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MASS SPECTRAL STUDIES ON SOME 1,3-DIOXABORINANE ESTERS

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Summary

The complete mass spectra of the compounds $R\overline{BOCHMeCH_2CHMeO}$ (R = 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.

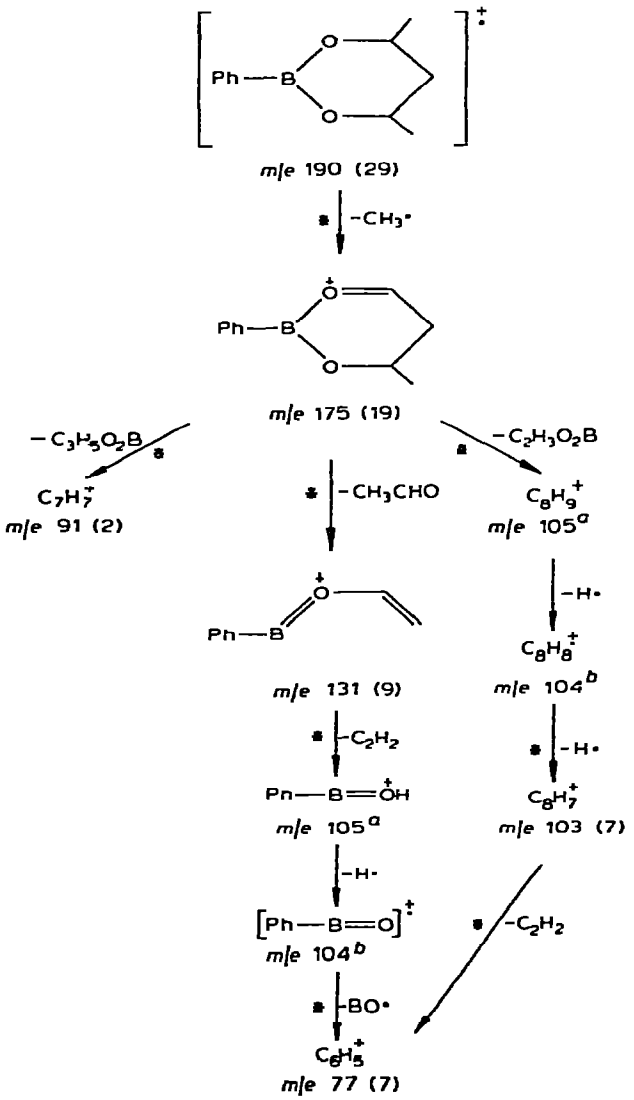
The formation of hydrocarbon rearrangement ions in the mass spectra of a range of cyclic esters of phenylboronic acid has attracted considerable attention in recent years. Cragg and Todd [1] reported initial studies on $Ph\overline{BOCH_2CH_2O}$ (I), which was shown to form the $C_7H_7^+$ ion directly 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 $Ph\overline{BOCD_2CD_2O}$ [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 $Ph\overline{BOCR^1R^2CR^3R^4O}$ (R^1 = Me, $R^2 = R^3 = R^4$ = H; $R^1 = R^3$ = Me, $R^2 = R^4$ = H; $R^1 = R^2 = R^3 = R^4$ = 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 $Ph\overline{BO(CH_2)_3O}$ (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 $C_8H_9^+$, $C_9H_{11}^+$ and $C_{10}H_{12}^+$ 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-dioxa-

borinane, PhOBOCHMeCH$_2$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 PhBOCDMeCH$_2$CDMeO (IV) and (CH$_3$)$_3$COBOCHMeCH$_2$CHMeO (V).

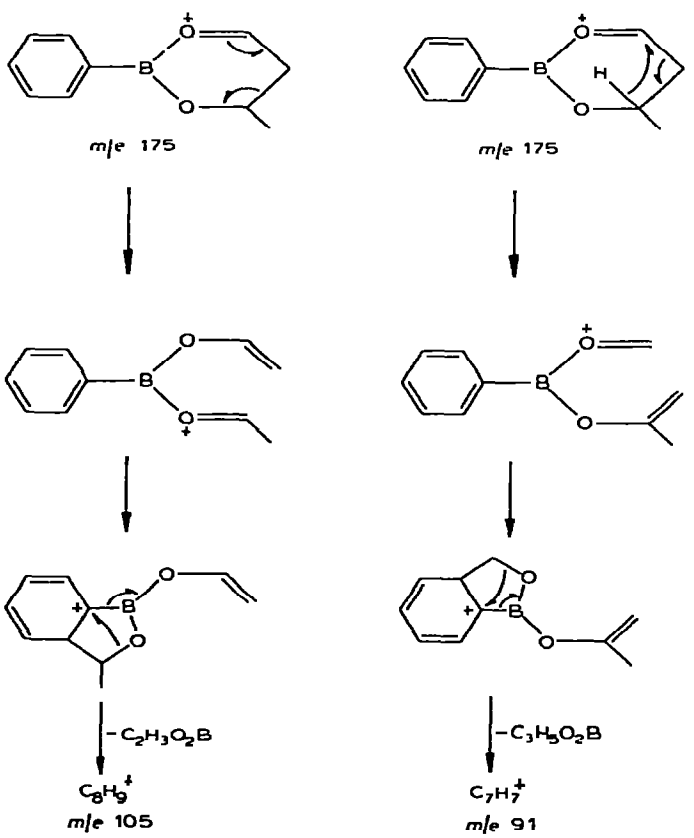
Results and discussion

The formation of hydrocarbon rearrangement ions by PhBOCHMeCH$_2$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). [a] Total relative intensity of ions at *m/e* 105 is 100%. [b] Total relative intensity of ions at *m/e* 104 is 30%.

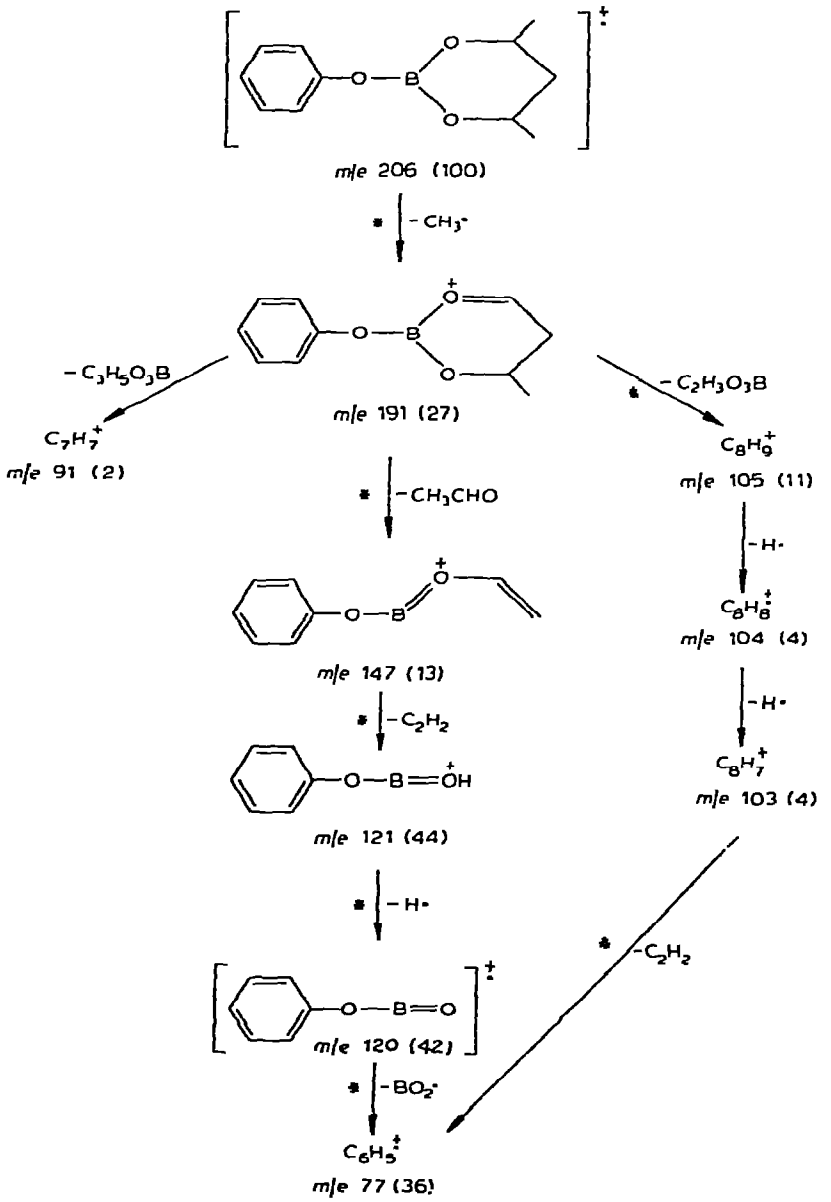
shows the fragmentation behaviour of VI and on the basis of observed metastable ions, the molecular ion of this compound appears to decompose exclusively via the resonance stabilised oxonium ion (*m/e* 175). Successive losses of CH_3CHO and C_2H_2 from the oxonium ion lead to the formation of PhB=$\overset{+}{O}$H (*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 $C_6H_5{}^{11}BOH^+$. On the basis of these results, we suggest that the former ion is produced by direct loss of $C_2H_3O_2B$ 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 $H^\cdot$ 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 cleanly 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 deutero-analogues.

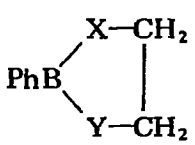


Scheme 3. Fragmentation of compound III (relative intensities given in brackets, all *m/e* values based on ^{11}B; * metastable ion).

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 cleanly 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.

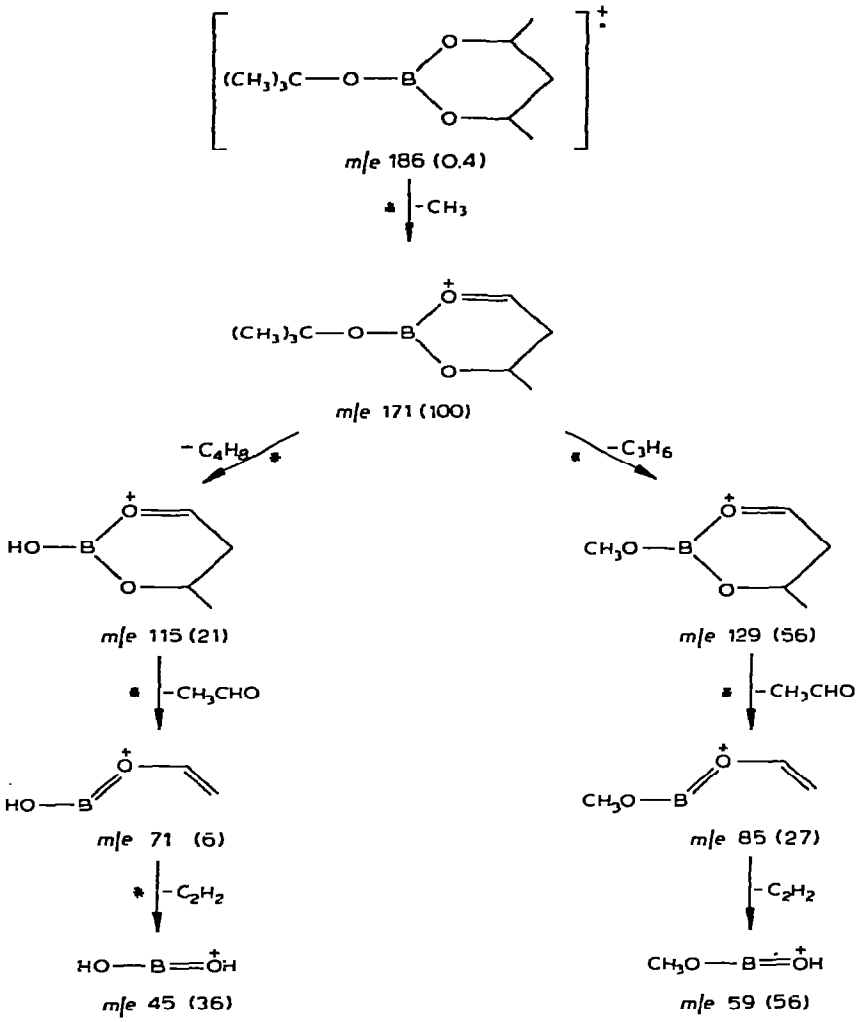
However, given that a 1,3-hydrogen migration process does occur together with cleavage of the 2,3-bond in these compounds, it is possible to rationalise this rearrangement as one involving the carbon atom adjacent to the charge carrying oxygen atom of the oxonium ion, this presumably being the site of 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-

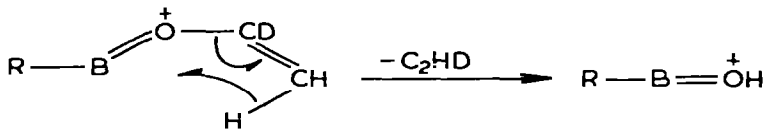


Scheme 4. Fragmentation of compound IV (relative intensities given in brackets, all *m/e* values based on ^{11}B; * metastable ion).

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 $C_6H_5OB{=}O^+$ (*m/e* 120 based on ^{11}B) to $C_6H_5^+$ ions and not to $C_6H_5O^+$. 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 (R = PhO and Ph respectively). The oxonium ions formed by both these molecules show exclusive loss of 45 a.m.u. corresponding

to the expulsion of CH_3CDO. The ions resulting from these losses can thus be represented as VIII, and these, in turn, show exclusive loss of 27 a.m.u., corresponding to the expulsion of C_2HD. Thus the last of these two processes must involve a four-membered transition state (VIII → IX).



(VIII) (IX)

Experimental

Preparation of 4,6-dimethyl-1,3,2-dioxaborinanes

Pentane-2,4-diol, prepared by high pressure hydrogenation of acetylacetone using Raney nickel catalyst, was separated into its *meso* and racemic isomers by the method of Pritchard and Vollmer [8], viz. by conversion into the cyclic sulphites, fractional distillation and hydrolysis of the separated sulphites back to the diols. The diol which crystallises at room temperature has been assigned the racemic configuration [8].

The three esters used in this study were 2-phenyl-, 2-phenoxy- and 2-t-butoxy-4,6-dimethyl-1,3,2-dioxaborinanes. They were prepared by distillation of a toluene solution of the respective alcohols with boric acid or phenylboronic anhydride in stoichiometric proportions followed by distillation under vacuum. The esters were characterised by elemental analysis, IR and ^1H NMR spectroscopy. The proton resonances of the 2-phenyl-4,6-dimethyl-1,3,2-dioxaborinanes were examined in some detail. Racemic ester (found: doublet, τ 8.73, J 6.0 Hz, CH_3; triplet, τ 8.42, J 5.0 Hz, CH_2; sextet, τ 5.78, CH (this signal was shown by double resonance to be a quartet of triplets)). *meso*-Ester (m.p., 46-47°C) (found: doublet, τ 8.73, CH_3; four triplets, τ 8.05, 8.27, 8.40, 8.57, CH_2; multiplet, τ 5.6-6.15, CH). The CH multiplets of both the *meso* and racemic isomers did not change their shape or position over the temperature range +60 to −70°C when run in CF_3Cl.

The aromatic resonances occurred as two multiplets at τ 2.1-2.35 and τ 2.6-2.85 in the case of the phenylborinane, but were a single complex multiplet at τ 2.7-3.2 for the phenoxyborinane. t-Butoxy-ester (found: singlet, τ 8.68, exocyclic CH_3; doublet, τ 8.77, ring CH_3). There was no difference between the mass spectral fragmentation patterns of the respective *meso* and racemic esters.

Preparation of 2-phenoxy-5,5-dideutero-4,6-dimethyl-1,3,2-dioxaborinane

Acetylacetone (5 ml) was shaken with excess D_2O (24 h) when deuteration of the labile methylene protons occurred. The deuterated acetylacetone was hydrogenated in n-pentane at 100°/100 atm. using Raney nickel (1 g). Filtration and distillation yielded the glycol which was further exchanged with D_2O in order to replace the hydroxyl protons. From a consideration of the ^1H NMR, IR and mass spectra it was concluded that the acetylacetone tautometric equilibria had resulted in a product which was 20% non-deuterated, 50% mono-deu-

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-dideuteroborinane 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 μA 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.

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