ in 400 ml. of diethyl ether at 25°. The usual workup gave a yellow oil. Distillation through a Vigreux column gave 13.5 g. of the aminoborazine, b.p. 101–103° at 1.3 mm.

Reaction of B-Dimethylamino-B-dimethyl-N-trimethylborazine with Phosphorus Trichloride.— To a stirred solution of 5.0 g. (0.026 mole) of the aminoborazine in 15 ml. of benzene was added dropwise 3.6 g. (0.026 mole) of freshly distilled phosphorus trichloride. The exothermic reaction warmed the solution to *ca.* 45°. The mixture was refluxed for 3 hr. and then the solution was concentrated and cooled to crystallize the product. After filtering and drying, the crude product was purified by sublimation at 60–70° and 1 mm. to give 4.1 g. (86% yield) of white crystals, m.p. 127.0–128.5°. *Anal.* Calcd. for $Cl(CH_3)_2[BN]_3(CH_3)_3$: B, 17.5; N, 22.7; Cl, 19.2. Found: B, 17.3; N, 23.2; Cl, 19.4.

Reaction of B-Bis-(dimethylamino)-B-dimethyl-N-trimethylborazine with Phosphorus Trichloride.—Five g. of the aminoborazine (0.021 mole) in 25 ml. of benzene was treated with 8.1 g. (0.043 mole) of phosphorus trichloride dissolved in 25 ml. of benzene. The mixture was refluxed for 1 hr. and the solvent and other volatiles were removed under vacuum. The crude product was recrystallized from acetonitrile to give 3.9 g. (90% yield) of $Cl_2(CH_3)[BN]_3(CH_3)_3$, m.p. 145–147°. *Anal.* Calcd: B, 16.0; N, 20.4; Cl, 34.5. Found: B, 15.7; N, 20.4; Cl, 34.3.

Purification of B-Chloro-B-methyl Derivatives.—During some preparations of the partially alkylated borazines, the product was recovered as a yellowish solid of low melting point but having the same chlorine content as the desired compound. Attempted purification of these materials by sublimation or recrystallization did not remove the yellowish impurities. It was found, however, that a favorable distribution of impurity and borazine occurred in the two-phase solvent system dimethylformamide–petroleum ether. This property was employed to purify the borazines, the procedure for which is illustrated by the following example.

A yellowish sample (60 g.) of B-chloro-B-dimethyl-N-trimethylborazine containing 19.2% chlorine and melting over the range 112–117° was dissolved in 1500 ml. of petroleum ether in a separatory funnel. This solution was shaken with successive 15-ml. portions of dimethylformamide (DMF) until the DMF layer was colorless (three portions required). The ether layer then was concentrated by distillation and the solution cooled to give white crystals, m.p. 126–128°. *Anal.* Calcd. for $Cl(CH_3)_2[BN]_3(CH_3)_3$: B, 17.5; N, 22.7; Cl, 19.2. Found: B, 17.2; N, 22.4; Cl, 19.5.

Pyrolysis of B-Triamino-N-triphenylborazine.—A 0.48-mmole sample of B-triamino-N-triphenylborazine was heated at 300° for 18 hr. in a Pyrex glass tube on the vacuum line. The sample tube was connected to a −196° trap so that the volatile products were removed as rapidly as they formed. The products were a volatile liquid which was retained in the trap at −196°, a white solid which condensed on a cool portion of the sample tube, and a non-volatile, white residue. The volatile liquid was fractionated through a −78° trap and a trace of gas, presumed to be ammonia, was separated. The liquid retained at −78° was 0.0344 g. (0.37 mmole) of aniline, identified by its infrared spectrum and through the tribromo derivative, m.p. 116–119° (lit. 119°). The non-volatile residue contained 52.1% nitrogen and 47.6% boron; calcd. for BN, 56.5% N, 43.5% B. The weight of residue, 0.0098 g., corresponded to 0.39 mmole of BN, so that very nearly 1 mole of BN remained as residue per mole of aniline formed. The weight of the white sublimate could not be ascertained accurately, but its melting point, 245–247°, and analysis, 24.1% N, indicated essentially unchanged $(H_2N)_3[BN]_3(C_6H_5)_3$.

The pyrolysis of B-triamino-N-triphenylborazine also was carried out in an evacuated sealed tube. A 0.305-mmole sample was heated at 400° for 2 hr. The tube was opened on the vacuum line and 0.491 mmole of aniline, identified by its infrared spectrum, was obtained. A trace of ammonia was detected in the aniline by its odor. Further heating of the non-volatile residue at 330° for 1 hr. under vacuum gave no additional volatile products.

Pyrolysis of B-Tris-(methylamino)-N-triphenylborazine.—On the vacuum line, 1.34 mmoles of B-tris-(methylamino)-N-triphenylborazine began to evolve a volatile liquid at 170°. The sample was heated for 2 hr. at 280° and for 4 hr. at 360°. The volatile liquid, 0.94 mmole, was identified as aniline by its infrared spectrum and through the Hinsberg test. The other products were a sublimate and a non-volatile residue.

A 0.52-mmole sample of B-tris-(methylamino)-N-triphenylborazine was heated at 400° for 4 hr. in a sealed, evacuated tube. After opening the tube 0.131 mmole of aniline was obtained. Heating at 350° for an additional 0.5 hr. on the vacuum line produced no additional volatile compounds.

Pyrolysis of B-Tris-(dimethylamino)-N-triphenylborazine.—A sample of B-tris-(dimethylamino)-N-triphenylborazine underwent no change when heated at 350° for 2.5 hr. in an evacuated sealed tube.

Pyrolysis of B-Triamino-N-trimethylborazine.—A 5.92-mmole sample of the aminoborazine began to evolve gaseous products at 120°. Gas evolution ceased above 180° and no further change was observed to 350°. After heating at 180° for 3 hr., 3.31 mmoles of gas was obtained. The gaseous products were transferred to a tube containing 2 ml. of 6 *N* hydrochloric acid and the solution then was evaporated to dryness. The white solid residue gave well defined diffraction patterns of both ammonium chloride and methylammonium chloride. The molar ratio of methylamine to ammonia in the mixture was determined to be 1.7 from nitrogen analysis.

During the pyrolysis approximately 0.1 g. of unchanged B-triamino-N-trimethylborazine was sublimed to a cool part of the sample tube. The non-volatile residue weighed 0.71 g., so that close to 0.7 mole of gas was evolved per mole of compound decomposed. X-Ray analysis showed this residue to be amorphous.

In another experiment, 0.402 mmole of B-triamino-N-trimethylborazine was heated in a sealed, evacuated tube at 300° for 4 hr. After opening the tube on the vacuum line, 0.253 mmole of gas was obtained and an additional 0.201 mmole of gas was evolved when the non-volatile residue was heated at 350° for 1 hr. on the vacuum line. The total quantity of gas, 0.454 mmole, was converted to the hydrochloride and, after drying, 0.0285 g. of amine hydrochloride mixture was obtained. The average molecular weight of the amine hydrochloride mixture was, therefore, 62.9, corresponding to a molar ratio for methylamine to ammonia of 2.0.

Pyrolysis of B-Tris-(methylamino)-N-trimethylborazine.—B-Tris-(methylamino)-N-trimethylborazine evolves methylamine slowly at 100° and more rapidly at 150°. A 2.33-mmole sample was heated on the vacuum line under reflux at 300° for 2 hr. The non-volatile residue was a yellow solid foam. The total gaseous product, 1.86 mmoles, was converted to the hydrochloride, which was identified as methylamine hydrochloride by its X-ray diffraction pattern and through elemental analyses: found 52.2% Cl, calcd. for CH_3NH_3Cl, 52.6% Cl. The non-volatile pyrolysis residue was amorphous. Analysis of this residue indicated a N/B ratio of 1.85.

In a sealed, evacuated tube, 1.04 mmoles of B-tris-(methylamino)-N-trimethylborazine evolved 0.20 mmole of methylamine when heated at 400° for 3 hr. The non-volatile pyrolysis residue evolved an additional 0.27 mmole of methylamine when heated at 350° for 1 hr. on the vacuum line.

Pyrolysis of B-Tris-(dimethylamino)-N-trimethylborazine.—A 0.94-mmole sample of B-tris-(dimethylamino)-N-trimethylborazine underwent only minor decomposition when heated at 360° for 4 hr. on the vacuum line. About 90% of the sample was sublimed to a cooler part of the apparatus. Formation of the small amount of non-volatile residue, which was solid at 300°, was accompanied by evolution of a trace amount of gas.

After 4 hr. at 400° in a sealed tube, a 0.55-mmole sample of the compound had evolved 0.10 mmole of gas. Heating an additional 1 hr. at 300° on the vacuum line produced 0.067 mmole of gas. No products were identified.

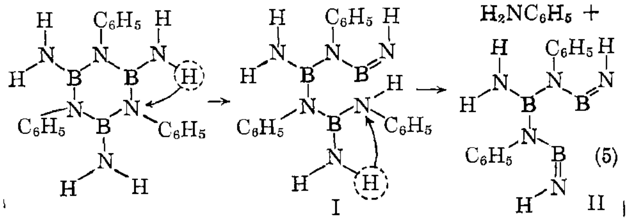
Transformation of B-Tris-(methylamino)-N-triphenylborazine at its Melting Point.—A purified sample of the compound in a capillary tube melted to a clear colorless fluid at 165° and then solidified between 60 and 50°. The substance then remelted to an opaque viscous fluid between 60 and 70°.

In order to obtain a larger sample of the transformed substance the following experiment was carried out. One arm of an inverted V-tube was charged with 7.33 g. of B-tris-(methylamino)-N-triphenylborazine. The other arm of the V-tube was connected to the high vacuum system. The apparatus was evacuated to a pressure of less than 10^{-3} mm. and the arm containing the sample was heated slowly to 200°. A pale yellow glass began to deposit in the cool arm of the apparatus. The distillation was continued for 5 hr. at temperatures between 200 and 230°. The distillate was 5.26 g. of brittle glass which was readily ground to a white powder, m.p. 60–70°. Analysis of this distillate gave 8.14% boron and 21.09% nitrogen; *i.e.*, an identical composition as the starting material $(CH_3NH)_3[BN_3]_3(C_6H_5)_3$: B, 8.20%; N, 21.23%. After standing at room temperature for 3 days the powder had fused to a glass. The distillate was soluble in hot *n*-heptane and reprecipitated from solution without apparent change. Two cryoscopic molecular weight determinations, at concentrations of 6 and 21 g. of solute per 1000 g. of benzene, indicated molecular weights of 357 and 347, respectively.

The distillation was accompanied by some decomposition of the aminoborazine. This was evidenced by collection of 0.28 g. of aniline in the vacuum system. This amount of aniline corresponds to approximately 0.6 mole per mole of decomposed aminoborazine (taken as weight of non-volatile residue plus weight of aniline evolved). The non-volatile residue was solid at 230° and was insoluble in hot *n*-heptane.

Discussion

Pyrolysis of B-Triaminoborazines.—Although no detailed description of the thermal reactions can be given on the basis of the present data, some aspects of their mechanism may be suggested. The initial step in the decomposition of B-triamino-N-triphenylborazine appears to result from a hydrogen atom or proton shift from the amino nitrogen to an adjacent ring nitrogen with subsequent breaking of a ring B–N bond. Transfer of a second hydrogen atom or proton to the ring nitrogen then would permit loss of an aniline molecule



I

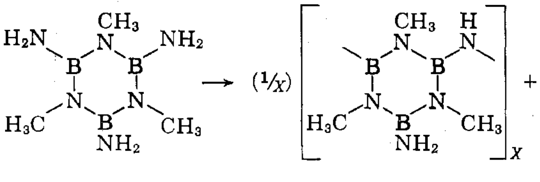
II

(5)

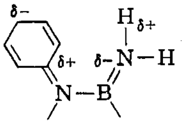
Decomposition of B-tris-(methylamino)-N-triphenylborazine must follow an analogous course because no methylamine or N-methylaniline is produced. In this case, however, the polymeric residue contains N-phenyl groups as required by the composition of the aminoborazine. Furthermore, although decomposition of this compound under vacuum starts at a lower temperature than required for decomposition of B-triamino-N-triphenylborazine, not all of the amino hydrogen is lost as aniline even at 350°.

The transformation which occurs during melting of B-tris-(methylamino)-N-triphenylborazine may be thought to result from intramolecular rearrangement of an intermediate analogous to I with the net effect being an interchange of methyl and phenyl groups. Isomerization in this manner could lead to a mixture of four isomers, a composition not inconsistent with the observed properties of the transformed substance.

Evolution of methylamine from B-triamino-N-trimethylborazine suggests that the borazine ring is cleaved in this decomposition. However, ammonia also is evolved, indicating that the "normal" polymerization reaction[8,10] takes place concurrently. Decomposition of B-tris-(methylamino)-N-trimethylborazine also may be expected to take both paths.


(6)

The factors controlling the thermal reactions are not evident. The π-bond interactions between the amino nitrogens and the ring boron atoms could give protic character to the amino hydrogen atoms and migration of these protons to the ring nitrogen atom then could occur. Using this criterion, molecules with minimum π-bonding between ring nitrogen and boron atoms should be most susceptible to ring cleavage by proton migration. N-Phenyl borazines fit this category because of competition for the unshared electron pair of the ring nitrogens by the phenyl groups. Spectral evidence[11] suggests that in the compounds $R_3[BN]_3(C_6H_5)_3$, where R is larger than a hydrogen atom, the phenyl and borazine rings cannot be coplanar and hence π-bonding between the ring nitrogens and the phenyl groups cannot be strong. These steric restrictions would not be severe at higher temperatures, however, and conjugated structures such as



could become important.

Partial Alkylation of B-Trichloroborazines.—The stepwise reaction of the Grignard reagent with the trichloroborazine may be described by the equations

$$Cl_3[BN]_3(CH_3)_3 + CH_3MgBr \longrightarrow Cl_2CH_3[BN]_3(CH_3)_3 + MgBrCl \quad (7)$$

$$Cl_2CH_3[BN]_3(CH_3)_3 + CH_3MgBr \longrightarrow Cl(CH_3)_2[BN]_3(CH_3)_3 + MgBrCl \quad (8)$$

$$Cl(CH_3)_2[BN]_3(CH_3)_3 + CH_3MgBr \longrightarrow (CH_3)_3[BN]_3(CH_3)_3 + MgBrCl \quad (9)$$

Our results show that, when the concentration of Grignard reagent is kept low, reaction 7 takes preference to reaction 8, which, in turn, is favored over reaction 9. This difference in reactivity of the Cl–B< bonds in the three chloroborazines implies that substitution of one methyl group for a chlorine atom alters appreciably the electronic environment about the remaining Cl–B< bonds. The effect with respect to the Grignard reagent is a decreased reactivity of the Cl–B< bond. Qualitatively a similar decrease in reactivity of Cl–B< bonds with increasing B-methyl substitution is noted in the behavior of the three chloroborazines toward water. Whereas B-trichloro-N-trimethylborazine reacts vigorously with water, the B-dichloro derivative dissolves without violence and dissolution of the monochloro compound requires several hours at 25°.

Although a number of unsymmetrically substituted borazines are known,[12] few examples of selective partial substitution at the boron atoms have been reported. Smalley and Stafiej[13] found selective reaction in the alkylation of N-triphenylborazine with Grignard reagents but the corresponding alkylations of N-trimethylborazine gave more or less random distribution of products. Our studies with B-chloroborazines indicate that selective partial alkylation occurs for N-trimethyl compounds but that in the N-triphenyl series the reactions are less selective.[14]

This inversion of properties with respect to Grignard alkylation of the B–H and B–Cl compounds cannot be understood without additional study. It seems likely that the most important factor governing substitution on the borazine ring is the aromatic nature of the ring and in this respect the relative donor properties of the chlorine, hydrogen, and methyl substituents and the acceptor properties of the phenyl groups must be considered.

Very recently Wagner and Bradford[15] reported the preparation of B-chloro-B-dimethyl-N-trimethylborazine and B-dichloro-B-methyl-N-trimethylborazine by a method different from ours. They obtained pure compounds by chlorination of B-methyl- and B-dimethyl-N-trimethylborazine with hydrogen chloride. Attempted partial alkylation of B-trichloro-N-trimethylborazine with methyllithium, however, failed to give pure products. It thus seems that the balance between selective and random substitution reactions on the borazine ring is rather tenuous.

Infrared Spectra.—The infrared spectra of the B-aminoborazines are recorded in Table II. The charac-

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(10) H. J. Emeléus, *Proc. Chem. Soc.*, 202 (1959).

(11) H. J. Becher and S. Frick, *Z. physik. Chem.* (Frankfurt), **12**, 241 (1957).

(12) See, for example, G. W. Schaeffer, R. Schaeffer, and H. I. Schlesinger, *J. Am. Chem. Soc.*, **73**, 1612 (1951); E. Wiberg, *Naturwissenschaften*, **35**, 212 (1948); H. I. Schlesinger, D. M. Ritter, and A. B. Burg, *J. Am. Chem. Soc.*, **60**, 1296 (1938).

(13) J. H. Smalley and S. F. Stafiej, *ibid.*, **81**, 582 (1959).

(14) We have made a concerted effort to prepare B-methyl-B-dichloro-N-triphenylborazine and B-dimethyl-B-chloro-N-triphenylborazine by alkylation of B-trichloro-N-triphenylborazine with methylmagnesium bromide. Although we believe that reasonably pure products were obtained in some of the preparations, the reaction is quite unpredictable and isolation of the desired product is largely a matter of chance. Furthermore, yields in these reactions were always in the 20–50% range due to extensive side reactions. The purest products obtained were characterized as given below: For $Cl(CH_3)_2[BN]_3(C_6H_5)_3$, m.p. 254–264°. *Anal.* Calcd.: B, 8.74; Cl, 9.55; N, 11.3; C, 64.7; H, 5.70. Found: B, 8.79; Cl, 8.99; N, 10.9; C, 66.0; H, 6.37. For $Cl_2(CH_3)[BN]_3(C_6H_5)_3$, m.p. 261–268°. *Anal.* Calcd.: B, 8.29; Cl, 18.1; N, 10.7; C, 58.3; H, 4.63. Found: B, 8.34; Cl, 18.5; N, 10.9; C, 58.3; H, 4.73.

(15) R. I. Wagner and J. L. Bradford, *Inorg. Chem.*, **1**, 93 (1962).

teristic borazine ring absorptions are found near 1400 cm.$^{-1}$ in the N-phenyl derivatives and between 1460 and 1450 cm.$^{-1}$ in the N-methylborazines. Absorption at 1492 and 1497 cm.$^{-1}$ in $(CH_3HN)_3[BN]_3(CH_3)_3$ and $[(CH_3)_2N]_3[BN]_3(CH_3)_3$ may be due to an antisymmetrical deformation mode of the aminomethyl group, since no corresponding band is found in the spectrum of $(H_2N)_3[BN]_3(CH_3)_3$. These bands are at higher frequency than normally expected for CH_3 deformation modes but analogous shifts of the methyl deformation bands in the borate esters have been noted.[16] The B-tris-(methylamino)- and B-tris-(dimethylamino)-N-triphenylborazines absorb at 1450 and 1460 cm.$^{-1}$ and no corresponding band is found for B-triamino-N-triphenylborazine. Accordingly, this band could be assigned to an aminomethyl deformation mode. If reliable assignments of the methyl deformation bands could be made, correlation with the electronic environment of the nitrogen atoms might be possible.[17]

Niedenzu and Dawson[2] have suggested that the side chain B–N vibrational mode absorbs at 1350 cm.$^{-1}$. No distinct bands were observed at that frequency, for compounds reported here, although weak bands near 1350 cm.$^{-1}$ generally appeared as shoulders on the stronger bands in the 1400 cm.$^{-1}$ region. Medium intensity bands near 700 cm.$^{-1}$ were found for all the B-aminoborazines and these bands may be due to a skeletal $N_3B_3N_3$ vibration as suggested by Aubrey and Lappert.[3] However, it should be noted that the 697 cm.$^{-1}$ band is characteristic of monosubstituted aromatics and N-trimethylborazine and its B-trichloro derivative absorb near 670 cm.$^{-1}$.

The spectra of the pyrolysis products, obtained from the solids in KBr matrix, were similar to those of the parent compounds. In general, however, all the bands were broadened and this was particularly true for the bands due to borazine ring vibrations and methyl deformation modes. This effect probably reflects the great multitude of structural features present in the polymeric residues.

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Borazole Exchange Reactions[1]

BY H. C. NEWSOM, W. G. WOODS, AND A. L. McCLOSKEY

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Hexamethylborazole was found to exchange boron substituents with B-trichloro-N-trimethylborazole at 250–350°. An apparent equilibrium is established between starting materials and the unsymmetrical species, B-chloro-B-dimethyl-N-trimethylborazole and B-dichloro-B-methyl-N-trimethylborazole. The equilibrium concentrations do not correspond to a random distribution and indicate the operation of electronic effects in the exchange process. Hexamethylborazole and N-trimethylborazole were observed to exchange boron substituents slowly at 175°.

Introduction

Substituted borazoles have been reported to undergo exchange with trimethylborane,[2] trihaloboranes,[3] and with amino-(dimethyl)-borane.[4] Evidence for exchange of B-chloro and B-ethyl groups during attempted distillation of a B-chloro-(ethyl)-N-trimethylborazole mixture was observed by Sisler, *et al.*[5] Schaeffer[3] has reported hydrogen–chlorine exchange between borazole and B-trichloroborazole. Substituent exchange is well known in other boron systems, such as alkylvinylboranes,[6] alkylhaloboranes,[7,8] trialkylboranes,[9] and haloboranes.[10] In the present study, exchange reactions of hexamethylborazole with B-trichloro-N-trimethylborazole and with N-trimethylborazole have been observed.

Results and Discussion

The exchange reactions were carried out by heating the borazole mixtures in sealed Pyrex tubes. In the B-trichloro-N-trimethylborazole–hexamethylborazole

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[1] This research was sponsored by Wright Air Development Division, Air Research and Development Command, United States Air Force, under Contract AF 33(616)-7303.

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