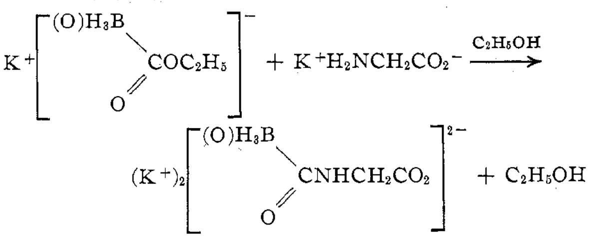
$$2OCOOC_2H_5^- + H_2NCH_2CH_2NH_2 \longrightarrow (CO_2)HNCH_2CH_2NH(CO_2)^{2-} + 2C_2H_5OH$$

Since these reactions appear to proceed stepwise by an SN2 mechanism, the difference in reactivity of these isoelectronic analogs should be effected by the difference in the effect of the $H_3B \cdot CO$ and CO_2 moieties on the nitrogen environment. If the $H_3B \cdot CO$ is less electronegative than CO_2, this should render the nitrogen more nucleophilic in the former reaction and thus rationalizing the more extensive substitution.

$K_2O_2CNHCH_2CO_2$ and the $K_2H_3BCONHCH_2CO_2$ were also prepared as shown in



$$K^+\left[(O)H_3B\text{-}C(=O)OC_2H_5\right]^- + K^+H_2NCH_2CO_2^- \xrightarrow{C_2H_5OH} (K^+)_2\left[(O)H_3B\text{-}C(=O)NHCH_2CO_2\right]^{2-} + C_2H_5OH \quad (4)$$

This reaction procedure has been reported previously for the preparation of boranocarbamates.[5]

The structure proposed for these compounds was consistent with elemental analyses and equivalent weight data as reported in the Experimental Section and with infrared spectra which showed a sharp peak at 3421 cm^{-1} for the oxygen compound and at 3380 cm^{-1} for the borane analog which is consistent with the N–H stretching vibration usually found for secondary amides.[11] The borane compound also had strong absorptions at 2280 and 1618 cm^{-1} typical of boranocarboxylate groups.[1,5]

If glycine is stirred with an ethanol solution of $KH_3BCOOC_2H_5$, the same borane compound described above is produced as shown in

$$2KH_3BCOOC_2H_5 + H_3NCH_2CO_2 \longrightarrow K_2H_3BCONHCH_2CO_2 + (C_2H_5O)_2BCH_2OH + H_2 \quad (5)$$

The fact that III is not produced by this reaction by substitution of $H_3B \cdot CO$ for an H^+ is further evidence that such a reaction would require a lone pair of electrons on the nitrogen so as to proceed by an SN2 mechanism.[5] In this reaction glycine apparently protonates the $H_3BCOOC_2H_5^-$ ion producing the ethyl ester of hydroxymethylboronic acid and hydrogen as in reactions previously observed.[6] The glycinate ion then reacts as shown in (4).

Carbon monoxide–borane also reacted with potassium sarcosinate $K(CH_3)HNCH_2CO_2$ under the same conditions but a pure product was not isolated. Potassium *N*-methyl-*N*-boranocarboxylatoaminoacetate ($K_2H_3BCO(CH_3)NCH_2CO_2$) was prepared, however, in a similar manner as shown in reaction 4.

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Preparation and Spectral Characterization of Unsymmetrically Substituted Borazines

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The ten possible *B*-phenyl-, -methyl-, and -chloro-substituted derivatives of *N*-trimethylborazine, as well as $(C_2H_5)(CH_3)_2B_3N_3(CH_3)_3$, $[(CH_3)_5C_6](CH_3)_2B_3N_3(CH_3)_3$, $[(CH_3)_3N_3B_3(CH_3)_2]_2$, and $[(CH_3)_3N_3B_3(CH_3)_2]_2O$, have been synthesized and characterized, and their infrared spectra have been determined. Correlation techniques are used to establish the characteristic frequencies associated with the absorptions of the B and N substituents.

Introduction

It is well known that substitution reactions occur at the boron site of a borazine nucleus more readily than at the nitrogen position. Thus, *B*-halogeno[1] and *B*-H[2] substituents react with Grignard reagents or organolithium reagents to yield the corresponding *B*-alkyl or -aryl derivatives. Evidence is available to show that *B*-alkyl and *B*-aryl substituents can also react with Grignard reagents to form a different B-substituted derivative.[3] The hydridic nature of a *B*-H moiety in borazines can be used to form the corresponding *B*-Cl substituents.[4–6] We present here several synthetic routes to a series of unsymmetrically B-substituted borazines which are potentially useful intermediates for other compounds containing the borazine nucleus.

Experimental Section

All reactions were carried out under an inert atmosphere (N_2 or Ar) using conventional techniques developed for the preparation of air-sensitive, volatile compounds. Melting points are uncorrected.

Preparation of Compounds. $Cl_3B_3N_3(CH_3)_3$.—This compound was prepared by the method of Haworth and Hohnstedt[7] in 78.7% yield based on the amount of $CH_3NH_2 \cdot HCl$ taken; mp 150–153°, lit.[8] mp 153–156°.

$Cl(CH_3)_2B_3N_3(CH_3)_3$.—This compound was prepared by the following modification of the method of Wagner and Bradford.[9] Methylmagnesium bromide (0.68 mol in 250 ml of ether) was

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[9] R. T. Wagner and J. L. Bradford, *Inorg. Chem.*, **1**, 93 (1962).

allowed to react with 77.15 g of $Cl_3B_3N_3(CH_3)_3$ dissolved in 250 ml of anhydrous ether. The resulting reaction mixture was filtered and the solid residue was washed with several portions of ether. The washings were added to the filtrate and the solvent was removed *in vacuo*. The residue was extracted several times with hot *n*-hexane, the extracts were combined, the solvent was removed *in vacuo*, and the resulting residue was sublimed *in vacuo* at 55°. This process yielded 38.1 g of the desired product, mp 124–127°, lit.[9] mp 127–128.5°.

$Cl_2(CH_3)B_3N_3(CH_3)_3$.—The modification of the method of Wagner and Bradord[9] described for the preparation of $Cl(CH_3)_2B_3N_3(CH_3)_3$ was used for the synthesis of this compound. The crude product formed from the reaction of 20.0 ml of 2.98 *M* methylmagnesium bromide in ether with 13.50 g of $Cl_3B_3N_3(CH_3)_3$ dissolved in 250 ml of ether obtained after removal of the solvent was extracted with hot *n*-hexane. The extract was evaporated and the resulting solid was sublimed twice *in vacuo* at 70° yielding 9.84 g of $Cl_2(CH_3)B_3N_3(CH_3)_3$, mp 148–149°, lit.[9] mp 145–146°.

$C_6H_5(CH_3)_2B_3N_3(CH_3)_3$ and $(C_6H_5)_2CH_3B_3N_3(CH_3)_3$.—These compounds were prepared from the reaction of C_6H_5MgBr with the corresponding chloride. Since *B*-monochloro- and *B*-dichloro-*N*-trimethylborazine are often obtained as tediously separable mixtures it was of interest to devise a method of using such mixtures as starting materials to prepare a mixture of the corresponding alkyl or aryl derivatives which might be more easily separated. In a typical reaction, a mixture of $Cl(CH_3)_2B_3N_3(CH_3)_3$ (60%) and $Cl_2CH_3B_3N_3(CH_3)_3$ (40%) (11.23 g in 250 ml of ether) and the appropriate amount of C_6H_5MgBr in ether, the latter being added over a 25-min period, was refluxed for 4 hr. The solvent was removed from the reaction mixture, the resulting residue extracted twice with *n*-hexane, the solvent removed from the extract *in vacuo* at room temperature, and the remaining liquid distilled to yield $C_6H_5(CH_3)_2B_3N_3(CH_3)_3$, bp 83–92° (0.01 Torr). The proton nmr spectrum of the product showed it to be contaminated with biphenyl which could not be separated from the borazine by either sublimation or distillation. The analysis of the final product corresponded to a mixture of 91.5% borazine and 8.5% biphenyl. *Anal.* Calcd for $C_{12}H_{20}B_3N_3$: C, 58.26; H, 8.89; N, 18.53. Found: C, 58.37; H, 8.54; N, 16.94.

The solid residue which remained after $C_6H_5(CH_3)_2B_3N_3(CH_3)_3$ had been removed by distillation was sublimed at 100° *in vacuo* and resublimed in a 48-in. linear gradient furnace designed for fractional sublimation.[6] The final product was colorless and produced a pale blue fluorescence under ultraviolet irradiation; mp 125.5–126.5°, lit.[10] mp 124°. *Anal.* Calcd for $C_{16}H_{22}B_3N_3$: C, 66.53; H, 7.68; N, 14.55. Found: C, 66.57; H, 7.92; N, 14.83.

$(C_6H_5)_3B_3N_3(CH_3)_3$.—*N*-Trimethyl-*B*-triphenylborazine was prepared by the following modification of the Ryschkewitsch method[11] which involves the reaction of $Cl_3B_3N_3(CH_3)_3$ and C_6H_5MgBr in ether. The Grignard reagent (0.7338 mol) was added to an ether solution of the borazine (0.1845 mol in 200 ml of ether) over a 90-min period. The reaction mixture was refluxed for 6 hr and allowed to stand overnight. The brown supernatant ether solution was discarded, dry benzene (600 ml) was added to the residue, and the mixture was stirred for 1 hr, allowed to stand overnight, and filtered. The residue was extracted four times with hot benzene, the extracts were combined with the original filtrate, and the solvent was removed *in vacuo*. The resulting white crystals were recrystallized twice from benzene and dried *in vacuo* to yield 40 g of product, mp 265–268°, lit.[11] mp 270°. The mass spectrum of the product showed it to be free of *B*-triphenylboroxole. *Anal.* Calcd for $C_{21}H_{24}B_3N_3$: C, 71.88; H, 6.89; N, 11.98. Found: C, 72.27; H, 6.93; N, 12.13.

$(C_6H_5)Cl_2B_3N_3(CH_3)_3$.—This compound was prepared by the reaction of $Cl_3B_3N_3(CH_3)_3$ (0.0604 mol in 250 ml of ether) with C_6H_5MgBr (0.0604 mol) which was added over a 2-hr period. The mixture was refluxed for 3 hr and treated as described in the preparation of $Cl(CH_3)_3B_3N_3(CH_3)_3$. The liquid remaining after the removal of the solvent hexane was distilled *in vacuo* to yield 4.5 g (28% based on the original borazine taken) of final product, bp 95–99° (0.01 Torr). The product, which is extremely air sensitive, gives a blue-purple fluorescence under ultraviolet irradiation. *Anal.* Calcd for $C_9H_{14}B_3N_3(CH_3)_3$: C, 40.39; H, 5.27; Cl, 26.50; N, 15.70. Found: C, 41.31; H, 5.22; Cl, 26.22; N, 15.72.

$Cl(C_6H_5)_2B_3N_3(CH_3)_3$.—This compound was prepared from the reaction of $Cl_3B_3N_3(CH_3)_3$ (0.060 mol) in 200 ml of ether with C_6H_5MgBr (0.120 mol) which was added over a period of 3.5 hr. The reaction mixture was refluxed for 2.5 hr and then treated as described in the preparation of $Cl(CH_3)_2B_3N_3(CH_3)_3$. The resulting solid was sublimed *in vacuo* at 125° using a hot water (100°) heated cold finger to facilitate the removal of $C_6H_5Cl_2B_3N_3(CH_3)_3$ which was also present in the residue (nmr). This sublimation process was repeated three times to yield 8.41 g of $Cl(C_6H_5)_2B_3N_3(CH_3)_3$, mp 148–150.5°. *Anal.* Calcd for $C_{15}H_{19}B_3ClN_3$: C, 58.28; H, 6.19; Cl, 11.47; N, 13.59. Found: C, 61.02; H, 6.81; Cl, 11.72; N, 14.41.

$Cl(CH_3)(C_6H_5)B_3N_3(CH_3)_3$.—This borazine was prepared by the reaction of $Cl_2CH_3B_3N_3(CH_3)_3$ (0.0248 mol) in 200 ml of ether with C_6H_5MgBr (0.0257 mol) which was added over a 1-hr period. The reaction mixture was treated as described in the preparation of $Cl(CH_3)_2B_3N_3(CH_3)_3$. The resulting viscous liquid was distilled twice *in vacuo* to yield the final product, bp 92–94° (0.01 Torr). *Anal.* Calcd for $C_{10}H_{17}B_3ClN_3$: C, 48.59; H, 6.93; Cl, 14.34; N, 17.00. Found: C, 48.19; H, 6.63; Cl, 14.12; N, 16.60.

$C_2H_5(CH_3)_2B_3N_3(CH_3)_3$.—This compound was prepared by the reaction of $Cl(CH_3)_2B_3N_3(CH_3)_3$ (0.054 mol) in 200 ml of ether with C_2H_5MgBr (0.062 mol) which was added over a 0.5-hr period. The reaction mixture was refluxed for 3 hr and treated as described in the preparation of $Cl(CH_3)_3B_3N_3(CH_3)_3$. The crude product, 7.2 g, was distilled to yield $C_2H_5(CH_3)_2B_3N_3(CH_3)_3$, bp 68–70° (0.01 Torr). *Anal.* Calcd for $C_7H_{20}B_3N_3$: C, 47.07; H, 11.30; N, 23.50. Found: C, 45.06; H, 11.12; N, 23.30.

After several days at room temperature, the mass spectrum and nmr spectrum of the product indicated that it had disproportionated to form a mixture containing $(CH_3)_n(C_2H_5)_{3-n}B_3N_3(CH_3)_3$ (n = 1, 2, 3).

$C_{12}H_{15}(CH_3)_2B_3N_3(CH_3)_3$.—*B*-Mono(pentamethylphenyl)-pentamethylborazine was prepared by the reaction of $(CH_3)_5C_6MgBr$ with $Cl(CH_3)_2B_3N_3(CH_3)_3$ in butyl ether at 65°. The Grignard reagent was prepared by an entrainment procedure[12] from bromopentamethylbenzene (0.044 mol), magnesium turnings (0.088 g-atom), and ethyl bromide (0.044 mol). The cream-colored product was washed twice with 20 ml of ethyl ether and allowed to react with the borazine (0.043 mol in 250 ml of ether) over a 3-day period. The reaction mixture was filtered and evaporated, and the residue was extracted with hot hexane (100 ml). The solvent was removed from the extract *in vacuo* and the resulting solid was sublimed. The sublimate obtained at 50° was discarded, and the sublimate which formed at 120° was crystallized from $CHCl_3$–CH_3CN to yield 2.0 g of final product, mp 215–216°. *Anal.* Calcd for $C_{17}H_{30}B_3N_3$: C, 64.73; H, 10.18; N, 14.15. Found: C, 64.89; H, 9.97; N, 14.40.

$[(CH_3)_3N_3B_3(CH_3)_2]_2$.—This compound was prepared by treating a suspension of potassium sand (0.114 g-atom) prepared in heptane with $Cl(CH_3)_2B_3N_3(CH_3)_3$ (0.055 mol). The mixture was stirred overnight at 50° and allowed to settle, the solid residue was removed by filtration, the filtrate was evaporated *in vacuo*, and the solid residue was sublimed at 120° *in vacuo*. The sublimate was then resublimed slowly at 80° *in vacuo* to yield 7.1 g of $[(CH_3)_3N_3B_3(CH_3)_2]_2$, mp 171–173°, lit.[13] mp 165–166°. *Anal.* Calcd for $C_{10}H_{30}B_6N_6$: C, 40.13; H, 10.10; N, 28.00. Found: C, 40.42; H, 9.80; N, 27.30.

The reaction of potassium sand suspended in refluxing benzene with $Cl(CH_3)_2B_3N_3(CH_3)_3$ yielded a dark blue mixture. The solution was cooled and filtered, the solvent was removed from the filtrate *in vacuo*, and the residue was sublimed *in vacuo* giving a viscous liquid on the water-cooled cold finger, identified as $C_6H_5(CH_3)_2B_3N_3(CH_3)_3$ by its infrared spectrum, proton nmr spectrum, and mass spectrum. *B,B'*-decamethylbis(borazine) was also obtained from the mixture at 120°.

The reaction of a solution of *B,B'*-decamethylbis(borazine) in CCl_4 with water was followed by recording the proton nmr spectrum of the borazine in the organic phase after it had been equilibrated with water. The spectrum indicated that the borazine was essentially unreacted after the organic phase had been equilibrated three times with fresh samples of water.

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$[(CH_3)_3N_3B_3(CH_3)_2]_2O$.—*B,B′*-Bis(pentamethylborazinyl) oxide was first prepared by the method of Wagner and Bradford[14] to yield a product, mp 135–140°, lit. mp 133–135[14] and 132°,[15] which exhibited the infared spectrum reported. The proton nmr spectrum of this product in CCl_4 and in C_6H_6 solutions showed that it was a mixture of at least three borazines. A single product was obtained only after repeated sublimation *in vacuo* followed by recrystallization from CCl_4 in air; mp 130.5–132°. The mass spectrum of this product was consistent with that expected for the desired compound; however, elemental analyses were not reproducible and corresponded best with the composition of a trihydrate. *Anal.* Calcd for $C_{10}H_{36}B_6N_6O_4$: C, 32.50; H, 9.85; N, 22.75. Found: C, 33.34, 33.37; H, 8.41, 8.87; N, 22.81, 23.29.

A pure sample of $[(CH_3)_3N_3B_3(CH_3)_2]_2O$ was eventually obtained by refluxing a mixture of sodium sand suspended in xylene with $Cl(CH_3)_2B_3N_3(CH_3)_3$ overnight. The reaction was filtered, and the solvent was removed from the filtrate *in vacuo* to yield a solid which was a mixture of $[(CH_3)_3N_3B_3(CH_3)_2]_2O$ and $[(CH_3)_3N_3B_3(CH_3)_2]_2$. After repeated careful sublimation *in vacuo*, a small amount of the oxide was isolated as indicated by its proton nmr spectrum, mass spectrum, and infrared spectrum. *Anal.* Calcd for $C_{10}H_{30}B_6N_6O$: C, 38.10; H, 9.59; N, 26.66. Found: C, 38.05; H, 9.52; N, 26.65.

Infrared Spectra.—Spectra in the sodium chloride region were obtained with a Beckman IR-7 spectrophotometer. The spectra of solid substances were determined as CCl_4 solutions; the region 700–800 cm^{-1} was supplemented as Nujol overlays. The spectra of liquid borazines were determined as the pure liquids.

Infrared spectra in the 115–800-cm^{-1} region were obtained with a Beckman IR-11 spectrophotometer using Nujol mulls and thin polyethylene windows. The results of these experiments appear in Tables I and II.

TABLE I

FAR-INFRARED ABSORPTION BANDS (CM^{-1}) OF SOME B-SUBSTITUTED *N*-TRIMETHYLBORAZINES[a]

$[(CH_3)_3N_3B_3(CH_3)_2]_2$	$(CH_3)_3N_3B_3$-$(CH_3)_2C_6(CH_3)_5$	$[(CH_3)_3N_3B_3(CH_3)_2]_2O$
		180 m
193 s	203 mw	
	239 mw	
397 m	397 w	400 w
426 w		417 w
		484 w
548 ms		537 m
	564 m	
646 s		
667 w		677 ms
675 w		
	682 s	
	702 w	700 w

[a] Key: s, strong; ms, medium strong; vs, very strong; m, medium; mw, medium weak; w, weak; vw, very weak.

Discussion

Syntheses.—Although several potential routes are available for the syntheses of unsymmetrically substituted borazines, the most efficient method, in our hands, from the standpoint of yields, ease of purification, and time, involved *N*-trimethyl-*B*-trichloroborazine as the prime source of the ring system. The addition of 1 (eq 1) or 2 (eq 2) mol of Grignard reagent

$$(CH_3)_3N_3B_3Cl_3 + RMgBr \longrightarrow \underset{\text{I}}{(CH_3)_3N_3B_3RCl_2} + MgBrCl \quad (1)$$

$$(CH_3)_3N_3B_3Cl_3 + 2RMgBr \longrightarrow \underset{\text{II}}{(CH_3)_3N_3B_3R_2Cl} + 2MgBrCl \quad (2)$$

gave the expected compounds in good yield. Subsequent reactions of these mono- or dichloro derivatives with a different Grignard reagent lead to unsymmetrically B-substituted borazines (eq 3 and 4). In reactions

$$(CH_3)_3N_3B_3RCl_2 + R'MgBr \longrightarrow (CH_3)_3N_3B_3RR'Cl + MgBrCl \quad (3)$$

$$(CH_3)_3N_3B_3R_2Cl + R'MgBr \longrightarrow (CH_3)_3N_3B_3R_2R' + MgBrCl \quad (4)$$

where a *B*-chloro derivative was the desired product (eq 1–3), a stoichiometric amount of Grignard reagent was used; no more than a 5% excess was used for the preparation of completely B-substituted derivatives. This procedure minimized the presence of partially substituted products in the reaction mixture. When more than the stoichiometric amount of Grignard reagent was used in the preparation of compounds in which at least one *B*-Cl moiety was required, the product was contaminated with the next higher alkylated compounds. If more than a 5% excess of Grignard reagent was present in the preparation of a completely B-substituted borazine (eq 4), exchange of *B*-alkyl or *B*-aryl groups occurred.[3] The most practical order of treating borazines with Grignard reagents in terms of the ease of purification of the products involved reaction with CH_3MgBr before C_2H_5MgBr; reaction with C_6H_5MgBr was always the last of any series. Replacement of a *B*-methyl group by a phenyl moiety is slower than the reverse reaction under the same conditions. The properties of the *B*-phenyl derivatives also differ markedly from those of the corresponding alkyl compounds. Reactions with C_6H_5MgBr required considerably longer reflux times than those with the alkyl Grignard reagents to obtain comparable yields. Our observation that stoichiometric quantities of Grignard reagent react with *B*-dichloro- and *B*-trichloroborazines to give good yields of the desired products with only small amounts of more highly substituted derivatives indicates that a stepwise[2] rather than a statistical process[11] occurs under these conditions.

A number of the unsymmetrically B-substituted borazines readily undergo exchange reactions to yield a mixture of products. Thus, carefully purified samples of *B*-monophenylpentamethylborazine upon distillation always give hexamethylborazine, *B*-diphenyltetramethylborazine, and *B*-triphenyl-*N*-trimethylborazine. This reaction does not occur appreciably at room temperature but occurs readily at elevated temperatures. The preparation of some unsymmetrically substituted borazines containing *B*-alkyl moieties is complicated by relatively rapid exchange processes. For example the liquid compound $C_2H_5(CH_3)_2B_3N_3(CH_3)_3$ rapidly equilibrates to a mixture of products at 40°. On the other hand the solid derivative $Cl(C_6H_5)_2B_3N_3(CH_3)_3$ required about 4 months to yield a mixture of the four possible exchange products.

The reaction of $Cl(CH_3)_2B_3N_3(CH_3)_3$ with a suspension of potassium sand in benzene which was reported to form $[(CH_3)_3N_3B_3(CH_3)_2]_2$ (III)[13] gave the expected product together with $C_6H_5(CH_3)_2B_3N_3(CH_3)_3$ in about 15% yield; when the reaction was conducted in heptane, only III was formed. The reaction mixture using benzene as a solvent acquires a dark blue color suggesting the presence of radical species. It is possible that $C_6H_5(CH_3)_2B_3N_3(CH_3)_3$ which was isolated from this reaction was formed from the reaction of the chloroborazine with phenylpotassium (eq 5), the latter compound arising from the attack of a borazinylpotassium

$$Cl(CH_3)_2B_3N_3(CH_3)_3 + C_6H_5K \longrightarrow C_6H_5(CH_3)_2B_3N_3(CH_3)_3 + KCl \quad (5)$$

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[14] R. I. Wagner and J. L. Bradford, *Inorg. Chem.*, **1**, 99 (1962).

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TABLE II

FAR-INFRARED SPECTRA OF B-SUBSTITUTED *N*-TRIMETHYLBORAZINES

	B substituents									
	Me	Me	Me	Cl	Me	Ph	Ph	Ph	Me	Me
	Me	Me	Cl	Cl	Ph	Ph	Cl	Ph	Ph	Me
	Me	Cl	Cl	Cl	Cl	Cl	Cl	Ph	Ph	Ph
Phenyl ring					157 w	178 w	157 m	157 m	155 m	159 w
BN ring	180 s	180 s	181 s	185 s						
					194 w	191 m				197 w
			218 w	214 w			215 m		217 m	
									225 m	
		245 w								
					253 w	255 w		253 s		
							264 m	276 m	266 m	
			283 vw							
		296 m					298 w	295 vw		
			326 w	323 s		325 m	320 m			
		347 m		368 w			364 m			
Me_5 confign	397 s	397 m					395 vw	400 vw		397 mw
			440 vw						414 w	
		472 m					473 w		470 vw	
				485 w	485 m	486 m		488 s		480 m
	495 vw		503 vw				496 ms		500 s	
		523 w	513 w							
							550 w	555 m	541 vw	542 m
	575 s	577 w	578 vw			577 m		578 w		560 m
				587 mw	590 ms	590 w	587 w		590 m	
					600 m	606 m	608 mw	613 vw		608 w
					621 w	623 m	620 w	618 vw	618 vw	617 w
								640 vw	637 w	
		627 vs	635 m							
		645 m	647 s							
		657 w	660 s							
			665 m							
		687 m	674 w	682 vs		675 s				
					693 m					685 s

derivative on the solvent. Morton and Richardson[16] have proposed that amylsodium attacks benzene at room temperature to form phenylsodium.

The reaction of $Cl(CH_3)_2B_3N_3(CH_3)_3$ with sodium sand always yielded varying amounts of $[(CH_3)_3N_3B_3(CH_3)_2]_2O$ (IV), possibly by the reaction of the chloroborazine with sodium oxides present on the surface of the metal. The possibility that IV arises from the hydrolysis of III during the work-up procedure was investigated in several ways. A pure sample of III which was exposed to the atmosphere for 1 month was virtually unchanged over this period of time. Attempted reaction of a CCl_4 solution of III with water over a 1-hr period also gave little indication that IV had been formed in the process.

Finally we were unable to repeat the reported[13] cleavage of the boron–boron bond in III by bromine to yield *B*-bromopentamethylborazine. Meller and Mareck[13] reported their product of this reaction to melt at 116–118° which is considerably lower than that originally reported (127–129°) for *B*-bromopentamethylborazine.[9]

Infrared Spectra.—The B-substituted borazines[17] reported here might be expected to exhibit a large number of vibrational modes. Theoretically, symmetrically B-substituted *N*-trimethylborazines exhibit D_{3h} symmetry and should give ten fundamental infrared-active modes, while the B-mono- or B-disubstituted derivatives (C_{2v}) should exhibit 27 infrared-active modes.[18,19] The completely unsymmetrically B-substituted borazines such as $Cl(CH_3)(C_6H_5)B_3N_3(CH_3)_3$ possess the lowest symmetry of the compounds prepared (C_s) and the largest number of infrared-active modes. Because of the obvious difficulties of applying a rigorous analysis to the spectra of these compounds using the usual group theoretical arguments, we have assigned the observed bands using correlation methods. The assignments were verified for the most part using the relative intensities of the substitutents in question, because the compounds prepared incorporated several series with zero, one, two, and three B substituents. In such cases the relative intensity of the vibrations associated with the *B*-X moieties increased regularly along this series.

B-**CH**$_3$.—A *B*-CH_3 mode, previously assigned as ν(B–C),[19,20] $\rho(CH_3)$,[21] and $\nu(B–CH_3)$[22] is affected only slightly by changing the nature of the remaining B substituents, changes in the symmetry, or coupling with other vibrations. The data in Table III sum-

TABLE III

THE POSITION OF THE *B*-CH_3 MODE IN SUBSTITUTED *N*-TRIMETHYLBORAZINES

B substituents[a]			Band position, cm^{-1}	B substituents[a]			Band position, cm^{-1}
R_2	R_4	R_6		R_2	R_4	R_6	
CH_3	CH_3	CH_3	888	CH_3	CH_3	PMB	883
CH_3	CH_3	Cl	885	CH_3	CH_3	PMBO	883
				CH_3	CH_3	C_2H_5	882
CH_3	CH_3	$(CH_3)_5C_6$	884	CH_3	Cl	Cl	881
CH_3	CH_3	C_6H_5	883				
CH_3	C_6H_5	C_6H_5	883				

[a] PMB = $(CH_3)_3N_3B_3(CH_3)_2$; PMBO = $[(CH_3)_3N_3B_3(CH_3)_2]O$.

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[16] A. A. Morton and G. M. Richardson, *J. Amer. Chem. Soc.*, **62**, 123 (1940).

[17] In the following discussions the boron substituents are numbered R_2, R_4, and R_6 in accordance with the usual nomenclature of the parent compound, *i.e.*, 1,3,5-trimethylborazine.

[18] G. A. Anderson and J. J. Lagowski, *Spectrochim. Acta, Part A*, **26**, 2013 (1970).

[19] A. Meller, *Organometal. Chem. Rev.*, **2**, 1 (1967).

[20] A. Meller and R. Schlegel, *Monatsh. Chem.*, **96**, 1209 (1965).

[21] A. Meller and M. Wechsberg, *ibid.*, **98**, 513 (1967).

[22] H. Watanabe, M. Narisada, T. Nakagawa, and M. Kubo, *Spectrochim. Acta*, **16**, 78 (1960).

marize the position of the *B*-CH_3 absorptions for all of the compounds containing this group. There appears to be a decrease in energy for this vibration with increasing chloro or phenyl substitution suggesting that the net inductive effects of these groups are similar in magnitude and direction.

B-**Cl.**—The band patterns for borazines containing this group which appear in the ranges 600–700 cm^{-1} (A) and 900–1000 cm^{-1} (B) have been assigned to *B*-Cl vibrations[19,22,23] (Table IV). These bands are sensitive to electronic effects and symmetry changes brought about by changes in the nature of the substituents at the other boron positions. Electronic effects shift the centers of gravity of the patterns whereas symmetry changes cause a broadening of the envelope of band A. For example, $Cl_3B_3N_3(CH_3)_3$ exhibits a closely spaced triplet for band A which becomes markedly broader for $(CH_3)_2ClB_3N_3(CH_3)_3$. The spectra of the *B*-phenyl derivatives are more difficult to assign because the bands characteristic of a monosubstituted phenyl group which occur in the 800–650 cm^{-1} region partially obscure the *B*-Cl vibrations. Our observations are essentially in agreement with Meller,[19] who suggested that band A arises from an out-of-plane vibration which is strongly coupled to the ring vibrations. The center of gravity of A moves to lower energy with an increase in methyl substitution.

TABLE IV

THE POSITIONS OF THE *B*-Cl MODES IN SUBSTITUTED *N*-TRIMETHYLBORAZINES

B substituents			Band positions,[a] cm^{-1}	
R_2	R_4	R_6	A	B
Cl	CH_3	CH_3	689, 646, 628	(1008), 1003
Cl	Cl	CH_3	667, 660, 649, 635	997, (990)
Cl	CH_3	C_6H_5	684,[b] 622	995, (980)
Cl	Cl	Cl	680, 670, 667	(981), 975
Cl	Cl	C_6H_5	675,[b] 625	(975), 970
Cl	C_6H_5	C_6H_5	678, 626	(972), 967

[a] Positions given in parentheses are shoulders. [b] Bands partially obscured by C_6H_5–X vibrations.

Band B, assigned to ν(B–Cl),[22,23] is a broad singlet with evidence for shoulders arising from ^{37}Cl and ^{10}B isotopes. The center of band B moves to higher energies on increased methyl substitution on contrast to band A.

N-**CH_3**.—The bands which occur in the 1083–1175-cm^{-1} region are tentatively assigned to a combination of ν(N–C) and methyl deformation vibrations (Table V). They appear to be only weakly coupled with the ring vibrations and not significantly affected by inductive or mesomeric effects. However, the band positions in the region are very sensitive to steric influences of the substituents (R_2 and R_6) on the adjacent boron sites. The correlation of the position of the *N*-CH_3 vibration with the nature of the ortho substituents is shown in Table V. *N*-Methyl groups which have C_5H_6–Cl, CH_3–Cl, or Cl–Cl ortho substituents exhibit overlapping bands in this spectral range. When more than one of these combinations occur in the same molecule, the bands are frequently unresolved. Conceivably the patterns developed in Table V can be used in a diagnostic sense to establish the substitution in other mixed borazines.

TABLE V

THE POSITION OF THE *N*-CH_3 MODES IN SUBSTITUTED *N*-TRIMETHYLBORAZINES

			Band position,[b] cm^{-1}					
B substituents[a]			Nature of R_2 and R_6 B substituents					
R_2	R_4	R_6	C_6H_5, C_6H_5	C_6H_5, CH_3	CH_3, CH_3	Cl, Cl	C_6H_5, Cl	CH_3, Cl
CH_3	CH_3	CH_3			1105 (1112)			
Cl	Cl	Cl				1088 (1092)		
C_6H_5	C_6H_5	C_6H_5	1173 (1180)					
C_6H_5	C_6H_5	CH_3	1172 (1185)	1114 (1122)				
C_6H_5	C_6H_5	Cl	1176 (1187)				1085 (1089)	
Cl	Cl	CH_3				1090[c]		1085[c]
Cl	Cl	C_6H_5				1085	1085	
CH_3	CH_3	C_6H_5		1124 (1130)	1106			
CH_3	CH_3	Cl			1106			1085
C_6H_5	CH_3	Cl		1116 (1124)			1083 (1090)	1083 (1090)
PMB	CH_3	CH_3		1133[d]	1107			
PMBO	CH_3	CH_3		1120[e]	1110			
C_2H_5	CH_3	CH_3			1106			
CH_3	CH_3	$(CH_3)_5C_6$			1106			

[a] PMB = $[(CH_3)_3N_3B_3(CH_3)_2]$; PMBO = $[(CH_3)_3N_3B_3(CH_3)_2]O$. [b] Bands in parentheses are shoulders. [c] Overlapping bands. [d] $R_2 = (CH_3)_3N_3B_3(CH_3)_2$. [e] $R_2 = (CH_3)_3N_3B_3(CH_3)_2O$.

B-**C_6H_5**.—Several of the bands which appear in the spectra of *B*-phenylborazines are associated vibrations arising from a monosubstituted phenyl group.[20] The bands which appear above 3000 cm^{-1} undoubtedly belong to the C–H frequencies of the phenyl substituent.[24] The band at about 1600 cm^{-1} is characteristic of a monosubstituted phenyl derivation and has been assigned to a skeletal in-plane vibration. The strong band at about 1460 cm^{-1} tends to confuse the assignment of the CH_3 deformation mode which also occurs near this position. The C–H out-of-plane deformation modes, which appear in the 770–693-cm^{-1} region, and characteristic bands for a monosubstituted

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[23] V. Gutmann, A. Meller, and R. Schlegel, *Monatsh. Chem.*, **94**, 1071 (1963).

[24] L. J. Bellamy, "The Infrared Spectra of Complex of Complex Molecules," Methuen, London, 1954, pp 54–71.

phenyl derivative, which appears in the 950–1225 cm^{-1} region, are also present.

CH_3 Deformations and Ring Vibrations.—The two strongest bands in the infrared spectra of the *N*-methylborazines occur in the 1440–1475-and 1395–1424-cm^{-1} regions. The latter is assigned to a symmetric B–N stretching frequency, while the former corresponds to a methyl deformation. The methyl deformation, which is strongly coupled to B–N ring vibrations,[20] is split whenever a *B*-phenyl substituent is present (Table VI); this effect likely arises from the superposition of one or more phenyl ring absorptions which also overlap into this region.

TABLE VI

CH_3 DEFORMATIONS AND RING VIBRATIONS FOR SUBSTITUTED *N*-TRIMETHYLBORAZINES

B substituent[a]				Ring vibration, cm^{-1}	
R_2	R_4	R_6	$\delta(CH_3)$, cm^{-1}	C	D
CH_3	CH_3	CH_3	1470	1415, 1395	1325
Cl	Cl	Cl	1453	1405	1288
C_6H_5	C_6H_5	C_6H_5	1467, 1443	1406	1350, 1312, 1305
Cl	Cl	CH_3	1475	1416, 1395	1302, 1294
C_6H_5	C_6H_5	Cl	1470, 1455	1419, 1395	1325
C_6H_5	C_6H_5	CH_3	1475, 1443	1418, 1394	1333, 1325
CH_3	CH_3	Cl	1465	1416, 1382	1325
CH_3	CH_3	C_6H_5	1475, 1460	1424	1320, 1305
Cl	Cl	C_6H_5	1475, 1455	1415, 1387	1325
C_6H_5	CH_3	Cl	1475, 1458	1418, 1386	1325, 1312
PMB	CH_3	CH_3	1450	1410	1317
PMBO	CH_3	CH_3	1450	1410	1325
C_2H_5	CH_3	CH_3	1464, 1447	1405	1317, 1306
$(CH_3)_5C_6$	CH_3	CH_3	1446	1405	1320, 1313

[a] PMB = $[(CH_3)_3N_3B_3(CH_3)_2]$; PMBO = $[(CH_3)_3N_3B_3(CH_3)_2]O$.

Two patterns exist for the ring vibrations (Table VI). The first (C) is very intense and centered near 1400 cm^{-1}, and the second (D) is usually markedly weaker and centered near 1315 cm^{-1}. These bands are very often split. Band C is split only in the unsymmetrically substituted borazines that have a chloro substituent. Band D is split in some instances if certain substituents are present, but because the band is weak, it is difficult to establish a pattern of splitting with the data available. Both bands C and D move to higher energy as the number of *B*-CH_3 groups in the borazine increases; the change, however, is not regular.

Combination Bands.—The assignment of the two bands at 1278 and 1026 cm^{-1} which occur in the spectrum of hexamethylborazine has been in conflict.[21,25] These bands are also present in the compounds $(CH_3)_3N_3B_3(CH_3)_2X$ [X = Cl, C_6H_5, $(CH_3)_3N_3B_3(CH_3)_2$, $(CH_3)_3N_3B_3(CH_3)_2O$, C_2H_5]. The band at 1278 cm^{-1} has been assigned to ν(BN)[21] and ν(B–CH_3),[25] while the band at 1026 cm^{-1} is described as ν(NC).[21]

These bands appear to be strongly coupled with a ring vibration which is markedly affected by chloro or phenyl substitution. An out-of-plane ring vibration has been postulated as the cause of the lower effective symmetry of the borazine nucleus observed in an electron diffraction study.[26] Whether the ring motion is indeed an out-of-plane vibration, the fact that both bands at 1278 and 1026 cm^{-1} disappear upon deuteration of the *B*- or *N*-methyl groups[25] strongly suggests that these are coupled modes and not fundamentals although their high intensities would seem to indicate otherwise.

Tables I and II show the bands present in the far-infrared spectra (800–115 cm^{-1}) of the compounds synthesized in this work. Although the data show some features expected for these compounds such as the phenyl ring vibrations at about 155 cm^{-1}, the most interesting feature is the band at about 397 cm^{-1} in compounds of the type $(CH_3)_3N_3B_3(CH_3)_2X$. The band at about 1278 cm^{-1} (E) for these compounds appears to be a combination of ν(B–CH_3) with the band at 397 cm^{-1}; the results of these calculations are shown in Table VII. In a similar way, the bands near 1026 cm^{-1} (F) appear to be combination (difference) bands originating from the ring vibrations (1425–1405 cm^{-1}) and the band at 397 cm^{-1} (Table VII).

TABLE VII

CALCULATED AND OBSERVED COMBINATION BANDS IN $(CH_3)_3N_3B_3(CH_3)_2X$

	E band, cm^{-1}		F band, cm^{-1}	
X	Calcd	Obsd	Calcd	Obsd
CH_3	1285	1278	1018	1026
Cl	1282	1282	1027	1026
C_6H_5	1280	1273	1027	1026
$(CH_3)_3N_3B_3(CH_3)_2$	1280	1273	1013	1015
$(CH_3)_3N_3B_3(CH_3)_2O$	1280	1281	1013	1022
$(CH_3)_5C_6$	1281	1276	1008	1015

Borazine Dimers.—The spectra of $[(CH_3)_3N_3B_3(CH_3)_2]_2$ and $[(CH_3)_3N_3B_3(CH_3)_2]_2O$ show absorption bands typical of pentamethylborazines. The most definitive features in the spectrum of $[(CH_3)_3N_3B_3(CH_3)_2]_2$ are the bands at 987 and 1014 cm^{-1}; the oxide does not possess strong bands which are unique. The weak band observed in the oxide at 950 cm^{-1} has been assigned[14] to a B–O–B stretching frequency. It is present in other borazinyl oxides carrying *N*-methyl groups but is absent in borazinyl oxides which contain *N*-ethyl groups[15] and does not appear in a spectrum of a borazinyl oxide reported by Gutmann, *et al.*[23] Thus, it appears that the band at 950 cm^{-1} does not originate solely from a boron–oxygen stretching mode but is dependent on the presence of *N*-methyl groups. The boron–oxygen stretching modes in borates and *B*-alkoxyborazines have been reported for the region 1350–1310 cm^{-1}, whereas the same modes in $[(C_6H_5)_2B]_2O$ appear at 1262 and 1378 cm^{-1}.[27] The boron–oxygen stretching frequencies are probably masked by the B–N stretching absorption bands or they could be assigned to the band at 1261 cm^{-1}.

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(25) T. Totani and H. Watanabe, *Spectrochim. Acta*, **25**, 585 (1969).

(26) W. Harschbarger, G. Lee, R. F. Porter, and S. H. Bauer, *Inorg. Chem.*, **8**, 1683 (1969).

(27) W. Gerrard, "The Organic Chemistry of Boron and Its Compounds," Wiley, New York, N. Y., 1967, p 534.