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Free-Radical Intermediates in the Photochemistry of Alkylborazines. Synthetic Applications

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Received June 10, 1976

AIC60432S

Mercury photosensitization of alkylborazine–H_2 mixtures at 2537 Å leads to products identified as dimers of an intermediate radical formed by H abstraction from the alkyl group. Reactions of *N*-mono-, -di-, and -trimethylborazine yield exclusively C–C bonded diborazinyl derivatives; B–B bonded products are not observed. The dimer formed by photolysis of *N*-triethylborazine, a 2,3-disubstituted butane, indicates that the intermediate radical is formed at the carbon atom α to the borazine ring. Reactions of *B*-trimethylborazine involve formation of an intermediate radical at a carbon and H–CH_3 exchange at a boron site. Hexamethylborazine reacts with H atoms by H–CH_3 exchange at the boron sites.

Introduction

It has previously been demonstrated that mercury photosensitization of gaseous mixtures of *N*-trimethylborazine and H_2 with radiation at 2537 Å yields a well-defined crystalline product, 1,2-bis[*N*-(3′,5′-dimethylborazinyl)]ethane (DMBE).[1] It is believed that the mechanism of the reaction involves abstraction of a methyl hydrogen by an H atom to form the intermediate radical $H_3B_3N_3(CH_3)_2CH_2\cdot$ which then dimerizes to form a stable product. We have now tested the generality of this radical mechanism for a number of alkyl-substituted borazines, including the *N*-methylborazines, *N*-triethylborazine, and *B*-trimethylborazine. For all of the *N*-methylborazines studied the reaction product obtained is an *N*-diborazinylethane. The product of the *N*-triethylborazine reaction is an *N*-diborazinylbutane. The product with *B*-trimethylborazine is predominantly a *B*-diborazinylethane. The photochemical mechanism for hexamethylborazine is somewhat complicated by competing processes. Throughout this paper we will use the following abbreviations: *N*-trimethylborazine, *N*-TMB; *N*-dimethylborazine, *N*-DMB; *N*-methylborazine, *N*-MB; *N*-triethylborazine, *N*-TEB; *B*-trimethylborazine, *B*-TMB; $(CD_3)_3B_3N_3H_3$, *B*-TMB-d_9; hexamethylborazine, HMB.

Experimental Section

The unsymmetrically substituted *N*-methylborazines were prepared by the method of Beachley,[2] using dimethoxyethane solvent dried over $NaBH_4$, CH_3NH_3Cl, and NH_4Cl under a helium atmosphere. *N*-MB and *N*-DMB were separated by vacuum distillation through U-tube traps. Product purities were checked by mass spectrometry. *N*-TMB was similarly prepared using CH_3NH_3Cl and $NaBH_4$. Purification by vacuum distillation was checked by mass and infrared[3] spectra. *N*-TEB was prepared from $C_2H_5NH_3Cl$ and $NaBH_4$. Purity of the product, separated by vacuum distillation, was checked by mass spectrometry,[4] proton NMR,[5] and vapor pressure measurements.[6]

Hexamethylborazine was prepared by the method of Haworth and Hohnstedt[7] using CH_3I, Mg, and $Cl_3B_3N_3(CH_3)_3$ in diethyl ether solvent under dry N_2. Purity of the product collected by vacuum distillation was checked by mass spectrometry[8] and its melting point, 98–99 °C (lit.[7,9] mp 97.1 °C). *B*-TMB was similarly prepared from $Cl_3B_3N_3H_3$. Its purity was checked by mass spectrometry,[10] infrared spectroscopy,[11,12] and vapor pressure measurements.[13] The partially deuterated compound, *B*-TMB d_9, was prepared by the same procedure, starting with CD_3I. These Grignard reactions were performed by slowly adding the CH_3I (CD_3I) to a stirred reaction mixture containing Mg in diethyl ether under dry N_2.

Table I. Partial Mass Spectra of the Dimers of the *N*-Methylborazine Radicals

$[H_3B_3N_3\text{-}H_2CH_2]_2$		$[H_3B_3N_3\text{-}HCH_3CH_2]_2$		$[H_3B_3N_3\text{-}(CH_3)_2CH_2]_2$	
m/e	Rel ion intens	*m/e*	Rel ion intens	*m/e*	Rel ion intens
187	8	215	8.5	244	3
186	12.5	214	12.5	243	26.5
185	10	213	9.5	242	36
184	4	212	4.5	241	22
183	3	109	7	240	8
182	1.5	108	100	239	2
95	4.5	107	74.5	123	4.5
94	100	106	21.5	122	100
93	73	105	4	121	75
92	19			120	19
91	3			119	2

Mass spectra were obtained on a Consolidated Electrodynamics Corp. Model 21-103A spectrometer with gas inlet. An AEI-MS902/CIS-2 mass spectrometer was used for high-resolution spectra, chemical ionization spectra, and spectra of samples of low volatility. The sample inlet probe temperature was approximately 30 °C. Electron impact mass spectra were run at 70 eV.

Proton NMR spectra were obtained with a Varian A-60A spectrometer or with a Bruker HX-90 high-resolution spectrometer with a Digilab NMR-3 Fourier transform system with Alpha Data Disc memory storage of 128K and a Fourier transform radiofrequency probe amplifier, Model 400-2. Proton chemical shifts were obtained relative to the residual protons in deuterated solvents. Using downfield shifts from TMS as positive δ (ppm), the following relationships were used: $\delta_{TMS} = 7.28 + \delta_{CHCl_3}$, $\delta_{TMS} = 7.20 + \delta_{C_6D_5H}$, $\delta_{TMS} = 2.05 + \delta_{CD_3COCD_2H}$. Resonances for protons bound to nitrogen or boron atoms were too broad and weak for accurate measurement.

Infrared spectra were recorded on either a Perkin-Elmer Model 337 or Model 521 grating spectrophotometer.

The photolysis cell was a 2-l. Pyrex vessel equipped with a quartz immersion well. The light source was a medium-pressure Hanovia mercury arc lamp surrounded by a Vycor sleeve. The lamp and surroundings were purged with cool dry N_2. A pool of triply distilled Hg at the bottom of the photolysis vessel was agitated with a Teflon-clad stir bar during the photolysis. Fisher High-Purity grade H_2

Table II. Partial Mass Spectrum of the Dimer of the *N*-Triethylborazine Radical[a]

m/e	Rel ion intens	*m/e*	Rel ion intens
327	1.5	160	1.5
326	2	149	1
325	1.5	148	2
165	7.5	147	1
164	100	109	4.5
163	74.5	108	2
162	22.5	107	1
161	3.5		

[a] In the parent region relative ion intensities are *m/e* 328:327:326:325 = 9.5:66:100:69.

or Air Products and Chemicals, Inc., Research grade D_2 was used.

Results

N-Methylborazine (5 mm) and H_2 (33 mm) were photolyzed for $^3/_4$ h. The products of the reaction were pumped into a U-tube trap at −196 °C. This trap was found to contain predominantly unreacted *N*-MB. A viscous liquid, free of *N*-MB, remaining in the photolysis vessel gave a mass spectrum (Table I) with a characteristic six-boron isotopic distribution pattern between masses 182–187 and a three-boron fragment ion between masses 91–94. In another experiment 9 mm of *N*-MB and 180 mm of H_2 were photolyzed for 1 h. Under these conditions, approximately 60% of the *N*-MB reacted. The mass spectrum of the product was the same as in the previous experiment. The sample, which has a small but observable volatility, was condensed in a U-tube at liquid N_2 temperature. The sample was transferred to an NMR tube with $CDCl_3$ solvent and sealed under vacuum. A single ethylene proton resonance was observed at δ 3.44.

N-Dimethylborazine (25 mm) and H_2 (120 mm) were photolyzed for 1 h. Unreacted *N*-DMB was pumped into a −196 °C U-tube trap. A crystalline product remaining in the reaction vessel gave a melting point of 57 °C. The mass spectrum (Table I) of this compound indicates an ion with a six-boron isotopic pattern in the mass range 212–215 and a three-boron fragment ion in the mass range 105–108. The NMR sample was prepared in the same manner as for the product of *N*-MB and sealed with $CDCl_3$ under vacuum. A methyl proton resonance is observed at δ 3.11 and an ethylene proton resonance at δ 3.40.

The products for the photolysis of *N*-TMB have been described previously.[1] The mass spectrum (Table I) has been reproduced for comparison. Gaseous *N*-TMB and Hg were photolyzed for 30 min without any added H_2. Crystalline DMBE formed and H_2 was detected by mass spectrometry.

For photolysis studies of *N*-TEB, liquid *N*-TEB was present in the photolysis vessel. The vapor pressure of *N*-TEB (~2 mm) at room temperature is sufficient for gas-phase photochemical studies. In one experiment gaseous *N*-TEB was photolyzed for 50 min with Hg in the absence of added H_2. The mass spectra of the noncondensable products showed evidence for formation of some H_2 and CH_4. In a separate experiment gaseous *N*-TEB was photolyzed in the presence of 27 mm of H_2 for 100 min while the outer Pyrex wall of the reaction vessel was maintained between 60 and 70 °C. The unreacted *N*-TEB and H_2 were pumped off and the vessel was allowed to remain under vacuum for 12 h. Small, colorless crystals collected on the inner wall were removed. The crystals melted at 84–86 °C in a sealed capillary. The 70-eV electron impact spectrum on the MS902 mass spectrometer is indicated in Table II. A six-boron fragmentation corresponding to the $(P - 1)^+$ ion was observed in the mass range 323–327. A three-boron fragment ion was observed in the mass range 160–164. A sample of the crystalline product for NMR analysis was obtained by repeating the same procedure. Several proton NMR samples were prepared and run at 60 and 90 MHz, Table III and Figure 1. These spectra will be discussed later.

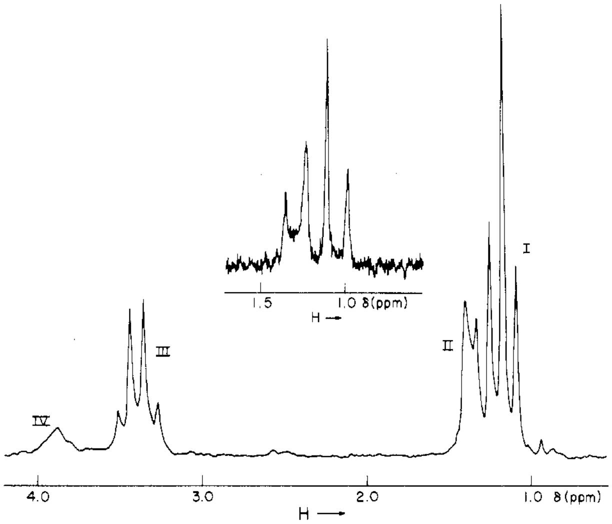


Figure 1. The 90-MHz proton NMR spectrum of the dimer of the *N*-triethylborazine radical (6% in C_6D_6): I, C_β(H)'s; II, X_3(H)'s; III, C_α(H)'s; IV, A(H)'s. Inset: portion of the 60-MHz proton NMR spectrum.

Hexamethylborazine was photolyzed at its equilibrium vapor pressure for 1 h with H_2 (10 mm). The infrared and mass spectra of the volatile products of this reaction indicated ethane and *N*-TMB. When the vapor was photolyzed in the presence of 53 mm of H_2, only *N*-TMB was observed as a product. In a separate experiment, HMB at a vapor pressure corresponding to 55 °C was photolyzed in the absence of H_2 for $^1/_2$ h. Mass spectral analysis of the noncondensable products indicated the formation of C_2H_6, CH_4, and H_2. The condensable products collected at −196 °C in a U-tube trap were analyzed without further separation. The infrared spectrum of this fraction indicated the absence of an N–H stretching frequency at about 3500 cm^{-1} but the presence of a B–H stretching vibration near 2500 cm^{-1}. From the mass spectrum of this mixture we identified the components as *N*-TMB and $H_2CH_3B_3N_3(CH_3)_3$. HMB was photolyzed at room temperature for $^1/_2$ h. The mass spectral analysis of the products indicated the presence of $H(CH_3)_2B_3N_3(CH_3)_3$, $H_2CH_3B_3N_3(CH_3)_3$, *N*-TMB, C_2H_6, CH_4, and H_2. When a mixture of HMB at its equilibrium vapor pressure and 53 mm of D_2 was pho-

Table III. Proton NMR Data for the Dimer of the *N*-Triethylborazine Radical[a]

			δ, ppm			
Solvent	Wt % solute	Rf (MHz)	C_α(H) quartet	C_β(H) triplet	X_3(H) mult	A(H) mult
$CDCl_3$	2	60	3.35 ± 0.01	1.17 ± 0.01	1.14 ± 0.05	*b*
CD_3COCD_3	1	60	3.33 ± 0.01	1.13 ± 0.01	1.15 ± 0.05	*b*
C_6D_6	6	60	3.34 ± 0.01	1.12 ± 0.01	1.30 ± 0.05	*b*
C_6D_6	6	90	3.38 ± 0.01	1.18 ± 0.01	1.36 ± 0.02	3.86 ± 0.02

[a] Proton NMR shifts for *N*-TEB[5] are $\delta(C_\alpha(H))$ 3.34 and $\delta(C_\beta(H))$ 1.14. [b] Resonances too weak or masked for observation.

Table IV. Mass Spectra of $[CH_2(CH_3)_2B_3N_3H_3]_2$

70-eV electron impact (3% cutoff)				Chem ionization (in methane)	
m/e	Rel ion intens	*m/e*	Rel ion intens	*m/e*	Rel ion intens
245	3.5	189	9	273	21.5
244	46	188	18.5	272	29
243	68.5	187	18.5	271	17
242	46.5	186	10.5	270	6
241	18.5	185	6	246	6
240	4	184	6	245	59.5
229	8	183	3.5	244	100
228	9	174	7.5	243	79.5
227	6.5	173	9	242	37.5
226	3.5	172	5.5	241	13
216	5	171	4.5	240	3.5
215	70.5	160	3.5	230	3
214	100	159	4	229	27.5
213	64.5	135	3	228	37
212	24.5	120	9	227	24.5
211	10.5	119	7	226	8
210	4.5	108	28.5	215	10
203	3.5	107	20	214	12.5
202	13.5	106	5.5	213	8.5
201	16.5	93	4	212	3.5
200	12	92	6.5	188	6
199	51.5	91	11	187	7
198	69	90	7	186	4
197	44	67	36		
196	16.5	66	25.5		
195	3	65	5.5		

High Resolution (EI)

Nominal *m/e*	Obsd *m/e*	Calcd *m/e*	Empirical formula
244	244.2468	244.2464	$C_6B_6N_6H_{22}^+$
229	229.2230	229.2229	$C_5B_6N_6H_{19}^+$
215	215.2090	215.2073	$C_4B_6N_6H_{17}^+$

tolyzed for $^1/_2$ h, an increase in pressure was noted. An infrared spectrum of the condensable products indicated a weak band corresponding to a C–D stretching vibration near 2230 cm^{-1} and a stronger band corresponding to C–H stretching vibration near 2960 cm^{-1}. A strong B–D stretching absorption was observed near 1900 cm^{-1}, but an expected B–H stretching absorption was absent near 2500 cm^{-1}.

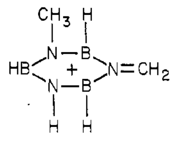
B-Trimethylborazine at its normal vapor pressure was photolyzed for 1 h in the presence of H_2 at 71 mm pressure. Colorless crystals collected on the walls of the reaction vessel were removed by transferring to a cold finger by vacuum sublimation. These crystals, removed from the system under dry N_2, melted between 47 and 48 °C in sealed capillaries. A second sample of crystals formed by photolysis of *B*-TMB vapor and H_2 (13 mm) also melted between 47 and 48 °C. Electron impact mass spectra (Table IV) of these crystals showed a six-boron molecular ion in the mass range 241–244 and a six-boron fragment ion in the mass range 211–215. The chemical ionization mass spectrum of this compound in methane is also indicated in Table IV. Major features of this spectrum are the $(P + 1)^+$ and the $(P + C_2H_5)^+$ ions in the mass ranges 241–245 and 271–273, respectively. The high-resolution mass spectrum of the product is also indicated (Table IV). The proton NMR spectrum of the product in $CDCl_3$ shows a methyl proton resonance at δ 0.35 and an ethylene proton resonance at δ 0.88 with relative intensities of 3:1. The infrared and mass spectra of the unreacted *B*-TMB indicated no changes from the original starting material. When a mixture of *B*-TMB (2 mm) and H_2 (209 mm) was photolyzed for $^1/_2$ h, hydrogen–methyl exchange at boron sites was observed as noted by changes in the infrared and mass spectra. When mixtures of *B*-TMB and D_2 at 2.5 and 205 mm, respectively, were photolyzed for 45 min, a strong B–D stretching absorption appeared in the volatile reaction product around 1900 cm^{-1}.

$(CD_3)_3B_3N_3H_3$, *B*-TMB-d_9, was photolyzed with D_2 at several pressures (12, 18, 20, 37, 63, 200 mm). Under these conditions, a major product was $D(CD_3)_2B_3N_3H_3$. In the run at 18 mm of D_2, a clear filmy liquid was formed along with $D(CD_3)_2B_3N_3H_3$. The mass spectrum of this liquid indicated that it was a mixture of products that were not strictly analogous to the product obtained in the photolysis of *B*-TMB and H_2. These products were not obtained in the absence of D_2. The mass spectrum of the liquid product appeared to be derivatives of the six-boron compound in which methyl groups had been replaced by D. CD_4 was observed as a noncondensable product.

A vapor mixture of *B*-TMB and *N*-TMB was photolyzed in the presence of H_2 (pressures between 9 and 16 mm). After $1^1/_2$ h of photolysis, a solid formed on the inner walls of the reaction vessel was analyzed by proton NMR in $CDCl_3$ and by its mass spectrum to be DMBE. After a total photolysis period of 3 h, it was found that the *N*-TMB had been completely consumed but no evidence was found for a hypothetical compound formed by linking *B*- and *N*-borazinyl groups.

Discussion

Irradiation of *N*-methylborazines and H_2 in the presence of Hg at 2537 Å was found to produce higher molecular weight products. The mass spectra of these products have base peaks at the same *m/e* as in the mass spectra of the corresponding *N*-methylborazine. Product parent ions are indicated at twice the *m/e* of their respective base peaks. The mass spectra of branched *N*-alkylborazines[4,15] and for DMBE[1] have been interpreted previously. A representative base peak fragment ion is I, found at *m/e* 108 in the mass spectrum of *N*-dimethylborazine and in the product formed from photolysis of *N*-DMB and H_2. The photolysis products of the series of *N*-methylborazines studied each have characteristic six-boron isotopic distributions at $(P - 1)^+$ in their respective mass spectra (Table I). The proton NMR spectra of the *N*-methylborazine photolysis products (Table V) contain integrated methyl and ethylene proton resonance intensities consistent with the ratio expected for a compound with two rings linked by an ethane structure. The small downfield shifts observed for the ethylene proton resonances are comparable to the case of DMBE and the trend observed in toluene and



I

Table V. Proton NMR Summary of Dimers of Methylborazine Radicals in $CDCl_3$

Compd	δ, ppm Methyl protons	Compd		Wt % solute	δ, ppm Methyl protons	δ, ppm Ethylene protons
N-MB	3.01	$[H_3B_3N_3H_2CH_2]_2$		2		3.44 ± 0.01
N-DMB	3.11	$[H_3B_3N_3HCH_3CH_2]_2$		1	3.11 ± 0.01	3.40 ± 0.01
N-TMB	3.08	$[H_3B_3N_3(CH_3)_2CH_2]_2$	ref 14		3.10 ± 0.01	3.36 ± 0.01
			this work	1	3.07 ± 0.01	3.34 ± 0.01
B-TMB	0.35	$[CH_2(CH_3)_2B_3N_3H_3]_2$		1	0.35 ± 0.01	0.88 ± 0.01

dibenzyl.[16] The following mechanism for the photolysis of *N*-methylborazine is proposed

$$Hg(^1S_0) + h\nu(2537\ \text{Å}) \rightarrow Hg(^3P_1) \quad (1)$$

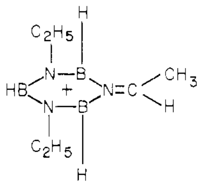
$$Hg(^3P_1) + H_2 \rightarrow Hg(^1S_0) + 2H\cdot \quad (2)$$

$$H\cdot + N\text{-MB} \rightarrow H_2 + {>}N\text{-}CH_2\cdot\ (R^1) \quad (3)$$

$$2R^1 \rightarrow {>}NCH_2CH_2\text{-}N{<} \quad (4)$$

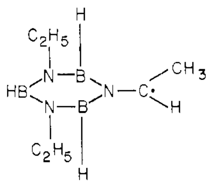
Hydrogen abstraction is believed to occur, eq 3, producing a stabilized "benzyl"-like radical. No product containing a B–B link has been observed in these studies. Protonation studies[17] have demonstrated that in the proton-transfer reaction between $H_3B_3N_3(CH_3)_3^+$ and $H_3B_3N_3(CH_3)_3$ the proton transfer originates from the exocyclic methyl group on the cation. The indication that the methyl proton is more labile than the proton on boron strengthens the assertion that hydrogen abstraction occurs at a methyl site as in eq 3 and not at a boron.

The photolysis of *N*-triethylborazine and H_2 in the presence of Hg at 2537 Å produced a higher molecular weight product with a mass spectrum following the same pattern as for the *N*-methylborazines (Table II). The observed base peak in the mass spectrum of the photolysis product of *N*-TEB was at the same *m/e* as the $(P - 1)^+$ peak of the *N*-TEB (II) spectrum.

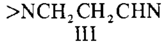


II

The proton NMR spectrum of the *N*-TEB photolysis product was examined and found to compare with a 2,3-disubstituted butane structure.[18,19] Bothner-By and Naar-Colin[18] interpreted the spectrum of 2,3-diphenylbutane. The similarities of benzene and borazine rings suggest that the relative rotamer populations of 2,3-diphenylbutane and 2,3-bis[*N*-(3′,5′-diethylborazinyl)]butane could be qualitatively compared. The exocyclic ethyl groups were interpreted as in *N*-TEB, the ring-linking group as a 2,3-disubstituted butane, an $X_3AA'X'_3$ system with $J_{XX'} = 0$ and $\nu_{AX} >> J_{AX}, J_{AX'}$. The *N*-TEB photolysis product is an unresolved mixture of *dl* and meso isomers. In $CDCl_3$ solvent the X protons could not be resolved from the C_β protons of the ethyl groups at 60 MHz nor 90 MHz. Anisotropic benzene-d_6 solvent affects the magnetic environment of protons dependent upon their orientation to the solvent molecule.[20] At 90 MHz, the X and C_β protons are resolved. The signal to noise enhancement of the Fourier transform NMR allowed the methine, A, protons to be located in the benzene-d_6 solvent. This structural evidence for the photolysis product of *N*-TEB suggests the existence of a radical intermediate, R^2, which subsequently dimerizes by radical combination. No product was observed with a structure similar to III, indicating that the radical R^2 is stable compared to R^3.



R^2



$${>}NCH_2CH_2\overset{CH_3}{\underset{|}{C}}HN{<}$$

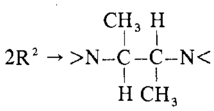
III

$${>}NCH_2CH_2\cdot$$

R^3

The proposed mechanism for the formation of 2,3-bis[*N*-(3′,5′-diethylborazinyl)]butane is shown by (5) and (6).

$$H\cdot + N\text{-TEB} \rightarrow H_2 + R^2 \quad (5)$$



$$2R^2 \rightarrow {>}N\text{–}\overset{CH_3}{\underset{H}{C}}\text{–}\overset{H}{\underset{CH_3}{C}}\text{–}N{<} \quad (6)$$

Irradiation of *B*-trimethylborazine and H_2 in the presence of Hg at 2537 Å produced a solid product. The electron impact mass spectrum of the product indicated a molecular ion at *m/e* 244 (Table IV) for the ^{11}B isotopic species. The base peak of the mass spectrum appeared at *m/e* 215, indicating a loss of two carbons and five hydrogens. The composition of these ions was confirmed in the high-resolution mass spectrum. The chemical ionization mass spectrum in methane supported the EI mass spectral analyses by indicating intense peaks at $(P + 1)^+$ corresponding to proton addition and $(P + 29)^+$ corresponding to $C_2H_5^+$ addition. Addition of $C_2H_5^+$ to borazine by chemical ionization in methane has been observed.[21] Proton NMR was employed to determine the molecular structure of the product molecule. A spectrum analogous to the results for the DMBE molecule was observed (Table V), with relative integrated intensities of methyl to ethylene protons of 3:1 and a small downfield shift for the ethylene protons. When a mixture containing a high ratio of H_2 to *B*-TMB was irradiated, no solid product was observed, but some hydrogen–methyl exchange occurred. Irradiation of a mixture of *B*-TMB-d_9 and D_2 produced a mixture of products. Irradiation at 2537 Å with a high ratio of D_2 to *B*-TMB-d_9 resulted in significantly more D–CD_3 exchange than in the H–CH_3 case. The loss of methyl groups was consistent with the low mass products observed in the radical dimerization experiment. The following mechanism is proposed.

$$H\cdot + B\text{-TMB} \xrightarrow[k_7]{} H_2 + \underset{R^4}{{>}BCH_2\cdot} \quad (7)$$

$$2R^4 \rightarrow {>}BCH_2CH_2B{<} \quad (8)$$

$$H\cdot + {>}BCH_3 \xrightarrow[k_9]{} {>}BH + CH_3\cdot \quad (9)$$

$$Hg(^3P_1) + D_2 \rightarrow Hg(^1S_0) + 2D\cdot \quad (10)$$

$$D\cdot + B\text{-TMB-}d_9 \xrightarrow[k_{11}]{} D_2 + \underset{R^5}{{>}BCD_2\cdot} \quad (11)$$

$$2R^5 \rightarrow {>}BCD_2CD_2B{<} \quad (12)$$

$$D\cdot + {>}BCD_3 \xrightarrow[k_{13}]{} {>}BD + CD_3\cdot \quad (13)$$

Comparing the results observed for *B*-TMB and *B*-TMB-d_9

$$k_7/k_9 > k_{11}/k_{13} \quad (14)$$

A possible explanation for the inequality in (14) is a kinetic isotope effect. Substituting D for H on the methyl groups should result in a more significant lowering of the zero-point energy for the C–D bonds than for the B–C bonds. This could have the effect of lowering the rate of reaction 11 relative to reaction 7 through changes in the relative activation energies for the two processes.

Photolysis of hexamethylborazine and H_2 with Hg at 2537 Å produced mainly *N*-TMB when the H_2 pressure was high. At low H_2 pressures, *N*-TMB was still observed as a photolysis product along with the formation of ethane. The mechanism (15)–(17) is proposed for the formation of *N*-TMB and ethane.

$$Hg(^3P_1) + H_2 \rightarrow Hg(^1S_0) + 2H\cdot \quad (15)$$

$$H + {>}BCH_3 \rightarrow {>}BH + CH_3\cdot \quad (16)$$

$$2CH_3\cdot \rightarrow C_2H_6 \quad (17)$$

A series of substitution reactions (reaction 16) will account for the formation of *N*-TMB from HMB.

Photolysis of *B*-TMB + *N*-TMB mixtures led to a solid product identified as DMBE. The *N*-TMB was completely consumed in the reaction, but most of the *B*-TMB was recovered unchanged, except for some hydrogen–methyl exchange. To account for this behavior it appears that the radical formed from *B*-TMB reacts with *N*-TMB

$$>BCH_2\cdot + N\text{-TMB} \rightarrow B\text{-TMB} + >NCH_2\cdot \qquad (18)$$

Equation 18 implies that $>NCH_2\cdot$ is thermodynamically more stable than $>BCH_2\cdot$.

Acknowledgment. We are grateful for support of this work by the National Science Foundation (Grant GH 33637) through the Material Science Center, Cornell University, and Grant No. CHE76-02477.

Registry No. *N*-MB, 21127-94-6; *N*-DMB, 23208-28-8; *N*-TMB, 1004-35-9; *N*-TEB, 7360-03-4; *B*-TMB, 5314-85-2; $[H_3B_3N_3H_2CH_2]_2$, 60607-08-1; $[H_3B_3N_3HCH_3CH_2]_2$, 60607-09-2; $[H_3B_3N_3(CH_3)_2CH_2]_2$, 54517-76-9; $[H_3B_3N_3(CH_2CH_3)_2CHCH_3]_2$, 60607-10-5; $[CH_2(CH_3)_2B_3N_3H_3]_2$, 60607-11-6.

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Proton–Proton Spin Coupling in Metallocarboranes. Triple-Resonance Nuclear Magnetic Resonance Spectroscopy as a Structural Probe for Boron Compounds[1]

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Received July 26, 1976 AIC60538N

Three-bond proton–proton spin coupling in 2,4-$C_2B_5H_7$ and a number of metallocarboranes have been examined in detail via triple-resonance NMR spectroscopy, in which ^{11}B and selective ^1H decouplings are conducted simultaneously while observing the proton NMR spectrum. Spin–spin coupling constants were obtained by direct measurement or by computer simulation of line spectra. The ranges were 10–20 Hz for H–C–C–H, 1–10 Hz for H–C–B–H, and 0–4 Hz for H–B–B–H. In the closo seven-atom cages, equatorial–equatorial proton interactions are stronger than those between equatorial and apical nuclei. The triple-resonance technique is shown to be a useful tool for investigating structure, frequently removing uncertainties in the interpretation of conventional NMR spectra and allowing unequivocal assignments of resonances.

Introduction

Proton nuclear magnetic resonance, in contrast to its overriding importance to organic chemists, has been a tool of only secondary interest to workers in the field of cage boron compounds. In the usual proton NMR spectrum of a borane or carborane, the resonances of hydrogen atoms bound to a ^{11}B atom (80% natural abundance, spin $^3/_2$) appear as broad, widely spaced quartets ($J \approx 180$ Hz) which are difficult to detect and often disappear entirely into the baseline noise.[2] Even when the H–B quartets can be identified, they rarely add significantly to the structural insights which are gleaned from the ^{11}B NMR spectrum of the same compound.

Recently, however, it has become clear that the proton spectra of carboranes contain inherently a wealth of information which is relevant to electronic and geometric structure, to a degree comparable to that seen in organic compounds. Several years ago we observed that certain metallocarboranes exhibit proton NMR spectra (undecoupled) in which the cage H–C resonances appear as multiplets instead of the usual broad singlets, and we postulated H–C–B–H proton–proton coupling as the cause of the observed fine structure.[3-7] With the aid of ^{11}B decoupling, Onak and Wan[8] have found similar three-bond proton–proton interactions in small carboranes; long-range coupling has also been reported in some of the lower boron hydrides.[9] We became interested in the systematic exploitation of proton–proton coupling as a structural tool in boron chemistry and initiated the present study which utilized a "triple-resonance" technique in which both ^{11}B decoupling and selective ^1H decoupling are simultaneously employed during observation of the 100-MHz proton NMR spectrum. The compounds examined included some whose structures are established and others of less well-defined geometry in which the ^1H–^1H coupling patterns could be used to remove structural ambiguities.

Experimental Section

Materials. The metallocarboranes studied were prepared by previously described methods as cited in the text; *closo*-dicarbaheptaborane(7) ($C_2B_5H_7$) was purchased from Chemical Systems, Inc., and used as received. Solvents were reagent grade and used as received.

Spectra. All metallocarboranes were examined in $CDCl_3$ solution in capped 5-mm tubes, while the $C_2B_5H_7$ spectra were obtained in acetone-d_6 solution in a sealed 5-mm tube under vacuum. Spectra were recorded in the pulse Fourier transform mode on a JEOL PS-100 P/EC spectrometer, using a deuterium lock.

Double-resonance experiments involving decoupling of ^1H and ^{11}B were conducted with the standard JEOL accessories JNM-OA-1M and JNM-SD-HC, respectively. The only modification required for triple-resonance experiments (decoupling ^{11}B and ^1H nuclei si-