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MASS SPECTRA OF ORGANOBORON COMPOUNDS

III*. MASS SPECTRA OF SOME 2-PHENYL-1,3,2-DIOXABOROLANS

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Summary

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

Introduction

Although the application of mass spectrometry to the study of organoboranes has been extensive [2] there has been virtually no systematic mass spectral study of organoboron heterocycles. Our initial communication on the mass spectrum of 2-phenyl-1, 3, 2-dioxaborolan [3] appears to have aroused interest in this area with the publication of a number of communications concerned with the mass spectra of organoboron heterocycles [4—8].

Interest has been centred on the novel electron-impact rearrangements to form hydrocarbon ions. In the mass spectral fragmentation patterns of aromatic hydrocarbons the occurrence of the tropylium ion rearrangement has been fully documented [9, 10]. However at the commencement of this present work there was only one example of this type of rearrangement in compounds where the contributing carbon atom is not directly bonded to the phenyl group in the parent molecule, and that was in the case of alkylphenylphosphonates [11].

With the exception of 2-phenyl-1, 3, 2-dioxaborolan [12, 13] and 2-phenyl-1,3,2-dioxaborinan [13] there have been no detailed studies reported concerning the mass spectra of heterocyclic organoboranes containing two oxygen atoms and we now report our results and observations in this area.

Results

4-Methyl-2-phenyl-1, 3, 2-dioxaborolan (I) (Scheme 1) was observed to fragment via cleavage of one of two bonds.

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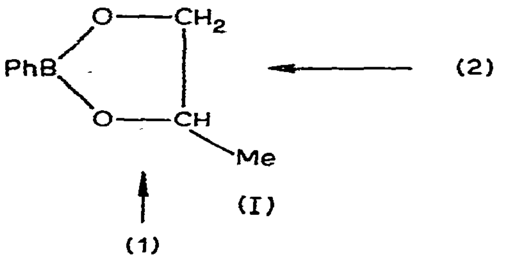
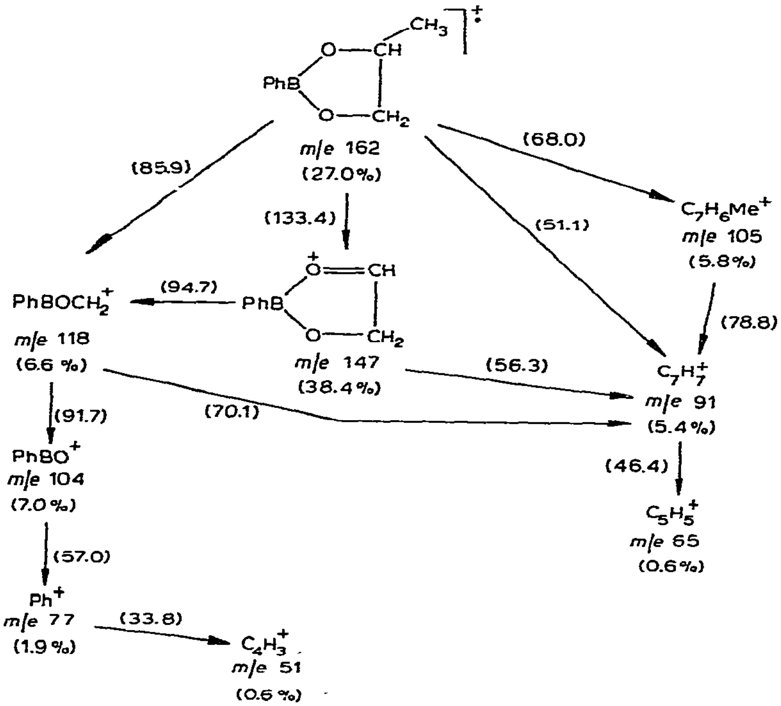
[*] For Part II see ref. 1.

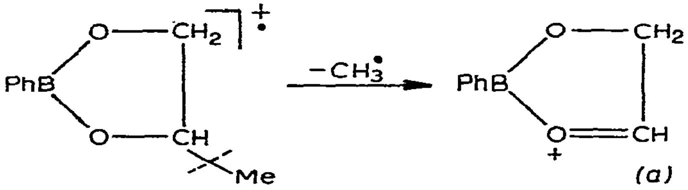


Process 1 produced a reducing ring species whilst process 2 led to one of two fragmentation modes resulting in rearrangement by phenyl ring expansion or loss of a neutral alkoxy grouping.

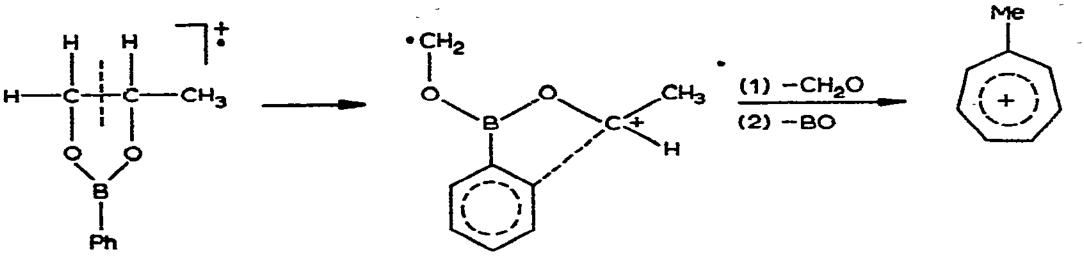
SCHEME 1. FRAGMENTATION PATTERN FOR 4-METHYL-2-PHENYL-1, 3, 2-DIOXABOROLAN



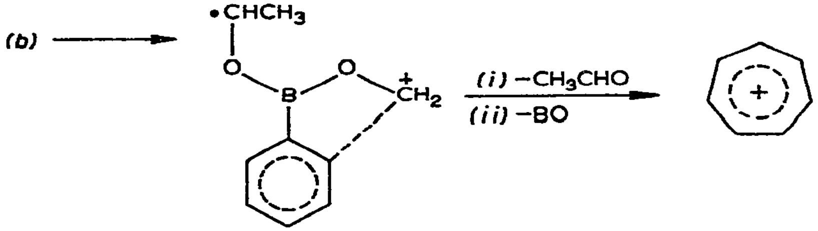
Process 1 involved the loss of a methyl radical whilst process 2 involved



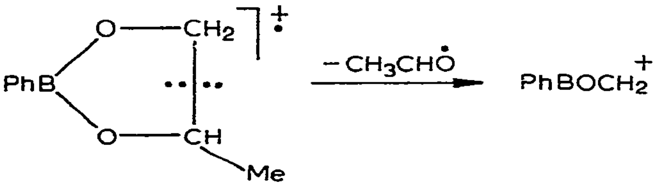
C_4—C_5 fission. This was followed either by B—O cleavage to give an ion *m/e* 118, which was also formed from ion (*a*), or by rearrangement to give both the tropylium and methyltropylium ions.



(b)

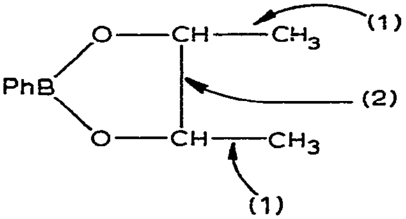


The counterpart of *m/e* 118, PhB$\overset{+}{O}$CHCH$_3$, was also formed by the C_4—C_5 fission, but it was observed only in very low yield.



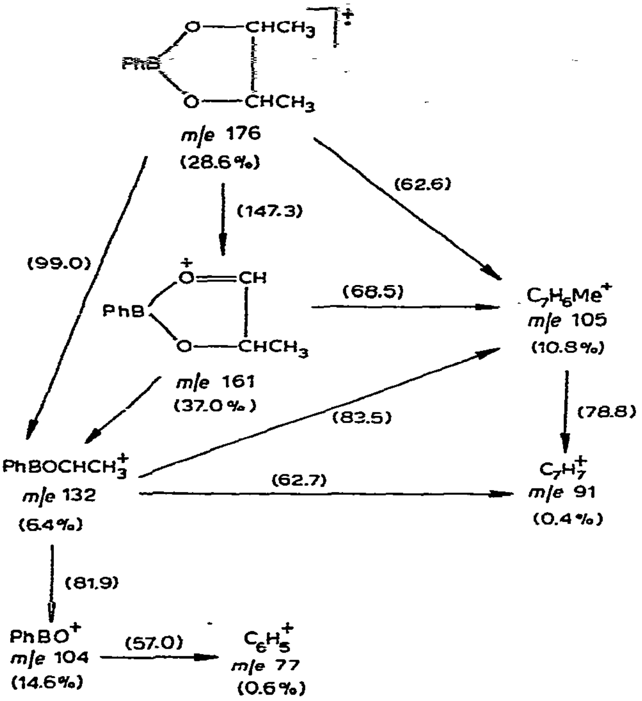
Further fragmentation of the PhBOCH$_2^+$ ion was via PhBO$^+$, the route described for it via PhBCH$_2^+$ in the spectrum of 2-phenyl-1, 3, 2-dioxaborolan [12] was observed to produce ions of very low abundance. Thus the major fragmentation observed was similar to that observed in the spectrum of 2-phenyl-1, 3, 2-dioxaborolan and is in agreement with a recent communication [7].

Methylation of the dioxaborolan ring at both C_4 and C_5 in 4, 5-dimethyl-2-phenyl-1,3,2-dioxaboralan (II) (Scheme 2) led to two major fragmentation modes analogous with those observed for 4-methyl-2-phenyl-1, 3, 2-dioxaborolan.

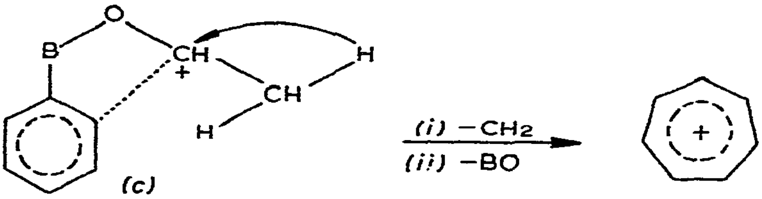


(II)

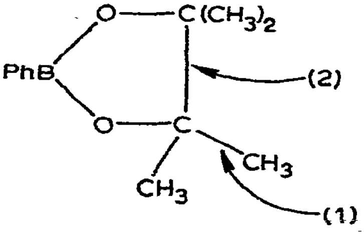
SCHEME 2. FRAGMENTATION PATTERN FOR 4,5-DIMETHYL-2-PHENYL-1,3,2-DIOXABOROLAN



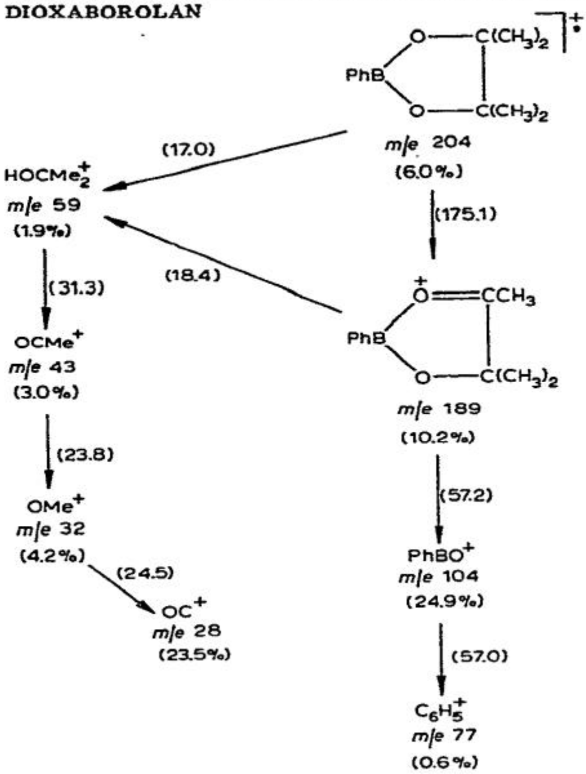
In this compound fragmentation by process 1 involved loss of either of the methyl substituents which were chemically identical. Process 2 led to either the $PhBOCHCH_3^+$ ion or to a rearrangement to give the methyltropylium ion. The tropylium ion itself was formed by methyltropylium fragmentation or rearrangement of the $PhBOCHCH_3^+$ ion (*c*), further fragmentation of (*c*) gave the $PhBO^+$ ion.



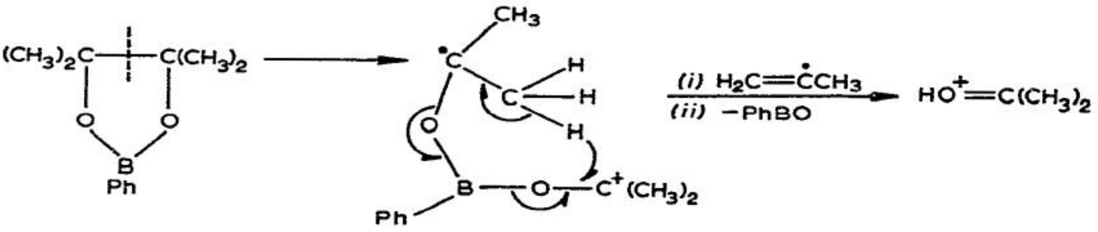
Dimethylation of both C_4 and C_5 in 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolan (Scheme 3) did not alter the primary bond cleavage. A methyl radical was lost by process 1, but C_4—C_5 bond breakage by process 2 to form a $PhBOC(CH_3)_2^+$ ion or a tropylium type rearrangement was not observed.



SCHEME 3. FRAGMENTATION PATTERN FOR 4,4,5,5-TETRAMETHYL-2-PHENYL-1,3,2-DIOXABOROLAN

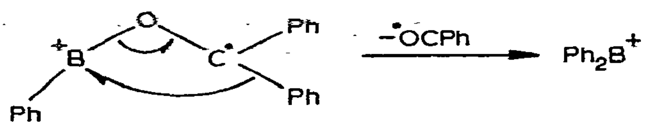


Dimethylation of the annular carbon atoms stabilised the fragments produced from secondary B—O bond fission and enabled the HOC(Me)$_2$ fragment to carry the charge.

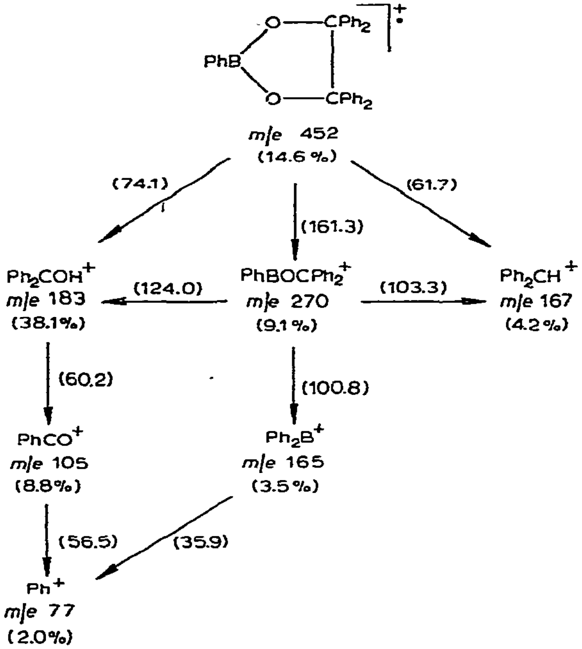


This is the first example of a charged alkoxy fragment produced from a 2-phenyl-1,3,2-dioxaboracycloalkane and shows that ring fragments which contain disubstituted carbon atoms are able to become charge carriers.

In order to test this conclusion further, the spectrum of 2,4,4,5,5-pentaphenyl-1,3,2-dioxaborolan was measured (Scheme 4). The alkoxy fragment Ph$_2$COH$^+$ was the base peak of the spectrum with a total ion abundance of 38.1%. Tropylium type rearrangement was not observed, and the ion formed by phenyl radical loss from the parent was of very low intensity, but the ion PhBOCPh$_2$$^+$ formed by C$_4$—C$_5$ fission was observed. It further fragmented by a rearrangement which appeared to involve B—C bond formation (see over).



SCHEME 4. FRAGMENTATION PATTERN FOR 2, 4, 4, 5, 5-PENTAPHENYL-1, 3, 2-DIOXABOROLAN



The major ions observed for the 2-phenyl-1,3,2-dioxaborolans are shown in Table 1. Monomethylsubstitution in the borolan ring altered the fragmentation skeleton proposed by McKinley [7] very little and methyltropylium ion formation was observed. Disubstitution of each carbon atom in the borolan ring led to a major fragmentation route which involved formation of an R_2COH^+ ion. As can be seen from Table 1, this had the effect of greatly reducing the total percentage of ions containing an intact borolan ring whereas monomethylation of the ring carbon atoms had increased this percentage. The corresponding figure for 2-phenyl-1, 3, 2-dioxaborolan was 44% [12].

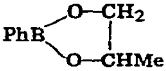
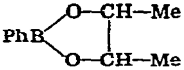
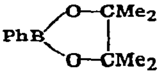
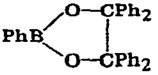
The main feature of the mass spectra of 2-phenyl-1,3,2-dioxaborolans is the formation of hydrocarbon ions by electron-impact-induced rearrangement processes.

Experimental

The mass spectra were recording using an AEI MS902 mass spectrometer operating with an electron beam energy of 70 eV. The source was maintained at 170° and the compounds were introduced as neat liquids using an unheated direct-insertion probe. The 2-phenyl-1, 3, 2-dioxaborolans were prepared by the interaction of dichlorophenylborane with the corresponding diol [14].

TABLE 1

PRINCIPAL IONS OF INTEREST IN THE MASS SPECTRA OF 2-PHENYL-1, 3, 2-DIOXABOROLANS (RELATIVE INTENSITY AS A % OF THE TOTAL IONISATION)

Compound	$[P]^+$ *m/e* (%)	$[P-1]^+$ *m/e* (%)	$PhBO^+$ *m/e* (%)	$C_8H_9^+$ *m/e* (%)	$C_7H_7^+$ *m/e* (%)	Base *m/e* (%)	Ions containing an intact ring (%)
	162 (27.0)	161 (0.2)	104 (7.0)	105 (5.8)	91 (5.4)	*P*-15 (38.4)	65.6
	176 (28.6)	175 (0.4)	104 (14.6)	105 (10.8)	91 (0.4)	*P*-15 (37.0)	66.9
	204 (6.0)	203 (0.3)	104 (24.9)	105 (0.5)	91 (0.2)	28 (23.5)	16.5
	452 (14.6)	451	104	105	91 (0.2)	183 (38.1)	14.6

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