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(22) Numbering of compounds in our total compilation of alkene reactivities[5] is **1 (103), 2 (104), 3 (105), 5 (106), 6 (107),** (*E*)-MeCH=C(Ph)NMe$_2$ **(110),** Me$_2$C=CH(NC$_5$H$_{10}$) **(111)** (NC$_5$H$_{10}$ = 1-piperidino), *p*-H$_2$NC$_6$H$_4$CH=CH$_2$ **(108),** and *p*-Me$_2$NC$_6$H$_4$CH=CH$_2$ **(109).**
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Structures and Mass Spectral Behavior of the Inositol Cyclic Boronic Esters

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Abstract: The structures of the cyclic tris(boronic) esters of each of the inositols have been examined by electron ionization mass spectrometry. Structural assignments have been made from mass spectral features and from mixed boronic ester experiments. The structures appear to fall into three related groups: *myo*- and *muco*-inositol, the former with two α,γ- and one α,β-cyclic ester, the latter with two α,γ- and one α,δ-cyclic esters: *cis*- and *allo*-inositol, each with two α,β- and one α,δ-ester; *neo*-, *chiro*-, and *epi*-inositol each with three α,β-cyclic boronates, one of which is trans in each case. *scyllo*-Inositol, which does not form a triboronate, was found to produce, after sequential butaneboronation and trimethylsilylation, a bis(trimethylsilyl)bis-(butaneboronate) derivative.

The inositols (Figure 1) are useful candidates for studying the effects of stereochemical features on fragmentation following electron ionization in the mass spectrometer. We have noted earlier that trimethylsilyl ethers of the inositols show much larger variations in the intensities of ions in their mass spectra than do the inositol acetates.[1] We attributed this to an expression of the stereochemistry of each isomer, enhanced by the effect of bulky trimethylsilyl groups. In the present study we report the behavior of each of the inositols when they are reacted with boronic acids, derivatizing reagents which themselves have steric requirements for the formation of stable cyclic esters. As previously reported,[2] *myo*-, *muco*-, *neo*-, and *chiro*-inositols form derivatives, on reaction with butaneboronic acid, which readily undergo gas chromatography. *scyllo*-Inositol does not form volatile products under these conditions. We have found that the remaining isomers (*epi*-, *allo*-, and *cis*-inositols) also react readily with butaneboronic acid. Methane-, octane-, and benzeneboronates were examined as well.

Results and Discussion

Each of the inositols, except *scyllo*-inositol, which is discussed below, on reaction with butaneboronic acid, gives a product which gas chromatographs as a single peak. Eisenberg[3] first reported that *myo*-inositol forms a tributaneboronate and we find that the rest of the inositols, with the exception noted, also form triesters.

The structures of these cyclic boronates can be divided into three groups on the basis of similarities in their mass spectra: first, the butaneboronate derivatives of *myo*-inositol (Figure 2) and *muco*-inositol have comparatively simple mass spectra with an abundant ion at *m/e* 139 and a much less intense ion at *m/e* 126 (the structurally diagnostic usefulness of these two ions is discussed below); second, *cis*-inositol (Figure 2) and *allo*-inositol cyclic butaneboronates have complex spectra with an ion $[M - C_4H_9]^+$ (*m/e* 321) as base peak; and third, *neo*-inositol (Figure 2), *chiro*-inositol, and *epi*-inositol butaneboronates have spectra with the *m/e* 126 ion approximately three times more intense than the ion *m/e* 139.

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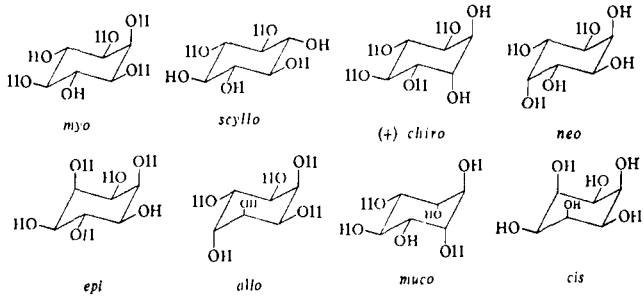
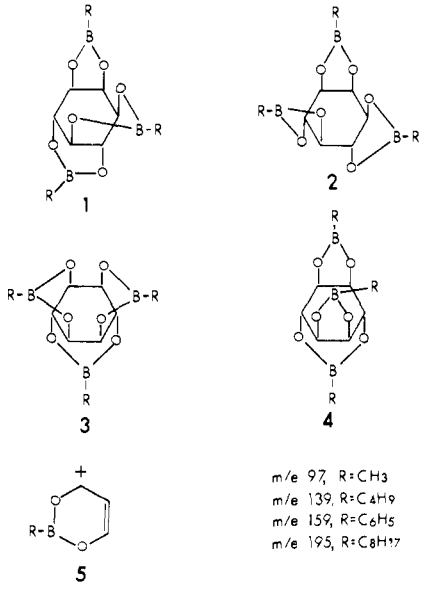


Figure 1. The inositol diastereomers.

scyllo-Inositol, which has all its hydroxyls trans to their neighbors (Figure 1), does not produce a triester under the conditions described here. However, if trimethylsilylation follows the reaction with butaneboronic acid, several products are formed, as shown by gas chromatography. One of these is a bis(trimethylsilyl)bis(butaneboronate), as shown by its mass spectrum, suggesting that the boronation proceeds only to the extent of forming the bis(butaneboronate), which cannot be detected by gas chromatography. Subsequent trimethylsilylation produces the volatile derivative observed. Further details are given in the Experimental Section.

***myo*- and *muco*-Inositol.** Each of these diastereomers forms a single stable product, as shown by gas chromatography, with either alkane- or benzeneboronic acids. In each case the *myo*- and *muco*-inositol boronates have nearly identical mass spectra which possess molecular ions of significant abundance (cf. Figure 2). Structure **1** is the logical choice for the *myo*-inositol derivatives since, in the alternate structure **2**, two of the three



α,β-cyclic moieties would have to be trans. Evidence for structure **1** was obtained by an experiment in which *myo*-inositol formed a mixture of triesters in a simultaneous reaction with both methane- and butaneboronic acids. This reaction mixture gave rise to three gas chromatographic peaks as observed by mass chromatography[4] of the molecular ion (*m/e* 336) of the mono(methaneboronate) bis(butaneboronate) derivatives. The alternate structure **2** can also have three isomers, only two of which would be expected to separate by gas chromatography.

The *muco*-inositol boronates can have either structures **3** or **4**; however, the mixed ester experiment cannot distinguish between them. An argument in favor of structure **3** is based on the presence of an intense ion at *m/e* 139 in the spectrum of both this compound and *myo*-inositol butaneboronate (Figure 2). The ion *m/e* 139 has been found in earlier studies to predominantly have the composition $C_7H_{12}BO_2$ and to be largely formed by rearrangement in the fragmentation of reducing sugar boronates.[5,6] We have proposed the resonance-stabilized α,γ-cyclic ester **5** for the structure of this ion.[5]

Table I. Intensities of Ion **5** in Inositol Cyclic Boronates at 70 eV

	Σ_{40}, %[a]			
	methane boronates (*m/e* 97)	butane boronates (*m/e* 139)	octane boronates (*m/e* 195)	benzene boronates (*m/e* 159)
myo-inositol	41	23	12	29
muco-inositol	28	15	8.6	12
cis-inositol	18	2.7	1.1	8.4
allo-inositol	10	4.3	2.1	7.2

[a] Percent of total ion abundance summed from *m/e* 40.

The spectra of each of the inositol boronates contain ion **5**; however, the abundance of this ion is markedly greater in the spectra of *myo*- and *muco*-inositol boronates than in the cases of the other inositols (Figure 2 and Table I). We will provide evidence that the enhanced abundance in the myo and muco esters is due to the presence of an α,γ-boronate moiety in the parent molecule from which ion **5** can be produced in greater abundance than when it is formed by rearrangement. Of all the possible inositol boronate structures only *myo*- and *muco*-inositol structures **1** and **3** can accommodate an α,γ-cyclic ester and thus be capable of generating this ion directly. In the other cases all of ion **5** must be produced by rearrangement.

That ions of type **5** can be produced by the simple extrusion of this moiety without rearrangement can be shown by a comparison of the abundance ratios of *m/e* 139 (**5**, R = C_4H_9) to *m/e* 97 (**4**, R = CH_3) in the spectra of the mixed methane-butaneboronates of *myo*-inositol. As mentioned, three isomers of the monomethane-dibutaneboronate of *myo*-inositol are separable by gas chromatography. The *m/e* 139:97 intensity ratios (Σ_{40}) of these isomers are 0.26, 4.5 and 2.2, in order of elution. It is clear from the large variation of the ratios that little scrambling of the methane- and butaneboronate moieties is taking place. One can assign to the first gas chromatographic peak the structure with the α,γ-cyclic methaneboronate on the opposite side of the molecule from the other two cyclic esters (cf. **1**).

muco-Inositol mixed boronates display similar ion **5** intensity ratio behavior suggesting that in *muco*-inositol boronates, as in the *myo*-inositol derivatives, the α,γ-cyclic boronate exists in the parent molecule (i.e., structure **3**). For example, in the two isomers of *muco*-inositol monomethanedibutaneboronate the ratios of *m/e* 139 to *m/e* 97 (Σ_{40}) are 0.24 and 2.97, in order of elution. Based on structure **3** we propose that these isomers have structures **6** and **7**, respectively. A similar result is obtained with the mono(benzeneboronate)-bis(butaneboronate) of *muco*-inositol where, in order of elution, the *m/e* 139:159 (**5**, R = C_6H_5) abundance ratios are 1.8 and 0.3. In this case the first chromatographic peak must be the symmetrical isomer.

Additional evidence consistent with structure **3** representing *muco*-inositol is found in the spectra of the *cis*-inositol boronates. *cis*-Inositol butaneboronate (**8**, R = C_4H_9) has a mass spectrum with ion **5** (*m/e* 139) in low abundance (Figure 2), consistent with a structure containing no α,γ-cyclic boronic ester. Since in this case ion **5** must be formed by a rearrangement process, the abundance ratios of these ions should be similar when produced from different isomers of mixed boronates, since their ease of formation would be governed mainly by factors other than the structures of the precursor boronates. The two isomeric *cis*-inositol monobutanedimethaneboronates have Σ_{40} abundance ratios (*m/e* 139:97) of 0.25 and 0.26.

We give evidence (vide infra) that *allo*-inositol boronates

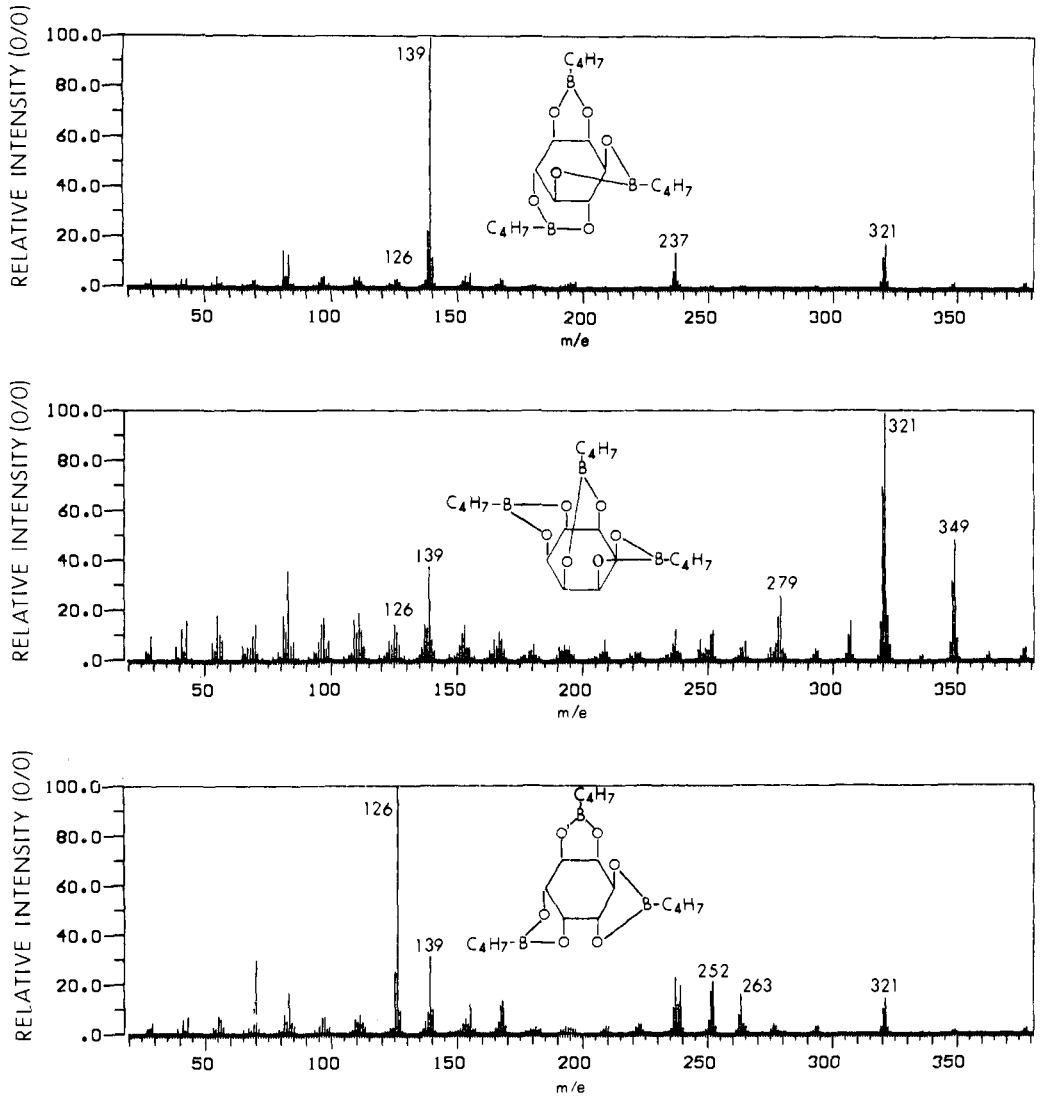
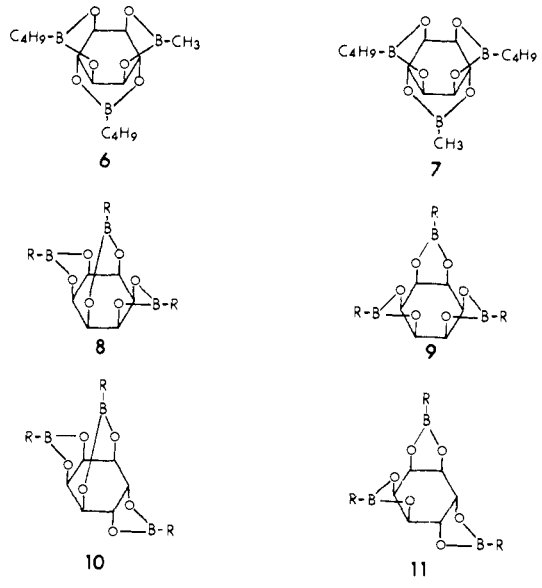


Figure 2. (Top) The 70-eV mass spectrum of (±)-*myo*-inositol 1,2:3,5:4,6-tris(butaneboronate)[11] (**1**) normalized to *m/e* 139 (ion **5**). (Center) The 70-eV mass spectrum of *cis*-inositol 1,2:3,6-4,5-tris(butaneboronate) (**8**) normalized to *m/e* 321 ([M − C_4H_9]$^+$). (Bottom) The 70-eV mass spectrum of (±)-*neo*-inositol 1,2:3,4:5,6-tris(butaneboronate) (**12**) normalized to *m/e* 126 (ion **17**).



have structure **10**. As with *cis*-inositol mixed boronates the *allo*-inositol monobutanedimethaneboronates have similar *m/e* 139:97 ratios (0.42 and 0.30). The two *allo*-inositol monomethanedibutaneboronates each have *m/e* 139:97 ratios of 0.83. Thus the *cis*- and *allo*-inositols are similar to each other in this respect but differ from *muco*-inositol and *myo*-inositol boronates in the generation of type **5** ions. However, it should be noted that the alternate structure of *muco*-inositol boronate (**4**) is quite similar to structures **8** and **10** which are assigned to the *cis*- and *allo*-boronates. It is, therefore, unlikely that structure **4** is tenable as the structure of *muco*-inositol boronate.

The arguments regarding the simple extrusion of ion **5** and the relationship between its mass spectral abundance and its precursor structure contain the assumption that other structural features (e.g., neighboring group participation, steric effects) do not influence the extrusion process. The validity of this assumption is supported by the observation that the total Σ_{40} values for ion **5** in *myo*-inositol and in *muco*-inositol are very similar regardless of whether their origin is the homogeneous or a mixed boronate. For example, in Table I it can be seen that *myo*-inositol tributane- and tribenzeneboronate each have similar ion **5** abundances. We find that the four isomers of *myo*-inositol mixed butanebenzeneboronates which can be chromatographically separated (i.e., two monobutane-dibenzeneboronates and two monobenzene-dibutaneboronates) have an average Σ_{40} value of ions **5** (R = C_4H_9 and R = C_6H_5) of 26%, close to the value of the homogeneous ions **5** in Table

Table II. Intensities of M^+ and $[M - R]^+$ in Inositol Boronate Derivatives at 70 eV

	Σ_{40}, %[a]							
	methaneboronates		butaneboronates		octaneboronates		benzeneboronates	
	M^+	$[M - CH_3]^+$	M^+	$[M - C_4H_9]^+$	M^+	$[M - C_8H_{17}]^+$	M^+	$[M - C_6H_5]^+$
myo-inositol	1.4	0.95	1.4	4.4	1.4	6.2	21	
muco-inositol	2.7	1.3	1.8	2.8	3.8	3.5	24	
allo-inositol	3.6	1.3	1.1	7.7	1.6	8.5	17	
cis-inositol	2.7	1.3	1.0	7.7	1.9	7.6	25	

[a] Percent of total ion abundance summed from *m/e* 40.

I. *muco*-Inositol behaves similarly, the four mixed benzene-butaneboronate isomers in this case having an average ion **5** Σ_{40} abundance of 13%.

***cis*- and *allo*-Inositols.** Two structures, **8** and **9**, are possible for the *cis*-inositol boronates. As discussed earlier *cis*-inositol mono(butaneboronate)bis(methaneboronate) exists in two isomers separable by gas chromatography. Only structure **8** is compatible with this finding.

allo-Inositol boronates can have either structure **10** or **11**; however, only two isomers are observed in a mixed ester experiment, thus this approach is inconclusive.

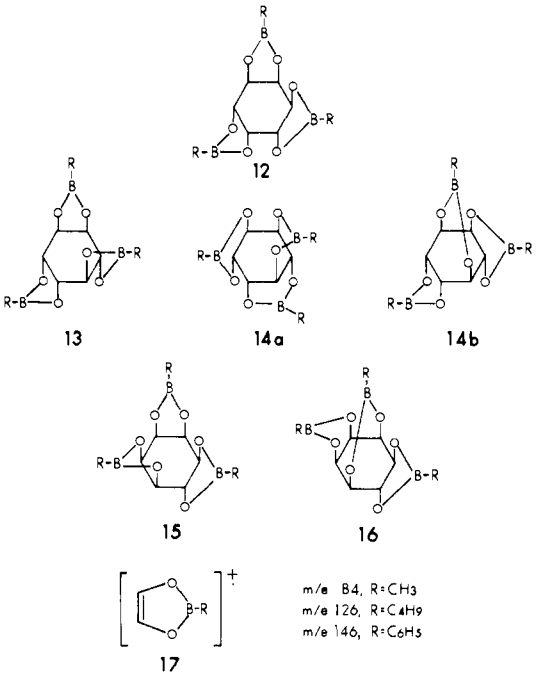
allo-Inositol and *cis*-inositol boronates have mass spectra which are similar to each other and very different from the spectra of the other inositol boronates. The spectra are highly complex and fragmented with, in the butaneboronate derivatives, $[M - C_4H_9]^+$ (*m/e* 321) as base peak (Figure 2). In Tables I and II it can be seen that *cis*- and *allo*-inositol boronates form a pair with mass spectral similarity as do *myo*- and *muco*-inositol boronates. These features suggest structure **10** for the *allo*-inositol boronates.

Another finding which is consistent with structure **10** over **11** is that one of the two *allo*-inositol mono(benzeneboronate) bis(butaneboronate) derivatives has an intense $[M - C_4H_9]^+$ (*m/e* 341, Σ_{40} 16.4%) with a molecular ion intensity of (Σ_{40}) 0.70%. For the other isomer the values are 18.6 (molecular ion) and 1.3% for $[M - C_4H_9]^+$, which is more typical of benzeneboronate spectra (vide infra). An explanation consistent with structure **10** is that, in the first instance, the loss of the butyl radical and the stabilization of the resulting charge involve participation of the phenyl group, placing the phenyl on the same side of the structure from which the butyl radical is lost. In the second case, the phenyl is on the side of the structure opposite to that of the butyl groups. Furthermore, while structure **10** has the symmetry necessary for this interaction, structure **11** does not.

The interaction between a phenyl and an adjacent boron described above is not observed in the mixed butane-benzeneboronates of *cis*-inositol. A possible explanation is that a comparable situation occurs with the butaneboronate derivatives of D-glucose 6-phosphate dimethyl ester and D-mannose 6-phosphate dimethyl ester[5] and also with the butaneboronate-acetate derivatives of D-glucose and D-mannose.[6] In each case, the $[M - C_4H_9]^+$ ion in the mannose derivative is much less abundant than in the glucose derivatives. As in the *cis*- and *allo*-inositol examples the situation in which $[M - C_4H_9]^+$ is enhanced is the one where crowding between cyclic boronate moieties is minimized because one of the cyclic esters is on the remote side of the ring system.

***neo*-, *chiro*-, and *epi*-Inositols.** The triboronates of these inositols are unstable in solution, converting to products of unknown structures with long gas chromatographic retention times following prolonged standing at room temperature. This instability probably results from the obligatory formation of one trans cyclic boronate in each of these isomers, a structure not found in the previously discussed inositols, all of which form boronates that are stable in solution.

Only one structure (**12**) is possible for *neo*-inositol boronates while three are possible for the *chiro*-inositol derivatives (**13, 14a, 14b**) and two for the *epi*-inositol boronates (**15, 16**). The mass spectra of the *chiro*- and *epi*-inositol esters do not rule out the alternate structures; however, the similarity of their spectra to that of the neo-inositol derivative (Figure 2) suggests structures **13** and **15.**



Each of these spectra has *m/e* 126 as the base peak. This ion, with the probable structure **17,** is prominent in the spectra of aldopyranose butaneboronates with α,β-cyclic moieties[6] where its abundance, as may be the case here, is associated with the ease of its expulsion from a molecule having such groups. This expulsion in the present cases may be aided by considerable torsional strain due to the presence of the trans cyclic ester. In the spectra of the other inositol butaneboronates, the ratio is 1:3 or greater. A low abundance of *m/e* 139 would not be expected with the alternate structure **14a** of the *chiro*-inositol derivative.

A further observation which is consistent with structures **13** and **15** but not with the alternate *chiro*- and *epi*-inositol boronate structures is that molecular models of **14a, 14b,** and **16** all show the trans α,β-cyclic ester of these structures to be under greatly increased strain relative to the trans moieties in structures **13** and **15.** In the case of **14a** this is because of the rigid nature of the interlocking α,γ-boronates which reduce the flexibility of the cyclitol ring. In the base of **14b** and **16** it is because the α,δ-boronate forces the inositol into a boat conformation, exaggerating the trans character of the remaining hydroxyls.

Effects of Alkyl Group Size in the Spectra of Alkaneboronates. The nature of the alkaneboronate side chains influences the spectra of the inositol boronates in two general ways. First, the general appearance of the inositol methaneboronate spectra shows less variation from one isomer to another than is seen with the butane- and octaneboronates. This is typified by ion

5, the abundances for which are given in Table I for the *myo*-, *muco*-, *cis*-, and *allo*-inositol derivatives. The second effect, which is shown in Table II, is that $[M - C_4H_9]^+$ and $[M - C_8H_{17}]^+$ ions occur in larger abundance than $[M - CH_3]^+$ ions.

Inositol Benzeneboronate Spectra. The tris(benzeneboronate) derivatives of *myo*-, *muco*-, *cis*-, and *allo*-inositol were found to gas chromatograph as single peaks. The mass spectra of these derivatives have intense molecular ions and an absence of $[M - C_6H_5]^+$ ions (Table II). This reflects the expected instability of phenyl radical as a leaving moiety and perhaps the ability of benzene to stabilize the molecular ion. Another effect of the phenyl group is found in the intensity of *m/e* 146 (**17**, R = phenyl), which carries a significant portion of the ion current in the spectra of *myo*-, *muco*, *cis*, and *allo*-inositols (Σ_{40} of 4.6, 6.0, 7.5, and 7.3%, respectively, at 70 eV). This is compared with *m/e* 126 in the spectra of the corresponding butaneboronates, which have Σ_{40} values of 0.8, 1.7, 0.7, and 1.3%.

It can be argued that, in the benzeneboronate case, this odd electron ion is increased in intensity as a result of partitioning of the fragmentation in favor of *m/e* 146 because the loss of a phenyl group is an unfavored process.

Experimental Section

Samples. *allo*-, *cis*-, and *epi*-inositols were the gift of Professor S. J. Angyal, University of New South Wales. *muco*-Inositol was the gift of Professor C. E. Ballou, University of California, Berkeley. *scyllo*-Inositol was prepared by the method of Stanacev and Kates[7] and *neo*-inositol by the method of Angyal and Matheson.[8] *myo*- and (+)-*chiro*-inositol were commercial samples. Octaneboronic acid was prepared by a modification of the procedure of Brown and Gupta.[9] Methane-, butane-, and benzeneboronic acids were purchased from the Alfa Division of Ventron Corp.

Boronation. A typical derivatization procedure was as follows. A suspension of 1 mg of an inositol in 0.15 mL of pyridine solution containing a 3-6-equiv excess of the boronic acid was agitated on a mechanical shaker for 24 h. When necessary the reaction was completed by heating on a steam bath. Gas chromatographic retention times of the inositol tris(butaneboronates) at 230 °C on a 6-ft glass column packed with 3% OV-17 on Gas Chrom Q (30 mL He per min) are as follows (inositol followed by retention times in min) (Table III): *allo*-, 5.2; *muco*-, 5.5; *myo*-, 5.6; *neo*-, 6.2; *chiro*-, 9.2; *epi*-, 10.0; *cis*-, 12.0. Similar conditions were used for chromatography of the other boronates. The stationary phases, column lengths and temperatures, and the approximate ranges of chromatographic retention times were as follows: trimethaneboronates, 3% OV-17, 6 ft, 140 °C, 6-8 min; tribenzeneboronates, 1% SE-30, 1 ft, 230 °C, 8-12 min; trioctaneboronates, 1% SE-30, 2 ft, 240 °C, 10-15 min.

Solutions of mixed triboronates of *myo*-, *muco*-, *cis*-, and *allo*-inositols were prepared in the same way as the homogeneous boronates except that 24 h at room temperature was allowed for equilibration, following complete dissolution of the inositol. The conditions and results for those mixed derivatives described in the text were as follows.

***myo*-Inositol Methane-Butaneboronates:** 6 ft, 3% OV-17 on Gas Chrom Q, temperature programmed from 150 °C at 1 °C/min, peaks identified at 18 and 19 (monobutane-dimethaneboronates) and at 41, 42, and 43 min (monomethane-dibutaneboronates).

***muco*-Inositol Butane-Benzeneboronates:** 1.5 ft, 3% SE-30 on Gas Chrom Q, temperature programmed for 210 °C at 1 °C min, peaks identified at 11 and 19 (monobenzene-dibutaneboronates) and at 29 and 34 min (monobutane-dibenzeneboronates).

***cis*-Inositol Methane-Butaneboronates:** 6 ft, 3% OV-17 on Gas Chrom Q, temperature programmed from 150 °C at 1 °C/min to give peaks at 18 and 42 (monobutane-dimethaneboronate) and at 68 min (monomethane-dibutaneboronate).

Bis(trimethylsilyl)-*scyllo*-inositol Di-1-butaneboronate. *scyllo*-Inositol (5 mg) was suspended in 0.2 mL of pyridine containing 25 mg of butaneboronic acid by sonication and then heated at about 80 °C for 6 h. Only partial dissolution could be achieved. The clear supernatant (0.1 mL) was, after centrifugation, reacted with 0.2 mL of *N,O*-bis(trimethylsilyl)trifluoroacetamide containing 10% trimethylsilyl chloride (Regis) at room temperature for 12 h. Gas chromatography on a 6-ft 3% SE-30 column at 210 °C (other parameters as above) revealed three peaks with relative areas of approximately 1:1:2 and retention times of 4.5, 5.4, and 7.7 min, respectively. The last of these was identified as a bis(trimethylsilyl) dibutaneboronate of an inositol by GC-MS. The second peak was hexakis(trimethylsilyl)-*scyllo*-inositol, while the first peak (containing both silicon and boron) remains unidentified.

Table III. Gas Chromatographic Retention Times (min) of Inositol Tris(butaneboronate) Derivatives[a]

allo-inositol	5.2	*chiro*-inositol	9.2
muco-inositol	5.5	*epi*-inositol	10.0
myo-inositol	5.6	*cis*-inositol	12.0
neo-inositol	6.2		

[a] Chromatographed at 230 °C on a 6-ft glass column packed with 3% OV-17 on Gas Chrom Q using a helium carrier flow rate of 30 mL/min.

Gas Chromatography-Mass Spectrometry. An LKB-9000/PDP-12 system[10] was used for all experiments. The mass spectrometer was operated with 70-eV electron beam ionization energy, while the source and separator temperatures were 270 and 240 °C, respectively. In the case of mixed-ester experiments scans every 3-10 s were taken across detectable peaks (as indicated by the total ion current monitor) and these stored on magnetic tape. Mass chromatograms were reconstructed from the stored spectra. Other spectra were obtained with 2-s scans across the center of the gas chromatographic peak, during the period of minimum sample concentration change.

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Supplementary Material Available: A listing of the mass spectra of the following inositol boronates: *scyllo*-inositol bis(*n*-butaneboronate) bis(trimethylsilyl) ether; the tris(*n*-butaneboronates) of *myo*-, *muco*-, *cis*-, *allo*-, *neo*-, *chiro*-, and *epi*-inositols; the trismethaneboronates of *myo*-, *muco*-, *cis*-, and *allo*-inositols; the tris(*n*-octaneboronates) of *myo*-, *muco*-, *cis*-, and *allo*-inositols; the trisbenzeneboronates of *myo*-, *muco*-, *cis*-, and *allo*-inositols (15 pages). Ordering information is given on any current masthead page.

Reference and Notes

(1) W. R. Sherman, N. C. Eilers, and S. L. Goodwin, *Org. Mass Spectrom.*, **3**, 829 (1970).
(2) F. Eisenberg, Jr., *Methods Enzymol. B*, **28**, 168-178 (1973).
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(4) In mass chromatography sequential scans of the mass spectrometer, collected and stored during the gas chromatographic elution of a group of substances, are reassembled to give an ion abundance vs. time profile for specified ions.
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(9) H. C. Brown and S. K. Gupta, *J. Am. Chem. Soc.*, **93**, 1816 (1971).
(10) W. F. Holmes, W. H. Holland, and J. A. Parker, *Anal. Chem.*, **43**, 1806 (1971).
(11) The IUPAC-IUB nomenclature for the inositol boronates will not be used in the text of the paper. However, for reference purposes, the correct nomenclature of the structures we have assigned to these compounds are as follows: **1**, (±)-1,2,3,5/4,6-cyclohexanehexol-1,2:3,5:4,6-tris(butaneboronate); **3**, 1,2,4,5/3,6-cyclohexanehexol-1,5:2,4:3,6-tris(butaneboronate); **8**, 1,2,3,4,5,6/0-cyclohexanehexol-1,2:3,6:4,5-tris(butaneboronate); **10**, 1,2,3,4/5,6-cyclohexanehexol-1,4:2,3:5,6-tris(butaneboronate); **12**, (±)-1,2,3/4,5,6-cyclohexanehexol-1,2:3,4:5,6-tris(butaneboronate); **13**, (±)-1,2,4/3,5,6-cyclohexanehexol-1,2:3,4:5,6-tris(butaneboronate); **15**, (±)-1,2,3,4,5/6-cyclohexanehexol-1,2:3,4:5,6-tris(butaneboronate).