$(DPPE)_2$ (see Scheme II), while isomerization could occur from a species void of hydrides, possibly through a π-allyl complex. But this point requires further study, since 1-pentene is not isomerized on the same time scale.

Mechanism aside, the photochemistry of $H_4M(DPPE)_2$ in the presence of olefins is unique both in terms of its relatively high quantum efficiency and selectivity toward reduction. The quantum efficiencies for the stoichiometric reduction of 1-pentene using $H_4Ru_4(CO)_{12}$[8d] and $H_2Os_3(CO)_{10}$[8e] are about 2 orders of magnitude less than that observed with $H_4Mo(DPPE)_2$. The cluster hydrides also isomerize 1-pentene to its internal isomers, even when irradiated under H_2. The rate of olefin isomerization far exceeds that of olefin reduction. The photoreduction of neat olefin solutions under 20 psi of H_2 with $Fe(CO)_5$ can occur with quantum efficiencies greater than 1.0, but again olefin isomerization occurs.[27] The experiments with $H_4M(DPPE)_2$ show no 1-pentene isomerization with or without H_2 present. Also, all well-known thermal olefin hydrogenation catalysts, though being selective catalysts for reducing olefins under H_2, isomerize olefins in the absence of H_2.

Conclusions

Replacement of ^1H by ^2H in $H_4M(DPPE)_2$ does not significantly alter the nonradiative decay rate from the emissive state that is triplet in character. Further, photoreduction of 1-pentene occurs at the same rate, using either $H_4W(DPPE)_2$ or $D_4W(DPPE)_2$. The loss of H_2 upon photoexcitation of $H_4M(DPPE)_2$ in solution is consistent with a lowest excited state that is M → P charge transfer in character that tends to labilize the H_2 with respect to reductive elimination, since the metal is partially oxidized in the excited state. Alternatively, the lowest excited state may involve population of an orbital that is antibonding with respect to the M-H_2 interaction that leads to a sufficiently distorted excited state that little isotope effect on nonradiative decay rate would be expected. All of the data seem to be best interpreted with the M-H_2 antibonding type of excited state as proposed for certain Ir(III) polyhydrides,[29] since strongly antibonding character in an excited state is usually responsible for efficient dissociative type processes in organometallic molecules.[8a] For $H_4M(DPPE)_2$ photoextrusion of H_2 leads to a reactive dihydride that will efficiently reduce, but not rapidly isomerize, alkenes. The photoreduction has good quantum efficiency for alkenes having a terminal double bond, and irradiation under H_2 leads to sustained conversion to alkane.

Acknowledgment. We thank the National Science Foundation for support of this research.

Registry No. $H_4Mo(DPPE)_2$, 32109-09-4; $D_4Mo(DPPE)_2$, 83632-65-9; $Mo(N_2)_2(DPPE)_2$, 41700-58-7; $H_4W(DPPE)_2$, 36352-27-9; $D_4W(DPPE)_2$, 83632-66-0; $W(N_2)_2(DPPE)_2$, 55954-53-5; D_2, 7782-39-0; ethylene, 74-85-1; propene, 115-07-1; 1-pentene, 109-67-1; *n*-pentane, 109-66-0; *cis*-2-pentene, 627-20-3; 3,3-dimethyl-1-pentene, 3404-73-7; cyclopentene, 142-29-0; 4-phenyl-1-butene, 768-56-9; 3,3-dimethylpentane, 562-49-2; cyclopentane, 287-92-3; 1,2-dideuteriopentane, 83615-82-1; 1,2-dideuteriobut-4-ylbenzene, 83615-83-2.

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(28) (a) Parshall, G. W. "Homogeneous Catalysis"; Wiley-Interscience: New York, 1980. (b) James, B. R. *Adv. Organomet. Chem.* **1979**, *17*, 319. (c) James, B. R. "Homogeneous Hydrogenation"; Wiley-Interscience: New York, 1973.
(29) Geoffroy, G. L.; Pierantozzi, R. *J. Am. Chem. Soc.* **1976**, *98*, 8054.

Photochemistry of Divinylboranamines

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Abstract: The photochemistry of the divinylboranamines was explored in order to define structure–photoreactivity relationships for unsaturated organoboranes. Ultraviolet irradiation of the *N,N*-dimethyldivinylboranamines in cyclohexane gave cis–trans isomerization about the carbon–carbon double bonds to approximately statistical distributions of the three possible geometric isomers. Photolysis of the *N*-phenyldivinylboranamines gave nonoxidative photocyclization to azaboranaphthalenes in high yields. An investigation into the scope of cyclization revealed that chloro and bromo substitutents were tolerated on the aromatic ring, while compounds with methyl, ethyl, and *tert*-butyl groups on the vinyl moieties cyclized without difficulty. Quantum yields of cyclization ranged from 0.06 to 0.34 mol einstein^{-1}. Photoproduct structure determinations were accomplished from spectroscopic data and chemical degradation reactions. Cyclization was found to occur in a variety of solvents including pentane, cyclohexane, dioxane, and acetonitrile. In carbon tetrachloride, a carbon–boron bond-cleavage reaction occurred, giving an *N*-phenylvinylchloroboranamine as the only identifiable photoproduct. A new synthetic route for selective ortho-alkylation of anilines was developed via divinylboration, photocyclization, protonolysis, and hydrolysis. The alkylation is comparable in yields to known methods and tolerates introduction of a wide variety of alkyl groups.

The photochemical 1,2-boron shift and α-elimination processes, reported to date only in tetraarylborates[1] and trinaphthylborane,[2] are connected through the putative di-π-methane-type intermediate **1** (Scheme I). The unknown generality of these rearrangements in the photochemistry of di-π-borane systems suggested a systematic investigation into the governing structure–reactivity relationships. We, therefore, chose to study the photochemistry of various divinylboranamines.[3] The results to be discussed here indicate that rotational deactivation and nonoxidative photocyclization can occur in place of the di-π-methane-type rearrangement where structurally permitted.

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(1) Eisch, J. J.; Tamao, K.; Wilcsek, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 895-7.
(2) Ramsey, B. G.; Anjo, D. M. *J. Am. Chem. Soc.* **1977**, *99*, 3182-3.
(3) Current nomenclature practices of Chemical Abstracts Services designates boron–nitrogen compounds as boranamines. IUPAC uses the name aminoboranes as well.

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Scheme I

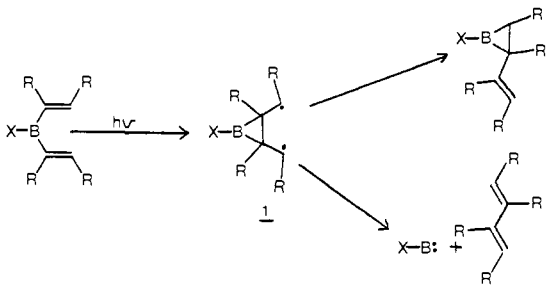


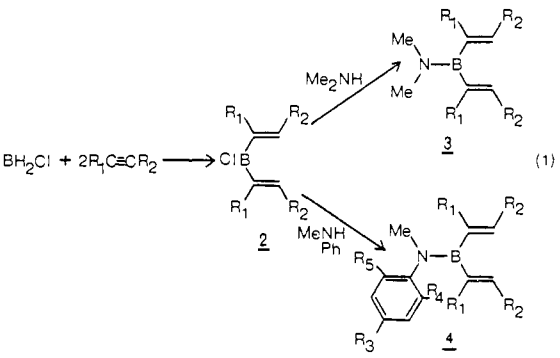
Table I. Divinylboranamines Synthesized

boranamine	R_1	R_2	R_3	R_4	R_5	yield,[a] %	synthetic method[b]
3a	H	Et				45	1
3b	Me	Me				30	1
4a	H	Et	H	H	H	52	1
4b	Me	Me	H	H	H	53	1
4c	Et	Et	H	H	H	60	1
4d	H	*t*-Bu	H	H	H	54	1
4e	H	H	H	H	H	16	3
6a	H	Et	H	H	H	84	2
6b	H	Et	H	H	Cl	78	2
6c	H	Et	H	H	Br	80	2
6d	Me	Me	H	Br	H	40[c]	2
6e	Me	Me	Me	Me	H	70	2
6f	H	Et	H	H	NO_2	10[c]	2

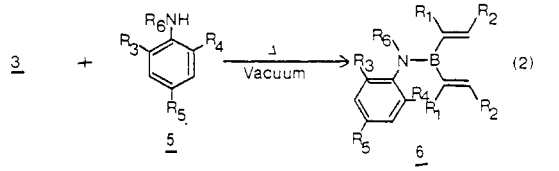
[a] On the basis of moles of BH_2Cl or divinyl-*N*,*N*-dimethylboranamine reacted. [b] Methods 1, 2, and 3 as defined in text by eq 1, 2, and 3. [c] Low yields result from the inherent difficulties of distilling 5–10 mmol quantities.

Results and Discussion

Synthesis. The divinylboranamines were prepared by one of three methods. The first method (eq 1) involved the reaction of



monochloroborane with the appropriate acetylene to give a divinylchloroborane (**2**). In the same reaction flask, **2** was reacted with a secondary amine and the resulting amine–borane complex was dehydrohalogenated with triethylamine to give the desired product (**3** or **4**) in yields ranging from 40 to 60%. This method works well with amines such as dimethylamine and *N*-methylaniline that form stable complexes with **2**. For less reactive aromatic amines (second method), a thermal aminolysis reaction had to be carried out between the aniline of choice and a *N*,*N*-dimethyldivinylboranamine (**3**) (eq 2). This procedure has been



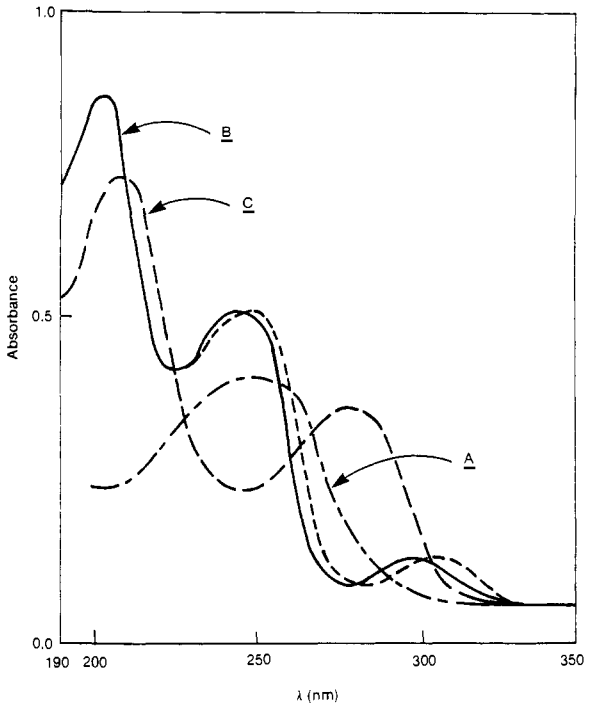
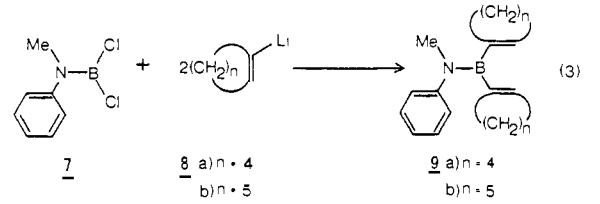


Figure 1. Ultraviolet spectra of the divinyl-*N*-phenylboranamines (—), the 1-aza-2-boranaphthalenes (– – –), and the divinyl-*N*,*N*-dimethylboranamines (- - -). The dotted line (- - -) shows the bathochromic shift that takes place in going from cyclohexane to acetonitrile as the solvent.

employed by other workers in the preparation of various *N*-phenylboranamines;[4] however, reactions were carried out at temperatures in excess of 150 °C (760 mm), and reaction times of 96 h were required for conversions greater than 90%. Under vacuum, dimethylamine was removed efficiently at reaction temperatures of only 70–120 °C and reaction times of 1–6 h. Isolated yields ranged from 60 to 90%.[5] The third method of preparation involved a coupling reaction between *N*-methyl-*N*-phenyldichloroboranamine (**7**) and 2 equiv of a cycloalkenyl lithium (**8**) (eq 3). The desired products (**9**) were obtained in ca. 40% yield (Table I).



Absorption Spectra. Typical ultraviolet spectra of the divinylboranamines and the respective photoproducts in cyclohexane and acetonitrile are shown in Figure 1. The *N*,*N*-dimethyldivinylboranamines (**3**) give one maximum at 240 nm (curve A) while the *N*-phenyldivinylboranamines (**4** and **6**) show three maxima in the regions of 300, 240, and 200 nm (curve B) with slight variations in the λ_{max} and ϵ values. The broken line shows the bathochromic shift in the absorption spectrum that takes place in going from cyclohexane to acetonitrile as a solvent and demonstrates the $\pi \rightarrow \pi^*$ character of the responsible transitions. The two longer wavelength peaks in curve B closely resemble the ultraviolet spectra of aniline (λ_{max} at 230 nm (25 000) and 280 nm (1600))[6] and *N*-methylaniline (λ_{max} 242 nm (11 000) and 290

(4) Kramer, J. D. Ph.D. Dissertation, University of California, Davis, CA, 1973.

(5) NMR spectra typically indicated quantitative conversion to the *N*-phenylboranamine. Isolated yields less than 80% were attributed to inherent losses in distilling 10–20-mmol quantities.

(6) Becher, H. J.; Baechle, H. T. *Adv. Chem. Ser.* **1964**, *No. 42*, 71–7. Baechle, H. T. Ph.D. Dissertation, Technische Hochschule, Stuttgart, 1963.

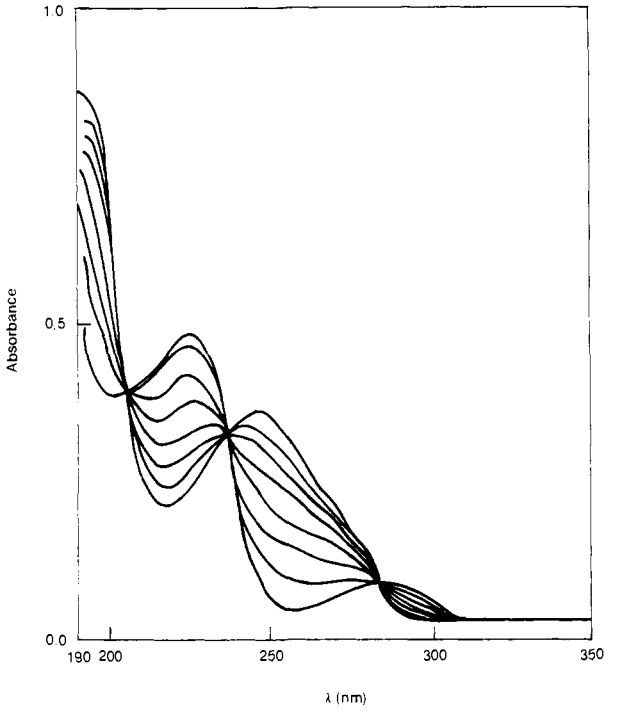
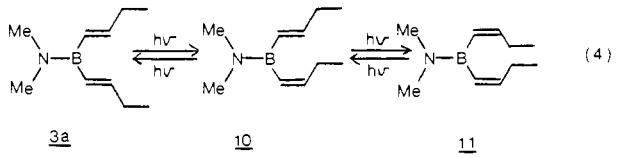


Figure 2. Ultraviolet spectra recorded during the photolysis of bis(*cis*-2-buten-2-yl)-*N*-phenylboranamine (**4b**) in cyclohexane.

nm (1900)).[6] A spectroscopic similarity between *N*-phenylboranamines and anilines has been previously noted[7] and suggests the intimate involvement of an aniline-type $\pi \rightarrow \pi^*$ absorption in the observed photochemical reactivity. Photoproducts of **4** and **6** typically show two maxima in the regions of 260 nm and 212 nm (curve C).

Ultraviolet spectra recorded during the photolysis of **4b** in cyclohexane are shown in Figure 2. Isosbestic points at 225, 252, and 293 nm indicate that nonabsorbing side products are not formed during photolysis and a linear conversion process from starting material to photoproduct is occurring.

Photochemical Cis–Trans Isomerization. Ultraviolet irradiation of a 1.0 M solution of bis(*trans*-1-buten-1-yl)-*N*,*N*-dimethylboranamine (**3a**) in cyclohexane gives cis–trans isomerization about the carbon–carbon double bonds (eq 4). Evidence for this



(4)

scheme stems from NMR spectral data and chemical degradation studies on the starting material and photoproduct. Deuterolysis of **3a** in acetic-*d* acid gives 2 equiv of *trans*-1-deuterio-1-butene (**12**) and *N*,*N*-dimethylacetamide (**13**). After irradiation, deuterolysis gave a 50:50 mixture of **12** and *cis*-1-deuterio-1-butene (**14**). Therefore, prolonged irradiation of **3a** in hydrocarbon solvent generates a steady-state mixture of **3a**, **10**, and **11** in close to statistical proportions.

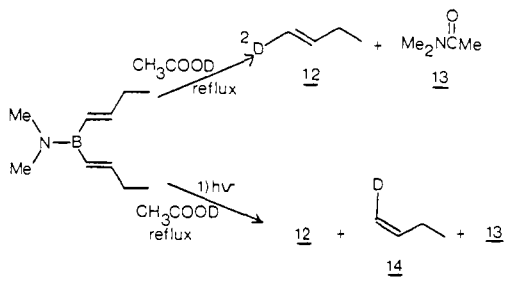
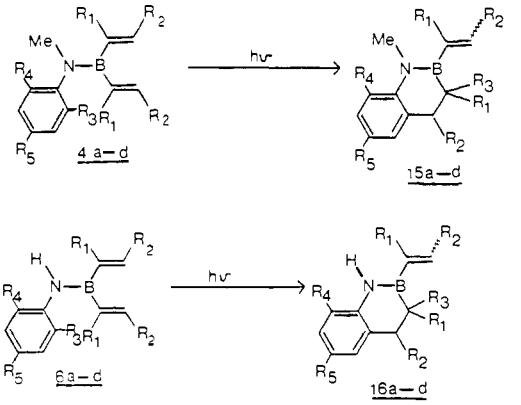


Table II. Irradiation Times and Isolated Yields of Nonoxidative Photocyclization Products

starting material	irradiation[a] time, h	photoproduct	isolated yield, %
4a	140	15a	95
4b	86	15b	95
4c	36	15c	66
4d	530	15d	80
6a	16	16a	90
6b	170	16b	68
6c	170	16c	35[c]
6d	22	16d	*b*
9a	50	23a	80
9b	20	23b	*b*

[a] All irradiations indicated were carried out in cyclohexane at concentrations of 0.8 to 1.0 M. [b] Irradiations were run on a millimolar scale (20–200 mg) suitable for NMR analysis. [c] Low yield is due to the inherent difficulties in distilling and recovering 5–10-mmol quantities.

Nonoxidative Photocyclization. Photolysis of the divinyl-*N*-phenylboranamines **4a–d** and **6a–d** at 254 nm caused, in each case, nonoxidative cyclization to the dihydro-1-aza-2-boranaphthalenes **15a–d** and **16a–d** (Table II). Photolyses were monitored by NMR

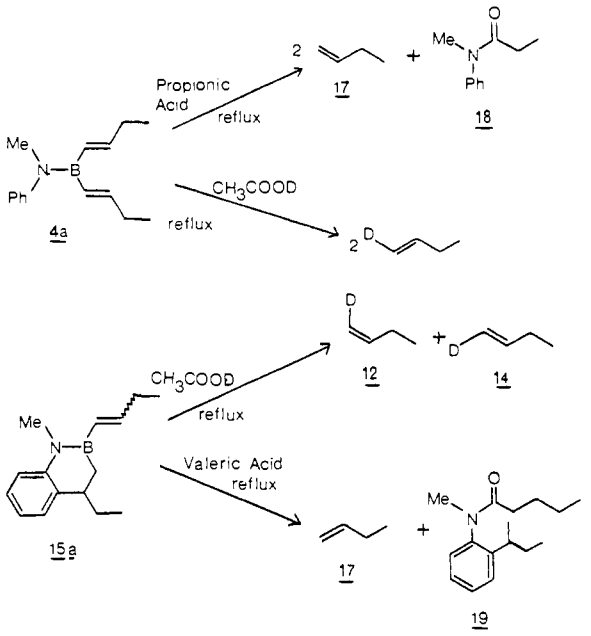


and UV spectroscopy. In preparative irradiations, photolyses were continued until no further changes were observed in the NMR spectra. The final spectra typically indicated quantitative conversion of the starting material to photoproduct (cf. Figure 2). Photoproducts were isolated by vacuum distillation, which wholly accounted for the less than quantitative isolated yields (Table II).

The assignment of structures **15** and **16** as photoproducts was based on spectral data and identification of the protonolysis products of **4a** and **15a**. Protonolysis of **4a** in refluxing propionic acid gave 2 equiv of 1-butene (**17**) and *N*-methyl-*N*-phenylpropionamide (**18**). Anilide **18** was identified by comparison of spectral and physical data with those of an independently and unambiguously synthesized sample. As expected, deuterolysis of **4a** gave 2 equiv of *trans*-1-deuterio-1-butene. Degradation of **15a** in refluxing acetic-*d* acid cleaved only the vinylic boron–carbon bond[8] to yield 1 equiv of a 50:50 mixture of **12** and **14** and an unidentified, not necessarily homogeneous, boron-containing compound. Protonolysis of **15a** in refluxing valeric acid, however, afforded 1 equiv of **17** and amide **19**; i.e., in valeric acid, protonolysis occurred with cleavage of both boron–carbon bonds and the boron–nitrogen bond. These data establish the gross cyclic structure of photoproducts **15** and **16**; details of the stereochemistry of cyclization are discussed in the accompanying paper.

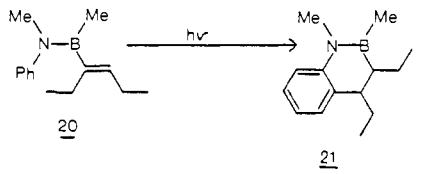
(7) Hancock, K. G.; Ko, Y.; Dickinson, D. A.; Karmer, J. D. *J. Organomet. Chem.* **1975**, *90*, 23–39.

(8) Brown, H. C. "Boranes in Organic Chemistry"; Cornell University Press: Ithaca, NY, 1972; p 313. Brown, H. C. "Organic Synthesis via Boranes"; Wiley: New York, 1975; p 81.



A limited investigation into the scope of cyclization revealed that both chloro and bromo substitutents were tolerated on the aniline ring. In addition, compounds containing methyl, ethyl, and *tert*-butyl vinyl substituents cyclized without difficulty. Of particular interest was the cyclization of **6d** exclusively on the unsubstituted side of the aromatic ring. This result was surprising since structurally similar bromoenaminones[9] and (2-iodophenyl)-*N*,*N*-diphenylboranamines[10] cyclized oxidatively with the loss of HBr and HI, respectively. The boranamines **4e**, **6e**, and **6f** failed to cyclize, even after prolonged ultraviolet irradiation.

The nonoxidative photocyclization of (*cis*-3-hexen-3-yl)-methyl-*N*-methyl-*N*-phenylboranamine (**20**) to **21** demonstrates

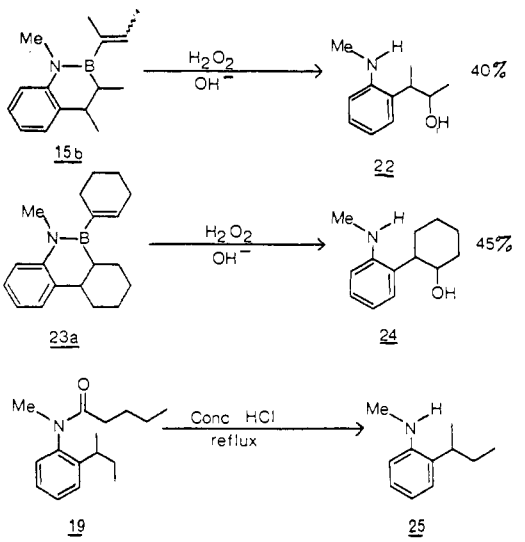


that two boron vinyl groups are not required as part of the chromophore in order to observe cyclization. The difficulty in preparing **20**, however, detracts from its general synthetic utility.

Chemical Degradation Reactions. Generally, when the divinylboranamines and respective photoproducts were refluxed in an organic acid, an amide was formed. The size of the acid employed depended upon the refluxing temperature required to complete the protonolysis reaction in a reasonable time period. Attempts to degrade **15a** in refluxing propionic acid and **15b** in refluxing valeric acid were unsuccessful, presumably because cleavage of the unsaturated boron–carbon bonds, primary in **15a** and secondary in **15b**, was too slow at the respective boiling points of the solvents employed.[8]

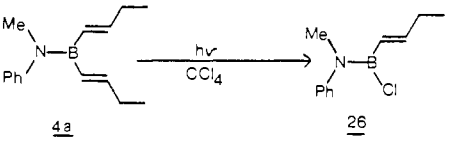
Although protonolysis reactions of photoproducts containing secondary carbon atoms bonded to boron proved difficult, such compounds could be successfully oxidized under basic hydrogen peroxide conditions. For example, **15b** and 10-(1-cyclohexenyl)-9-methyl-1,2,3,4,4a,9,10,10a-octahydro-9-aza-10-borophenanthrene (**23a**) were readily oxidized to the hydroxyanilines **22** and **24** in moderate yields. Conditions were not optimized for these reactions, and low yields were attributed to the formation of water-soluble amine oxides, which were lost during work up.

Acid hydrolysis of the amide **19** afforded *o*-*sec*-butyl-*N*-methylaniline (**25**) in an overall yield of 35% on the basis of the



original amount of *N*-methylaniline used in the preparation of **4a**. The sequence of reactions summarized by divinylboration of an aniline, photolysis, protonolysis, and hydrolysis constitutes an effective procedure for ortho-alkylation of an aromatic amine. This procedure admits introduction of primary, secondary, and tertiary alkyl groups, is comparable to other available methods in overall yield,[11] and may offer advantages in certain synthetic circumstances.

Solvent Effects. Nonoxidative cyclization of compounds **4** and **6** occurred in a variety of solvents including pentane, cyclohexane, benzene, dioxane, and acetonitrile. In carbon tetrachloride, however, inhibition of both nonoxidative photocyclization and rotational deactivation about the carbon–carbon double bonds was observed. Instead, a carbon–boron bond-cleavage reaction occurred, yielding the chloroboranamine **26** as as the only identified

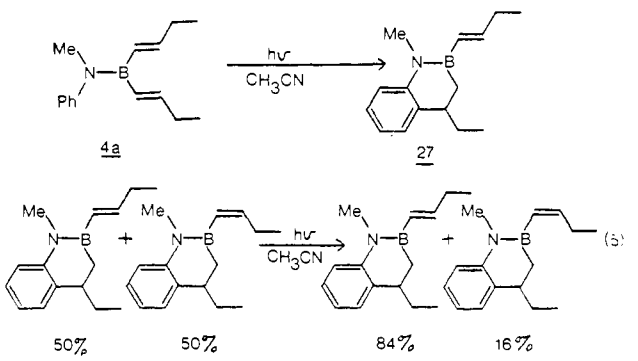


photoproduct. The fate of the lost vinyl group was not determined. Irradiation of all other *trans*-divinylboranamines in carbon tetrachloride gave complex mixtures; isolated photoproducts were not pure enough or quantitatively large enough for reliable analysis. Compounds with trisubstituted vinyl moieties such as **4b** and **4c**, when irradiated in carbon tetrachloride, gave cyclization in competition with other photodegradation processes, possibly boron–carbon homolysis in both the starting material and cycloadduct.[12] For all carbon tetrachloride irradiations, a majority of the starting material was lost to an unidentified carbon tetrachloride insoluble solid. Typically, less than 10% of the starting material by weight was recovered after irradiation.

Photolysis of **4a** in acetonitrile apparently inhibited trans–cis photoisomerization about the carbon–carbon double bonds and yielded **27** stereoselectively as the major photoproduct (90%). In contrast, preparation of **15a** by photolysis of **4a** in cyclohexane gave a 50:50 mixture of the *cis*- and *trans*-vinyl isomers (vide supra). This conclusion was verified by both NMR integration ratios and deuterolysis reactions. When **15a**, obtained from the cyclization of **4a** in cyclohexane, was irradiated in acetonitrile, the original 50:50 mixture of *cis*- and *trans*-vinyl isomers was converted to a 16:84 mixture (eq 5). Thus, a clear preference for the *trans*-vinyl isomer is exhibited in acetonitrile.

A detailed high-resolution NMR study of **15b** prepared from the full-arc irradiation of **4b** in acetonitrile revealed that olefin *E*-to-*Z* isomerization was partially inhibited and that the ste-

(9) Iida, H.; Yuasa, Y.; Kibayashi, C. *J. Chem. Soc., Chem. Commun.* **1978**, 766–7.
(10) Grisdale, P. J.; Williams, J. L. R. *J. Org. Chem.* **1969**, *34*, 1675–7.
(11) Gassman, P. G.; Gruetzmacher, G. D. *J. Am. Chem. Soc.* **1974**, *96*, 5487–95. Coates, R. M.; Said, I. Md. *Ibid.* **1977**, *99*, 2355–7.
(12) Hancock, K. G.; Uriarte, A. K. *J. Am. Chem. Soc.* **1970**, *92*, 6374–6. Hancock, K. G.; Dickinson, D. A. *Ibid.* **1973**, *95*, 280–2.



reoisomer of **15b** resulting from cyclization with an *E*-vinyl group resulted as the primary constituent in the photolysate. In contrast, irradiation in cyclohexane gave a near 50:50 mixture of the *E* and *Z* cycloadducts. A detailed explanation of these results is given in the following paper.

Quantum Yields. Quantum yields for cyclization (Φ_{cyc}) were determined relative to a valerophenone actinometer.[13] Values from multiple runs were extrapolated to zero conversion and are listed in Table III. The low values for **4b** and **6a** in cyclohexane were not unexpected since cyclization is competing with highly efficient rotational deactivation processes about the C=C (Φ_{c-t} = 0.4–0.5)[14] and B=N (Φ_{c-t} = 0.3)[15] double bonds. This effect can be seen in **9a**, where supression of olefin isomerization has possibly resulted in a corresponding increase in Φ_{cyc}. Nevertheless, the values in Table III are comparable to those obtained for the nonoxidative cyclization of various 2-vinylbiphenyls (Φ_{cyc} = 0.02–0.04)[16] and acrylic acid anilides (Φ_{cyc} = 0.2–0.3).[17]

Figure 3 shows a plot of percent conversion vs. time for the irradiation of a 0.1 M solution of **4b** in cyclohexane. Surprisingly, this curve is linear up to 70% conversion and implies that the quantum yield of cyclization is roughly constant at conversions between 0 and 70%. Since both **4b** and **15b** absorb in the same region of the UV, a highly efficient energy-transfer process must be occurring between electronically excited **15b** and ground-state **4b**. Similar results were obtained in the Norrish type II reaction of valerophenone,[18] which led to the usefulness of valerophenone as a photochemical actinometer.

Summary. From this study we conclude that the di-π-methane reaction is not the only primary photochemical pathway open to unsaturated organoboranes. Both nonoxidative photocyclization and rotational deactivation can take place where structurally permitted. In carbon tetrachloride, however, a boron–carbon bond-cleavage reaction is observed. The reason for this solvent dependence on reactivity is currently unknown. A nearly linear relationship in the percent conversion vs. time plot for the cyclization of **4b** was obtained for conversions as high as 70%, making these photocyclizations practical on synthetically useful scales. Since the cycloadducts could also be chemically degraded under protolytic or oxidative conditions to give ortho-substituted anilines, the sequence of reactions described herein provides not only evidence for new photochemistry in organoboranes but also constitutes a useful new synthesis of ortho-alkylated anilines.

Experimental Section

Instrumentation. Nuclear magnetic resonance spectra were recorded on the Varian Models A60A and EM360 60-MHz spectrometers. Chemical shifts are reported in parts per million on the δ scale, with tetramethylsilane as an internal standard. Infrared spectra were obtained on the Beckman IR-8 spectrometer. Mass spectra were taken on the DuPont Model 492 spectrometer equipped with a Finnigan-Inco data system. Ultraviolet spectra were recorded on the Cary Model 17 spectrometer. Boiling points and melting points are uncorrected.

Table III. Quantum Yields of Cyclization

compound	Φ_{cyc}
4b	0.15,[a] 0.35[b]
6a	0.06[a]
9a	0.34[a]

[a] In cyclohexane. [b] In acetonitrile.

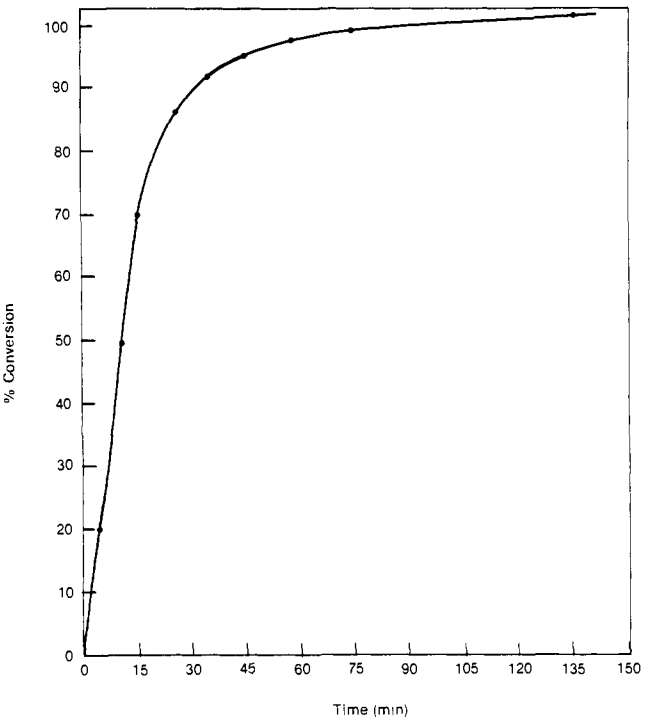


Figure 3. Percent conversion vs. time plot for the photolysis of a 0.1 M solution of **4b** in cyclohexane at 254 nm.

Materials. Unless otherwise specified, anhydrous diethyl ether (Mallinckrodt AR) was used directly without further purification. Triethylamine (Aldrich), *N*-methylaniline (Aldrich), and aniline were routinely distilled from potassium hydroxide prior to use. The purification of *n*-pentane was carried out as described by Vogel.[19] 2,6-Dimethylaniline, *p*-chloroaniline, *p*-bromoaniline, *o*-bromoaniline, and dimethylamine were used as recieved from Aldrich Chemical Co. Benzene, cyclohexane, and acetonitrile used in syntheses, photolyses, and spectral measurements were routinely distilled from freshly ground calcium hydride. Dichloro-*N*-methyl-*N*-phenylboranamine was routinely distilled prior to use. All distillations were carried out under a nitrogen atmosphere. Freshly distilled reagents and solvents were stored under an argon or a nitrogen atmosphere. The divinyl-*N*-phenylboranamines were distilled prior to use only in the case of discoloration. These compounds were stored in screw-cap vials or glass ampules in a nitrogen glove box for several months without discoloration or any noticeable change in the NMR spectrum. When exposed to the air, the divinylboranamines slowly turned red. *N*-Methyl-*N*-phenylpropionamide,[20] 1-chlorocyclohexene,[21,22] 1-chlorocycloheptene,[22] dichloroborane,[23] monochloroborane,[23] bis(*cis*-3-hexen-3-yl)chloroborane,[23] dichloro-*N*,*N*-dimethylboranamine,[24] and dichloro-*N*-methyl-*N*-phenylboranamine[25] were prepared as previously described.

Techniques. All preparations of air-sensitive compounds were carried out in flame-dried or oven-dried glassware under an atmosphere and positive pressure of argon or nitrogen. Air-sensitive compounds and solutions were transfered according to general methods already described.[26]

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Chloro(*cis*-3-hexen-3-yl)-*N*-methyl-*N*-phenylboranamine. Into a dry 1-L, three-necked Morton flask equipped with an overhead stirrer, 50-mL graduated addition funnel, and glass stopper were placed 200 mL of dry benzene and 12.3 g (0.074 mol) of (*cis*-3-hexen-3-yl)dichloroborane[23] under a nitrogen atmosphere. This solution was immersed in an ice bath, and 7.94 g (0.074 mol) of *N*-methylaniline in 30 mL of benzene was added dropwise. After being stirred for 5 min, 7.92 g (0.074 mol) of triethylamine in 30 mL of benzene was added to the solution, causing formation of solid triethylamine hydrochloride. The reaction mixture was stirred for 4 h at room temperature, filtered in a nitrogen atmosphere, and concentrated through a solvent stripper. The last traces of solvent were removed under a vacuum of 1.0 torr. The resulting yellow liquid was distilled in vacuo through a 10-cm Vigreux column to give 8.5 g (50%) of a colorless liquid: bp 65–68 °C (0.02 torr); NMR (CCl_4) δ 0.70 (t, J = 8 Hz, 3 H), 0.90 (t, J = 7 Hz, 3 H), 1.90 (m, 4 H, methylene), 3.30 (s, 3 H, *N*-methyl), 5.35 (t, J = 7 Hz, 1 H, vinyl), 7.07 (br s, 5 H, phenyl); IR (neat film) 2980, 2950, 2890, 1620, 1600, 1495, 1400 (B–N), 1275, 1250, 1200, 1120, 1070, 1030, 1020, 980, 830, 770 (phenyl), and 700 (phenyl) cm^{-1}.

Bis(*trans*-1-buten-1-yl)-*N*,*N*-dimethylboranamine (3a). The preparation of **3a** served as a general procedure used for the preparation of all *N*,*N*-dimethylboranamines (compounds **3**) and *N*-methyl-*N*-phenylboranamines (compounds **4**).

A dry 2-L, three-necked Morton flask equipped with a 250-mL graduated addition funnel, overhead stirrer, and nitrogen inlet was charged with 240 mL of diethyl ether and 27 g (0.52 mol, 30 mol % excess) of 1-butyne (Farchan). The 1-butyne gas was passed through a calcium chloride drying tube prior to being condensed in a graduated cold trap at −78 °C under a nitrogen atomsphere.[27] Once the desired volume had been condensed, the liquid acetylene was rapidly transferred to the reaction flask. The ether–acetylene solution was immersed in an ice bath, and 205 mL of monochloroborane (0.980 M solution in diethyl ether, 0.200 mol) was added over a 0.5-h period. The reaction mixture was stirred at 0 °C for 1 h followed by 1 h at room temperature. After the solution was recooled to 0 °C, 9.0 g (0.20 mol) of dimethylamine (Eastman) in 100 mL of anhydrous diethyl ether was added dropwise. To the resulting cloudy mixture was added 20.2 g (0.200 mol) of dry triethylamine in 100 mL of diethyl ether, giving rise to a heavy white precipitate. The reaction mixture was stirred for 4 h at room temperature and filtered in a nitrogen glove box through a sintered-glass funnel. The filtrate was concentrated by evaporation of the solvent at reduced pressure,[28] and the remaining clear viscous liquid was distilled in vacuo through a 10-cm Vigreux column to give 15 g (45%) of a colorless liquid: bp 81–84 °C (9 torr); NMR (CCl_4) δ 1.02 (t, J = 7 Hz, 6 H, methyl), 2.11 (m, 4 H, methylene), 2.68 (s, 6 H, *N*-methyl), 5.87 (ABX_2, J_{AB} = 18 Hz, J_{BX} = 5 Hz, 4 H, *trans*-vinyl); IR (neat film) 2960, 2920, 2870, 1625, 1505, 1455, 1408 (B–N), 1320, 1240, 1215, 1140, 1100, 995 (vinyl) cm^{-1}; UV (cyclohexane) 227 (ϵ 13 300) nm.

Anal. Calcd for $C_{10}H_{20}BN$: M^+ 165.1689. Found: 165.1710.

Bis(*cis*-2-buten-2-yl)-*N*,*N*-dimethylboranamine (3b). Distillation at reduced pressure through a 7-cm Vigreux column[29] gave 20 g (60% based on a 0.2-mol reaction scale) of a colorless liquid: bp 35–36 °C (0.7 torr); NMR (CCl_4) δ 1.56, 1.66 (m, 12 H, vinyl methyl), 2.73 (s, 3 H, *N*-methyl), 5.38 (m, 4 H, vinyl); IR (neat film) 2950, 2890, 1630, 1505, 1440, 1400 (B–N), 1375, 1250, 1195, 1125, 1060, 1010, 810 cm^{-1}; UV (cyclohexane) 220 (ϵ 7600) nm.

Anal. Calcd for $C_{10}H_{20}BN$: M^+ 165.1689. Found: 165.1691.

Bis(*trans*-1-buten-1-yl)-*N*-methyl-*N*-phenylboranamine (4a). The resulting clear liquid was distilled at reduced pressure through a 10-cm Vigreux column to give 19 g (49% on the basis of 0.172-mol reaction scale) of a colorless liquid: bp 76–82 °C (0.01 torr); NMR (CCl_4) δ 0.97 (t, J = 7 Hz, methyl), 2.10 (m, 4 H, methylene), 3.18 (s, 3 H, *N*-methyl), 5.90 (br m, 4 H, vinyl), 7.04 (m, 5 H, phenyl); IR (neat film) 2965, 2950, 1620, 1595, 1495, 1430, 1385 (B–N), 1250, 1125, 1100, 995, 770 (phenyl), 700 (phenyl) cm^{-1}; UV (cyclohexane) 292 (ϵ 2400), 233 (ϵ 22 500), and 201 (ϵ 36 000) nm, (acetonitrile) 296 (ϵ 2400), 235 (ϵ 20 000), and 202 (ϵ 36 000) nm.

Anal. Calcd for $C_{15}H_{22}BN$: M^+ 227.1845. Found: 227.1870.

Bis(*cis*-2-buten-2-yl)-*N*-methyl-*N*-phenylboranamine (4b). The crude product was placed in a 250-mL single-necked round-bottom flask with 10 mL of Dow Corning Antifoam A compound[29] and distilled at reduced pressure through a 7-cm Vigreux column, giving 22 g (53% on the basis of a 0.178-mol reaction scale) of a colorless liquid: bp 70–78 °C (0.01 torr); NMR (CCl_4) δ 1.40 (br s, 6 H, vinyl methyl), 1.55 (br d, J = 7 Hz, 6 H, vinyl methyl), 3.10 (s, 3 H, *N*-methyl), 5.55 (q, J = 7 Hz, 2 H, vinyl), 7.00 (m, 5 H, phenyl); IR (neat film) 2990, 2930, 2880, 1624, 1600, 1495, 1430, 1385 (B–N), 1260, 1120, 1078, 1040, 830, 770 (phenyl), 700 (phenyl) cm^{-1}; UV (cyclohexane) 293 (ϵ 2400), 240 (ϵ 16 700), and 202 (ϵ 34 000) nm, (acetonitrile) 296 (ϵ 2000), 244 (ϵ 13 000), and 201 (ϵ 30 000) nm.

Anal. Calcd for $C_{15}H_{22}BN$: M^+ 227.1845. Found: 227.1860.

Bis(*cis*-3-hexen-3-yl)-*N*-methyl-*N*-phenylboranamine (4c). Distillation of the crude product at reduced pressure through a 10-cm Vigreux column gave 34 g (60% on the basis of a 0.2-mol reaction scale) of a colorless liquid: bp 94–98 °C (0.01 torr); NMR (CCl_4) δ 0.87 (br m, 12 H, alkyl methyl), 2.00 (br m, 8 H, alkyl methylene), 3.20 (s, 3 H, *N*-methyl), 5.35 (br t, J = 7 Hz, 2 H, vinyl), 7.07 (m, 5 H, phenyl); IR (neat film) 2980, 2940, 2880, 1615, 1595, 1490, 1455, 1425, 1380 (B–N), 1295, 1280, 1245, 1170, 1120, 1060, 1030, 860, 800, 765 (phenyl), 700 (phenyl) cm^{-1}; UV (cyclohexane) 280 (ϵ 2800), 250 (ϵ 7380), 200 ϵ 28 900) nm.

Anal. Cacld for $C_{19}H_{30}BN$: M^+ 283.2471. Found: 283.2462.

Bis(*trans*-3,3-dimethyl-1-buten-1-yl)-*N*-methyl-*N*-phenylboranamine (4d).[30] The remaining yellow viscous liquid was distilled at reduced pressure through a 10-cm Vigreux column, giving 31 g (56% on the basis of a 0.2-mol reaction scale) of a colorless liquid: bp 98–104 °C (0.01 torr); NMR (CCl_4) δ 0.96 (br s, 18 H, *t*-Bu), 3.17 (s, 3 H, *N*-methyl), 5.50 (br m, 2 H, vinyl), 6.10 (br d, J = 18 Hz, 2 H, vinyl), 7.04 (m, 5 H, phenyl); IR (neat film) 2975, 2920, 2880, 1616, 1598, 1495, 1460, 1430, 1385 (B–N), 1360, 1288, 1260, 1110, 1005, 915, 770 (phenyl), 700 (phenyl) cm^{-1}; UV (cyclohexane) 221 (ϵ 15 610), 200 (ϵ 21 600) nm.

Anal. Calcd for $C_{19}H_{30}BN$: M^+ 283.2471. Found: 283.2478.

Bis(cyclohexenyl)-*N*-methyl-*N*-phenylboranamine (9a). Into a dry 500-mL, three-necked Morton flask equipped with an overhead stirrer, addition funnel, and nitrogen inlet were placed 370 mL of diethyl ether and 2.29 g (0.165 mol) of finely cut lithium wire. To this mixture was added 17.5 g (0.150 mol) of 1-chlorocyclohexene. This reaction mixture was refluxed for 6 h, and the resulting alkenyl lithium solution was standarized according to the single-titration technique already reported.[31] The solution was found to be 0.368 M in 1-lithiocyclohexene.

A solution of 8.0 g (0.043 mol) of freshly distilled dichloro-*N*-methyl-*N*-phenylboranamine in 150 mL of diethyl ether was placed in a dry 1-L three-necked Morton flask fitted with an addition funnel, nitrogen inlet, and glass stopper. The mixture was immersed in an ice bath, and 246 mL of 1-lithiocyclohexene (0.368 M solution in diethyl ether, 0.091 mol) was added during a period of ca. 5 min. After 3 h of stirring at room temperature, the reaction mixture was filtered through an oven-dried sintered-glass funnel in a nitrogen-filled glove box and concentrated by evaporation of the solvent at reduced pressure. Distillation of the remaining yellow viscous liquid through a short-path distillation apparatus gave 5.6 g (47%) of a colorless liquid: bp 137 °C (0.6 torr); NMR (CCl_4) δ 1.30–2.30 (br m, 16 H, methylene), 3.23 (s, 3 H, *N*-methyl), 5.83 (m, 2 H, vinyl), 7.20 (m, 5 H, phenyl); IR (neat film) 3010, 2920, 2840, 1620, 1598, 1495, 1430, 1385 (B–N), 1275, 1255, 1212, 1180, 1120, 1075, 1030, 980, 970, 955, 855, 770 (phenyl), 700 (phenyl) cm^{-1}; UV (cyclohexane) 294 (ϵ 2200), 241 (ϵ 16 500), 203 (ϵ 22 100) nm.

Anal. Calcd for $C_{19}H_{26}BN$: M^+ 279.2158. Found: 279.2144.

Bis(1-cycloheptenyl)-*N*-methyl-*N*-phenylboranamine (9b). Into a 500-mL, single-necked round-bottom flask were placed 20.3 g (0.156 mol) of 1-chlorocycloheptene, 200 mL of diethyl ether, and 2.38 g (0.343 mol, 10 mol % excess) of finely divided lithium wire under a nitrogen atmosphere. This mixture was stirred overnight at room temperature and titrated.[31] The solution was found to be 0.205 M in 1-lithiocycloheptene.

A 500-mL three-necked Morton flask was equpped with an overhead stirrer, addition funnel, and nitrogen inlet. In the flask were placed 3.38 g (0.018 mol) of dichloro-*N*-methyl-*N*-phenylboranamine and 100 mL of anhydrous diethyl ether. This solution was immersed in an ice bath and 176 mL (0.036 mol) of 1-lithiocycloheptene was slowly added. After 3 h of stirring at room temperature, the reaction mixture was filtered through a sintered-glass funnel in a nitrogen-containing glove box and

(26) Kramer, G. W.; Levy, A. B.; Midland, M. "Organic Synthesis via Boranes"; Brown, H. C., Ed.; Wiley: New York, 1975; Chapter 9.

(27) Liquid acetylenes were used as recieved from commercial sources (Farchan).

(28) Due to the slight solubility of triethylamine hydrochloride in diethyl ether, a solid may appear after removing the solvent. The resulting cloudy oil is diluted with 30 mL of pentane, filtered under an inert atmosphere, and concentrated in vacuo. Most of the triethylamine should be removed at this point since it tends to sublime into the condenser during distillation.

(29) The bis(*cis*-2-buten-2-yl)boranamines have a tendency to foam during distillation. For this reason, 10 mL of Dow Corning Antifoam A compound was added before distillation.

(30) The ethereal solution of monochloroborane was added as rapidly as possible to the neat liquid acetylene (cooled on ice) without allowing the resulting exothermic reaction to boil the solvent. Once the addition was completed, the reaction mixture was stirred for 1 h at 0 °C and 1 h at room temperature and diluted to 1.0 L with diethyl ether.

(31) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165–8.

concentrated by evaporation of the solvent at reduced pressure. Distillation of the remaining viscous liquid through a short-path distillation apparatus gave 3.5 g (63%) of a colorless liquid: bp 130–137 °C (0.05 torr); NMR (CCl_4) δ 0.80 to 2.50 (br m, 20 H, cycloheptenyl methylene), 3.20 (s, 3 H, *N*-methyl), 5.92 (br m, 2 H, vinyl), 7.07 (m, 5 H, phenyl); IR (neat film) 3015, 2960, 2870, 2840, 1618, 1600, 1495, 1430, 1380 (B–N), 1276, 1255, 1195, 1130, 1090, 1075, 1027, 1010, 1000, 925, 795, 765 (phenyl), 700 (phenyl) cm^{-1}.

Anal. Calcd for $C_{21}H_{30}BN$: M^+ 307.2471. Found: 307.2482.

Bis(ethenyl)-*N*-methyl-*N*-phenylboranamine (4e). Into a 500-mL, three-necked round-bottom flask, equipped with an overhead stirrer, rubber septum, and glass stopper were placed 100 mL of diethyl ether and 6.44 g (34.3 mmol) of dichloro-*N*-methyl-*N*-phenylboranamine. This solution was cooled to 0 °C and 74.4 mL of vinylmagnesium bromide in tetrahydrofuran (0.91 M, 68.8 mmol) was slowly syringed into the reaction flask, causing formation of a white precipitate. After 1 h of stirring at room temperature, the reaction mixture was filtered through a dry sintered-glass funnel in a nitrogen-filled glove box and concentrated by evaporation of the solvent at reduced pressure. Distillation through a 7-cm Vigreux column gave 1.0 g (16%) of a colorless liquid: bp 70 °C (0.04 torr); NMR (CCl_4) δ 3.20 (s, 3 H, *N*-methyl), 5.60–6.70 (br m, 6 H, vinyl), 7.10 (m, 5 H, phenyl). An IR spectrum was not obtained due to the presence of an impurity peak at δ 3.00 in the NMR that could not be removed after several distillations.

(*cis*-3-Hexen-3-yl)methyl-*N*-methyl-*N*-phenylboranamine (20). A flame-dried 500-mL three-necked round-bottom flask was equipped with an overhead stirrer, nitrogen inlet, and rubber septum. Into the flask were placed 8.54 g (0.036 mol) of chloro(*cis*-3-hexen-3-yl)-*N*-methyl-*N*-phenylboranamine and 100 mL of diethyl ether. This solution was immersed in an ice bath, and 18.2 mL of methyl lithium (2.00 M solution in diethyl ether, Aldrich, 0.036 mol) was added by syringe, causing formation of a white precipitate. The reaction mixture was stirred for 1 h at 0 °C, filtered in a nitrogen-containing glove box, and concentrated by evaporation of the solvent at reduced pressure. The resulting clear liquid was distilled through a 10-cm Vigreux column, giving 5.0 g (65%) of a colorless liquid: bp 60–70 °C (0.03 torr); NMR (CCl_4) δ 0.27 (br s, 3 H, *B*-methyl), 0.94 (br t, J = 8 Hz, 6 H, alkyl methyl), 2.10 (br m, 4 H, methylene), 3.27 (s, 3 H, *N*-methyl), 5.40 (br t, J = 7 Hz, 1 H, vinyl), 7.30 (m, 5 H, phenyl); IR (neat film) 2970, 2940, 2880, 1600, 1500, 1385 (B–N), 1310, 1250, 1130, 1120, 1080, 850, 778 (phenyl), 705 (phenyl) cm^{-1}.

Anal. Calcd for $C_{14}H_{22}BN$: M^+ 215.1881. Found: 215.1846.

Bis(*trans*-1-buten-1-yl)-*N*-phenylboranamine (6a). Into a dry 25-mL single-necked round-bottom flask, equipped with a total reflux head, were placed 2.00 g (12.1 mmol) of **3a** and 1.63 g (17.5 mmol) of aniline under a nitrogen atmosphere. This mixture was slowly heated under a vacuum of 50 torr. At 80 °C, dimethylamine gas evolution started. After 1.5 h at 110 °C, the reaction mixture was fractionally distilled, giving 1.8 g (70%) of a colorless liquid: bp 95–97 °C (0.01 torr); NMR (CCl_4) δ 1.06 (t, J = 7 Hz, 6 H, methyl), 2.20 (m, 4 H, methylene), 5.60–6.70 (m, 5 H, vinyl and N–H), 7.20 (m, 5 H, phenyl); IR (neat film) 3480, 2980, 2940, 2880, 1625, 1600, 1495, 1335 (B–N), 1190, 1140, 1095, 1070, 995, 755 (phenyl), 695 (phenyl) cm^{-1}; UV (cyclohexane) 280 (ε 2200), 230 (ε 21 400), and 199 (ε 37 000), (acetonitrile) 287 (ε 1900), 232 (ε 21 000), and 199 (ε 38 000) nm.

Anal. Calcd for $C_{14}H_{20}BN$: M^+ 213.1689. Found: 213.1712.

Bis(*trans*-1-buten-1-yl)-*N*-(4-chlorophenyl)boranamine (6b). A dry 15-mL single-necked round-bottom flask was fitted with a total reflux head. In the flask were placed 1.02 g (6.19 mmol) of **3a** and 1.57 g (12.4 mmol) of 4-chloroaniline under a nitrogen atmosphere. This mixture was slowly heated under a vacuum of 50 torr. Evolution of dimethylamine gas commenced at 60 °C. After 2 h at 110 °C, the reaction mixture was distilled under vacuum. The first fraction of distillation contained unreacted solid 4-chloroaniline and had to be collected by sublimation. Continued distillation through a short-path apparatus gave 1.2 g (78%) of a clear liquid: bp 116–117 °C (0.01 torr); NMR (CCl_4) δ 1.05 (t, J = 7 Hz, 6 H, methyl), 2.16 (m, 4 H, methylene), 5.50–6.70 (m, 5 H, vinyl and N–H), 6.90–7.16 (AB q, J = 9 Hz, 4 H, phenyl); IR (neat film) 3390, 2970, 2940, 2880, 1625, 1590, 1495, 1390, 1340, 1300, 1275, 1200, 1170, 1140, 1090, 1010, 990, 830 (phenyl) cm^{-1}; UV (cyclohexane) 298 (ε 1970), 235 (ε 21 200), and 200 (ε 35 500), (acetonitrile) 300 (ε 1950), 235 (ε 20 000), and 200 (ε 38 000) nm.

Anal. Calcd for $C_{14}H_{19}B^{35}ClN$: M^+ 247.1299. Found: 247.1293.

Bis(*trans*-1-buten-1-yl)-*N*-(4-bromophenyl)boranamine (6c). Into an oven-dried 15-mL single-necked round-bottom flask, equipped with a total reflux head, were placed 1.35 g (8.12 mmol) of **3a** and 2.81 g (16.2 mmol) of 4-bromoaniline. This heterogeneous mixture was heated at 90 °C for 2 h and 150 °C for an additional 2 h. Distillation of the resulting dark red mixture under vacuum gave unreacted 4-bromoaniline in the first fraction, which had to be collected by sublimation. Continued distillation through a short-path apparatus gave 1.5 g (65%) of a colorless liquid: bp 108–117 °C (0.01 torr); NMR (CCl_4) δ 1.05 (t, J = 7 Hz, 6 H, methyl), 2.17 (m, 4 H, methylene), 5.40–6.20 (br m, 5 H, vinyl and N–H), 6.86–7.00 (AB q, J = 8 Hz, 4 H, phenyl); IR (neat film) 3390, 2980, 2940, 2880, 1620, 1590, 1490, 1385, 1340 (B–N), 1300, 1280, 1200, 1170, 1140, 1100, 1070, 995, 830 (phenyl) cm^{-1}; UV (cyclohexane) 297 (ε 1750), 234 (ε 22 300), and 201 (ε 36 100), (acetonitrile) 300 (ε 1600), 234 (ε 19 000), and 201 (ε 36 500) nm.

Anal. Calcd for $C_{14}H_{19}B^{79}BrN$: M^+ 291.0794. Found: 291.0782.

Bis(*trans*-1-buten-1-yl)-*N*-(4-nitrophenyl)boranamine (6f). A dry 25-mL single-necked round-bottom flask was equipped with a total reflux head. In the flask were placed 1.15 g (6.99 mmol) of **3a** and 1.96 g (14.0 mmol) of 4-nitroaniline under a nitrogen atmosphere. This heterogeneous mixture was heated for 0.5 h at 110 °C under a vacuum of 55 torr, followed by 1 h at 15 torr and 120 °C. Distillation under vacuum of the resulting brown residue through a short-path apparatus gave 0.2 g (11%) of a yellow liquid: bp 142–147 °C (0.03 torr); NMR (CCl_4) δ 1.05 (t, J = 7 Hz, 6 H, methyl), 2.20 (m, 4 H, methylene), 5.85, 6.33, 6.57 (ABX_2, J_{AB} = 18 Hz, J_{AX} = 5 Hz, 4 H, vinyl), 6.40 (br s, 1 H, N–H), 7.06–8.05 (AB q, J = 9 Hz, 4 H, phenyl); Ir (neat film) 3370 , 2970, 2940, 2880, 1620, 1590, 1515, 1500, 1480, 1400, 1325 (B–N), 1300, 1260, 1195, 1175, 1140, 1110, 1070, 995, 850, 750, 700 cm^{-1}.

Bis(*cis*-2-buten-2-yl)-*N*-(2-bromophenyl)boranamine (6d). Into a dry 25-mL single-necked round-bottom flask, equipped with a total reflux head, were placed 2.70 g (17.5 mmol) of **3b** and 3.00 g (18.0 mmol) of 2-bromoaniline under a nitrogen atmosphere. The reaction was slowly heated to 140 °C under a vacuum of 40 torr. Dimethylamine gas evolution started at 70 °C and slowed down after 0.5 h at 140 °C. The pressure was cautiously lowered to 5 torr at 140 °C for an additional 0.5 h. Distillation of the crude product under vacuum through a 10-cm Vigreux column gave 2.0 g (40%) of a colorless liquid: bp 95–96 °C (0.03 torr); NMR (CCl_4) δ 1.68 and 1.78 (pair of br s, 12 H, vinyl methyl), 5.20–6.50 (m, 3 H, vinyl and N–H), 6.50–7.50 (m, 4 H, phenyl); IR (neat film) 3400, 2920, 2860, 1615, 1585, 1495, 1375, 1315, 1225, 1150, 1020, 750, 700 cm^{-1}; UV (cyclohexane) 293 (ε 2200), 230 sh, 204 (ε 31 100) nm.

Anal. Calcd for $C_{14}H_{19}B^{79}BrN$: M^+ 291.0794. Found: 291.0775.

Bis(*cis*-2-buten-2-yl)-*N*-(2,6-dimethylphenyl)boranamine (6e). An oven-dried 25-mL single-necked round-bottom flask was fitted with a total reflux head. In the flask were placed 2.99 g (12.1 mmol) of **3b** and 2.4 g (20 mmol) of 2,6-dimethylaniline under a nitrogen atmosphere. The pressure was gradually lowered to 55 torr since excessive foaming was encountered. The reaction was heated for 0.5 h at 110 °C and 55 torr, followed by 0.5 h at 110 °C and 20 torr. Distillation of the crude product at reduced pressure through a 7-cm Vigreux column gave 2.0 g (70%) of a colorless liquid: bp 83–85 °C (0.18 torr); NMR (CCl_4) δ 1.26 (s, 3 H, vinyl methyl), 1.52 (d, J = 7 Hz, 3 H, vinyl methyl), 2.76 (br s, 6 H, vinyl methyl), 2.20 (s, 6 H, phenyl methyl), 5.10 (br s, 1 H, N–H), 5.50–6.08 (br m, 2 H, vinyl), 6.90 (br s, 3 H, phenyl); IR (neat film) 3400, 2940, 2880, 1625, 1500, 1460, 1380, 1320, 1240, 1170, 1155, 1100, 1040, 920, 875, 820, 775, 690, 665 cm^{-1}; UV (cyclohexane) 282 (ε 2000), 230 sh, 204 (ε 30 200) nm.

Anal. Calcd for $C_{16}H_{24}BN$: M^+ 241.2002. Found: 241.1970.

General Procedure for the Photolysis of the Divinyl-*N*-phenylboranamines. A general procedure for the irradiation of small- and large-scale reaction mixtures is described. Solution concentrations, solvents used, irradiation times, and isolated yields are listed in Table II. Physical properties and spectral data of the resulting photoproducts follow.

Small-scale irradiations were carried out in dry 5-mm quartz tubes. A solution of starting material in the desired deuterated solvent was placed in the tube and irradiated with the unfiltered arc of a water-cooled 450-W medium-pressure mercury lamp under a nitrogen atmosphere. Photolyses were monitored by NMR spectroscopy, and products were distilled through a molecular distillation apparatus.

Large-scale irradiations were carried out in an oven-dried quartz vessel. A solution of starting material in dry cyclohexane was placed in the quartz vessel and irradiated as described above. The solvent was removed in vacuo, and the remaining oil was distilled through either a short-path apparatus or a 7-cm Vigreux column.

2-(1-Buten-1-yl)-4-ethyl-1-methyl-1,2,3,4-tetrahydro-1-aza-2-boranaphthalene (15a). Distillation of the crude product through a 7-cm Vigreux column gave a colorless liquid: bp 74–78 °C (0.01 torr); NMR (CCl_4) δ 0.60–1.70 (m, 10 H), 2.10 (m, 2 H, allylic methylene), 2.55 (m, 1 H, benzylic methine), 3.15 (pair of s, 3 H, *N*-methyl), 5.50–6.60 (m, 2 H, vinyl), 6.97 (m, 4 H, phenyl); IR (neat film) 3010, 2960, 2865, 1620, 1600, 1475, 1455, 1430, 1380 (B–N), 1300, 1260, 1200, 1125, 1110, 1055, 985, 895, 755 (phenyl) cm^{-1}; UV (cyclohexane) 267 (ε 9100), 209 (ε 25 200) nm.

Anal. Calcd for $C_{15}H_{22}BN$: M^+ 227.1845. Found: 227.1849.

2-(2-Buten-2-yl)-1,3,4-trimethyl-1,2,3,4-tetrahydro-1-aza-2-boranaphthalene (15b). Distillation of the crude product through a 7-cm Vigreux column gave a colorless liquid: bp 88–90 °C (0.01 torr); NMR (CCl_4) δ 0.70–1.30 (m, 7 H, alkyl methyl and α-boron methine), 1.65 (m, 6 H, vinyl methyl), 2.67 (m, 1 H, benzylic methine), 3.10 (s, 3 H, *N*-methyl), 5.63 (m, 1 H, vinyl), 6.90 (m, 4 H, phenyl); IR (neat film) 2960, 2940, 2880, 1620, 1598, 1475, 1450, 1426, 1385 (B–N), 1270, 1255, 1120, 1050, 1020, 980, 820, 755 (phenyl), 745 (phenyl) cm^{-1}; UV (cyclohexane) 258 (ϵ 9300), 210 (ϵ 27 600) nm.

Anal. Calcd for $C_{15}H_{22}BN$: M^+ 227.1845. Found: 227.1862.

2-(3-Hexen-3-yl)-3,4-diethyl-1-methyl-1,2,3,4-tetrahydro-1-aza-2-boranaphthalene (15c). Distillation of the crude photoproduct through a short-path apparatus gave a colorless liquid: bp 98–100 °C (0.01 torr); NMR (CCl_4) δ 0.60–2.70 (m, 22 H), 3.12 (s, 3 H, *N*-methyl), 5.35 (m, 1 H, vinyl), 6.93 (m, 4 H, phenyl); IR (neat film) 2970, 2940, 2880, 1615, 1600, 1590, 1475, 1430, 1380 (B–N), 1260, 1125, 1055, 865, 790, 765 (phenyl), 755 (phenyl) cm^{-1}; UV (cyclohexane) 258 (ϵ 9100), 210 (ϵ 29 100) nm.

Anal. Calcd for $C_{19}H_{30}BN$: M^+ 283.2471. Found: 283.2506.

2-(3,3-Dimethyl-1-buten-1-yl)-4-*tert*-butyl-1-methyl-1,2,3,4-tetrahydro-1-aza-2-boranaphthalene (15d). The crude photoproduct was distilled through a short-path apparatus to give a clear liquid: bp 100–102 °C (0.01 torr); NMR (CCl_4) δ 0.83, 0.93, 1.00 (three s, 18 H, *t*-Bu), 1.70 (m, 1 H, α-boron methine), 2.38 (d, J = 8 Hz, 1 H, benzylic methine), 3.03, 3.13 (two s, 3 H, *N*-methyl), 5.53–5.86 (AB q, J = 15 Hz, *cis*-vinyl), 5.93–6.56 (AB q, J = 18 Hz, *trans*-vinyl), 6.92 (m, 4 H, phenyl); IR (neat film) 2965, 2910, 2880, 1615, 1595, 1470, 1425, 1400, 1380 (B–N), 1360, 1320, 1290, 1262, 1195, 1060, 990, 895, 750 (phenyl) cm^{-1}; UV (cyclohexane) 262 (ϵ 9100), 212 (ϵ 30 000) nm.

Anal. Calcd for $C_{19}H_{30}BN$: M^+ 283.2471. Found: 283.2489.

10-(1-Cyclohexenyl)-9-methyl-1,2,3,4,4a,9,10,10a-octahydro-9-aza-10-boraphenanthrene (23a). Distillation of the crude product through a short-path apparatus gave 4.96 g (81% on the basis of 6.19 g of starting material) of a colorless liquid: bp 157 °C (0.01 torr); NMR (CCl_4) δ 0.80–2.50 (br m, 18 H), 3.20 (s, 3 H, *N*-methyl), 5.58 (br m, 1 H, vinyl), 7.10 (br m, 4 H, phenyl); IR (neat film) 2920, 1840, 1625, 1595, 1580, 1470, 1450, 1440, 1420, 1380 (B–N), 1285, 1260, 1190, 1175, 1130, 1120, 1055, 1010, 995, 850, 820, 800, 755 (phenyl), 710 cm^{-1}; UV (cyclohexane) 254 (ϵ 8900), 208 (ϵ 26 900) nm.

Anal. Calcd for $C_{19}H_{26}BN$: M^+ 279.2158. Found: 279.2167.

2-(1-Cycloheptenyl)-1-methyl-3,4-cyclohepta-1,2,3,4-tetrahydro-1-aza-2-boranaphthalene (23b). Distillation of the crude photoproduct through a molecular distillation apparatus gave a clear liquid; NMR (CCl_4) δ 0.30–2.50 (br m, 22 H), 3.41 (s, 3 H, *N*-methyl), 6.15 (br t, 1 H, vinyl), 7.45 (m, 4 H, phenyl); IR (neat film) 2840, 2765, 1625, 1595, 1470, 1450, 1375 (B–N), 1285, 1268, 1170, 1120, 1055, 960, 855, 780, 750 (phenyl), 720 cm^{-1}. No boiling point was obtained since distillations were carried out on milligram quantities. A vacuum of less than 0.1 torr is required during distillation.

Anal. Calcd for $C_{21}H_{30}BN$: M^+ 307.2471. Found: 307.2473.

1,2-Dimethyl-3,4-diethyl-1,2,3,4-tetrahydro-1-aza-2-boranaphthalene (21). Distillation of the crude product through a molecular distillation apparatus gave a colorless liquid: NMR (CCl_4) δ 0.56 (s, 3 H, *B*-methyl), 0.60–1.80 (m, 11 H), 2.26 (t, J = 6 Hz, 1 H, benzylic methine), 3.08 (s, 3 H, *N*-methyl), 6.86 (m, 4 H, phenyl); IR (neat film) 2970, 2880, 1600, 1480, 1380 (B–N), 1300, 1270, 1130, 755 (phenyl), 745 (phenyl) cm^{-1}. No boiling point was obtained since distillations were carried out on milligram quantities. A vacuum of less than 0.1 torr is required during distillation.

1-(1-Buten-1-yl)-4-ethyl-1,2,3,4-tetrahydro-1-aza-2-boranaphthalene (16a). Distillation of the crude photoproduct through a 7-cm Vigreux column gave a colorless liquid: bp 83 °C (0.01 torr); NMR (CCl_4) δ 0.60–1.80 (m, 10 H), 2.20 (m, 2 H, allylic methylene), 2.65 (m, 1 H, benzylic methine), 5.30–6.60 (m, 3 H, vinyl and N–H), 6.83 (m, 4 H, phenyl); IR (neat film) 3380, 2970, 2940, 2880, 1625, 1600, 1495, 1425, 1295, 1120, 990, 895 , 745 (phenyl) cm^{-1}; UV (cyclohexane) 273 (ϵ 13 000), 214 (ϵ 24 600) nm.

Anal. Calcd for $C_{14}H_{20}BN$: M^+ 213.1689. Found: 213.1713.

2-(1-Buten-1-yl)-6-chloro-4-ethyl-1,2,3,4-tetrahydro-1-aza-2-boranaphthalene (16b). Distillation of the crude product through a short-path apparatus gave a colorless liquid: bp 94 °C (0.01 torr); NMR (CCl_4) δ 0.70–1.80 (m, 12 H), 2.26 (m, 2 H, allylic methylene), 2.60 (m, 1 H, benzylic methine), 5.30–7.10 (complex m, 6 H, vinyl, N–H, phenyl); IR (neat film) 3410, 2980, 2940, 2880, 1625, 1600, 1490, 1460, 1390, 1350, 1295, 1210, 1190, 1140, 1095, 1070, 1010, 990, 880, 865, 815, 650 cm^{-1}; UV (cyclohexane) 276 (ϵ 14 800), 213 (ϵ 25 400) nm.

Anal. Calcd for $C_{14}H_{19}B^{35}ClN$: M^+ 247.1299. Found: 247.1284.

2-(1-Buten-1-yl)-6-bromo-4-ethyl-1,2,3,4-tetrahydro-1-aza-2-boranaphthalene (16c). The crude photoproduct was distilled through a molecular distillation apparatus to give a colorless liquid: NMR (CCl_4) δ 0.60–1.80 (m, 12 H), 2.56 (m, 1 H, benzylic methine), 5.40–7.30 (m, 6 H, vinyl, N–H, phenyl); IR (neat film) 3390, 2980, 2930, 2870, 1625, 1600, 1450, 1390, 1340, 1290, 1220, 1210, 1190, 1140, 1080, 1070, 990, 875, 860, 810, 645 cm^{-1}; UV (cyclohexane) 275 (ϵ 13 000), 211 (ϵ 24 300) nm.

Anal. Calcd for $C_{14}H_{19}B^{79}BrN$: M^+ 291.0794. Found: 291.0796.

2-(2-Buten-2-yl)-8-bromo-3,4-dimethyl-1,2,3,4-tetrahydro-1-aza-2-boranaphthalene (16d). The crude product was distilled through a molecular distillation apparatus to give a clear liquid: NMR (CCl_4) δ 0.80 (d, J = 7 Hz, 3 H, α-boron methyl), 1.03 (d, J = 7 Hz, 3 H, benzylic methyl), 1.20–2.00 (m, 7 H, vinyl methyl and α-boron methine), 2.60 (m, 1 H, benzylic methine), 6.10–7.30 (m, 5 H, phenyl vinyl, N–H); IR (neat film) 3405, 3020, 2960, 2920, 1620, 1600, 1575, 1550, 1470, 1415, 1375, 1350, 1285, 1235, 1183, 1142, 1073, 1025, 988, 905, 845, 825, 810, 778, 750, 735, 685, 655 cm^{-1}; UV (cyclohexane) 268 (ϵ 12 600), 219 (ϵ 26 800) nm. No boiling point was obtained since distillations were carried out on milligram quantities. A vacuum of less than 0.1 torr is required during distillation.

Anal. Calcd for $C_{14}H_{19}B^{79}BrN$: M^+ 291.0794. Found: 291.0764.

Photolysis of 3a. Into a 50-mL quartz tube were placed 1.52 g (9.20 mmol) of boranamine and 15 mL of dry cyclohexane. This mixture was degassed with three freeze–pump–thaw cycles and irradiated for 67 h with the full arc of a Hanovia 450-W medium-pressure mercury lamp. Distillation of the crude photoproduct through a short-path apparatus gave 1.0 g (66%) of a clear liquid: bp 34 °C (0.05 torr); NMR (CCl_4) δ 1.00 (m, 6 H), 2.00 (m, 4 H), 2.58, 2.61, 2.66 (three s, 3 H, *N*-methyl), 5.50–6.20 (m, 4 H, vinyl); IR (neat film) identical with that of the starting material.

Photolysis of 4a in Carbon Tetrachloride. A 1.0 M solution of boranamine in carbon tetrachloride was placed in a 5-mm quartz tube and irradiated for 250 h with the full arc of a 450-W Hanovia medium-pressure mercury lamp. Vacuum distillation of the photolysate through a molecular distillation apparatus gave (1-buten-1-yl)chloro-*N*-methyl-*N*-phenylboranamine: NMR (CCl_4) δ 0.90 (t, J = 7 Hz, 3 H, methyl), 2.33 (m, 2 H, methylene), 3.30 (s, 3 H, *N*-methyl), 5.00–6.90 (ABX_2, J_{AB} = 18 Hz, J_{BX} = 6 Hz, 2 H, vinyl), 7.17 (m, 5 H, phenyl); IR (neat film) 2965, 2920, 1618, 1587, 1485, 1430, 1390 (B–N), 1247, 1120, 1067, 1025, 1011, 985, 764 (phenyl), 696 (phenyl) cm^{-1}. A boiling point was not obtained since distillations were carried out on milligram quantities. A vacuum of 1.0 torr is required during distillation.

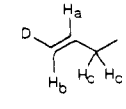
Anal. Calcd for $C_{11}H_{15}B^{37}ClN$: M^+ 207.0985. Found: 207.0989.

Photolysis of 4a in Acetonitrile. A 0.8 M solution of boranamine in acetonitrile-d_3 was placed in a 5-mm quartz tube and irradiated for 136 h with the full arc of a 450-W Hanovia medium-pressure mercury lamp. The NMR spectrum of the distilled photoproduct was identical with that of the expected cycloadduct with the exception of a 90:10 *trans*:*cis*-vinyl isomer ratio, which was identified by NMR peak integration.

Photolysis of 15a in Acetonitrile. A 0.8 M solution of azaboranaphthalene in acetonitrile-d_3 was placed in a 5-mm quartz tube and irradiated for 166 h with the full arc of a 450-W Hanovia medium-pressure mercury lamp. The NMR spectrum of the distilled photoproduct showed an 83:17 *trans*:*cis*-vinyl isomer ratio.

Photolysis of 6e. Into a 5-mm quartz tube was placed a 0.8 M solution of boranamine in benzene-d_6 under a nitrogen atmosphere. This solution was irradiated for 162 h with the full arc of a Hanovia 450-W medium-pressure mercury lamp. In the NMR spectrum, constant-peak integration ratios and an increase in peak complexity indicated that only cis–trans isomerization about the vinylic carbon–carbon double bonds was taking place.

Deuterolysis of 3a. A dry 10-mL single-necked round-bottom flask was fitted with a total reflux head. Into the flask were placed 1.1 g (7.5 mmol) of **3a** and 5 mL of acetic-*d* acid (Thompson Packard, 99 atom % D). This mixture was refluxed for 2 h, evolving 319 mL (14.3 mmol, 96%) of *trans*-1-deuterio-1-butene gas: NMR (CCl_4) δ 1.00 (t, J = 7 Hz, 3 H, methyl), 2.00 (m, 2 H, methylene), 4.92 (d, J_{ab} = 18 Hz, vinyl),



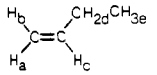
5.50–6.20 (dt of 1:1:1 t, J_{ba} = 18 Hz, J_{ac} = 6 Hz, J_{aD} = 1.5 Hz, vinyl). Distillation of the reaction mixture through a short-path apparatus gave *N*,*N*-dimethylacetamide: bp_{760} 165–175 °C (lit.[32] 165 °C); NMR (CCl_4) δ 2.0 (s, 3 H, acetyl methyl), 2.83 and 3.00 (pair of s, 6 H, *N*-methyl).

Deuterolysis of Irradiated 3a. Into a 10-mL single-necked round-bottom flask were placed 0.85 g (5.00 mmol) of photoproduct and 5 mL of acetic-*d* acid (Packard Thompson, 99 atom % D). This solution was refluxed for 2 h, generating 230 mL (9.20 mmol, 92%) of a mixture of

(32) Coppinger, G. M. *J. Am. Chem. Soc.* **1954**, *76*, 1372–3.

cis- and *trans*-1-deuterio-1-butene: NMR (CCl_4) δ 1.00 (t, J = 7 Hz, 3 H, methyl), 2.00 (m, 2 H, methylene), 4.60–5.20 (pair of d, J_{cis} = 10 Hz, J_{trans} = 18 Hz, 1 H, vinyl), 5.40–6.10 (m, 1 H, vinyl).

Protonolysis of 4a in Propionic Acid. A 50-mL single-necked round-bottom flask was equipped with a total reflux head. In the flask were placed 1.13 g (5.00 mmol) of **4a** and 10 mL of propionic acid. This mixture was refluxed 1 h, during which time 217 mL (8.9 mmol, 89%) of 1-butene gas was evolved. The reaction mixture was made basic with an excess of 2 N aqueous sodium hydroxide and extracted with two 50-mL portions of *n*-pentane. The combined pentane extracts were dried over anhydrous sodium sulfate and concentrated by rotary evaporation of the solvent. The remaining white solid was found to be *N*-methyl-*N*-phenylpropionamide by comparison of spectral data with those of an independently synthesized sample. A total of 0.73 g (90%) was collected: mp 56.5–57.5 °C (lit.[20] 55–56 °C); NMR (CCl_4) δ 1.00 (t, J = 7 Hz, 3 H, methyl), 2.02 (q, J = 7 Hz, 2 H, methylene), 3.18 (s, 3 H, *N*-methyl), 7.25 (m, 5 H, phenyl). For 1-butene, NMR (CCl_4) resonances occur at δ 1.00 (t, J_{de} = 7 Hz, 3 H, methyl), 2.06 (m, 2 H, methylene), 4.70–5.20 (dd, J_{ac} = 9 Hz, J_{bc} = 17 Hz, 2 H, vinyl), and 5.50–6.20 (m, 1 H, vinyl).

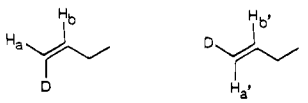


Anal. Calcd for $C_{10}H_{13}NO$: M^+ 163.0998. Found: 163.1013.

Protonolysis of 15a in Valeric Acid. Into a 50-mL single-necked round-bottom flask, fitted with a total reflux head, were placed 4.20 g (18.5 mmol) of **15a** and 12 mL of valeric acid. This mixture was refluxed for 18 h and poured into 50 mL of 2 N aqueous sodium hydroxide. The resulting oil was extracted with two 30-mL portions of diethyl ether. The combined ether extracts were dried over anhydrous sodium sulfate and concentrated by rotary evaporation. The remaining oil was distilled through a short-path apparatus, giving 4.2 g (92%) of a colorless liquid: bp 109–110 °C (0.04 torr); NMR (CCl_4) resonances at δ 0.60–2.00 (m, 17 H, methyl and methylene), 2.78 (m, 1 H, benzylic methine), 3.12 (s, 3 H, *N*-methyl), 7.20 (m, 4 H, phenyl); IR (neat film) 2980, 2955, 2890, 1655 (C=O), 1490, 1450, 1420, 1384, 1287, 1130, 1085, 775 (phenyl), 760 (phenyl) cm^{-1}.

Anal. Calcd for $C_{16}H_{25}NO$: M^+ 247.1936. Found: 247.1938.

Deuterolysis of 15a. Into a 50-mL single-necked round-bottom flask, equipped with a total reflux head, were placed 1.0 g (4.4 mmol) of boranamine and 5 mL of acetic-*d* acid (Thompson Packard Inc., 99 atom % D). This mixture was refluxed for 16 h, yielding a nonhomogeneous unidentified boron-containing compound and 60 mL (60%) of a mixture of *cis*- and *trans*-1-deuterio-1-butene gas: NMR (CCl_4) δ 1.00 (t, J = 7 Hz, 3 H, methyl), 2.00 (q, J = 7 Hz, 2 H, methylene), 4.60–5.20 (pair of d, J_{ab} = 10 Hz, $J_{a'b'}$ = 18 Hz, 1 H, vinyl), 5.40–6.10 (m, 1 H, vinyl).



***N*-Methyl-2-(2-butyl)aniline (25).** A 50-mL single-necked round-bottom flask was fitted with a total reflux head. In the flask were placed 2.83 g (9.46 mmol) of *N*-(2-(2-butyl)phenyl)-*N*-methylvaleramide (**19**) and 20 mL of concentrated hydrochloric acid. This mixture was refluxed for 60 h and made strongly basic with an excess of 5 N aqueous sodium hydroxide. A yellow oil formed, which was extracted with two 30-mL portions of diethyl ether. The combined ether extracts were dried over anhydrous sodium sulfate and concentrated by rotary evaporation. The remaining liquid was spectroscopically pure without further treatment. A total of 1.3 g (85%) of a colorless liquid was collected: NMR (CCl_4) δ 0.86 (t, J = 7 Hz, 3 H, alkyl methyl), 1.17 (d, J = 7 Hz, 3 H, homobenzylic methyl), 1.53 (m, 2 H, methylene), 2.55 (m, 1 H, benzylic methine), 2.80 (s, 3 H, *N*-methyl), 3.50 (br s, 1 H, N–H), 6.20–7.20 (m, 4 H, phenyl); IR (neat film) 3460, 3080, 3038, 2980, 2940, 2880, 2820, 1601, 1585, 1475, 1404, 1358, 1167, 745 (phenyl) cm^{-1}.

Anal. Calcd for $C_{11}H_{17}N$: M^+ 163.1361. Found: 163.1388.

Basic Hydrogen Peroxide Oxidation of 15b. A 100-mL three-necked round-bottom flask was equipped with an addition funnel, thermometer, and glass stopper. Into the flask were placed 2.0 g (8.9 mmol) of azaboranaphthalene, 30 mL of THF, and 5 mL of 3 N aqueous sodium hydroxide. This mixture was placed in a water bath at 20 °C, and 4 mL of 30% hydrogen peroxide (Mallinckrodt) was added at such a rate as to maintain the internal temperature between 35 and 40 °C. After the addition was completed, the reaction mixture was stirred for 1 h. The resulting clear solution was diluted with 20 mL of water and extracted with two 30-mL portions of diethyl ether. The combined ether extracts were dried over anhydrous sodium sulfate and concentrated by rotary evaporation. The remaining oil was distilled through a short-path apparatus, giving 1.0 g (62%) of a yellow viscous liquid: bp 104 °C (0.05 torr); NMR (CCl_4) δ 0.70–1.40 (m, 6 H, methyl), 2.66 (s, 3 H, *N*-methyl), 2.73 (m, 1 H, benzylic methine), 3.69 (m, 1 H, α-hydroxy methine), 4.10 (br s, 2 H, N–H and O–H), 6.30–7.20 (m, 4 H, phenyl); IR (neat film) 3380, 2980, 2880, 2810, 1601, 1585, 1505, 1450, 1330, 1300, 1255, 1160, 1080, 1000, 905, 745 (phenyl) cm^{-1}.

Anal. Calcd for $C_{11}H_{17}NO$: M^+ 179.1311. Found: 179.1313.

Basic Hydrogen Peroxide Oxidation of 23a. A 250-mL three-necked round-bottom flask was fitted with an addition funnel, thermometer, and glass stopper. Into the flask, were placed 5.0 g (18 mmol) of photoproduct, 60 mL of THF, and 15 mL of 3 N aqueous sodium hydroxide. Hydrogen peroxide (6 mL of 30% solution) was slowly added to the mixture, maintaining the internal temperature at 40 °C. The reaction mixture was stirred for 1 h at room temperature, diluted with 75 mL of water, and extracted with two 50-mL portions of diethyl ether. The combined ether extracts were dried over anhydrous sodium sulfate and concentrated. The remaining oil (3.1 g) was chromatographed on 100 g of basic alumina (Baker, 9.0 pH), eluting with 300 mL of anhydrous diethyl ether followed by 300 mL of fat-extraction diethyl ether (Mallinckrodt). Concentration of the fat-extraction ether fraction gave 1.8 g (48%) of 2-(2-hydroxycyclohexyl)-*N*-methylaniline: NMR (CCl_4) δ 1.00–2.00 (br m, 8 H), 2.00–2.90 (m and s, 4 H, *N*-methyl and benzylic methine), 2.90–3.80 (br m, 3 H, α-hydroxy methine, N–H, and O–H), 6.30–7.30 (m, 4 H, phenyl); IR (neat film) 3400, 2940, 2865, 1690, 1600, 1577, 1505, 1445, 1305, 1275, 1180, 1164, 1150, 1119, 1060, 960, 868, 845, 810, 750 (phenyl) cm^{-1}.

Anal. Calcd for $C_{13}H_{19}NO$: M^+ 205.1467. Found: 205.1472.

Actinometry. Quantum yields for cyclization of the *N*-phenyldivinylboranamines were determined relative to the quantum yield of acetophenone formation (0.33)[13] upon irradiation of a 0.1 M solution of valerophenone in benzene. The valerophenone actinometer was selected because the similarity between its absorption spectrum and those of the boranamines made it easy to ensure equal absorption of light by actinometer and sample. Actinometer solutions containing known quantities of valerophenone and tetradecane as an internal standard (0.004 M) were prepared in the appropriate volumetric glassware. Valerophenone was purified by passage through neutral alumina and distillation; tetradecane and benzene were distilled from freshly ground calcium hydride. Irradiations were carried out on 5-mL portions of actinometer and boranamine in 13 × 100 mm Pyrex tubes degassed with three freeze–pump–thaw cycles. Conversions of actinometer were limited to less than 10%. Analysis for acetophenone after irradiation was carried out on a Varian-Aerograph 1400 gas chromatograph fitted with a 0.25 in. × 10 ft column containing 5% Carbowax 20M on 80-mesh Chromsorb G. Area ratios were converted to mole ratios by calibration with known mixtures of valerophenone, acetophenone, and tetradecane in benzene.

Quantum Yields. Multiple samples of actinometer and boranamine of similar volumes and concentrations were simultaneously irradiated for various time intervals. All samples were degassed with three freeze–pump–thaw cycles. Irradiations were carried out on a "merry-go-round" apparatus with Pyrex-filtered light from a Hanovia 450-W medium-pressure mercury lamp contained in a water-cooled quartz immersion well. Boranamine samples were analyzed by ultraviolet spectroscopy in the region where the largest difference between starting material and photoproduct absorptivities occurred.

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Registry No. 3a, 83720-43-8; **3b**, 83720-44-9; **4a**, 83721-06-6; **4b**, 83720-45-0; **4c**, 83731-14-0; **4d**, 83720-46-1; **4e**, 83720-47-2; **6a**, 83720-48-3; **6b**, 83720-49-4; **6c**, 83720-50-7; **6d**, 83720-51-8; **6e**, 83720-52-9; **6f**, 83720-53-0; **7**, 1125-73-1; **8a**, 37609-34-0; **8b**, 38202-46-9; **9a**, 83720-54-1; **9b**, 83720-55-2; **11**, 83720-71-2; **12**, 18457-64-2; **13**, 127-19-5; **14**, 10036-59-6; **15a**, 83720-56-3; **15b**, 83720-57-4; **15c**, 83720-58-5; **15d**, 83720-59-6; **16a**, 83720-60-9; **16b**, 83720-61-0; **16c**, 83731-15-1; **16d**, 83720-62-1; **17**, 106-98-9; **18**, 5827-78-1; **19**, 83720-68-7; **20**, 83720-70-1; **21**, 83720-66-5; **22**, 83720-73-4; **23a**, 83720-63-2; **23b**, 83720-64-3; **24**, 83720-69-8; **25**, 83720-67-6; **26**, 83720-74-5; **27**, 83720-72-3; BH_2Cl, 10388-28-0; Me_2NH, 124-40-3; chloro(*cis*-3-hexen-3-yl)-*N*-methyl-*N*-phenylboranamine, 83720-65-4; (*cis*-3-hexen-3-yl)dichloroborane, 51207-22-8; *N*-methylaniline, 100-61-8; 1-butyne, 107-00-6; 1-chlorocyclohexene, 930-66-5; 1-chlorocycloheptene, 13294-30-9; vinyl bromide, 593-60-2; aniline, 62-53-3; 4-chloroaniline, 106-47-8; 4-bromoaniline, 106-40-1; 4-nitroaniline, 100-01-6; 2-bromoaniline, 615-36-1; 216-dimethylaniline, 87-62-7.