first step in this reaction would form the species proposed as the intermediate in the reaction of diamines with an amine–iodoborane, *i.e.*, a cation in which trimethylamine and one end of the diamine are coordinated to BH_2^+ (step 1 above). Ring closure (step 2a) should be relatively more favorable since the competing reaction, leading to polynuclear species, is now another transamination rather than iodide displacement from amine–iodoborane as in step 2b. Transaminations on bis(trimethylamine)boronium ion are indeed very slow reactions as was shown in separate experiments here and elsewhere.[12]

Ebullioscopic experiments in acetonitrile solution were made for a number of salts and confirmed the structure assignments (Figure 1). Comparison with known compounds showed that 1+ ions gave nearly the expected apparent molecular weights in this solvent.[13] An increase in charge produced progressively larger deviations from the expected values in the direction expected for association of ions. The data for the polynuclear species derived from tetramethylbutanediamine suggest that extensive association exists in these materials and that the charge on the species is 3+ or larger. It is probable that the charge is not very great because the polynuclear species showed similar deviation from ideality as did an authentic 3+ ion. If this is true, then the elemental analysis which agrees with the formula $(\text{diamineBH}_2\text{PF}_6)_n$ suggests that the product contains large rings, rather than linear structures which would require additional terminal groups. There is little doubt, however, that the basic structural units have been correctly assigned, since, except for the generally broader appearance of absorption bands, the ir and nmr spectra closely correspond to those for the low molecular weight chelated species. These characteristics were invariant in materials obtained from reactions under different conditions. However, since solubilities in various solvents and exact elemental composition differed somewhat depending upon reaction conditions, it is likely that mixtures of polymers had been produced.

Acknowledgment.—Support of this research under Grant GM-13650, sponsored by the National Institutes of Health, is gratefully acknowledged.

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[12] T. E. Sullivan, M.S. Thesis, University of Florida, 1967.

[13] E. L. Muetterties, *J. Inorg. Nucl. Chem.*, **15**, 182 (1960); $(py)_2BI_2^+I^-$ gave an apparent molecular weight of 312 g; calcd 275 g.

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Photochemistry of Borazine. B-Halogenation Reactions

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Received September 9, 1969

B-Monobromoborazine has been obtained by the photolysis of a borazine–methyl bromide mixture in the gas phase with 1849-Å radiation. B-Monochloroborazine may be obtained by the photolysis of low-pressure mixtures of borazine and HCl, CH_3Cl, $CHCl_3$, CCl_4, or HSO_3Cl. Infrared spectra were obtained for monochloro- and monobromoborazine and the B-dideuterated derivatives. Aspects of the photochemical mechanism are discussed.

Introduction

Several monosubstituted borazines, including B-amino, B-hydroxy, and B-alkoxy derivatives, have been prepared by a photochemical procedure. We have now extended this procedure to halogenation reactions and in this paper we focus special attention on the reactions of borazine with methyl chloride and methyl bromide.

Experimental Section

Mixtures of borazine and halogenating reagent in the gas phase were irradiated with 1849-Å radiation in a procedure described earlier.[1] The initial ratio of borazine to reactant was about 5:1 with a total pressure between 10 and 15 mm. The series of halogenating reagents included CHF_3, HCl, CH_3Cl, $CHCl_3$, CCl_4, HSO_3Cl, CH_3Br, and CH_3I. B-Trideuterioborazine, prepared by the photochemical exchange of borazine and deuterium,[2] was also allowed to react with CH_3Cl and CH_3Br. Experiments designed to aid in establishing mechanisms included irradiation of borazine with CH_3Br and a fivefold excess of argon and irradiation of borazine–Br_2 mixtures with radiation of wavelengths above 3000 Å. After irradiation, the reaction mixture was opened to a −130° trap, allowing the most volatile products to pass through for sampling for mass spectral analysis. The portion of the reaction mixture frozen in the −130° trap was then warmed and pumped through traps at −65 and −196°. The −65° trap was then warmed to −45° and residual borazine was removed. Mass spectral analysis showed that the material remaining in the −45° trap was the monohaloborazine. Infrared spectra of the products were obtained on a Perkin-Elmer Model 521 spectrophotometer using a 9-cm gas cell equipped with CsI windows. Far-infrared spectra were obtained on a Beckman IR-11 spectrophotometer in cells with polyethylene windows. Borazine was prepared by the reaction of $LiBH_4$ and NH_4Cl[3] and was purified by addition of ammonia to precipitate diborane and aminodiborane which are obtained as by-products.

Results

Photochemical reactions of borazine with HCl,

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[1] G. H. Lee, II, and R. F. Porter, *Inorg. Chem.*, **6**, 648 (1967).

[2] R. F. Porter and E. S. Yeung, *ibid.*, **7**, 1306 (1968).

[3] G. W. Shaeffer, R. Schaeffer, and H. J. Schlesinger, *J. Amer. Chem. Soc.*, **73**, 1612 (1951).

CH_3Cl, $CHCl_3$, CCl_4, or HSO_3Cl in the gas phase yielded a product identified as B-monochloroborazine.[4] In a typical experiment, irradiation of a borazine–CH_3Cl mixture for 1 hr yielded 5–10 mg of isolated product. Irradiation of a borazine–CH_3Br mixture yielded B-monobromoborazine. The B-dideuterated derivatives were produced by irradiating B-trideuterioborazine and the methyl halide. Mass spectra of chloro- and bromoborazine are given in Figure 1 and the infrared spectra are shown in Figure 2. In Tables I and II are listed spectral data for the compounds and the B-dideuterated derivatives. Vapor pressures, measured at 0° with a silicone oil manometer, were about 6 mm for chloroborazine and 2 mm for bromoborazine. The compounds undergo some decomposition with repeated condensation and rewarming. Reaction of borazine and CH_3I produced no isolable derivative. Although fluoroborazine was detected in the borazine–CHF_3 reaction mixture, it was not in sufficiently large quantities for useful analysis. For the borazine-CH_3Cl and borazine–CH_3Br reactions the only other products observed aside from the haloborazine were CH_4 and a smaller amount of C_2H_6. Mass spectral analysis of the products of the B-trideuterioborazine–CH_3Br reaction indicated that the methane formed was predominantly CH_3D.

Discussion

Vibrational Assignments.—A partial vibrational analysis of B-monochloro- and B-monobromoborazine was obtained by comparing observed frequencies with the spectrum of borazine and from the deuterium isotope effects. It was assumed that the monosubstituted borazines have C_{2v} symmetry. The reduction in symmetry from borazine to the monohaloborazine results in 30 nondegenerate modes: 11 A_1, 3 A_2, 10 B_1, 6 B_2, with only the A_2 mode inactive in the infrared spectrum. For the chloro- and bromoborazines, the largest moment of inertia is the one with respect to the axis perpendicular to the ring. For motions parallel to this axis, bands with a prominent Q branch would be predicted. Motions parallel to the symmetry axis should exhibit band structure with P, Q, and R branches. The in-plane asymmetric vibrations should show B-type contours.

The band at 3475 cm^{-1} in chloro- and bromoborazine is clearly due to an N–H stretching motion. The position of the band, which has a B-type shape, is very close to that of the E′ stretching mode in borazine at 3486 cm^{-1}. Bands near 2530 and 1450 cm^{-1} are readily assigned to the B–H and ring stretching modes, respectively (2520 and 1465 cm^{-1} in borazine). The B–H in-plane bending vibrations at 1025 and 1000 cm^{-1} in chloroborazine and bromoborazine, respectively, are easily identified by the large isotope shift on deuterium substitution. Bands in the region near 1000 cm^{-1} showing P, Q, and R structure are interpreted as symmetric N–H bending and ring-stretching vibrations. The strong bands with prominent Q-branch

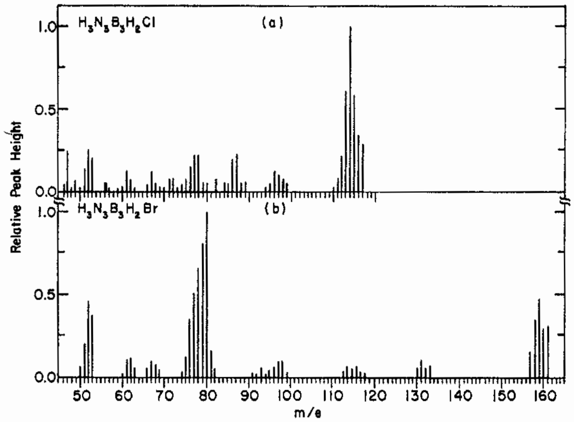

Figure 1.—(a) Portion of mass spectrum of B-monochloroborazine. (b) Portion of mass spectrum of B-monobromoborazine.

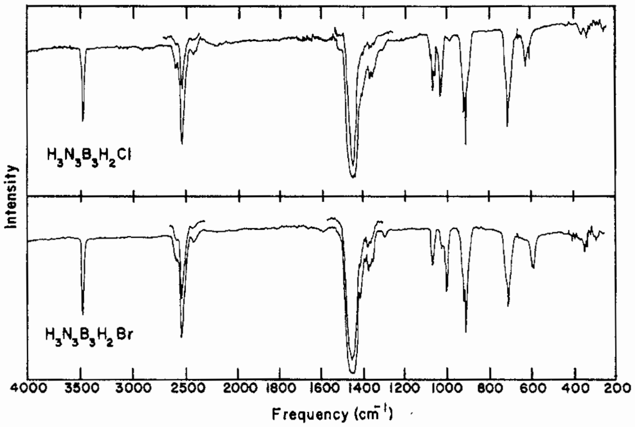

Figure 2.—Infrared spectra of B-monochloroborazine and B-monobromoborazine. For both compounds, sample pressure was *ca.* 6 mm for the complete spectrum and *ca.* 3 mm for the partial spectrum.

structure at 908 cm^{-1} in chloroborazine and at 914 cm^{-1} in bromoborazine are assigned to the out-of-plane B–H bending vibration (912 cm^{-1} in borazine). Other bands near 600 and 700 cm^{-1} also have band shapes expected for out-of-plane vibrations. The relatively broad bands at 625 cm^{-1} in chloroborazine and at 595 cm^{-1} in bromoborazine probably involve the boron–halogen stretch. Band contours for these vibrations may not be reliable for identification of the species of vibration because of complication of the halogen isotopes. Bands analogous to these are not observed in borazine and the isotope shifts upon deuterium substitution are slight.

Mechanism.—For radiation at 1849 Å the extinction coefficients for borazine, CH_3Cl, and CH_3Br have been determined in these experiments to be 810, 88, and <7 l./mol cm, respectively. Hence borazine absorbs a major fraction of the light at 1849 Å under the conditions of the photolysis experiments. Photolysis of CH_3Br in the absence of borazine did not yield notable quantities of CH_4 and C_2H_6 during a period of irradiation equal to that employed for the borazine–CH_3Br reactions. This observation and the detection of CH_3D in the products of the $D_3B_3N_3H_3$–CH_3Br re-

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[4] R. Maruca, O. T. Beachley, Jr., and A. W. Laubengayer, *Inorg. Chem.*, **6**, 575 (1967).

TABLE I

INFRARED SPECTRA OF B-MONOCHLOROBORAZINE AND B-DEUTERIOMONOCHLOROBORAZINE[a]

$H_2ClB_3N_3H_3$			$D_2ClB_3N_3H_3$		
Freq, cm^{-1}	Intens	Remarks	Freq, cm^{-1}	Intens	Remarks
3480, 3475	m	Asym N–H str	3480, 3475	m	Asym N–H str
2600, 2590	vw				
			2540, 2530[b]	w	Due to HD species
2530	s	B–H str.			
2420	vw				
			1930 sh	vw	
			1905, 1895	s	Asym B–D str
1520	vw				
1450	vs	B–N ring str			
			1445	vs	B–N ring str
1420 sh, 1410 sh	vw				
			1400 sh, 1370	vw	B–N ring str
1345–1370	w	B–N ring str			
			1335	w	
1310	vw				
			1250	vw	
			1210	vw	
1080, 1075, 1070 (PQR)[c]	w				
			1078, 1072, 1068 (PQR)[c]	w	
1070, 1065, 1060 (PQR)	m	Sym in-plane N–H def	1065?	vw	
			1050, 1045, 1040 (PQR)	m	Sym in-plane N–H def
1033, 1025, 1020 (PQR)	m	Sym in-plane B–H def			
985	vw				
			975, 970, 965 (PQR)	w	
920, 908	s	Out-of plane B–H def			
			910[b]	vw	Due to HD species
			806, 803, 796, 782[d]	m	Out-of-plane B–D def
			750, 745	vw	In-plane B–D def
710	s	Out-of-plane N–H def	710, 705	s	Out-of-plane N–F def
625	w	Mainly B–Cl str			
605	w	Out-of-plane def			
			600	w	Mainly B–Cl str
			590	w	Out-of-plane def
360	vw	Mainly B–Cl in-plane def or B–N out-of-plane ring def	360	vw	Mainly B–Cl in-plane de for out-of-plane B–N ring def
345	vw				

[a] Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; str, stretch; sym, symmetric; asym, asymmetric; def, deformation. [b] Due to partially deuterated species ($ClHDB_3N_3H_3$). [c] Due to B^{10} species. [d] Partially deuterated species account for some of the peaks.

action indicate that the presence of borazine is essential to the formation of methane. The possibility that Br atoms are required for the formation of bromoborazine seems unlikely since the product was not detected in the photolysis of borazine–Br_2 mixtures at wavelengths above 3000 Å. Under these conditions borazine does not absorb light but Br atoms can be formed from Br_2.[5] The addition of excess argon to the borazine–CH_3Br mixture did not result in a lowering of the yield of bromoborazine as might be expected if Br atoms, which can be deactivated by gas-phase collisions, were essential to the mechanism.

Photochemical experiments in borazine–D_2 exchange were interpreted on the basis of an excited-state mechanism rather than the formation of a borazinyl and H radical in the primary step. From these considerations and the present evidence on the halogenation reaction it is probable that the reaction to form monobromoborazine involves reaction of CH_3Br with an excited borazine intermediate which is formed after the initial act of absorption. We have discussed previously the possibility that the intermediate is the $^1A_1$ excited state.[6]

The reaction

$$H_3B_3N_3H_3^* + CH_3Br \longrightarrow H_2BrB_3N_3H_3 + CH_4 \qquad (1)$$

will account for the formation of methane, but the presence of C_2H_6 in significant amounts is more difficult to explain. At least two explanations can be offered for the formation of C_2H_6 consistent with an excited-state mechanism. These are (1) that methyl bromide is photosensitized by the excited state of borazine

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(5) J. Franck, *Trans. Faraday Soc.*, **21**, 536 (1926).

(6) M. P. Nadler and R. F. Porter, *Inorg. Chem.*, **8**, 599 (1969).

TABLE II

INFRARED SPECTRA OF B-MONOBROMOBORAZINE AND B-DEUTERIOMONOBROMOBORAZINE[a]

$H_2BrB_3N_3H_3$			$D_2BrB_3N_3H_3$		
Freq, cm⁻¹	Intens	Remarks	Freq, cm⁻¹	Intens	Remarks
3480, 3470	m	Asym N–H str	3480, 3470	m	Asym N–H str
2600, 2590	vw				
2535	s	B–H str			
2530	vw				
			2515[b]	w	Due to HD species
			1905	s	B–D str
1450	vs	B–N ring str			
			1440	vs	B–N ring str
1413	vw				
			1370, 1330	w	B–N ring str
1350–1390	w	B–N ring str			
1295	vw				
1072, 1067, 1062 (PQR)	m	Sym in-plane N–H def			
			1059, 1055, 1050 (PQR)	m	
			1042, 1039, 1034 (PQR)	m	Sym in-plane N–H def
1032, 1025, 1020 (PQR)	vw				
1010	m				
1004, 1000, 996 (PQR)	m	Sym in-plane B–H def			
			994[b]	vw	Due to HD species
			966	w	
			956, 953, 948 (PQR)	m	
925, 917, 914	s	Out-of-plane B–H def			
			911[b]	vw	Due to HD species
854	vw				
			813, 809, 806, 799[c]	s	Asym out-of-plane B–D def
			740	w	In-plane B–D def
715	m	Out-of-plane N–H def			
			714, 706	m	Out-of-plane N–H def
595	w	Mainly B–Br str			
590	w	Out-of-plane def			
			580	w	Out-of-plane def
			570	w	Mainly B–Br str
340	vw	Mainly B–Br str or out-of-plane B–N ring def			
			290	vw	
285	vw				

[a] Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; str, stretch; sym, symmetric; asym, asymmetric; def, deformation. [b] Due to partially deuterated species ($BrHDB_3N_3H_3$). [c] Partially deuterated species account for some of the peaks.

leading to CH_3 radicals that can recombine and (2) that reaction 1 yields CH_3 and H radicals through release of the excess energy. Further quantum yield experiments may help to resolve this problem.

Several chlorinating reagents were found to be photochemically reactive with borazine. Methyl chloride, chloroform, and carbon tetrachloride were all used efficiently. As a preparative tool photochemical halogenations of borazine may have some advantages because of the simplicity of the halogenating reagents used. The yields of monosubstituted product depend mainly on the irradiation time, and competing thermal reactions that yield undesired products may be reduced by working with low pressures.

Acknowledgments.—We gratefully acknowledge financial support from the Army Research Office—Durham and the Advanced Research Projects Agency (Materials Science Center, Cornell University).