Mechanism of Cyclization of Divinyl-*N*-phenylboranamines[1]

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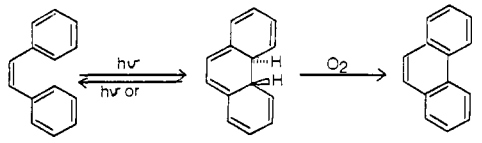
Abstract: High-resolution NMR and mass spectral data were used to deduce the mechanism of nonoxidative photocyclization of divinyl-*N*-phenylboranamines. Cyclization was found to proceed through an excited singlet state conrotatory electrocyclic ring closure between phenyl and adjacent vinyl groups, followed by an intramolecular suprafacial 1,5-hydrogen shift. Such a mechanism was found to be operating in both the divinylboranamines and the dicycloalkenylboranamines. Irradiation in acetonitrile inhibited vinylic photochemical trans–cis isomerization, yielding predominantly the cycloadduct from starting material vinyl stereochemistry.

Intramolecular nonoxidative photocyclization reactions occur primarily between an aromatic ring and adjacent vinyl group.[2-7] Oxidative photocyclizations typically take place between two aromatic rings and are commonly found among stilbene (**1**) and



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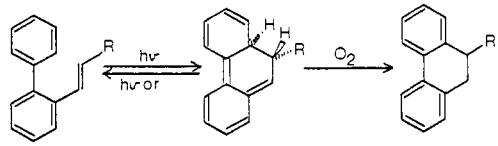
a wide variety of stilbene analogues.[8,9] Both reaction types apparently proceed through a Woodward–Hoffmann allowed electrocyclic ring closure from the first excited state.[10,11] In the presence of a mild oxidant such as oxygen or iodine, the cyclized dihydrophenanthrene intermediate **2** is oxidized to phenanthrene. Nonoxidative cyclization arises via an intramolecular 1,5-hydrogen shift from cyclized intermediates similar to **5**. Under the appropriate electronic and structural constraints, both oxidative and nonoxidative photocyclization reactions have been observed in various stilbene derivatives[12] and 2-vinylbiphenyls.[4]



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This paper presents a mechanistic investigation into the photochemical nonoxidative cyclization of divinyl-*N*-phenylboranamines.[13] Emphasis was placed on the use of high-resolution NMR spectral techniques to define the various stereochemical pathways taken during cyclization. With such information, conclusions on both the mechanism and excited-state multiplicity were made possible. Indeed, without high-resolution NMR spectroscopy, such an investigation would have been a truly formidable task.

Results and Discussion

Excited-State Multiplicity. Attempts to sensitize the nonoxidative cyclization of the divinyl-*N*-phenylboranamines with 4-bromobiphenyl (E_T = 67 kcal/mol)[14] gave only small amounts of cyclized product after extended irradiations. Typically, optical densities were adjusted such that greater than 90% of the incident light was absorbed by the sensitizer. Appearance of some photoproduct in sensitization samples was caused by residual direct absorption of light by the starting material. This result gives an indication that cyclization is occurring from either the first excited singlet state (S_1) or a "vibrational excited state" (S_0*). Of course, the possibility that ineffective sensitization results from a highly inefficient energy-transfer process between the triplet state (T_1) of 4-bromobiphenyl and ground-state (S_0) boranamine cannot be excluded.

Given the reported enhancement of S_1-to-T_1 intersystem crossing by the nitro group,[15] the failure of bis(*trans*-1-buten-1-yl)-*N*-(4-nitrophenyl)boranamine (**7**) to cyclize also supports the conclusion that cyclization is occurring from S_1 or S_0*. In addition, the failure of thermolysis experiments to induce cyclization gives evidence against the involvement of S_0* and suggests that cyclization may be occurring only from S_1. This conclusion is not without precedent. Most oxidative and nonoxidative photocyclization reactions reported to date are believed to proceed through S_1.[16] Only certain 2-vinylbiphenyls are known to cyclize through both S_1 and T_1.[17]

In spite of the failure of **7** to cyclize, bis(*trans*-1-buten-1-yl)-*N*-(4-bromophenyl)boranamine and bis(*cis*-2-buten-2-yl)-*N*-(2-bromophenyl)boranamine cyclized readily.[10] The bromine atom, which is also known to enhance S_1-to-T_1 intersystem crossing,[15] apparently does not effect the cyclization process. A similar situation exists in the oxidative photocyclization of substituted stilbenes; nitrostilbenes do not cyclize while bromostilbenes cyclize without difficultly.[18] These results suggest that factors

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(1) Current nomenclature practices of Chemical Abstracts Service designates boron–nitrogen compounds as boranamines. IUPAC uses the name aminoboranes as well.

(2) Chapman, O. L.; Cleveland, P. G. *Chem. Commun.* **1967**, 1064–5.
(3) Chapman, O. L.; Eian, G. L.; Bloom, A.; Clardy, J. *J. Am. Chem. Soc.* **1971**, *93*, 2918–28.
(4) Morgan, D. D.; Horgan, S. W.; Orchin, M. *J. Org. Chem.* **1973**, *38*, 3801–3.
(5) Laarhoven, W. H.; op het Veld, P. H. G.; Langendam, J. C. *Tetrahedron Lett.* **1975**, 231–2.
(6) Padwa, A.; Doubleday, C.; Mazzu, A. *J. Org. Chem.* **1977**, *42*, 3271–9.
(7) Ninomiya, I.; Naito, T.; Kiguchi, T. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2257–61, and references therein.
(8) Woods, W. G.; Strong, P. L. *J. Am. Chem. Soc.* **1966**, *88*, 4667–71. Stermitz, F. R., "Organic Photochemistry"; Chapman, O. L., Ed.; Marcel Dekker: New York, 1967, Vol. 1, p 247.
(9) Blackburn, E. V.; Timmons, C. J. *Q. Rev., Chem. Soc.* **1967**, *23*, 482–503.
(10) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Academic Press: New York, 1970.
(11) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781–853.
(12) Sargent, M. V.; Timmons, C. J. *J. Chem. Soc.* **1964**, 5544–52.
(13) Sobieralski, T. J.; Hancock, K. G. *J. Am. Chem. Soc.*, preceding paper in this issue.
(14) O'Donnell, C. M.; Harbaugh, K. F.; Winefordner, J. D.; Fisher, R. P. *Anal. Chem.* **1973**, *45*, 609–11.
(15) Lower, S. K.; El-Sayed, M. A. *Chem. Revs.* **1966**, *66*, 199–241.
(16) Muszkat, K. A.; Fisher, E. *J. Chem. Soc. B* **1967**, 662–78.
(17) Lapouyade, R.; Fornier de Violet, P.; Koussini, R. *J. Am. Chem. Soc.* **1978**, *100*, 6679–87.

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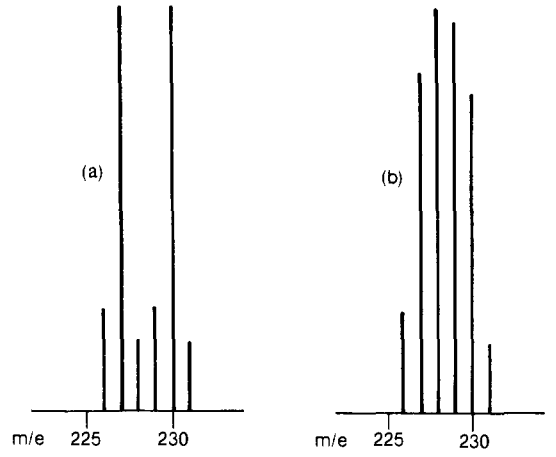
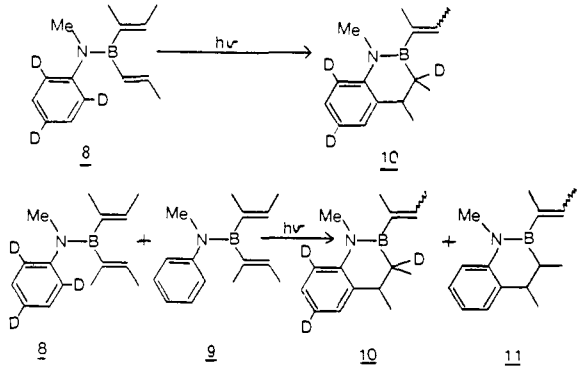


Figure 1. Predicted molecular ion peak patterns possible from the photolysis of a mixture of **8** and 9.

other than excited-state multiplicity may be involved in determining the photochemical reactivity of the divinylboranamines toward nonoxidative photocyclization.

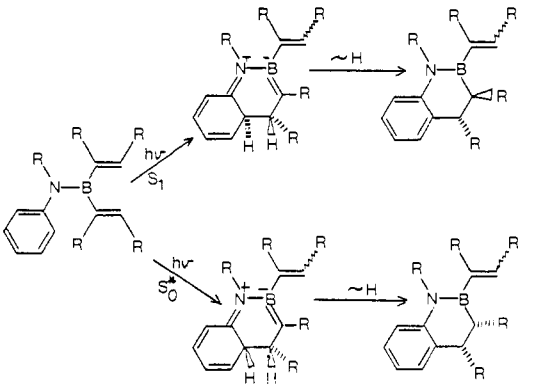
A correlation between the observation of cyclization and the electron density, or free-valence indicies ($\sum F_r^*$), at the positions of cyclization in the first excited state has been made among numerous stilbene and 2-vinylbiphenyl derivatives.[19] Free-valence numbers greater than unity are required to observe cyclization. The failure of divinyl-*N*-methyl-*N*-phenylboranamine[16] and **7** to cyclize may, therefore, be due to electronic factors. Nevertheless, additional detailed experimentation is required before more definite conclusions can be made regarding this aspect of the photoreactivity of the divinyl-*N*-phenylboranamines.

1,5-Hydrogen Sigmatropic Shift. A priori, the 1,5-prototropic shift following cyclization can occur in either a concerted, intramolecular Woodward–Hoffmann fashion,[10,11] or through an intermolecular proton-exchange process. In order to distinguish between these two mechanisms, **8** was prepared and irradiated. Photocyclization of **8** gave preferential migration of deuterium from C-2, or equivalently C-6, to the carbon atom α to boron. Irradiation of a mixture of **8** and **9** clearly gave **10** and **11** without

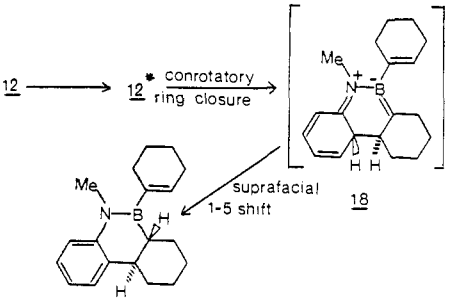


the formation of mono- and dideuterated crossover products. Evidence for this scheme was given in the mass spectrum. Figure 1 shows the predicted molecular ion peak patterns possible from the photolysis of a mixture of **8** and **9**. A pattern similar to that in Figure 1b would result from an intermolecular 1,5-shift giving an equimolar mixture of the mono-, di-, tri-, and undeuterated products. On the other hand, a pattern like that shown in Figure 1a would result from a concerted intramolecular process. The pattern obtained experimentally was clearly that of Figure 1a,

Scheme I



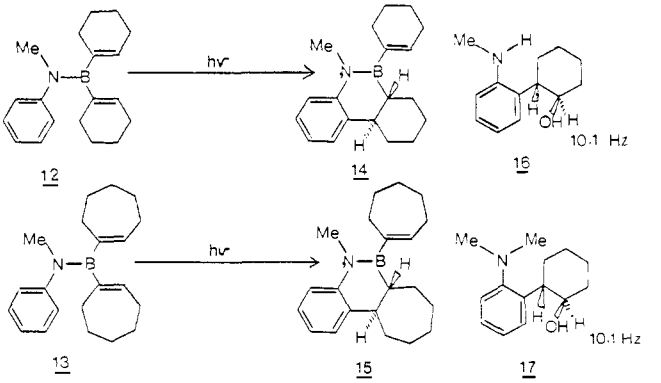
Scheme II



showing, therefore, that the 1,5-hydrogen shift is occurring primarily, perhaps exclusively, in an intramolecular, stereoselective fashion.

Stereochemistry of Cyclization. In principle, distinction between reaction from an electronically excited singlet state and a vibrationally excited state can be made from the stereochemistry of cyclization. Since similar nonoxidative photocyclization reactions have been reported to proceed through a concerted 6-π-electron ring closure followed by a 1,5-hydrogen sigmatropic shift, cyclization from S_1 should occur in a conrotatory fashion while cyclization from S_0* will give disrotatory ring closure.[10,11] The stereochemical consequences corresponding to each mechanism are illustrated in Scheme I. If cyclization occurs from the *E*-vinyl isomer only, excited-state ring closures gives a product with R groups in the trans configuration while thermal ring closure gives the cis configuration.

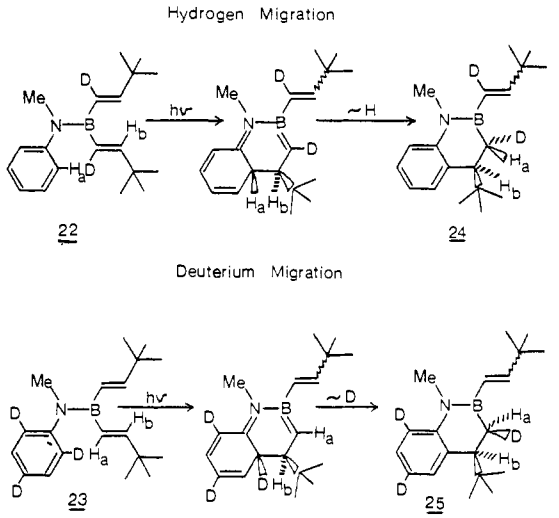
Cyclization of the cycloalkenylboranamines **12** and **13** to the trans-fused **14** and **15**, respectively, demonstrates that a concerted



mechanism is indeed operating in these systems. Coupling constants of 14.5 and 15.0 Hz were observed between bridgehead protons in **14** and **15**, respectively, indicative of the trans stereochemistry.[19] In addition, hydrogen peroxide oxidation of **14** yields the 2-hydroxycyclohexylaniline **16**,[13] which gives a coupling constant of 10.1 Hz between the benzylic proton and the α-hydroxy proton. This value compares identically with that obtained for

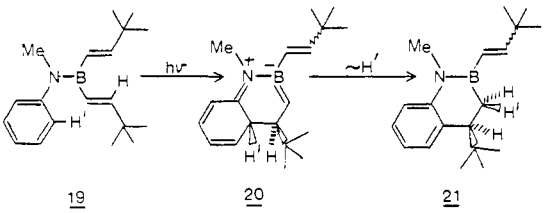
(18) Mallory, F. B.; Wood, C. S.; Gordon, J. T. *J. Am. Chem. Soc.* **1964**, *86*, 3094–102.
(19) Laarhoven, W. H.; Cuppen, Th. J. M.; Nivard, R. J. F. *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 687–98. Blackburn, E. V.; Timmons, C. J. *J. Chem. Soc. C* **1970**, 172–5.

Scheme III



independently synthesized 2-(*o*-dimethylaminophenyl)cyclohexanol (**17**)[24] and gives further for the trans stereochemistry in **14** and **15**.[19] Therefore, cyclization is occurring from an electronically excited state and not from S_0*. The mechanism is represented in Scheme II. Conrotatory ring closure of **12*** to **18** followed by an intramolecular suprafacial 1,5-hydrogen shift results in the observed stereochemistry.

In order to determine whether the same mechanism applies to photocyclization of straight-chain divinylboranamines, an investigation into the stereochemistry of cyclization of bis(*trans*-3,3-dimethyl-1-buten-1-yl)-*N*-methyl-*N*-phenylboranamine (**19**) was



carried out. The reason for choosing this particular compound was twofold: first, cyclization would probably occur from the *trans*-vinyl isomer only, since cyclization from the cis isomer would be sterically inhibited by the *tert*-butyl group; secondly, the benzylic proton NMR absorption would show coupling to only two vicinal protons, and this coupling could be employed for stereochemical analysis.

Close examination of the cycloadduct (**21**) reveals the presence of an asymmetric center on the benzylic carbon atom and a pair of diastereomeric protons on the carbon atom α to boron. One of the diastereomeric protons results from a 1,5-hydrogen shift in intermediate **20**, while the other, which was originally vinylic, remains stationary throughout cyclization. If cyclization proceeds from the *trans*-vinyl isomer in a concerted fashion and the 1,5-hydrogen shift occurs suprafacially, the shifting proton ends up cis to the *tert*-butyl group and the stationary proton ends up trans to the *tert*-butyl group.[10,11] Substitution of one of the diastereomeric protons with deuterium leaves only two vicinal protons that can interact magnetically with each other. Thus, the Karplus relation[20] can be used to deduce the stereochemistry in this region.

Separate substitution of the diastereomeric protons of **21** with deuterium was accomplished by irradiating compounds in which deuterium migrates and deuterium remains stationary (Scheme III). Cyclization is shown in Scheme III to take place on the front side of the aromatic ring with the *trans*-vinyl isomer in a Woodward–Hoffmann fashion. Only one of the two possible enantiomeric products is shown. In the "hydrogen migration case",

(20) Jackman, L. M.; Sternhell, S. "Applications of NMR Spectroscopy in Organic Chemistry"; Pergamon: New York, 1969.

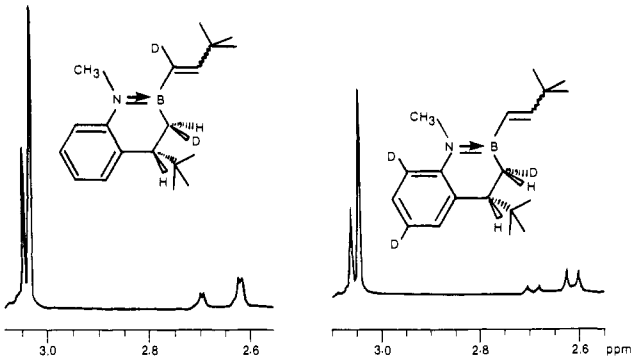
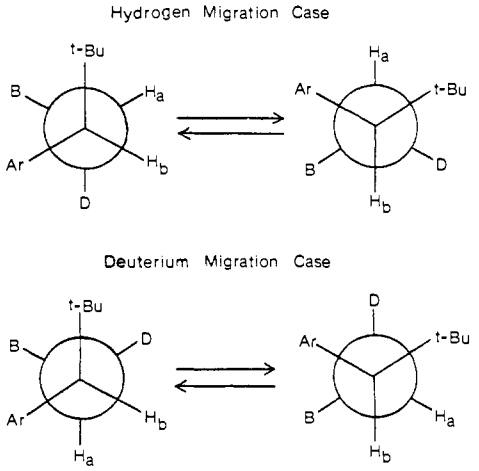


Figure 2. NMR spectra of **24** and **25** showing the *N*-methyl and benzylic proton absorptions.

Scheme IV



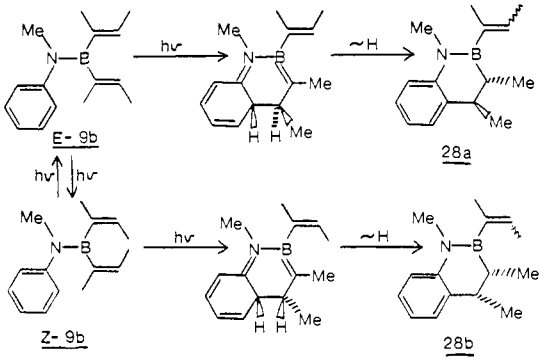
the two methine protons (H_a and H_b) result in the trans configuration, while in the "deuterium migration case", the methine protons end up in the cis configuration.

Newman projection formulas of the structures **24** and **25** reveal a further complexity in the stereochemistry in the region of interest (Scheme IV). Structures are drawn in Scheme IV with the benzylic carbon atom in front. In each case there are two possible rotational isomers related by a ring inversion and likely to be in thermal equilibrium. The "hydrogen migration product" shows dihedral angles of 60° and 180° between vicinal protons in these two conformers, giving predicted coupling constants of either 2 or 10 Hz, respectively.[20] A coupling constant of 6–7 Hz would be observed if the equilibrium gives a 50:50 mixture of each rotomer at room temperature. In the "deuterium migration case", only one dihedral angle results (60°), predicting a coupling constant of about 2 Hz.

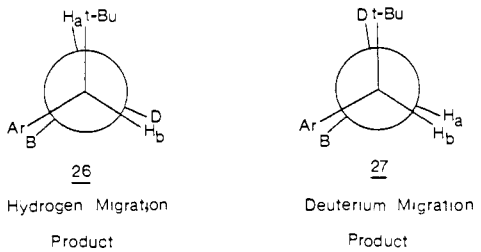
The *N*-methyl and benzylic proton absorptions for compounds **24** and **25** at 360 MHz are shown in Figure 2. Two peaks were observed for each absorption due to the presence of the *cis*- and *trans*-vinyl isomers in the unreacting side chain. In the hydrogen migration case, a coupling constant of 6–7 Hz was predicted, while a constant of only 2 Hz could be identified in the spectrum after resolution enhancement. For the deuterium migration case, a coupling constant of 8 Hz was found as compared to the predicted value of 2 Hz. These results appeared to be the opposite of what was predicted on the basis of thermally equilibrating photoproduct conformers with gauche substituents. One possible explanation is that cyclization takes place from the *cis*-vinyl isomer, which is highly unlikely. The fact that a spectral difference exists between **24** and **25** implies that a concerted cyclization process is indeed operating.

An attempt was made to distinguish between the *trans*-H_a,H_b isomer and *cis*-H_a,H_b isomer of **24** and **25** in a variable temperature NMR experiment. Since the trans isomer gives a thermal equilibrium between rotomers with dihedral angles of 60° and

Scheme V



180°, a thermal dependence of the coupling constant should be observable.[21] The coupling constant for the cis isomer should be invariant with temperature since an equilibrium is established between rotomers of essentially identical dihedral angles. Both **24** and **25**, in fact, displayed an invariance in coupling constant from −50 to +50 °C, suggesting either that the thermal equilibration was unperturbed even at −50 °C or that no thermal equilibrium was present. Inspectation of space-filling models of **24** and **25** shows that these molecules are extremely crowded along the 3,4-bond axis and that the eclipsed configuration is probably actually preferred. Newman projection formulas of eclipsed **24** and **25** show dihedral angles of 0° for the deuterium migration product (**26**) and 60° for hydrogen migration product (**27**). These



angles correspond to predicted coupling constants of about 8 and 2 Hz, respectively, which compare well with the observed values. Cyclization in the straight-chain systems is, therefore, most likely to occur through a concerted mechanism similar to that observed for the cycloalkenylboranamines (Scheme II).

Effect of Acetonitrile on the Photocyclization of 9. Since cyclization in the straight-chain divinylboranamines occurs through a concerted mechanism, different stereochemical consequences will result, depending upon the vinyl isomer from which cyclization occurs. In the irradiation of **9**, cyclization from the *E*-vinyl isomer gives the trans stereochemistry in the 3- and 4-positions while cyclization from the *Z*-vinyl isomer gives the cis stereochemistry (Scheme V). The observation that photochemical *E*-to-*Z* isomerization is inhibited in acetonitrile[13] will allow for a variation in the relative amounts of **28a** and **28b** formed during photolysis. Also, since **28a** and **28b** are diastereomers, they should be distinguishable in the NMR.

Figures 3 and 4 show expanded 360-MHz NMR spectra of the alkyl methyl absorptions of **28** prepared in cyclohexane and acetonitrile, respectively. The methyl group α to boron appears as four doublets between 0.7 and 1.0 ppm. Clearly, a difference in peak intensities in the α-boron methyl absorptions can be seen between Figures 3 and 4. When **28** is prepared in cyclohexane, the four doublets occur with almost equal intensities; in acetonitrile, the two upfield peaks increase in intensity at the expense of the two low-field peaks.

Assignment of these four doublets to particular stereoisomers of **28** was made from the results of a low-temperature NMR

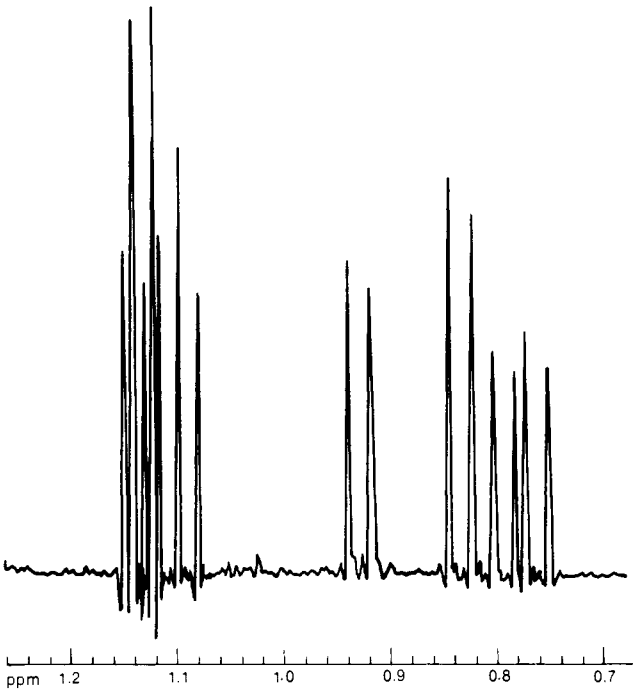


Figure 3. Alkyl methyl NMR absorptions of **28** prepared in cyclohexane.

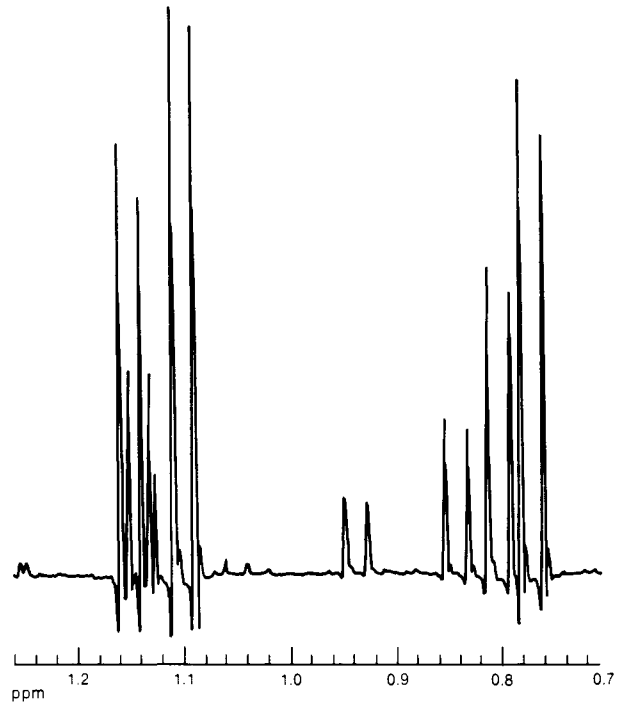


Figure 4. Alkyl methyl NMR absorptions of **28** prepared in acetonitrile.

experiment carried out on the photoproduct prepared in acetonitrile (Figure 5). The two downfield peaks of the α-boron methyl give significant line broadening from −30 to −50 °C. In fact, the peak at 0.95 ppm broadens to coalescence between −30 and −40 °C and resolves into two separate peaks at 0.91 and 0.98 ppm as the temperature approaches −60 °C. These results indicate that an equilibrium exists between two species in solution where the doublet at 0.95 ppm (room temperature) represents a "fast exchange" situation and the pair of doublets observed at −60 °C represents a "slow exchange" situation on the NMR time scale. The peaks at 0.76 and 0.79 ppm simply give line broadening at temperatures as low as −80 °C. The lack of coalescence in the two upfield peaks at −80 °C indicates that the equilibrium they represent has a much lower free energy of activation than that represented by the two low-field peaks.

(21) Laarhoven, W. H.; op het Veld, P. H. G. *J. Chem. Soc., Perkin Trans. 2* **1978**, 915–27.

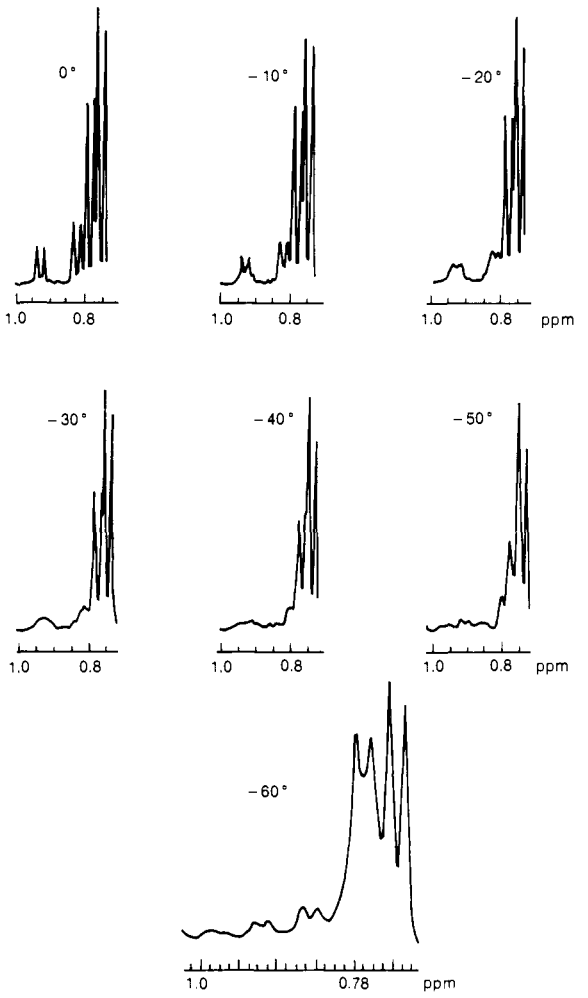
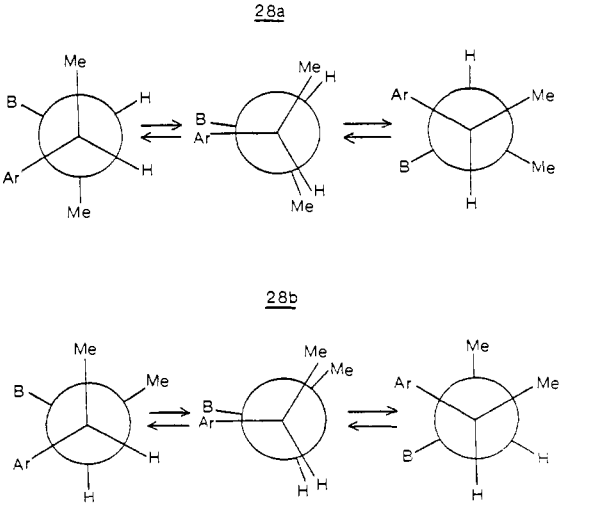


Figure 5. Low-temperature NMR experiment on **28** prepared in acetonitrile showing the α-boron methyl absorptions.

Scheme VI



In Scheme VI, Newman projection formulas show the thermal equilibria that are taking place between rotational isomers in **28a** and **28b** and offer an explanation of the observations made in the NMR spectra at reduced temperatures. Structures are drawn with the benzylic carbon atom in the front. Clearly, interconversions between rotomers in **28a** eclipse adjacent methyl and hydrogen groups. In contrast, **28b** gives eclipsed methyl groups. The higher energy required to eclipse vicinal methyls in **28b** would give a slower rate of exchange between rotomers as compared to **28a**. Therefore, the two methyl absorptions at 0.84 and 0.95 ppm can be assigned to **28b** and the two absorptions at 0.76 and 0.79 ppm can be assigned to **28a**. As was observed for **24** and **25**, two doublets occur for each methyl of **28** due to the presence of *E*- and *Z*-vinyl isomers at the unreacted side chain.

Taking into consideration the relative abundance of **28a** and **28b** formed in acetonitrile, one finds that the above peak assignments are consistent with the proposed mechanism of cyclization (Schemes II and V). Irradiation of **9** in cyclohexane gives nearly a 50:50 mixture of **28a** and **28b**, since photochemical *E*-to-*Z* isomerization is occurring much more efficiently than cyclization. In acetonitrile, vinyl *E*-to-*Z* isomerization is inhibited sufficiently to give **28a** as the major product. In addition, the quantum yield of cyclization of **9** increases from 0.15 mol einstein^{-1} in cyclohexane to 0.34 mol einstein^{-1} in acetonitrile.[13] Therefore, an increase in the efficiency of cyclization coupled with a decrease in the efficiency of vinyl *E*-to-*Z* isomerization in going from cyclohexane to acetonitrile as the solvent accounts for the observed results.

Summary. From high-resolution NMR data, the nonoxidative photocyclization of the divinyl-*N*-phenylboranamines was found to proceed through a conrotatory ring closure, followed by a concerted, intramolecular 1,5-hydrogen shift. Such a mechanism excludes the possibility of cyclization from a vibrationally excited state (S_0*). The failure of **7** to cyclize suggests that photocyclization is occurring primarily, if not exclusively, from S_1. In the straight-chain divinylboranamines, irradiation in cyclohexane gives olefin cis–trans isomerization more efficiently than cyclization. Thus, a relatively equal distribution of stereoisomers is obtained. In acetonitrile, cyclization is slightly more efficient than olefin cis–trans isomerization, giving the cycloadduct from starting material vinyl stereochemistry as the primary photoproduct.

Experimental Section

Instrumentation. High-resolution nuclear magnetic resonance spectra were recorded on the Nicolet NT360 Fourier Transform spectrometer. 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 Du Pont Model 492 spectrometer equipped with a Finnigan-Inco data system. Ultraviolet spectra were recorded on the Cary Model 17 spectrometer. Boiling points are uncorrected.

Materials. Unless otherwise specified, anhydrous diethyl ether (Mallinckrodt AR) was used directly without further purification. Triethylamine (Aldrich) and *N*-methylaniline (Aldrich) were routinely distilled from potassium hydroxide prior to use. The purification of *n*-pentane was carried out as described by Vogel.[22] 2,4,6-Trideuterioaniline was prepared as previously reported.[23] Benzene, cyclohexane, and acetonitrile used in the syntheses, photolyses, and spectral measurements were distilled from freshly ground calcium hydride. 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 when necessary. 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 left exposed to the air, the divinylboranamines slowly turned red.

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 transferred according to general methods already described.[24]

Attempted Sensitization of the Cyclization of Bis(*trans*-1-buten-1-yl)-*N*-methyl-*N*-phenylboranamine[13] with 4-Bromobiphenyl. A solution containing a 5:1 molar ratio of 4-bromobiphenyl and boranamine, respectively, in benzene-d_6 was placed in a 5-mm quartz tube under a nitrogen atmosphere. A control sample was similarly prepared without the sensitizer. Both samples were degassed with three freeze–pump–thaw cycles and irradiated for 41 h with an unfiltered, water-cooled 450-W medium-pressure mercury lamp. The NMR spectra showed complete conversion to the cyclized product in the control sample while <5% conversion was observed in the experimental sample. Cyclization in the

(22) Vogel, A. I. "Practical Organic Chemistry", Wiley: New York, 1966.
(23) Best, A. P.; Wilson, C. L. *J. Chem. Soc.* **1946**, 239–43. Carter, R. E. *Acta Chem. Scand.* **1967**, *21*, 75–86.
(24) Kramer, G. W.; Levy, A. B.; Midland, M. "Organic Synthesis via Boranes"; Borwn, H. C., Ed.; Wiley: New York, 1975; Chapter 9.

experimental sample containing bromobiphenyl was attributed to direct absorption of light by the boranamine.

Photolysis of Bis(*trans*-1-buten-1-yl)-*N*-(4-nitrophenyl)boranamine (7).[13] A 0.8 M solution of boranamine in dioxane-d_8 was placed in a 5-mm quartz tube under an atmosphere of dry nitrogen. After 150 h of irradiation with an unfiltered 450-W medium-pressure mercury lamp, no change had occurred in the NMR spectrum.

Thermolysis of Bis(*trans*-1-buten-1-yl)-*N*-methyl-*N*-phenylboranamine.[13] A 20% solution of boranamine in dry hexadecane (distilled from calcium hydride) was placed in a 5-mm Pyrex tube and heated for 100 h at 220 °C. Distillation of the thermolysate in vacuo gave a small amount of an unidentified complex mixture. Most of the material remained as an undistillable oligomer.

Bis(*cis*-2-buten-2-yl)-*N*-methyl-*N*-(2,4,6-trideuteriophenyl)boranamine (8). As described for the preparation of bis(*cis*-2-buten-2-yl)-*N*-methyl-phenylboranamine,[13] but substituting *N*-methyl-2,4,6-trideuterioaniline for *N*-methylaniline, the reaction was carried out on a 40-mmol scale. Distillation of the crude product at reduced pressure through a 7-cm Vigreux column gave 3.0 g (33%) of a colorless liquid: bp 78–79 °C (0.02 torr); NMR (CCl_4) δ 1.40 (br s, 6 H, vinyl methyl), 1.55 (d, J = 6 Hz, 6 H, vinyl methyl), 3.13 (s, 3 H, *N*-methyl), 5.51 (q, J = 6 Hz, 2 H, vinyl), 7.08 (s, 2 H, phenyl); IR (neat film) 3060, 2910, 2865, 2275, 1830, 1620 (vinyl), 1580, 1420, 1380 (B–N), 1255, 1170, 1120, 1085, 1070, 1030, 920, 820, 795, 775, 765, 700, 650 cm^{-1}; UV (Cyclohexane) 292 (ϵ 2040), 240 (ϵ 15 000), 201 (ϵ 31 900) nm.

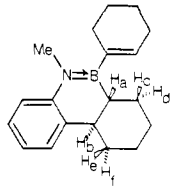
Anal. Calcd for $C_{15}H_{19}D_3BN$: M^+ 230.2031. Found: 230.2051.

2-(2-Buten-2-yl)-1,3,4-trimethyl-3,6,8-trideuterio-1,2,3,4-tetrahydro-1-aza-2-boranaphthalene (10). Into a 5-mm quartz tube was placed 2 mL of a 25% solution of **8** in dry cyclohexane-d_{12} under a nitrogen atmosphere. This sample was irradiated for 30 h with unfiltered light from a 450-W Hanovia medium-pressure mercury lamp and concentrated by vacuum evaporation of the solvent. Distillation of the crude photoproduct through a short-path apparatus gave a colorless liquid: bp 77–79 °C (0.01 torr); NMR (CCl_4) δ 0.6–1.3 (m, 6 H, alkyl methyl), 1.3–1.8 (m, 6 H, vinyl methyl), 2.60 (m, 1 H, benzylic methine), 3.10 (s, 3 H, *N*-methyl), 5.56 (m, 1 H, vinyl), 7.00 (br s, 2 H, phenyl); IR (neat film) 2960, 2930, 2870, 1625 (vinyl), 1595, 1575, 1485, 1450, 1430, 1380, 1290, 1260, 1125, 1100, 1080, 1020, 900, 810, 780, 640 cm^{-1}; UV (cyclohexane) 257 (ϵ 9650), 209 (ϵ 28 400) nm.

Anal. Calcd for $C_{15}H_{19}BD_3N$: M^+ 230.2031. Found: 230.2066.

Irradiation of a Mixture of Bis(*cis*-2-buten-2-yl)-*N*-methyl-*N*-phenylboranamine and Bis(*cis*-2-buten-2-yl)-*N*-methyl-*N*-(2,4,6-trideuteriophenyl)boranamine (8). Into a 13 × 100 mm quartz tube were placed 0.70 g (3.1 mmol) of each boranamine and 5 mL of dry cyclohexane under a nitrogen atmosphere. This sample was irradiated for 35 h with an unfiltered, water-cooled 450-W medium-pressure mercury lamp. The solvent was removed in vacuo, and the remaining clear oil was subjected to mass spectral analysis.

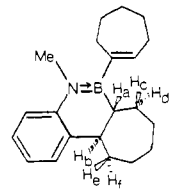
10-(1-Cyclohexenyl)-9-methyl-1,2,3,4,4a-9,10,10a-octahydro-9-aza-10-boraphenanthrene (14). Into a 100-mL quartz tube were placed 6.19 g of 1,1-bis(1-cyclohexenyl)-*N*-methyl-*N*-phenylboranamine (**12**)[13] and 30 mL of dry cyclohexane under a nitrogen atmosphere. This solution was irradiated for 50 h with a 450-W medium-pressure mercury lamp and concentrated by vacuum evaporation of the solvent. Distillation of the crude product through a short-path apparatus gave 4.97 g (81% on the basis of 6.19 g of starting material) of a colorless liquid: bp 157 °C (0.01 torr); NMR (360-MHz, benzene-d_6) δ 0.078 (ddd, J_{ab} = 14.5 Hz,



J_{ad} = 12.8 Hz, J_{ac} = 3.09 Hz, α-boron methine), 1.34 (m), 1.70 (br s), 1.84 (m), 1.95 (m), 2.02 (m), 2.13 (m), 2.34 (m), 3.06 (s, *N*-methyl), 5.60 (m, vinyl), 6.90–7.33 (m, phenyl); IR (neat film) 2920, 2840, 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} (phenyl); UV (cyclohexane) 254 (ϵ 8900), 208 (ϵ 26 900) nm.

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

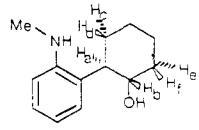
2-(1-Cycloheptenyl)-1-methyl-3,4-cyclohepta-1,2,3,4-tetrahydro-1-aza-2-boranaphthalene (15). A 5-mm quartz tube containing a 25% solution of bis(1-cycloheptenyl)-*N*-methyl-*N*-phenylboranamine (**13**)[13] in dry cyclohexane under nitrogen was irradiated for 20 h with a 450-W medium-pressure mercury lamp. Distilltion of the crude photoproduct through a molecular still gave a clear liquid: NMR (360-MHz, CCl_4) δ 0.77 (ddd, J_{ab} = 15 Hz, J_{ad} = 10 Hz, J_{ac} = 2.0 Hz, 1 H, α-boron



methine), 1.20–2.25 (complex m, 20 H), 2.53 (dt, J_{ba} = 15 Hz, J_{be} = J_{bf} = 5.6 Hz, 1 H, benzylic methine), 3.02 (s, 3 H, *N*-methyl), 5.74 (t, J = 7 Hz, vinyl), 6.80–7.25 (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.

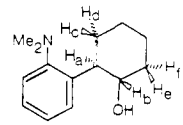
Anal. Calcd for $C_{21}H_{30}BN$: M^+ 307.2471. Found: 307.2473.

2-(*o*-(Methylamino)phenyl)cyclohexanol (16).[13] NMR (360-MHz, benzene-d_6) δ 1.10 (m, 2 H), 1.33 (m, 2 H), 1.51 (m, 1 H), 1.61 (m, 2 H), 1.97 (m, 1 H), 2.44 (s, 3 H, *N*-methyl), 2.55 (dt, J_{ab} = 10.1 Hz, J_{ad}



= 10.1 Hz, J_{ac} = 3.5 Hz, 1 H, benzylic methine), 3.31 (dt, J_{ba} = 10.1 Hz, J_{be} = 10.1 Hz, J_{bf} = 4.2 Hz, 1 H, hydroxy methine), 6.58–7.22 (m, 4 H, phenyl).

2-(*o*-(Dimethylamino)phenyl)cyclohexanol (17).[25] NMR (360-MHz, benzene-d_6) δ 1.14–1.71 (m, 6 H), 1.77 (m, 1 H), 2.19 (m, 1 H), 2.64 (s, 6 H, *N*-methyl), 3.32 (dt, J_{ab} = 10.1 Hz, J_{ac} = 10.1 Hz, J_{ad} = 4.2 Hz,



1 H, benzylic methine), 3.54 (dt, J_{ba} = 10.1 Hz, J_{bf} = 10.1 Hz, J_{be} = 3.5 Hz, 1 H, α-hydroxy methine), 6.78–7.28 (m, 4 H, phenyl).

Bis(1-deuterio-*trans*-3,3-dimethyl-1-buten-1-yl)-*N*-methyl-*N*-phenylboranamine (22). Into a dry 250-mL, single-necked round-bottom flask equipped with an additional funnel were placed 1.64 g (0.200 mol) of *tert*-butylacetylene (Farchan) and 100 mL of anhydrous diethyl ether under a nitrogen atmosphere. This mixture was immersed in an ice bath, and 75 mL of *n*-butyllithium (2.68 M solution in *n*-hexane, Alfa Ventron, 0.20 mol) was added dropwise. The reaction was allowed to warm to room temperature for 1 h and was recooled to 0 °C. The slow addition of 30 mL of deuterium oxide (Bio Rad, 99.8 atom % D) produced a vigorous reaction and a white precipitate. After 3 h at room temperature, the reaction mixture was distilled into a receiver cooled to −78 °C. The distillation was discontinued at a head temperature of 70 °C, and the distillate was used directly in the next step.

A dry 1-L, three-necked Morton flask was equipped with a mechanical stirrer, 300-mL graduated addition funnel, and nitrogen inlet. The ethereal deuterioacetylene solution prepared above was placed in the flask, immersed in an ice bath, and 100 mL of the monochloroborane (0.79 M solution in diethyl ether, 0.079 mol) added as rapidly as possible without causing the solvent to boil. The reaction mixture was stirred for 1 h at 0 °C and 1 h at room temperature. After dilution with anhydrous ether to a total volume of 500 mL, 8.45 g (0.079 mol) of *N*-methylaniline in 50 mL of anhydrous diethyl ether was added dropwise at 0 °C. This was followed immediately with the rapid addition of 7.98 g (0.079 mol) of dry triethylamine (Aldrich) in 50 mL of anhydrous diethyl ether. The reaction mixture was stirred overnight at room temperature, filtered with suction through an oven-dried sintered-glass funnel in a nitrogen-filled glove box, and concentrated by evaporation of the solvent at reduced pressure. The resulting cloudy, viscous liquid was diluted with 25 mL of dry *n*-pentane, filtered, and concentrated as described above. The crude product was distilled twice through a 7-cm Vigreux column, giving 4.4 g (22%) of a colorless liquid: bp 92 °C (0.03 torr); NMR (CCl_4) δ 1.00 (br s, 18 H, *t*-Bu), 3.20 (s, 3 H, *N*-methyl), 6.05 (br s, 2 H, vinyl), 7.10 (m, 5 H, phenyl); IR (neat film) 3060, 3030, 2960, 2940, 2910, 2210

(25) Lepley, A. R.; Dohn, V. C.; Giumanini, A. G. *J. Org. Chem.* **1969**, *34*, 3042–6.

(C–D), 1600, 1490, 1455, 1425, 1370 (B–N), 1300, 1250, 1200, 1165, 1115, 1060, 1030, 1020, 925, 910, 770 (phenyl), 740, 695 (phenyl) cm^{-1}.

Anal. Calcd. for $C_{19}H_{28}D_2BN$: M^+ 285.2597. Found: 285.2607.

Bis(3,3-dimethyl-*trans*-1-buten-1-yl)-*N*-methyl-*N*-(2,4,6-trideuteriophenyl)boranamine (23). Prepared as described for 1,1-bis(3,3-dimethyl-*trans*-1-buten-1-yl)-*N*-methyl-*N*-phenylboranamine,[13] but substituting *N*-methyl-2,4,6-trideuterioaniline[15] for *N*-methylaniline, the crude product was distilled at reduced pressure through a 7-cm Vigreux column, giving 2.0 g (15%) of a colorless liquid: bp 94 °C (0.01 torr); NMR (CCl_4) δ 1.00 (br s, 18 H, *t*-Bu), 3.21 (s, 3 H, *N*-methyl), 5.50 (br m, 2 H, vinyl), 6.10 (br d, J = 18 Hz, 2 H, vinyl), 7.20 (s, 2 H, phenyl); IR (neat film) 3075, 2975, 2925, 2890, 2300 (C–**D**), 2210 (C–**D**), 1820 (C–D), 1620, 1549, 1480, 1453, 1430, 1365, 1323, 1290, 1265, 1225, 1180, 1130, 1090, 1060, 1030, 1000, 914, 900, 838, 808, 718, 692, 670, 637 cm^{-1}.

Anal. Calcd for $C_{19}H_{27}D_3BN$: M^+ 286.2660. Found: 286.2677.

2-(3,3-Dimethyl-1-buten-1-yl)-4-*tert*-butyl-1-methyl-3,6,8-trideuterio-1,2,3,4-tetrahydro-1-aza-2-boranaphthalene (25). Into a 5-mm quartz tube was placed a 25% solution of bis(3,3-dimethyl-1-buten-1-yl)-*N*-methyl-*N*-(2,4,6-trideuteriophenyl)boranamine (**23**) in cyclohexane under a nitrogen atmosphere. This solution was irradiated for 140 h with a 450-W medium-pressure mercury lamp and concentrated by vacuum evaporation of the solvent. Distillation of the crude product through a molecular still gave a colorless liquid: bp 100–102 °C (0.01 torr); NMR (360-MHz, benzene-d_6) δ 0.90, 0.94, 1.01, 1.11 (four s, 18 H, *t*-Bu), 1.22 (d, J = 8 Hz, α-boron methine, *trans*-vinyl isomer), 2.54 (d, J = 8 Hz, benzylic methine, *cis*-vinyl isomer), 2.62 (d, J = 8 Hz, benzylic methine, *trans*-vinyl isomer), 2.95 and 2.89 (pair of s, 3 H, *N*-methyl), 5.74 and 5.95 (AB q, J = 15 Hz, *cis*-vinyl), 6.70 and 6.95 (AB q, J = 18 Hz, *trans*-vinyl), 7.05–7.17 (m, 2 H, phenyl); IR (neat film) 3023, 2980, 2905, 2865, 1620, 1590, 1475, 1450, 1427, 1380, 1360, 1320, 1300, 1270, 1250, 1185, 1125, 1080, 1048, 1035, 995, 900, 860, 830, 795, 705 (phenyl), 680, 660, 620 cm^{-1}.

Anal. Calcd for $C_{19}H_{27}D_3BN$: M^+ 286.2660. Found: 286.2626.

2-(1-Deuterio-3,3-dimethyl-1-buten-1-yl)-4-*tert*-butyl-1-methyl-3-deuterio-1,2,3,4-tetrahydro-1-aza-2-boranaphthalene (24). A 25% solution of bis(1-deuterio-3,3-dimethyl-1-buten-1-yl)-*N*-methyl-*N*-phenylboranamine (**22**) in cyclohexane was placed in a 5-mm quartz tube under a nitrogen atmosphere. This solution was irradiated for 135 h with a 450-W medium-pressure mercury lamp and concentrated by vacuum evaporation of the solvent. The crude photoproduct was distilled through a molecular distillation apparatus to yield a clear liquid: NMR (360-MHz, benzene-d_6) δ 0.89, 0.95, 1.02, 1.11 (four s, 18 H, *t*-Bu), 1.66 (d, J = 2.4 Hz, α-boron methine, *cis*-vinyl isomer), 1.93 (d, J = 2.4 Hz, α-boron methine, *trans*-vinyl isomer), 2.54 (d, J = 2.4 Hz, benzylic methine, *cis*-vinyl isomer), 2.61 (d, J = 2.4 Hz, benzylic methine, *trans*-vinyl isomer), 2.96 and 2.98 (pair of s, 3 H, *N*-methyl), 6.15 (s, *cis*-vinyl), 6.74 (s, *trans*-vinyl), 6.87–7.25 (m, 4 H, phenyl); IR (neat film) 2960, 2920, 2870, 1600, 1475, 1425, 1375, 1360, 1265, 1180, 1120, 1060, 1045, 1035, 995, 970, 925, 855, 790, 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.

Anal. Calcd for $C_{19}H_{28}D_2BN$: M^+ 285.2597. Found: 285.2604.

Variable-Temperature 360-MHz NMR Experiment on 2-(3,3-Dimethyl-1-buten-1-yl)-4-*tert*-butyl-1-methyl-3,6,8-trideuterio-1,2,3,4-tetrahydro-1-aza-2-boranaphthalene (25) and 2-(1-Deuterio-3,3-dimethyl-1-buten-1-yl)-4-*tert*-butyl-1-methyl-3-deuterio-1,2,3,4-tetrahydro-1-aza-2-boranaphthalene (24). A ca. 25% solution of azaboranaphthalene in toluene-d_8 was placed in a Pyrex NMR tube. The 360-MHz NMR spectra were recorded at −50, −20, 10, and 50 °C. No significant change was observed in the coupling constants between the proton α to boron and the benzylic proton.

360-MHz NMR Data for 2-(2-Buten-2-yl)-1,3,4-trimethyl-1,2,3,4-tetrahydro-1-aza-2-boranaphthalene (28).[13] NMR (CD_2Cl_2) δ 0.77, 0.80, 0.84, 0.94 (four d, J = 7.0 Hz, 3 H, methyl α to boron), 1.10, 1.12, 1.14, 1.15 (four d, J = 7.0 Hz, 3 H, benzylic methyl), 1.30, 1.42 (complex m, 1 H, α to boron methine), 1.56, 1.74 (complex m, 6 H, vinyl methyl), 2.57, 2.76 (pair of dt, J_{ab} = 6.5 Hz, J_{ac} = 6.5 Hz, 1 H, benzylic methine, pair of dt results from the presence of *E* and *Z* vinyl isomers), 3.14, 3.15, 3.16 (three s, 3 H, *N*-methyl), 5.49, 5.62 (pair of m, 1 H, *E* and *Z* vinyl protons), 7.08 (m, 4 H, phenyl). This sample was subjected to a low-temperature NMR experiment with spectra recorded at room temperature −10, −20, −30, −40, −50, −60, −70, −80, and −90 °C.

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Registry No. 7, 83721-07-7; **8**, 83721-08-8; (*Z*)-**9b**, 83720-45-0; (*E*)-**9b**, 83721-10-2; **10**, 83721-09-9; **12**, 83720-54-1; **13**, 83720-55-2; **14**, 83721-11-3; **15**, 83721-12-4; **16**, 83721-13-5; **17**, 83731-21-9; **18**, 83721-05-5; **19**, 83721-14-6; **20**, 83731-20-8; **21**, 83720-59-6; **22**, 83731-22-0; **23**, 83721-15-7; **24**, 83721-16-8; **25**, 83721-17-9; **28a**, 83721-18-0; **28b**, 83721-19-1; 4-bromobiphenyl, 92-66-0; bis(*trans*-1-buten-1-yl)-*N*-methyl-*N*-phenylboranamine, 83721-06-6; *tert*-butylacetylene, 917-92-0; monochloroborane, 10388-28-0; *N*-methylaniline, 100-61-8.