carbon triple bond and not an allenic group, and also as in the trivalent compound no stretches attributable to either $=CH_2$ wagging or a C≡CH are present.[18,19] The infrared spectrum is listed in Table I.

The ^{19}F and ^1H nmr spectra support the prop-1-ynyl structure.[21-26] As in all RPF_4 compounds (R = alkyl) the fluorines appear to be equivalent over a wide range of temperatures. The ^{19}F nmr spectrum consists of a doublet of quartets ($J_{PF} = 896$ Hz, $J_{FH} = 2.6$ Hz) from −10 to −80°. The spectrum could not be taken any lower than −80° as $PF_4C_3H_3$ began to freeze from the isopentane solution. J_{PF} and J_{FH} do not vary over this range of temperatures while the chemical shift from external $CFCl_3$ varies from +41.7 ppm (−10°, $CHCl_3$) to +40.7 ppm (−80°, isopentane). These spectra are typical of a tetrafluorophosphorane except that the chemical shift is slightly out of the range normally observed for these compounds (∼+45 to +55 ppm).[35] No nmr spectra have been obtained on neat samples because of preparative difficulties.

As in $PF_2C_3H_3$, the simplicity of the ^1H spectra confirm the 1-alkynyl rather than the allenic or terminal acetylenic structure.[21-26] The spectrum is a doublet of pentets ($J_{FH} = 2.6$ Hz, $J_{PH} = 2.6$ Hz, δ(relative to internal tetramethylsilane) 1.98 ppm (−10°, $CHCl_3$)).

Prop-1-ynyltetrafluorophosphorane has also been obtained in the decomposition of $PF_2C{\equiv}CCH_3$ and from the reaction of SbF_3 (catalytic amount of $SbCl_5$[35]) with $PF_2C_3H_3$. No reaction occurs unless the catalyst is present. The infrared and ^{19}F and ^1H nmr spectra of the compound prepared from these reactions are identical with those of the compound prepared from the reaction of BF_3 and $PF_2C_3H_3$.

Registry No. $PF_2C_3H_3$, 37805-59-7; LiC_3H_3, 4529-04-8; PF_2Br, 15597-40-7; B_2H_6, 1928-74-57; $PF_2C_3H_3BH_3$, 37805-62-2; BF_3, 763-70-72; $PF_4C_3H_3$, 37805-63-3; SbF_3, 7783-56-4.

Acknowledgment. The authors are grateful for the assistance of John Gray with the ^{19}F nmr, Richard Cox with the ^{31}P and ^{11}B nmr, and Roy Jones with the mass spectrometer. We also thank the Air Force for the use of a Jeol 60-MHz nmr at Robins Air Force Base and gratefully acknowledge the Petroleum Research Fund administered by the American Chemical Society for support of this work.

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Mass Spectra of Unsymmetrically B-Substituted Borazines

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The mass spectra of B-substituted derivatives of borazine and of *N*-trimethylborazine were recorded and analyzed in terms of the relative contribution of the parent ion and certain fragment ion intensities. A method of spectral analysis was developed to separate the observed distribution of mass peaks into overlapping distributions of parent and fragment ions. The results are discussed in terms of the relative stabilities of parent fragment ions arising from substituent effects. B-Substituents are more labile than the corresponding N-substituents, the six-membered ring fragments being stabilized by release of electron density from the adjacent nitrogen atoms. On the other hand, borazines containing *N*-methyl substituents lose a hydrogen atom to form immonium-like fragment ions.

Introduction

During the course of preparing a series of unsymmetrically B-substituted borazines for other purposes,[1,2] we became interested in the use of mass spectrometry as a method for establishing criteria of purity for these compounds. Such criteria were especially important for this series of borazines because the synthetic methods employed generally yield mixed substitution products; some of the pure compounds also undergo spontaneous redistribution reactions.[3] The results reported here verify the validity of our original interest in using mass spectrometry to characterize these compounds. In addition, the mass spectra contain features which can be related to the constitution of these compounds.

Experimental Section

The details of the preparation of the unsymmetrically B-substituted borazines used in this study are reported elsewhere.[1,2] Mass spectra were recorded with either a Consolidated Electrodynamics Corp. Type 21-1030 or a Bell and Howell 21491 mass spectrometer; both instruments operate with an ionization potential of 70 V and an ionizing current of 50 mA. The former instrument incorporated a heated inlet system; samples were introduced in capillary tubes that were broken either immediately prior to introduction or internally by a heat sensitive, bimetallic strip. The Bell and Howell spectrometer used a direct-probe system, solid samples being introduced in sealed capillary tubes opened immediately prior to introduction and liquid samples with a syringe. Experiments involving compounds with a *B*-halogeno moiety invariably yielded hydrolysis products when the capillary tube was broken immediately prior to introduction into the spectrometer.

The mass distribution of the molecular ion peak was calculated by a binomial expansion method described elsewhere[4] using a program available at the Mass Spectrometry Laboratory of the University of Texas. The following isotope abundances were used in the calculation: ^{10}B, 19.61%; ^{11}B, 80.39%; ^{12}C, 98.89%; ^{13}C, 1.11%; ^{35}Cl, 75.77%; ^{37}Cl, 24.23%; ^{79}Br, 50.54%; ^{81}Br, 49.46%.[5]

Discussion

General Features. Typical mass spectra observed for the borazines are shown in Figures 1 and 2. The lower mass range contains doubly charged species and fragment group

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[1] G. A. Anderson and J. J. Lagowski, *Spectrochim. Acta, Part A*, 26, 2013 (1970).

[2] L. A. Melcher, J. L. Adcock, and J. J. Lagowski, *Inorg. Chem.*, 11, 1247 (1972).

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[5] A. E. Cameron and E. Wichers, *J. Amer. Chem. Soc.*, 84, 4175 (1962).

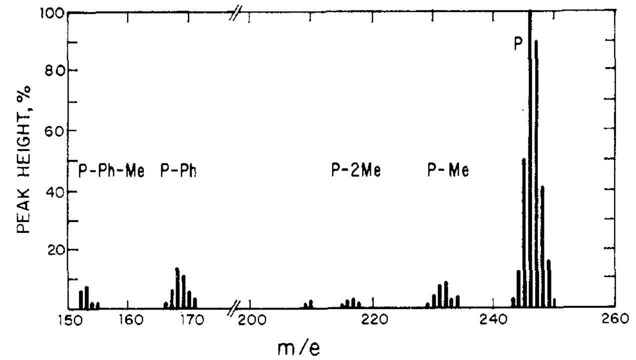

Figure 1. The upper mass spectral range for $(C_6H_5)(CH_3)ClB_3N_3(CH_3)_3$; P designates the parent molecular ion distribution.

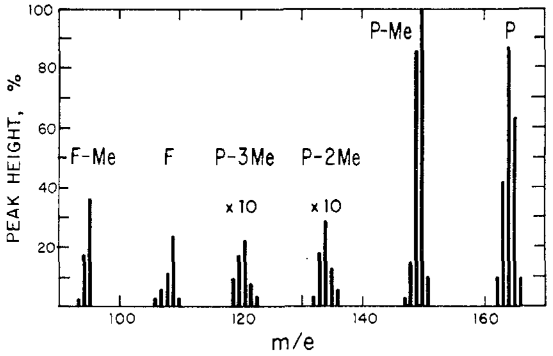

Figure 2. A portion of the mass spectrum for $(CH_3)_3B_3N_3(CH_3)_3$. P designates the parent molecular ion and F the fragment $(CH_3)_2B_2N_2(CH_3)_2$.

distributions which overlap extensively. In addition, the mass spectra of the *B*-haloborazines show the presence of hydrolysis products, *i.e.*, peak distributions containing *B*-OH groups, if the sample capillary was opened in the atmosphere or if it was opened internally without evacuating the sample compartment for a suitable period of time. Hydrolysis products were never observed when *B*-halogen moieties were absent.

The spectra contain mass peaks characteristic of the fragment $R_2N_2B_2R'_2$ which has been observed previously and assigned a cyclic structure,[6,7] the presence of which has been used as evidence for resonance stabilization in the parent borazine.[8] The same basic ring fragment, $C_6H_5(CH_3)B_2N_2(CH_3)_2$, arises from both $(C_6H_5)_2(CH_3)B_3N_3(CH_3)_3$ [by loss of $C_6H_5BNCH_3$] and $(C_6H_5)(CH_3)_2B_3N_3(CH_3)_3$ [by loss of CH_3BNCH_3]. If the fragmentation process is random, the fragments $(C_6H_5)_2B_2N_2(CH_3)_2$ or $(CH_3)_2B_2N_2(CH_3)_2$ should also be observed; however the mass spectra of these compounds are devoid of traces of these species. The fragments $(CH_3)_2B_2N_2(CH_3)_2$ and $(C_6H_5)_2B_2N_2(CH_3)_2$ are observed, however, in the mass spectra of hexamethylborazine and *B*-triphenyl-*N*-trimethylborazine, respectively, indicating that the exclusion of these fragments from the previous spectra cannot be interpreted in terms of an inability of these systems to stabilize a positive charge.

Parent Ion Distribution. The ionization of borazine derivatives in a mass spectrometer yields a number of parent ions which differ in *m/e* values because of the presence of appreciable amounts of ^{10}B and ^{11}B isotopes; if chlorine is present, an additional isotopic distribution occurs. Thus, the mass spectra of borazines exhibit a distribution of parent ions rather than a single peak.[5] It follows that species arising from such a distribution of parent ions will appear as a fragment ion distribution. If a fragment is formed with a mass near that of the parent, the resulting spectrum will be the sum of two overlapping mass distributions.

Table I. Partial Mass Spectrum of Borazine

	Intensities			
m/e	P	P − H	P + (P − H)[a]	Obsd
75	0.0	0.0	0.0	4.1
76	0.0	0.0	0.0	9.3
77	0.0	1.4	1.1	13.3
78	1.4	17.1	14.0	23.2
79	17.1	72.7	61.5	64.8
80	72.2	100.0	100.0	100.0
81	100.0	1.2	32.9	35.5
82	1.2	0.0	0.4	0.0

[a] 29.4% P, 70.6% (P − H).

For our purposes, the term parent ion distribution is defined as the distribution of mass peaks which results from the presence of two or more isotopic species in the parent ion and is symbolized by P. The largest peak in the parent ion distribution is defined as the reference peak of the distribution; the intensities of other peaks in the distribution are reported relative to the reference peak. The loss of an atom or group from the molecular ion species yields a fragment ion species which exhibits a new peak distribution, but at lower *m/e* values. The fragment ion peak distribution is represented by P − Z,[9] where Z is the mass of the group lost. In the mass spectrum of borazine derivatives, P and P − H peak distributions are both present but overlap to yield a composite distribution. The relative contributions of the P and P − H species to the overlapping peak distribution observed in the mass spectrum of borazine can be calculated from a set of simultaneous equations using a matrix-inversion technique.[10,11] For example, the intensity of the distribution of peaks which occur about mass 80 in the spectrum of borazine is best described as being composed of 29.4% of the parent ion distribution (P) and 70.6% of the fragment ion distribution (P − H) with a standard deviation from the observed spectrum of ±6.5%. The details are shown in Table I.

The relative contributions of the parent ion distribution and the fragment ion distribution are useful concepts because comparison of the peaks in the mass spectra of different compounds is of little significance unless the peaks are expressed in terms of their contribution to the spectrum.[11] Comparison of the peak heights as a percentage of the total ion current, $\%\Sigma_m$,[4,11] necessitates summation of the intensities of all the peaks in the mass spectrum above mass *m*, a tedious process. Consequently, we have found it convenient to define the per cent relative contribution of the parent ion given by eq 1 for comparing the relative contributions of the molecular ion peak distributions in different spectra. The relative intensities of the reference peaks of the parent ion distribution and of the fragment ion distribution are given by P and F, respectively. The quantity %P expresses the contribution of the parent ion to the mass spectrum in terms of the

$$\%P = [P/(P + F)] \times 100\% \qquad (1)$$

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[6] J. H. Beynon, "Mass Spectrometry and Its Application to Organic Chemistry," Elsevier, Amsterdam, 1960, pp 407-408.

[7] W. Snedden, *Advan. Mass Spectrom.*, 2, 456 (1963).

[8] E. D. Loughran, C. L. Mader, and W. G. McQuiston, U. S. Atomic Energy Commission Report No. LA-2368, Los Alamos Scientific Laboratory, Jan 14, 1960.

[9] The symbolism P − Z refers to a fragment the mass of which is that of the parent (P) minus that of the group lost (Z).

[10] G. A. Anderson, Ph.D. Dissertation, The University of Texas at Austin, 1969, pp 80-85.

[11] K. Bieman, "Mass Spectrometry, Organic Chemical Applications," McGraw-Hill, New York, N. Y., 1962, pp 44-45.

fragment ion. The complement of %P is the per cent relative contribution of the fragment ion, %F.

Borazines which fragment by the loss of a hydrogen atom require computer analysis to resolve the overlapping P and P − H ion contributions from the experimentally observed distributions. However, the relative contributions of the P and P − H peak distributions to the observed distribution are in the same ratio as the respective relative intensities of the distributions and are, therefore, the per cent relative contributions of the parent ion and the P − H fragment ion to the mass spectrum. By contrast, borazines which fragment by the loss of methyl, halogen, or phenyl groups yield mass spectra in which the parent ion distribution and the fragment ion distribution do not overlap; the ratios of the parent ion intensities to the fragment ion intensities are identical with the ratios of the relative intensities of the respective distributions. Consequently, the per cent relative contribution for the parent ion distributions to the mass spectra can be calculated directly from the absolute intensities of the corresponding reference peaks without prior normalization of the mass spectra. Since the relative contributions to the mass spectra are expressed in terms of the fragment ions, it is necessary to specify the nature of the fragment ion when indicating its per cent relative contribution, *viz.*, %(P − H), %(P − Cl), %(P − CH_3), etc. Defined in this fashion, the per cent relative contributions of the parent ions in the mass spectra of different compounds are directly comparable and indicate the effects of substitution on the relative stabilities of the parent ions.

It is well known that the character of the recorded mass spectrum of a compound is dependent upon the instrument and conditions under which the sample was run. The concept of the relative contribution of the parent and the fragment ions described here serves as a reliable index for a comparison of data obtained under different conditions. Table II contains results of calculating the relative contribution of parent and fragment ions for several borazines from data collected under different conditions. It is apparent that the calculated values are in reasonable agreement in spite of the inherent differences in sampling techniques and instruments.

The Loss of B-Substituents. The mass spectra of the mixed *B*-methyl- and *B*-phenylborazines indicate that the relative peak intensity of the P − CH_3 fragment decreases regularly from hexamethylborazine to *B*-triphenyl-*N*-trimethylborazine (Table III). These results suggest that the methyl group lost in the fragmentation comes from a boron site; an *N*-methyl group is markedly less labile than a *B*-methyl group. The loss of *B*-alkyl or -aryl substituents in preference to a nitrogen substituent suggests that a positive charge is more readily stabilized at the boron site; a similar conclusion arises from the mass spectra of alkylboranes.[12] In the case of borazines, the loss of a B-substituent could be stabilized by an increase in electron donation from the adjacent nitrogen atoms.

A comparison of %P and %(P − H) in the mass spectra of the series of compounds $H_3N_3B_3H_{3-x}Y_x$ (Y = Cl or CH_3; x = 0, 1, 2, 3) clearly indicates that the P − H fragment ion arises primarily by the loss of a hydrogen atom from the boron site (Table IV); this observation is in agreement with the results for *B*-alkyl- or -arylborazines which lose boron substituents rather than nitrogen substituents.

The order of the lability of boron substituents can be determined by comparison of the per cent relative contributions of the parent ions and the fragment ions to the mass spectra (Table V). Since hydrogen atoms at a nitrogen site are not significantly labile (Table IV), the data in Table V indicate that the order of bond breaking is B-Cl < B-H < B-CH_3. This trend is in agreement with the order predicted from the bond strengths of simple boron compounds, *viz.*, 109 kcal for BCl_3, *ca.* 93 kcal for BH_3, and 89 kcal for $B(CH_3)_3$.[13]

Table II. Comparison of the Relative Contributions of the Parent and the P − H Fragment Ions for Several Borazines

Compd	Rel contribution, % P	Rel contribution, % P − H	Comments
$H_3N_3B_3H_3$	29.4	70.6	*a*
	30.2	69.8	*b*
$H_3N_3B_3F_3$	95.1	4.9	*a*
	96.4	3.6	*c*
$(CH_3)_3N_3B_3H_3$	21.3	78.7	*a*
	22.1	77.9	*d*
$(CH_3)_3N_3B_3(CH_3)_3$	52.9	47.1	*a*
	57.3	42.7	*d*
$(CH_3)_3N_3B_3Cl_3$	22.9	77.1	*a*
	24.7	75.3	*d*

[a] This work performed with the CEC 21-1030 spectrometer. [b] Reference 8. [c] A. W. Laubengayer, K. Watterson, P. R. Bidinosti, and R. F. Porter, *Inorg. Chem.*, 2, 519 (1963). [d] This work performed with the Bell and Howell 21491 spectrometer.

Table III. Relative Contributions of the Parent Ions and the P − CH_3 Fragment Ions of Methyl and Phenyl B-Substituted Borazines

Compd	Rel contribution, % P	Rel contribution, % P − CH_3	Rel contribution, % P − C_6H_5
$(CH_3)_3N_3B_3(CH_3)_3$	87	100	
$(CH_3)_3N_3B_3(CH_3)_2C_6H_5$	100	27	50
$(CH_3)_3N_3B_3(CH_3)(C_6H_5)_2$	100	8	54
$(CH_3)_3N_3B_3(C_6H_5)_3$	100	2	40

Table IV. Relative Contributions of P and P − H Ion Distributions in the Mass Spectra of Some B-Substituted Borazines

Compd	Rel contribution, % P	Rel contribution, % P − H
$H_3N_3B_3H_3$	29.4	70.6
$H_3N_3B_3H_2Cl$	36.0	64.0
$H_3N_3B_3HCl_2$	45.6	54.0
$H_3N_3B_3Cl_3$	97.3	2.7
$H_3N_3B_3H_2CH_3$ [a]	55.4	44.6
$H_3N_3B_3H(CH_3)_2$ [a]	79.0	21.0
$H_3N_3B_3(CH_3)_3$	96.2	3.8

[a] Calculated from the data of R. Maruca, O. T. Beachley, Jr., and A. W. Laubengayer, *Inorg. Chem.*, 6, 575 (1967), using the method outlined in this paper.

The Loss of N-Substituents. The resistance to loss of hydrogen atoms from the nitrogen sites (Table IV) is supported by the small relative contribution of the species P − H to the spectrum of *B*-trimethylborazine: %P = 96.2, %(P − H) = 3.8. In contrast, the per cent relative contributions of the parent ions and the P − H fragment ions to the mass spectra of *N*-trimethylborazine and the *B*-chloro derivatives of *N*-trimethylborazine are striking (Table VI). While the P − H fragment ion contributions to the mass spectra of *N*-trimethyl-*B*-chloroborazine and *N*-trimethyl-*B*-dichloroborazine could result from the loss of *B*-hydrogen atoms and/or hydrogen atoms from methyl groups, all of the P − H fragment ion contributions to the mass spectrum of *N*-trimethyl-*B*-trichloroborazine must arise from the loss of hydrogen atoms from a methyl group. Consequently, replacement of the relatively labile *B*-hydrogen substituents must be offset by the effect that *B*-chlorine substituents exert on the borazine ring. To

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(12) I. Shapiro, C. O. Wilson, J. F. Ditter, and W. J. Lehman, *Advan. Chem. Ser.*, No. 32, 127 (1961).

(13) T. L. Cottrell, "The Strengths of Chemical Bonds," Academic Press, New York, N. Y., 1958, pp 270-273.

Table V. Relative Contributions of P and P – X Ion Distributions in Some Borazines

Compd	P – X	Rel contribution, % P – X	P
$H_3N_3B_3Cl_3$	P – Cl	48.7	51.3
$H_3N_3B_3H_3$	P – H	70.6	29.4
$H_3N_3B_3(CH_3)_3$	P – CH_3	77.5	22.5

Table VI. Relative Contributions of P and P – H Ion Distributions of *B*-Chloro-*N*-trimethylborazines

Compd	Rel contribution, % P	P – H
$(CH_3)_3N_3B_3H_3$	21.3	78.7
$(CH_3)_3N_3B_3H_2Cl$	19.4	80.6
$(CH_3)_3N_3B_3HCl_2$	24.4	75.6
$(CH_3)_3N_3B_3Cl_3$	19.8	80.2

Table VII. Relative Contributions of P and P – H Ion Distributions of *B*-Halo-*N*-trimethylborazines

Compd	Rel contribution, % P	P – H
$(CH_3)_3N_3B_3H_2F$	26.4	73.6
$(CH_3)_3N_3B_3HF_2$	18.3	81.7
$(CH_3)_3N_3B_3F_3$	22.5	77.5
$(CH_3)_3N_3B_3H_2Br$	38.6	61.4
$(CH_3)_3N_3B_3HBr_2$	35.5	64.5
$(CH_3)_3N_3B_3Br_3$	44.2	50.8
$(CH_3)_3N_3B_3H_2I$	75.0	25.2
$(CH_3)_3N_3B_3HI_2$	94.5	5.2

Table VIII. Relative Contributions of P and P – H Ion Distributions of *N*-Trimethylborazines Containing the *B*-Cl and *B*-CH_3 Moieties

Compd	Rel contribution, % P	P – H
$(CH_3)_3N_3B_3Cl_3$	24.7	75.3
$(CH_3)_3N_3B_3Cl_2CH_3$	33.3	66.7
$(CH_3)_3N_3B_3Cl(CH_3)_2$	45.5	54.5
$(CH_3)_3N_3B_3(CH_3)_3$	57.3	42.7

Table IX. Relative Contributions of P and P – H Ion Distributions in *N*-Trimethylborazines

Compd	Rel contribution, % P	P – H
$(CH_3)_3N_3B_3Cl_3$	24.7	75.3
$(CH_3)_3N_3B_3Cl_2C_6H_5$	54.9	45.1
$(CH_3)_3N_3B_3Cl(C_6H_5)_2$	69.9	30.1
$(CH_3)_3N_3B_3(C_6H_5)_3$	76.6	23.4
$(CH_3)_3N_3B_3C_6H_5ClCH_3$	56.3	43.7
$(CH_3)_3N_3B_3(CH_3)_3$	57.3	42.7
$(CH_3)_3N_3B_3(CH_3)_2C_6H_5$	68.6	31.4
$(CH_3)_3N_3B_3CH_3(C_6H_5)_2$	76.6	23.4
$(CH_3)_3N_3B_3(C_6H_5)_3$	76.6	23.4

Table X. Relative Contributions of P and P – H Ion Distributions in B-Substituted Borazines

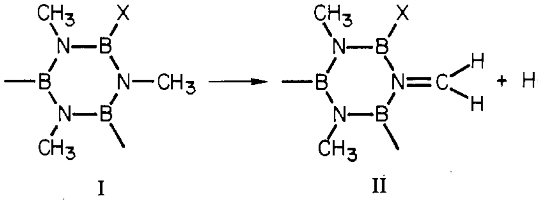
Compd	Rel contribution, % P	P – H	Ref
$H_3N_3B_3H_2Br$	74.6	25.4	*a*
$H_3N_3B_3H_2CH_3$	55.4	44.6	*b*
$H_3N_3B_3H_2(OCH_3)$	44.1	55.9	*a*
$H_3N_3B_3H_2Cl$	36.0	64.0	*c*
$H_3N_3B_3H_2F$	31.5	68.5	*a*
$H_3N_3B_3HBr_2$	95.4	4.6	*a*
$H_3N_3B_3H(CH_3)_2$	79.0	21.0	*b*
$H_3N_3B_3HCl_2$	45.6	54.4	*c*
$H_3N_3B_3HF_2$	31.0	69.0	*a*
$H_3N_3B_3(CH_3)_3$	96.2	3.8	*d*

[a] O. T. Beachley, Jr., *Inorg. Chem.*, 8, 981 (1969). [b] R. Maruca, O. T. Beachley, Jr., and A. W. Laubengayer, *Inorg. Chem.*, 6, 575 (1967). [c] O. T. Beachley, Jr., *J. Amer. Chem. Soc.*, 92, 5372 (1970). [d] This work.

understand the basis of this effect, it is necessary to examine the relative contributions of the parent ions of other B-halogenated derivatives of *N*-trimethylborazine. From the data in Table VII it is apparent that molecular ion species are stabilized by halogen substitution in the order F ~ Cl < Br < I. An identical trend is observed in the mass spectra of halogenated aromatic compounds.[14]

The P – H fragment is also prominent in the *B*-chloro- and *B*-methyl-substituted *N*-trimethylborazines although there are no *B*-H moieties in these compounds (Table VIII). The trend observed in the data given in Table VIII indicates that despite the increased number of hydrogen atoms in this series of compounds, the P – H contribution decreases. This result clearly indicates that the P – H distribution arises primarily from the loss of hydrogen atoms from an *N*-methyl group and that the *B*-chloro substituents destabilize the parent ion with respect to the P – H fragment. The destabilizing influence of a *B*-chloro substituent on the parent ion is also observed in the spectra of the mixed *B*-chloro, -methyl, and -phenyl derivatives of *N*-trimethylborazine (Table IX). The large relative contribution of the parent ion in the phenyl derivatives can be attributed to the large number of positions in the phenyl ring over which positive charge may be delocalized.[7] In general parent ions are stabilized by groups containing π-electron systems.[15]

The relative contributions of the parent and the P – H ions in the *N*-trimethylborazines depend partially on the stability of the radical cation I relative to the "immonium" ion II



I II

formed when the parent molecule loses a hydrogen atom. If the B-substituents are capable of stabilizing a positive charge, a relatively greater amount of the parent ion distribution will be observed regardless of the mechanism of stabilization. If, however, the substituent group cannot stabilize, or, indeed, destabilizes, a positive charge, a relatively greater amount of the P – H distribution will be observed in the spectrum. The data summarized in Tables VII-IX indicate that B-substituents in the *N*-trimethylborazines increase the parent ion stability in the order Cl ~ F < Br ~ CH_3 < C_6H_5 ~ I which is in general agreement with other experiments. Phenyl groups are known to delocalize positive charge readily.[15] The ability of halogens to accommodate positive charge decreases in the order I > Br > Cl > F.[16,17] Within the halogen series of derivatives the relative stabilities of the molecular ions is understandable. Chlorine and fluorine withdraw electrons from the ring more than do bromine and iodine thus destabilizing the parent ion with respect to the P – H fragment ion. The

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(14) F. W. McLafferty, *Anal. Chem.*, 34, 16 (1962).

(15) K. Biemann, "Mass Spectrometry, Organic Chemical Applications," McGraw-Hill, New York, N. Y., 1962, p 51.

(16) G. A. Olah and J. M. Ballinger, *J. Amer. Chem. Soc.*, 89, 4744 (1967).

(17) L. A. Clarke and D. H. L. Williams, *J. Chem. Soc. B*, 1126 (1966).

increased stability of the parent ion on increased methyl substitution could be attributed to the ability of the methyl group to release electron density into the borazine ring thus stabilizing the parent ion.

The general substituent effects on the relative stability of the parent ion observed for the B-substituted *N*-trimethylborazines also obtains for the B-substituted borazines. Mass spectral data available in the literature were analyzed by the method described here and the results summarized in Table X. The stability of the parent ion of B-monosubstituted borazines increases in the order F < Cl < OCH_3 < CH_3 < Br; for the known B-disubstituted derivatives the same order is observed. The results in both series of compounds are in general agreement with the data obtained for the corresponding *N*-trimethylborazine derivatives. A comparison of the results in Tables IV and VIII indicates that the loss of a hydrogen atom from an *N*-methyl group is more facile than from a *B*-methyl group, which is in agreement with the more ready formation of an immonium ion (II).

Registry No. $H_3N_3B_3H_3$, 6569-51-3; $H_3N_3B_3F_3$, 13779-24-3; $(CH_3)_3N_3B_3H_3$, 1004-35-9; $(CH_3)_3N_3B_3(CH_3)_3$, 877-07-6; $(CH_3)_3N_3B_3Cl_3$, 703-86-6; $(CH_3)_3N_3B_3(CH_3)_2C_6H_5$, 32386-02-0; $(CH_3)_3N_3B_3(CH_3)(C_6H_5)_2$, 28075-19-6; $(CH_3)_3N_3B_3(C_6H_5)_3$, 909-21-7; $H_3N_3B_3H_2Cl$, 15061-65-1; $H_3N_3B_3HCl_2$, 15259-40-2; $H_3N_3B_3Cl_3$, 933-18-6; $(CH_3)_3N_3B_3H_2Cl$, 13401-07-5; $(CH_3)_3N_3B_3HCl_2$, 13401-08-6; $(CH_3)_3N_3B_3H_2F$, 29812-74-6; $(CH_3)_3N_3B_3HF_2$, 29812-75-7; $(CH_3)_3N_3B_3H_2Br$, 13401-09-7; $(CH_3)_3N_3B_3HBr_2$, 13401-10-0; $(CH_3)_3N_3B_3Br_3$, 703-85-5; $(CH_3)_3N_3B_3H_2I$, 29812-76-8; $(CH_3)_3N_3B_3HI_2$, 29812-77-9; $(CH_3)_3N_3B_3Cl_2CH_3$, 7387-21-5; $(CH_3)_3N_3B_3Cl(CH_3)_2$, 13058-05-4; $(CH_3)_3N_3B_3Cl_2C_6H_5$, 36972-50-6; $(CH_3)_3N_3B_3Cl(C_6H_5)_2$, 36972-51-7; $(CH_3)_3N_3B_3C_6H_5ClCH_3$, 36972-52-8; $H_3N_3B_3H_2(OCH_3)$, 18277-68-4.

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Deprotonation of Tetraborane(10)

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The deprotonation of tetraborane(10) by methyllithium was found to proceed smoothly in ethyl ether at −78°. The reaction produced methane and the lithium salt of the nonahydrotetraborate(1−) ion. Reprotonation of the anion with HCl and DCl regenerated tetraborane(10) and monodeuterated tetraborane(10), respectively. The infrared spectrum of B_4H_9D indicated that the deuterium atom entered the bridge position only. The LiB_4H_9 was thermally unstable even for moderate periods of time at −78° and decomposed irreversibly at higher temperatures. Relative Bronsted acidities were determined by displacement reactions and found to increase in the order B_5H_9, B_4H_{10}, $B_{10}H_{14}$.

Introduction

The results of a study of the deprotonation of tetraborane(10) by $LiCH_3$ in ethyl ether have recently appeared in a brief report.[1] Both the Bronsted acidity of the tetraborane(10) and the reactivity of the product lithium nonahydrotetraborate(1−) were examined. At the same time Johnson and Shore[2] reported the results of a similar study using NH_3 and KH as deprotonating agents. Both of these studies confirm that tetraborane(10) is a Bronsted acid and forms the $B_4H_9^-$ anion intact at low temperatures. Previous studies had demonstrated that tetraborane(10) could be cleaved across the bridge bonds symmetrically yielding BH_3 and B_3H_7 generally as base adducts or asymmetrically in polar environments giving BH_2^+ and $B_3H_8^-$ fragments.[3]

In this article we present the experimental details of our study.

Experimental Section

Materials. All volatile compounds were handled using standard high vacuum procedures. Preparations of the nonahydrotetraborate(1−) anion and subsequent reactions were done in sealed tubes as shown in Figure 1. The capillary tubing on the side arms D provided a means of sealing off the reaction vessel under vacuum. The side arm could be fastened to a tube opener through a greaseless threaded adapter with a Viton O ring (Ace 5027-20). Sealed-tube reactions avoided contamination with stopcock grease and allowed reaction pressures of up to 5 atm.

Methyllithium [Alfa Inorganics], a 2.3 *M* solution in ethyl ether, was routinely diluted with ethyl ether in a syringe to avoid clogging the syringe needle and to provide additional solvent for the reaction. The bottle of $LiCH_3$ solution was always opened under a stream of dry nitrogen. B_4H_{10} was prepared by a modified method of Schaeffer and Tebbe[4] as described elsewhere.[5] Ethyl ether was distilled from sulfuric acid and stored in a dry nitrogen-filled bottle over molecular sieves (Linde 4A). The ether was checked periodically for peroxides.

A codistillation condensation column[5] was used to determine the purity of volatile compounds and, when possible, the composition of mixtures. All volatile starting materials were determined to be chromatographically pure by this method. Decaborane(14) was sublimed before use. Diborane(6) was prepared by adding an I_2 solution in diglyme to a $NaBH_4$–diglyme slurry.[6] Pentaborane(9) was prepared by the method of DeAcetis and Trotz.[7] Anhydrous aluminum chloride [Merck] was used as received. Boron trifluoride [Matheson] was taken from a tank directly into the vacuum line and purified. Both HCl and DCl gases [Stohler Isotopes] were prepared by pumping on their respective concentrated aqueous solutions through −78° traps.

All infrared spectra were taken on a Perkin-Elmer 521 grating spectrometer. Mass spectra were run on a double-focusing Hitachi Perkin-Elmer RMU-7 mass spectrometer.

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