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ORGANOBORON COMPOUNDS

XI*. MASS SPECTRAL STUDIES ON SOME 2-PHENYL-1,3,2-DIOXABORINANES

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Summary

2-Phenyl-1,3,2-dioxaborinanes have been found to undergo electron impact-induced rearrangements resulting in the formation of hydrocarbon ions.

Introduction

Our initial communications [2,3] concerning the electron impact-induced rearrangement to form hydrocarbon ions from phenylboranes has aroused considerable interest [4-8]. We recently published the results of our mass spectral studies on a series of 2-phenyl-1,3,2-dioxaborolans [9] and in view of the recent paper concerning the mass spectra of some 1,3-dioxaborinane esters [10] we wish to report our results of an extensive study of 2-phenyl-1,3,2-dioxaborinanes and to make some generalisations with regard to their mode of fragmentation in the mass spectrometer. The main interest in the mass spectra of 2-phenyl-1,3,2-dioxaboracycloalkanes has been due to their electron impact-induced rearrangements to form hydrocarbon ions such as the tropylium ion and the methyltropylium ion.

Results and discussion

The major ions of interest in the mass spectra of 2-phenyl-1,3,2-dioxaboranes are given in Table 1. One interesting feature is the presence of a peak of *m/e* 105 which in the case of compounds I, III-VI was found by precise mass

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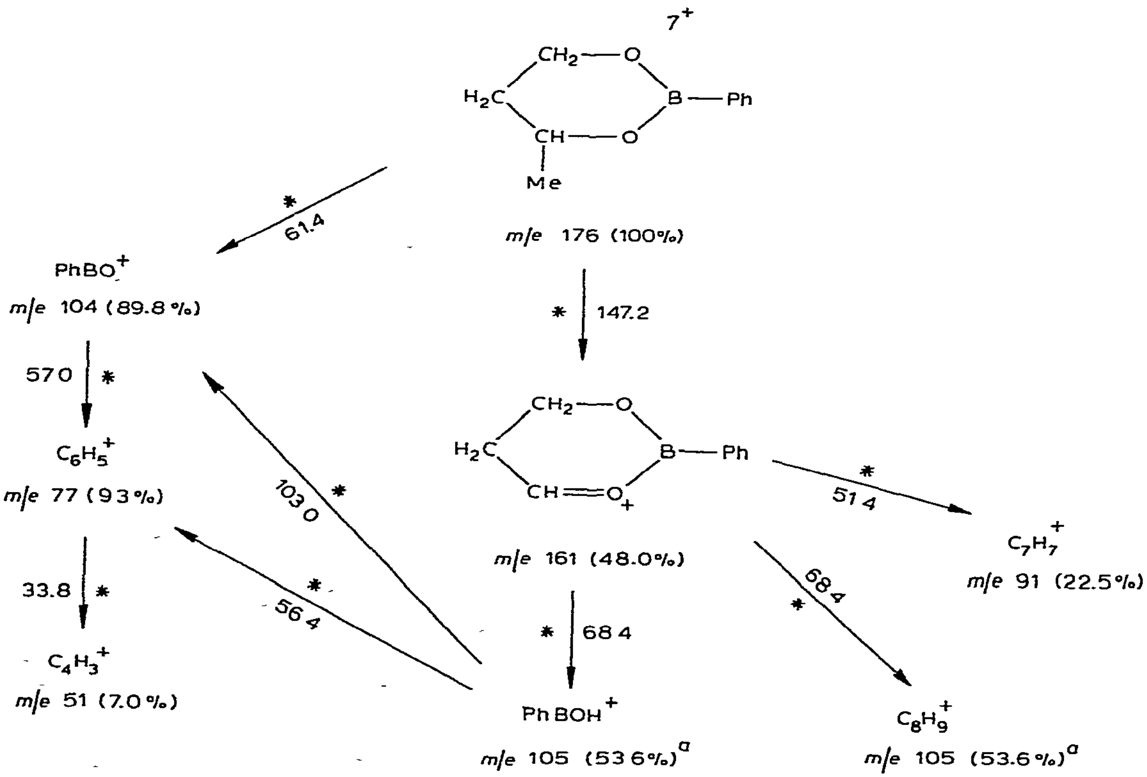
* For part X see ref. 1.

measurements to be due to the $C_8H_9^+$ and $PhBOH^+$ ions in the approximate ratio of 1/3. Surprisingly in a communication [5] the $C_8H_9^+$ ion was identified by precise mass measurement but there was no mention that the peak was a doublet and contained a contribution due to the $PhBOH^+$ ion. The mass spectrum of 4-methyl-2-phenyl-1,3,2-dioxaborinane is discussed in detail because it demonstrates all the general features of the fragmentation patterns of 2-phenyl-1,3,2-dioxaborinanes.

In the mass spectrum of 4-methyl-2-phenyl-1,3,2-dioxaborinane the molecular ion, *m/e* 176, was the base peak with the ion *m/e* 104 being the second most intense peak. The fragmentation pattern for this compound is given in Scheme 1. The molecular ion fragmented by loss of a methyl radicle to give an oxonium ion, *m/e* 161, and a double charged ion was observed at *m/e* 80.5 which suggests that the oxonium ion has considerable stability. The oxonium ion then fragmented to give hydrocarbon ions, namely the tropylium and methyltropylium ions. The ion *m/e* 104 previously identified as the $C_8H_8^+$ ion was shown by precise mass determination to be due mainly to the $PhBO^+$

SCHEME 1

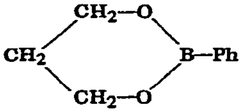
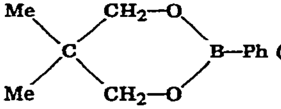
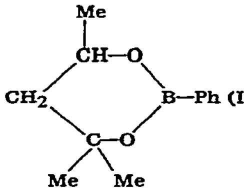
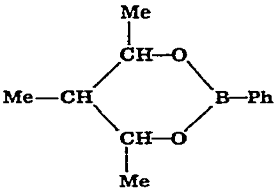
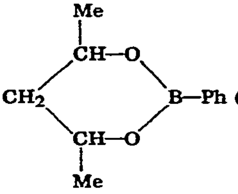
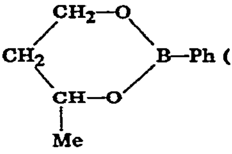
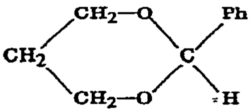
FRAGMENTATION OF 4-METHYL-2-PHENYL-1,3,2-DIOXABORINANE
(relative intensities given in brackets, all *m/e* values based on ^{11}B; * metastable ion)



^{a} Total relative intensity of ions *m/e* 105 is (53.6%).

TABLE I

MAJOR IONS OF INTEREST IN THE MASS SPECTRA OF 2-PHENYL-1,3,2-DIOXABORINANS [d]

Compound	*P* (*m/e*)	Base (%)	Base peak	*m/e* 105	*m/e* 104	*m/e* 91 (%) [c]
 (I)	162	98.6	104	19.4 [a]	100	15.6
 (II)	190	68.9	56	27.5	13.7	7.2
 (III)	204	39.6	43	88.8 [a]	44.7 [b]	2.5
 (IV)	204	32.3	56	55.2 [a]	17.6 [b]	1
 (V)	190	57.6	105	100 [a]	25.4	1
 (VI)	176	100	176	52.7 [a]	88.8 [b]	22.2
 (VII)	164	51.4	105	100	1.1	4.0

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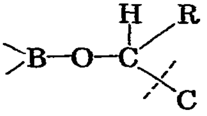
[a] *m/e* 105 determined by precise mass measurements to be a mixture of $C_8H_9^+$ and $PhBOH^+$. [b] *m/e* 104 determined by precise mass measurements to be a mixture of $C_8H_8^+$ and $PhBO^+$. [c] $C_7H_7^+$ tropylium ion. [d] Relative intensities as % of the base peak.

ion with only a small contribution due to the $C_8H_8^+$ ion. One further interesting feature is the presence of an ion *m/e* 105 which was found by precise mass determination to be a doublet consisting of the $C_8H_9^+$ and $C_6H_5BOH^+$ ions.

Increasing the number of methyl groups in the ring introduced a new feature in the mass spectra of dioxaborinanes. In the mass spectra of 5,5-dimethyl-1,3,2-dioxaborinane and 4,6-dimethyl-1,3,2-dioxaborinane the ion *m/e* 56 was found to be the base peak in both spectra and we suggest that in the former compound it is due to the 1,1-dimethylethylene ion and in the latter compound 1,2-dimethylethylene ion. Formation of the tropylium ion in compound IV was observed in about 1% abundance whereas in compound II it was 7.2% intensity. We rationalise this result as follows. In compounds II and IV cleavage of a C—C bond in the grouping A would result in migration of a CH_2 grouping towards the phenyl group in the former and a MeCH— grouping in the latter. The low intensity of the $C_7H_7^+$ ion in compounds IV and V is expected due to the lack of a CH_2 group next to oxygen to which boron is attached.



(A, R = H, Me)

In those compounds in which there is a $>$B—OCHMe— group the ion *m/e* 105 is found in high abundance and in compound V was observed to be the base peak. With the information obtained from our mass spectral study we are able to make the following general observations.

a. With the exception of compound VI ions containing carbon and hydrogen were the base peaks.

b. All spectra contained an ion *m/e* 105 of high intensity which was confirmed by precise mass measurements, in the cases of compounds I, III-VI, to be a mixture of the methyltropylium ion and the $PhBOH^+$ ion. This is in contrast to the previously published data which identified this ion as being solely due to the methyltropylium ion. In some cases a small peak due to the $C_5{}^{13}CH_5BO^+$ ion was also observed.

c. All the spectra contained an ion *m/e* 104 of high intensity which was shown by precise mass measurements, in compounds III, IV and VI to be a mixture of $PhBO^+$ and $C_8H_8^+$ in contrast to a previous publication which identified it solely as the latter ion.

d. The formation of ion *m/e* 104 via *m/e* 105 was observed in all compounds and was accompanied by the metastable ion at 103.0.

e. In the majority of compounds the molecular ion fragmented to give an oxonium ion from which the major fragmentation routes occur.

f. With the exception of compound II all the spectra contained double charged ions which were identified as being due to an oxonium ion formed by loss of H in the case of compound I and loss of Me for the rest of the compounds.

Finally in view of the communication [6] concerning the formation of hydrocarbon rearrangement ions from 4,6-dimethyl-2-phenoxy-1,3,2-dioxaborinan we decided to study the series of 2-phenoxy-1,3,2-dioxaboracycloalkanes. However we found these compounds to be very sensitive towards moisture and were unable to record their spectra without the presence of $PhOH^+$ one of the hydrolysis products. This confirms the observation by Davis in his communication but we find it difficult to understand why no mention was made of this ion in his recently published paper on the same compound [10].

Experimental

All the 2-phenyl-1,3,2-dioxaborinanes were prepared by the refluxing of phenylboroxine with the corresponding diol in benzene using a Dean—Stark apparatus until the stoichiometric amount of water had been eliminated. The benzene was removed under vacuum and the residue afforded on distillation the required product. The mass spectra were recorded, using an A.E.I. MS 902 mass spectrometer at 70 eV. The source was maintained at 170°C and the compounds were introduced as neat liquids using an unheated direct-insertion probe.

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