molar ratio[27] Eu(hfc)$_3$/(2*R*)-1α 0.22, *c* (1α) 0.58 M, 1.2-ml solution in a 12-mm o.d. NMR tube with a vortex plug; (2*S*)-1α (120 mg), molar ratio Eu(hfc)$_3$/(2*S*)-1α 0.29, *c* (2*S*)-1α 2.2 M, 320 μl total solution in a 5-mm o.d. NMR tube; (2*R*)-1α (78 mg), molar ratio Eu(hfc)$_3$/(2*R*)-1α 0.26, *c* (2*R*)-1α 2.5 M, 185 μl total solution in a 5-mm o.d. tube.

The ^{13}C NMR spectra were obtained by pulsed Fourier transform NMR as follows: broad-band (noise modulated) ^{1}H decoupling, pulse width 78 μs, acquisition time 0.8 s, no pulse delay; transients, (racemic 1α) 62K; (2*R*)-1α 232K; (2*S*)-1α 71K. The changes in chemical shifts for the C-1 signals[28] in the presence of Eu(hfc)$_3$ were racemic 1α, $\Delta\delta$ 16.9, $\Delta\Delta\delta$ 1.9 ppm; (2*S*)-1$\alpha\Delta\delta$ 14.9, $\Delta\Delta\delta$ 1.6 ppm.

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Registry No.—(±)-1α, 54815-06-4; (−)-1α, 59014-03-8; (+)-1α, 59014-04-9; (±)-1β, 54832-20-1; (−)-1β, 59014-05-0; (+)-1β, 59014-06-1; (±)-1γ, 54832-21-2; (−)-1γ, 54832-22-3; (+)-1γ, 59014-07-2; (±)-1δ, 59014-08-3; (−)-1δ, 59014-09-4; (+)-1δ, 59014-10-7; (±)-**5**, 50304-40-0; (2*S*)-(+)-**5**, 59014-11-8; (2*R*)-(−)-**5**, 20626-49-7; **6**, 59014-12-9; **7**, 58977-11-0; **8**, 6125-73-1; **10** isomer I, 58977-12-1; **10** isomer II, 58977-13-2; **11**α, 58977-14-3; **11**β, 59014-13-0; **11**γ, 59014-14-1; **11**δ, 59014-15-2; **15**, 58977-15-4; **16**, 59014-16-3; **20**, 58977-16-5; **21**, 58977-17-6; tosyl chloride, 98-59-9; 3-pentanone, 96-22-0; cyclohexylamine, 108-91-8; (+)-α-methylbenzylamine, 3886-69-9; (−)-α-methylbenzylamine, 2627-86-3.

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(26) The chemical ionization mass spectra were run by Dr. J. Henion and his staff at the Department of Chemistry, Cornell University, Ithaca, N.Y. The system was a Finnigan Model 3300 GC-MS, GC Model 9500, interfaced with a Systems Industries 150 computer.
(27) The optimum molar ratio [Eu(hfc)$_3$/1α] for obtaining good enantiomeric separation was determined by previous runs at (E/1α) = 0.024 and 0.14.
(28) The assignment of the ^{13}C signals of 1α–γ will be discussed in a later publication.

Synthesis and Competitive Mechanism of Formation of Phenyl-Substituted 1,2-Azaborolidines and 1-Aza-5-borabicyclo[3.3.0]octanes[1]

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1,5-Diphenyl-1-aza-5-borabicyclo[3.3.0]octane, 1,2-diphenyl-1,2-azaborolidine, and propene were isolated as the major products of the reaction of triethylamine phenylborane with *N,N*-diallylaniline. These compounds were characterized by nuclear magnetic resonance, infrared, mass spectroscopy, and elemental analyses. Two mechanisms were proposed for the formation of propene and 1,2-diphenyl-1,2-azaborolidine. Triethylamine dideuteriophenylborane reacted with *N,N*-diallylaniline to give 3,7-dideuterio-1,5-diphenyl-1-aza-5-borabicyclo[3.3.0]octane, 3-deuterio-1,2-diphenyl-1,2-azaborolidine, and 3-deuteriopropene. These products are consistent with one of the proposed mechanisms, a concerted, facile elimination of propene. This elimination mechanism was supported by model studies of the transition states. Triethylamine phenylborane reacted with *N,N*-di-3-butenylaniline to give 1,2-diphenyl-1-(3-butenyl)-2-hydroazaboracyclohexane and 1,6-diphenyl-1-aza-6-borabicyclo[4.4.0]decane. No butene gas was eliminated, giving further support for the proposed mechanism. Several substituted derivatives of 1,5-diphenyl-1-aza-5-borabicyclo[3.3.0]octane and 1,2-diphenyl-1,2-azaborolidine were also prepared and characterized.

Previous studies[2,3] in our laboratories showed that the reaction of triethylamine phenylboranes with tertiary diallylamines yielded a new class of compounds, 1-aza-5-borabicyclo[3.3.0]octanes, as well as 1,2-azaborolidines. The formation of the azaborolidines was thought to occur with elimination of an allyl group from nitrogen, although no attempt was made to trap the evolved propene in the earlier work. We would now like to report mechanistic studies on this

Table I

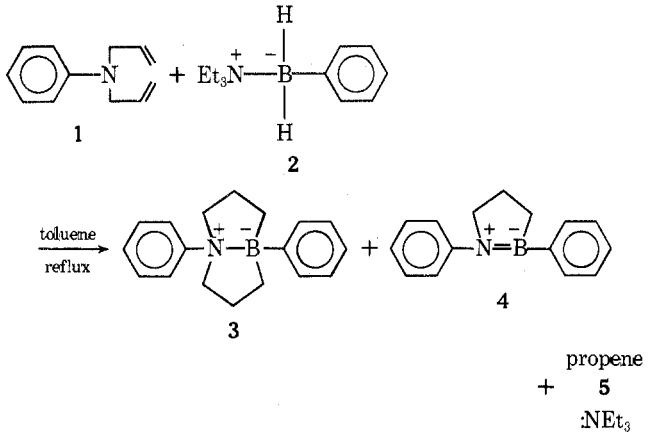
Compd	Name	Formula	%	Mp or bp, °C (mm)	Chemical shift	Anal., %
3	1,5-Diphenyl-1-aza-5-borabicyclo-[3.3.0]octane	$C_{18}H_{22}BN$	51	80–81 (mp)	6.85 (10) 3.3 (4) 2.1 (4) 1.1 (4)	Calcd: C, 82.13; H, 8.42; N, 5.32; B, 4.11 Found: C, 82.15; H, 8.51; N, 5.41; B, 4.21
18	3-Deuterio-1,2-diphenyl-1,2-azaborolidine	$C_{15}H_{15}DBN$	42	50–54 (0.15 mm) (bp)	7.15 (10) 3.75 (2) 2.0 (1) 1.65 (2)	
20	3,7-Dideuterio-1,5-diphenyl-1-aza-4-borabicyclo[3.3.0]octane	$C_{18}H_{20}D_2BN$	53	78–79 (mp)	7.0 (10) 3.45 (4) 2.15 (2) 1.1 (4)	Calcd: C, 81.52; H, 7.60; C, 1.52; N, 5.28; B, 4.08 Found: C, 81.74; N, 5.18; B, 4.20
29	1-(4-Bromophenyl)-5-phenyl-1-aza-5-borabicyclo[3.3.0]octane	$C_{18}H_{21}BNBr$	41	116–118 (mp)	6.9 (9) 3.3 (4) 2.1 (4) 1.1 (4)	Calcd: C, 63.19; H, 6.19; N, 4.09; B, 3.16; Br, 23.36 Found: C, 63.11; H, 6.29; N, 3.96; B, 2.90; Br, 23.24
39	1,2-Diphenyl-1,2-azaborolidine	$C_{15}H_{16}BN$	44	84–86 (0.30 mm) (bp)	7.2 (10) 3.8 (2) 1.8 (4)	Calcd: C, 81.47; H, 7.29; N, 6.34; B, 4.89 Found: C, 81.42; H, 7.31; N, 6.21; B, 5.01
40	1-(4-Bromophenyl)-2-phenyl-1,2-azaborolidine	$C_{15}H_{15}BNBr$	53	120–123 (0.15 mm) (bp)	7.2 (9) 3.8 (2) 1.7 (4)	Calcd: C, 60.03; H, 5.04; N, 4.67; B, 3.61; Br, 26.65 Found: C, 60.14; H, 5.12; N, 4.58; B, 3.64; Br, 26.52

novel elimination as well as details of the synthesis of several of these phenyl-substituted compounds.

Results and Discussion

Equimolar quantities of triethylamine phenylborane (**2**) and *N,N*-diallylaniline (**1**) were dissolved in toluene and slowly heated (Scheme I). Gas samples from the reaction, as

Scheme I

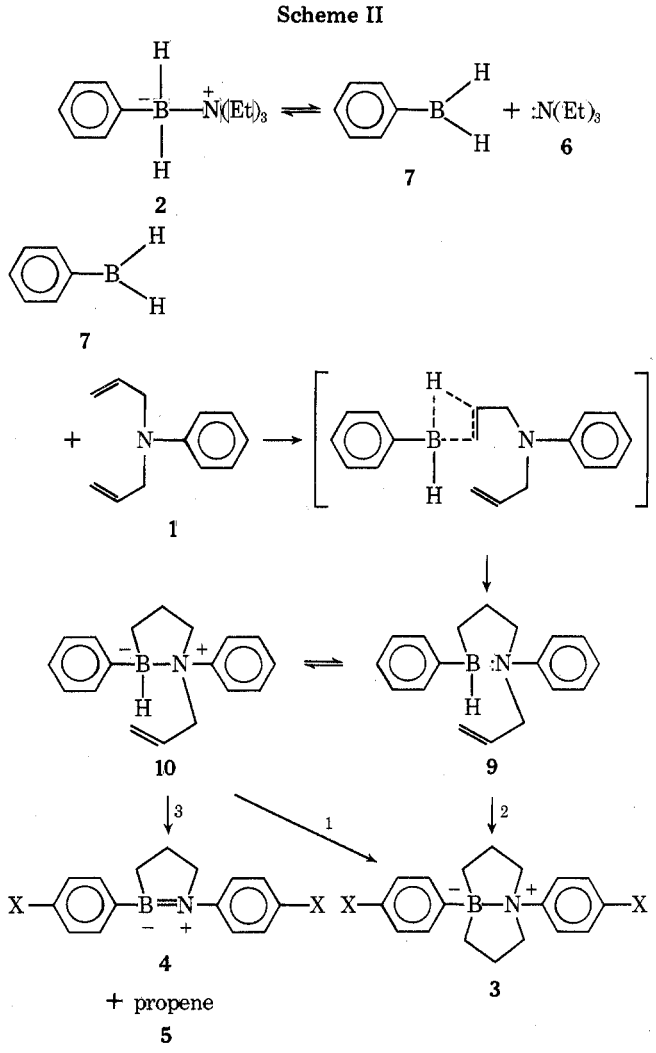


well as solution samples, were monitored by infrared spectroscopy over the temperature range 26–110 °C. The boron–hydrogen bond absorbance at 2340 cm^{-1} was monitored, and it was found that the initial hydroboration occurred near 50 °C. Little change in the intensity was noted up to 95 °C at which point the B–H intensity decreased with time. The infrared spectra began to show traces of propene as indicated by the broad, spiked peak at 910 cm^{-1}. Two products, a colorless liquid and a white solid,[3] were isolated and characterized. A small amount of apparently polymeric, viscous material was also formed; however, attempts to characterize this material were unsuccessful. The liquid was identified as 1,2-diphenyl-1,2-azaborolidine[3] (**4**) and the solid as 1,5-diphenyl-1-aza-5-borabicyclo[3.3.0]octane[3] (**3**).

Several para-substituted derivatives of 1,2-diphenyl-1,2-azaborolidine (**4**) and 1,5-diphenyl-1-aza-5-borabicyclo-[3.3.0]octane (**3**) were prepared by modification of the above procedure as described in the Experimental Section. Physical properties, analyses, and spectral data are given in Table I for selected compounds.[8]

A general mechanism for the formation of **3** and **4** is outlined in Scheme II. The triethylamine phenylborane (**2**) is postu-

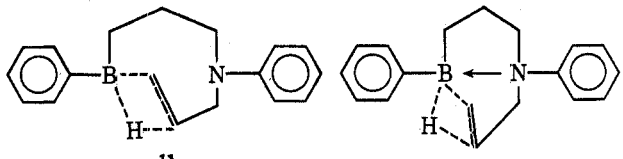
Scheme II



lated to dissociate in solution to give the free phenylborane 7 and triethylamine.

One of the allyl groups of the *N,N*-diallylaniline (1) is hydroborated to give the uncoordinated intermediate 9 which would be expected to exist in equilibrium with its coordinated form 10. The initial hydroboration likely occurs after coordination of the free phenylborane (7) with *N,N*-diallylaniline (1).

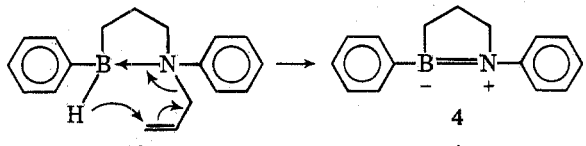
Competitive pathways (Scheme II) could yield products 3 and 4. The 1,5-diphenyl-1-aza-5-borabicyclo[3.3.0]octane (3) could be formed by a second hydroboration with boron adding to the terminal end of the remaining double bond. This might occur by either pathway 1 or pathway 2. Brown[4] has proposed a four-centered transition state for the general process of hydroboration. Following this proposal, the transition state (11) for the coordinated form would be much less favorable than that of the uncoordinated form (12). This, of course, is



11 12

the result of the additional strain imposed by the coordinate bond. Therefore, the second hydroboration should occur along pathway 2.

The formation of the 1,2-diphenyl-1,2-azaborolidine (4) is accompanied by the elimination of propene (5). Amine boranes have been reported to dealkylate at high temperatures under vacuum.[5] This system, however, appears to be a special one which allows for very facile propene elimination at relatively low temperatures, atmospheric pressure, and mild conditions. The coordinated intermediate (10) is well suited for a concerted elimination of propene as shown below:

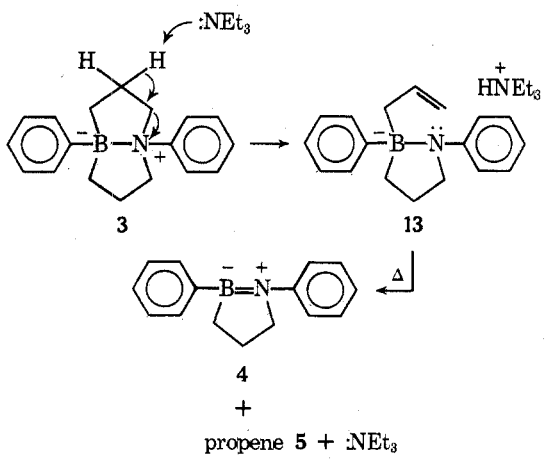


10 → 4 + propene 5

A six-membered transition state would allow for a relatively strain-free addition of hydrogen to the terminal end of the double bond of the allyl group and the ensuing electron shifts.

A second mechanism which might lead to formation of the 1,2-diphenyl-1,2-azaborolidine (4) is given in Scheme III. The

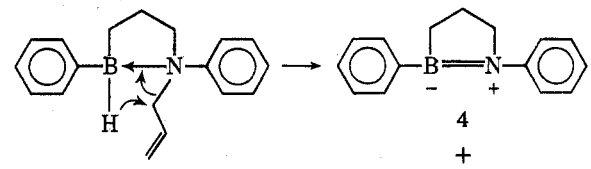
Scheme III



3 → 13 → 4 + propene 5 + :NEt$_3$

triethylamine in the refluxing reaction solution could act as the base in a Hofmann-type elimination, abstracting a proton of the 1,5-diphenyl-1-aza-5-borabicyclo[3.3.0]octane (3) at either of the two carbon atoms in the β position to the quaternary ammonium group. The resulting allylborane (13) then could conceivably undergo thermal cleavage to give 1,2-diphenyl-1,2-azaborolidine (4). Alkylboranes have been reported to undergo this type of cleavage.[6]

A third mechanism for formation of 4 could be proposed involving a four-centered reduction of the allyl group of intermediate 10 as shown below:

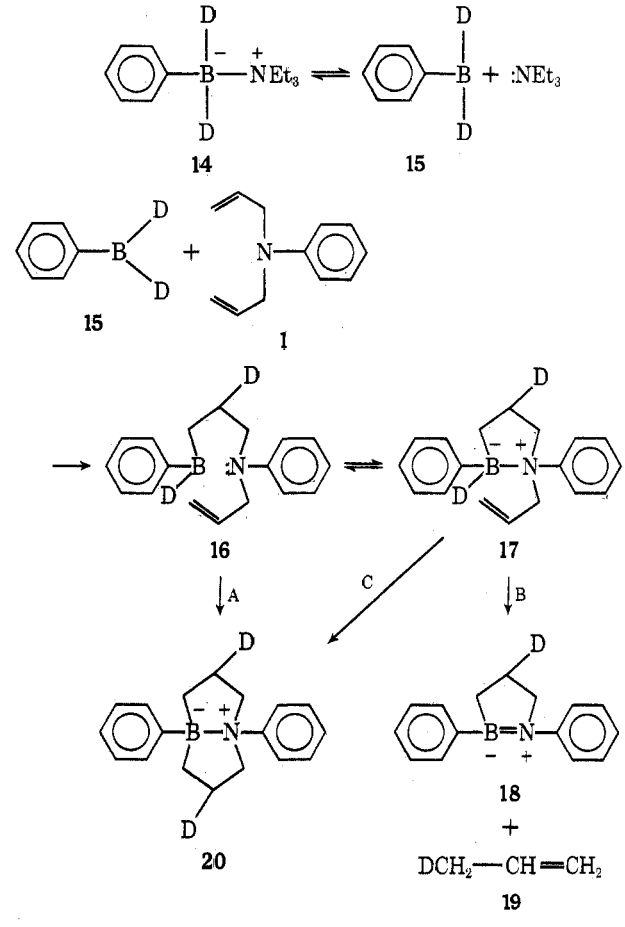


10 → 4 + propene 5

Two separate studies were necessary to give strong support to one of these mechanisms.

Deuterium labeling studies should distinquish quite clearly between the first two proposed mechanisms. The proposed concerted mechanism is shown in Scheme IV. The triethyl-

Scheme IV



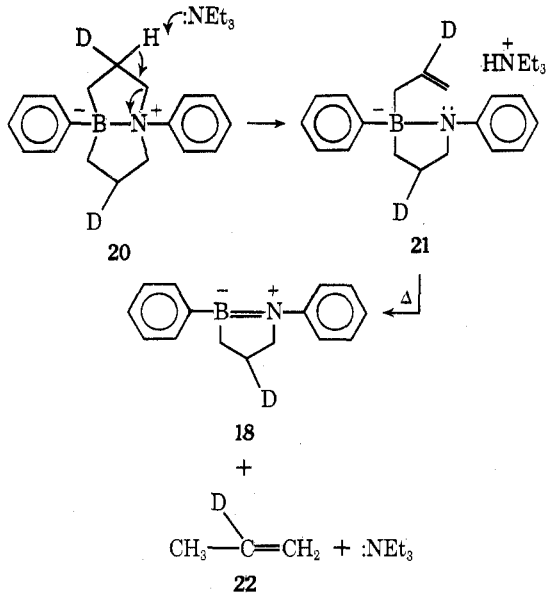
14 ⇌ 15 + :NEt$_3$; 15 + 1 → 16 ⇌ 17; 16 → (A) 20; 17 → (B) 18 + DCH$_2$—CH=CH$_2$ 19; (C)

amine dideuteriophenylborane (14) would dissociate to give the free dideuteriophenylborane (15) which would undergo an initial deuterioboration to give intermediate 16. An equilibrium would exist between the dissociated form (16) and the coordinated form (17). Note that the deuterium is in the 2 position of the ring. A second deuterioboration through pathway A would lead to the dideuterated bicyclic product (20). A concerted elimination, with deuterium adding to the

terminal end of the double bond in intermediate **17** and the ensuing electron shifts, would yield the monodeuterated azaborolidine (**18**) and 3-deuteriopropene (**19**).

The proposed Hofmann elimination mechanism is shown in Scheme V. Triethylamine would attack **20** at hydrogen or

Scheme V



deuterium on the β carbon to nitrogen. Abstraction of a proton should be favored over deuterium abstraction, owing to an isotope effect. Intermediate **21** could then undergo thermal cleavage to give the monodeuterated azaborolidine (**18**) and 2-deuteriopropene (**22**). If deuterium were abstracted rather than proton, propene gas would be generated.

Triethylamine dideuteriophenylborane (**14**) was prepared by reducing diethyl phenylboronate with lithium aluminum deuteride in ether with triethylamine at low temperature. The triethylamine dideuterioborane structure (mp 64–65 °C, 84%) was characterized by mass spectral, NMR, ir, and elemental analyses. The infrared spectrum showed a broad boron–deuterium absorbance at 1680–1765 cm^{-1}.

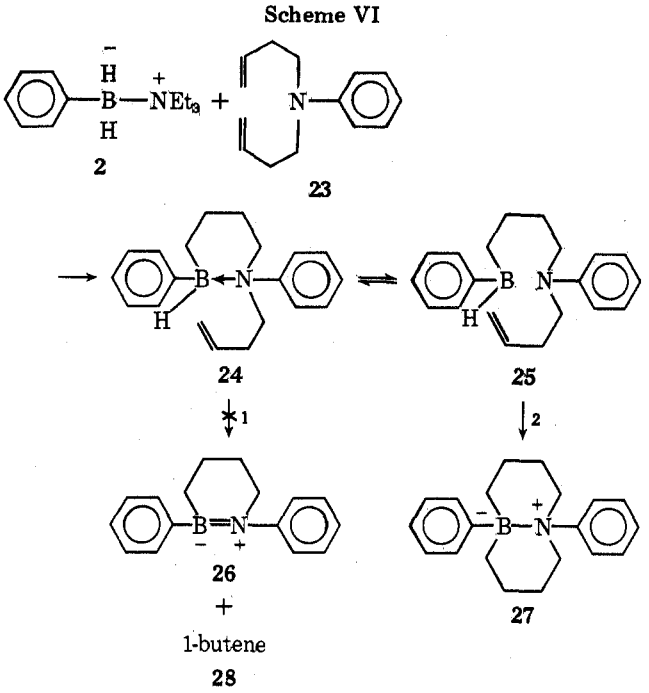
N,N-Diallylaniline (**1**) was added to an equimolar quantity of the triethylamine dideuteriophenylborane (**14**) in *p*-xylene. Above 95 °C deuteriopropene was evolved. The infrared absorbance at 2175 cm^{-1} was consistent with that expected for the allylic carbon–deuterium stretching frequency. NMR, ir, and mass spectral evidence conclusively identified the gas as 3-deuteriopropene rather than 2-deuteriopropene. Final confirmation of structure came from generation of 3-deuteriopropene from the reaction of allylmagnesium bromide with D_2O. The NMR and ir spectra were identical with those of the reaction product.

The structure of 3-deuterio-1,2-diphenyl-1,2-azaborolidine (**18**) was confirmed by mass, NMR, and ir spectra. The structure of **20** was also confirmed by spectral data and elemental analyses (Table I).

Further evidence against the second mechanism (Hofmann-type elimination) was that no propene gas could be generated by heating **3** in toluene with triethylamine; **3** was recovered quantitatively.

Evidence supporting the concerted elimination of propene through a six-centered transition state (Scheme II, path 3) over a four-centered elimination was obtained by the model reaction of *N,N*-di-(3-butenyl)aniline (**23**) with triethylamine phenylborane (**2**) as outlined in Scheme VI. This reaction would be expected to yield 1,6-diphenyl-1-aza-6-borabicyclo[4.4.0]decane (**27**). 1,2-Diphenylazaboracyclohexane (**26**) should not be formed by a concerted mechanism as was the case for the azaborolidines in the previous studies. This compound could, however, conceivably be formed by a four-centered mechanism. The elimination could be tested, as before, by monitoring gases produced from the reaction in *p*-xylene. If the competing pathway 1 (Scheme VI) were followed at the reaction temperature, butene gas would be detected. If only pathway 2 were followed, the bicyclic compound should be formed in relatively higher yield.

Scheme VI



N,N-Di-3-butenylaniline (**23**), triethylamine phenylborane (**2**), and *p*-xylene were slowly heated under nitrogen. Gas samples were taken at various temperatures and time intervals. A bright-green color developed during heating, but no butene gas was evolved during the course of the reaction. A white, crystalline solid was isolated; spectral and analytical results were consistent with the structure of 1,6-diphenyl-1-aza-6-borabicyclo[4.4.0]decane. A second fraction yielded ir and NMR data consistent with the structure 1,2-diphenyl-1-(3-butenyl)-2-hydroazaboracyclohexane (**25**). Spectral data and elemental analyses of these products are detailed in the Experimental Section.

These results offer strong support to the proposed mechanism for facile, concerted elimination of propene in the competitive formation of 1,5-diphenyl-1-aza-5-borabicyclo-[3.3.0]octanes (**3**) and 1,2-diphenyl-1,2-azaborolidine (**4**) (Scheme II).

Experimental Section

Equipment and Data. Nuclear magnetic resonance (NMR) spectra were obtained with a Varian A-60A analytical NMR spectrometer. Chemical shifts were measured in deuteriochloroform, unless otherwise specified, relative to tetramethylsilane. Infrared (ir) spectra were obtained with a Beckman IR-8 infrared spectrophotometer. ^{11}B NMR spectra were obtained with a Varian XL-100 high-resolution NMR spectrometer. Mass spectra were obtained with a Hitachi Perkin-Elmer RMU mass spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc. Knoxville, Tenn.

Syntheses of Para-Substituted *N,N*-Diallylanilines. The general procedure for preparation of substituted diallylanilines was a slight modification of that of Butler and Bunch.[7]

Preparation of *N,N*-Di-3-butenylaniline. Aniline (14.0 g, 0.15 mol), sodium carbonate (32.0 g), and 50 ml of water were placed in a 250-ml, three-necked, round-bottomed flask equipped with a me-

chanical stirrer, addition funnel, and cold-water condenser. The mixture was heated to reflux and 4-bromo-1-butene (40 g, 0.30 mol) added dropwise with constant stirring. The reaction was allowed to proceed for 24 h after which the contents were cooled and filtered. The amine layer was separated, dried over sodium sulfate, and distilled under vacuum. A clear, colorless liquid (11.2 g, 37%) was obtained [bp 74–75 °C (0.10 mm)].

Syntheses of Triethylamine Phenylboranes. Para-substituted triethylamine phenylboranes were prepared by modifications of the method of Statton and Butler.[2]

1,2-Diphenyl-1,2-azaborolidine (4) and 1,5-Diphenyl-1-aza-5-borabicyclo[3.3.0]octane (3). These compounds were prepared for purposes of this study by use of the procedure reported by Butler, Statton, and Brey[3] with slight modifications. The spectral data agreed with the literature assignments[3] for these compounds.

A typical procedure for the para-substituted derivatives is given below. (See supplemental tables for other compounds.)

1-(4-Bromophenyl)-2-phenyl-1,2-azaborolidine (28) and 1-(4-Bromophenyl)-5-phenyl-1-aza-5-borabicyclo[3.3.0]octane (29). Triethylamine phenylborane (19.3 g, 0.1 mol) 25.2 g (0.1 mol) of *p*-bromo-*N,N*-diallylaniline, and 1.25 l. of toluene were placed in a 2-l. round-bottomed flask. The toluene was slowly distilled from the flask through a fractionating column. Upon initial heating, the contents of the flask turned bright yellow-green. When the temperature at the distilling head reached 120 °C, the residual green liquid was transferred to a 50-ml round-bottomed flask and distilled on a spinning band column. The lower boiling fraction was a clear to pale yellow, viscous liquid, bp 120–123 °C (0.15 mm), yield 7.8 g. NMR and ir data were consistent with those expected for the azaborolidine (Table III).

The higher boiling fraction, bp 130–132 °C (0.15 mm), was dissolved in acetone and cooled in a dry ice–2-propanol bath to yield 6.7 g of a crystalline compound, mp 116–118 °C. The ir, NMR, and mass spectra and elemental analysis were consistent with the structure 1-(4-bromophenyl)-5-phenyl-1-aza-5-borabicyclo[3.3.0]octane (Tables I and II).

Preparation of Dideuteriophenylborane Triethylamine (14). Lithium aluminum deuteride (3.36 g, 0.08 mol) was added to 200 ml of anhydrous diethyl ether (distilled from lithium aluminum hydride) in a three-necked, 500-ml, round-bottomed flask equipped with mechanical stirrer, addition funnel, condenser with drying tube, low-temperature thermometer, and nitrogen inlet tube. The lithium aluminum deuteride–ether mixture was refluxed for 20 min and then cooled to −72 °C in a dry ice–2-propanol bath. Triethylamine (15.2 g, 0.15 mol) was added in one portion. Diethyl phenylborane (19.0 g, 0.107 mol) was added dropwise with stirring; the temperature was kept below −65 °C during the entire addition. The mixture was allowed to stir until it had warmed to room temperature. The resulting mixture was filtered through a sintered glass funnel to remove the excess lithium aluminum deuteride. The filtrate was cooled in a dry ice–2-propanol bath. White, needlelike crystals of dideuteriophenylborane triethylamine, 17.5 g (84%), were filtered and dried (mp 64–65 °C). The infrared spectrum showed a strong absorbance at 1765 cm^{-1} which was assigned to the B–D stretching frequency. The NMR spectrum exhibited resonances at δ 1.2 (t, 9), 2.75 (quartet, 6), and 7.3 (m, 5). Anal. Calcd for $C_{12}H_{20}D_2BN$: C, 74.63; H, 10.44; N, 7.25; B, 5.60; D, 2.08. Found: C, 73.05; H, 11.12; N, 6.31; B, 5.83.

Preparation and Isolation of 3,7-dideuterio-1,5-diphenyl-1-aza-5-borabicyclo[3.3.0]octane (20), 3-Deuterio-1,5-diphenyl-1,2-azaborolidine (18), and 3-Deuteriopropene (19). Dideuteriophenylborane triethylamine (15.6 g, 0.08 mol), *N,N*-diallylaniline (13.8 g, 0.08 mol), and *p*-xylene (300 ml) were placed in a three-necked, 1-l., round-bottomed flask equipped with a mechanical stirrer, thermometer, and gas outlet. The outlet was connected by Tygon tubing to an infrared gas cell and then to a gas trap cooled by a dry ice–2-propanol mixture. The temperature of the solution was slowly raised and several gas samples were taken at 90, 98, 104, 96, and 97 °C. The infrared spectrum showed absorbances at 912 (s, spike on broad peak), 985 (w), 1002 (w), 1012 (w), 1080 (w), 1140 (s), 1260–1310 (m, broad, detailed), 1350–1400 (m, detailed), 1410–1490 (m, broad, detailed), 1638 and 1655 (double peak, s), 1820 and 1840 (double peak, w), 2175 (spiked peak), 2880 (s), 2940–3020 (s, broad, detailed), and 3090, 3110 cm^{-1} (double peak, s). The peak at 2175 cm^{-1} was consistent with the carbon–deuterium stretching frequency of 3-deuteriopropene. The threshold temperature for propene formation appeared to be 95–96 °C. The liquefied, trapped gas was mixed with deuteriochloroform for analysis by NMR. The NMR spectrum exhibited resonances at δ 1.7 (finely split doublet, 2), 5.0 (finely split triplet), and 5.8 (multiplet with fine splitting). The assignments in the NMR along with comparison with butene as a model, and with 3-deuteriopropene, synthesized for this purpose, confirm the identity of this gas as 3-deuteriopropene. The mass spectrum showed a peak at *m/e* 43. The reaction was allowed to continue for 12 h. The pale green reaction mixture was filtered and the filtrate was evacuated to remove the solvent. The remaining viscous, green liquid was placed in a 50-ml round-bottomed flask and distilled under vacuum on a spinning band column. The first fraction, 1.3 g (bp 50–54 °C, 0.15 mm) gave spectra consistent with 3-deuterio-1,2-diphenyl-1,2-azaborolidine (Table III). The azaborolidine was unstable in air and formed a white, insoluble material (mp 90–100 °C). The other fraction, 1.8 g (bp 64–68 °C, 0.15 mm), was recrystallized from ethanol yielding a white, crystalline compound (mp 77–79 °C). The residue from the distillation flask was recrystallized from ethanol, yielding 3.2 g of white crystals (mp 78–79 °C). Spectral data and elemental analyses confirmed the assignment of the structure for 3,7-dideuterio-1,5-diphenyl-1-aza-5-borabicyclo[3.3.0]octane (Tables I and II).

Reaction of *N,N*-Di-3-butenylaniline (23) with Triethylamine Phenylborane Complex (2). *N,N*-Di-3-butenylaniline (11.2 g, 0.056 mol), triethylamine phenylborane complex (14.1 g, 0.072 mol), and 500 ml of *p*-xylene were placed in a 1-l., three-necked flask equipped with a magnetic stirrer, nitrogen inlet tube, and cold-water condenser. The temperature was varied from 80 to 110 °C. A bright green color developed during heating. Gas samples were taken at regular intervals for infrared analysis. No butene gas was observed during the course of the reaction. The reaction was allowed to proceed for 24 h. The resulting solution was filtered, evaporated, and divided into two portions. The first portion was placed on the spinning band column for distillation. The first fraction (0.8 g, bp 75 °C, 0.5 mm) proved to be unreacted *N,N*-di-3-butenylaniline. The second fraction (1.2 g, bp 75–78 °C, 0.5 mm) gave spectral data consistent with the structure 1,2-diphenylazaboracyclohexane; however, as shown below, the elemental analysis failed to support this structural assignment for this compound. The infrared spectrum exhibited absorbances at 700 (s), 750 (s), 865 (w), 930 (m), 965 (w), 1000 (m), 1048 (m), 1065 (m), 1120 (w), 1280 and 1300 (double peak, m), 1220 (w), 1310 (s), 1400 (s), 1410 (m), 1450 and 1460 (double peak, m), 1515 (s), 1610 (s), and 2900–3150 cm^{-1} (s, broad, detailed). The NMR spectrum gave resonance signals at δ 0.82 (m, 2), 1.5 (m, 4), 3.5 (m, 2), and 7.2 (m, 10.5). The mass spectrum gave a peak at *m/e* 235 ± 1. Anal. Calcd for $C_{16}H_{18}BN$: C, 81.73; H, 7.72; B, 4.60; N, 5.96. Found: C, 78.42; H, 8.19; B, 4.99; N, 3.75 (not consistent with the above structure). The third fraction (1.4 g, bp 90–95 °C, 0.5 mm) gave spectral data consistent with the structure 1,2-diphenyl-1-(3-butentyl)-2-hydroazaboracyclohexane (25). The ir exhibited absorbances at 700 (s), 750 and 765 (double peak, s), 800–880 (w, detailed), 890–950 (m, detailed), 1995 (double peak, m), 1028 (m), 1150 (m), 1190 (m), 1325–1450 (broad, s), 1445 (m), 1500 (s), 1600 (s), 2300 (broad, m), and 2900–3100 cm^{-1} (s). The NMR spectrum showed resonance signals at δ 0.8 (m, 2), 1.65 (m, 6), 3.35 (m, 4), 5.1 (m, 1), 5.8 (m, 0.5), and 7.4 (m, 12). The fourth fraction (1.2 g, bp 95–105 °C, 0.50 mm), a light-yellow oil which solidified in the side arm, was recrystallized from ethanol. A white, crystalline solid (mp 140–143 °C) was obtained. The structure assigned was 1,6-diphenyl-1-aza-6-borabicyclo[4.4.0]decane (27). The infrared spectrum showed absorbances at 700 (s), 755 (s), 768 (s), 810 (m), 870 (w), 910 (double peak, s), 970 (w), 1000 (s), 1030 (s), 1066 (s), 1180 and 1200 (double peak, s) 1250–1430 (broad, s), 1450 (s), 1510 (s), 1610 (s), 2900–3300 cm^{-1} (broad, s, detailed). The NMR exhibited resonances at δ 0.95 (m, 4), 1.6 (m, 8), 3.5 (m, 4), and 7.3 (m, 10). The mass spectrum gave a parent peak at *m/e* 291 ± 1. Identical spectra were obtained from the second portion of the original reaction solution. The material was chromatographed on a silica gel column in benzene. The eluted solution was evaporated and the residue recrystallized from ethanol. A white, crystalline material (1.1 g, mp 143–145 °C) was obtained. Anal. Calcd for $C_{20}H_{26}BN$: C, 82.48; H, 9.00; B, 3.71; N, 4.81. Found: C, 81.98; H, 8.81; B, 3.64; N, 4.76.

A solid material (1.4 g, mp >350 °C) was recovered from the reaction vessel. The NMR showed only aromatic absorption at δ 7.3. This material was shown to be triphenylcycloborazene.

Preparation of 3-Deuteriopropene (19). Allylmagnesium bromide (20 ml, 0.5 ml/l. in ether) was placed in a 500-ml round-bottomed flask. A few drops of deuterium oxide were added, resulting in gas evolution. The gas was condensed in a trap cooled in dry ice–2-propanol. The condensed gas was mixed with carbon tetrachloride and deuteriochloroform for NMR studies. An infrared gas cell was used to trap some of the gas for analysis. The NMR showed resonance signals at δ 1.65 (finely split signal, 2), 4.8 (finely split triplet, 2), and 5.65 (m, 1). The infrared spectrum exhibited absorbances at 855 and 865 (s, double peak), 940 (broad, s), 1006 (m), 1100 (broad, s), 1330 (s), 1455 (s, spiked), 1675 (m, spiked), 1870 (w), 1995 (s), 2200 (m), 2340 (w), and 2940–3300 cm^{-1} (broad, s, detailed).

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Registry No.—**2,** 15068-65-2; **3** uncoordinated, 4529-26-4; **3** coordinated, 7800-63-7; **14,** 59318-44-4; **18,** 59318-45-5; **19,** 1117-89-1; **20** uncoordinated, 59318-46-6; **20** coordinated, 59350-20-8; **23,** 13369-16-9; **25,** 59318-47-7; **27** uncoordinated, 59318-48-8; **27** coordinated, 59350-19-5; **29** uncoordinated, 59318-49-9; **29** coordinated, 59368-11-5; **30** uncoordinated, 59318-50-2; **30** coordinated, 59349-70-1; **31** uncoordinated, 59318-51-3; **31** coordinated, 59368-12-6; **32** uncoordinated, 59318-52-4; **32** coordinated, 59350-26-4; **33** uncoordinated, 59318-53-5; **33** coordinated, 59350-25-3; **34** uncoordinated, 59318-54-6; **34** coordinated, 59350-24-2; **35** uncoordinated, 59318-55-7; **35** coordinated, 59350-23-1; **36** uncoordinated, 59318-56-8; **36** coordinated, 59350-22-0; **37** uncoordinated, 59318-57-9; **37** coordinated, 59368-09-1; **38** uncoordinated, 59318-58-0; **38,** coordinated, 59350-21-9; **39,** 4529-23-1; **40,** 59318-59-1; **41,** 59318-60-4; **42,** 59318-61-5; **43,** 59318-62-6; **44,** 59318-63-7; aniline, 62-53-3; 4-bromo-1-butene, 5162-44-7; *p*-bromo-*N,N*-diallylaniline, 30438-95-0; triethylamine, 121-44-8; diethylphenylborane, 56797-48-9; *N,N*-diallylaniline, 6247-00-3; *N,N,N',N'*-tetrallyl-*p*-phenylenediamine, 59318-64-8; *p*-phenylenediamine, 106-50-3; 3-bromopropene, 106-95-6; *p*-chloro-*N,N*-diallylaniline, 30438-94-9; *p*-chlorophenylborane triethylamine, 59318-65-9; *p*-methylphenylborane triethylamine, 59318-66-0; *p*-methyl-*N,N*-diallylaniline, 3480-96-4; *p*-ethoxyphenylborane triethylamine, 59318-68-2; *p*-methoxyphenylborane triethylamine, 59318-69-3; *p*-methoxy-*N,N*-diallylaniline, 59318-70-6.

Supplementary Material Available. Tables of physical constants and experimental details on syntheses (16 pages). Ordering information is given on any current masthead page.

References and Notes

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Investigations on the Photochemical Ring Expansion of Ring Fused β-Lactams

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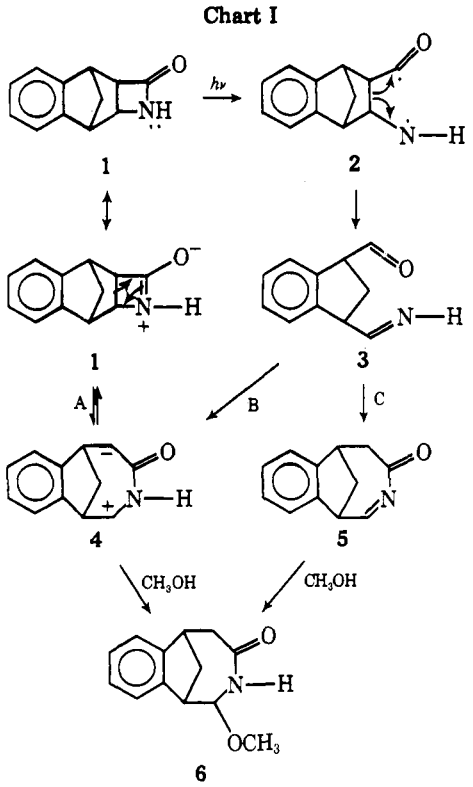
The photochemical ring expansion of *exo*-3-aza-4-ketobenzotricyclo[4.2.1.$0^{2,5}$]non-7-ene (**1**) in the presence of methanol to *exo*-2-methoxy-3-aza-4-keto-7,8-benzobicyclo[4.2.1]nonene (**6**) was studied. Data on the relative quantum yields for product (**6**) formation and starting material (**1**) disappearance as a function of methanol concentration suggest a dipolar intermediate in the reaction. A variety of other ring fused β-lactams were subjected to the reaction conditions and, of materials studied, only those β-lactams fused to the bicyclo[2.2.1]heptane ring system were found to undergo the rearrangement.

In an earlier report[1] on the photochemical ring expansion of the β-lactam **1**, in alcoholic solution, to the lactam ether **6** a number of mechanistic possibilities were suggested (Chart I). We now report investigations directed at further elucidating the mechanism of this reaction and studies of a series of β-lactams designed to delineate the scope of the reaction.

Chart I



Results and Discussion

The three logical mechanistic routes for the reaction center on the formation of two intermediates (**4** and **5**), one of which, (**4**), is common to two of the routes (A and B). Routes B and C are initiated by C(O)–N bond cleavage[2] to biradical **2** followed by β-bond cleavage to afford the imine ketene[3] **3** which can react either by addition of the N–H across the ketene[4] moiety to afford acylimine **5** or by collapse to zwitterion[5] **4**. A third alternative (path A) involves electrocyclic ring opening to **4**,[7] a route which is difficult to distinguish from path B which we favor. In either case[4,5a,6] addition of methanol to **4** or **5** would afford the observed product. Our discussions will center on path B although it should be kept in mind that path A remains a viable, but perhaps indistinguishable, alternative.

Our first attempt at differentiating paths B and C was based on the fact that, in the formation of acylimine **5**, the N–H must add across the C=C of the ketene moiety, i.e., a proton is transferred from N to C. We reasoned that N-alkylation of **1** would block this path and that the formation of N-alkylated