Organoborazines. Part 2.[1] Synthesis of Alkenyltriborazines

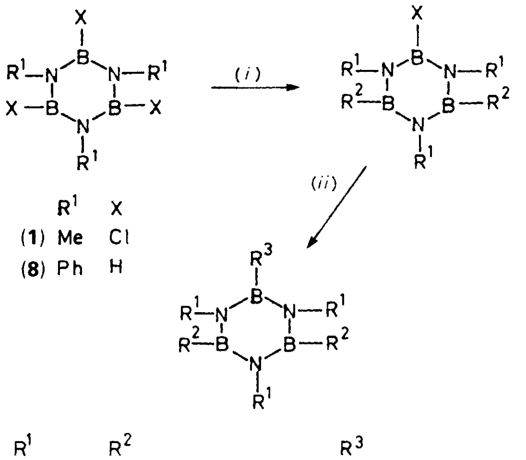
Logan A. Jackson and Christopher W. Allen *
Department of Chemistry, University of Vermont, Burlington, Vermont, 05405, U.S.A.

A series of unsymmetrically B-substituted N-methyl and N-phenyl borazines $R^3(R^2)_2B_3N_3(R^1)_3$ (R^3 = vinyl, allyl, or *p*-vinylphenyl; R^2 = methyl or phenyl; R^1 = methyl or phenyl) were prepared by substitution reactions of $Cl_3B_3N_3Me_3$ and $H_3B_3N_3Ph_3$ using Grignard reagents. Substituent exchange processes in these reactions were monitored by gas chromatography–mass spectrometry. These compounds were prepared in moderate yields and characterized by a combination of i.r. spectroscopy, ^1H, ^{13}C, and ^{11}B n.m.r. spectroscopy, mass spectrometry, and elemental analysis. N.m.r. evidence for the existence of mesomeric interactions of the borazines with the vinyl substituent and lack of such interactions with the *p*-vinylphenyl substituent was obtained.

Considerable interest exists in the development of precursors to boron nitride solid-state ceramic materials. Typically these materials are prepared by high energy means (high temperature, high pressures, pyrolysis, *etc.*) involving simple starting materials.[2–4] Recently alternative routes have been investigated which involve the combination of the boron and nitrogen atoms as adducts or strategically prepared polymeric precursors which allow for easier handling and lowering of the necessary energy required for ceramic formation.[5–7] The concept has been quite successfully applied to the preparation of silicon carbide and silicon nitride ceramic materials.[8]

Unfortunately, polymers containing a boron–nitrogen backbone are difficult to prepare due to the thermodynamic stability of the trimeric borazine rings. Therefore, most BN polymer precursors involve the linking together of borazine rings as described in the preparation of a number of cyclomatrix and cyclolinear polymers.[5,7] It is important to investigate alternative precursors which do not incorporate the boron–nitrogen bonds in the polymer backbone. We have previously shown that cyclophosphazenes can be incorporated as pendant groups in carbon chains by polymerization of the appropriate organofunctional phosphazene.[9] In this and in succeeding papers we shall demonstrate how this concept may be applied to cycloborazine chemistry.

It is well known that substitution of B-halogeno[10–12] and B-hydrido[13] borazines can be accomplished using alkyl and aryl Grignard reagents. The replacement of the chlorine and hydrogen atoms of the N-methyl- and N-phenyl-borazines is a stepwise process and allows for the preparation of unsymmetrically B-substituted borazines.[12,13] Therefore it should be possible to prepare a variety of monosubstituted borazine rings which contain a single organofunctional unit that allows for polymerization by conventional methods. In this paper we describe a series of molecules which contain the vinyl functionality and are potential monomers for the preparation of borazine-containing polymers.



	R^1	X
(1)	Me	Cl
(8)	Ph	H

R^1	R^2	R^3
Me	Me	vinyl (2), allyl (3), *p*-vinylphenyl (4)
Me	Ph	vinyl (5), allyl (6), *p*-vinylphenyl (7)
Ph	Me	vinyl (9), allyl (10), *p*-vinylphenyl (11)
Ph	Ph	vinyl (12), allyl (13), *p*-vinylphenyl (14)

Scheme. (*i*) $2MgR^2(X)$–diethyl ether; (*ii*) $MgR^3(X)$

Table. Alkenylborazines

Compound	Yield/%
(2)	63
(3)	66
(4)	30
(5)	51
(6)	50
(7)	28
(9)	63
(10)	63
(11)	48
(12)	28
(13)	29

Results and Discussion

A series of unsymmetrically B-substituted cyclic borazines were prepared by the reactions of the appropriate Grignard reagents with B-chloro-N-methyl and B-hydrido-N-phenyl borazines as shown in the Scheme. The reactions were carried out in the following general manner. The starting borazine was dissolved in diethyl ether and 2.0 equivalents of the Grignard reagent (methyl- or phenylmagnesium bromide in ether) were added slowly at room temperature. After a period of time, 1.0 equivalent of the vinyl functional Grignard reagent [vinylmagnesium chloride–tetrahydrofuran (thf), allylmagnesium bromide–thf, or *p*-vinylphenylmagnesium bromide–ether] was added. The subsequent work-up of the reaction yielded the desired product or a mixture of products. The yields for the compounds prepared are summarized in the Table.

It has been previously reported that the preparation of unsymmetrically substituted borazines by reactions of Grignard reagents with the B-chloro-N-methyl borazine proceeded with some degree of alkyl/aryl exchange.[12] This was found to be true for the preparations of compounds (**2**)—(**7**). The B-vinyl- (**2**) and B-allyl-pentamethyl (**3**) compounds were not isolated in analytically pure form due to difficulties in separation. Compounds (**2**) and (**3**) were obtained as mixtures with the B-divinyl- or B-diallyl-B-methyl-N-trimethylborazines and hexamethylborazine. Attempted vacuum distillation of the resulting oils was unsuccessful. The percentage composition of each component in the mixtures was determined by using capillary gas chromatography.* The synthesis of compound (**2**) has previously been reported.[14] The B-(*p*-vinylphenyl)-B-dimethyl-N-trimethylborazine, compound (**4**), was found to be a solid and could be isolated by vacuum sublimation.

The exchange of substituent groups also occurred in the preparations of the unsymmetrically substituted B-vinyl- (**5**) and B-allyl-B-diphenyl-N-trimethylborazines (**6**), however the desired products were solids and could be isolated by crystallization. Compound (**7**) was also obtained as a mixture with B-di(*p*-vinylphenyl)-B-phenyl-N-trimethyl- and B-triphenyl-N-trimethylborazine. Pure product was isolated by successive recrystallization. Attempted separation of all the B-substituted-N-trimethylborazines by chromatography on silica gel resulted in the decomposition of the material.

The extent of exchange was studied by careful examination of the reaction for the preparation of B-vinyl-B-dimethyl-N-trimethylborazine (**2**) and B-allyl-B-dimethyl-N-trimethylborazine (**3**) by using capillary gas chromatography (g.c.) and g.c.–mass spectrometry (m.s.). In each case the stepwise (0.25 equivalent) addition of 2.0 equivalents of methylmagnesium bromide (in diethyl ether) to a diethyl ether solution of $Cl_3B_3N_3Me_3$ (**1**) was monitored. After addition of a slight excess (5%) of methylmagnesium bromide only B-chloro-B-dimethyl-N-trimethylborazine and hexamethylborazine were detected by g.c. and g.c.–m.s. After addition of the first 0.25 equivalents of the vinyl Grignard reagent four compounds were detected, the expected B-chloro-B-dimethyl-N-trimethylborazine, B-vinyl-B-dimethyl-N-trimethylborazine (**2**), and hexamethylborazine as well as a small amount of B-divinyl-B-methyl-N-trimethylborazine. Previous reports suggest that exchange occurred upon addition of excess of Grignard reagent.[12] The results obtained in this study show that exchange was found to occur throughout the addition of the vinyl Grignard to the reaction mixture. Addition of excess of vinylmagnesium bromide resulted in further exchange and was evident in these studies by the presence of the B-trivinyl-N-trimethylborazine.

The preparation of the desired monomers from the B-hydrido-N-triphenylborazine proceeded with no apparent exchange of substituents. Again the substitution of the hydrogen atoms has been shown to be a stepwise process[13] and allowed for the preparation of good yields of the desired unsymmetrically substituted borazines, compounds (**9**)—(**11**) (Table). The products obtained were solids and could be isolated in pure form by crystallization. Compounds (**12**)—(**14**) were more difficult to prepare due to the poor solubility of the intermediate B-hydrido-B-diphenyl-N-triphenylborazine in ether. Compound (**14**) could not be obtained in pure form and was only detected, in small amounts, in the product mixture after work-up.

Characterization of the Reaction Products.—The compounds prepared were characterized by a combination of ^{1}H, ^{13}C, and ^{11}B n.m.r. spectroscopy, i.r. spectroscopy, m.s., and elemental analysis. The ^{1}H n.m.r. data for the compounds prepared were found to be consistent with the unsymmetrical structures described. The B-methyl protons were observed as singlets between δ −0.15 and 0.60[14,15] while the N-methyl signals were found between δ 2.5 and 3.0.[14–17] The complex multiplets due to phenyl proton resonances occurred at δ 7.0—8.0 for B-phenyl and 6.0—8.0 for N-phenyl groups. The resonances for the alkene functionality were typical and found between δ 4.9 and 7.0.[14–17] The integration of each of the spectra was found to be in agreement with the assigned structure.

The ^{13}C n.m.r. spectrum for each compound could be clearly assigned using the data obtained from the coupled and decoupled spectra. The carbon atoms of the methyl groups attached to boron atoms [compounds (**2**)—(**4**) and (**9**)—(**11**)] were observed as broad resonances, due to quadrupolar boron–carbon coupling, between −1.0 and 2.0 p.p.m., while the N-methyl carbon resonances occurred between 34 and 37 p.p.m.[18] The B-phenyl signals were observed in the range of 124—147 p.p.m. and N-phenyl signals in the range of 124—149 p.p.m. The vinylic carbon atoms were assigned by examining both the coupled and decoupled spectra. The α carbons were observed between 135 and 139 p.p.m. as broad resonances. The resonances for the β carbons of the vinyl groups were found between 126 and 132 p.p.m. The broad resonance for the methylene carbon attached to the boron atom of the allyl group was found between 22 and 24 p.p.m. The resonances for the carbon atoms α and β to the methylene carbon were observed between 135 and 136 and 113 and 115 p.p.m. respectively. The resonances of the α and β carbons atoms of the vinyl group of the *p*-vinylphenyl borazines were found between 137 and 138 and 112 and 114 p.p.m.

The ^{11}B n.m.r. spectra of compounds (**2**)—(**7**) and (**9**)—(**14**) consisted of broad resonances. The resonances for the two types of boron nuclei present were often overlapping and not well resolved. The chemical shifts for the compounds prepared were found between 29.0 and 38.0 ppm.[19]

The question of possible mesomeric interactions between boron π-acceptor sites and unsaturated organic substituents is a fundamental one for understanding details of the chemistry, *e.g.* polymerization behaviour, which may occur at the organic substituent. Previous studies have demonstrated that the favoured solution conformation in B-aryl derivatives is one in which the aryl group is perpendicular to the borazine ring.[20,21] The resulting restrictions of overlap of C_π donor and B_π acceptor orbitals suggests that the vinylphenyl derivatives (**4**), (**7**), (**11**), and (**14**) should exhibit spectroscopic parameters which are consistent with these structural demands. The β-carbon ^{13}C n.m.r. chemical shifts of the vinyl groups are typical of those found for styrenes which have weak electron donors in the *para* position.[22] These observations can be accounted for by the σ-electron donating capacity of the boron atom due to its decreased electronegativity relative to the sp^2 carbon atom. The vinyl borazines (**2**), (**5**), (**9**), and (**12**) present a more complex situation. Previous u.v. studies show evidence for significant conjugative effects.[17] In an attempt to investigate the conformational preference of the vinyl group, we examined the variable-temperature ^{1}H n.m.r. spectrum of compound (**2**). The chemical shifts of the flanking N-methyl groups remained equivalent down to 130 K. While this may indicate lack of a significant barrier to boron–carbon bond rotation, it also may result from insufficient chemical shift non-equivalence to be detected. The vinyl group could be non-planar with respect to the borazine ring and still maintain C_π to B_π overlap as long as the orbitals do not approach the orthogonal limit. The β-carbon ^{13}C n.m.r. chemical shifts of the vinyl groups fall in the range for monosubstituted vinyl groups with electron-withdrawing substituents.[22] Since the borazine will be σ-electron donating to

---

* The response factors for each component to the flame ionization detector were assumed to be equivalent in these determinations.

the olefin (see above), the electron-withdrawing effect must be a π donation from the olefin to the borazine. The downfield shift of the β-carbon resonance on going from the N-methyl[(**2**), (**5**)] to the N-phenyl[(**9**), (**12**)] derivatives suggests an increase in π donation to boron. The ^{11}B n.m.r. spectrum of (**2**) shows two resolved resonances one in the range of B-methyl (37.1) and the other (33.8) due to the B-vinyl centre. The lower ^{11}B shift is associated with better shielding due to π charge donation to boron.[19]

The i.r. spectra for all of the compounds exhibited strong bands between 1 350 and 1 500 cm^{-1} which are typical of borazine ring compounds.[12,15–17,23] The band for the vinyl group present in each compound was found near 1 600 cm^{-1}. The m.s. data for these compounds were consistent with the structures assigned.

Conclusions

It was possible to prepare a series of unsymmetrically substituted borazines which bear an alkenyl functionality using known methods. These new compounds were well characterized by standard techniques. Polymerization studies of the compounds are presently being carried out in our laboratories.

Experimental

Materials.—All reactions were carried out under an inert nitrogen atmosphere using Schlenk techniques. 2,4,6-Trichloro-1,3,5-trimethylborazine (**1**),[24] 1,3,5-triphenylborazine (**8**),[13] and 1,2,3,4,5-pentaphenylborazine[13] were prepared by published procedures and handled in a nitrogen atmosphere glove-box. Methylmagnesium bromide (3.0 mol dm^{-3} in diethyl ether), vinylmagnesium bromide (1.0 mol dm^{-3} in thf), allylmagnesium chloride (2.0 mol dm^{-3} in thf), phenylmagnesium bromide (3.0 mol dm^{-3} in diethyl ether), and 4-bromostyrene were purchased from the Aldrich Chemical Company and were used as obtained. Vinylphenylmagnesium bromide was prepared by addition of the required amount of 4-bromostyrene to an excess (5%) of magnesium metal in thf. Diethyl ether was distilled from lithium aluminium hydride and thf from potassium metal directly before use.

Gas chromatography was performed on a Varian model 3700 gas chromatograph using a 30-m (0.25 mm I.D.) RTX-5 cross-bonded SE-54 WCOT fused quartz capillary column. The same capillary column was used in the g.c.–m.s. studies. The ^1H and ^{13}C n.m.r. spectra (in $CDCl_3$) were recorded on a Bruker 270 MHz Fourier-transform n.m.r. spectrometer operating at 270.13 and 67.93 MHz. Chloroform (^1H) and tetramethylsilane (^{13}C) were used as the internal references. The ^{11}B n.m.r. spectra were obtained on a Bruker WM-250 spectrometer operating at 80.24 MHz, and referenced to an external sample of $BF_3 \cdot OEt_2$. All of the chemical shifts upfield of the reference were assigned positive values. Infrared spectra were recorded on a Perkin-Elmer 1430 ratio recording spectrometer, mass spectra and g.c.–m.s. spectra on a Finnigan 4000 automated gas chromatograph/EI-CI mass spectrometer operating at 80 eV (*ca.* 1.28×10^{-17} J). Elemental analyses were performed by Robertson Laboratories.

Synthesis of B-*Alkenylpentamethylborazines* (**2**)—(**4**).—The preparations of the unsymmetrically substituted pentamethyl borazines were accomplished by the following general procedure. A solution of methylmagnesium bromide (14.8 cm^3, 22.0 mmol, 3.0 mol dm^{-3}) in diethyl ether was added dropwise (0.5 h) to a solution of $Cl_3B_3N_3Me_3$ (**1**) (5.0 g, 22.0 mmol) in diethyl ether (150 cm^3) at room temperature. The mixture was allowed to stir for 1 h then 1.0 equivalent of the appropriate Grignard reagent was added [vinylmagnesium bromide (22.0 cm^3, 1.0 mol dm^{-3}, 22.0 mmol), allylmagnesium chloride (11.0 cm^3, 22.0 mmol, 2.0 mol dm^{-3}) or *p*-vinylphenylmagnesium bromide (22.0 mmol)] dropwise. The reaction mixtures were allowed to stir overnight at room temperature. The solvent was removed by a rotary evaporator and the resulting material was extracted with hot hexane (2 × 100 cm^3). Removal of the solvent from the hexane extracts yielded a mixture of the desired products.

Compounds (**2**) *and* (**3**). The yields for compounds (**2**) and (**3**) were determined by g.c. The major products were the B-vinyl-(**2**) (63%) and B-allyl-pentamethylborazines (**3**) (66%). Also present in each case were B-divinyl-(7%), diallyl-tetramethylborazine (7%), and hexamethylborazine (16, 3%). The major products were not successfully isolated by distillation and attempted chromatography on silica gel resulted in decomposition.

Compound (**2**): n.m.r., ^1H, δ 6.26 [J_{HCCH} = 15.58 (*cis*), 20.27 (*trans*), $BCH{=}CH_2$], 5.77 [J_{HCH} = 3.84, $BCH{=}CH_2$ (*cis*)], 5.40 [$BCH{=}CH_2$ (*trans*)], 2.87(2) and 2.88(1) (NCH_3), and 0.47 (BCH_3); ^{13}C, δ 138.3 ($BCH{=}CH_2$), 126.1 (J_{CH} = 156.0, $BCH{=}CH_2$), 35.1(2) and 34.4(1) (J_{CH} = 133.5 Hz, NCH_3), and −0.5 p.p.m. (BCH_3); ^{11}B, δ 33.8 ($BCH{=}CH_2$) and 37.1 p.p.m. (BCH_3); i.r. 1 385s (B–N str), 1 440s (C–N def), 1 607m (C=C str), and 2 950m cm^{-1} (CH str); *M* 176 (m.s.).

Compound (**3**): n.m.r., ^1H, δ 5.91 (J_{HCCH} = 10.25, $BCH_2CH{=}CH_2$), 4.97 [J_{HCCH} (*trans*) = 17.08, $BCH_2CH{=}CH_2$ (*trans*)], 4.90 [J_{HCH} = 1.71, J_{HCCH} = 10.25, $BCH_2CH{=}CH_2$ (*cis*)], 2.92(2) and 2.86(1) (NCH_3), 2.01 (J_{CH} = 6.83, $BCH_2CH{=}CH_2$), and 0.47 (BCH_3); ^{13}C, δ 135.3 (J_{CH} = 150.6, $BCH_2CH{=}CH_2$), 114.3 (J_{CH} = 150.7, $BCH_2CH{=}CH_2$), 34.4(1) and 34.0(2) (J_{CH} = 135.4 Hz, NCH_3), 22.3 ($BCH_2CH{=}CH_2$), and −0.2 (BCH_3); ^{11}B, δ 35.1 ($BCH_2CH{=}CH_2$) and 37.1 p.p.m. (BCH_3); i.r. 1 397s (B–N str), 1 450s (C–N def), 1 629m (C=C str), and 2 950m (CH str); *M* 190 (m.s.).

Compound (**4**). Sublimation of the crude material at 40 °C (0.03 mmHg, *ca.* 4 Pa) for 4 h allowed removal of the hexamethylborazine produced in the reaction. The desired product (2.5 g, 30%, m.p. = 60—61 °C) (Found: C, 60.90; H, 9.00; N, 16.05. Calc. for $C_{13}H_{22}B_3N_3$: C, 61.75; H, 8.75; N, 16.60%) was isolated by further sublimation (5 h) under the same conditions. Attempted sublimation at higher temperatures resulted in decomposition of the material.

N.m.r.: ^1H, δ 7.35 (complex m, $BC_6H_4CH{=}CH_2$), 6.72 (J_{CH} = 17.72, $BC_6H_4CH{=}CH_2$), 5.76 [J_{CH} = 0.85, BC_6H_4-$CH{=}CH_2$ (*cis*)], 5.23 [J_{HCH} = 0.85, J_{HCCH} = 10.80, $BC_6H_4CH{=}CH_2$ (*trans*)], 2.97(1) and 2.69(2) (NCH_3), and 0.54 (BCH_3); ^{13}C, δ 142—125 ($BC_6H_4CH{=}CH_2$), 137.2 (J_{CH} = 150.5, $BC_6H_4CH{=}CH_2$), 113.1 (J_{CH} = 154.5, $BC_6H_4CH{=}CH_2$), 35.8(2) and 34.5(1) (J_{CH} = 135.4 Hz, NCH_3), and −0.4 p.p.m. (BCH_3); ^{11}B, δ 37.0 p.p.m. (overlapping $BC_6H_4CH{=}CH_2$ and BCH_3). I.r.: 1 395s (B–N str), 1 445s (C–N def), 1 603w (C=C str aromatic), 1 627w (C=C str vinyl), 2 950m (CH str), and 3 020s cm^{-1} (CH str aromatic). *M* 252 (m.s.).

Synthesis of B-*Alkenyldiphenyl*-1,3,5-*trimethylborazines* (**5**)—(**7**).—The preparation of the unsymmetrically substituted B-diphenyl-N-trimethyl borazines was accomplished by the following general procedure. Phenylmagnesium bromide (15.4 cm^3, 3.0 mol dm^{-3}, 46.0 mmol) was added dropwise to a solution of $Cl_3B_3N_3Me_3$ (**1**) (5.0 g, 22.0 mmol) in diethyl ether (150 cm^3) at room temperature. The mixture was allowed to stir for 1 h then 1.0 equivalent of the appropriate Grignard reagent was added [vinylmagnesium bromide (22.0 cm^3, 1.0 mol dm^{-3}, 22.0 mmol), allylmagnesium chloride (11.0 cm^3, 22.0 mmol, 2.0 mol dm^{-3}), *p*-vinylphenylmagnesium bromide (22.0 mmol)] dropwise. The reaction mixtures were allowed to stir overnight at room temperature. The solvent was removed by a rotary evaporator and the resulting material was extracted with hot hexane (2 × 100 cm^3) to yield the crude products.

Compounds (**5**) *and* (**6**). These compounds were easily purified by crystallization from hexane–methylene chloride mixtures. The 1,3,5-trimethyl-2,4,6-triphenylborazine was removed with the initial crystallization. The desired products were then isolated and the yields obtained are shown in the Table.

Compound (**5**) [Found: C, 67.65; H, 7.25; N, 13.80%; *M* 301 (m.s.). Calc. for $C_{17}H_{22}B_3N_3$: C, 67.85; H, 7.35; N, 13.95%]: m.p. 95—96 °C; n.m.r., ^1H, δ 7.35 (complex m, BC_6H_5), 6.32 [J_{HCCH} = 15.34 (*cis*), 20.40 (*trans*), $BC\mathit{H}{=}CH_2$], 5.84 [J_{HCH} = 3.80 Hz, $BCH{=}C\mathit{H}_2$ (*cis*)], 5.56 [$BCH{=}C\mathit{H}_2$ (*trans*)], 2.76(2) and 2.48(1) (NCH_3); ^{13}C, δ 140—127 (BC_6H_5), 137.3 ($B\mathit{C}H{=}CH_2$), 127.0 (J_{CH} = 155.0, $BCH{=}\mathit{C}H_2$), 36.9(1) and 36.3(2) p.p.m. (J_{CH} = 135.4 Hz, NCH_3); ^{11}B, δ 32.9 p.p.m. (overlapping $BCH{=}CH_2$ and BC_6H_5); i.r. 1 395s (B–N str), 1 440s (C–N def), 1 597w (C=C str aromatic), 1 610w (str vinyl), and 2 950m cm^{-1} (CH str).

Compound (**6**) [Found: C, 67.80; H, 7.35; N, 12.85%; *M* 377 (m.s.). Calc. for $C_{18}H_{24}B_3N_3$: C, 68.65; H, 7.70; N, 13.35%]: m.p. 91—93 °C; n.m.r.; ^1H, δ 7.34 (complex m, BC_6H_5), 5.98 (J_{CH} = 9.82, $BCH_2C\mathit{H}{=}CH_2$), 5.05 [J_{HCCH} (*trans*) = 16.65, $BCH_2CH{=}C\mathit{H}_2$ (*trans*)], 4.97 [J_{HCH} = 1.71, J_{HCCH} = 9.82, $BCH_2CH{=}C\mathit{H}_2$ (*cis*)], 2.82(2) and 2.44(1) (NCH_3), and 2.12 (J_{CH} = 7.26 Hz, $BC\mathit{H}_2CH{=}CH_2$); ^{13}C, δ 141—127 (BC_6H_5), 134.8 (J_{CH} = 150.6, $BCH_2\mathit{C}H{=}CH_2$), 114.9 (J_{CH} = 150.7, $BCH_2CH{=}\mathit{C}H_2$), 37.15(1) and 35.49(2) (J_{CH} = 135.4 Hz, NCH_3), and 22.3 p.p.m. ($B\mathit{C}H_2CH{=}CH_2$); ^{11}B, 36.7 p.p.m. (overlapping $BCH_2CH{=}CH_2$ and BCH_3); i.r. 1 395s (B–N str), 1 445s (C–N def), 1 597w (C=C str vinyl), 1 625w (C=C str aromatic), 2 950m (CH str), and 3 015s cm^{-1} (CH str aromatic).

Compound (**7**). This compound was isolated by successive recrystallizations from hexane [Found: C, 73.60; H, 6.30; N, 10.95%. *M* 377 (m.s.). Calc. for $C_{23}H_{26}B_3N_3$: C, 73.30; H, 6.95; N, 11.15%], m.p. 190—240 °C. N.m.r.: ^1H, δ 7.37 (complex m, $BC_6\mathit{H}_4CH{=}CH_2$), 7.37 (complex m, BC_6H_5), 6.72 (J_{CH} = 17.50, $BC_6H_4C\mathit{H}{=}CH_2$), 5.76 [$BC_6H_4CH{=}C\mathit{H}_2$ (*cis*)], 5.22 [J_{HCCH} = 10.68 Hz, $BC_6H_4CH{=}C\mathit{H}_2$ (*trans*)], 2.54(2) and 2.53(1) (NCH_3); ^{13}C, δ 141—125 ($B\mathit{C}_6H_4CH{=}CH_2$), 137.2 ($BC_6H_4\mathit{C}H{=}CH_2$), 113.3 ($BC_6H_4CH{=}\mathit{C}H_2$), and 37.0(3) p.p.m. ($NCH_3$); ^{11}B, δ 37.0 p.p.m. (overlapping $BC_6H_4CH{=}CH_2$ and BCH_3). I.r.: 1 395s (B–N str), 1 445s (C–N def), 1 585w (C=C str aromatic), 1 615w (C=C str vinyl), 2 950m (CH str), and 3 020s cm^{-1} (CH str aromatic).

Synthesis of B-*Alkenyldimethyl*-1,3,5-*triphenylborazines* (**9**)—(**11**).—Compounds (**9**)—(**11**) were prepared by the following general procedure. A solution of methylmagnesium bromide (3.0 mol dm^{-3}, 10.8 cm^3, 32 mmol) in diethyl ether was added dropwise (0.5 h) to a solution of $H_3B_3N_3Ph_3$ (**8**) (5.0 g, 16 mmol) in diethyl ether. The mixture was allowed to stir for 1 h then 1.0 equivalent of the appropriate Grignard reagent was added [vinylmagnesium bromide (17.0 cm^3, 1.0 mol dm^{-3}, 17.0 mmol), allylmagnesium chloride (8.5 cm^3, 2.0 mol dm^{-3}, 17.0 mmol), or *p*-vinylphenylmagnesium bromide (17.0 mmol)] dropwise. The reaction mixture was then allowed to stir overnight. The solution was filtered to remove the precipitated salts then the solvent was removed and the resulting material was extracted with hexane (150 cm^3). The extracts were filtered and the solvent was removed to give the crude product. The material was found to be a mixture of the desired product and trimethyltriphenylborazine. Successive recrystallizations from hexane provided the pure products (Table).

Compound (**9**) [Found: C, 72.60; H, 6.60; N, 11.55%; *M* 362 (m.s.). Calc. for $C_{22}H_{24}B_3N_3$: C, 72.80; H, 6.65; N, 11.55%]: m.p. 197—198 °C; n.m.r., ^1H, δ 7.18 (complex m, NC_6H_5), 5.46 [J_{HCCH} = 14.50 (*cis*), 20.06 (*trans*), $BC\mathit{H}{=}CH_2$], 5.22 [J_{HCH} = 3.80 Hz, $BCH{=}C\mathit{H}_2$ (*cis*)], 4.61 [$BCH{=}C\mathit{H}_2$ (*trans*)], and −0.13 (BCH_3); ^{13}C, δ 148—124 (NC_6H_5), 136.2 ($B\mathit{C}H{=}CH_2$), 130.9 (J_{CH} = 144.9 Hz, $BCH{=}\mathit{C}H_2$), and 1.9 p.p.m. (BCH_3); ^{11}B, δ 28.1 ($BCH{=}CH_2$) and 33.8 p.p.m. (BCH_3); i.r. 1 370s (B–N str), 1 490s, 1 595s (C=C str aromatic), 1 615w (C=C str vinyl), 2 950m (CH str), and 3 025s cm^{-1} (CH str aromatic).

Compound (**10**) [Found: C, 73.55; H, 6.90; N, 10.90%; *M* 377 (m.s.). Calc. for $C_{23}H_{26}B_3N_3$: C, 73.30; H, 6.95; N, 11.15%]: m.p. 110—112 °C; n.m.r., ^1H, δ 7.20 (complex m, NCH_3), 5.27 [J_{HCCH} (*cis*) = 9.82, $BCH_2C\mathit{H}{=}CH_2$], 4.53 [J_{HCH} = 2.14, $BCH_2CH{=}C\mathit{H}_2$ (*cis*)], 4.22 [J_{HCCH} (*trans*) = 17.04, $BCH_2CH{=}C\mathit{H}_2$ (*trans*)], 1.41 (J_{CH} = 7.68 Hz, $BC\mathit{H}_2CH{=}CH_2$), and −0.17 (BCH_3); ^{13}C, δ 149—124 (complex m, NC_6H_5), 135.1 (J_{CH} = 152.9, $BCH_2\mathit{C}H{=}CH_2$), 113.9 (J_{CH} = 154.5 Hz, $BCH_2CH{=}\mathit{C}H_2$), 23.4 ($B\mathit{C}H_2CH{=}CH_2$), and 1.9 p.p.m. (BCH_3); ^{11}B, δ 37.3 p.p.m. (overlapping $BCH_2CH{=}CH_2$ and BCH_3); i.r. 1 380s (B–N str), 1 490s, 1 595s (C=C str aromatic), 1 630w (C=C str vinyl), 2 950m (CH str), and 3 020s cm^{-1} (CH str aromatic).

Compound (**11**) [Found: C,76.30; H, 6.40; N, 9.65%; *M* 439 (m.s.). Calc. for $C_{28}H_{28}B_3N_3$: C, 76.60; H, 6.45; N, 9.55%]: m.p. 191—193 °C; n.m.r., ^1H, δ 7.10 (complex m, NC_6H_5), 7.10 (complex m, $BC_6\mathit{H}_4CH{=}CH_2$), 6.42 ($J_{CH}$ = 10.70, $BC_6H_4C\mathit{H}{=}CH_2$), 5.50 [$J_{HCCH}$ (*trans*) = 10.70, $BC_6H_4CH{=}C\mathit{H}_2$ (*trans*)], 5.02 [J_{HCH} = 1.30 Hz, $BC_6H_4CH{=}C\mathit{H}_2$ (*cis*)], and −0.07 (BCH_3); ^{13}C, δ 137.2 (J_{CH} = 148.7, $BC_6H_4\mathit{C}H{=}CH_2$), 132—125 ($B\mathit{C}_6H_4CH{=}CH_2$ and NC_6H_5), 112.6 (J_{CH} = 160.2 Hz, $BC_6H_4CH{=}\mathit{C}H_2$), and 2.2 p.p.m. ($BCH_3$); ^{11}B, δ 36.0 p.p.m. (overlapping $BC_6H_4CH{=}CH_2$ and BCH_3); i.r. 1 370s (B–N str), 1 490s, 1 595s (C=C str aromatic), 1 630w (C=C str vinyl), 2 950m (CH str), and 3 025s cm^{-1} (CH str aromatic).

Synthesis of B-*Alkenylpentaphenylborazines* (**12**)—(**14**).—Compounds (**12**)—(**14**) were prepared by the following general procedures. The desired Grignard reagent [vinylmagnesium bromide (11.0 cm^3, 1.0 mol dm^{-3}, 11.0 mmol), allylmagnesium chloride (5.5 cm^3, 2.0 mol dm^{-3}, 11.0 mmol) or *p*-vinylphenylmagnesium bromide (11.0 mmol)] was added dropwise to an ether solution of $H(Ph)_2B_3N_3Ph_3$ (5.0 g, 11.0 mmol). The reaction mixture was allowed to stir overnight then a saturated aqueous solution of NH_4Cl was added slowly until the salts precipitated. The solvent was removed and the residue extracted with methylene chloride (100 cm^3). The desired products were isolated by recrystallization from methylene chloride–hexane mixture to give the pure compounds.

Compound (**12**) [Found: C, 79.20; H, 5.75; N, 7.95%; *M* 487 (m.s.). Calc. for $C_{32}H_{28}B_3N_3$: C, 78.90; H, 5.80; N, 8.65%]: m.p. 282—284 °C; n.m.r., ^1H, δ 6.90 (complex m, BC_6H_5), 6.90 (complex m, NC_6H_5), 5.56 [$BCH{=}C\mathit{H}_2$ (*trans*)], 5.28 [J_{HCH} = 3.42, $BCH{=}C\mathit{H}_2$ (*cis*)], and 4.66 [J_{HCCH} 15.37 (*cis*), 20.06 Hz (*trans*), $BC\mathit{H}{=}CH_2$]; ^{13}C, δ 148—124 (BC_6H_5 and NC_6H_5), 135.8 ($B\mathit{C}H{=}CH_2$), and 131.4 p.p.m. ($BCH{=}\mathit{C}H_2$); ^{11}B, δ 29.4 ($BCH{=}CH_2$) and 34.9 p.p.m. (BC_6H_5); i.r. 1 380s (B–N str), 1 491s, 1 597s (C=C str aromatic), 1 610w (C=C str vinyl), 2 950m (CH str), and 3 020s cm^{-1} (CH aromatic).

Compound (**13**) [Found: C, 78.90; H, 5.85; N, 8.40%; *M* 501 (m.s.). Calc. for $C_{33}H_{30}B_3N_3$: C, 79.10; H, 6.05; N, 8.40%]: m.p. 289—291 °C; n.m.r., ^1H, δ 6.91 (complex m, NC_6H_5), 6.90 (complex m, BC_6H_5), 5.29 [J_{HCCH} (*cis*) = 9.81, $BCH_2C\mathit{H}{=}CH_2$], 4.57 [J_{HCH} = 2.56, $BCH_2CH{=}C\mathit{H}_2$ (*cis*)], 4.28 [J_{HCCH} (*trans*) = 17.01, $BCH_2CH{=}C\mathit{H}_2$ (*trans*)], and 1.58 (J_{HCH} = 7.25 Hz, $BC\mathit{H}_2CH{=}CH_2$); ^{13}C, δ 148—124 (complex m, BC_6H_5 and NC_6H_5), 135.2 (J_{CH} = 150.7, $BCH_2\mathit{C}H{=}CH_2$), 114.4 (J_{CH} = 152.5 Hz, $BCH_2CH{=}\mathit{C}H_2$), and 23.9 p.p.m. ($B\mathit{C}H_2CH{=}CH_2$); ^{11}B, 29.5 ($BCH_2CH{=}CH_2$) and 35.5 p.p.m. (BC_6H_5); i.r. 1 380s (B–N str), 1 490s, 1 600s (C=C str aromatic), 1 630w (C=C str vinyl), 2 950m (CH str), and 3 020s cm^{-1} (CH aromatic).

G.C. Study of the Exchange Reaction.—The exchange process was examined by capillary g.c. and g.c.–m.s. according to the following general procedure. The $Cl_3B_3N_3Me_3$ (1.0 g, 4.4 mmol) was dissolved in ether (25 cm^3). To this solution was added 0.25 equivalent of methylmagnesium bromide–ether (3.0 mol dm^{-3}). After each addition an aliquot (0.25 cm^3) was removed and analyzed by capillary g.c. A slight excess of methyl Grignard was added until only $Cl_3B_3N_3Me_3$ and hexamethylborazine were present. The presence of only these two compounds was confirmed by g.c.–m.s. Two equivalents of vinylmagnesium bromide–thf (1.0 mol dm^{-3}) or allylmagnesium–thf (2.0 mol dm^{-3}) were then added in 0.25 equivalent portions. Aliquots were taken after each addition and analysed by g.c.–m.s.

Acknowledgements

This work has been supported in part by a grant from the Office of Naval Research. The assistance of Ms. Christine DiMeglio in obtaining the variable-temperature n.m.r. spectra and Mr. Rodney Parsons in g.c.–m.s. is greatly appreciated.

References

1 L. A. Jackson and C. W. Allen, *Phosphorus Sulfur, Silicon*, 1989, **41**, 341.
2 A. Meller, Gmelin Handbuck der Anorganische Chemie, Boron Compounds, Second Supplement, 1983, vol. 1, p. 304.
3 C. S. Kalyoncu, *Ceram. Eng. Sci. Proc.*, 1985, 1356.
4 N. J. Archer, *Spec. Publ.*, The Royal Society of Chemistry, 1977, no. 30, p. 167.
5 C. K. Narula, R. T. Paine, and R. Schaeffer, *ACS Symp. Ser.*, 1988, **360**, 378.
6 S. Y. Shaw, D. A. Dubois, and R. H. Neilson, *ACS Symp. Ser.*, 1988, **360**, 385.
7 K. J. Paciorek, W. Krone-Schmidt, D. H. Harris, R. H. Kratzer, and K. J. Wynne, *ACS Symp. Ser.*, 1988, **360**, 392.
8 K. J. Wynne and R. W. Rice, *Annu. Rev. Mater. Sci.*, 1984, **14**, 297.
9 C. W. Allen, *ACS Symp. Ser.*, 1988, **360**, 290.
10 D. T. Haworth and L. F. Hohnstedt, *J. Am. Chem. Soc.*, 1960, **82**, 3860.
11 G. E. Ryschkewitsch, J. J. Harris, and H. H. Sisler, *J. Am. Chem. Soc.*, 1958, **80**, 4515.
12 L. A. Melcher, J. L. Adcock, and J. J. Lagowski, *Inorg. Chem.*, 1972, **11**, 1247.
13 J. H. Smalley and S. F. Stafiej, *J. Am. Chem. Soc.*, 1959, **81**, 582.
14 A. J. Klanica and J. P. Faust, *Inorg. Chem.*, 1968, **7**, 1037.
15 P. Powell, *Inorg. Chem.*, 1973, **12**, 913.
16 O. T. Beachly, *J. Am. Chem. Soc.*, 1972, **94**, 4223.
17 T. Yoshizaki, H. Watanabe, K. Nagasawa, T. Totani, and T. Nakagawa, *Inorg. Chem.*, 1965, **4**, 1016.
18 H. Noth and B. Wrackmeyer, *Chem. Ber.*, 1981, **114**, 1150.
19 H. Noth and B. Wrackmeyer, 'NMR, Basic Principles and Progress,' Springer, Berlin, Heidelberg, 1979, vol. 14, p. 1.
20 E. F. Mooney, *Spectrochim. Acta*, 1962, **18**, 1355.
21 P. M. Johnson, jun., and E. K. Mellon, *Inorg. Chem.*, 1974, **13**, 2769.
22 J. B. Strothers, 'Carbon-13 NMR Spectroscopy,' Academic Press, New York, 1972.
23 T. Totani, H. Watanabe, and M. Kubo, *Spectrochim. Acta*, 1969, **25**, 585.
24 C. H. Brown and A. W. Laubengayer, *J. Am. Chem. Soc.*, 1955, **77**, 3699.

Received 17th February 1989; *Paper* 9/00751B