BORENIUM IONS:
A MASS SPECTROMETRIC INVESTIGATION

by 557

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

g	gram
mmole	millimole
ml	milliliter
mp	melting point
vp	vapor pressure
torr	millimeters mercury (pressure)
mm	millimeter
cm	centimeter
min	minute
hr	hour
M	molar (concentration)
eV	electron volts
Ph	phenyl (C_6H_5)
Me	methyl
Et	ethyl
Kcal	Kilocalorie
Fc	ferrocenyl
AP	appearance potential

A. Introduction

For many years the structure of ions in the gas phase has been a topic of concern in several fields of chemistry. There are a number of methods by which one can obtain information leading toward the elucidation of ionic structures; however, with the exception of optical spectroscopy, there are no methods which lead directly to gaseous ion structures. The use of mass spectroscopy can provide information which will favor one structure over another but it cannot definitely designate the structure of an ion. Energetics of ion formation, metastable ion characteristics and molecular substituent effects are techniques which employ mass spectroscopy in ion structure determinations.

The appearance potentials for ions of the same composition obtained from different parent molecules allow a comparison of the enthalpies of formation of the ions. These enthalpy values have been suggested as a means of deciding whether or not two ions have the same structure and they may also aid in deciding between two or more possible structures.[1] Before discussing how a comparison of enthalpies of formation can be helpful in structure determination, it is necessary to show how the measurement of the appearance potential of an ion can be used to calculate the enthalpy of formation of the ion.[2,3,4]

Upon electron impact a molecule (M) may merely be ionized (to give $M^{+}\cdot$) or the initially formed molecular ion may fragment to form a positively charged daughter ion ($D^{+}\cdot$ or D^{+}) and a neutral fragment (N or $R\cdot$).

$$M + e \rightarrow M^{+\cdot} + 2e \quad (1)$$

$$M + e \rightarrow D^{+\cdot} + N + 2e \quad (2)$$

$$M + e \rightarrow D^{+} + R^{\cdot} + 2e \quad (3)$$

From an ionization efficiency curve one can obtain the appearance potential (AP). There is a certain amount of uncertainty in the value obtained from ionization efficiency curves since, depending on the method of measurement, the curve can approach the voltage axis asymptotically.[1] The asymptotic nature of the ionization efficiency curve, obtained by electron impact, is in part due to the energy spread of the bombarding electrons[5] and also due to the thermal internal energy of the molecule prior to ionization.[6] Errors due to the above problems generally will not cause errors in the appearance potential value greater than a few tenths of an eV. Retarding potential difference techniques can be used to obtain more accurate values,[7,8] while methods other than electron impact can also be used.[9,10]

Thermodynamic consideration of equation (2) leads to the following equation:

$$AP(D^{+\cdot}) = \Delta H_f(D^{+\cdot}) + \Delta H_f(N) - \Delta H_f(M) + E \quad (4)$$

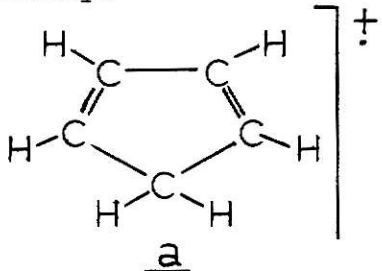
The term E accounts for the fact that production of $D^{+\cdot}$ or N may occur with excess energy at the threshold. Usually $\Delta H_f(N)$ and $\Delta H_f(M)$ are known,[1] thus the major problems involved in calculating $\Delta H_f(D^{+\cdot})$ arise from errors in determining and interpreting $AP(D^{+\cdot})$[6] and in estimating the amount of excess energy, E.[6]

The appearance potential, as measured in a mass spectrometer, is the amount of energy required to form the ion in question plus the energy required for the formation to proceed

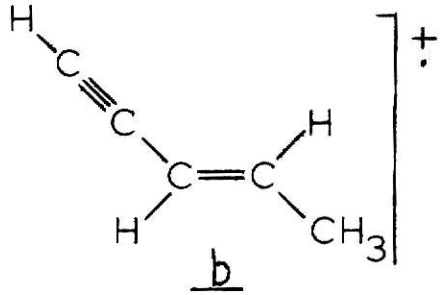
at a rate appropriate to the instrumental measurement. This extra energy is known as the kinetic shift. Thus, the kinetic shift energy is that energy which is required to produce a detectable ion current in a time of about 10^{-5} seconds.[5] The excess energy due to the kinetics of the dissociation may not be more than a few tenths of an eV;[6] however, there are cases where this factor causes a large error in the measured appearance potential.[11]

A major problem arises when one attempts to estimate the value of E. In a simple bond dissociation the E term can be neglected.[6] In rearrangements, where there is bond formation as well as bond cleavage, one cannot assume E to be negligible, since the products may be stabilized relative to the activated complex.

An example of how enthalpy of formation data can be used in ion structure determination is found in a paper by Occolowitz and White.[1] They reported the enthalpies of formation of the ion $(C_5H_6)^{+\cdot}$ obtained from phenol (ΔH_f = 284 Kcal/mole), aniline (ΔH_f = 278 Kcal/mole), cyclopentadiene (ΔH_f = 237 Kcal/mole) and 3-penten-1-yne (ΔH_f = 273 Kcal/mole). The $(C_5H_6)^{+\cdot}$ ions formed from aniline and from phenol involve the loss of the neutrals HCN and CO respectively. Since the formation of the $(C_5H_6)^{+\cdot}$ ions from cyclopentadiene and from 3-penten-1-yne involve only ionization, probable structures for the $(C_5H_6)^{+\cdot}$ ions are (a) and (b) respectively.



a



b

The ΔH_f values for the formation of ions (a) and (b) are quite different in magnitude, but the ΔH_f values obtained for the formation of the $(C_5H_6)^{+\cdot}$ ions from aniline and phenol are similar to the ΔH_f for the ionization of 3-penten-1-yne. Therefore, one can reasonably assume that (b) represents the structure of the $(C_5H_6)^{+\cdot}$ ions obtained from phenol and aniline.

This method is not an infallible way to infer structures because there is no way to accurately predict the excess energy term. It is, nevertheless, a technique which has provided some self consistent structural inferences.

Metastable ions have characteristics which can be useful in distinguishing the structures of gaseous ions. The abundance of a daughter ion relative to the abundance of the metastable ion can provide structural information. Rosenstock and Krauss[12] discuss the quasi-equilibrium theory (QET) of mass spectrometry which can be simplified to the rate equation

$$k = \nu \left(\frac{E - E_o}{E} \right)^{S-1} \qquad (5)$$

where k is the rate constant, ν is the frequency factor, E is the internal energy, E_o is the activation energy and S is the number of effective oscillators.

It has been estimated that ions typically spend between one and five microseconds in the source, require about one microsecond for acceleration and then spend about five microseconds in a field free region before they reach the magnetic sector.[13] If a metastable transition is to be recorded, the ion must

fragment somewhere in this field free region. If the rate constant for the dissociation is greater than 10^{-6} sec.$^{-1}$, fragmentation will occur largely in the source and daughter ions will be predominant in the spectrum. If the rate constant is less than 10^{-5} sec.$^{-1}$, most of the ions will traverse the flight tube without dissociating and will be detected as the parent ion. However, if the rate constant is between 10^{-6} and 10^{-5} sec.$^{-1}$, fragmentation of the ion will occur in the field free region and the metastable transition will be detected. From equation (5) it is obvious that by changing the energy of the bombarding electrons one can control the relative abundances of parent, metastable and daughter ions formed. The activation energies for fragmentations which involve skeletal and hydrogen rearrangements generally are smaller than those for simple bond cleavage.[6] Thus, if the energy of the ionizing electrons is lowered, there will be a correspondingly greater decrease in the abundance of daughter ions for simple bond cleavage than for a dissociation process involving a rearrangement. This particular method can be valuable in identifying rearrangement processes[14] which in turn can provide evidence concerning product ion structures.

When different precursor ions (of the same elemental composition) fragment, in a metastable process, to produce daughter ions (also of the same composition), if the metastable ion abundances are equal, then it is assumed that the structures of the precursor ions are identical. If the metastable ion abundances are not equal it cannot be said that the precursor ions are structurally dissimilar, since there are a number of energy

considerations which can affect the results.[6] Also, even if the metastable ion abundances are equal, this may be only accidental and it is conceivable that errors may arise in assuming similar ion structures.

The appearance of flat-topped or concave-topped metastable peaks has been determined as being due to release of kinetic energy during dissociation.[14] From the measured width of the peak and the instrumental parameters, it is possible to determine the amount of kinetic energy involved.[15,16,17,18] Structural inferences have been drawn from such data in several cases.[19,20]

The amount of energy transferred from the bombarding electrons to the ions formed varies over a wide range of values.[21] Thus it can be seen that the ions leaving the source have a wide distribution of internal energies. The rate at which a molecular ion dissociates is dependent upon the amount of energy transferred during ionization.[21] Upon electron impact some of the energy transferred is used in ionizing the molecule with the residual amount remaining as internal energy. Upon adding a substituent to a molecule it may be possible to lower the ionization energy, thus the number of ions leaving the source with enough energy to dissociate is increased.[21] This causes a decrease in the molecular ion abundance and an increase in the daughter ion abundance, if its appearance potential remains constant. The rate of decomposition of a particular molecular ion can indicate the molecular environment at the reaction site.[22]

Consideration must be given to the possibility that by changing the substituent one also changes the rate of competitive fragmentation,[21] thereby altering a particular ion abundance. This could lead to misinterpretation of the significance of the substituent effect and thus an error in structural implication would result.

Bursey and McLafferty[23] have employed the concept of metastable peak widths and substituent effects to show that in order for various nitroaromatic compounds to release kinetic energy along with the loss of NO, it is necessary to have stabilization of the product ion by the substituents. This gives an indication of the various resonance hybrids which are important in the over-all ion structure.

Whereas the information regarding ion structure obtained from mass spectrometric investigations is inference data, one can get much more definitive structural data from the electronic emission spectrum of a molecule. Emission spectra of only three polyatomic gaseous ions have been reported. Duffendack and Smith[24] first reported the simultaneous ionization and excitation of the CO_2 which was formed from either a mixture of helium, CO and O_2 or a mixture of neon, CO and O_2 in a continuous flow discharge tube. Duncan[25] was able to show that the emission spectrum obtained was that of the CO_2^+ ion. Subsequent investigation by Bueso-Sanllehi[26] and Mrozowski[27,28,29] produced a complete vibrational and rotational analysis of the CO_2^+ gaseous ion spectrum which indicated that CO_2^+ is linear.

In 1951 Schüler and Reinebeck reported a new spectrum which was observed in the glow discharge of benzene vapors.[30] They also observed the same spectrum from the glow discharge of naphthalene,[31] phenylacetylene[32] and acetylene.[32] It was postulated that the spectrum was due to diacetylene.[33] However, J. H. Callomon[34] has shown that the new spectrum was due to the diacetylene ion ($C_4H_2^+$) which has a linear structure.

The third polyatomic gaseous ion reported was CS_2^+.[35] The vibrational and rotational analysis of the spectrum obtained indicated that CS_2^+ is linear in structure.

To obtain the emission spectra of gaseous ions requires a large amount of expensive and sophisticated equipment. It is necessary to have a resolving power exceeding 300,000 in order to obtain the fine structure essential to a complete rotational analysis. Thus 21-30 foot grating spectrographs must be used. Excitation conditions need to be carefully studied to determine the source which will give an intense spectrum without producing high concentrations of interfering ions. The wave-lengths must be measured very accurately if the data obtained are to be of any significance. A careful study has shown that errors in the shape of the grating and the photographic plate emulsions can produce errors in the wave-lengths measured.[27] Constant observation of the barometric pressure is also necessary during the time of exposure since a change of 2.5 torr can cause a significant shift in the lines at the dispersion used.[26] For the same reason it is essential to maintain the temperature of the grating

within 0.1° C. Thus, with exposures which many times last 50 hours, the difficulty encountered in obtaining accurate and useful data is obvious.

This thesis is concerned primarily with the structural implications of observations on borenium ion abundances. From the appearance potential of various ions it is possible to calculate the enthalpies of formation of the ions in question. Dibeler and Liston[36] employed the BF_3 and B_2F_4 systems to calculate the enthalpies of formation of a large number of ions and radicals. The ion of particular interest was BF_2^+. From a photoionization efficiency curve of BF_3 it was determined that the threshold energy for the formation of BF_2^+ is 15.81 eV or 364.6 Kcal $mole^{-1}$. The equation involved in the formation of BF_2^+ is shown as follows:

$$BF_3 + h\nu \longrightarrow BF_2^+ + F + e \qquad (6)$$

Assuming the threshold energy to be the ΔH_o for the reaction, it is possible to substitute $\Delta H_f(BF_3) = -271.08$ Kcal $mole^{-1}$ and $\Delta H_f(F) = 18.6$ Kcal $mole^{-1}$ into the proper thermodynamic equation to obtain $\Delta H_f(BF_2) = 75.1$ Kcal $mole^{-1}$. Dibeler and Liston calculated the enthalpy of formation for a number of other ions and radicals. BF_2^+ illustrates the method used to calculate the enthalpies of formation of various other borenium ions.

A list of ΔH_f values for a number of borenium ions is given in Table I.

It is evident that there is some discrepancy in the ΔH_f values listed in Table I. For instance, there are three values

given for $\Delta H_f(BBr_2^+)$, and in Table I $\Delta H_f(BF_2^+)$ = 87 Kcal mole^{-1}, whereas Dibeler and Liston[36] obtained $\Delta H_f(BF_2^+)$ = 75.1 Kcal mole^{-1}.

TABLE I

ΔH_f Values for Various Borenium Ions[37]

Borenium Ion	ΔH_f Kcal/mole	Precursor molecule
BH_2^+	274	BH_2
BBr_2^+	171,173,178	BBr_3
BMe_2^+	175	BMe_3
BEt_2^+	159	BEt_3
BCl_2^+	147,151	BCl_3
BF_2^+	87	BF_3
$B(OMe)_2^+$	85	$B(OMe)_3$

The major reason for the variance in values for $\Delta H_f(BF_2^+)$ is that Dibeler and Liston used a photoionization source to obtain a threshold energy of 15.81 eV and a value of 16.2 eV[38] would have been obtained if an electron impact source had been used. Other causes for a deviation in results are the difficulties involved in interpreting ionization efficiency curves; this problem has been discussed earlier.

It can be seen from the ΔH_f values listed in Table I that BH_2^+ is the least stable and $B(OMe)_2^+$ is the most stable of the borenium ions given. Thus a borenium ion stability order can be written as follows:

$B(OMe)_2^+ \geqslant BF_2^+ > MeBF^+ > BCl_2 \geqslant BEt_2^+ > BMe_2^+, \quad BBr_2^+ > BH_2^+$

It is apparent that borenium ions are stabilized by substituents bearing lone pairs of electrons. Stabilization of the borenium ion may result when the substituent donates its lone pair to the unfilled orbital of boron thus increasing the bond order of the boron substituent bond. Not only must the substituent contain a lone pair, but the lone pair must also be available for bonding with the boron atom. This is why, even though bromine contains lone pairs of electrons, $\Delta H_f(BBr_2^+)$ is quite large relative to ΔH_f for the other dihalogen borenium ions. The bromine atom is too large, compared to the size of the boron atom, to allow for any effective donation of lone pairs of electrons from the bromine atom onto the boron atom.

A further indication of the relative stability of borenium ions is the fact that the mass spectral data for the precursor molecules shows that in nearly all cases the borenium ion is more abundant than the molecular ions. This can be seen in Table II.

The major concern of this thesis is the interpretation of experimental results which show the nearly complete absence of the possible borenium ions when the boron atom is enclosed in a five-membered ring. The compounds studied are shown in structures 1-12. It may be argued that the lack of a borenium ion peak in the mass spectrum is due to removal of the ion by further fragmentation. Low electron energy spectra showed that this could not be the case. It was also possible that the aromatic backbone of the compounds 1-10 could cause stabilization

TABLE II

Mass Spectral Data for Selected Borenium Ion Precursor Molecules

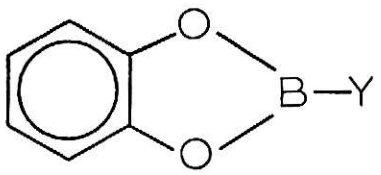
TABLE II

Mass Spectral Data for Selected Borenium Ion Precursor Molecules

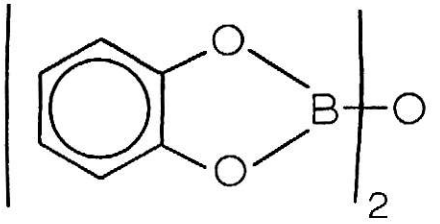
Molecular Ion	% Relative Abundance	100% Relative Intensity Ion	Borenium Ion Abundance	Reference
$B(CH_3)_3^+$	1.4	$B(CH_3)_2^+$	100%	37
$B(C_2H_5)_3^+$	3.7	Mass 41	68.2%	37
$B(OCH_3)_3^+$	35.1	$B(OCH_3)_2^+$	100%	37
$HB(OCH_3)_2^+$	2.7	$B(OCH_3)_2^+$	100%	37
$B(OC_2H_5)_3^+$	44.0	EtO^+, $B(OH)_2^+$	79%	38
BF_3^+	5.5	BF_2^+	100%	39
BCl_3^+	33.4	BCl_2^+	100%	39

Explanation of Figure 1

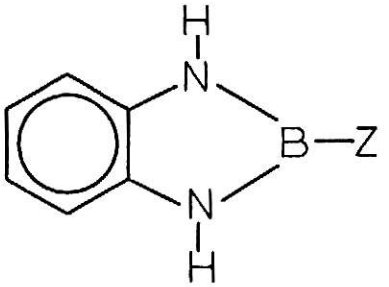
Boron Compounds Studied



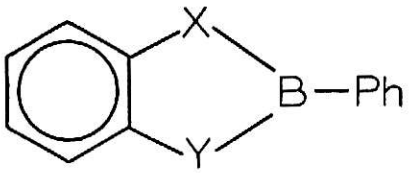
1 Y = Ph
2 Y = Cl
3 Y = Et
4 Y = Me
5 Y = OH



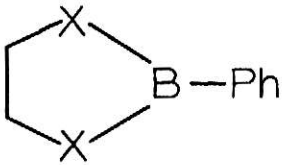
6



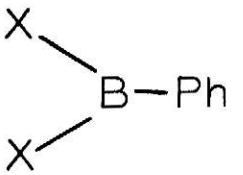
7 Z = Me
8 Z = Ph



9 X = NH, Y = O
10 X = NH, Y = S



11 X = O
12 X = NMe

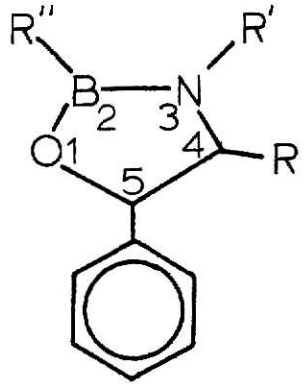


13 X = NMe_2
14 X = OMe

of their molecular ions and so prevent observation of the borenium ions. However, this can be disproved since compounds 11 and 12 did not give a borenium ion peak greater than 1%. To rule out the possibility of stabilization by multiple bond formation between the boron atom and the phenyl group, it was necessary to obtain the specta of compounds 2-7. In not one case was the relative abundance of borenium ion greater than 1%. The spectrum of compound 2 was obtained also to see if a good leaving radical could facilitate the formation of borenium ions.

The literature covering the mass spectra of heterocyclic boron compounds is fairly restricted, especially regarding studies on five-membered cyclic compounds.

Brooks, Middleditch, and Anthony[41] reported the spectra of a series of alkylphenyl-1,3,2-oxazaborolidines, (c).



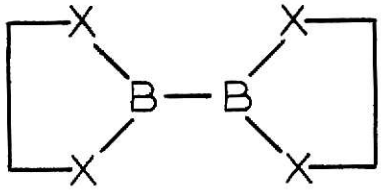
C

R'' = Me, n-Bu, Ph.
R' = H, Me.
R = H, Me.

They report that there is a tendency for the loss of R" since in the mass spectra of the compounds in which R" equals n-butyl, there are peaks corresponding to $[M-R"]^+$. It is quite possible

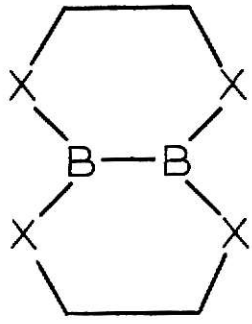
however, that this ion is generated by loss of propene and the C_4-methyl group. Moreover, the spectra of the compounds where R" = Ph do not show intense $[M-Ph]^+$ ions. It is possible that phenyl loss occurs from C_5. Thus it is not established that compounds (c) tend to lose R".

Brubaker and Shore[42] employed mass spectrometry to distinguish between the two possible structures of $B_2(X_2C_2H_4)_2$.



X = O, S, or NCH_3

d



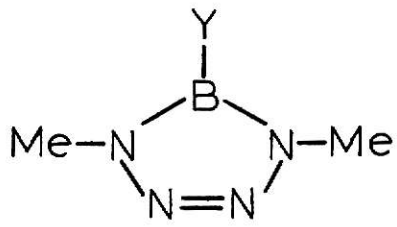
X = O, S, or NCH_3

e

If the structures were bicyclic (d), the mass spectra would parallel the mass spectra of the acyclic analogs. The abundance of the ions corresponding to half the mass of the parent molecular ions for the acyclic compounds indicated symmetrical cleavage of the B-B bond. Since the intensities of the half-mass peaks were between 16.1 and 20.7% in the spectra of the cyclic compounds, Brubaker and Shore concluded that the fused ring structures (e) were probably correct.

Cragg and Todd[43] reported that the mass spectrum of 2-phenyl-1,3-dioxa-2-borole indicated the stability of phenyldioxaborole is greater than the stability of the analogous 2-phenyldioxolanes reported by Marshall and Williams.[44] In

another paper the spectra of various 2,5-dimethylcyclotetrazenoboranes (f) were reported.[45]



f

Y = D
Y = Et
Y = CH=CH$_2$
Y = Cl
Y = Br

In the mass spectra of these compounds the expected occurs: N_2 is readily lost.

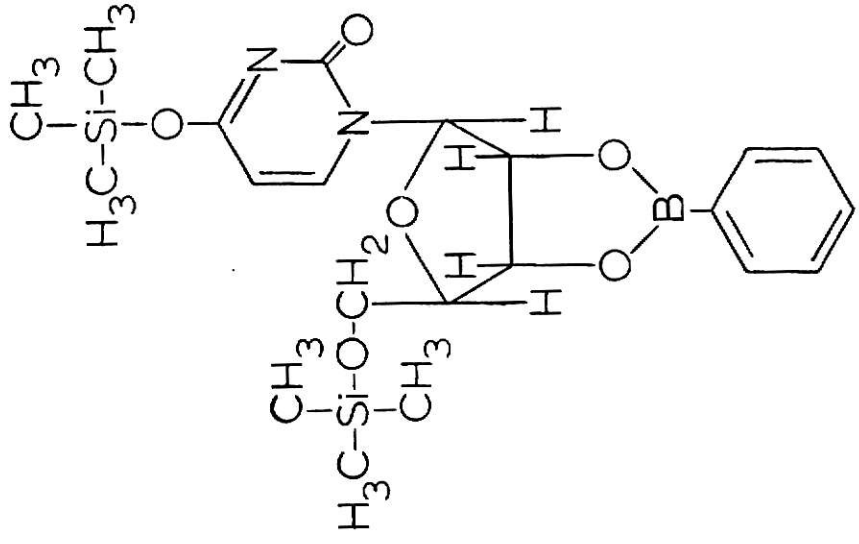
Dolhun and Wiebers[46] reported the mass spectra of two nucleoside derivatives, (g) and (h), which did give borenium ions of approximately 22% and 7% relative abundance respectively.

The mass spectra of trimethylboroxine,[47] trifluoroboroxine,[48,49] difluoroboroxine,[49] and boroxine[49,50] were reported in the early 1960's. In all cases, except trifluoroboroxine, the base peak was due to the loss of either CH_3 or an H atom. In the mass spectrum of trifluoroboroxine the molecular ion was the base peak and the $[M-F]^+$ ion had only 9.6% of the total ion intensity. Recently Brooks, Harvey and Middleditch[51] reported the mass spectra of triphenylboroxine, tricyclohexylboroxine, tri-t-butylboroxine and tri-n-butylboroxine. In the case of triphenylboroxine the base peak was due to the molecular ion and in the other three cases the base peak was due to a fragment ion. It is interesting to note that only for tri-n-butylboroxine was the $[M-R]^+$ ion (where R is the substituent attached to the boron atom) of any appreciable abundance. Post,

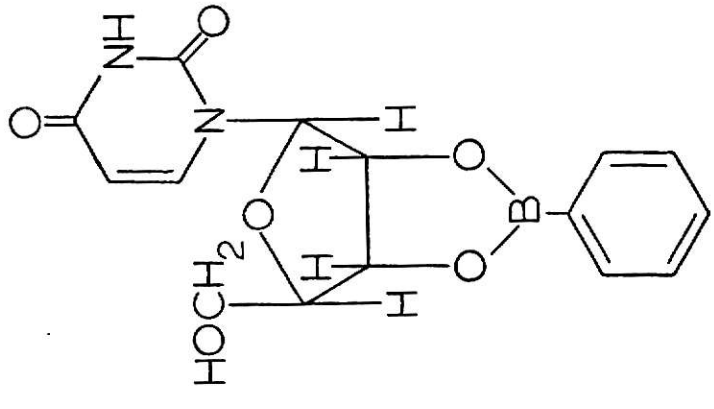
Explanation of Figure 2

Structures of Uridine Phenylboronate

and its Trimethylsilyl Ether Derivative



h



g

Cooks, and Kotz[52] reported similar results for the spectrum of triphenylboroxine. They also found that the spectrum of triferrocenylboroxine is devoid of $[M\text{-}Fc]^+$ ions.

In the case of most boroxine derivatives the loss of substituent attached to the boron atom was not a facile process. However, in borazine derivatives, cleavage of the boron-substituent bond apparently can occur quite readily. This can be seen from a careful study of an article by Snedden.[53] However, Painter[54] reported that the spectrum of B-triferrocenylborazine did not include a $[M\text{-}Fc]^+$ ion.

Although none of the boron ring compounds studied in this research gave abundant borenium ions, this is not taken to imply that there are no similar systems which will give abundant borenium ions. It is fully expected that there exists such a system; however, it has not been uncovered.

B. Experimental Methods and Data

1. Equipment and Techniques

Vacuum Line. The vacuum line was a Pyrex system similar to the basic Stock design,[55] equipped with a two-stage mercury diffusion pump and a Welsh Duo Seal No. 1400B mechanical pump. The fractionation manifold consisted of five U-traps connected in series with mercury float valves.

Dry Box. The dry box was a Model No. DRI-LAB HE-43-2 from Vacuum Atmospheres Corp. The nitrogen atmosphere was dried by passing through a P_2O_5 column before entering the dry box. The atmosphere was kept clean by circulating through a series of three columns; the first column containing Linde 4A molecular sieves removed water, the second column containing Linde 13X molecular sieves removed organic molecules, and the third column containing MnO suspended on vermiculite removed any oxygen in the atmosphere.

Infrared Spectroscopy. The IR spectra were obtained with a Perkin-Elmer 337 grating spectrophotometer.

Mass Spectrometry. An Associated Electronics Industries, Ltd., MS-9 high resolution mass spectrometer was used to record the mass spectra. Samples were introduced through the direct inlet, heated inlet or gas inlet systems. For direct introduction of air sensitive compounds, an I^2R glove bag was attached to the direct inlet system and purged with nitrogen before use. To introduce air sensitive compounds through the heated inlet system, the sample flask was filled in the dry box, plugged with Apiezon T

grease, and sealed in a small glass bottle. Once the sample flask was attached to the mass spectrometer, the grease plug was easily removed by vacuum.

Melting Point Apparatus. Melting points were determined in sealed capillary tubes with a MEL-TEMP melting point apparatus.

Distillation Column. Nearly all solvents and reagents used were dried, except where noted, by distillation using a three foot vacuum jacketed glass column packed with glass helices.

2. Reagents and Solvents

o-Aminophenol (Aldrich) was purified by repeated recrystallization from ethanol and dried under reduced pressure.

2-Aminothiophenol (Aldrich) was used as received.

Benzene (Mallinckrodt, Analytical Reagent, thiophene free) was refluxed at least six hours over CaH_2, distilled, and stored in a stoppered flask in the dry box.

Boron Trichloride (Matheson, technical) was purified by repeated fractionations through U-traps at -78, -112, and -196° C until the vapor pressure at 0° C was 476±1 torr (lit.[56] vp at 0° C is 476 torr).

Catechol (Eastman Organic Chemicals) was purified by vacuum sublimation at 55-60° C. Recrystallization from methylene chloride was an alternative method of purification.

Diethyl Ether (B & A, Reagent, anhydrous) was refluxed over $LiAlH_4$ for at least eight hours, distilled, and stored in a stoppered flask in the dry box.

Dimethylamine (Matheson, anhydrous) was dried over CaH_2 overnight before used.

sym-Dimethylethylenediamine (Aldrich) was used as received.

Ethanol, 95%, was used directly as received.

Ethyllithium (Foote Mineral Co.) was received dissolved in benzene as a 5.07% solution. It was stored at 0^{o} C.

Ethylene Glycol (Fisher, Certified) was vacuum distilled from $MgSO_4$ and stored in a stoppered flask in the dry box.

Hexane (Mallinckrodt, Analytical Reagent) was refluxed over CaH_2 for at least four hours, distilled, and stored in a stoppered flask in the dry box.

Methanol was refluxed over magnesium turnings for at least ten hours, distilled, and stored in a stoppered flask in the dry box.

Methylboron Dibromide was synthesized by following reported procedures,[57] and the IR spectrum obtained agreed very well with the literature spectrum.[58]

Methylene Chloride (Fisher, Certified) was refluxed over P_2O_5 for at least six hours, distilled, and stored in a stoppered flask in the dry box.

Methyl Magnesium Iodide was prepared by the reaction of metallic magnesium on methyliodide in diethyl ether.

Phenylboron Dichloride (Alpha Inorganics) was used as received.

o-Phenylenediamine (Aldrich) was purified by recrystallization from $CHCl_3$ and dried under reduced pressure.

Skelly B (Skelly Oil Co.) was refluxed at least four hours over CaH_2, distilled, and stored in a stoppered flask in the dry box.

Toluene-3,4-dithiol (Eastman Organic Chemicals) was used as received.

3. Preparations and Data

The experimental procedures employed in the preparations of 2-phenyl-1,3-dioxa-2-borole, 2-phenyl-1,3-diaza-2-borole, 2-phenyl-1-oxa-3-aza-2-borole, and 2-phenyl-1,3-thiaza-2-borole have been reported by Dewar, Kubba, and Pettit.[59] The experimental methods listed were followed precisely except that in the case of the latter three compounds, the refluxing times were lengthened to between 24 and 39 hours. The products were all recrystallized from Skelly B in the dry box to safeguard against air oxidation. The experimentally determined melting points were, in all cases, slightly higher than those listed by Dewar, Kubba, and Pettit.

2-Phenyl-1,3-dioxa-2-borole. (Exp. m. p. 116-117° C, lit.[59] m. p. 109-110° C)

Mass spectrum at 70 eV. (direct inlet; source temp. 150° C)

m/e = 197(15.5%), 196(81), 195(26), 168(1.3), 167(1.2), 157(1.5), 152(0.9), 151(1.2), 150(0.7), 149(0.5), 145(1.0), 144(5.4), 143(2.1), 142(1.0), 141(1.8), 140(1.6), 139(1.7), 138(0.7), 137(0.5), 126(0.6), 125(0.6), 120(3.2), 119(1.2), 115(1.8), 114(1.6), 113(2.7), 112(1.1), 105(2.1), 104(3.2),

103(2.2), 102(1.2), 101(1.9), 100(1.1), 99(1.1), 98.5(2.0), 98(10.7), 97.5(3.2), 93(2.3), 92(23), 91(2.4), 90.5(0.9), 90(1.3), 89(1.6), 88(1.2), 87(1.5), 86(0.8), 85(2.6), 84.5(1.3), 84(1.0), 79(1.2), 78(4.3), 77(17), 76(6.5), 75(5.1), 74(4.8), 73(1.7), 72(1.0), 71(0.8), 66(4.4), 65(19), 64(100), 63(95), 62(25), 61(13), 60(5.7), 59(3.0), 58(2.3), 57(1.3), 56(1.2), 55(1.7), 54(1.8), 53(28), 52(13), 51(30), 50(24), 49(5), 48(2.7), 47(1.0), 45(1.5), 44.5(1.0), 44(1.7), 43(1.8), 42(1.5), 40(2.7).

m* = 44.5, m* = 43.2, m* = 105.2-105.6

Mass spectrum at 20 eV.

m/e = 197(20%), 196(100), 195(34), 92(7.6), 77(2.6), 64(11), 50(2).

2-Phenyl-1,3-diaza-2-borole. (Exp. m. p. 217° C, lit.[59] m. p. 204-206° C)

Mass spectrum at 70 eV. (direct inlet; source temp. 110° C)

m/e = 195(14%), 194(100), 193(31), 192(7.1), 191(3.1), 168(1.5), 167(1.5), 166(3.7), 165(1.4), 164(0.8), 142(1.2), 141(0.9), 140(0.9), 139(0.8), 138(0.6), 118(1.3), 117(0.7), 116(1.9), 115(1.6), 114(1.3), 113(1.3), 97(7.3), 96.5(2.5), 96(1.1), 90(0.9), 89(2.2), 88(1.2), 87(1.3), 84(1.6), 83.5(0.9), 83(1.3), 78(2.2), 77(1.0), 76(0.8), 71(2.0), 64(0.8), 63(1.5), 62(1.2), 61(1.5), 52(1.7), 51(1.3), 50(0.7), 39(1.2).

m* = 72.8, m* = 145.5

Mass spectrum at 18 eV.

m/e = 195(30%), 194(100), 193(16), 78(3.6).

m* = 105

2-Phenyl-1-oxa-3-aza-2-borole. (Exp. m. p. 105-107° C, lit.[59] m. p. 105-106° C)

Mass spectrum at 70 eV. (direct inlet; source temp. 150° C)

m/e = 196(15%), 195(100), 194(28), 193(3.0), 192(1.0), 180(0.3), 179(0.2), 169(1.0), 167(2.0), 166(2.0), 156(0.6), 149(0.6), 143(1.4), 134(2.0), 119(1.0), 114(1.0), 113(1.0), 105(1.4), 98(1.0), 97.5(7), 97(2.0), 91(3.0), 90(1.5), 89(1.0), 78(1.0), 77(2.0), 65(2.0), 64(4.0), 63(3.0), 62(1.0), 61(1.0), 53(1.0), 52(2.0), 51(2.0), 50(1.0), 43(2.0), 42(2.0), 41(1.0), 39(3.0), 38(1.0).

m* = 146.8 (ca), m* = 73.2

2-Phenyl-1,3-thiaza-2-borole. (Exp. m. p. 158-160° C, lit.[59] m. p. 154-156° C)

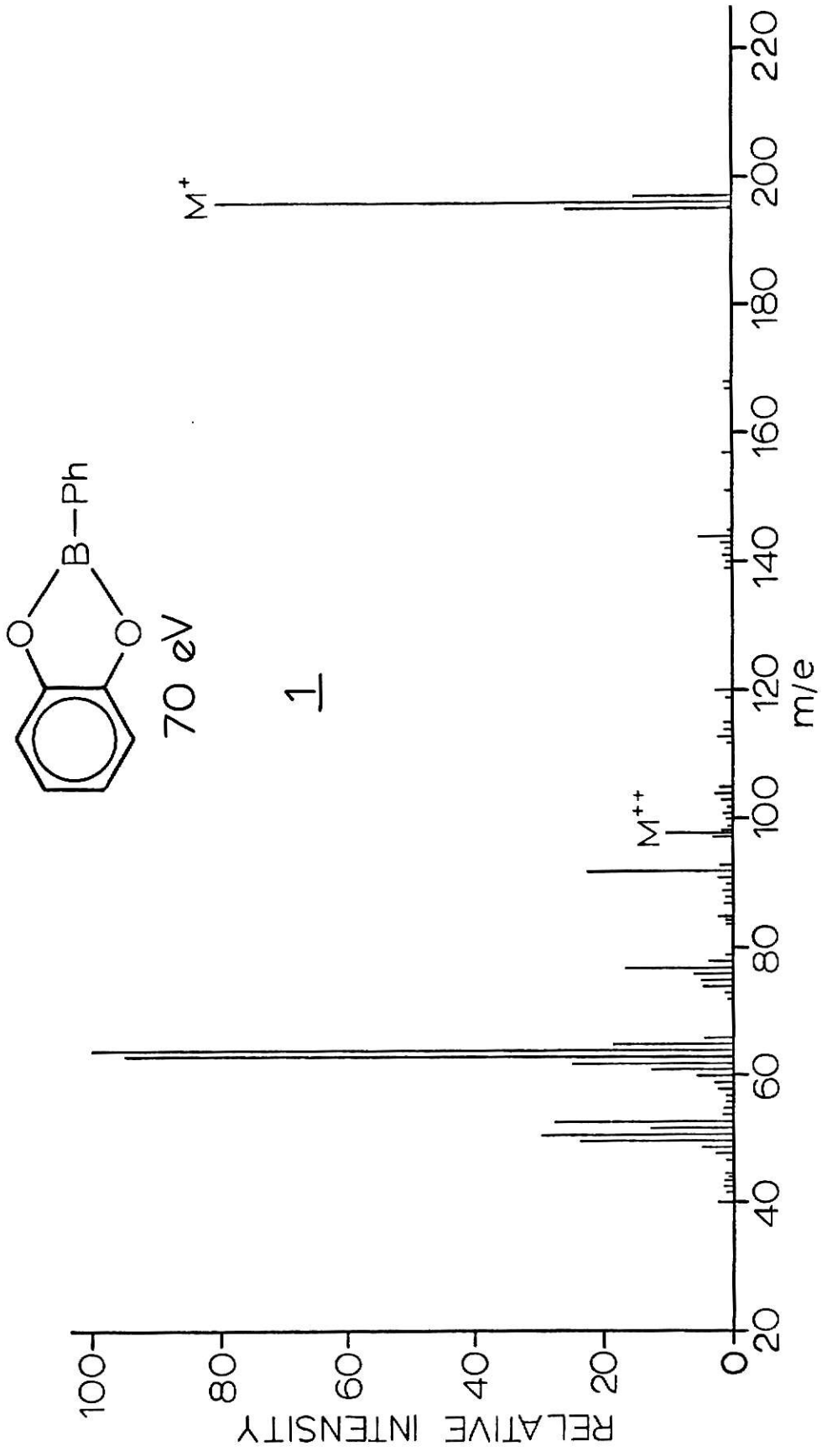
Mass spectrum at 70 eV. (direct inlet; source temp. 150° C)

m/e = 213(5%), 212(16), 211(100), 210(29), 209(5), 208(3.0), 185(1.4), 184(1.0), 183(1.4), 178(1.0), 177(1.0), 166(1.8), 165(1.3), 159(1.1), 150(2.5), 135(1.4), 134(1.0), 133(2.6), 132(1.0), 120(1.0), 115(1.1), 114(1.0), 113(1.0), 108(1.0), 106(1.7), 105.5(6.2), 105(2.5), 104.5(1.4), 104(1.0), 93(1.0), 92.5(1.6), 92(1.4), 91(2.4), 90(1.3), 89(1.5), 88(1.0), 87(1.5), 78(1.0), 77(3.0), 76(1.0), 75(1.0), 69(2.0), 65(1.7), 64(2.2), 63(3.5), 62(1.7), 61(2.3), 52(1.8), 51(3.0), 50(1.8), 43(1.6), 39(4.0), 38(1.0), 37(1.0).

Explanation of Figure 3

Mass Spectrum at 70 eV of 2-Phenyl-1,3-dioxa-2-borole

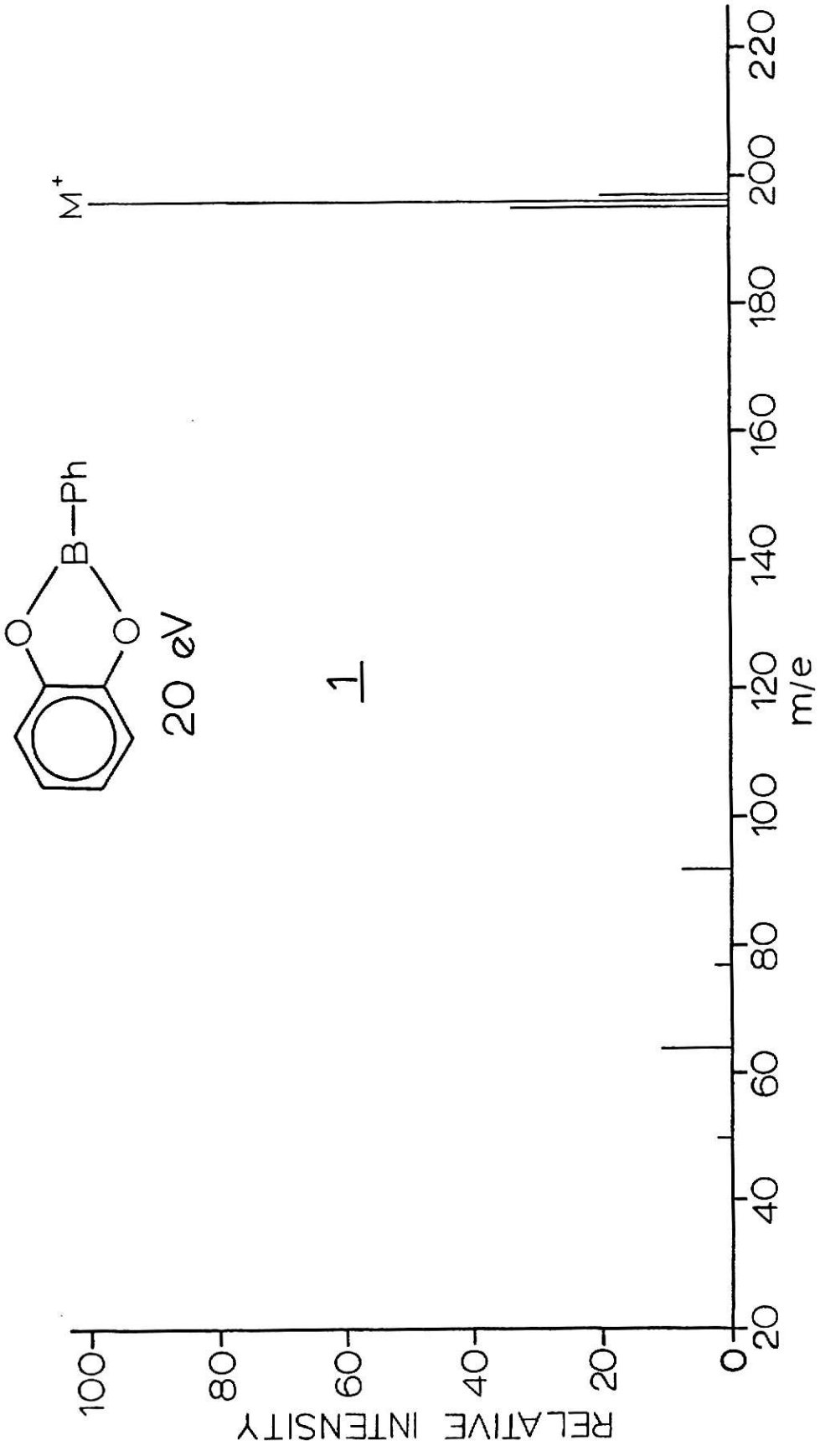
(Direct inlet; source temp. 150° C)


B—Ph
O
O
70 eV
1
M+
M++
RELATIVE INTENSITY
m/e
0
20
40
60
80
100
120
140
160
180
200
220

Explanation of Figure 4

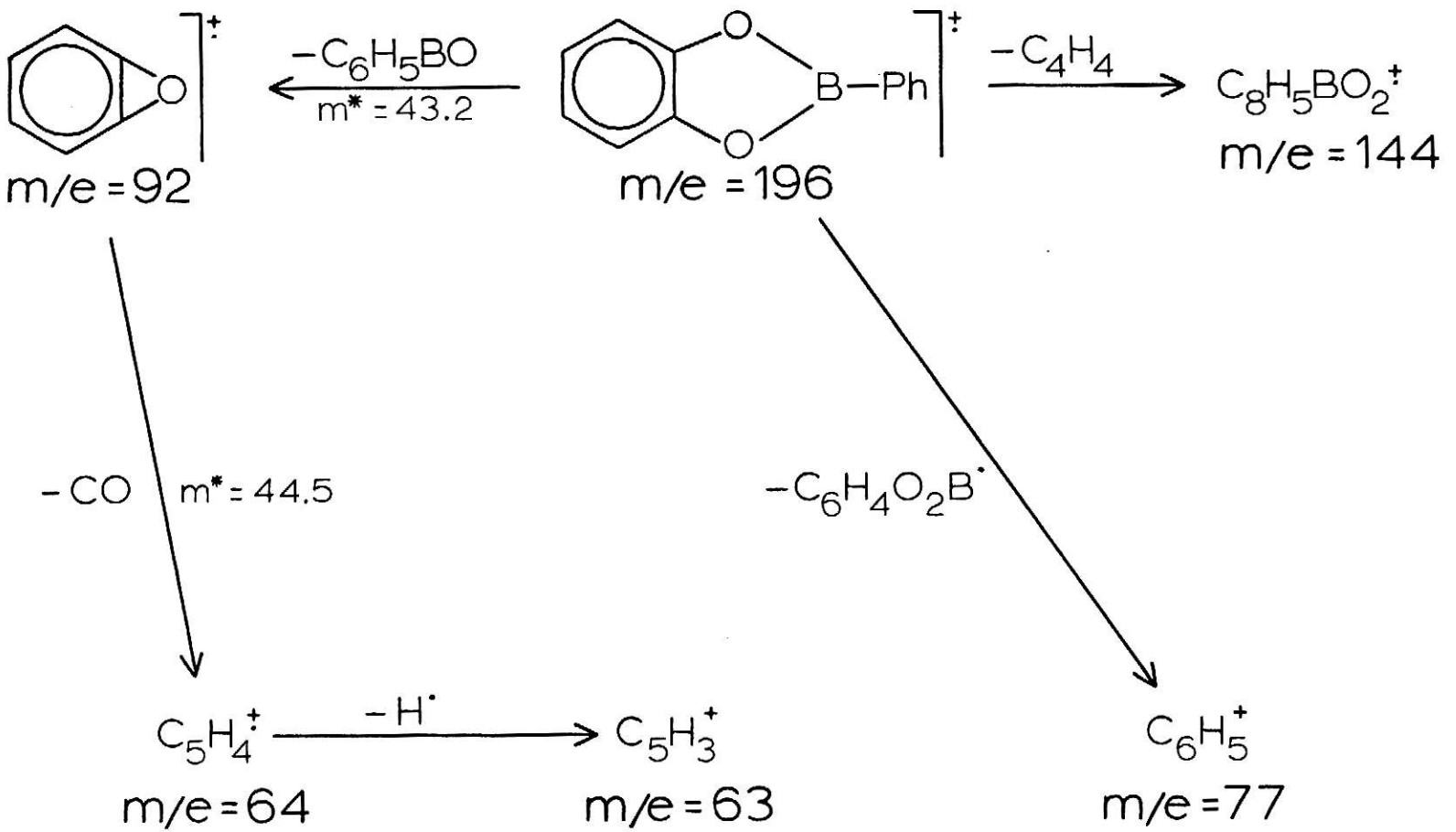
Mass Spectrum at 20 eV of 2-Phenyl-1,3-dioxa-2-borole

(Direct inlet; source temp. 150^{o} C)


M+
B—Ph
O
O
20 eV
1
RELATIVE INTENSITY
100
80
60
40
20
0
20
40
60
80
100
120
140
160
180
200
220
m/e

Explanation of Figure 5

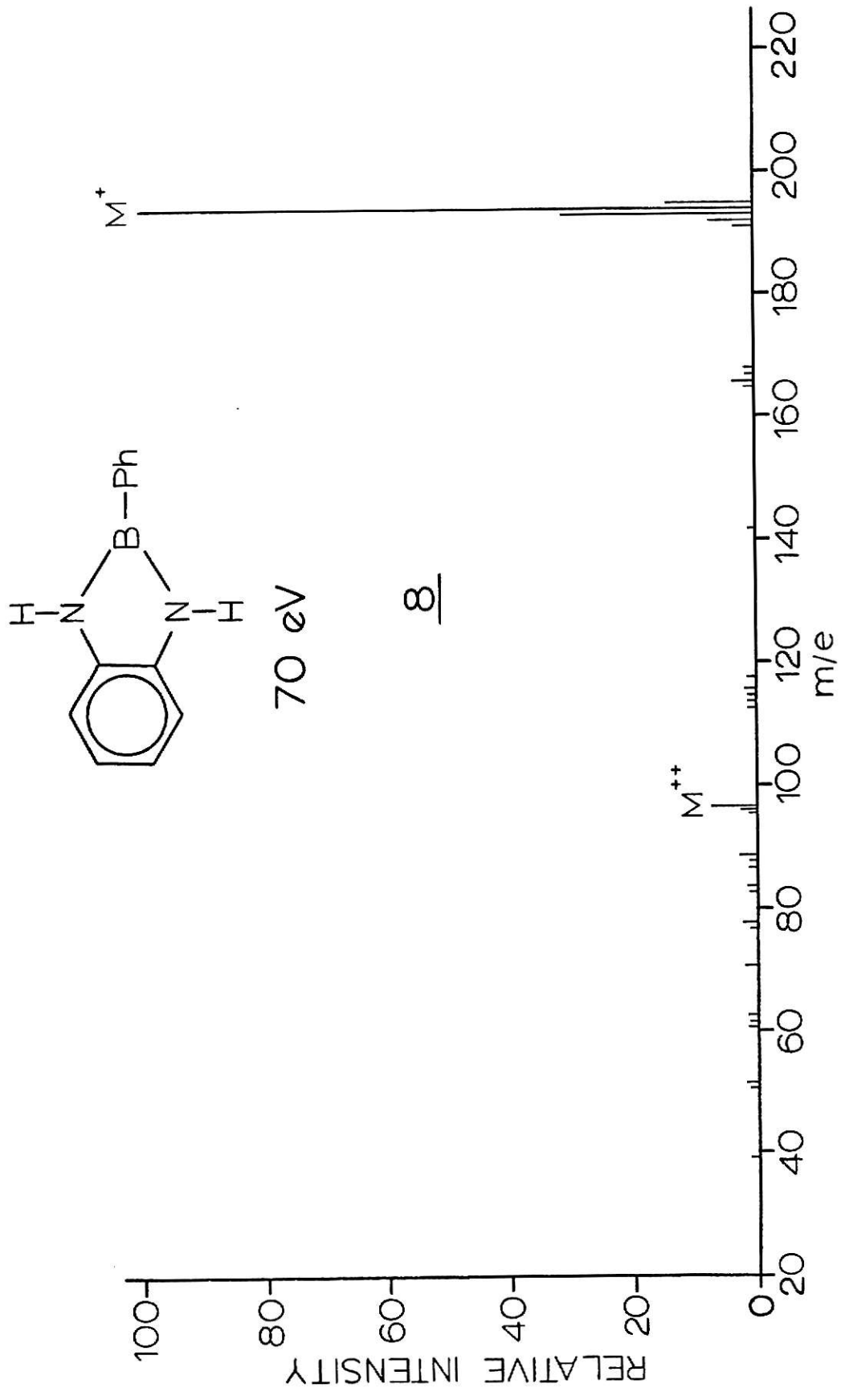
Partial Fragmentation Scheme of 2-Phenyl-1,3-dioxa-2-borole


m/e = 92
−C6H5BO
m* = 43.2
m/e = 196
−C4H4
C8H5BO2+
m/e = 144
− CO
m* = 44.5
−C6H4O2B·
C5H4+
−H·
C5H3+
m/e = 64
m/e = 63
C6H5+
m/e = 77

Explanation of Figure 6

Mass Spectrum at 70 eV of 2-Phenyl-1,3-diaza-2-borole

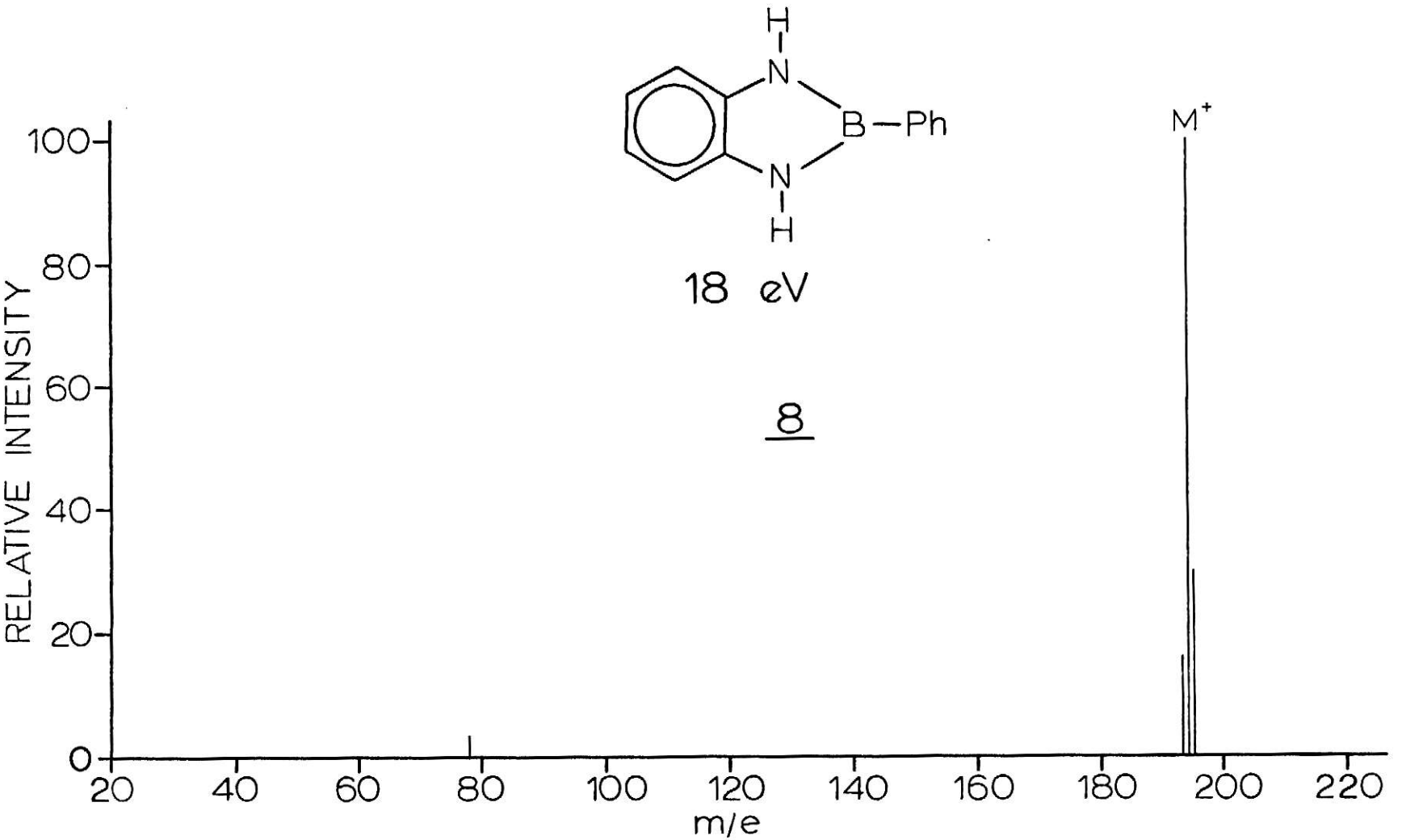
(Direct inlet; source temp. 110° C)


RELATIVE INTENSITY
100
80
60
40
20
0
20
40
60
80
100
120
140
160
180
200
220
m/e
M+
M++
B—Ph
H—N
N—H
70 eV
8

Explanation of Figure 7

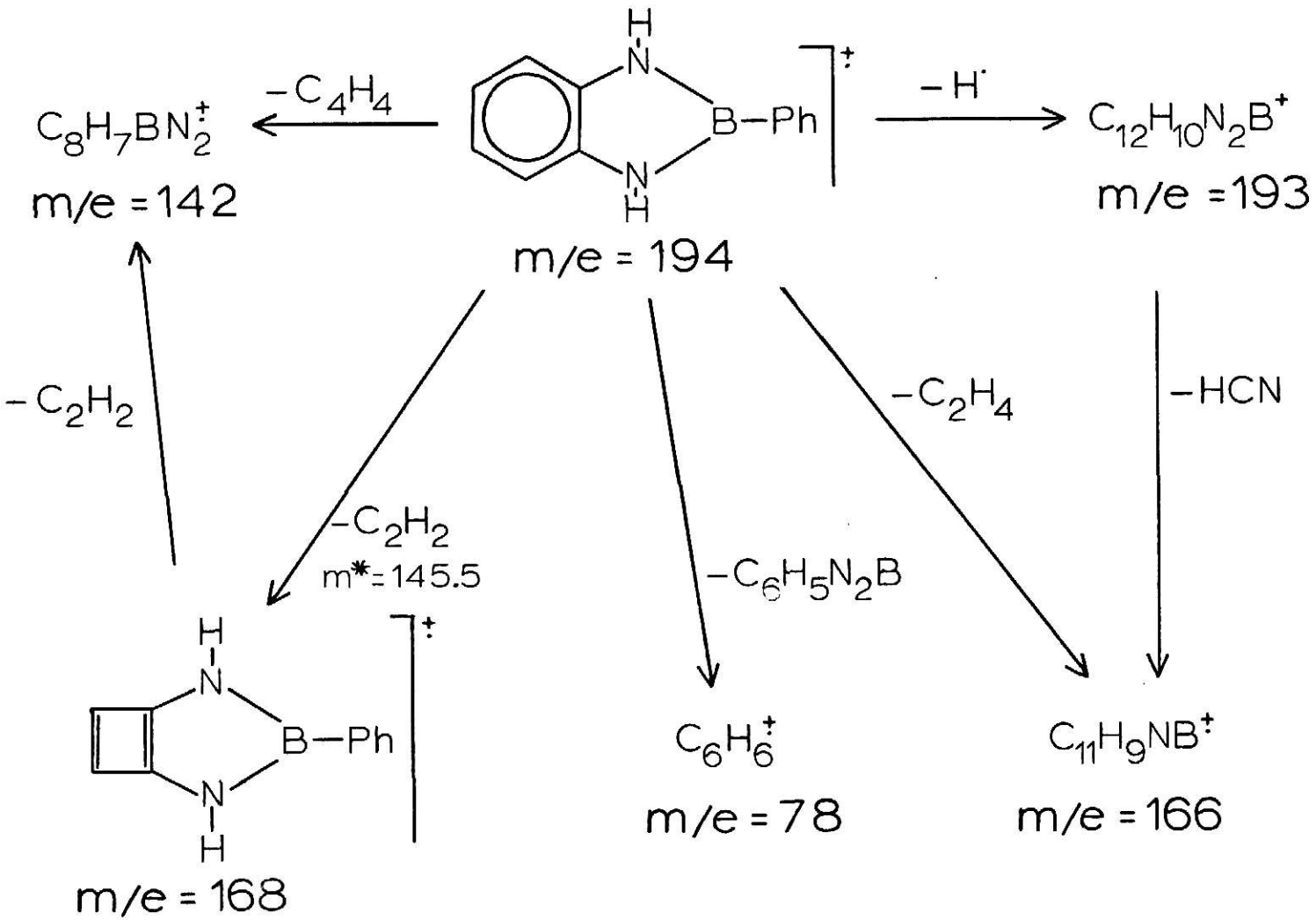
Mass Spectrum at 18 eV of 2-Phenyl-1,3-diaza-2-borole

(Direct inlet; source temp. 110^{o} C)


H
N
B—Ph
N
H
18 eV
8
M+
100
80
60
40
20
0
RELATIVE INTENSITY
20
40
60
80
100
120
140
160
180
200
220
m/e

Explanation of Figure 8

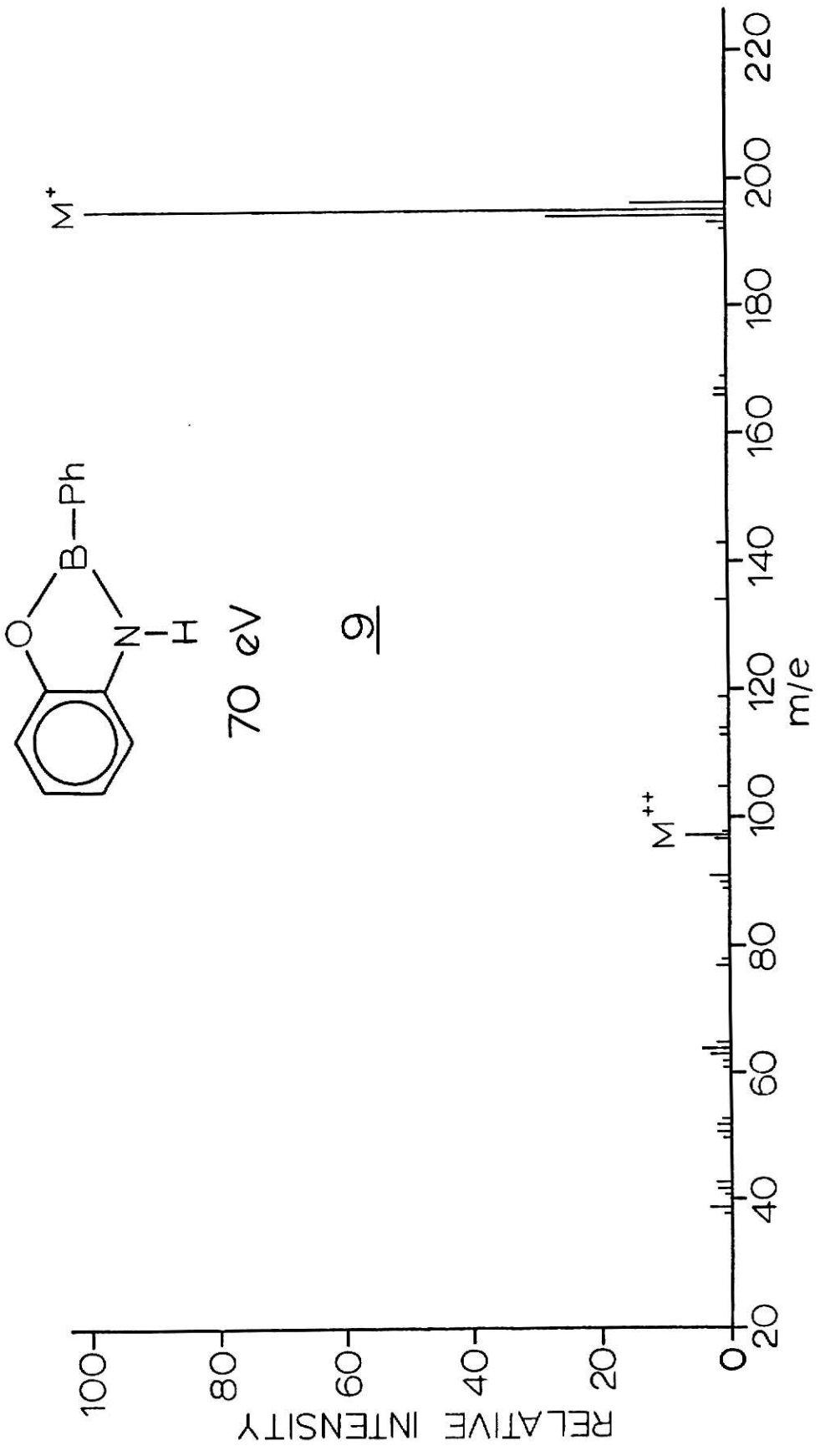
Partial Fragmentation Scheme of 2-Phenyl-1,3-diaza-2-borole


$C_8H_7BN_2^+$
m/e = 142
$-C_4H_4$
$-H^\cdot$
$C_{12}H_{10}N_2B^+$
m/e = 193
m/e = 194
$-C_2H_2$
$-C_2H_2$
m* = 145.5
$-C_6H_5N_2B$
$-C_2H_4$
$-HCN$
$C_6H_6^+$
m/e = 78
$C_{11}H_9NB^+$
m/e = 166
m/e = 168

Explanation of Figure 9

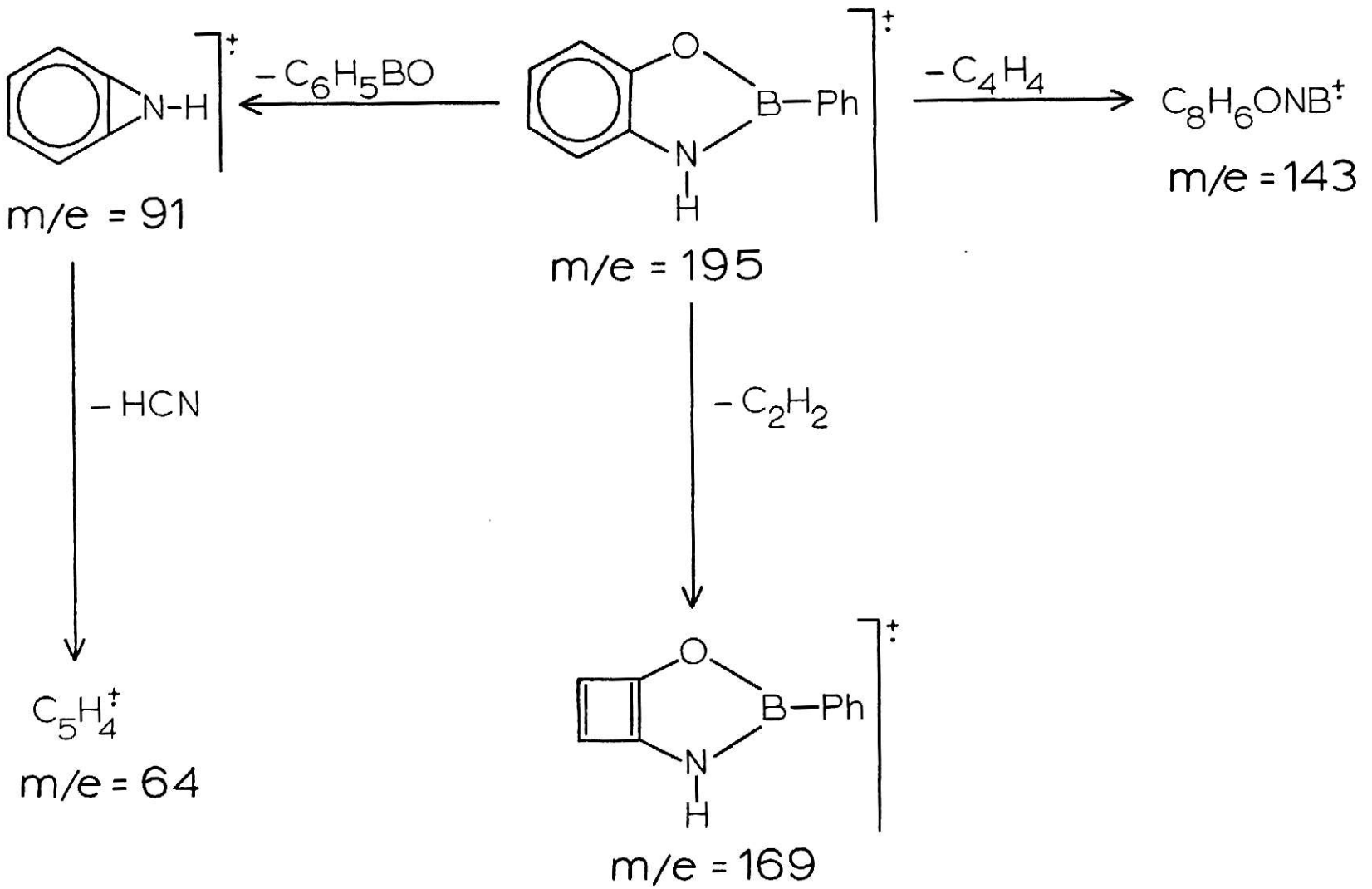
Mass Spectrum at 70 eV of 2-Phenyl-1-oxa-3-aza-2-borole

(Direct inlet; source temp. 150^{o} C)


RELATIVE INTENSITY
100
80
60
40
20
0
20
40
60
80
100
120
140
160
180
200
220
m/e
M++
M+
O
B—Ph
N—H
70 eV
9

Explanation of Figure 10

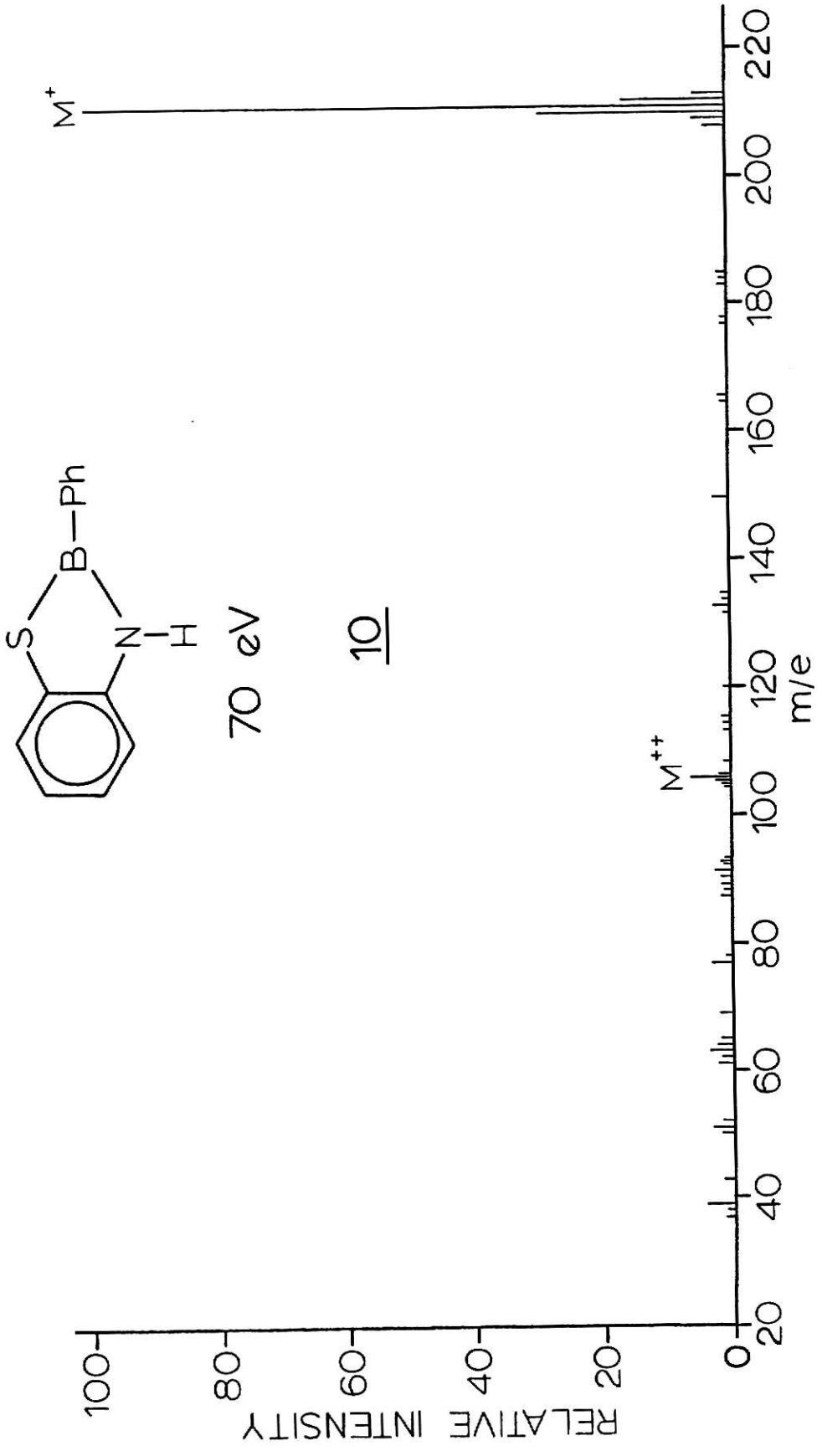
Partial Fragmentation Scheme of 2-Phenyl-1-oxa-3-aza-2-borole


N-H
m/e = 91
– C_6H_5BO
O
B–Ph
N
H
m/e = 195
– C_4H_4
$C_8H_6ONB^{+\cdot}$
m/e = 143
– HCN
$C_5H_4^{+\cdot}$
m/e = 64
– C_2H_2
O
B–Ph
N
H
m/e = 169

Explanation of Figure 11

Mass Spectrum at 70 eV of 2-Phenyl-1,3-thiaza-2-borole

(Direct inlet; source temp. 150^{o} C)


RELATIVE INTENSITY
100
80
60
40
20
0
20
40
60
80
100
120
140
160
180
200
220
m/e
M+
M++
70 eV
10
S
B—Ph
N—H

Gerrard, Lappert, and Mountfield[60] have reported the synthesis of o-phenylene chloroboronate and o-phenylene hydrogen borate. o-Phenylene chloroboronate was prepared using the literature procedure, but not without some difficulty. Gerrard, Lappert, and Mountfield added a suspension of catechol in methylene chloride to boron trichloride to obtain the product; however, it was found that if boron trichloride is added to a suspension of catechol, di-o-phenylene pyroborate and the anhydride of o-phenylene hydrogen borate were the products formed. To prepare o-phenylene hydrogen borate, 0.0585 g of o-phenylene chloroboronate was weighed out, in the dry box, into a small bottle which was then stoppered with a serum cap. Then an equimolar amount of water (0.0068 ml) was added using a hypodermic syringe to form o-phenylene hydrogen borate.

o-Phenylene chloroboronate. (Exp. m.p. 58° C, lit.[60] m. p. 57° C)

Mass spectrum at 70 eV. (direct inlet; source temp. 60° C)

m/e = 157(2.4%), 156(33), 155(15), 154(100), 153(25), 138(4.2), 137(1.0), 136(1.7), 120(1.0), 119(0.8), 103(1.2), 100(3.5), 99(1.6), 98(10.3), 97(3.5), 93(2.5), 92(35), 91(6), 90(3.5), 89(2.3), 82(1.4), 80(1.1), 78(1.2), 75(4.0), 74(4.0), 73(1.5), 71(2.8), 66(2.0), 65(5.8), 64(54), 63(61), 62(22.1), 61(18.5), 60(2.4), 59(1.3), 57(3.6), 56(9), 55(4.1), 53(11.4), 52(3.2), 51(4.4), 50(8.2), 49(4.0), 47(2.3), 46(2.2), 45(2.0), 43(3.8), 41(6.2).

m* = 44.5, m* = 54.8, m* = 62.1

Mass spectrum at 18 eV.

m/e = 157(2.3%), 156(34), 155(14), 154(100), 153(25), 138(1.7), 137(0.5), 136(0.6), 120(0.2), 119(0.2), 100(0.8), 99(0.3), 98(2.5), 97(0.6), 93(0.7), 92(9.5), 65(0.3), 64(3.8), 61(0.5), 56(1.2).

m* = 44.5, m* = 62.0, m* = 55.0

o-Phenylene hydrogen borate and its anhydride (these two compounds could not be separated since o-phenylene hydrogen borate dehydrates readily to its anhydride in a vacuum)

Mass spectrum at 70 eV. (direct inlet; source temp. 110° C)

m/e = 256(1.6%), 255(13), 254(100), 253(44), 252(5), 229(1.0), 228(9), 227(1.0), 196(2.0), 172(1.4), 171(1.4), 162(3.5), 161(1.4), 138(2.0), 137(6), 136(89), 135(24), 127(6), 126.5(2.5), 120(2.0), 110(5), 108(1.0), 107(1.0), 92(10), 91(1.0), 80(4.0), 79(1.5), 68(1.5), 65(1.0), 64(17), 63(12), 62(3.0), 61(1.0), 54(1.0), 53(4.0), 52(2.0), 51(1.5), 50(1.5), 39(2.0), 38(4.0), 37(2.0).

2-Ethyl-1,3-dioxa-2-borole was prepared in the dry box by dropwise addition of 5.4 ml of a 1.2 M solution of EtLi in benzene to 1.0 g of o-phenylene chloroboronate dissolved in benzene. The LiCl was filtered out of solution and the benzene distilled off under vacuum. The remaining clear liquid, upon studying its mass spectrum, appeared to be pure 2-ethyl-1,3-dioxa-2-borole.

Mass spectrum at 70 eV. (heated inlet; source temp. 170° C)

m/e = 149(4.0%), 148(40), 147(10.5), 146(1.4), 134(2.0), 133(7), 121(5.4), 120(100), 119(25), 105(1.0), 103(3.8), 102(1.0), 93(1.1), 92(5.8), 91(3.2), 90(1.0), 89(2.4), 65(5.5), 64(16), 63(24), 62(6), 61(2.8), 57(5), 56(1.8), 55(4.2), 54(1.2), 53(6.3), 46(3.8), 45(13), 44(1.1), 43(4.0), 42(1.5), 41(3.4), 40(1.5).

m* = 97.3, m* = 76.2

Mass spectrum at 18 eV.

m/e = 150(1.3%), 149(9), 148(100), 147(28), 121(4.8), 120(87), 119(22), 92(1.5), 91(0.5).

m* = 97.3

2-Methyl-1,3-dioxa-2-borole was prepared by adding 1.08 g of MeMgI, in ether, to 1.0 g of o-phenylene chloroboronate, dissolved in 10 ml of ether. By fractionation in a vacuum line and collecting in a -23° C trap one was able to purify the product formed. There was some doubt as to the purity of the product. The spectrum obtained indicated that the major impurities were HCl and Et_2O, thus it was necessary to subtract out the spectra of these two compounds.

Mass spectrum at 70 eV. (heated inlet; source temp. 100° C)

m/e = 135(10%), 134(100), 133(30), 132(1.0), 131(2.5), 107(2), 105(3.0), 104(10), 103(3.0), 101(6), 100(2.0), 97(2.0), 95(3.0), 93(3.0), 92(11), 91(4.0), 90(2.0), 89(3.0), 87(3.0) 85(2.0), 84(1.0), 83(2.0), 81(3.0), 79(1.0), 78(5), 77(6), 76(1.0), 75(1.1), 74(0.7), 73(3.1), 72(2.0), 71(3.0), 69(3.0), 67(3.5), 66(1.0), 65(3.0), 64(20), 63(23), 62(5), 61(2.0),

60(1.5), 59(4.3), 58(1.0), 57(4.0), 56(1.6), 55(4.5), 53(4.0), 52(2.0), 51(6), 50(5), 47(1.0), 45(14), 44(3.0), 43(12), 42(2.6), 40(6), 39(6), 35(4.5).

Mass spectrum at 20 eV.

m/e = 135(10%), 134(100), 133(26), 104(14), 101(2.0), 92(4.0), 64(2.0).

2-Methyl-1,3-diaza-2-borole was prepared by slowly adding 0.4487 g o-phenylenediamine to a stirred methylene chloride solution of 4.05 mmoles methylboron dibromide. The solution was refluxed, using a dry-ice condenser, for about eight hours, the remaining solvent removed and the solid sublimed twice; once at 80° C and the second time at room temperature. The melting point of the product was 89-90° C compared to the literature value of 94° C.[61] The mass spectrum of this compound contained a number of ions having a mass greater than the 132, the 2-methyl-1,3-diaza-2-borole molecular ion, indicating that the prepared sample was impure. Repeated attempts at purifying the compound failed, so the complete mass spectrum of this compound will not be reported. It is significant to point out, however, that the peak at m/e = 117 was less than 1% abundant relative to the molecular ion.

2-Phenyl-1,3-dioxa-2-borolane was prepared by the dropwise addition of 1.95 g of dry ethylene glycol to 5.00 g of phenylboron dichloride, with constant stirring. The solution was then stirred for about two hours, filtered and stored in the

dry box until its spectrum was obtained.

Mass spectrum at 70 eV. (heated inlet; source temp. 50° C)

m/e = 149(9%), 148(100), 147(27), 146(1.7), 121(1.3), 119(6), 118(44), 117(22) 116(3.0), 105(3.0), 104(5), 103(3.8), 92(7), 91(72), 90(3.2), 89(3.0), 88(1.0), 87(1.5), 79(3.7), 78(49), 77(20), 76(4.8), 75(1.7), 74(4.2), 73.5(4.4), 73(3.0), 71(0.8), 69(1.1), 66(1.5), 65(2.7), 63(2.5), 62(1.3), 61(2.1), 57(1.4), 56(1.2), 55(1.5), 53(3.0), 52(9), 51(14), 50(9), 49(1.3), 45(1.4), 44(3.0), 43(2.8), 42(1.0), 41(1.3), 39(7), 38(2.7), 37(1.8), 36(2.0).

m* = 56.1, m* = 70.2

Mass spectrum at 18 eV. (heated inlet; source temp. 50° C)

m/e = 149(9%), 148(100), 147(25), 119(3.0), 118(12), 117(5), 92(2.0), 91(21), 79(2.0), 78(30), 77(1).

1,3-Dimethyl-2-phenyl-1,3,2-diazaborolidine was not prepared using conventional methods.[62] To 1.11 g of sym-dimethylethylenediamine, dissolved in 15 ml of hexane, 1.0 g of phenylboron dichloride was added with constant stirring. The solution was stirred for about two hours, filtered and the hexane was removed by vacuum distillation.

Mass spectrum at 70 eV. (heated inlet; source temp. 60° C)

m/e = 176(0.5%), 175(6.5), 174(63), 173(100), 172(24), 171(2.7), 160(1.3), 159(6.8), 158(38), 157(15), 156(3.2), 155(2.2), 154(0.6), 146(0.7), 145(1.5), 144(3.2), 143(1.8), 142(1.6), 141(0.6), 133(1.0), 132(4.5), 131(2.6), 130(6.5), 129(2.7), 128(6.4), 127(1.2), 126(0.6), 119(0.8), 118(2.2),

117(5), 116(18), 115(6), 114(3.0), 113(0.8), 107(0.5), 106(1.0), 105(7), 104(6), 103(11), 102(5), 101(2.8), 100(1.5), 99(1.9), 97(1.0), 96(1.8), 95(2.2), 94(0.7), 93(0.7), 92(2.4), 91(17), 90(7), 89(47), 88(16), 87(13), 86(4.5), 85(1.9), 84(0.8), 83(1.4), 82(1.1), 81(1.9), 80(1.1), 79(2.8), 78(5.2), 77(9), 76(4.2), 75(3.5), 74(2.6), 73(1.3), 72(0.9), 71(4.5), 70(2.9), 69(1.6), 68(2.2), 67(3.2), 66(2.8), 65(4.0), 64(4.8), 63(14.9), 62(6.2), 61(10), 60(2.7), 59(0.8), 58(14.8), 57(9), 56(11.9), 55(5.1), 54(6.5), 53(2.9), 52(4.2), 51(10), 50(5.5), 49(1.5), 45(7.6), 44(90), 43(24), 42(38), 41(13), 40(9.6), 39(9.6).

m* = 144.2, m* = 68.2, m* = 143.5

Bis-(dimethylamino)phenylborane was prepared using reported procedures.[62] In the dry box, 1 g (6.28 mmoles) of phenylboron dichloride was dissolved in 15 ml of dry hexane. On the vacuum line, 27.6 mmoles of dimethylamine was condensed into the reaction flask at -196° C. The system was then allowed to gradually warm to room temperature, the precipitate was filtered off and the hexane was distilled away under vacuum leaving the clear liquid product.

Mass spectrum at 70 eV. (heated inlet; source temp. 180° C)

m/e = 177(12.5%), 176(100), 175(72), 174(17), 173(4.0), 162(7), 161(21), 160(5), 159(2.0), 145(5), 144(2.0), 133(9), 132(96), 131(23), 130(6), 119(2.0), 118(16), 117(19), 116(15), 115(4.0), 105(3.0), 104(2.0), 103(6), 102(2.0),

99(26), 98(11), 97(3.0), 95(2.0), 92(11), 91(62), 90(2.0), 89(14), 80(4.0), 79(4.0), 78(5), 77(7), 76(3.0), 72(2.0), 68(5), 67(5), 66(3.0), 65(5), 64(3.0), 63(6), 62(3.0), 61(3.0), 54(8), 53(11), 52(4.0), 51(10), 50(7).

m* = 108.1, m* = 99.2, m* = 62.8, m* = 37.4, m* = 36.5, m* = 27.4

Dimethoxyphenylborane was prepared by dropwise addition of 2.02 g of methanol with stirring to 5.00 g of phenylboron dichloride, in the dry box. The solution was stirred for an additional hour and then the excess methanol was distilled off under vacuum. The IR spectrum of the product agreed with the reported spectrum.[63]

Mass spectrum at 70 eV. (heated inlet; source temp. 50° C)

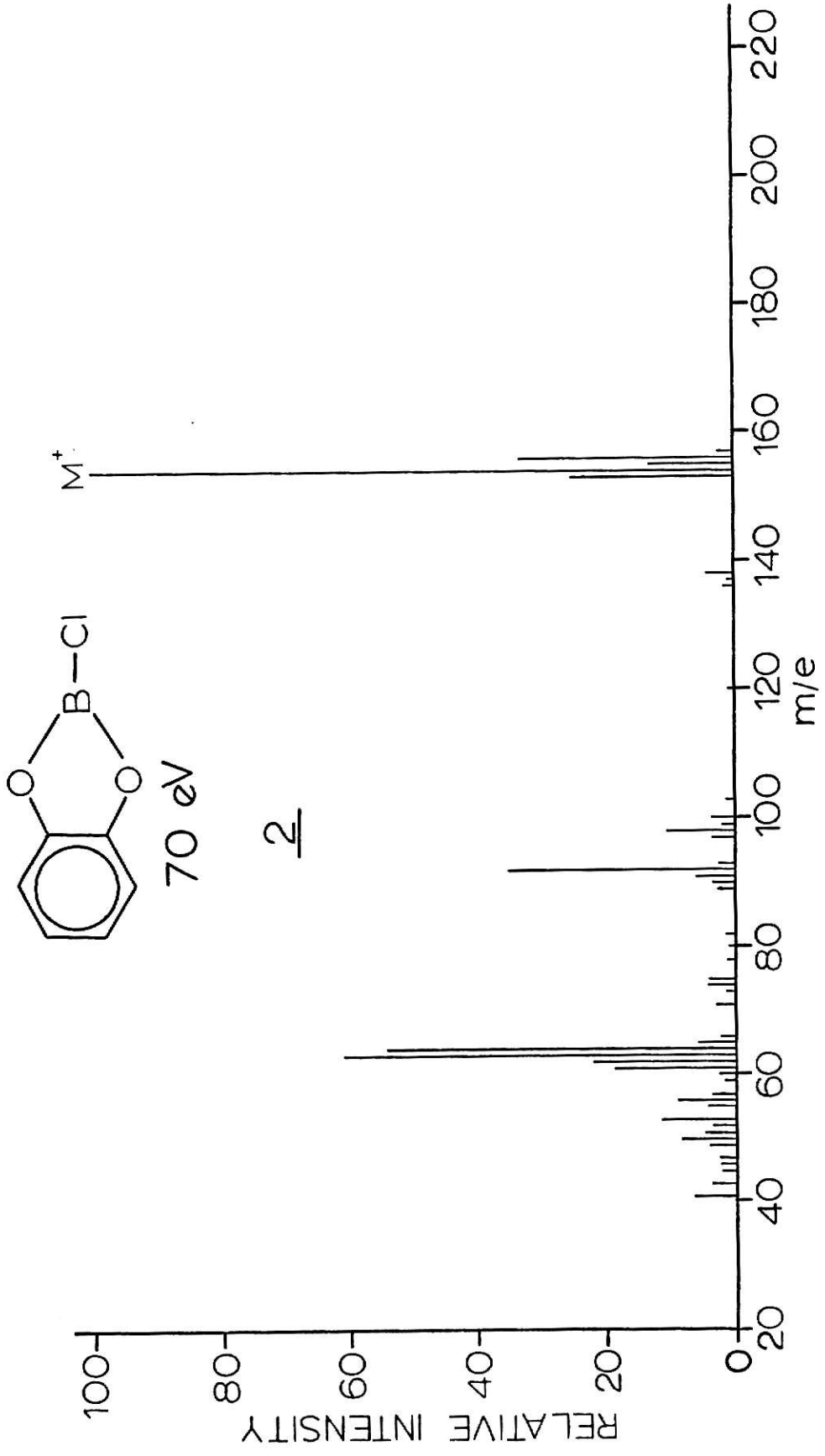
m/e = 151(7%) 150(75), 149(19), 120(7), 119(28), 118(9), 117(5.8), 116(1.5), 105(3.4), 104(10), 103(6.6), 102(1.4), 93(9), 92(98), 91(11), 90(1.2), 89(1.4), 77(12), 76(2.4), 75(1.4), 74(4.0), 73(100), 72(74), 71(12), 67(1.1), 65(2.1), 63(1.2), 59(1.8), 57(2.5), 53(3.2), 52(3.4), 51(9), 50(4.4), 43(17), 42(4.4), 39(3.3), 32(21), 31(24), 30(1.8), 29(9), 28(29), 27(1.5).

m* = 115.0, m* = 56.5, m* = 25.4

Explanation of Figure 12

Mass Spectrum at 70 eV of o-Phenylene Chloroboronate

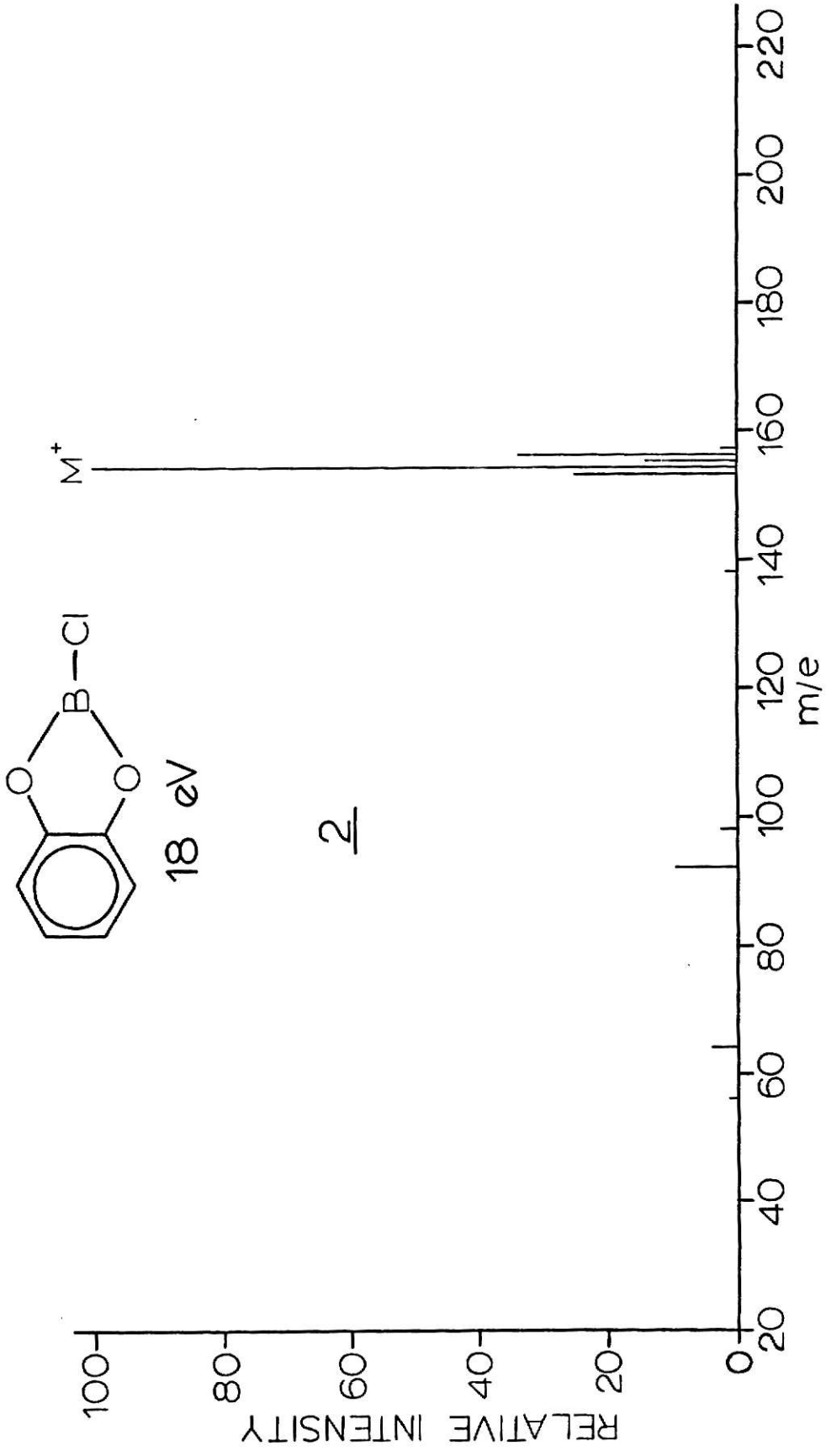
(Direct inlet; source temp. 60° C)


RELATIVE INTENSITY
100
80
60
40
20
0
20
40
60
80
100
120
140
160
180
200
220
m/e
M+
B—Cl
O
O
70 eV
2

Explanation of Figure 13

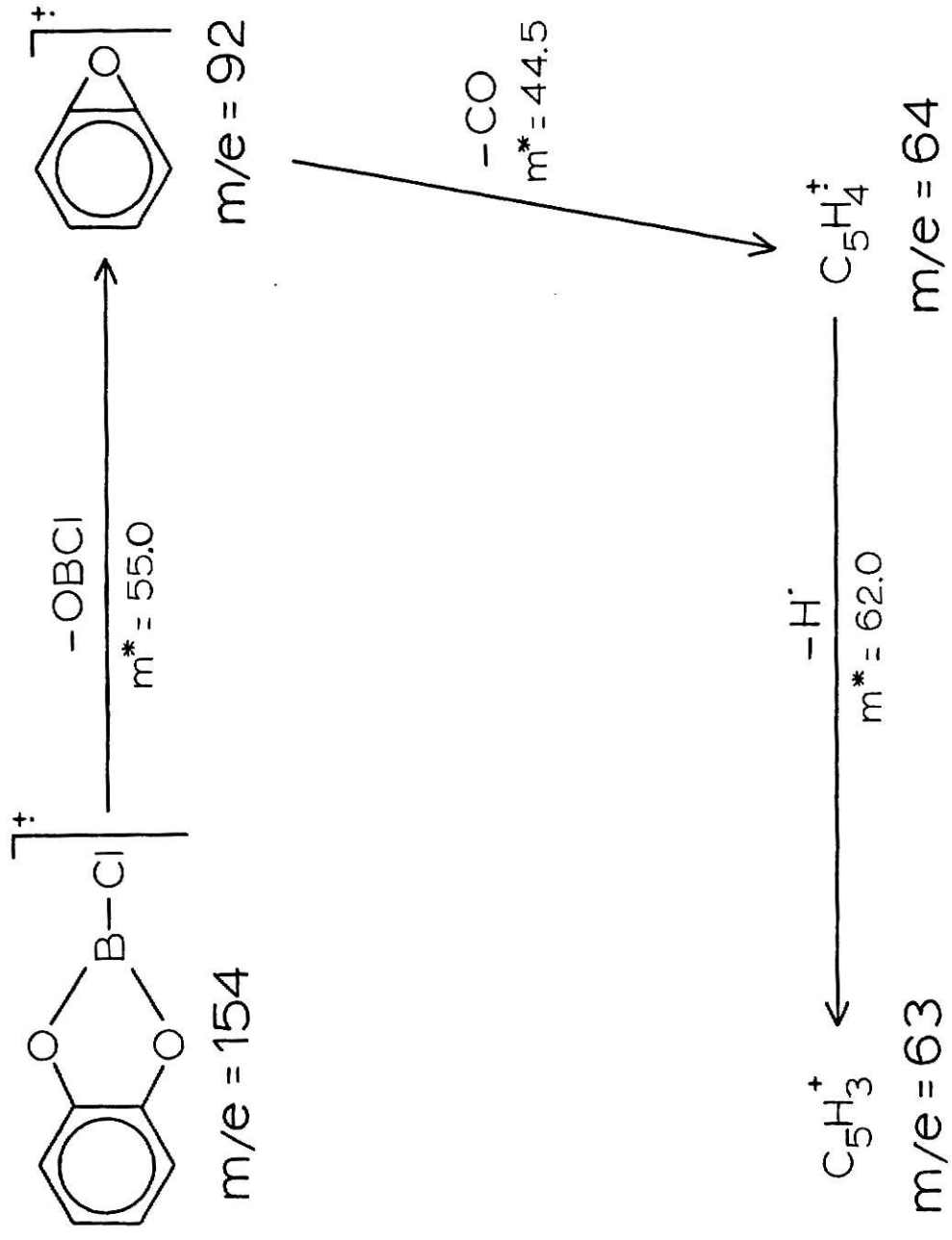
Mass Spectrum at 18 eV of o-Phenylene Chloroboronate

(Direct inlet; source temp. 60° C)


RELATIVE INTENSITY
100
80
60
40
20
0
20
40
60
80
100
120
140
160
180
200
220
m/e
M+
B—Cl
O
O
18 eV
2

Explanation of Figure 14

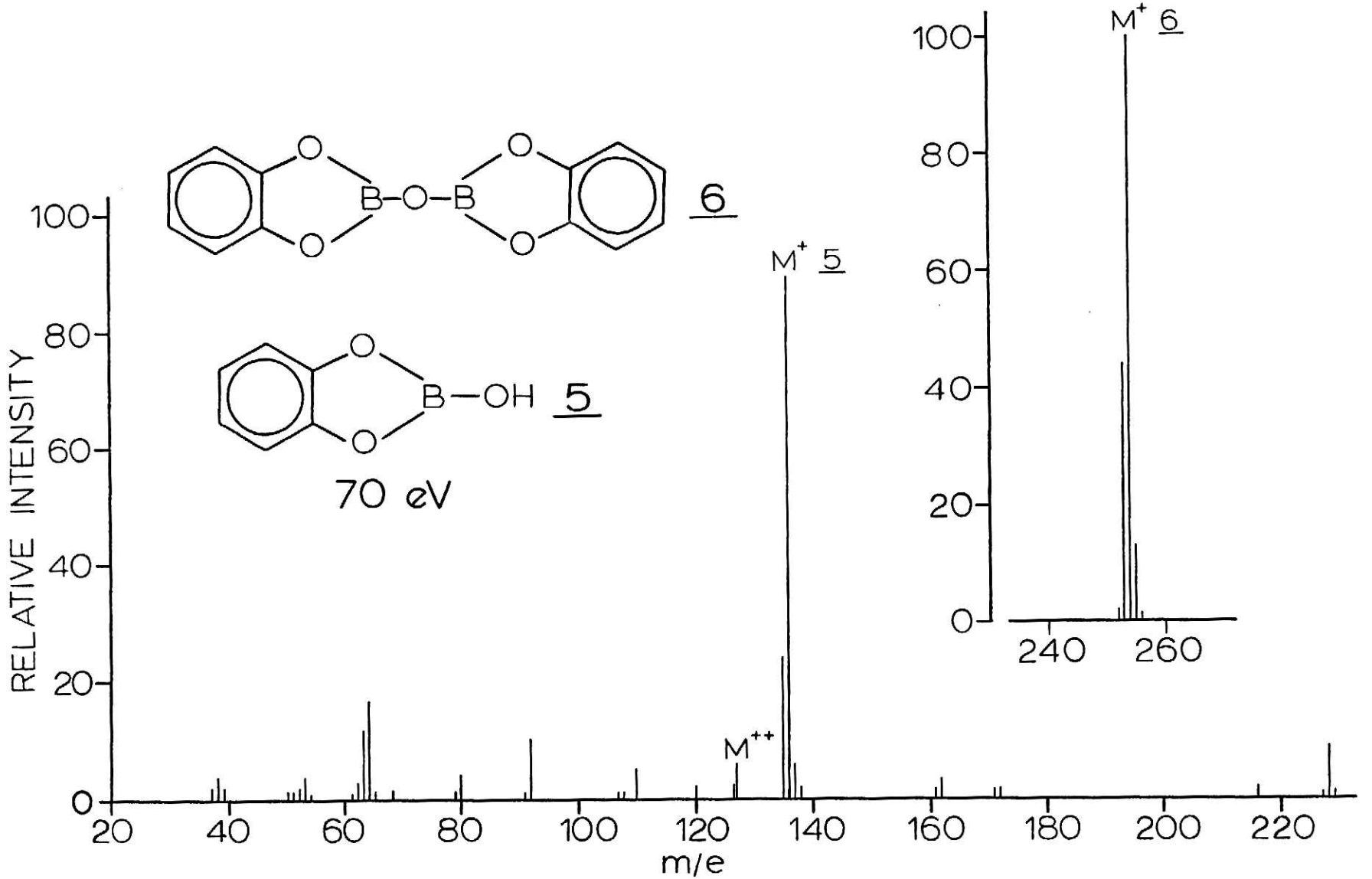
Partial Fragmentation Scheme of o-Phenylene Chloroboronate


m/e = 154
-OBCl
m* = 55.0
m/e = 92
-CO
m* = 44.5
m/e = 64
-H·
m* = 62.0
m/e = 63

Explanation of Figure 15

Mass Spectrum at 70 eV of o-Phenylene Hydrogen Borate and its Anhydride

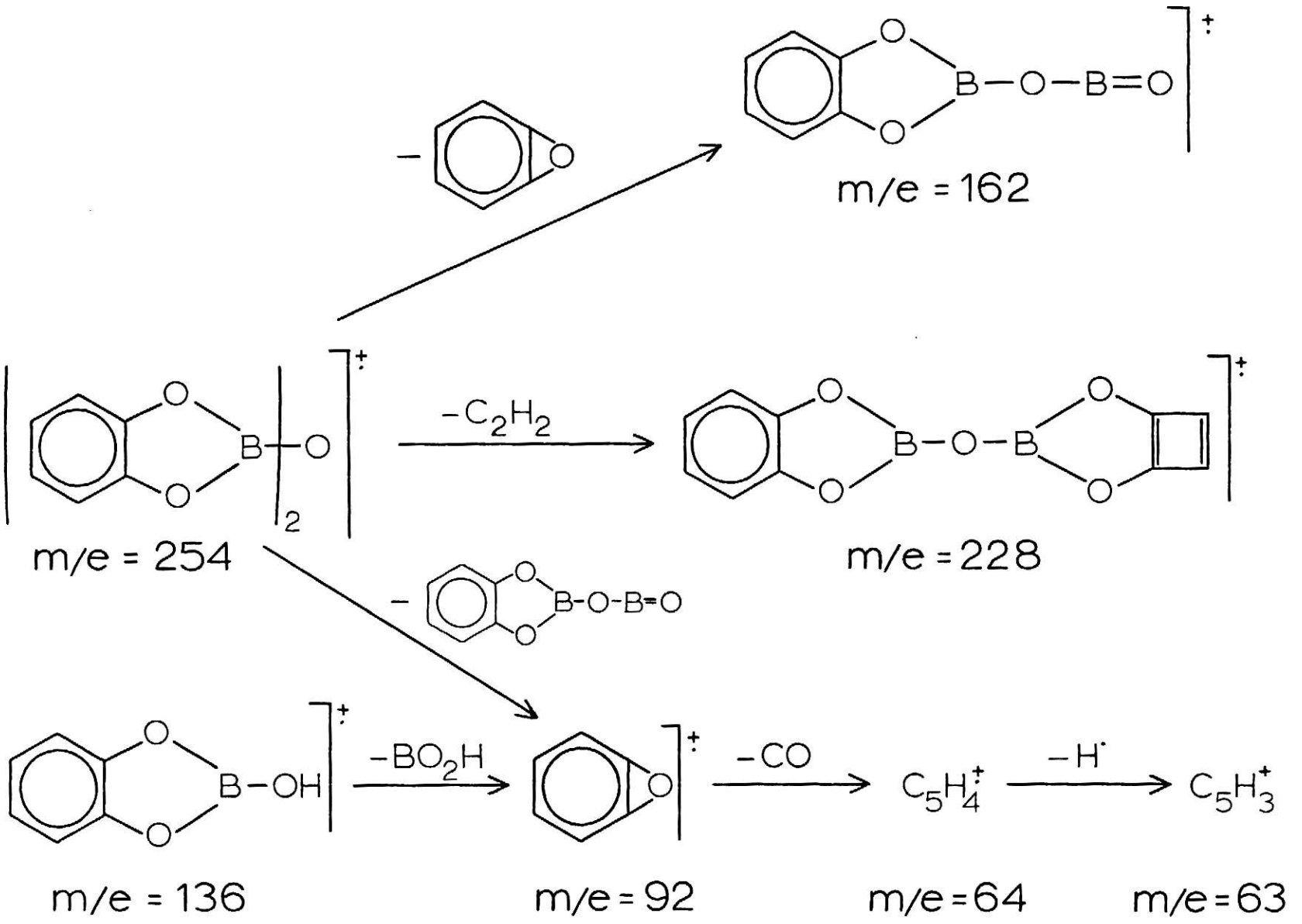
(Direct inlet; source temp. 110° C)


6
5
70 eV
M+ 5
M++
M+ 6
RELATIVE INTENSITY
m/e
100
80
60
40
20
0
20
40
60
80
100
120
140
160
180
200
220
240
260

Explanation of Figure 16

Partial Fragmentation Scheme of

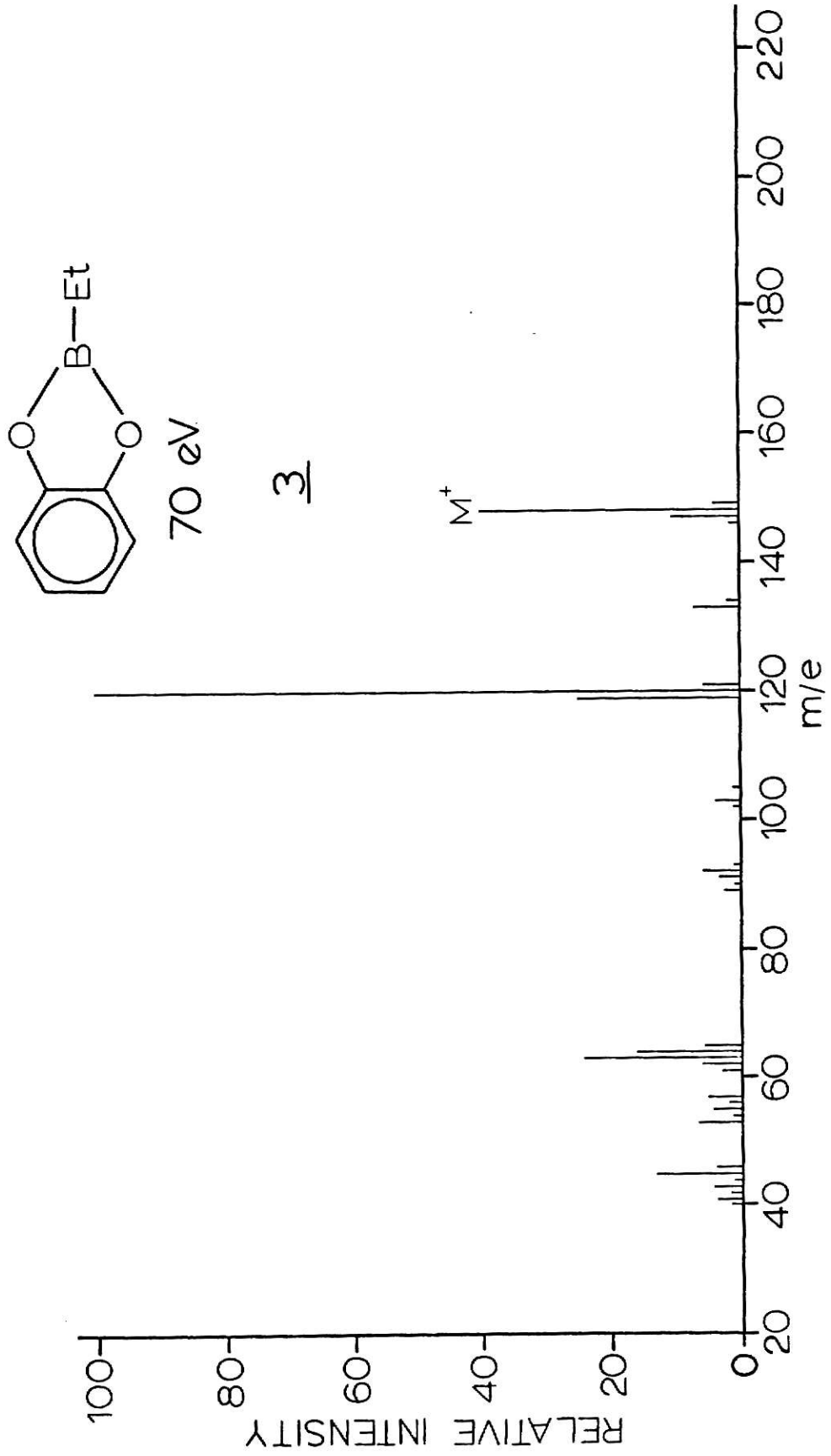
o-Phenylene Hydrogen Borate and its Anhydride


m/e = 254
m/e = 162
m/e = 228
m/e = 136
m/e = 92
m/e = 64
m/e = 63

Explanation of Figure 17

Mass Spectrum at 70 eV of 2-Ethyl-1,3-dioxa-2-borole

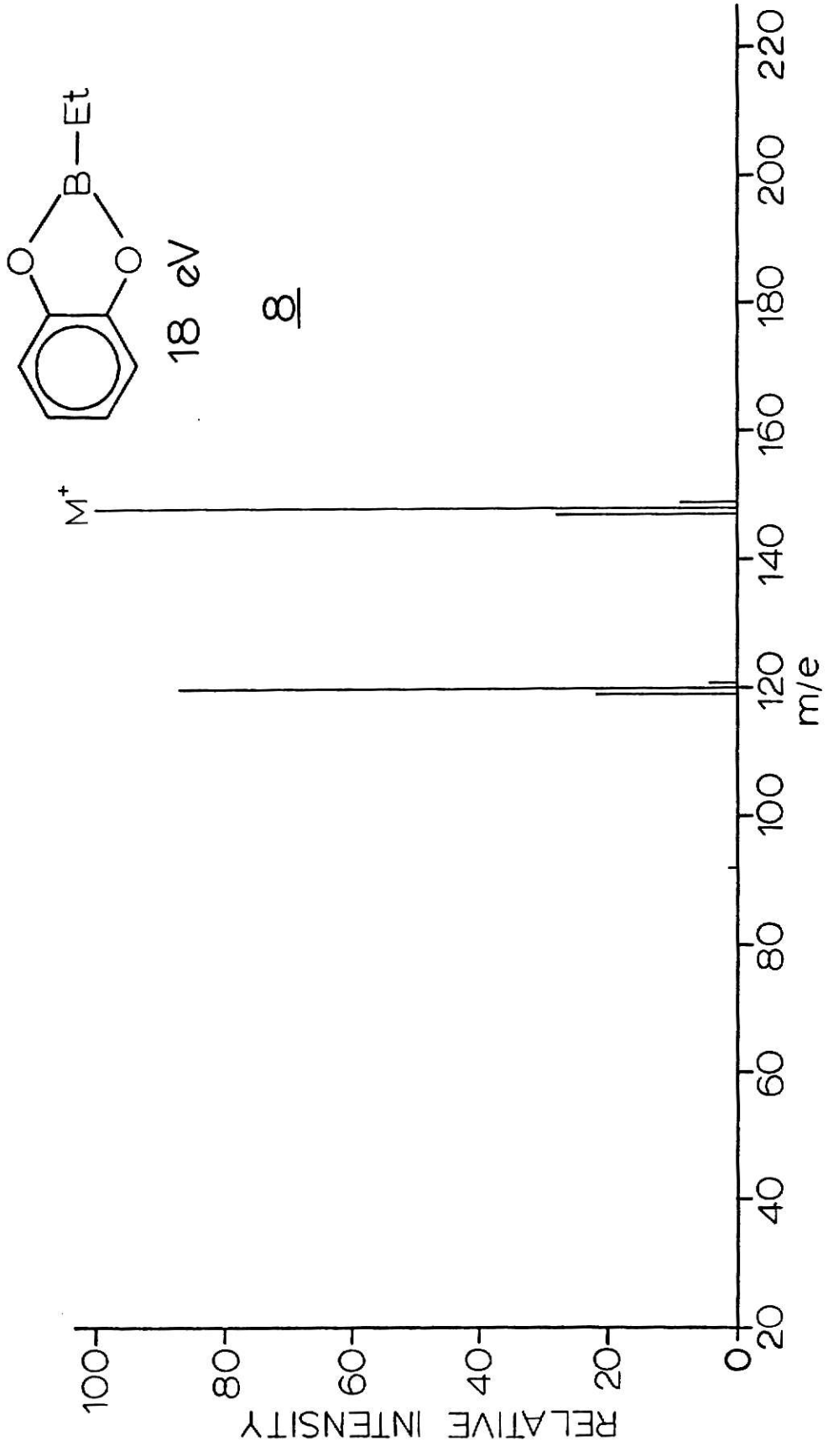
(Heated inlet; source temp. 170^{o} C)


B—Et
O
O
70 eV
3
M+
RELATIVE INTENSITY
100
80
60
40
20
0
20
40
60
80
100
120
140
160
180
200
220
m/e

Explanation of Figure 18

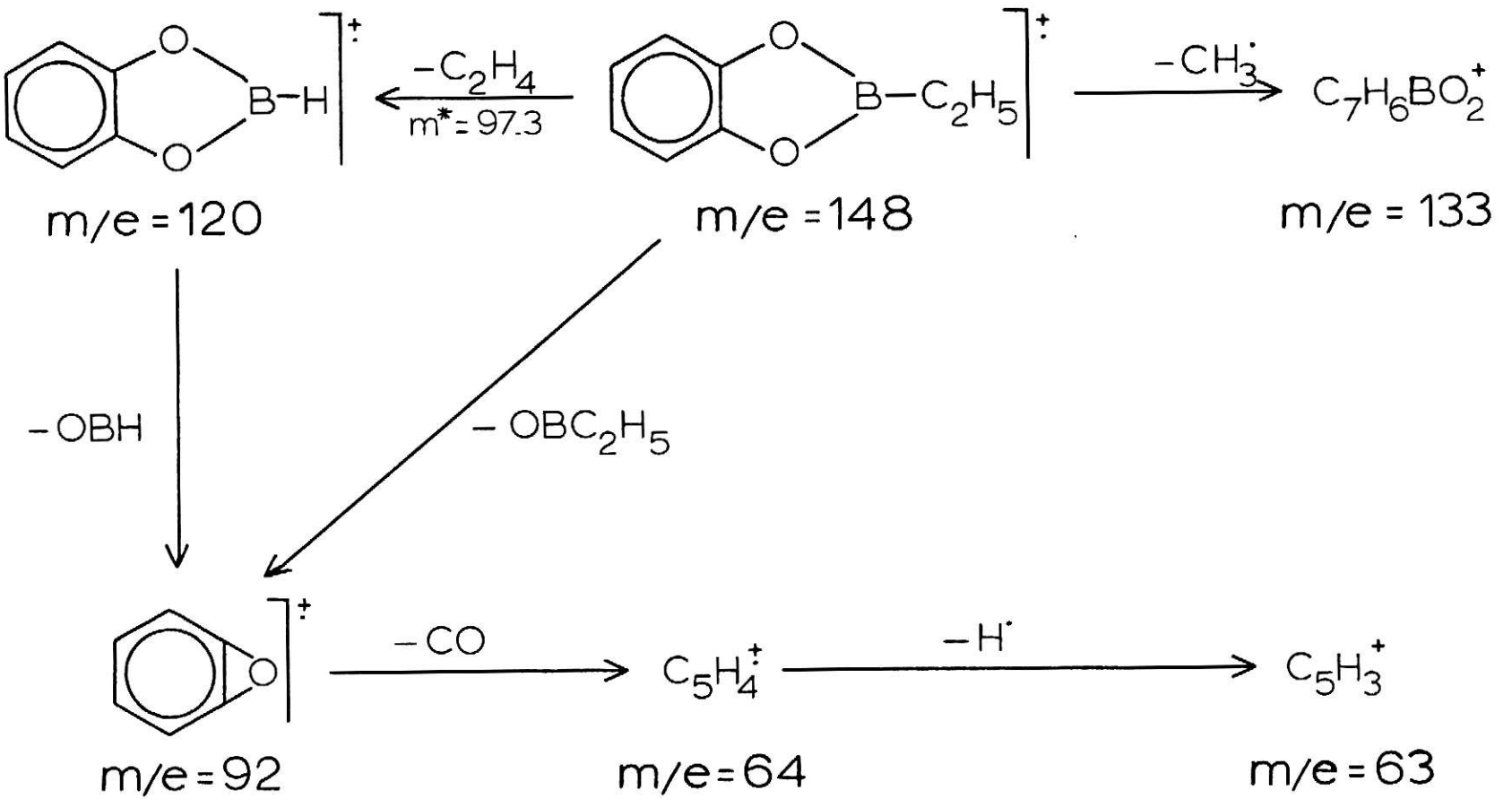
Mass Spectrum at 18 eV of 2-Ethyl-1,3-dioxa-2-borole

(Heated inlet; source temp. 170^{o} C)


B—Et
O
O
18 eV
8
M+
RELATIVE INTENSITY
100
80
60
40
20
0
20
40
60
80
100
120
140
160
180
200
220
m/e

Explanation of Figure 19

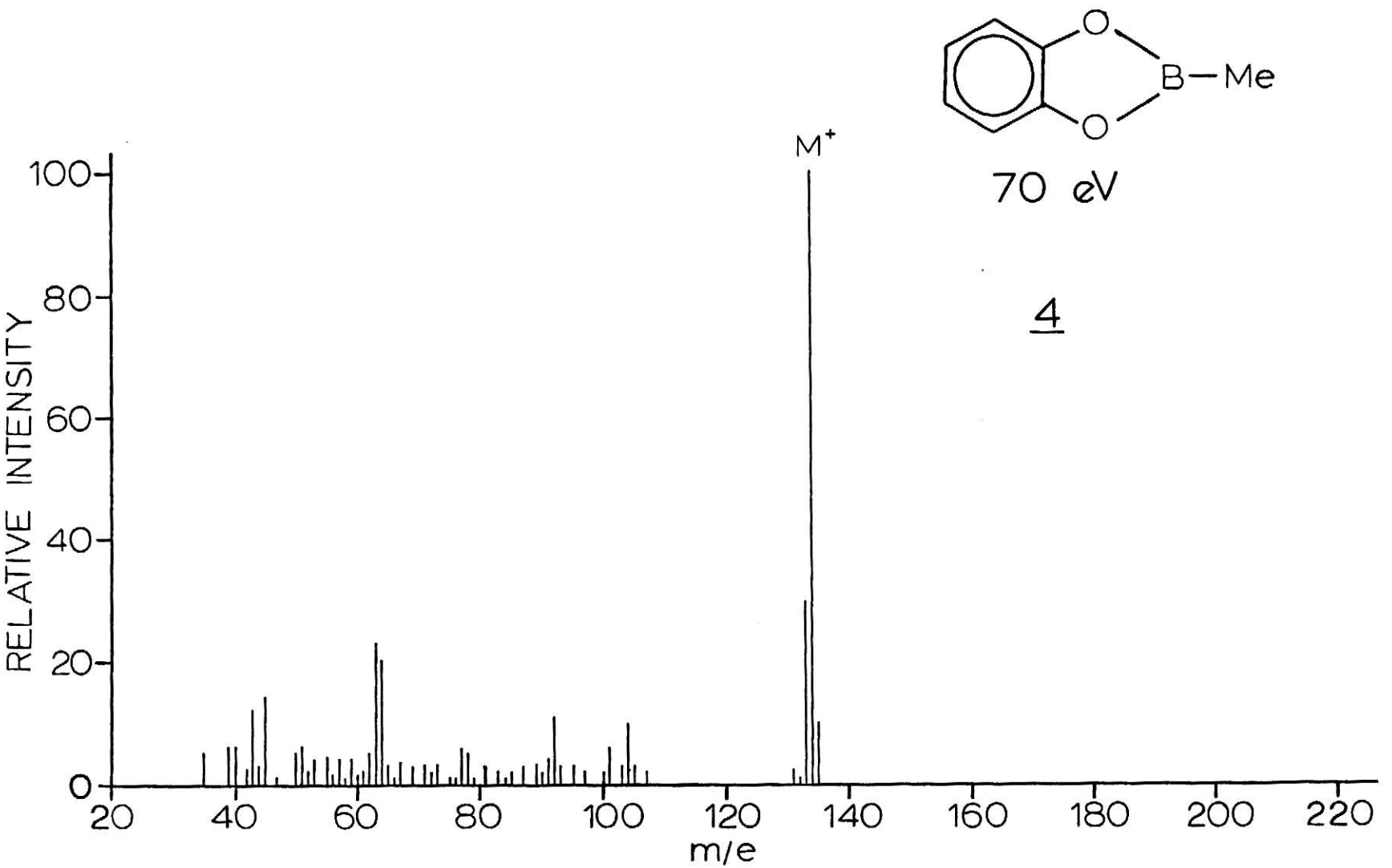
Partial Fragmentation Scheme of 2-Ethyl-1,3-dioxa-2-borole


B–H
$-C_2H_4$
m* = 97.3
$B-C_2H_5$
$-CH_3^{\cdot}$
$C_7H_6BO_2^+$
m/e = 120
m/e = 148
m/e = 133
– OBH
$-OBC_2H_5$
– CO
$C_5H_4^{+\cdot}$
$-H^{\cdot}$
$C_5H_3^+$
m/e = 92
m/e = 64
m/e = 63

Explanation of Figure 20

Mass Spectrum at 70 eV of 2-Methyl-1,3-dioxa-2-borole

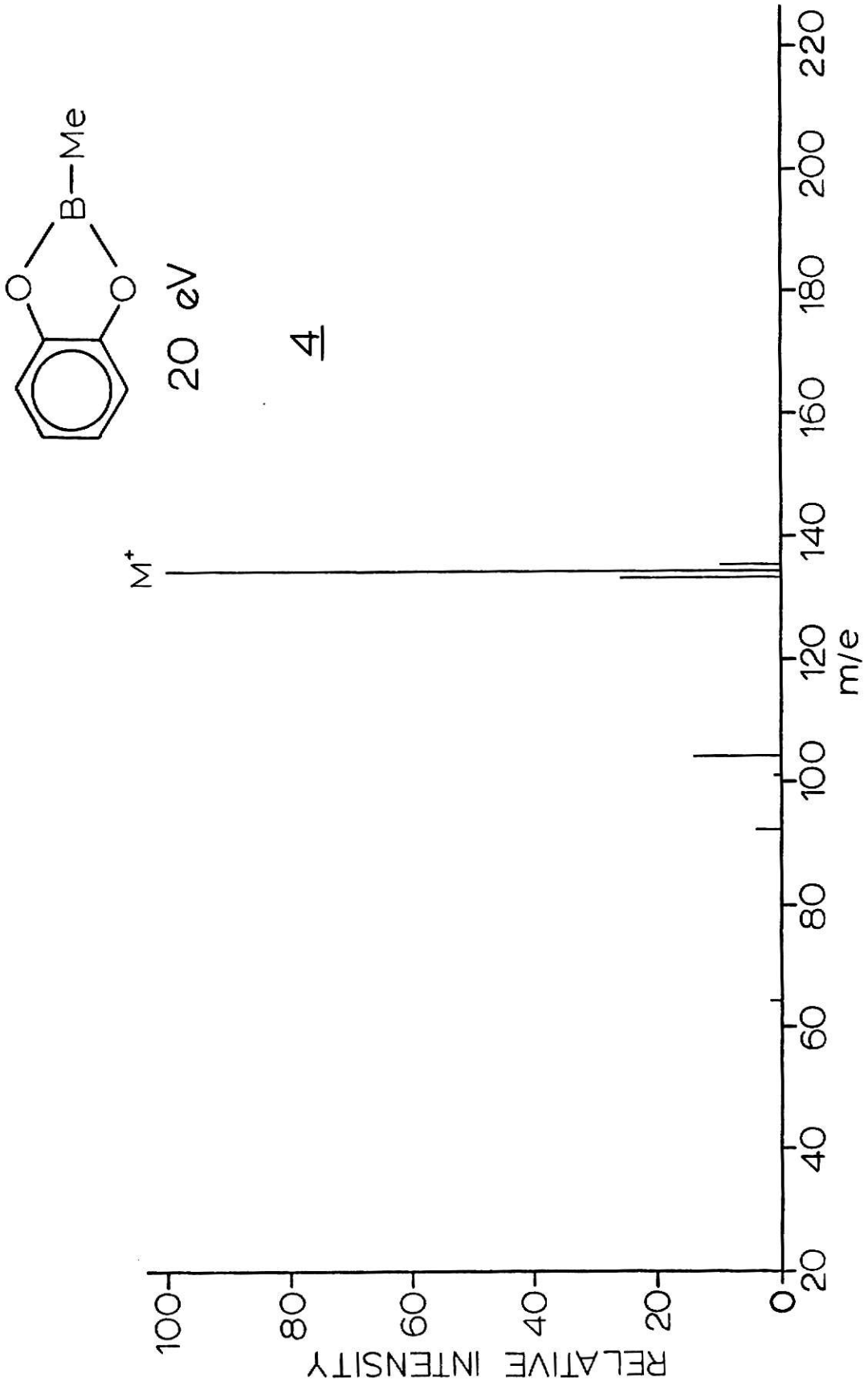
(Heated inlet; source temp. 100° C)


O
B—Me
O
M+
70 eV
4
RELATIVE INTENSITY
100
80
60
40
20
0
20
40
60
80
100
120
140
160
180
200
220
m/e

Explanation of Figure 21

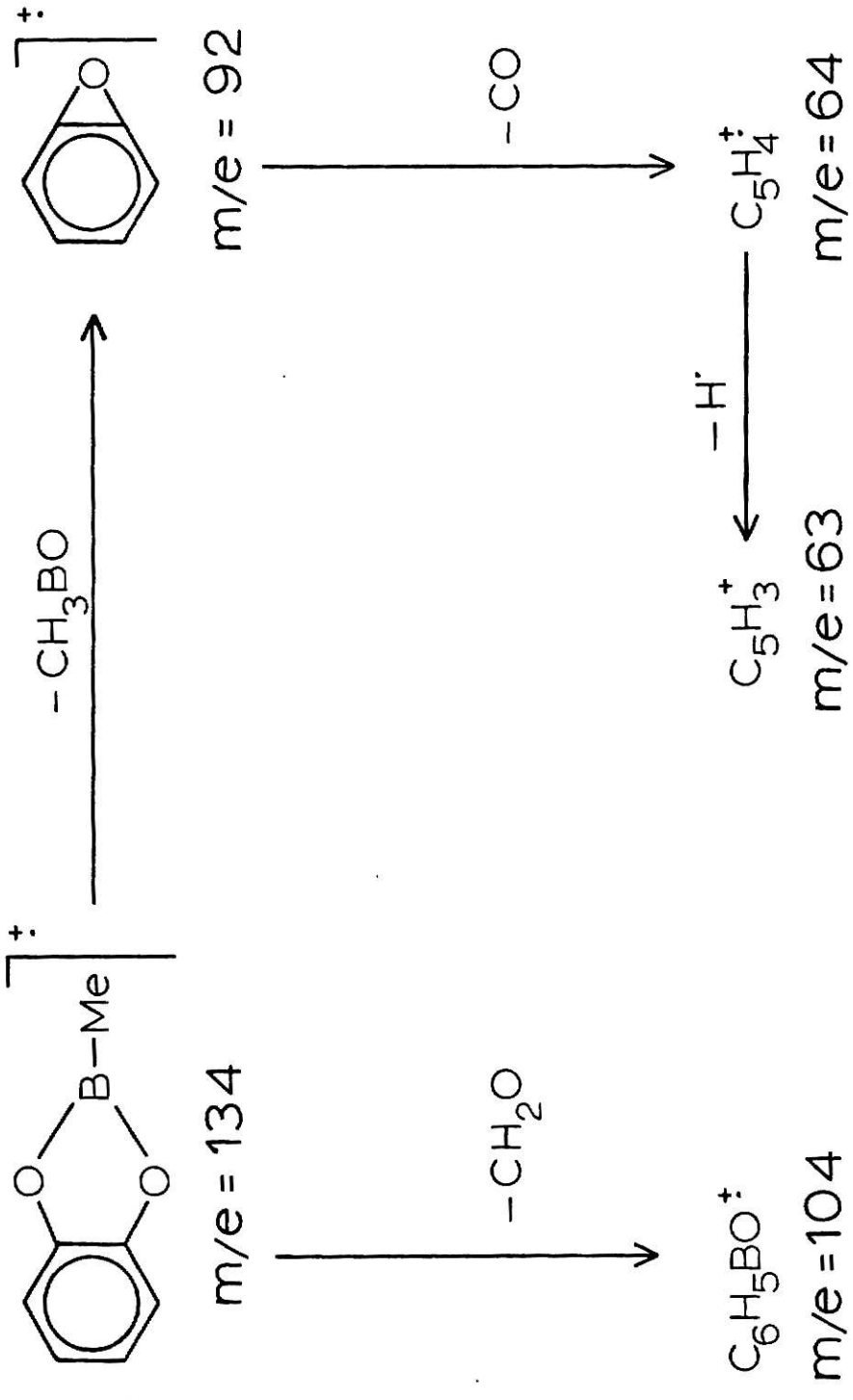
Mass Spectrum at 20 eV of 2-Methyl-1,3-dioxa-2-borole

(Heated inlet; source temp. 100^{o} C)


B—Me
O
O
20 eV
4
M+
RELATIVE INTENSITY
100
80
60
40
20
0
20
40
60
80
100
120
140
160
180
200
220
m/e

Explanation of Figure 22

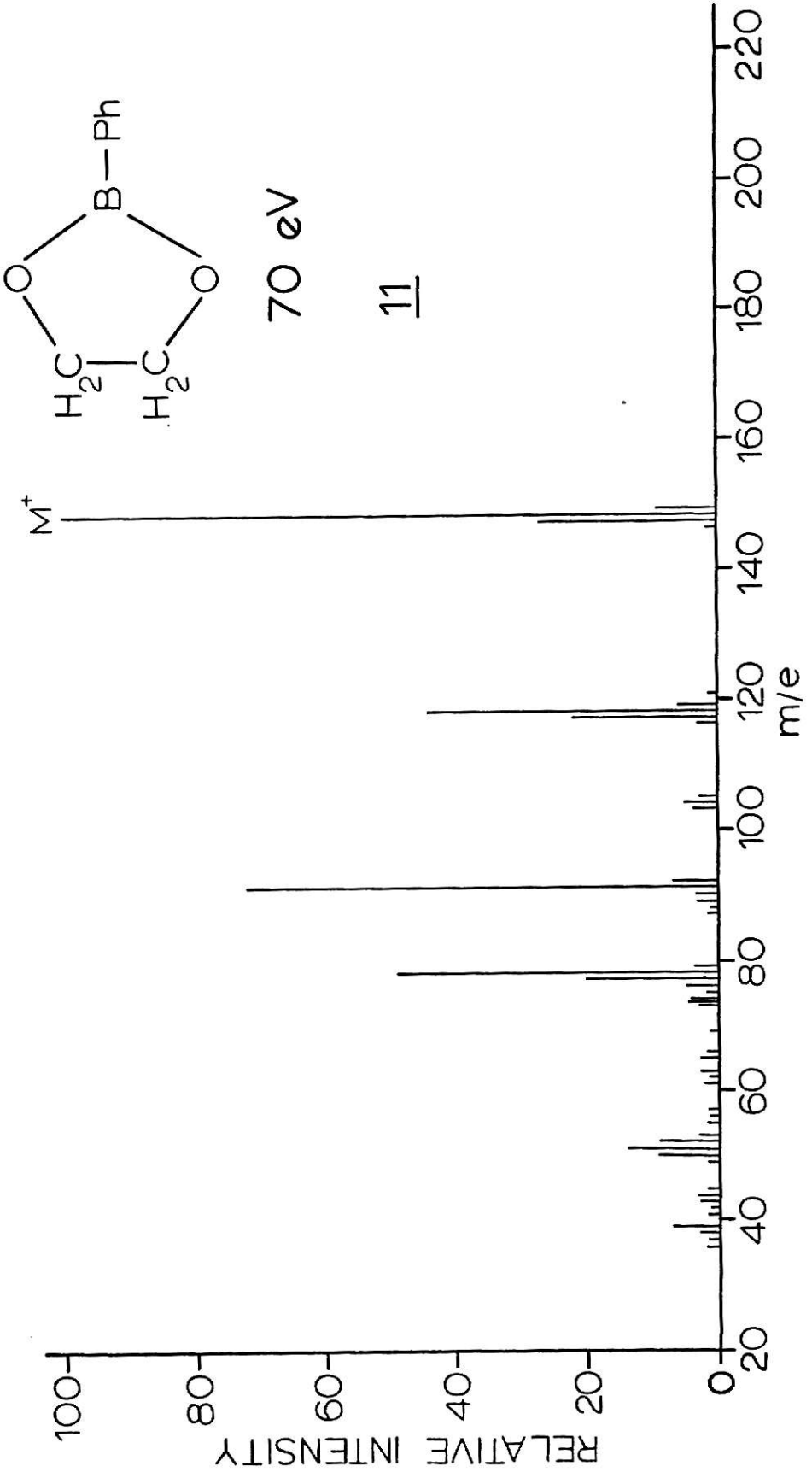
Partial Fragmentation Scheme of 2-Methyl-1,3-dioxa-2-borole


B–Me
O
O
+·
m/e = 134
$-CH_3BO$
$-CH_2O$
$C_6H_5BO^{+\cdot}$
m/e = 104
+·
m/e = 92
$-CO$
$C_5H_4^{+\cdot}$
m/e = 64
$-H^{\cdot}$
$C_5H_3^{+}$
m/e = 63

Explanation of Figure 23

Mass Spectrum at 70 eV of 2-Phenyl-1,3-dioxa-2-borolane

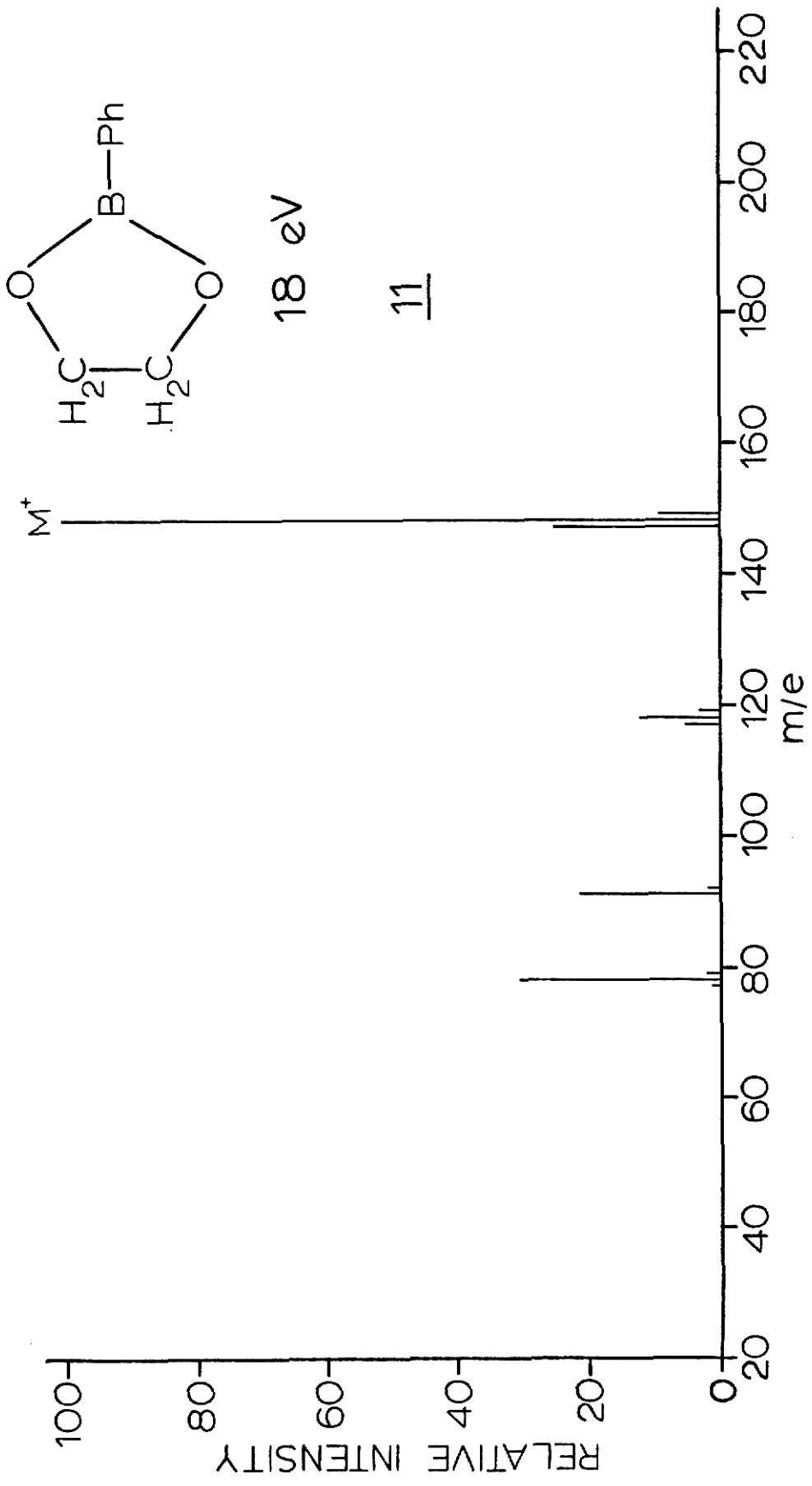
(Heated inlet; source temp. 50° C)


RELATIVE INTENSITY
100
80
60
40
20
0
20
40
60
80
100
120
140
160
180
200
220
m/e
M+
B—Ph
O
O
H2C
H2C
70 eV
11

Explanation of Figure 24

Mass Spectrum at 18 eV of 2-Phenyl-1,3-dioxa-2-borolane

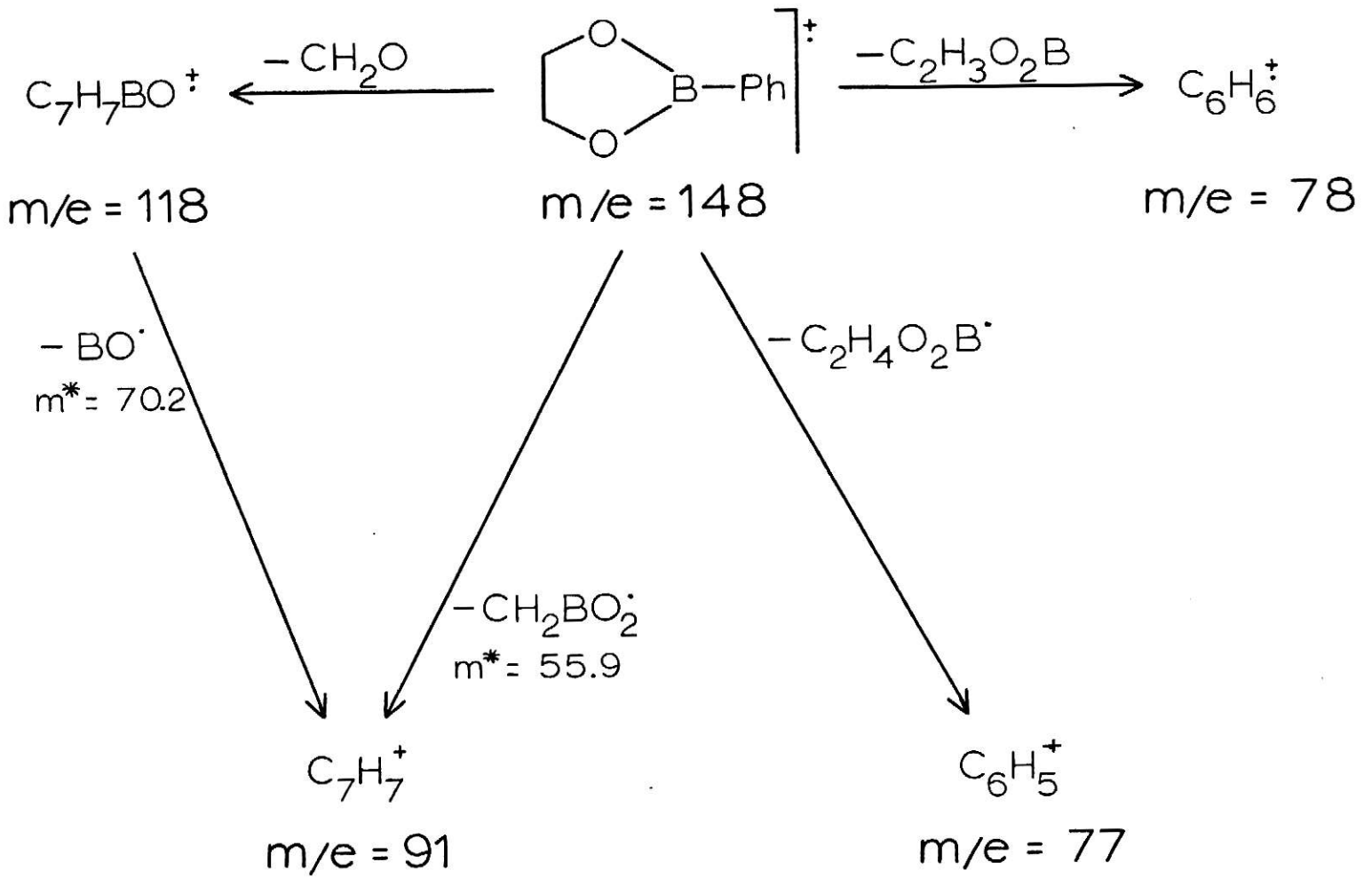
(Heated inlet; source temp. 50° C)


RELATIVE INTENSITY
100
80
60
40
20
0
20
40
60
80
100
120
140
160
180
200
220
m/e
M+
O
O
B—Ph
H2C
H2C
18 eV
11

Explanation of Figure 25

Partial Fragmentation Scheme of

2-Phenyl-1,3-dioxa-2-borolane

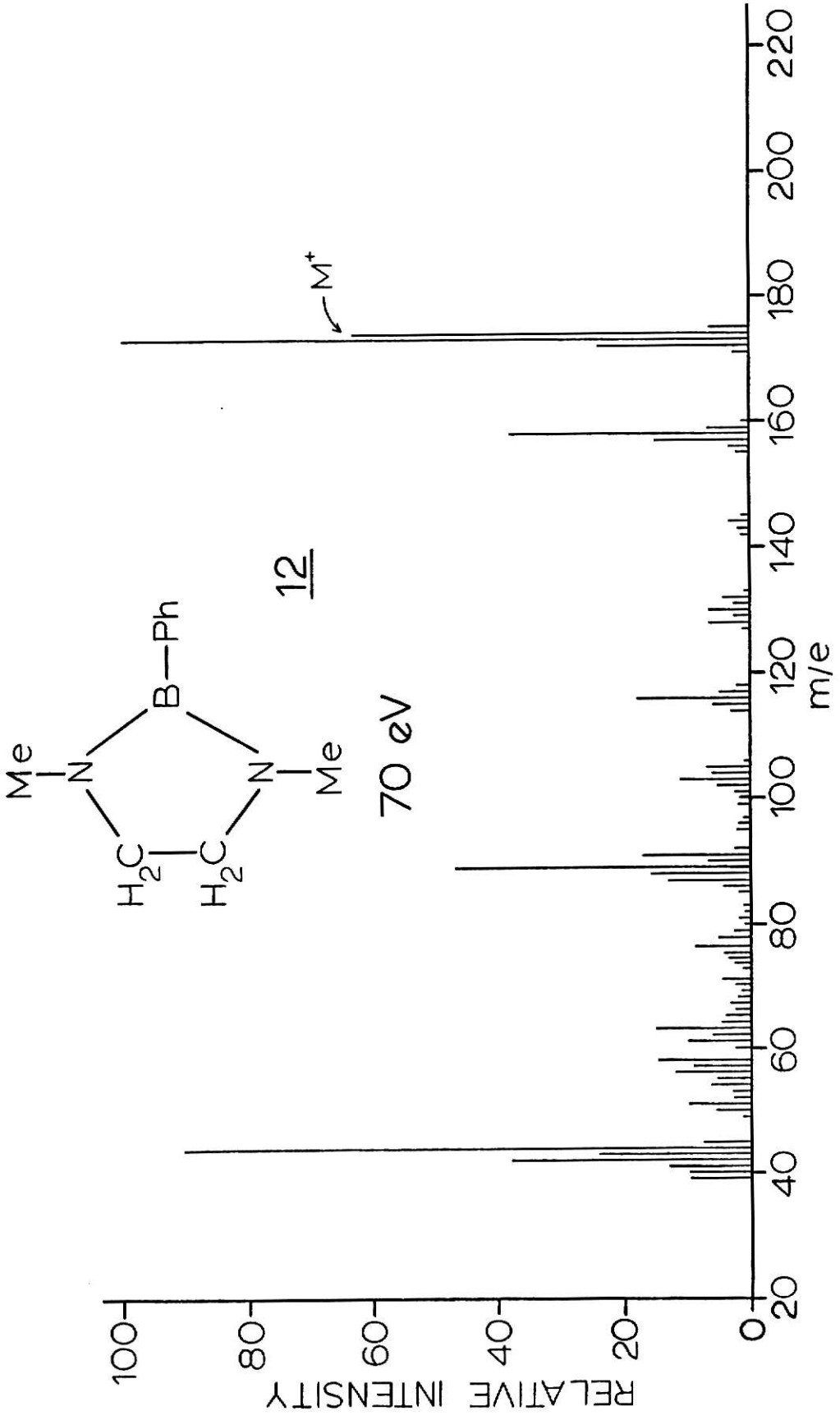

$C_7H_7BO^{+\cdot}$
$-CH_2O$
B—Ph
$-C_2H_3O_2B$
$C_6H_6^{+\cdot}$
m/e = 118
m/e = 148
m/e = 78
$-BO^{\cdot}$
m* = 70.2
$-C_2H_4O_2B^{\cdot}$
$-CH_2BO_2^{\cdot}$
m* = 55.9
$C_7H_7^{+}$
$C_6H_5^{+}$
m/e = 91
m/e = 77

Explanation of Figure 26

Mass Spectrum at 70 eV of

1,3-Dimethyl-2-phenyl-1,3,2-diazaborolidine

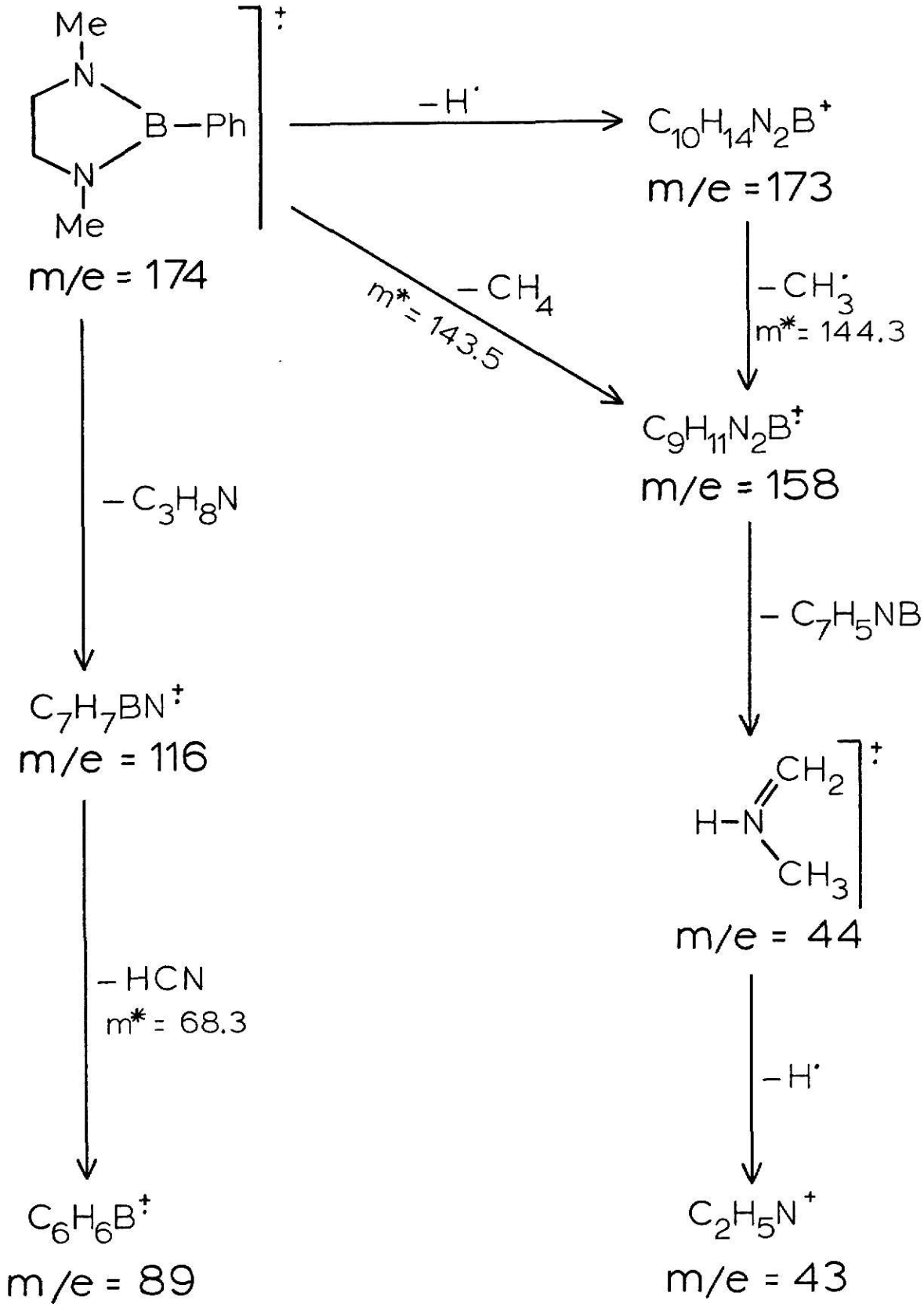
(Heated inlet; source temp. 60° C)


RELATIVE INTENSITY
100
80
60
40
20
0
20
40
60
80
100
120
140
160
180
200
220
m/e
M+
12
70 eV
Me
N
B
Ph
N
Me
H2C
H2C

Explanation of Figure 27

Partial Fragmentation Scheme of

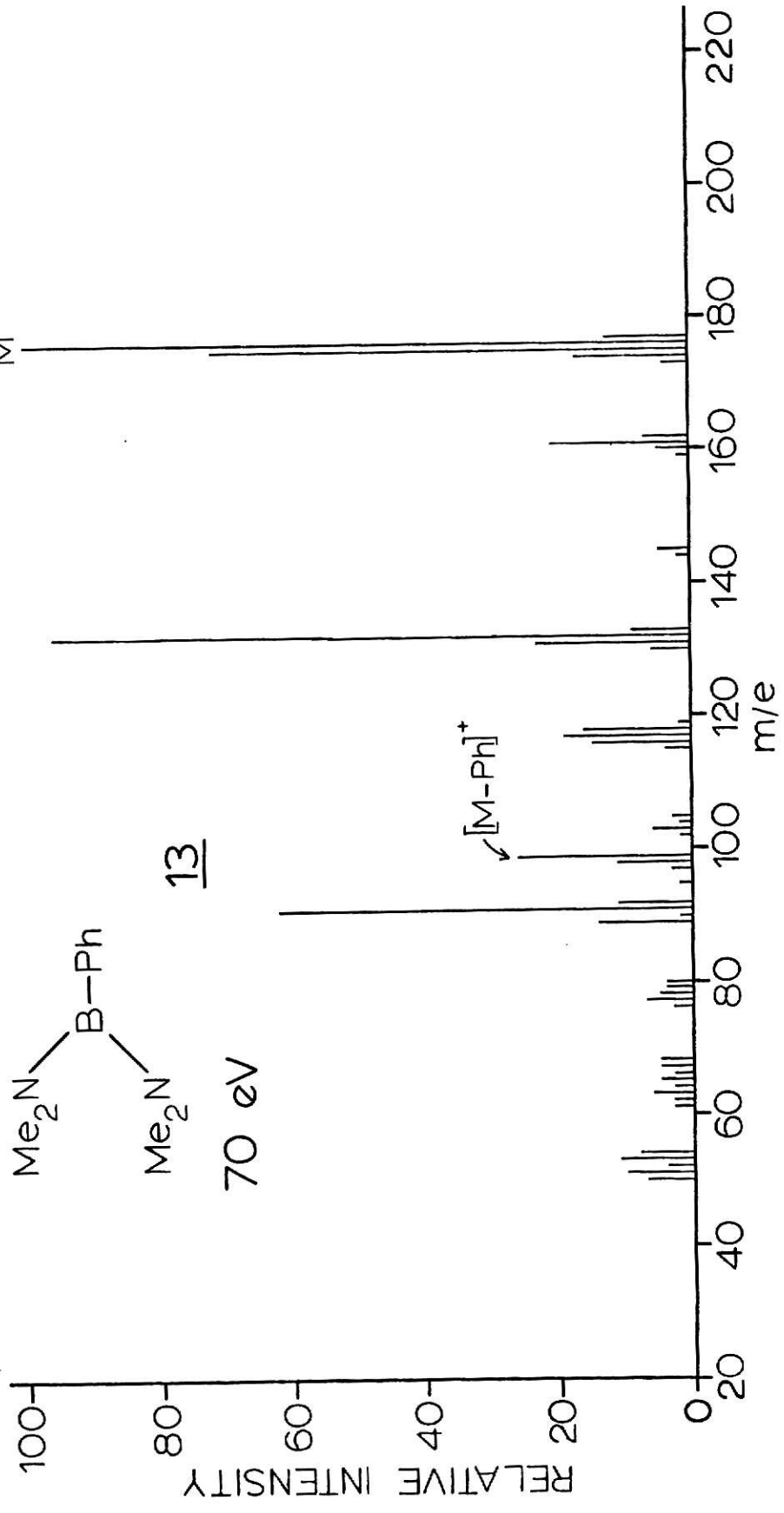
1,3-Dimethyl-2-phenyl-1,3,2-diazaborolidine


Me
N
B–Ph
N
Me
m/e = 174
–H·
$C_{10}H_{14}N_2B^+$
m/e = 173
–CH₄
m* = 143.5
–CH₃·
m* = 144.3
$C_9H_{11}N_2B^+$
m/e = 158
–C₃H₈N
–C₇H₅NB
$C_7H_7BN^+$
m/e = 116
CH₂
H–N
CH₃
m/e = 44
–HCN
m* = 68.3
–H·
$C_6H_6B^+$
m/e = 89
$C_2H_5N^+$
m/e = 43

Explanation of Figure 28

Mass Spectrum at 70 eV of Bis-(dimethylamino)phenylborane

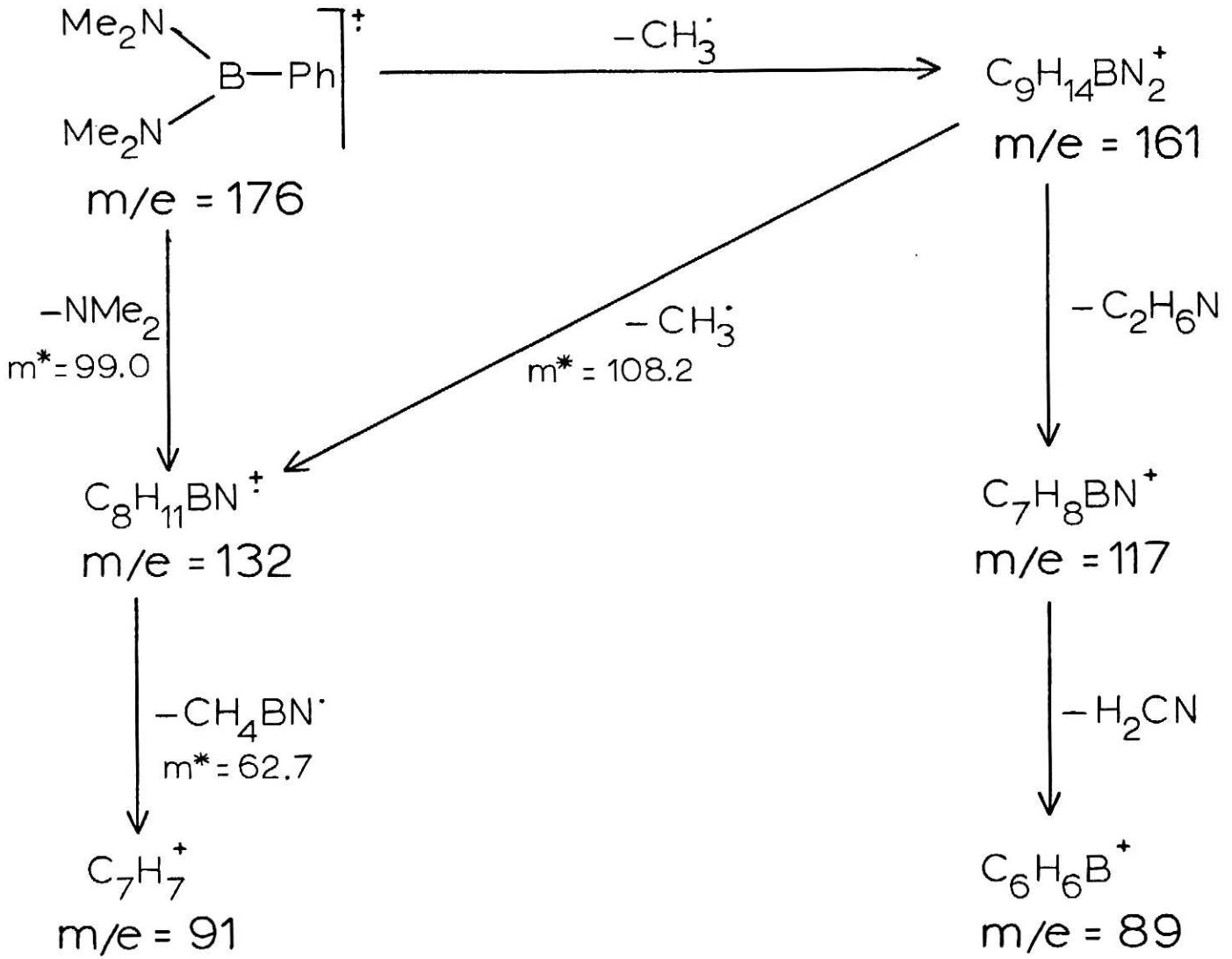
(Heated inlet; source temp. 180^{o} C)


RELATIVE INTENSITY
100
80
60
40
20
0
20
40
60
80
100
120
140
160
180
200
220
m/e
M+
[M-Ph]+
13
70 eV
Me2N
B—Ph
Me2N

Explanation of Figure 29

Partial Fragmentation Scheme of

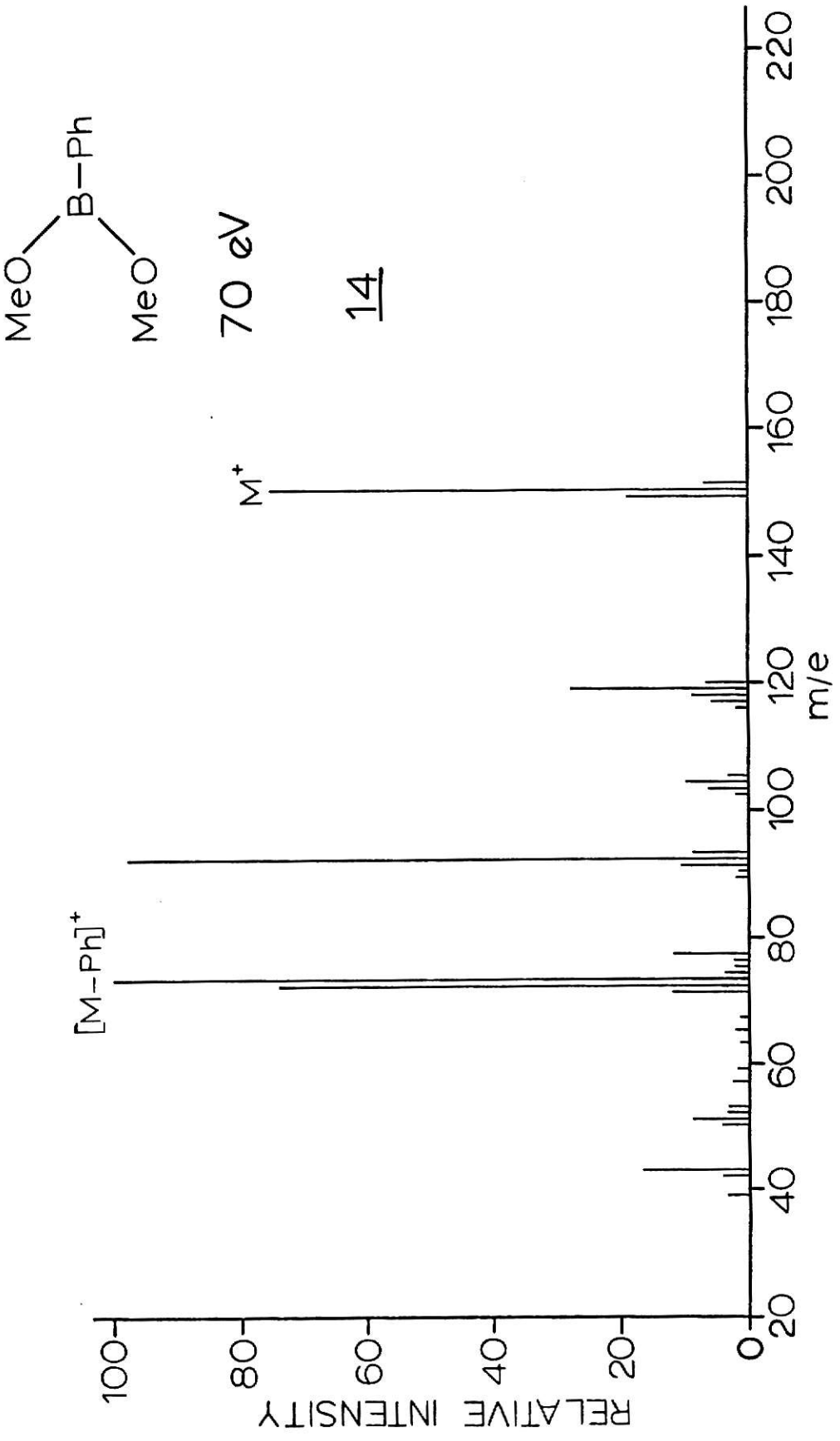
Bis-(dimethylamino)phenylborane


Me2N
B—Ph
Me2N
m/e = 176
−CH3·
C9H14BN2+
m/e = 161
−NMe2
m* = 99.0
−CH3·
m* = 108.2
−C2H6N
C8H11BN+·
m/e = 132
C7H8BN+
m/e = 117
−CH4BN·
m* = 62.7
−H2CN
C7H7+
m/e = 91
C6H6B+
m/e = 89

Explanation of Figure 30

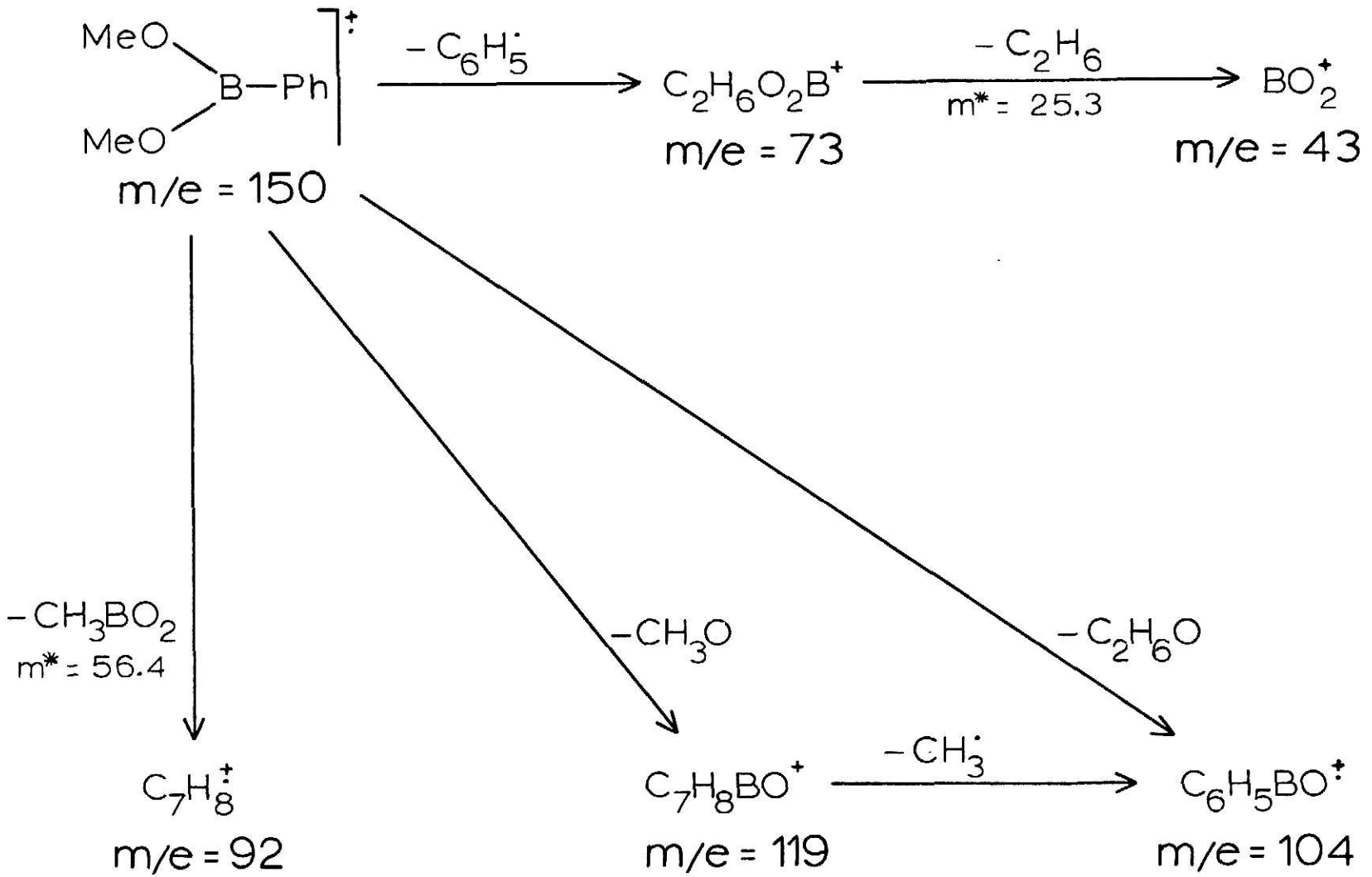
Mass Spectrum at 70 eV of Dimethoxyphenylborane

(Heated inlet; source temp. 50^{o} C)


MeO
B—Ph
MeO
70 eV
14
M+
[M-Ph]+
RELATIVE INTENSITY
m/e
0
20
40
60
80
100
120
140
160
180
200
220

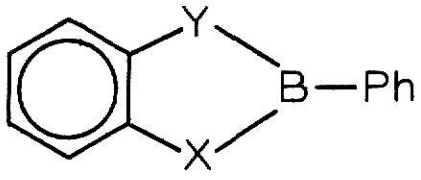
Explanation of Figure 31

Partial Fragmentation Scheme of Dimethoxyphenylborane


MeO
B—Ph
MeO
m/e = 150
$^{+\cdot}$
$-C_6H_5^{\cdot}$
$C_2H_6O_2B^+$
m/e = 73
$-C_2H_6$
m* = 25.3
BO_2^+
m/e = 43
$-CH_3BO_2$
m* = 56.4
$C_7H_8^{+\cdot}$
m/e = 92
$-CH_3O$
$C_7H_8BO^+$
m/e = 119
$-CH_3^{\cdot}$
$-C_2H_6O$
$C_6H_5BO^{+\cdot}$
m/e = 104

C. Conclusion and Discussion

The spectra of the boron-phenyl compounds 1, 8, 9, and 10 are all similar in that each fragments very little upon electron



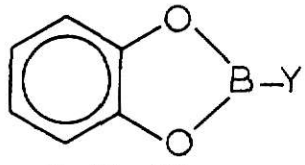
1 X=O, Y=O
8 X=NH, Y=NH
9 X=NH, Y=O
10 X=NH, Y=S

impact. The $[M-Ph]^+$ ion from each of the compounds is less than 1% abundant relative to the base peak. The intensities of the peaks corresponding to the loss of a phenyl group from the molecular ions are in some instances greater than 1% abundant. However, the isotopic contributions of neighboring ions must be subtracted which leaves less than 1% of the peak due to the $[M-Ph]^+$ ion. Each compound also gives an unusually intense doubly charged ion. This,[64] along with the failure of the molecular ion to fragment to any appreciable extent,[65] gives a good indication as to the stability of these species. Compound 1 does fragment much more than the other three compounds since the ions with mass 92 can readily lose CO to produce ions of mass 64 (see fragmentation scheme on page 33).

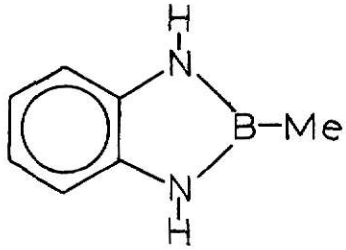
It is also interesting to note that when the phenyl-boron bond is cleaved, the charge accompanies the phenyl group as indicated by the ion at m/e = 77. This peak is especially intense in the spectrum of compound 1.

It has been shown that the phenyl-boron bond has a significant amount of double-bond character.[63] The spectra of boron-

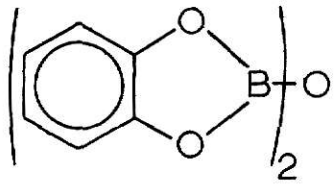
chloro compound (2), the boron-alkyl compounds (3, 4, and 7), the boron-hydroxyl compound (5), and the anhydride, (6), were



2 Y= Cl
3 Y= Et
4 Y= Me
5 Y= OH

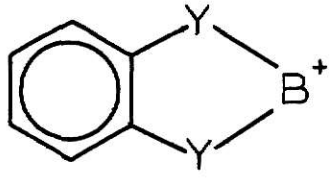


7



6

obtained to show that the above resonance effect was not the reason why the borenium ion (i) could not be observed.



i

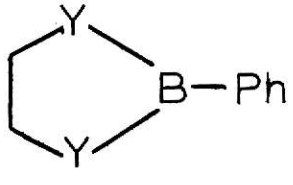
Since chlorine is a good leaving radical, one would expect the boron-chloro compound (2), to lose chlorine readily; however, the $[M\text{-}Cl]^+$ was less than 1% abundant. Interestingly, it appears that an oxygen atom is lost from the molecular ion, since there is a 4.2% $[M\text{-}16]^+$ peak at m/e = 138.

In discussing the mass spectrum of boron-phenyl compound 1, it was mentioned that when the boron-phenyl bond was cleaved, the charge accompanied the phenyl group. For that reason the boron-hydroxy compound (5) and its anhydride (6) were prepared and their spectra obtained. It was felt that the substituents attached to boron in these two compounds would assist in retaining the charge on the possible borenium ion. Even under these favorable conditions, borenium ions did not form.

To minimize resonance interaction between boron and the substituent, it was necessary to make an alkyl derivative. Boron-ethyl compound 3 was chosen because of the ease in which it could be prepared. However, upon electron impact a four-centered rearrangement took place in which ethylene was lost. Since this rearrangement process could provide a low energy pathway, it was essential to obtain the spectra of boron-methyl compounds 4 and 7. In both of these compounds a rearrangement process is not possible and the tendency for cyclic borenium ion formation should be high if such ions are not intrinsically unstable. However, the spectra of both compounds were devoid of a $[M-Me]^+$ peak.

The peak at m/e = 120 in the spectrum of the boron-ethyl compound (3) is due to the fragment ion formed by the loss of ethylene from the molecular ion. The peak at m/e = 119 is due entirely to the ^{10}B isotope of the m/e = 120 ion.

It might be argued that the aromatic nature of compounds 1-10 stabilizes the molecular ion to the extent of hampering further fragmentation, and that this, rather than the intrinsic instability of the cyclic borenium ions, accounts for the above observations. To answer this, the spectra of compounds 11 and 12 were obtained.

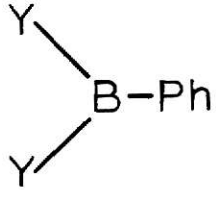


11 Y = O

12 Y = NMe

In both cases the loss of phenyl to form the borenium ion did not occur to any appreciable extent. There was loss of methane from the molecular ion of compound 12 and also loss of a methyl radical from the $[M-H]^+$ ion. Cragg and Todd have reported the mass spectrum of compound 11. Our spectrum was very similar except that the m/e = 78 peak in our spectrum is partially due to extraneous benzene. (Phenylboron dichloride, used to prepare compound 11, was synthesized by the reaction between boron trichloride and tetraphenyl tin in benzene.) It was evident that not all of the m/e = 78 peak intensity was due to a fragment ion since in changing from high to low eV it did not decrease in intensity as did all other ion intensities.

Since all the above compounds failed to produce borenium ions upon electron impact, it may be concluded that by encompassing the possible borenium ion into a five-membered ring one is attempting to form borenium ions which are unstable. If this is indeed so, compounds 13 and 14, which can give linear rather than cyclic borenium ions, should readily lose a phenyl group



13 Y = NMe_2

14 Y = OMe

upon electron impact. The spectra of these compounds very clearly shows that if the borenium ion formed can assume a linear

configuration, it will indeed be abundant. However, if the borenium ion formed cannot assume a linear configuration it will be unstable and thus will not be observed in the mass spectrum of its precursor molecule.

Employing the Walsh rules[66] one would expect the linear borenium ion to be the more stable; however, for more quantitative evidence a CNDO calculation was performed. The stability of BF_2^+ was calculated at various bond angles. (The B-F bond distance used was 1.380 Å.[67]) The results, given in Table III and Figure 32, show that the linear configuration is about 115 Kcal more stable than the configuration in which the F-B-F bond angle is 90°.

It is proposed that the instability of the cyclic borenium ion is due mainly to bond-pair and lone-pair repulsions. There are lone pairs of electrons on the nitrogen, oxygen, and sulfur atoms, and together with the bonded pairs of electrons between these atoms and boron the total repulsion is great enough to cause the linear borenium ion to be stabilized relative to the non-linear borenium ion.

Another factor which may aid in stabilizing the oxygen borenium ions is the fact that in the linear configuration the filled orbitals on the oxygen may overlap with the empty orbital on the boron.

In the following borenium ion (j) there is overlap of orbitals (α) to give aromatic character to the compound. However, if and only if the ion has a linear configuration will

TABLE III

Calculated Stability of BF_2^+ as the F-B-F Bond Angle Varies Between 180 and 90 Degrees

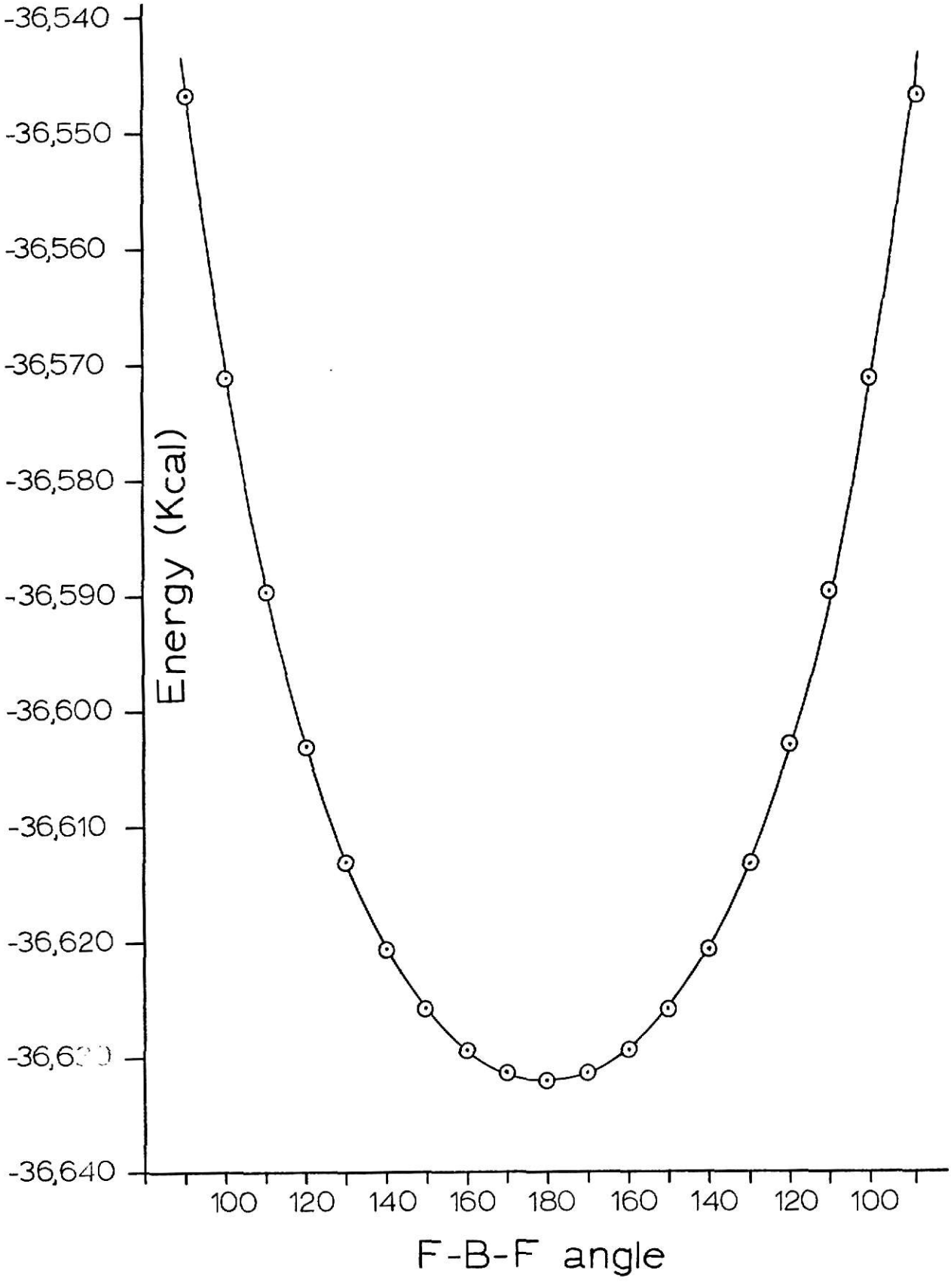
TABLE III

Calculated Stability of BF_2^+ as the F-B-F Bond Angle Varies from 180-90°

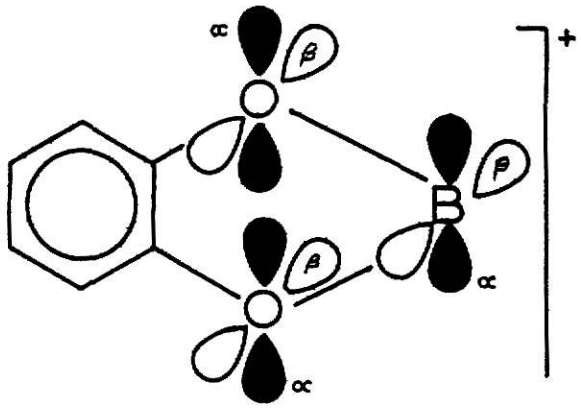
Bond Angle (degrees)	Total Energy		
	au	eV	Kcal
180	-58.38915	-1588.477	-36,631.864
170	-58.38811	-1588.448	-36,631.211
160	-58.38490	-1588.361	-36,629.198
150	-58.37929	-1588.209	-36,625.678
140	-58.37088	-1587.980	-36,620.402
130	-58.35907	-1587.658	-36,612.993
120	-58.34301	-1587.222	-36,602.917
110	-58.32147	-1586.636	-36,589.403
100	-58.29251	-1585.848	-36,571.235
90	-58.25314	-1584.777	-36,546.535

Explanation of Figure 32

Energy Plot of BF_2^+ as the F-B-F Bond Angle Varies Between 180 and 90 Degrees


-36,540
-36,550
-36,560
-36,570
-36,580
-36,590
-36,600
-36,610
-36,620
-36,640
Energy (Kcal)
100
120
140
160
180
160
140
120
100
F-B-F angle

j



the filled (β) orbitals on oxygen be able to overlap with the empty (β) orbital on the boron atom. In borenium ion (j) this type of overlap is not possible, consequently (j) is relatively unstable.

While there may well be some five-membered heterocyclic compounds which could produce borenium ions of measurable abundance in their mass spectra, the systematic search described above failed to uncover such compounds. Indeed, the most striking feature of our results was the evidence that typical five-membered cyclic borenium ions are destabilized to a relatively large extent.

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VITA

The author was born the tenth child in a family of fourteen, on December 14, 1945, to Martin and Marie Vander Zanden, in Appleton, Wisconsin. Shortly thereafter, the family moved to Shiocton, Wisconsin, where the author completed his first eight grades of formal education. After his eighth grade year the family moved to Combined Locks where the author attended Kimberly Senior High School, and graduated in June of 1964.

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On December 27, 1967, the author married Barbara A. Nack, the daughter of Robert and Alice Nack of Kaukauna, Wisconsin. One year later, on December 23, 1968, their first and only child, Holly Christine, was born.

The author is a member of the American Chemical Society and also a member of Alpha Chi Sigma professional chemical fraternity.

BORENIUM IONS: A MASS SPECTROMETRIC INVESTIGATION

by

ROBERT JOHN VANDER ZANDEN

B. S., Wisconsin State University-Platteville, 1968

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

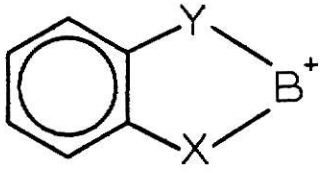
KANSAS STATE UNIVERSITY
Manhattan, Kansas

1971

The structure of ions in the gas phase is a topic of long-standing concern in several fields of chemistry. Reported in this thesis are some observations concerning the stabilities of borenium ions and the structural implications of these observations.

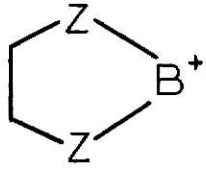
From the heats of formation of gaseous ions the following thermodynamic stability order can be derived:
$B(OMe)_2^+ \geqslant BF_2^+ > MeBF^+ > BCl_2 \geqslant BEt_2^+ > BMe_2^+, \quad BBr_2^+ > BH_2^+$.
It is apparent that borenium ions are stabilized by substituents bearing lone pairs of electrons. A further demonstration of this stability is found in numerous reported mass spectra of acyclic boron compounds in which borenium ions are abundant.

When potential borenium ions are encompassed in five-membered rings, the mass spectra are devoid of these ions. The compounds examined were chosen to optimize the possibility of generating the cyclic borenium ions, (a) and (b).



(a)

X and Y = O, S or NH



(b)

Z = NMe or O

The non-observation of borenium ions is not due to ready competitive fragmentations; the spectra are generally extremely simple with the molecular ions constituting the base peaks, while those fragment ions which do occur are mostly due to simple ring cleavages. Low electron energy spectra showed that the absence

of borenium ions could not be explained by their removal by further fragmentation. Furthermore, the absence of these ions could not be ascribed to any special molecular ion stability due to an aromatic backbone, as is evident from the failure to form borenium ions (b).

It is therefore concluded that the cyclic borenium ions (a) and (b) are thermodynamically unstable relative to their non-cyclic analogues. This stability of the non-cyclic borenium ions relative to the cyclic borenium ions may be taken as evidence that the acyclic borenium ions are probably linear. Also, the relative instability of the cyclic borenium ions is probably due to bond-pair and lone-pair repulsions. Thus it appears that the experimental evidence for the instability of five-membered cyclic borenium ions supports the view that for such ions a linear structure is the most stable.