12622-24-1; Cu_7Cl_7, 53906-70-0; Cu_8Cl_8, 53906-71-1; $Cu_{12}Cl_{12}$, 53906-72-2; $Cu_{15}Cl_{15}$, 53906-73-3; Na_2, 25681-79-2; Na_3, 37279-42-8; Na_4, 39297-86-4; Na_5, 39297-87-5; Na_6, 39297-88-6; Na_7, 39297-89-7; Na_8, 39297-90-0.

References and Notes

(1) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965).
(2) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).
(3) J. H. Sinfelt, *Chem. Eng. Progr., Symp. Ser.*, **63**, 16 (1967).
(4) J. H. Sinfelt, *J. Catal.*, **29**, 308 (1973).
(5) H. Stoll and H. Preuss, *Phys. Status Solidi*, **53**, 519 (1972).
(6) R. Hoffmann, *Tetrahedron*, **22**, 521 (1966).
(7) H. Dunken, *Z. Chem.*, **12**, 433, 475 (1972).
(8) G. Blyholder, *J. Chem. Soc., Chem. Commun.*, 625 (1973).
(9) R. C. Baetzold, *J. Chem. Phys.*, **55**, 4363 (1971).
(10) R. C. Baetzold, *J. Catal.*, **29**, 129 (1973).
(11) D. J. M. Fassaert, H. Verbeek, and A. Van der Avoird, *Surface Sci.*, **29**, 501 (1972).
(12) J. C. Robertson and C. W. Wilmsen, *J. Vac. Sci. Technol.*, **9**, 901 (1972).
(13) J. C. Robertson and C. W. Wilmsen, *J. Vac. Sci. Technol.*, **8**, 53 (1971).
(14) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).
(15) M. Guido, G. Balducci, G. Gigli, and M. Spoliti, *J. Chem. Phys.*, **55**, 4566 (1971).
(16) M. Guido, G. Gigli, and G. Balducci, *J. Chem. Phys.*, **57**, 3731 (1972).
(17) (a) E. J. Robbins, R. E. Leckenby, and P. Willis, *Advan. Phys.*, **16**, 739 (1967); (b) P. J. Foster, R. E. Leckenby, and E. J. Robbins, *Proc. Phys. Soc., London (At. Mol. Phys.)*, **2**, 478 (1969).
(18) R. C. Baetzold, *J. Chem. Phys.*, **55**, 4355 (1971).
(19) C. E. Moore, *Nat. Bur. Stand. (U.S.), Circ.*, No. 467 (1949).
(20) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).
(21) L. C. Cusachs and J. H. Corrington, "Sigma MO Theory," O. Sinanoglu and K. Widberg, Ed., Yale University Press, New Haven, Conn., 1970.
(22) L. C. Cusachs and J. W. Reynolds, *J. Chem. Phys.*, **43**, S160 (1965).
(23) M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20**, 837 (1952).
(24) J. J. Burton, *J. Chem. Phys.*, **52**, 345 (1970).
(25) C. Kittel, "Introduction to Solid State Physics," 3rd ed, Wiley, New York, N.Y., 1968.
(26) F. Herman and D. S. McClure, *Bull. Amer. Phys. Soc.*, **5**, 48 (1960).
(27) S. Kono, T. Ishii, T. Sagawa, and T. Kobayasi, *Phys. Rev. B*, **8**, 795 (1973).
(28) P. Ros and G. C. A. Schuit, *Theor. Chim. Acta*, **4**, 1 (1966).
(29) T. A. Koopmans, *Physica*, **1**, 104 (1933).

Notes

Contribution from the Department of Chemistry,
University of Utah, Salt Lake City, Utah 84112

Preparation of Bis(halodifluorophosphine)–Diborane(4) Complexes

R. T. Paine* and R. W. Parry

Received April 16, 1974 AIC40245Z

A few complexes of the bidentate Lewis acid B_2H_4 have been reported. Graybill and Ruff[1] prepared $[(C_6H_5)_3P]_2{\cdot}B_2H_4$ from $(CH_3)_3N{\cdot}B_3H_7$ through the reaction

$$(CH_3)_3N{\cdot}B_3H_7 + 3[(C_6H_5)_3P](\text{excess}) \xrightarrow[50^\circ]{\text{benzene}} [(C_6H_5)_3P]_2{\cdot}B_2H_4 + (C_6H_5)_3P{\cdot}BH_3 + N(CH_3)_3$$

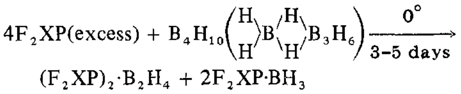
Deever, Lory, and Ritter, in a series of papers, described the preparation of B_2H_4 complexes of PF_3[2,3] and PF_2H[4] from $(CH_3)_2O{\cdot}B_3H_7$

$$(CH_3)_2O{\cdot}B_3H_7 + PF_3(\text{excess}) \xrightarrow{-16^\circ} (F_3P)_2{\cdot}B_2H_4 + F_3P{\cdot}BH_3$$

$$(CH_3)_2O{\cdot}B_3H_7 + PF_2H(\text{excess}) \xrightarrow{-16^\circ} (F_2HP)_2{\cdot}B_2H_4 + F_2HP{\cdot}BH_3$$

Lory and Ritter[4] prepared $(R_2NPF_2)_2{\cdot}B_2H_4$ and $(F_2HP)_2{\cdot}B_2H_4$ using B_4H_{10} as a B_2H_4 source instead of $(CH_3)_2O{\cdot}B_3H_7$. In the present study the bis(ligand)–diborane(4) complexes of PF_2X where X is F, Cl, and Br have been prepared from both $(CH_3)_2O{\cdot}B_3H_7$ and B_4H_{10}. The appropriate equations are

$$3F_2XP + (CH_3)_2O{\cdot}B_3H_7 \xrightarrow[5\ \text{hr}]{0^\circ} (F_2XP)_2{\cdot}B_2H_4 + F_2XP{\cdot}BH_3 + (CH_3)_2O$$



$$4F_2XP(\text{excess}) + B_4H_{10}\left(\begin{matrix}H\\H\end{matrix}B\begin{matrix}H\\H\end{matrix}B_3H_6\right) \xrightarrow[3\text{–}5\ \text{days}]{0^\circ} (F_2XP)_2{\cdot}B_2H_4 + 2F_2XP{\cdot}BH_3$$

The reactions involved and the products obtained can be analyzed in terms of base displacement processes which were considered in a general sense by Parry and Edwards[5] and in a more refined sense by Deever, Lory, and Ritter[3] and by Paine and Parry.[6]

Experimental Section

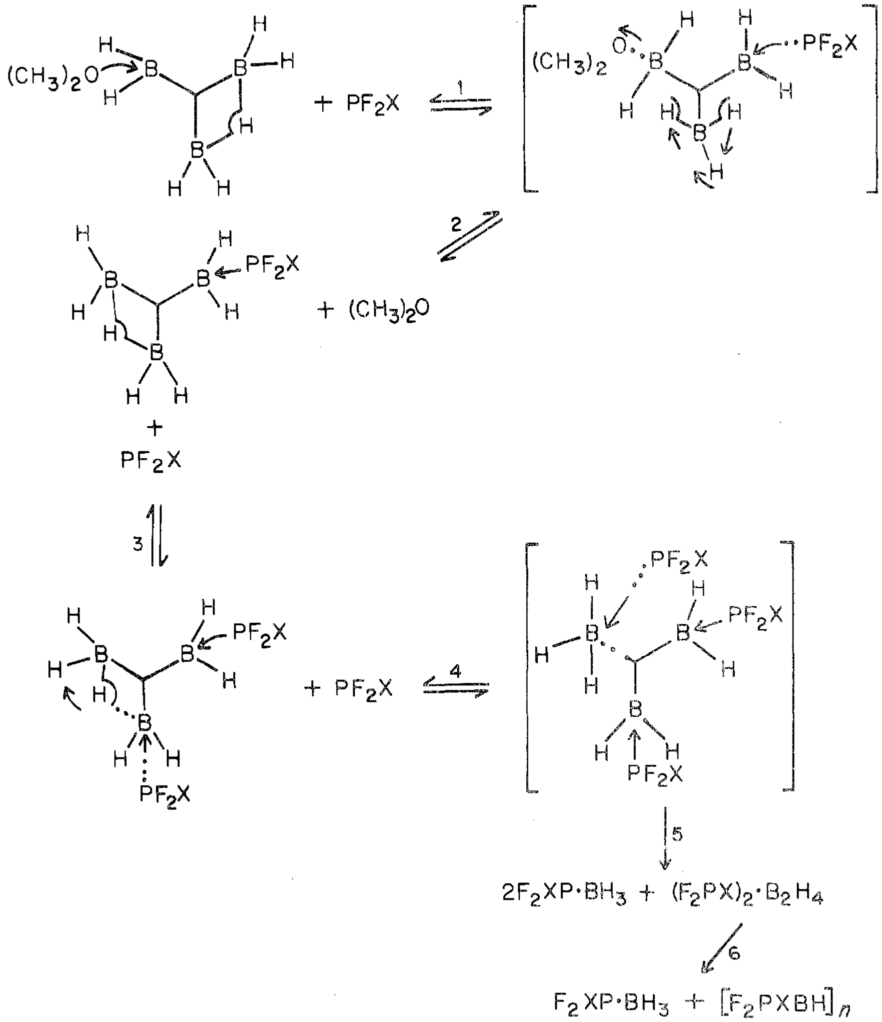
Equipment. Standard high-vacuum techniques were used for the manipulation of the volatile compounds. Infrared spectra were recorded on a Beckman IR20 spectrometer using a 70-mm path length gas cell with KBr windows. The nmr spectra were recorded on a Varian HA/HR 100 instrument operating at 32.1 MHz (^{11}B) and 94.1 MHz (^{19}F).[7] An external standard, $(CH_3)_3B$, was used for the ^{11}B nmr spectrum and an internal standard, $CFCl_3$, was used for the ^{19}F nmr spectrum. The $CFCl_3$ also served as the sample solvent.

Materials. Tetraborane(10) was prepared by the "hot–cold" tube pyrolysis of diborane(6) as described by Klein, Harrison, and Solomon.[8] The $(CH_3)_2O{\cdot}B_3H_7$ samples were prepared and purified as described by Deever and Ritter.[9] Trifluorophosphine was purchased from Ozark Mahoning Co. and was distilled through a −160° trap before using. The F_2ClP and F_2BrP ligands were prepared and purified by literature procedures.[10]

Reaction of B_4H_{10} with F_2XP. A 2.7-mmol sample of B_4H_{10} and a 12.5-mmol sample of F_2XP, X = F, Cl, or Br, were condensed into a 5.0-ml tube and sealed off. The tube was held at 0° for 3–5 days and then opened, and the contents were vacuum distilled through traps held at −96, −126, −160, and −196°. The $(F_3P)_2{\cdot}B_2H_4$ complex was retained at −126° and the $(F_2ClP)_2{\cdot}B_2H_4$ and $(F_2BrP)_2{\cdot}B_2H_4$ complexes were retained at −96°. The complexes were identified by infrared and nmr spectra. The yields of $(F_2XP)_2{\cdot}B_2H_4$ were 50–60% based on the B_4H_{10} consumed. When the same reactions were run in an nmr tube with a reactant ratio of $F_2XP{:}B_4H_{10} = 5{:}1$, the ^{19}F nmr spectra of the products showed $(F_2XP)_2{\cdot}B_2H_4$ and $F_2XP{\cdot}BH_3$, but no $F_2XP{\cdot}B_3H_7$.

Reaction of $(CH_3)_2O{\cdot}B_3H_7$ with Excess F_2XP. A 3.1-mmol sample of $(CH_3)_2O{\cdot}B_3H_7$ was prepared in a 10-ml reaction tube equipped with a Teflon stopcock. A 9.7-mmol sample of F_2XP, X = F, Cl, or Br, was added, the tube was closed, and then the system was held at 0° for 5 hr. After the reaction was complete, the tube was held at −78° and the volatile products were vacuum distilled as described above. The yields of $(F_2XP)_2{\cdot}B_2H_4$ complexes were approximately 40% based on the $(CH_3)_2O{\cdot}B_3H_7$ consumed. When the same reactions were run in an nmr tube with the reactant ratio $F_2XP{:}(CH_3)_2O{\cdot}B_3H_7 = 3{:}1$, the ^{19}F nmr spectra of the products showed large amounts of $(F_2XP)_2{\cdot}B_2H_4$ and $F_2XP{\cdot}BH_3$ and a very small amount of $F_2XP{\cdot}B_3H_7$.

Properties of $(F_2XP)_2{\cdot}B_2H_4$ Complexes. The infrared spectra of the $(F_2XP)_2{\cdot}B_2H_4$ complexes were similar to that reported by Deever and Ritter[2] for $(F_3P)_2{\cdot}B_2H_4$. The absorptions (cm^{-1}) and tentative assignments for $(F_2ClP)_2{\cdot}B_2H_4$ are as follows: 2400 [ν_{as}(B–H)], 2350 [ν_s(B–H)], 1100 [$\delta(BH_2)$], 1000 [?], 960 [ν(P–F)], 850 [ν(P–F)], 640 [ν(P–B)], 535 [ν(P–Cl)], 390 [δ(P–F)]. The spectrum of $(F_2BrP)_2{\cdot}B_2H_4$ is identical except for [ν(P–Br)]. (The symbols used above are defined as ν = stretch and δ = deformation.) The ^{11}B and ^{19}F nmr spectral parameters are summarized in the order X = F, Cl, Scheme I



Br, for $(F_2XP)_2 \cdot B_2H_4$: $\delta(^{11}B)$ 137.2, 127.9, 123.6 ppm; $\delta(^{19}F)$ −20.8, −29.9, −37.0 ppm; $J(PF)$ = 1259, 1357, 1340 Hz. (The spectra were recorded at −45° and the chemical shifts are relative to $(CH_3)_3B$ and CF_3COOH.)

Results and Discussion

A recent electron diffraction study by Lory, Porter, and Bauer[11] has shown that $(F_3P)_2 \cdot B_2H_4$ has the expected symmetrical structure containing a B–B linkage. Obvious similarities in the infrared and nmr spectra of $(F_2ClP)_2 \cdot B_2H_4$, $(F_2BrP)_2 \cdot B_2H_4$ and $(F_3P)_2 \cdot B_2H_4$ indicate that all three have similar geometry. The ^{11}B nmr spectrum of each compound consisted of a very broad singlet; no resolution of the B–H coupling was achieved. The ^{19}F spectrum showed a widely spaced doublet for $J(PF)$ with no resolvable fine structure. More detailed data showing the temperature dependence of the nmr spectra would be of interest.

Data on the progress of the reaction with various reaction conditions provide information on possible mechanisms. When $(CH_3)_2O \cdot B_3H_7$ and PF_2X were mixed in a 1:1 ratio at 0°, the fluorine-19 nmr spectrum showed about 30% $F_2XP \cdot B_3H_7$ after 30 min.[6] On standing at 0° the amount of $F_2XP \cdot B_3H_7$ gradually decreased and $(F_2XP)_2 \cdot B_2H_4$ formed. As the initial amount of F_2XP was increased, the maximum yield of $F_2XP \cdot B_3H_7$ found in the spectrum decreased. The reactions using B_4H_{10} as a boron source were much slower but showed similar trends. After a 1.5:1 mixture of B_4H_{10} and F_2XP was allowed to stand at 0° for 3–5 days, about 10% $F_2XP \cdot B_3H_7$ and no $(F_2XP)_2 \cdot B_2H_4$ were detected in the product mixture.[6] Under similar reaction conditions, a reactant ratio of 1:2 produced about 30% $(F_2XP)_2 \cdot B_2H_4$ and less than 10% $F_2XP \cdot B_3H_7$.[6] A reactant ratio of 1:5 produced 50–60% $(F_2XP)_2 \cdot B_2H_4$ and no $F_2XP \cdot B_3H_7$.

The data can be interpreted through an extrapolation of detailed reaction models suggested earlier by Ritter, Deever, and Lory[3,4] and by the authors.[6] It is assumed that the initial displacement reaction is reversible and that it can be represented as shown in Scheme I (steps 1 and 2). Because PF_2X appears to be comparable to or slightly weaker than $(CH_3)_2O$[12] as a Lewis base, the initial base displacement process does not go to completion and a sizable quantity of unreacted PF_2X remains in the system. Because PF_2X is a relatively weak base in combination with B_3H_7, the electron donation by phosphorus to the borane fragment is low, and the complex $F_2XP \cdot B_3H_7$ retains considerable Lewis acid strength.[4,6] Free PF_2X existing in the system then attacks the slightly acidic $F_2XP \cdot B_3H_7$ complex (eq 3) to give a double adduct which is vulnerable to further attack by PF_2X to give $H_3B \cdot PF_2X$ and $H_4B_2 \cdot 2PF_2X$ (eq 4 and 5) or $H_3B \cdot PF_2X$ and $[HBPF_2X]_n$ (eq 4–6).

This model rationalizes the initial appearance of $F_2XP \cdot B_3H_7$ and its conversion to $(F_2XP)_2 \cdot B_2H_4$ on standing. It also suggests that an excess of F_2XP should generate $(F_2XP)_2 \cdot B_2H_4$ rather than $F_2XP \cdot B_3H_7$. It further suggests that shifting of the equilibrium toward $F_2XP \cdot B_3H_7$ (eq 1 and 2) should convert free F_2XP to complexed $F_2XP \cdot B_3H_7$ and reduce attack by free F_2XP on the adduct $F_2XP \cdot B_3H_7$ (eq 3). If this fundamental process for decomposition of $F_2XP \cdot B_3H_7$ could be minimized, $F_2XP \cdot B_3H_7$ should be isolatable and relatively stable. This conclusion has been verified.[6] Addition of BF_3 to the system complexed the ether released; this shifted the equilibrium and permitted the isolation of formerly unattainable $F_2XP{\cdot}B_3H_7$ and OCB_3H_7 complexes. Stability data suggest that if a relatively strong base is bound to the B_3H_7 fragment, the *acid strength* of the base–B_3H_7 complex is inductively reduced.[4,6,13] Under these conditions, attack can only be by a very strong Lewis base. For this reason the $(CH_3)_3N{\cdot}B_3H_7$ complex, when once formed, is attacked only by excess $(CH_3)_3N$ or, better, by still stronger bases [*i.e.*, $P(C_6H_5)_3$].

As noted above, the equilibrium in the reversible displacement reaction (eq 1 and 2) is important. If the attacking base (L) is much stronger than the base which is being displaced (*i.e.*, $(CH_3)_2O$), the equilibrium in the 1:1 mixture goes rapidly to completion and the concentration of free base (L) capable of attacking the LB_3H_7 complex is reduced effectively to zero, thus minimizing conversion to $L_2{\cdot}B_2H_4$ through eq 3. This is observed when L is $(CH_3)_3N$.[13] Since the $(CH_3)_3N{\cdot}B_3H_7$ complex is stable enough to resist attack by ether, further decomposition does not occur.

In the case of the reaction of PF_2X and $(CH_3)_2O{\cdot}B_3H_7$, conversion to $(F_2XP)_2{\cdot}B_2H_4$ is promoted by the moderately high residual acid strength of the complex $F_2XP{\cdot}B_3H_7$ and by the high equilibrium concentration of F_2XP in the initial displacement process. The foregoing model suggests that as the attacking base F_2XP becomes weaker, the concentration of $F_2XP{\cdot}B_3H_7$ should decrease. This is in complete agreement with published work; *e.g.*, the decreasing base strength trend $X = (CH_3)_2N > F > Cl > Br$ parallels the decreasing stability of $F_2XP{\cdot}B_3H_7$.[6] Furthermore the presence of uncoordinated fluorophosphine in increasing equilibrium amounts in the order $X = (CH_3)_2N > F > Cl, Br$ should result in increasing degradation of the $F_2XP{\cdot}B_3H_7$ and increasing amounts of $(F_2XP)_2{\cdot}B_2H_4$. Analysis of the product yields from the 1:1 reaction of $(CH_3)_2O{\cdot}B_3H_7$ and F_2XP, in fact, shows a small relative increase in the amount of $(F_2XP)_2{\cdot}B_2H_4$ formed with decreasing base strength. Clearly, as noted by Ritter and his associates, both the relative strength of the bases which determine concentrations in the displacement reactions and the absolute strength of bases which determine strength of the base–B_3H_7 complex as a Lewis acid are important in determining products to be expected from these reactions.

The reactions of B_4H_{10} can be treated in a strictly analogous manner if a BH_3 group, coordinating through a double BHB bridge, is considered as an operational Lewis base comparable to $(CH_3)_2O$.[5] Indeed, these reactions of B_4H_{10} with a 2 mol sample of base can be considered as one of the first cases of an assisted displacement reaction since the operational base, BH_3, is tied up by the Lewis base NR_3 and removed from the system just as effectively as $(CH_3)_2O$ is removed by BF_3.[6]

Acknowledgment. We gratefully acknowledge the generous support of the National Science Foundation through Grant GP 14873 to the University of Utah.

Registry No. $(F_3P)_2{\cdot}B_2H_4$, 17239-60-0; $(F_2ClP)_2{\cdot}B_2H_4$, 53293-17-7; $(F_2BrP)_2{\cdot}B_2H_4$, 53229-22-4; B_4H_{10}, 18283-93-7; $(CH_3)_2O{\cdot}B_3H_7$, 53229-23-5; PF_3, 7783-55-3; PF_2Cl, 14335-40-1; PF_2Br, 15597-40-7.

References and Notes

(1) B. M. Graybill and J. K. Ruff, *J. Amer. Chem. Soc.*, **84**, 1062 (1962).

(2) W. R. Deever and D. M. Ritter, *J. Amer. Chem. Soc.*, **89**, 5073 (1967).

(3) W. R. Deever, E. R. Lory, and D. M. Ritter, *Inorg. Chem.*, **8**, 1263 (1969).

(4) E. R. Lory and D. M. Ritter, *Inorg. Chem.*, **10**, 939 (1971); E. R. Lory, Ph.D. Thesis, University of Washington, Seattle, Wash., 1969.

(5) R. W. Parry and L. J. Edwards, *J. Amer. Chem. Soc.*, **81**, 3554 (1959).

(6) R. T. Paine and R. W. Parry, *Inorg. Chem.*, **11**, 268 (1972).

(7) Nmr spectra were recorded by R. T. P., at Varian Associates, Analytical Division, Palo Alto, Calif.

(8) M. J. Klein, B. C. Harrison, and I. J. Solomon, *J. Amer. Chem. Soc.*, **80**, 4149 (1958).

(9) W. R. Deever and D. M. Ritter, *Inorg. Chem.*, **7**, 1036 (1968).

(10) J. G. Morse, K. Cohn, R. W. Rudolph, and R. W. Parry, *Inorg. Syn.*, **10**, 147 (1967).

(11) E. R. Lory, R. F. Porter, and S. H. Bauer, *Inorg. Chem.*, **10**, 1072 (1971).

(12) R. T. Paine, Ph.D. Thesis, University of Michigan, Ann Arbor, Mich., 1970.

(13) L. J. Edwards, W. V. Hough, and M. D. Ford, *Proc. Int. Congr. Pure Appl. Chem.*, **16** (1957).

Contribution from the Department of Chemistry,
Cornell University, Ithaca, New York 14850

Photochemical Reaction of Hexafluoroacetone with Borazine. Preparation of *B*-(2*H*-Hexafluoro-2-propoxy)borazine and *B*-(Perfluoro-*tert*-butoxy)borazine

Laura J. Turbini, George M. Golenwsky, and Richard F. Porter*

Received May 21, 1974 AIC40327N

Photochemical reactions of borazine in the absence of photosensitizing reagents have been interpreted as proceeding through an excited-state mechanism when borazine is the primary absorber.[1-3] Reactions involving free-radical intermediates have not been explored as potential sources of new borazine derivatives. We have now investigated the reaction of borazine in the presence of photochemically generated radicals from hexafluoroacetone (HFA). The photochemistry of HFA has been the subject of numerous studies,[4-6] and quantitative data for fluorescence[5b,7] and phosphorescence[5b,6] rate constants have been reported. Electronic excitation of borazine is observed at wavelengths below 2000 Å.[8-11] Thus, in mixtures of borazine and HFA, photolysis at wavelengths above 2000 Å will be controlled primarily by HFA intermediates. Two reports in the literature describe the photolysis of HFA with diborane[12] and with triethylborane.[13] However, the boron-containing products of these reactions were not identified.

Experimental Section

Borazine was prepared by the reduction of *B*-trichloroborazine with $NaBH_4$ (Alpha Chemical Co.) according to the method of Hohnstedt and Haworth.[14] *B*-Trideuterioborazine was prepared by the photolysis of borazine with excess D_2 (Matheson, CP grade, 99.5 atom %).[1] Hexafluoroacetone (Matheson), 2*H*-hexafluoro-2-propanol (E. I. du Pont de Nemours and Co., Inc.), and perfluoro-*tert*-butyl alcohol (Peninsula ChemResearch) were vacuum distilled through a trap maintained at −80°. Purity of these reagents was confirmed by infrared and mass spectra.

Photolyses of borazine–HFA mixtures (4:1 molar ratio, total pressure 5 mm) were carried out in a 2-l. vessel equipped with a quartz immersion well. The light source, a Hanovia medium-pressure mercury lamp, was purged with dry nitrogen during the 25-min photolysis periods. In separate experiments Vycor and Corex filters were used to block radiation below 2200 and 2700 Å, respectively. In one experiment, *B*-trideuterioborazine was photolyzed with HFA. The photochemical products were separated by conventional vacuum distillation through traps maintained at −55, −65, and −196°. The −55° trap was found to contain a new photochemical product subsequently identified as I, while analysis of the −65° trap revealed a mixture of I and a slightly more volatile product II. These products were obtained under all light filter conditions employed. Products I and II were also obtained in pure form by 1849-Å photolysis of hexafluoro-2-propanol–borazine and perfluoro-*tert*-butyl alcohol–borazine mixtures, respectively. For the latter experiments borazine–alcohol mixtures in a 4:1 ratio (total pressure 5 mm) were photolyzed for 30 min. In order to clarify the reaction mechanism, product I was photolyzed for 30 min with HFA. Neither I nor II is observed as a thermal product at the pressures studied. Products were analyzed by mass, infrared, and nmr spectroscopy. Mass spectra