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Studies of Boranes. XXXII. Reactions of *n*-Nonaborane(15)[1]

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Although *n*-nonaborane(15), *n*-B_9H_{15}, was isolated more than 10 years ago, little investigation of its chemistry has been reported. The complete structure (Figure 1) has been determined from the X-ray data[2,3] and has recently been found to be consistent with the solution structure with the aid of 70.6-MHz Fourier-transform ^{11}B nmr.[4] The mass spectrum has been determined and the decomposition kinetics of *n*-B_9H_{15} to B_8H_{12} in the mass spectrometer has been studied.[5]

Since *n*-B_9H_{15} was first prepared and isolated by decomposition of diborane in a silent discharge,[6] several methods of preparation have been developed;[7,8] however, the study of *n*-B_9H_{15} has been limited because of the inability to produce large amounts efficiently. In this laboratory several methods have recently been developed which allow the preparation of large amounts of *n*-B_9H_{15}[9] and the corresponding labeled compound, *n*-3-$^{10}B^{n}B_8H_{15}$.[10] It therefore seemed opportune to undertake an investigation at this time.

Experimental Section

Methods.—The high-vacuum techniques used in this investigation have been described elsewhere.[11,12] All materials used in this work were either reagent grade or were prepared and purified by standard methods.

The 70.6-MHz ^{11}B nmr spectra were obtained with a Varian Associates HR-220 MHz spectrometer equipped with standard Varian variable-temperature probe accessories. The ^{11}B chemical shift values were measured relative to $BF_3:O(C_2H_5)_2 = 0$ ppm using an external standard.

Mass spectra were obtained on the CH-7 mass spectrometer.

Preparation of Starting Materials.—*n*-Nonaborane(15) was prepared by reaction of diborane and pentaborane(9) in a hot-cold circulating system which is described elsewhere.[9] Isotopically labeled *n*-3-$^{10}B^{n}B_8H_{15}$ was prepared by the reaction of octaborane(12) with $^{10}B_2H_6$ and is also described elsewhere.[10] Samples were purified by low-temperature crystallization and by means of a low-temperature fractional distillation column until their ^{11}B nmr spectra appeared free of impurities.

Reactions of *n*-Nonaborane(15). Acetonitrile.—*n*-Nonaborane(15) (0.36 mmol) and acetonitrile (1.5 mmol) were transferred to an nmr tube which was then sealed under vacuum and warmed to room temperature. After 1 hr a white precipitate had formed, but only a trace of hydrogen was found upon opening the tube of the vacuum system. Fractionation of the volatiles established that 0.74 mmol of CH_3CN had been consumed. The precipitate dissolved upon the addition of 0.2 ml of acetonitrile and the ^{11}B nmr spectrum of this solution was identical with the spectrum of $B_8H_{12}NCCH_3$ formed from the reaction of B_8H_{12} and acetonitrile.[13] The only other product of this reaction was *n*-triethylborazine, which was identified by its mass spectrum.

An analogous experiment using the labeled compound, *n*-3-$^{10}B^{11}B_8H_{15}$, was performed and demonstrated that the $B_8H_{12}NCCH_3$ produced had an ^{11}B nmr spectrum identical with that from the unlabeled material proving that it is the boron(3) position (the doubly bridged $-BH_2$ group) which is cleaved in the reaction.

Water.—A U trap fitted with two Fischer–Porter valves was charged with *n*-nonaborane(15) (0.62 mmol) and diglyme (0.5 ml). Water was added in increments to the solution and the course of the reaction monitored by measuring the evolved hydrogen. For each addition of water the vessel was sealed from the vacuum system and water added with the aid of a syringe through a septum attached to the apparatus. The solution was then allowed to come to room temperature for about 5 min. During this time evolution of a gas (H_2) and formation of a white solid (B_2O_3) was apparent. The vessel was then reconnected to the vacuum system and the hydrogen evolved in the reaction was measured by means of a Toepler system. The following results were obtained

H_2O added, mmol	H_2 evolved, mmol
1.11	2.03
1.11	2.03
1.31	Trace
	4.06

The borane product was separated from the diglyme solution by distilling the mixture for about 3 hr from a −30° trap. The ^{11}B nmr spectrum and the infrared spectrum of the material passing the −30° trap proved it to be essentially pure hexaborane(10), B_6H_{10}. Only the white solid, B_2O_3, remained in the reaction vessel. No other borane product could be detected.

Ammonia.—*n*-Nonaborane(15) (0.5 mmol), ammonia (1.5 mmol), and either CH_2Cl_2 or diethyl ether (0.2 ml) were transferred to an nmr tube which was then sealed and warmed to −78° for 1 hr. The 70.6-MHz ^{11}B nmr (Figure 2) was then taken with the nmr probe cooled to −30°. The spectrum at this time was drastically changed from the initial spectrum of *n*-B_9H_{15} indicating a reaction had occurred at low temperature to produce what is probably a new $B_9H_{14}^-$ anion. The tube was next warmed to room temperature for 1 min and the nmr at −30° again taken. The only borane product at this time was $B_9H_{14}^-$ (a derivative of *i*-B_9H_{15}) which was identified by its ^{11}B nmr spectrum (Figure 3). No further reaction occurred upon continued warming of the reaction.

Only a trace of hydrogen could be detected upon reopening the reaction tube to the vacuum line.

The excess ammonia in each reaction was determined by conversion to NH_4Cl. Analysis of three samples gave values varying from 1.5 to 2.0 mmol of NH_3 consumed per mole of *n*-B_9H_{15}.

In an attempt to produce the nonsymmetrical cleavage product the reaction of ammonia and *n*-nonaborane(15) in a second experiment was allowed to age for 14 hr at −78°, but as in previous experiments no bridge cleavage products were formed.

Ethereal solutions of *n*-3-$^{10}B^{n}B_8H_{15}$ and ammonia were also allowed to react in the manner described above, producing the analogous labeled compounds (Figure 2b and 3b).

Sodium Amalgam.—*n*-Nonaborane(15) (2.44 mmol) and ethyl ether (2 ml) were transferred to a reaction tube containing an

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[1] Part XXXI: R. R. Rietz and R. Schaeffer, *J. Amer. Chem. Soc.*, **93**, 1263 (1971).

[2] R. E. Dickerson, P. H. Wheatly, P. A. Howell, and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 200 (1957).

[3] P. G. Simpson and W. N. Lipscomb, *ibid.*, **35**, 1340 (1961).

[4] A. Allerhand, A. O. Clouse, R. R. Rietz, T. Roseberry, and R. Schaeffer, *J. Amer. Chem. Soc.*, **94**, 2445 (1972).

[5] A. D. Norman, R. Schaeffer, A. B. Baylis, G. A. Pressley, Jr., and F. E. Stafford, *J. Amer. Chem. Soc.*, **88**, 2151 (1966).

[6] V. W. Kotlensky and R. Schaeffer, *ibid.*, **80**, 4517 (1958).

[7] A. B. Burg and R. Kratzer, *Inorg. Chem.*, **1**, 725 (1962).

[8] J. E. Dobson and R. Schaeffer, *ibid.*, **7**, 402 (1968).

[9] J. E. Dobson, R. Maruca, and R. Schaeffer, *ibid.*, **9**, 2161 (1970).

[10] R. Maruca, J. D. Odom, and R. Schaeffer, *ibid.*, **7**, 412 (1968).

[11] R. T. Sanderson, "High Vacuum Manipulation of Volatile Compounds," Wiley, New York, N. Y., 1948.

[12] D. F. Shriner, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.

[13] R. R. Rietz, private communication.

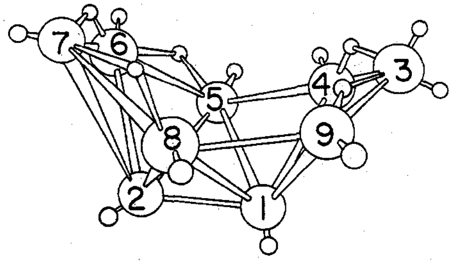

Figure 1.—The structure of *n*-nonaborane (15).

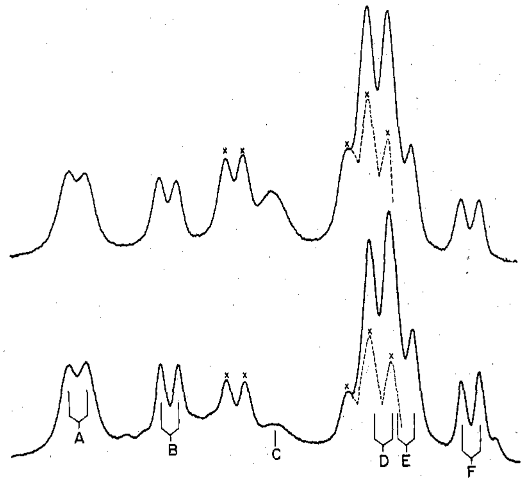

Figure 2.—The 70.6-MHz ^{11}B nmr spectra of the low-temperature product of the reaction of ammonia with (a) *n*-B_9H_{15} and (b) *n*-3-^{10}B^nB_8H_{15}.

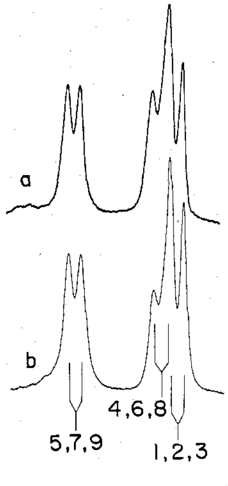

Figure 3.—The 70.6-MHz ^{11}B nmr spectra of (a) $B_9H_{14}^-$ and (b) 4(6,8)-^{11}B^n$B_8H_{14}^-$.

excess of sodium amalgam. Vigorous bubbling occurred upon warming the mixture to room temperature and a yellow color appeared. After 5 min the tube was opened to the vacuum line and the hydrogen produced (1.3 mmol) was measured in a Toepler system. The solid remaining in the reaction tube after removal of the condensables was dissolved in water and then added to an aqueous solution of tetramethylammonium chloride. The resulting precipitate was identified as $(CH_3)_4N^+B_9H_{14}^-$ (a derivative of *i*-B_9H_{15}) by comparison of its ir, ^{11}B nmr, and powder diffraction pattern with those of a known sample.

An analogous experiment was performed in a reaction flask consisting of a 15-mm nmr tube equipped with a side arm. The Na amalgam was first placed in the side arm while the *n*-B_9H_{15} and Et_2O were condensed into the bottom of the nmr tube. After the tube was sealed the reactants were mixed for 30 sec. The amalgam was then separated again into the side arm and the ^{11}B nmr taken of the ether solution. The only borane product was $B_9H_{14}^-$ and no intermediate could be detected.

Halogens.—The reaction of *n*-B_9H_{15} with halogens was tried using several different conditions. In a typical experiment, *n*-B_9H_{15} (0.5 mmol), ether (0.2 ml), and a slight excess of bromine (0.6 mmol) were transferred to an nmr tube which was then sealed from the vacuum system and allowed to stand at 0° until changes were detected in the ^{11}B nmr spectrum or yellow decomposition material was formed. The tube was then opened, and separation was attempted by use of a low-temperature fractionation column. In reactions using a large excess of bromine only BBr_3 was formed, whereas if a slight excess of bromine was used, as above, only orange decomposition material was formed. Reactions in which HCl and $AlCl_3$ were used gave similar results.

Several milder halogenating agents were also tried, including iodine trichloride in benzene solution and *n*-bromosuccimide in pentane solution. In both cases no reaction could be detected by ^{11}B nmr after 1 day at room temperature.

Results and Discussion

The structural similarity of *n*-nonaborane(15), *n*-B_9H_{15}, to tetraborane(10) in the region of the doubly bridged $-BH_2$ group (boron 3 in Figure 1) has been noted.[14] Previous studies of tetraborane(10) and other boranes containing this type of $-BH_2$ unit have established that certain reaction similarities of these compounds may be linked to the presence of this $-BH_2$ structural unit. Cleavage reactions occurring at the $-BH_2$ group involving either (1) symmetrical or BH_3 cleavage, or (2) nonsymmetrical or BH_2^+ cleavage, appear to be the characteristic reactions of each of these compounds, and it has been predicted[15] that *n*-B_9H_{15} should react accordingly.

Diborane(6), tetraborane(10), and pentaborane(11) have each been shown[16] to readily undergo symmetrical cleavage with a variety of Lewis bases.

$$B_2H_6 + L \longrightarrow 2LBH_3$$
$$B_4H_{10} + L \longrightarrow LBH_3 + LB_3H_7$$
$$B_5H_{11} + L \longrightarrow LBH_3 + LB_4H_8$$
$$L = \text{Lewis base}$$

Extrapolation to *n*-B_9H_{15} would predict that $B_8H_{12}L$ compounds should be the product of the reaction of *n*-B_9H_{15} and Lewis bases. As predicted, the reaction of *n*-B_9H_{15} with acetonitrile produces the symmetrical cleavage reaction

$$n\text{-}B_9H_{15} + 2CH_3CN \longrightarrow B_8H_{12}NCCH_3 + (-BNCCH_3-)_3$$

The use of the isotopically labeled compound *n*-3-^{11}B^nB_8H_{15} (boron-10 labeled in the doubly bridged $-BH_2$ group) confirmed that it was the 3 position which cleaved in the reaction.

Ammonia does not produce BH_3 cleavage at doubly bridged $-BH_2$ groups, but instead has been shown[16,17] to produce BH_2^+ cleavage.

$$B_2H_6 + 2NH_3 \longrightarrow [H_2B(NH_3)_2]^+[BH_4^-]$$
$$B_4H_{10} + 2NH_3 \longrightarrow [H_2B(NH_3)_2]^+[B_3H_8]^-$$
$$B_5H_{11} + 2NH_3 \longrightarrow [H_2B(NH_3)_2]^+[B_4H_9]^-$$

Nonsymmetrical cleavage of *n*-B_9H_{15} with ammonia was explored to be a possible means of preparing the previously unknown anion, $B_8H_{13}^-$.

$$n\text{-}B_9H_{15} + 2NH_3 \longrightarrow [H_2B(NH_3)_2]^+[B_8H_{13}]^-$$

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[14] W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963, p 39.

[15] Reference 14, p 171.

[16] Reference 14, pp 167–171, and references listed therein.

[17] G. Kodama, J. E. Dunning, and R. W. Parry, *J. Amer. Chem. Soc.*, **93**, 3372 (1971).

In contrast to the predicted result, the reaction of n-B_9H_{15} with ammonia yields deprotonation[18] followed by fast boron rearrangement to give the known $B_9H_{14}^-$ (a derivative of i-B_9H_{15}) and no bridge cleavage products are isolated. When this reaction is carried out at low temperature and monitored by 70.6-MHz ^{11}B nmr an intermediate is observed (Figure 2a) which may be an isomer of the known $B_9H_{14}^-$. This intermediate appears to be very unstable, since even at low temperatures some of the known $B_9H_{14}^-$ has formed (peaks denoted by ×'s in Figure 2). The spectrum of the intermediate consists of at least six separate resonances suggesting that the symmetry of n-B_9H_{15} is still maintained. Upon further warming of the reaction there appears to be a direct conversion of the intermediate to the known $B_9H_{14}^-$ (Figure 3a) and no other intermediates were observed. The chemical shifts and coupling constants for the intermediate are presented in Table I along with the reported values[18] of n-B_9H_{15}.

TABLE I

The 70.6-MHz ^{11}B Nmr Spectrum of the Low-Temperature Product of n-B_9H_{15} and NH_3

Resonance[a]	δ, ppm	*J*, cps
A	−10.4	140
B	−0.6	135
C	10.6	. . .
D	22.4	∼145
E	24.7	∼169
F	31.9	145

The 70.6-MHz ^{11}B Nmr Spectrum of n-B_9H_{15}[18]

	δ, ppm	*J*, cps
B(2)	46.0	157
B(4,9)	32.0	153
B(7,8 or 5,6)	−2.7	148
B(5,6 or 7,8)	−6.6	167
B(3)		
B(1)	−15.9	158

[a] See Figure 2.

The ammonia reaction was repeated using the specifically labeled compound, n-3-$^{10}B^nB_8H_{15}$. Comparison of the ^{11}B nmr spectra of the low-temperature products of the ammonia reaction with the unlabeled and labeled materials (Figure 2a and 2b, respectively) allows the assignment of resonance c as the boron-10 labeled position. This position was formerly the doubly bridged $-BH_2$ position in n-B_9H_{15}. When the ammonia reaction with the labeled material was allowed to go to completion the specifically labeled compound, 4(6,8)-$^{10}B^nB_8H_{14}^-$, was formed. The 70.6-MHz ^{11}B spectrum is presented in Figure 3b. The numbering and structure of $B_9H_{14}^-$ are presented in Figure 4.

TABLE II

THE 70.6-MHz ^{11}B NMR SPECTRUM OF $B_9H_{14}^-$

	δ, ppm	*J*, cps
B(5,7,9)	6.62	135
B(4,6,8)	19.7	∼145
B(1,2,3)	21.6	150

The reaction of n-B_9H_{15} with sodium amalgam leads to the deprotonation, rearrangement reaction discussed above for ammonia; however, attempts to observe an intermediate in this reaction were unsuccessful.

$$\text{Na–Hg} + n\text{-}B_9H_{15} \longrightarrow Na^+B_9H_{14}^- + {}^1/_2H_2$$

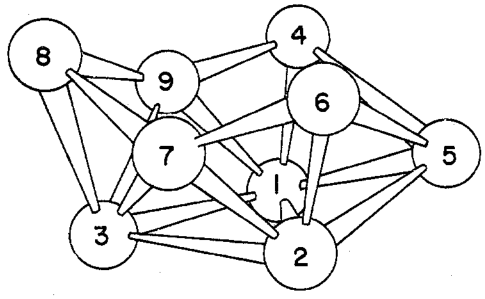

Figure 4.—The structure of $B_9H_{14}^-$.

The only borane detected upon the hydrolysis of n-B_9H_{15} was hexaborane(10), B_6H_{10}. Experimental agreement was found for the equation

$$2n\text{-}B_9H_{15} + 9H_2O \longrightarrow 2B_6H_{10} + 3B_2O_3 + 14H_2$$

Water required for complete hydrolysis: Calcd: 2.8 mmol. Found: 2.3 mmol. Hydrogen evolved in complete hydrolysis: Calcd: 4.3 mmol. Found: 4.1 mmol.

The formation of B_6H_{10} in hydrolysis of n-B_9H_{15} is not surprising since it was shown above that n-B_9H_{15} can undergo cleavage with suitable base to yield octaborane(12) derivatives. Octaborane(12) has been shown to undergo nearly quantitative hydrolysis[8] to hexaborane(10).

Although the ^{11}B nmr of n-B_9H_{15} has been analyzed as resulting from overlapping fragments similar to B_4H_{10} and B_5H_{11},[19] it was felt that if a halogen could be substituted in n-B_9H_{15} it might give complete final proof to the assignment. Substitution of halogens in other boranes has been useful for this purpose.[20] Unfortunately, no halogen derivative could be prepared in this investigation. In all cases where a reaction occurred, complete decomposition of the n-B_9H_{15} structure took place.

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[18] Recent studies have shown that deprotonation is also the initial step in the reaction of tetraborane(10) with ammonia. See H. D. Johnson, II, and S. G. Shore, *J. Amer. Chem. Soc.*, **92**, 7587 (1970).

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Nuclear Quadrupole Coupling of Copper Nuclei in Coordination Compounds of Copper(I) with Thiourea and Substituted Thioureas

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Since the advent of pure nuclear quadrupole resonance (nqr) spectroscopy, resonances for copper nuclei have been published for only two compounds Cu_2O[1] and

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(1) H. Kruger and V. Meyer-Berkhart, *Z. Phys.*, **132**, 171 (1952).