The Synthesis of Substituted 1,2-Azaborolidines and 1-Aza-5-borabicyclo[3.3.0]octanes[1]

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Four substituted 1-aza-5-borabicyclo[3.3.0]octanes, a new class of compounds, and four previously unreported 1,2-azaborolidines were prepared and characterized. The compounds were obtained from a novel reaction between triethylamine–phenylborane and tertiary diallylamines. A mechanism for the reaction was proposed, based on qualitative data, which involves reduction of an allylic carbon–nitrogen bond. Two of the 1,2-azaborolidines were also prepared from the reaction between triethylamine–phenylborane and secondary allylamines. The 1-aza-5-borabicyclo[3.3.0]octanes showed strong infrared absorption bands at 1250-1270 cm.$^{-1}$, which are assigned to the $^{-}$B–N^{+} coordinate bond. A new compound, 1-phenyl-1-bora-5-azoniaspiro[4.5]decane, was prepared by the reaction of triethylamine–phenylborane and N-allylpiperidine. A telomer with an unusual structure was prepared from N,N′-diallylpiperazine and triethylamine–phenylborane.

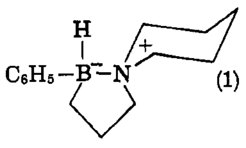
In a recent communication[2] from this laboratory, a novel reduction of an allylic carbon–nitrogen bond was reported. This reduction was observed during the synthesis of 1-aza-5-borabicyclo[3.3.0]octanes, a new class of compounds, and resulted in the formation of 1,2-azaborolidines. We would now like to report the details of synthesis and structure proof of these and related compounds, and an independent synthesis of two of the 1,2-azaborolidines.

During the course of this work, Adams and Poholsky[3] reported the synthesis of the first 1,2-azaborocycloalkane by refluxing a toluene solution of N,N-dimethylallylamine with trimethylamine–borane. A report of the preparations of 1-methyl-2-phenyl-1,2-azaborolidine and 2-phenyl-1,2-azaboracyclohexane from the reactions of N-methylallylamine and 3-butenylamine with trimethylaminephenylborane in diglyme soon followed.[4]

Discussion and Results

Syntheses of the boron heterocycles were first attempted by reduction of diethyl phenylboronate with lithium aluminum hydride in the presence of the unsaturated amine at low temperatures. The reaction mixtures were then distilled and isolation of products was attempted by crystallization at low temperatures or distillation. N,N-Diallylaniline was used in these attempts since the bicyclic product from this compound was considered to be the best model of the proposed structures. These reactions did not lead to the stable compounds which had been expected, and the easily oxidized products were not identified immediately. In order to determine whether this procedure was resulting in the hydroboration of the double bond, a less complex amine, N-allylpiperidine, was used since the number and complexity of the expected products would be decreased. The amine was treated in similar fashion and a small amount of the product (13%) was isolated in accordance with eq. 1. The product, 1-phenyl-1-bora-5-azoniaspiro[4.5]decane (I), was stable in the atmosphere. The presence of the nitrogen boron link was shown to be present by the shift of the boron–hydrogen stretching frequency from 4.5 (2220 cm.$^{-1}$) to 4.3 μ (2330 cm.$^{-1}$) both frequencies of which are indicative of coordination compounds of boranes.[5]

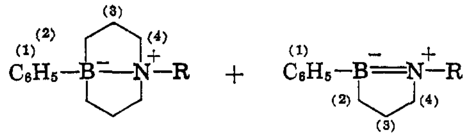
$C_6H_5BH_2$ + $CH_2CH—CH_2—NC_5H_{10}$ →



I (1)

Similar reactions were then carried out using diallylethylamine and diallyl-*n*-propylamine. The only products which could be isolated were small amounts of clear, colorless liquids which readily oxidized in air. These liquids were later proven to be substituted 1,2-azaborolidines. Since this procedure did not appear to give the desired products, the syntheses were attempted by the use of triethylamine–phenylborane and the unsaturated amines according to eq. 2. These reactions were performed by heating dilute toluene solutions of the reagents and slowly distilling the solutions. Two products could be isolated from these reactions: clear, colorless liquids and white solids. Apparent polymeric viscous liquids were also formed but were not investigated. The clear, colorless liquids oxidized easily in air, turning brown after a short period of time. The white solids were stable in air and were proven to be bicyclic compounds having structure II. The liquids were assigned structure III and were the major products. The physical properties, yields, and analytical data for compounds of structure III are shown in Table I, and those of II in Table II.

$C_6H_5BH_2N(C_2H_5)_3$ + $(CH_2{=}CHCH_2)_2NR$ ⟶ $N(C_2H_5)_3$ +



(2)

IIa, R = $\underset{(6)}{CH_3}\underset{(5)}{CH_2}$

b, R = $CH_3CH_2\underset{(5)}{CH_2}$

c, R = $\underset{(7)}{CH_3}\underset{(6)}{CH_2}CH(\underset{(8)}{CH_3})$

d, R = C_6H_5

IIIa, R = $\underset{(6)}{CH_3}\underset{(5)}{CH_2}$

b, R = $CH_3CH_2CH_2$

c, R = $\underset{(7)}{CH_3}\underset{(6)}{CH_2}\underset{(5)}{CH}(\underset{(8)}{CH_3})$

d, R = C_6H_5

The structural assignments were made on the basis

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[1] Taken from the Ph.D. Dissertation of G. L. Statton, Department of Chemistry, University of Florida, April 1964.

[2] G. B. Butler and G. L. Statton, *J. Am. Chem. Soc.*, **86**, 518 (1964).

[3] R. M. Adams and F. D. Poholsky, *Inorg. Chem.*, **2**, 640 (1963).

[4] D. G. White, *J. Am. Chem. Soc.*, **85**, 3634 (1963).

[5] B. Rice, R. Galiano, and W. J. Lehmann, *J. Phys. Chem.*, **61**, 1222 (1957).

TABLE I

PHYSICAL PROPERTIES, YIELDS, AND ANALYTICAL DATA FOR 1,2-AZABOROLIDINES

Compd.	Procedure	B.p., °C. (mm.)	Yield, %	Formula	Calcd, % C	Calcd, % H	Calcd, % B	Calcd, % N	Found, % C	Found, % H	Found, % B	Found, % N	Mol. wt. Calcd.	Mol. wt. Found
1-Ethyl-2-phenyl-	I	72.5–74.0 (1.3)	22.8	$C_{11}H_{16}BN$	76.33	9.32	6.25	8.09	76.27	9.23	6.30	8.06	...	...
	II	68–70 (1.0)	8.7											
1-*n*-Propyl-2-phenyl-	I	87.5–90 (2.0)	31.0	$C_{12}H_{18}BN$	77.04	9.69	5.78	7.48	77.73	9.35	5.62	7.40	187	187[a]
	II	71 (0.3)	14.0											
	III	78–79 (0.5)	47.0											
1-*sec*-Butyl-2-phenyl-	I	81–82 (0.8)	21.0	$C_{13}H_{20}BN$	77.64	10.02	5.38	6.96	77.61	10.22	5.76	7.00	201	201[a]
1,2-Diphenyl-	I	126–127 (1.1)	30.0	$C_{15}H_{16}BN$	81.47	7.29	4.89	6.34	81.38	7.42	5.35	6.14	...	...
	III	122–123 (0.65)	58.0											

[a] Mass spectral method.

TABLE II

PHYSICAL PROPERTIES, YIELDS, AND ANALYTICAL DATA FOR 1-AZA-5-BOROBICYCLO[3.3.0]OCTANES

Compd.	M.p. °C.	Yield, %	Formula	Calcd., % C	Calcd., % H	Calcd., % B	Calcd., % N	Found, % C	Found, % H	Found, % B	Found, % N	Mol. wt. Calcd.	Mol. wt. Found
1-Ethyl-5-phenyl-	58.3–59.3	7.0	$C_{19}H_{22}BN$	78.16	10.31	5.03	6.51	77.87	10.38	4.87	6.76	...	...
1-*n*-Propyl-5-phenyl-	61.9–63.0	8.0	$C_{15}H_{24}BN$	78.16	10.56	4.78	6.11	78.49	10.66	4.48	6.27	229	239[a]
1-*sec*-Butyl-5-phenyl-	59.9–61.4	9.5	$C_{16}H_{26}BN$	79.03	10.78	4.45	5.76	78.85	10.80	4.48	5.74	243	244[a]
1,5-Diphenyl-	81.6–82.6	22.0	$C_{18}H_{22}BN$	82.13	8.42	4.11	5.32	82.13	8.68	4.24	5.48	263	264[b]

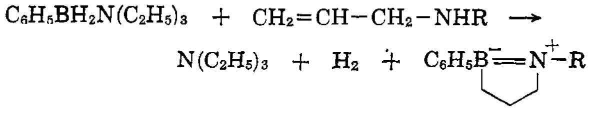
[a] Cryoscopic in cyclohexane. [b] Vapor pressure osmometer method.

of n.m.r. spectra, infrared spectra, and analyses. Mass spectral data and molecular weights were also obtained for several compounds. The mass spectrum of 1-*n*-propyl-2-phenyl-1,2-azaborolidine showed a parent ion peak at 187 mass units which agrees with the calculated molecular weight of 187.08. The most intense peak was found at 158 mass units, and small peaks were recorded at 116 and 89 mass units. The loss of an ethyl group gives the peak at 158 mass units. This is consistent with the most probable mode of rupture of amine compounds. The two weaker peaks are the result of loss of the C_3H_7N-CH_2 and C_3H_7N-C_3H_6 groups. The spectrum of 1-*sec*-butyl-2-phenyl-1,2-azaborolidine showed a parent ion peak at 201 in agreement with the mass number of the parent specie $^{12}C_{13}$-$^{1}H_{20}{}^{11}B^{14}N$. The most intense peak in the spectrum was at 172 mass units corresponding to loss of the ethyl group β to the nitrogen atom. Three other peaks of weaker intensity were found at 186, 130, and 89 mass units. These may be rationalized by considering the loss of CH_3, C_4H_9N, and C_4H_9N-C_3H_6 groups. The relative intensities of the peaks also are indicative of the structural assignment. The spectra showed that all peaks resulting from fragmentation in which two bonds were broken were less intense than the parent ion peak.

The infrared spectra of the liquids were in agreement with the assigned structures. It has been reported that boron–nitrogen bonds in amine–boranes absorb in the region of 6.6 to 7.3 μ (1515–1370 cm.$^{-1}$).[4,6,7] The boron–nitrogen absorption bands of the 1,2-azaborolidines were observed as follows: 1-ethyl-2-phenyl, 1512 cm.$^{-1}$; 1-*n*-propyl-2-phenyl, 1504 cm.$^{-1}$; 1-*sec*-butyl-2-phenyl, 1504 cm.$^{-1}$; 1,2-diphenyl, 1389 cm.$^{-1}$. The identity of the absorption bands were easily confirmed by partial hydrolysis of the substituted 1,2-azaborolidines which beraks the boron–nitrogen bond and results in disappearance of the boron–nitrogen absorption. The infrared spectra also showed the absence of boron–hydrogen and olefinic bonds.

N.m.r. spectra were obtained on several of the 1,2-azaborolidines. The boron resonance was obtained for the 1,2-azaborolidines and was found at −26 p.p.m. relative to trimethylborate. The proton magnetic resonance spectral data for three of the 1,2-azaborolidines are given in the Experimental Section. The spectra were obtained on the neat liquids using acetaldehyde as the external standard.

Two 1,2-azaborolidines were also prepared by the reaction of secondary allylamines and triethylamine–phenylborane according to eq. 3. Thus the reaction of triethylaminephenylborane with N-allylaniline resulted in isolation of 1,2-diphenyl-1,2-azaborolidine. Use of allyl-*n*-propylamine resulted in 1-*n*-propyl-2-phenyl-1,2-azaborolidine. The infrared spectra of the compounds prepared in this manner were identical with those from the tertiary diallylamines.



$$C_6H_5BH_2N(C_2H_5)_3 + CH_2{=}CH{-}CH_2{-}NHR \longrightarrow N(C_2H_5)_3 + H_2 + C_6H_5\overset{-}{B}{=}\overset{+}{N}{-}R \qquad (3)$$

III

The proton magnetic resonance spectral data for several of the 1-aza-5-borabicyclo[3.3.0]octanes in CCl_4 solutions are given in the Experimental Section. The hydrogen absorptions of the *sec*-butyl compound overlapped and could not all be definitely assigned, but

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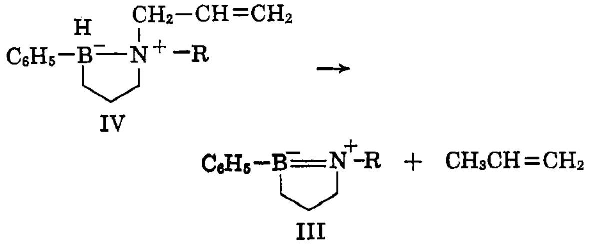
(6) K. Niedenzu, H. Beyce, and J. W. Dawson, *Inorg. Chem.*, **1**, 738 (1962).

(7) K. Niedenzu, G. W. Wyman, and J. W. Dawson, *J. Chem. Soc.*, 4068 (1962).

the total area agrees well with the theoretical number of hydrogens. The spectrum for the ethyl-substituted compound appears to agree well on the basis of the chemical shifts as well as on the total area. However, again, overlapping peaks were observed. The boron resonance absorption of 1-*n*-propyl-5-phenyl-1-aza-5-borabicyclo[3.3.0]octane was found at +8.9 p.p.m. relative to trimethylborate while those for the ethyl and *sec*-butyl derivatives were +6.0 and +8.0 p.p.m., respectively. These chemical shifts indicate the presence of the boron–nitrogen bond.[8] The 1,5-diphenyl compound showed no chemical shift.

The infrared spectra of the substituted 1-aza-5-borabicyclo[3.3.0]octanes showed the absence of boron–hydrogen and olefinic bonds in the compounds. There were strong absorptions in the 7.8- to 8.0-μ region (1248–1270 cm.$^{-1}$) which were tentatively assigned to the boron–nitrogen coordinate bond. The boron–nitrogen absorptions of 2′,2-iminodiethyl vinylbenzeneboronates and of pyridine complexes of boranes have been assigned near this region.[9,10]

The most plausible mechanism for the formation of the 1,2-azaborolidines isolated according to eq. 2 involves the formation of a cyclic amineborane which eliminates the allyl group from the nitrogen, according to eq. 4. Although no alkene was trapped from the reactions, probably due to the fact that it reacts rapidly with phenylborane, infrared spectra of samples taken during the course of the reaction offer some substantiation for this mechanism. The samples were taken while a solution of the phenylborane complex and diallyl-*n*-propylamine was being heated to reflux.

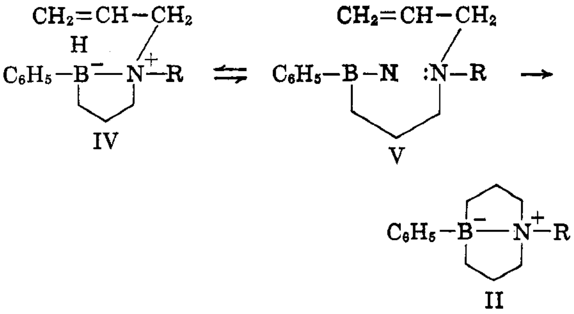


(4)

The boron–hydrogen absorption at 4.3 μ (2330 cm.$^{-1}$) was followed, and it was found that the initial hydroboration occurred between 47 and 60°. The sample at 90° showed little change in intensity from the sample at 73°. However at 112°, before the solution started refluxing, the intensity showed a marked decrease and after refluxing for 1.5 hr., no boron–hydrogen absorption was found. This suggests that the mechanism for loss of boron–hydrogen occurs in two successive steps, which is in agreement with the proposed mechanism.

The instability of the cyclic amine–borane toward elimination would be the result of the ease of replacement of the allyl group. The ability of an ethylenic bond of an allylic system to delocalize positive or negative charge over its π electron system greatly facilitates the reactions of a functional group attached. Quaternary ammonium salts containing allyl groups are known to undergo Hofmann degradation at much lower temperatures and result in better yields than corresponding alkyl ammonium compounds.[11] Allyl halides undergo S_N2 displacement reactions with ethoxide 37 to 95 times faster than their saturated counterparts.[12] Not only would the allyl group facilitate the elimination but the reduction of steric hindrance should also aid. In five-membered rings, the chief source of strain is interaction of nonbonded atoms; removal of the allyl group would reduce the strain.

The bicyclic compounds may be formed by initial intramolecular dihydroborations of the tertiary diallylamines before the nitrogen–boron bonds are formed or the bicyclic structures may result from an equilibrium dissociation of the cyclic amineboranes followed by hydroboration of the remaining double bond, according to eq. 5. The position of equilibrium of the reaction would be largely toward the cyclic amineborane. The stability of the boron–nitrogen bond of the cyclic amine–borane apparently limits the amount of bicyclic compound which can be formed.

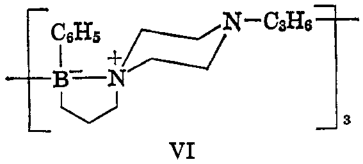


(5)

1-*sec*-Butyl-5-phenyl-1-aza-5-borabicyclo[3.3.0]octane was treated under conditions of the synthetic reactions and was found to be completely stable and not a precursor of any other product.

The synthesis of 1-phenyl-1-bora-5-azoniaspiro[4.5]decane (I) was repeated using the reaction of triethylamine–phenylborane and N-allylpiperidine. The infrared spectrum of this product was identical with the infrared spectrum of the product isolated by the other procedure. The yield was increased to 45%.

An attempt to prepare a polymer containing a cyclic unit was made with the reaction of triethylamine–phenylborane and N,N′-diallylpiperazine. Although the stable product was isolated in good yield, the average degree of polymerization was only 3. The infrared spectrum of the product showed an absence of any boron–hydrogen bonds but a small amount of vinyl absorption was present. The absence of boron–hydrogen bonds suggests that the structure of VI may be a macrocyclic structure although the presence of vinyl absorption supports an open-chain structure. The open-chain structure corresponding to VI would be expected to be terminated by both a boron–hydrogen bond and a vinyl group.



VI

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[8] (a) T. P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959); (b) H. Landesman and R. E. Williams, *J. Am. Chem. Soc.*, **83**, 1663 (1961); (c) T. P. Onak, R. E. Williams, and R. Swidler, *J. Phys. Chem.*, **67**, 1741 (1963).

[9] N. N. Greenwood and K. Wade, *J. Chem. Soc.*, 1130 (1960).

[10] W. J. Dale and J. E. Rush, *J. Org. Chem.*, **27**, 2598 (1962).

[11] R. Lukes and J. Trojanek, *Collection Czech. Chem. Commun.*, **16**, 603 (1951).

[12] R. H. Dewolfe and W. G. Young, *Chem. Rev.*, **56**, 758 (1956).

The 1-aza-5-borabicyclo[3.3.0]octanes were found to be unusually thermally stable. Thermal gravimetric analysis revealed that the 1-*sec*-butyl-5-phenyl derivative retained 90% of its original weight at 325° and disappeared completely either by thermal decomposition or volatilization at 390°. The 1,5-diphenyl derivative retained 90% of its original weight at 310° and 5% of the original weight at 400°.

Experimental Section

Materials.—*n*-Propyl bromide, *sec*-butyldiallylamine, and lithium aluminum hydride were obtained from Peninsular ChemResearch, Inc. The *n*-propyl bromide and *sec*-butyldiallylamine were distilled before use. Diallylamine and allylamine were obtained from the Shell Chemical Corp. and were distilled before use. Trimethylborate was obtained from Callery Chemical Co. and was used as received. N,N-Diallylaniline, N-allylaniline, N,N′-diallylpiperazine, and N-allylpiperidine were previously prepared in this laboratory and were distilled before use.

Equipment and Treatment of Data.—Infrared data were obtained with a Perkin-Elmer Infracord double-beam infrared recording spectrophotometer or with a Perkin-Elmer Model 421 grating spectrophotometer. N.m.r. data were obtained with a Varian DP-60 n.m.r. spectrometer. Mass spectral data were obtained on a Bendix time of flight mass spectrometer. Several molecular weights were obtained on a Mechrolab 302 vapor pressure osmometer. All apparatus used in the synthetic procedures were purged with dry nitrogen for several hours before use. All reactions and transfers, except recrystallizations, were carried out in a dry nitrogen atmosphere. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., or Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Syntheses Using Phenylborane and Unsaturated Amines.—The general procedure used for the reactions between phenylborane and the unsaturated amines involved placing lithium aluminum hydride with either tetrahydrofuran or diethyl ether in a nitrogen-purged, four-neck, round-bottom flask fitted with a mechanical stirrer, a low-temperature thermometer, an addition funnel, and a cold-water condenser fitted with a nitrogen inlet tube. The mixture was refluxed for 30 min. and then cooled to −72° with a Dry Ice–acetone bath. The amine was added all at once. The diethyl phenylboronate[13,14] was then added dropwise to the stirred mixture. After complete addition, the mixture was allowed to warm to room temperature. The mixture was filtered in a drybox, then distilled. Further purification depended on the compound being synthesized and will be described in detail for each individual compound.

Syntheses Using Triethylamine–Phenylborane[14] and Unsaturated Amines.—The reagents and approximately 2.0 l. of toluene were placed in a one-neck, round-bottom flask with a thermometer well. The flask was then connected to a 60-cm. packed column with a normal fractional distilling head. The solution was slowly heated to reflux and the triethylamine and toluene were slowly distilled. After the flask temperature reached 120°, the remaining small amount of toluene was removed under reduced pressure. The residual liquid was then distilled through a short Vigreux column into several crude fractions. For syntheses giving the 1,2-azaborolidines, the lower boiling fractions were redistilled through a 23-plate spinning-band column. The higher boiling fractions were individually dissolved in a small quantity of solvent and cooled to −72° where the solid compounds precipitated. They were then recrystallized. Purification details of the compounds synthesized in this manner are described under the individual compound sections.

1-Phenyl-1-bora-5-azoniaspiro[4.5]decane from Phenylborane and N-Allylpiperidine.—Diethyl ether (500 ml.) and 2.5 g. (0.06 mole) of lithium aluminum hydride were refluxed, then cooled to −72°. The N-allylpiperidine (12.5 g., 0.10 mole), was added to the stirred mixture followed by dropwise addition of 17.7 g. (0.10 mole) of diethyl phenylboronate. After warming to room temperature, the mixture was filtered. The ether was removed and the residual liquid was distilled under reduced pressure giving four crude fractions which ranged from 61° (34 mm.) to 160° (0.1 mm.). The fraction distilling at 135–145° (0.1 mm.) slowly crystallized on standing. The solid was dissolved in light petroleum ether (b.p. 30–40°) and then cooled to −72° where a white solid precipitated. On filtering, the solid melted, so the petroleum ether was decanted and the remainder was removed under reduced pressure. Repetition of the procedure yielded 3.0 g. (13%) of a white solid, m.p. 34.1–35.7°.

Anal. Calcd. for $C_{14}H_{22}BN$: C, 78.16; H, 10.31; B, 5.04; N, 6.51. Found: C, 77.98, H, 10.15; B, 5.17; N, 6.40.

1-Phenyl-1-bora-5-azoniaspiro[4.5]decane from Triethylamine–Phenylborane and N-Allylpiperidine.—A solution of 1.7 l. of toluene, 19.1 g. (0.10 mole) of triethylamine–phenylborane, and 12.0 g. (0.096 mole) of N-allylpiperidine was distilled at atmospheric pressure until the flask temperature reached 120°. After the remaining toluene was removed, the residual liquid was distilled into three crude fractions. The fractions were dissolved in pentane and cooled to −72°. A white solid precipitated from the fractions distilling at 114–120° (0.03–0.05 mm.) The pentane was decanted, the solids were combined, and the remaining liquid was removed under reduced pressure. Repetition of the crystallization gave 9.8 g. (45%) of a white solid, m.p. 34.1–35.2°. The infrared spectrum of this compound was identical with that prepared above.

1-Ethyl-2-phenyl-1,2-azaborolidine and 1-Ethyl-5-phenyl-1-aza-5-borabicyclo[3.3.0]octane from Triethylamine–Phenylborane and Diallylethylamine. Procedure I.—A solution of 2.0 l. of toluene, 28.8 g. (0.15 mole) of triethylamine–phenylborane, and 18.8 g. (0.15 mole) of diallylethylamine[15,16] was distilled at atmospheric pressure until the flask temperature reached 120°. After the remaining toluene was removed, the residual liquid was distilled into five crude fractions. The two lowest boiling fractions, 60–92° (0.8 mm.) and 92–107° (0.8 mm.), were redistilled through the spinning-band column giving 5.9 g. of 1-ethyl-2-phenyl-1,2-azaborolidine. The physical properties, yields, and analytical data for the 1,2-disubstituted-1,2-azaborolidines are shown in Table I.

The remaining three fractions were dissolved in a small amount of acetone and cooled in a Dry Ice–acetone bath where a white solid precipitated. The solids were filtered, combined, and recrystallized from acetone yielding 2.3 g. of 1-ethyl-5-phenyl-1-aza-5-borabicyclo[3.3.0]octane. The physical properties, yields, and analytical data for the 1,5-disubstituted 1-aza-5-borabicyclo-[3.3.0]octanes are shown in Table II.

1-Ethyl-2-phenyl-1,2-azaborolidine from Phenylborane and Diallylethylamine. Procedure II.—A solution of 500 ml. of dry tetrahydrofuran and 4.0 g. (0.11 mole) of lithium aluminum hydride was refluxed, then cooled to −72°. Diallylethylamine (25.0 g., 0.20 mole) was added to the stirred mixture followed by the dropwise addition of 35.4 g. (0.20 mole) of diethyl phenylboronate. After complete addition, the mixture was allowed to warm to room temperature. The mixture was filtered, and the filtrate was distilled at atmospheric pressure to remove the tetrahydrofuran. The remaining liquid was distilled through a spinning-band column yielding 3.0 g. of a clear, colorless liquid. The infrared spectrum of this compound was identical with the same compound prepared by procedure I.

1-*n*-Propyl-2-phenyl-1,2-azaborolidine from Triethylamine–Phenylborane and Allyl-*n*-propylamine.[17] Procedure III.—A solution of 2.0 l. of toluene, 10.4 g. (0.105 mole) of allyl-*n*-propylamine, and 20.0 g. (0.105 mole) of triethylamine–phenylborane was distilled at atmospheric pressure. Hydrogen evolution was evident soon after heating of the solution began. After the flask temperature reached 120°, the remaining toluene was removed under reduced pressure. The residual liquid was distilled through a spinning-band column yielding 9.2 g. of a clear, colorless liquid. The infrared spectrum and other physical properties of this compound were identical with those of the compound prepared by procedures I and II. 1,2-Diphenyl-1,2-azaborolidine was also prepared by this procedure.

Telomer from Triethylamine–Phenylborane and N,N′-Diallylpiperazine.—A solution of 400 ml. of toluene, 28.8 g. (0.15 mole)

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[13] R. M. Washburn, E. Levens, C. F. Albright, F. A. Billig, and E. S. Cernak, Advances in Chemistry Series, No. 23, American Chemical Society, Washington, D. C., 1959, pp. 102, 129.

[14] M. F. Hawthorne, *J. Am. Chem. Soc.*, **80**, 4291 (1958).

[15] L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961, p. 499.

[16] A. M. Weston, A. W. Ruddy, and C. M. Suter, *J. Am. Chem. Soc.*, **65**, 676 (1943).

[17] C. Liebermann and C. Paal, *Ber.*, **16**, 523 (1883).

of triethylamine–phenylborane, and 24.9 g. (0.15 mole) of N,N'-diallylpiperazine was slowly distilled at atmospheric pressure. After the flask temperature reached 120°, the remaining toluene was removed under reduced pressure. The residual white solid was dissolved in benzene and precipitated by pouring the solution into a large volume of pentane. The mixture was filtered and dried, yielding 28.8 g. (75%) of a stable white solid which melted completely over the temperature range of 208–230°.

Anal. Calcd. for $C_{16}H_{25}BN_2$: C, 75.01; H, 9.83; B, 4.22; N, 10.94. Found: C, 75.11; H, 9.77; B, 4.27; N, 10.70; mol. wt., 660 (vapor pressure osmometer).

Treatment of 1-*sec*-Butyl-5-phenyl-1-aza-5-borabicyclo[3.3.0]-octane under Reaction Conditions.—A solution of 100 ml. of toluene and 2.3 g. of 1-*sec*-butyl-5-phenyl-1-aza-5-borabicyclo-[3.3.0]octane was refluxed for 36 hr. The toluene was distilled at atmospheric pressure until the flask temperature reached 120°. The remaining toluene was removed under reduced pressure and the residual liquid was distilled giving only one fraction at 120° (0.1 mm.). The flask temperatures ranged from 160 to 230° during the distillation. A small amount of acetone was added to the liquid distillate and the solution was cooled in a Dry Ice–acetone bath yielding 2.1 g. of white solid, m.p. 58.8–60.9°.

Progress of the Reaction of Triethylamine–Phenylborane and Diallyl-*n*-propylamine as Followed by Infrared Absorption.—A solution of 2.0 l. of toluene, 28.8 g. (0.15 mole) of triethylamine–phenylborane, and 20.8 g. (0.15 mole) of diallyl-*n*-propylamine was placed in a three-neck flask fitted with a serum cap and a thermometer. The flask was connected to the distillation apparatus and slowly heated. Samples of 30 ml. each were withdrawn at various temperatures and immediately cooled. The samples were then concentrated to 1 ml. under reduced pressure and the infrared spectra of the samples were taken using a cell of 0.0258-mm. cell width. All spectra were obtained using this cell in order to assure uniformity. The intensity of the boron–hydrogen absorption at 4.3 μ (2330 cm.$^{-1}$) was measured from the base line to the peak. The following intensities were observed at the respective temperatures: 24°, 55%; 47°, 49%; 60°, 35%; 73°, 25%; 90°, 22%; 112°, 8%; and after refluxing for 1.5 hr. at 112°, 0%.

N.m.r. Data.—The proton magnetic resonance spectral data for three of the 1,2-azaborolidines (based on structure III) are as follows (peak assignment, τ, and peak area): for 1-ethyl-2-phenyl-, 1, 3.33, 5.0; 4 and 5, 7.41, 4.0; 3, 8.79, —; 2, 9.12, —; 6, 9.52, 7.53 (combined areas for 2, 3, and 6); for 1-*sec*-butyl-2-phenyl-, 1, 3.14, 5.2; 5, 6.70, 1.0; 4, 7.28, 2.0; 3, 8.63, —; 2, 9.04, —; 6, (hidden), —; 8, 9.30, 8.5 (combined areas for 2, 3, 6 and 8); and for 1,2-diphenyl-, 1, 3.06 and 3.42, 9.2; 4, 6.88, 2.0; 2, and 3, 8.70, 3.8.

The proton magnetic resonance spectral data for three of the 1-aza-5-borabicyclo[3.3.0]octanes are as follows: for 1-ethyl-5-phenyl-, 1, 3.01, 5.0; 4 and 5, 7.02, 1.1[18]; 4 and 5, 7.89, —; 3, 8.34, 7.9[18] (combined areas for 3, 4, and 5); 2, 9.20, —; 6, 9.68, 8.4[18] (combined areas for 2 and 6); for 1-*sec*-butyl-5-phenyl-, 1, 2.78, 4.9; 4 and 5, 7.30, 5.2; 3, 8.20, 5.4[18]; 2, 6, and 8, 9.09, 7.9[18]; 7, 9.82, 3.0; and for 1, 5-diphenyl-, 1,3.19, 10.0; 4, 6.76, 4.0; 3, 7.87, 4.0; 2, 8.92, 4.4.

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[18] Partial overlap of peaks made individual peak areas somewhat uncertain.

Dicyanodiazomethane[1]

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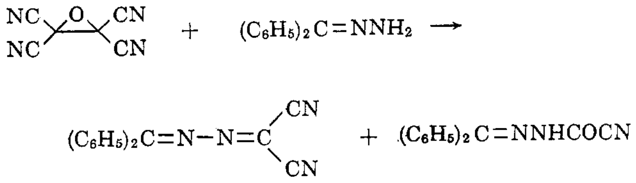
Dicyanodiazomethane, a highly electrophilic diazoalkane, has been prepared by lead tetraacetate oxidation of carbonyl cyanide hydrazone. Its properties are described. Some of its more unusual reactions include the diazo coupling with dimethylaniline, reaction with diazofluorene and diphenyldiazomethane to yield mixed azines, and the dehydrogenation of primary and secondary alcohols.

During an investigation of the chemistry of tetracyanoethylene epoxide,[2] a route to carbonyl cyanide hydrazone was discovered. This new hydrazone proved to be a convenient intermediate for the synthesis of dicyanodiazomethane, a molecule of interest both as an example of a highly electronegatively substituted diazoalkane and as a precursor of the heretofore unknown dicyanocarbene. The present paper is concerned with the synthesis and properties of dicyanodiazomethane as well as with its reactions to the extent that they do not involve a carbene intermediate. Reactions of dicyanocarbene will be described elsewhere.

Carbonyl Cyanide Hydrazone.—Tetracyanoethylene epoxide (TCNEO) has been shown to add to olefinic, acetylenic, and aromatic hydrocarbons yielding derivatives of tetracyanofuran.[2] Reactions of the epoxide with certain nucleophiles, on the other hand, proceed with cleavage of the molecule into carbonyl cyanide and products that are formally the adducts of dicyanocarbene to the nucleophile employed.[2] To determine the course of the reaction with a compound having both unsaturated and nucleophilic character, TCNEO was allowed to interact with benzophenone hydrazone. The products of this reaction, which occurred at 0°, were 1,1-dicyano-4,4-diphenyl-2,3-diazabutadiene (1)



1 (27%) 2 (45%)

and 1-cyanoformyl-2-diphenylmethylenehydrazine (2). The structures of the two products were determined by independent syntheses. Compound 2 was prepared in 77% yield by the reaction of benzophenone hydra-

[1] A preliminary report on the preparation of dicyanodiazomethane appeared: E. Ciganek, *J. Am. Chem. Soc.*, **87**, 652 (1965).

[2] W. J. Linn, O. W. Webster, and R. E. Benson, *ibid.*, **85**, 2032 (1963).