

MASS SPECTRAL STUDIES ON SOME 1,3-DIOXABORINANE ESTERS

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Summary

The complete mass spectra of the compounds $\text{RBOCHMeCH}_2\text{CHMeO}$ ($\text{R} = \text{Ph, PhO, t-BuO}$) are reported for the first time. The first two of these show rearrangement processes giving rise to C_8H_9^+ and C_7H_7^+ ions. Mechanisms for the formation of these ions are discussed in the light of studies on deuterium labelled compounds.

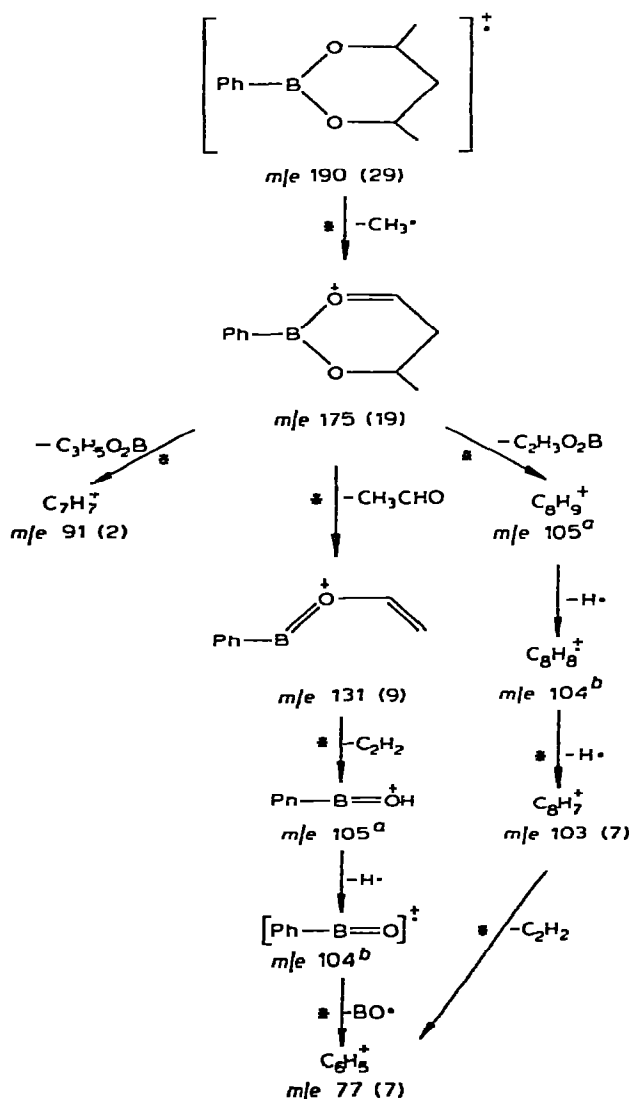
The formation of hydrocarbon rearrangement ions in the mass spectra of a range of cyclic esters of phenylboronic acid has attracted considerable attention in recent years. Cragg and Todd [1] reported initial studies on $\text{PhBOCH}_2\text{CH}_2\text{O}$ (I), which was shown to form the C_7H_7^+ ion directly from the molecular ion by two routes. These involved direct elimination of BO_2CH_2 and the two-step process of elimination of CH_2O followed by BO . A mechanism for these rearrangements has been proposed on the basis of a study of $\text{PhBOCD}_2\text{CD}_2\text{O}$ [2] and the effects of replacement of one or both of the oxygen atoms in I by sulphur has been discussed [3]. These studies have also been extended to a range of substituted 2-phenyl-1,3,2-dioxaborolanes, which show similar rearrangement processes [4]. In this case it was found that the molecules $\text{PhBOCR}^1\text{R}^2\text{CR}^3\text{R}^4\text{O}$ ($\text{R}^1 = \text{Me, R}^2 = \text{R}^3 = \text{R}^4 = \text{H; R}^1 = \text{R}^3 = \text{Me, R}^2 = \text{R}^4 = \text{H; R}^1 = \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{Me}$) all give rise to C_7H_7^+ ions, as well as the rearrangement product, C_8H_9^+ . McKinley and Weigel [5] found that C_7H_7^+ ions were also formed in the mass spectra of a wide range of cyclic esters of phenylboronic acid including $\text{PhBO}(\text{CH}_2)_3\text{O}$ (II) and its 4-methyl, 4,6-dimethyl and 5,5-dimethyl analogues. These authors also reported the formation of other hydrocarbon rearrangement ions such as C_8H_9^+ , $\text{C}_9\text{H}_{11}^+$ and $\text{C}_{10}\text{H}_{12}^+$ in the spectra of some of the methyl-substituted compounds. A mechanistic investigation of C_7H_7^+ ion formation by II has also been carried out with the aid of a study of its 5,5- d_2 analogue [2].

In a previous publication [6] we reported that C_7H_7^+ , C_8H_8^+ and C_8H_9^+ ions are also observed in the mass spectrum of 2-phenoxy-4,6-dimethyl-1,3,2-dioxaborolane.

borinane, $\text{PhO} \overline{\text{BOCHMeCH}_2\text{CHMeO}}$ (III). In an effort to gain further insight into the mechanism of formation of these ions, we have studied the mass spectral behaviour of deuterium labelled analogues of III, together with that of $\text{Ph} \overline{\text{BOCDMeCH}_2\text{CDMeO}}$ (IV) and $(\text{CH}_3)_3\text{CO} \overline{\text{BOCHMeCH}_2\text{CHMeO}}$ (V).

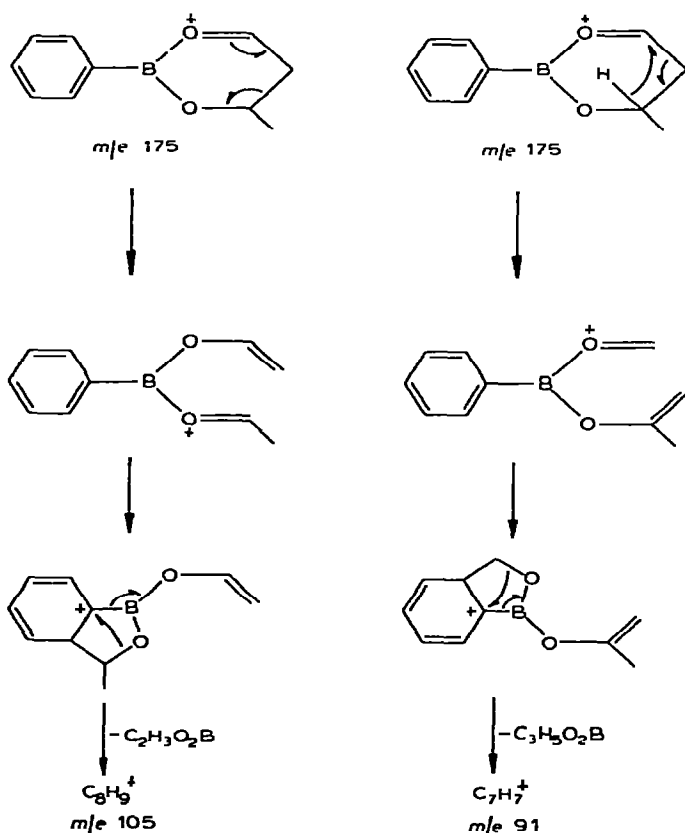
Results and discussion

The formation of hydrocarbon rearrangement ions by $\text{Ph} \overline{\text{BOCHMeCH}_2\text{CHMeO}}$ (VI) has been reported previously [5]. Although these authors reported only the intensities of the hydrocarbon ions, C_7H_7^+ , C_8H_8^+ and C_8H_9^+ in the spectrum of VI, our results appear to be completely in accord with those given. Scheme 1



Scheme 1. Fragmentation of compound VI (relative intensities given in brackets, all m/e values based on ^{11}B ; * metastable ion). ^aTotal relative intensity of ions at m/e 105 is 100%. ^bTotal relative intensity of ions at m/e 104 is 30%.

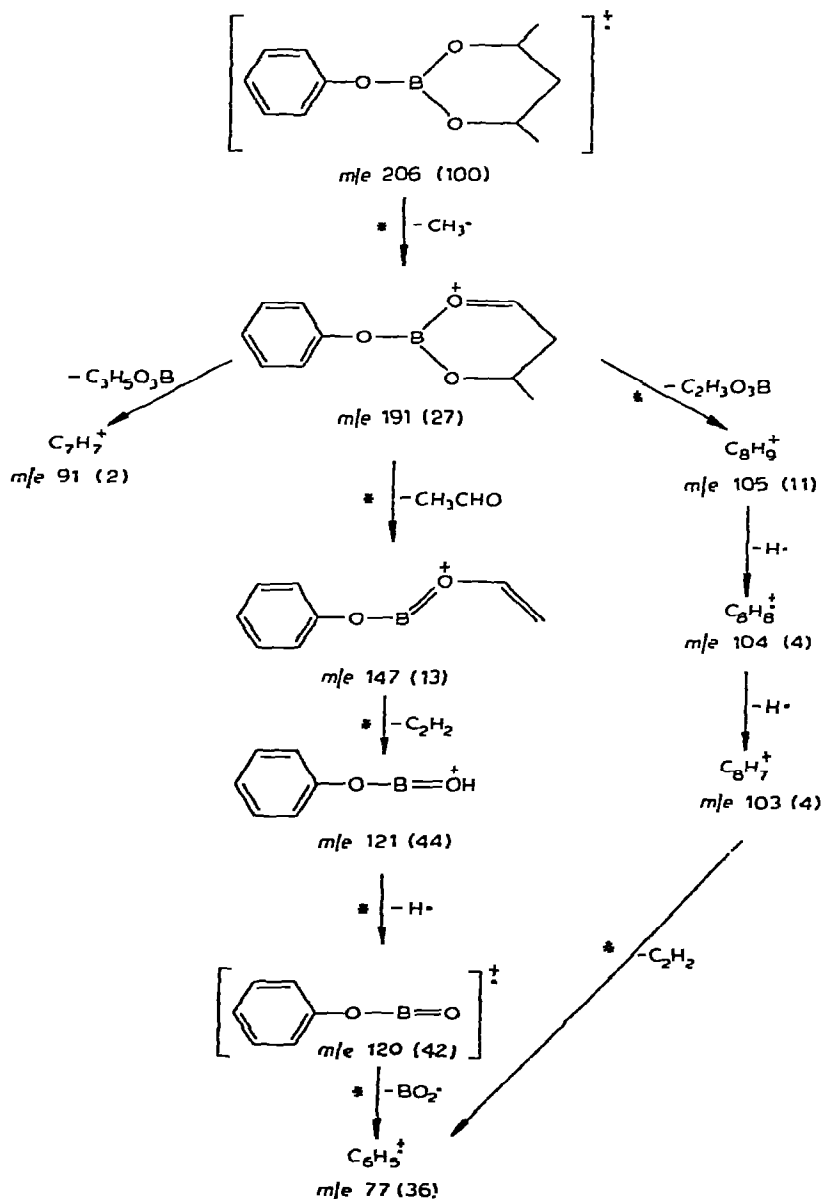
shows the fragmentation behaviour of VI and on the basis of observed metastable ions, the molecular ion of this compound appears to decompose exclusively via the resonance stabilised oxonium ion (m/e 175). Successive losses of CH_3CHO and C_2H_2 from the oxonium ion lead to the formation of $\text{PhB}=\dot{\text{O}}\text{H}$ (m/e 105, based on ^{11}B), both processes being supported by the presence of metastable ions. The oxonium ion also fragments directly to m/e 105 (metastable ion observed), however examination of the peak at m/e 105 under high resolution conditions showed it to be a doublet. Mass measurement of both components of this doublet are in agreement with the formulations C_8H_9^+ and $\text{C}_6\text{H}_5^{11}\text{BOH}^+$. On the basis of these results, we suggest that the former ion is produced by direct loss of $\text{C}_2\text{H}_3\text{O}_2\text{B}$ from the oxonium ion and that the latter is formed by the two-step process outlined above. From high resolution studies it appears that C_8H_9^+ constitutes approximately 30% of the total intensity of ions at m/e 105. Other hydrocarbon ions were identified at m/e 104 (C_8H_8^+) and m/e 103 (C_8H_7^+) and it is suggested that these arise via successive losses of H^+ from C_8H_9^+ . The second of these processes is supported by the presence of a metastable ion. A third route of decomposition available to the oxonium ion has been identified as that involving direct formation of C_7H_7^+ ions (m/e 91) and a weak metastable ion was observed indicating that this is a one-step process.



Scheme 2. The mechanism of formation of C_8H_9^+ and C_7H_7^+ ions from VI.

In order to further elucidate the mechanisms of these rearrangements, the mass spectrum of IV was examined.

For this compound the hydrocarbon rearrangement ion corresponding to $C_8H_9^+$ was observed at m/e 106 and, somewhat surprisingly, the ion corresponding to $C_7H_7^+$ is clearly shifted to m/e 93. On the basis of these results it appears that there is no H-D scrambling in the borinane ring prior to rearrangement and that the $C_8H_9^+$ and $C_7H_7^+$ ions are formed by the mechanisms shown in Scheme 2. Further discussion of these mechanisms is, however, deferred until after consideration of the fragmentation of III and its deuterio-analogues.

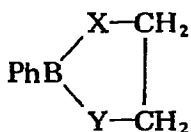


Scheme 3. Fragmentation of compound III (relative intensities given in brackets, all m/e values based on $^{11}\text{B-}^3$ metastable ion).

The fragmentation of III is shown in Scheme 3 and we suggest that again the principle fragmentation routes arise from the oxonium ion (m/e 191). Unfortunately, no metastable ions are observed that indicate the genesis of the ion $C_7H_7^+$. Nevertheless, it does not seem unreasonable to propose that this ion is formed directly from the oxonium ion as discussed above for compound VI. Such a mechanism is further substantiated by study of the 4,6- d_2 analogue of III and that with deuterium atoms at the 5-position. The preparation of the second of these labelled molecules led to formation of 5- d_1 compound as the major product, although low voltage mass spectrometry showed that appreciable quantities of 5,5- d_2 and the non-deuterated compounds were always present in the final product. Notwithstanding the fact that this product was a mixture, useful information was still obtained from its mass spectrum.

Deuteration at the 4 and 6 positions of the borinane ring again leads to $C_7H_7^+$ ions being clearly shifted to m/e 93 and $C_8H_9^+$ ions being similarly shifted to m/e 106. The mass spectrum of the mixture produced by deuteration at C-5 showed a complete absence of deuterium incorporation into the hydrocarbon rearrangement ions. These results are also consistent with the rearrangement mechanisms similar to those outlined in Scheme 2 in which C-5 of the borinane ring does not take part in hydrocarbon ion formation. Labelling studies on the related compound (II) [2] have also demonstrated the non-involvement of C-5 in formation of $C_7H_7^+$ ions directly from the molecular ion of this compound. The fact that the C-5 atom is not involved in the formation of such ions from III and VI is somewhat surprising, as this is the only site in the borinane ring that does not require hydrogen migration prior to rearrangement.

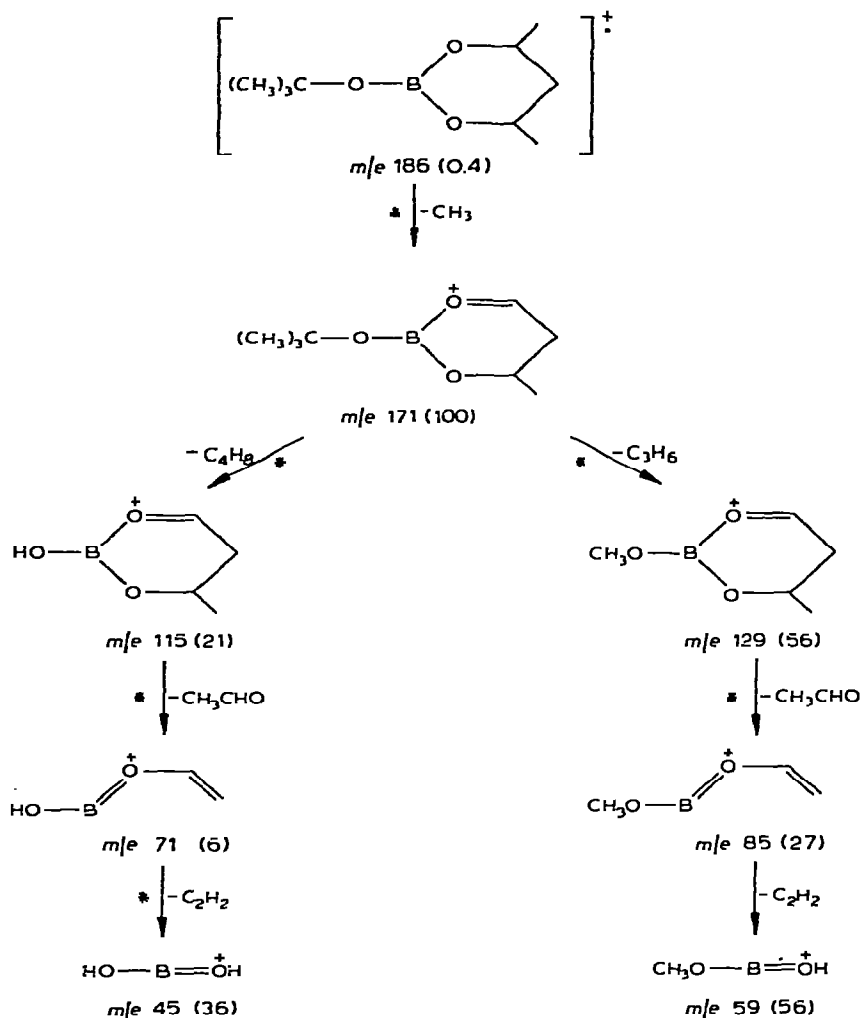
However, given that a 1,3-hydrogen migration process does occur together with cleavage of the 2,3-bond in these compounds, it is possible to rationalise this rearrangement as one involving the carbon atom adjacent to the charge carrying oxygen atom of the oxonium ion, this presumably being the site of highest electrophilicity. The fact that formation of $C_7H_7^+$ ions involves both hydrogen migration and cleavage of the borinane ring suggests that it is presumably a process of high activation energy. This would account for the low relative intensity of these ions, as other low energy fragmentation reactions of the oxonium ion are presumably able to compete effectively with tropylium ion formation. Similar findings have been reported [3] for the series of compounds VII, in which the yield of $C_7H_7^+$ depends markedly on X and Y. Thus the presence of



(VII) X = Y = O or S; X = O, Y = S

sulphur atoms allows the formation of $C_2H_4S^+$ ions to compete effectively with decomposition of the molecular ion to $C_7H_7^+$, whereas the molecular ion of the phenyldioxaborolane does not give rise to $C_2H_4O^+$. The low activation energy for the formation of $C_2H_4S^+$ ions compared to that for $C_2H_4O^+$ ions is reflected in a comparison of B—S and B—O bond strengths.

The formation of hydrocarbon rearrangement ions by the phenoxy com-



Scheme 4. Fragmentation of compound IV (relative intensities given in brackets, all m/e values based on ^{11}B ; * metastable ion).

pound (III) is somewhat surprising and presumably reflects the difference in B—O and C—O bond strengths (approx. 500 kJ mol^{-1} and approx. 360 kJ mol^{-1} respectively [7]). This difference in bond strengths is further evidenced by the exclusive fragmentation of $\text{C}_6\text{H}_5\text{OB}=\text{O}^+$ (m/e 120 based on ^{11}B) to C_6H_5^+ ions and not to $\text{C}_6\text{H}_5\text{O}^+$. Further evidence of the high B—O bond strength in such compounds is gained from the fragmentation of V. As can be seen from Scheme 4, the oxonium ion formed by this compound (m/e 171) fragments exclusively by rearrangement processes involving migration of either a hydrogen atom or a methyl radical from the tertiary butyl group, the acyclic B—O bond remaining intact in both cases.

Examination of the fragmentation of the oxonium ions formed from the 4,6- d_2 derivatives of III and VI also allows comment on the nature of the reactions leading to RBOH^+ ions ($\text{R} = \text{PhO}$ and Ph respectively). The oxonium ions formed by both these molecules show exclusive loss of 45 a.m.u. corresponding

terated and 30% di-deuterated glycol. The mixture of racemic and *meso* deuterated glycols was converted to the phenoxyborinane as described previously. B.p. 80°/0.05 mmHg.

Preparation of 2-phenoxy- and 2-phenyl-4,6-dideutero-4,6-dimethyl-1,3,2-dioxaborinane

To a methanol solution of acetylacetone (5 g) was added with stirring sodium borodeuteride (1.3 g) and sodium hydroxide (0.025 g in water). All the solvent was removed at reduced pressure and glycerol (5.0 g) was added to the residue. Distillation gave the 2,4-dideutero *meso* and racemic pentane-2,4-diol. b.p. 40°/0.3 mmHg. The phenoxy- and phenyl-4,6-dideutero-borinane esters were prepared as described previously.

Spectra

Mass spectra. These were recorded on an AEI MS 9 spectrometer. Electron beam energy was maintained at 70 eV and 100 μ A trap current. Fragmentation patterns were obtained at 1000 resolution and mass measurements performed at 10000 resolution by the peak matching technique. All spectra have been submitted to the Mass Spectrometry Data Centre, Aldermaston.

NMR spectra. These were recorded on a Perkin—Elmer R 10 spectrometer operating at 60 MHz.

References

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