affords white product, m.p. 183.5–184°. *Anal.* Calcd. for $C_{24}H_{24}O_3Br_3B_3$: C, 45.56; H, 3.82; Br, 37.90; B, 5.13. Found: C, 45.51; H, 3.97; Br, 38.16; B, 5.09.

p-Vinylphenylboronic Acid.[14]—p-(α-Bromoethyl)-phenylboroxine (10 g., 0.0155 mole), was placed in a 150-ml. erlenmeyer flask to which 20 g. of freshly distilled quinoline was added. The reaction mixture was heated at 130–140° for 0.5 hour with occasional stirring. During reaction the flask was protected by a calcium sulfate drying tube. At the end of the reaction time, the flask was cooled and the contents poured into 200 ml. of water. The reaction mixture was acidified with aqueous hydrochloric acid and extracted with ether. The ether was evaporated on the water-bath and the residual light orange solid was recrystallized from hot water in the presence of a small amount of charcoal. The yield of colorless p-vinylphenylboronic acid was 5.3 g. (74%), m.p. 179–182° dec. *Anal.* Calcd. for $C_8H_9O_2B$: C, 64.93; H, 6.13; B, 7.31. Found: C, 64.93, 64.20; H, 6.08, 6.43; B, 6.53, 7.07.

Iminodiethyl p-Vinylphenylboronate.—p-Vinylphenylboronic acid (5.0 g., 0.034 mole) was azeotroped in 200 ml. of toluene containing 3.6 g. (0.034 mole) of diethanolamine for 2 hours. At the end of this time, the reaction mixture was cooled and filtered. Recrystallization of the colorless product from acetone yielded 7.3 g. (99% of theory) of long glistening needles, m.p. 236–237° dec. *Anal.* Calcd. for $C_{12}H_{16}O_2NB$: C, 66.39; H, 7.43; N, 6.45; B, 4.98. Found: C, 66.42; H, 7.41; N, 6.44; B, 5.06.

p-Vinylphenylboroxine.—p-Vinylphenylboronic acid (10 g., 0.068 mole) was refluxed in 200 ml. of toluene until water no longer evolved. Evaporation of the toluene to a volume of 20 ml. led to the deposition of 8.4 g. of pale tan crystals of p-vinylphenylboroxine; yield 97%. Two recrystallizations of a small sample of the product from toluene afforded colorless needles, m.p. 195–196°. *Anal.* Calcd. for $C_{24}H_{21}B_3O_3$: C, 73.93; H, 5.43; B, 8.33. Found: C, 73.94; H, 5.45; B, 8.54.

Di-n-butyl p-Vinylphenylboronate.—p-Vinylphenylboronic acid (15.0 g., 0.10 mole) was azeotroped in 100 ml. of 1-butanol for several hours. The butanol was removed by distillation followed by vacuum evaporation at 100°. The residue was distilled and the yield of di-n-butyl p-vinylphenylboronate, b.p. 130° (1 mm.), was 14.4 g. (55%). *Anal.* Calcd. for $C_{16}H_{25}O_2B$: C, 73.84; H, 9.69; B, 4.16. Found: C, 73.21; H, 9.31; B, 4.09.

Polymerization of p-Vinylphenylboronic Acid and Derivatives.—Homopolymerization of p-vinylphenylboronic acid, p-vinylphenylboroxine or iminodiethyl p-vinylphenylboronate is accomplished readily by treating chloroform or methylene chloride solutions of the monomer with boron trifluoride diethyl etherate at 0–20°. The amount of catalyst required for complete conversion of monomer to polymer is high, of the order of 20–30 mole %. Di-n-butyl p-vinylphenylboronate does not form solid polymer under these conditions.

p-Vinylphenylboroxine in toluene solution or di-n-butyl p-vinylphenylboronate may be polymerized readily by 0.3 mole % free radical initiator such as α,α'-azodiisobutyronitrile or di-t-butyl peroxide at 80–100°

STAMFORD, CONN.

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[14] During the preparation of this manuscript a paper by H. R. Snyder, M. S. Konecky and W. J. Lennarz, THIS JOURNAL, **80**, 3611 (1958), has appeared in which salient features of the infrared spectra of p-vinylboronic acid and its boroxine have been discussed.

[CONTRIBUTION FROM THE STAMFORD LABORATORIES, RESEARCH DIVISION, AMERICAN CYANAMID CO.]

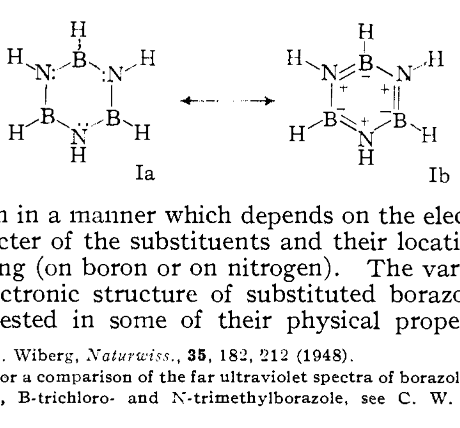
Organoboron Compounds. II. The B-Alkylation of N-Trisubstituted Borazoles

BY JANET HALL SMALLEY AND STANLEY F. STAFIEJ

RECEIVED JULY 22, 1958

The reaction of N,N',N''-triphenyl- and trimethylborazole with several Grignard and lithium reagents has been examined. From these reactions B-tri-alkylated and arylated borazoles have been isolated when three moles of the reagent to one mole of the borazole was used. From N,N',N''-triphenylborazole, B-mono- and disubstituted derivatives were obtained in good yields when the mole ratios of starting material to reagent were 1:1 and 1:2. The partially B-substituted N,N',N''-triphenylborazoles in turn were further alkylated to give unsymmetrically substituted compounds. The reaction of N,N',N''-trimethylborazole with fewer than three molar equivalents of a Grignard reagent is more complex, resulting in mixtures of mono-, di- and trisubstituted products. These results represent the first examples of the substitution of B–H containing borazoles by alkyl or aryl groups, *via* Grignard or lithium reagents.

The structure of borazole has been represented as a resonance hybrid in which the electron pairs on the nitrogen atoms are neither completely localized, as shown in structure Ia, nor completely shared by overlap with the vacant p-orbitals of the boron atoms, as shown in structure Ib, but have some intermediate electron distribution.[1] Substituents on the ring alter this electron distribution in a manner which depends on the electrical character of the substituents and their location on the ring (on boron or on nitrogen). The variation in electronic structure of substituted borazoles is manifested in some of their physical properties.[2] It might be expected that substituents would also affect the chemical behavior of the ring system, and that differences in substituents would be reflected in differences in reactivity. With this thought in mind, a study of the chemical behavior of B–H containing borazoles toward selected reagents was initiated. It has now been found that the B–H hydrogen atoms in these compounds can be replaced by the alkyl or aryl groups of Grignard or lithium reagents to give B-substituted products. An examination of the product composition, obtained from those reactions that lead to partial substitution, reveals that the rate of displacement depends on the nature of the groups attached to the nitrogen atoms of the ring and also on the degree of B-substitution. The present paper describes the results of this study with two members of this class of substituted borazoles, N,N',N''-triphenylborazole (II) and N,N',N''-trimethylborazole (V).



Ia Ib

Compound II, which has not previously been re-

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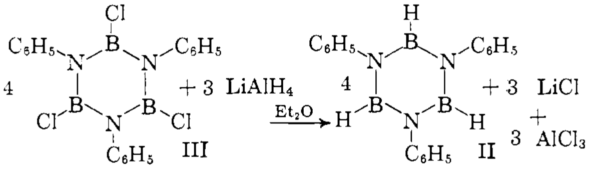
[1] E. Wiberg, *Naturwiss.*, **35**, 182, 212 (1948).

[2] For a comparison of the far ultraviolet spectra of borazole, B-trimethyl-, B-trichloro- and N-trimethylborazole, see C. W. Rector, G. W. Schaeffer and J. R. Platt, *J. Chem. Phys.*, **17**, 460 (1949). For differences in B–N bond lengths of several substituted borazoles, see S. H. Bauer, THIS JOURNAL, **60**, 524 (1938), and K. P. Coffin and S. H. Bauer, *J. Phys. Chem.*, **59**, 193 (1955).

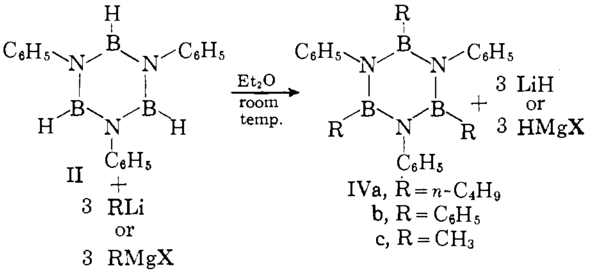
ported in the literature, was conveniently prepared in 85% yield by lithium aluminum hydride reduction of B,B′,B″-trichloro-N,N′,N″-triphenylborazole (III) in diethyl ether solution. None of the difficulties reported[3] in the lithium aluminum hydride reduction of B,B′,B″-trichloroborazole was encountered in this reaction. Moreover, it appears that all four of the hydrogen atoms of lithium aluminum hydride are utilized in this reduction, rather than only one as has been postulated.[3] Recently, Hohnstedt has reported[4] that compound III and several other B-trichloroborazoles can also be reduced by sodium borohydride in polyethylene glycol ethers. N,N′,N″-Triphenylborazole (II) is a white crystalline solid which slowly evolves hydrogen in the presence of moisture or hydroxylic solvents and, if not in a high state of purity, discolors on standing in dry air.



III

II

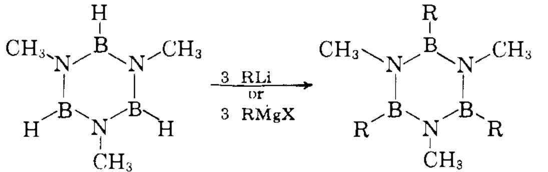
When treated with slightly more than three molar equivalents of either a Grignard or lithium reagent in diethyl ether solution at room temperature, N,N′,N″-triphenylborazole (II) was converted to B,B′,B″-trisubstituted products. From the reaction with *n*-butyllithium, B,B′,B″-tri-*n*-butyl-N,N′,N″-triphenylborazole (IVa) was obtained in 56% yield. Under similar conditions, phenyllithium gave hexaphenylborazole (IVb) in 33% yield. Grignard reagents gave the same results, although, in these cases, higher yields were obtained.[5] For example, with phenylmagnesium bromide, hexaphenylborazole (IVb) was isolated in 76% yield. With methylmagnesium iodide, compound II was converted into B,B′,B″-trimethyl-N,N′,N″-triphenylborazole (IVc) in 77% yield.[6]



II

IVa, R = *n*-C_4H_9
b, R = C_6H_5
c, R = CH_3

N,N′,N″-Trimethylborazole (V) also reacts with an excess of Grignard or lithium reagents, with apparently equal facility, to give B,B′,B″-trisubstituted products (VI). From methylmagnesium iodide and V, hexamethylborazole (VIa) was obtained in 83% yield. This compound has previously been prepared by the thermal reaction of trimethylboron and methylamine.[7] B,B′,B″-Triphenyl-N,N′,N″-trimethylborazole (VIb) was isolated from the reaction of V with either phenylmagnesium bromide or phenyllithium in yields of 61 and 49%, respectively. It is interesting to note that in contrast to compounds of the N-phenyl series, both of the N-methyl compounds VIa and VIb are sensitive to atmospheric moisture. Hydrolysis leads to ring cleavage with formation of the substituted boronic acid and methylamine.[7]



V

VIa, R = CH_3
b, R = C_6H_5

The replacement of B–H hydrogen by alkyl or aryl groups demonstrates the hydridic or pseudohalogen character of the hydrogen atoms linked to boron in compounds II and V. Furthermore, these reactions represent the first examples of the alkylation and arylation of B–H borazoles by lithium and Grignard reagents.[8] The only other reagents which have been reported to alkylate the B–H group of borazoles are trimethylboron and B,B-dimethylaminoborine, $(CH_3)_2BNH_2$.[9] Both reagents gave mixtures of B-mono-, di- and trimethylated derivatives, although trimethylboron gave better yields of the desired products.

By controlling the molar ratios of N,N′,N″-triphenylborazole (II) to the Grignard reagent, partially substituted borazoles have been prepared in good yields. Under the same reaction conditions found suitable for the preparation of B-trisubstituted products, treatment of II with slightly more than one molar equivalent of methylmagnesium iodide yielded B-monomethyl-N,N′,-N″-triphenylborazole (VIIa) in 93% yield. With two molar equivalents of methylmagnesium iodide B,B′-dimethyl-N,N′,N″-triphenylborazole (VIIIa) was isolated in 86% yield. The same results were obtained with phenylmagnesium bromide. Addition of one molar equivalent of this reagent to compound II gave B,N,N′,N″-tetraphenylborazole (VIIb) in 66% yield. With two molar equivalents of phenylmagnesium iodide, B,B′,N,N′,N″-pentaphenylborazole (VIIIb) was obtained in 86% yield. These partially substituted borazoles resemble N,N′,N″-triphenylborazole in their stability behavior; they are attacked slowly by moisture and

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[3] R. Schaeffer, M. Steindler, L. Hohnstedt, H. S. Smith, L. B. Eddy and H. I. Schlesinger, THIS JOURNAL, **76**, 3303 (1954).

[4] L. F. Hohnstedt and D. T. Haworth, Abstracts of Papers, 132nd National Meeting of the American Chemical Society, New York, N. Y., September, 1957, p. 8S.

[5] Contrast the difference in behavior of Si-H containing compounds toward lithium and Grignard reagents; H. Gilman and E. A. Zuech, THIS JOURNAL, **79**, 4560 (1957).

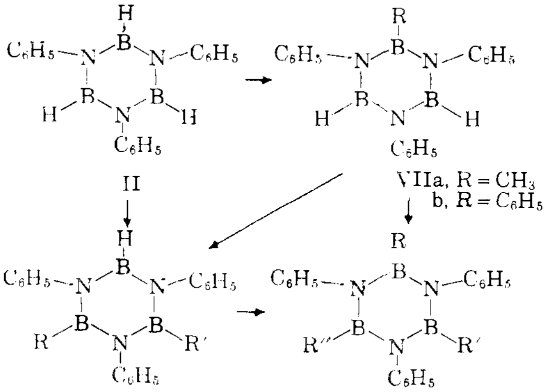
[6] These B-trisubstituted N,N′,N″-triphenylborazoles (IV) have been prepared previously by the reaction of B,B′,B″-trichloro-N,N′,-N″-triphenylborazole with Grignard reagents; S. J. Groszos and S. F. Stafiej, *ibid.*, **80**, 1357 (1958).

[7] E. Wiberg and K. Hertwig, *Z. anorg. allgem. Chem.*, **255**, 141 (1947).

[8] While this work was in progress, the paper of E. Wiberg and E. Strebel, *Ann.*, **607**, 9 (1957), was brought to our attention. These workers have found that the hydrogen atoms of diborane can be replaced by ethyl groups *via* ethylmagnesium halides to give triethylboron and HMgX according to the equation: $B_2H_6 + 6C_2H_5MgX \rightarrow 2B(C_2H_5)_3 + 6HMgX$.

[9] (a) H. I. Schlesinger, L. Horvitz and A. B. Burg, THIS JOURNAL, **58**, 409 (1936); (b) H. I. Schlesinger, D. M. Ritter and A. B. Burg, *ibid.*, **60**, 1296 (1938).

hydroxylic solvents with the liberation of hydrogen and also discolor on standing in dry air. However, since the colored decomposition products are insoluble in hydrocarbon solvents, the compounds are easily purified by recrystallization.


II

VIIa, R = CH_3
b, R = C_6H_5

VIIIa, R = R′ = CH_3
b, R = R′ = C_6H_5
c, R = CH_3, R′ = C_2H_5

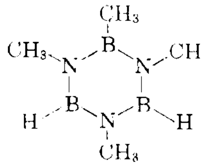
IXa, R = CH_3, R′ = C_2H_5
R″ = n-C_3H_7
b, R = R′ = CH_3,
R″ = n-C_4H_9

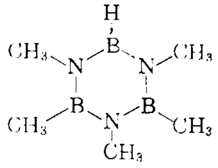
It has not been rigorously demonstrated that these are the exclusive products of the reaction, but they appear to be at least the predominant products. This has been shown for the B-monomethyl and B,B′-dimethyl compounds. Chromatography of once-recrystallized material on a column of activated alumina failed to give a separation into different components. However, a sample of the crude B,B′-dimethyl compound which was obtained when a 15% excess of Grignard reagent was used, could be separated into impure B,B′-dimethyl and B,B′,B″-trimethyl components. The fact that a statistical distribution[10] of products does not occur during the reactions that lead to partial substitution indicates that the introduction of a substituent on boron alters the reactivity of the remaining B–H centers toward further substitition. In the N-phenyl series, both methyl and phenyl groups attached to boron decrease the rate of further reaction so that the reactivity probably follows the order: unsubstituted > monosubstituted > disubstituted.

Practical use of this order of reactivity has led to the synthesis of N,N′,N″-triphenylborazoles, having one, two or three different R groups attached to the boron atoms. The ready preparation of several representative examples of this new class of compounds illustrates this point. The B-monomethyl compound VIIa, on treatment with one equivalent of ethylmagnesium bromide, was converted into B-methyl-B′-ethyl-N,N′,N″-triphenylborazole (VIIIc). The latter compound, on treatment with *n*-propylmagnesium bromide, yielded B-methyl-B′-ethyl-B″-*n*-propyl-N,N′,N″-triphenylborazole (IXa). In similar fashion B,B′-dimethyl-N,N′,N″-triphenylborazole (VIIIa) was converted into B,B′-dimethyl-B″-*n*-butyl-N,N′,N″-triphenylborazole (IXb) on addition of *n*-butylmagnesium bromide. The unsymmetrical trisubstituted products (IX) are nicely crystalline compounds which are sufficiently stable in methanol to permit recrystallization from this solvent and can be handled with no special precautions.

These results clearly indicate that a wide variety of N,N′,N″-triphenylborazoles, partially or completely substituted on boron, can now be prepared easily and conveniently in large quantities. The availability of the partially B-substituted compounds is of special interest in studying the effect of these added groups on the reactivity of the remaining B–H centers toward other reagents.

Differences in behavior between N,N′,N″-triphenylborazole (II) and N,N′,N″-trimethylborazole (V) appear when the latter is allowed to react with fewer than three molar equivalents of a Grignard reagent. Treatment with one mole of methylmagnesium iodide converts approximately 50% of compound V into B,N,N′,N″-tetramethylborazole (X). Smaller amounts of penta- (XI) and hexamethylborazole (VIa) also are obtained. With two equivalents of methylmagnesium iodide, 53% of the N,N′,N″-trimethylborazole can be accounted for as pentamethylborazole (XI) and another 19% as hexamethylborazole (VIa). These results contrast with the behavior of N,N′,N″-triphenylborazole, where mono- or disubstituted compounds were the only products isolated when one or two molar equivalents, respectively, of the Grignard reagent were used.


X


XI

It already has been pointed out that in the N-phenyl series, B-substitution decreases the reaction rate of the remaining B–H centers. In the N-methyl series, however, methyl groups newly attached to boron must deactivate the nucleus to further substitution *less* than in the N-phenyl series. The differences in reaction rates between the unsubstituted and partially substituted compounds, therefore, must be smaller in the N-methyl series than those encountered in the N-phenyl series. In the absence of a detailed kinetic study of these reactions, the factors which contribute to these differences in the two series of borazole derivatives cannot at present be assessed with assurance.

Acknowledgments.—The authors are indebted to the Microanalytical Group of these laboratories for the elemental analyses and to Dr. V. P. Wystrach for his continued interest and many helpful discussions during the course of this work.

Experimental[11]

1. **N,N′,N″-Triphenylborazole.**—In a three-liter, three-necked flask, provided with a stirrer, a condenser whose

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(10) For a 1:1 mole ratio of reactants the statistical composition of products would be: starting material, 29.6%; monosubstituted, 44.4%; disubstituted, 22.2%; and trisubstituted, 3.7%. For a 1:2 mole ratio: starting material, 3.7%; monosubstituted, 22.2%; disubstituted, 44.4%; and trisubstituted, 29.6%.

(11) Melting points were taken on a Fisher-Johns block and are uncorrected. All reactions were carried out under an atmosphere of nitrogen.

outlet was protected against moisture by a Drierite filled drying tube, and a Claisen head provided with a nitrogen inlet and a dropping funnel, was placed 15.2 g. (0.4 mole) of lithium aluminum hydride and 1 l. of anhydrous diethyl ether. A suspension of B,B',B''-trichloro-N,N',N''-triphenylborazole[6] (165 g., 0.4 mole) in 750 ml. of anhydrous diethyl ether was added (with stirring) at such a rate as to maintain gentle reflux. After the addition was complete, the reaction mixture was stirred for 2 hr. and allowed to stand overnight. With intermittent external cooling (ice-bath) a saturated aqueous ammonium chloride solution was added dropwise to the rapidly stirred reaction mixture. Because of the excess lithium aluminum hydride, this addition was carried out cautiously at first. Gradually, on further addition of the ammonium chloride solution, the salts separated from a cloudy solution and, finally, at the end-point coagulated and settled rapidly from a clear colorless solution. The ether layer was decanted from the insoluble salts, which were extracted with five 100-ml. portions of ether and two 75-ml. portions of warm hexane. The combined ether solution and extracts were evaporated to dryness. The white partially crystalline residue was recrystallized from hexane to give in two crops 103.9 g. (85%) of crystalline product, m.p. 160–161°. One additional crystallization from hexane furnished an analytical sample of unchanged melting point.

Anal. Calcd. for $C_{18}H_{18}B_3N_3$: C, 70.01; H, 5.87; N, 13.61; B, 10.51. Found: C, 69.77; H, 6.07; N, 13.43; B, 10.29.

2. **The Preparation of B-Substituted Borazoles.**—The addition of a Grignard or lithium reagent to a B–H borazole is a common feature shared by all of the reactions reported in this paper. Table I summarizes the quantities of reactants used and the yields of products isolated in typical experiments. The following experiments are described in detail to illustrate different procedures used for the isolation and purification of the B-substituted borazoles.

TABLE I

PREPARATION OF B-SUBSTITUTED BORAZOLES

Reactants[a,b]				Products	
Borazoles	Mole	RLi or RMgX	Mole	Borazoles	Yield, %
II	0.02	A	0.075	IVc	77
II	.02	B	.075	IVb	76
II	.025	C	.11	IVb	33
II	.02	D	.08	IVa	56
V	.03	A	.095	VIa	83
V	.03	B	.095	VIb	61
V	.03	C	.075	VIb	50.5
II	.07	A	.077	VIIa	95
II	.07	A	.142	VIIIa	86
II	.019	B[c]	.019	VIIb	66
II	.024	B[c]	.051	VIIIb	86
VIIa	.02	E	.022	VIIIc	79
VIIIc	.004	F	.008	IXa	54
VIIIa	.014	G[c]	.017	IXb	91
V	.093	A[c]	.088	V	12
				X	54
				XI + VIa	?
V	.078	A	.156	XI	53
				VIa	19

[a] The Roman numerals refer to structural formulas used in the text. [b] A = CH_3MgI, B = C_6H_5MgBr, C = C_6H_5Li, D = n-C_4H_9Li, E = C_2H_5MgBr, F = n-C_3H_7MgBr, G = n-C_4H_9MgBr. [c] These quantities represent the number of moles of Grignard or lithium reagents used in these reactions as determined by titration. The other quantities in this column refer to the number of moles of alkyl or aryl halide used to prepare the reagents.

a. **B-Methyl-N,N',N''-triphenylborazole.**—A solution of methylmagnesium iodide, prepared from magnesium (1.87 g., 0.077 g. atom) and methyl iodide (10.95 g., 0.077 mole) in 70 ml. of ether, was added to a stirred solution of II (21.6 g., 0.07 mole) in 300 ml. of ether over a one-hour period. After the addition was completed, the reaction mixture, which consisted of a lower black viscous layer and an upper cloudy ether solution, was stirred at room temperature for two hours and was titrated with ammonium chloride solution to the point at which the magnesium salts settled rapidly from solution. After being decanted from the precipitated salts, the ether solution was evaporated to dryness leaving 22.4 g. of product, m.p. 137–139°. Recrystallization from hexane yielded 20.6 g., m.p. 137–141°, and a second crop, 0.86 g., m.p. 136–139° (93% yield). Two further crystallizations of a small sample from petroleum ether (b.p. 30–60°) furnished the analytical sample, m.p. 140–142°.

A number of B-substituted borazoles also were prepared using this general procedure[12] B,B'-dimethyl- (hexane); B-methyl-B'-ethyl- (petroleum ether, b.p. 30–60°); B-methyl-B'-ethyl-B''-*n*-propyl- (methanol); B,B'-dimethyl-B''-*n*-butyl- (methanol); B,B',B''-trimethyl- (ether), and B,B',B''-tri-*n*-butyl- (ether–methanol) N,N',N''-triphenylborazoles. Hexamethylborazole, also obtained by this procedure from the reaction of N,N',N''-trimethylborazole[13] and methylmagnesium iodide, was purified by sublimation at 80° and 0.0026 mm. The analytical results and some of the physical properties of all the new compounds prepared in this investigation are listed in Table II.

b. **B,N,N',N''-Tetraphenylborazole.**—An ether solution (52 ml.) containing 0.019 mole of phenylmagnesium bromide was added dropwise over a 30-minute period to a stirred solution of 5.9 g. (0.019 mole) of N,N',N''-triphenylborazole in 250 ml. of ether. The reaction mixture was allowed to stand overnight at room temperature and then was decomposed with a saturated ammonium chloride solution as described above. In this reaction, the ether solution was not decanted from the insoluble salts because of the limited ether solubility of the product. Instead the ether was removed at reduced pressure and the total solid residue containing the product and inorganic salts was extracted with five 50-ml. portions of hot chloroform. Concentration and cooling led to the separation of 4.85 g. (66%) of nicely crystalline material, m.p. 212–216°. The analytical sample had m.p. 214–215° after three recrystallizations from chloroform.

B,B',N,N',N''-Pentaphenylborazole and hexaphenylborazole also are not appreciably soluble in ether. Both compounds were isolated and purified by the above procedure.

c. **B,B',B''-Triphenyl-N,N',N''-trimethylborazole.**—A solution of phenylmagnesium bromide (0.095 mole) in 200 ml. of ether was added dropwise over a 30-min. period to a stirred solution of N,N',N''-trimethylborazole[13] (0.03 mole) in 100 ml. of ether. The reaction mixture, which now contained some solid material, was refluxed for 2 hr. and allowed to stand overnight at room temperature. A considerable amount of solid, both amorphous and crystalline, had separated from solution. Without decomposition of the reaction mixture, the solvent was removed under vacuum and the residue was refluxed with 500 ml. of hexane for one hour. To remove insoluble material the solution was filtered through paper and sintered glass with Celite, neither of which was entirely satisfactory. The filtrates were generally cloudy, and only after three or four filtrations did they become clear, although colored yellow-green and slightly fluorescent. Concentration of the hexane solution furnished 5.0 g. of product, m.p. 267–269°, in two crops. The hexane-insoluble material was then extracted with hot benzene, filtered and hexane added to the boiling solution until more of the product separated. In this way, an additional 1.4 g. was obtained; total weight 6.4 g. (yield 61%). Two further recrystallizations from benzene–hexane furnished the analytical sample, m.p. 270°.

Using the same procedure and molar quantities of reagents as above (2c), except that phenyllithium was substituted for the Grignard reagent, B,B',B''-triphenyl-N,N',N''-trimethylborazole was isolated in 49% yield.

When these reaction mixtures were decomposed with saturated ammonium chloride solution and the precipitated salts extracted with benzene in a Soxhlet apparatus for 2.5 days, the only material isolated was a crystalline solid, m.p. 223–226° (from benzene–hexane) which was identified as B,B',B''-triphenyl*boroxole* by infrared comparison with a sample prepared by dehydration of phenylboronic acid.

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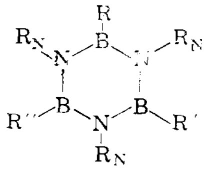
[12] The solvent used to purify these compounds is indicated in parentheses.

[13] Purchased from the Callery Chemical Co., Callery, Pa.

TABLE II

ANALYSES OF NEW B-SUBSTITUTED BORAZOLES



Compound R	Compound R′	Compound R″	R_N	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Boron, % Calcd.	Boron, % Found
CH_3	H	H	C_6H_5	142	70.68	70.24	6.24	6.11	13.02	12.85	10.05	10.26
C_6H_5	H	H	C_6H_5	215	74.89	74.54	5.76	5.86	10.92	11.07	8.43	8.40
CH_3	CH_3	H	C_6H_5	206	71.31	71.55	6.58	6.78	12.47	12.24	9.63	9.69
C_6H_5	C_6H_5	H	C_6H_5	207	78.16	78.55	5.69	5.97	9.12	9.15	7.04	6.71
CH_3	CH_3	n-C_4H_9	C_6H_5	113	73.35	73.22	7.70	7.97	10.69	10.52	8.26	8.15
CH_3	C_2H_5	H	C_6H_5	128	71.88	71.49	6.89	6.91	11.98	12.00	9.25	9.62
CH_3	C_2H_5	n-C_3H_7	C_6H_5	131	73.35	73.24	7.70	8.09	10.69	10.96	8.26	8.51
CH_3	H	H	CH_3	162[a]	35.17	35.56	10.33	10.96	30.76	30.59	23.76	20.17
CH_3	CH_3	H	CH_3	187[a]	39.85	40.04	10.70	11.04	27.89	28.11	21.54	21.42
CH_3	CH_3	CH_3	CH_3	99	43.76	43.39	11.00	10.83	25.52	25.43	19.71	19.91
C_6H_5	C_6H_5	C_6H_5	CH_3	270	71.88	71.86	6.89	6.87	11.97	11.54	9.25	8.81

[a] B.p. at atmospheric pressure.

d. **B,N,N′,N″-Tetramethylborazole.**—The reaction mixture obtained on treating 0.093 mole of N,N′,N″-trimethylborazole with 0.088 mole of methylmagnesium iodide was allowed to stand overnight at room temperature. The ether solution obtained after decomposing the reaction mixture with saturated ammonium chloride solution was distilled slowly at atmospheric pressure. After removal of solvent there was obtained 1.4 g. (12.3%) of unreacted N,N′,N″-trimethylborazole, b.p. 132–134°; 6.0 g. (54.0%) of B,N,N′,N″-tetramethylborazole, b.p. 161.5–162.5°; and 2.4 g. of a higher boiling residue. The latter was identified by infrared analysis as a mixture of B,B′,N,N′,N″-pentamethylborazole and B,B′,B″,N,N′,N″-hexamethylborazole.

Distillation of the crude product obtained from the reaction of 0.078 mole of N,N′,N″-trimethylborazole and 0.156 mole of methylmagnesium iodide furnished 6.2 g. (53%) of B,B′,N,N′,N″-pentamethylborazole, b.p. 186–187°, and a higher boiling residue which solidified on cooling. The partially crystalline solid was sublimed at 60–70° and 20 mm. to give 2.4 g. (18.7%) of crude B,B′,B″,N,N′,N″-hexamethylborazole, m.p. 82–89°. One recrystallization from acetonitrile gave needles, m.p. 93–97°.

3. **Chromatography of B-Methyl-N,N′,N″-triphenylborazole.**—One gram of the crude material, m.p. 137–139°, dissolved in hexane, was placed on a column of neutral alumina (17 g.; Woelm, activity 1) also prepared in hexane. The column was eluted with hexane and five 40-ml. fractions were collected. Crystalline material, m.p. 133–138°, was obtained on evaporation of the first two fractions. Recrystallization from petroleum ether (b.p. 30–60°) yielded 752 mg. of material, m.p. 139–141°. The three remaining fractions contained only traces of oily material.

4. **Chromatography of B,B′-Dimethyl-N,N′,N″-triphenylborazole.**—When 0.07 mole of II was treated with 0.154 mole of methylmagnesium iodide, 23.1 g. of crude product was obtained with m.p. 203–206°. A 1-g. sample was placed on a column of alumina (20 g.; Woelm, neutral, activity 1) and eluted with hexane. Five 40-ml. fractions were collected. Crystalline material was obtained in the first three fractions with the following melting points: I, m.p. 224–245°; II, m.p. 200–217°; III, m.p. 195–206°. Fraction 4 contained only a trace of solid, and evaporation of fraction 5 left no residue.

5. **Comparative Hydrolytic Stability. a. B,B′,B″-Triphenyl-N,N′,N″-trimethylborazole.**—A suspension of 354 mg. (1.01 millimoles) of B,B′,B″-triphenyl-N,N′,N″-trimethylborazole (solubility 1 mg./100 ml. at 25°) in 100 ml. of distilled water was refluxed gently for two hours. Methylamine evolution was detected at the condenser outlet during the reflux period. After being cooled to room temperature, the aqueous mixture was filtered through a sintered glass funnel; 25-mg. of insoluble material was collected. Titration of the filtrate with 0.100 *N* NaOH in the presence of mannitol indicated that 2.63 millimoles of phenylboronic acid had been formed. Since 3 moles of the acid would be formed by reaction of 1 mole of borazole with 6 moles of water, at least 86.8% of the compound was hydrolyzed under these conditions.

b. **B,B′,B″-Trimethyl-N,N′,N″-triphenylborazole.**—Under identical conditions, as described above, 351 mg. (1.00 millimole) of B,B′,B″-trimethyl-N,N′,N″-triphenylborazole (solubility 2 mg./100 ml. at 25°) was treated with boiling water. At the end of the reflux period there was recovered by filtration 98.9% (347 mg.) of the starting material, which showed no melting point depression on admixture with an authentic sample.

STAMFORD, CONN.