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THE MASS SPECTRA OF SOME 1,3,2-OXAZABOROLIDINES

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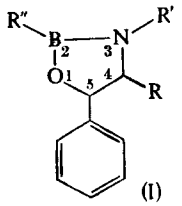
Abstract—Low resolution mass spectra of a series of alkylphenyl-1,3,2-oxazaborolidines are reported. The characteristic fragmentations are shown to be an aid to the elucidation of the substituents in the 1,3,2-oxazaborolidine ring by means of a 'substituent shift' technique.

INTRODUCTION

THE BEHAVIOUR of many five-membered heterocyclic ring systems upon electron-impact is now fairly well documented.[1,2,3] The mass spectra of several boroxines,[4,5] borazoles[6] and diazaboretanes[7] have also been reported, but no detailed study of the mass spectra of oxazaborolidines has been published. This paper deals with the mass spectra of a series of alkylphenyl-1,3,2-oxazaborolidines (I) prepared during a recent survey[8] of the use of cyclic boronate esters as derivatives for gas chromatography and gas chromatography-mass spectrometry (GC-MS). Representative spectra are shown in Figs. 1 to 9. The characteristic fragmentations are an aid to the elucidation of the identity of the substituents in the 1,3,2-oxazaborolidine ring.

Use has been made of a 'substituent shift' technique in the interpretation of the relevant ionic decompositions, and the elemental composition of several ions has been confirmed by high resolution mass measurement.*



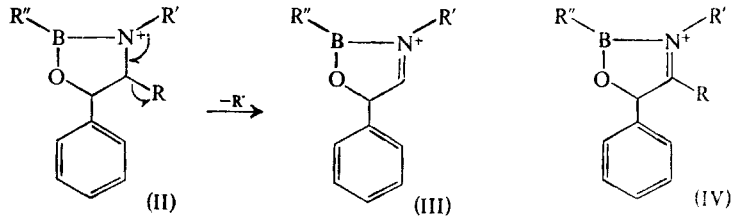
(I) R″ = Me,n-Bu,Ph.
R′ = H,Me.
R = H,Me.

RESULTS AND DISCUSSION

Molecular ion: In each spectrum, there is a relatively intense molecular ion (II). This is a useful feature of these cyclic boronate derivatives, particularly for GC-MS, since it gives their molecular weights directly.

$[M - R]^+$ *ion:* This gives an intense peak, often the base peak, in the spectrum of each of the samples under investigation. Its origin can be inferred from a comparison of the spectra of differently substituted compounds; for example, 2,5-*diphenyl*-1,3,2-*oxazaborolidine* (Ia; R = R′ = H, R″ = Ph) (Fig. 3) and 4-*methyl*-2,5-*diphenyl*-1,3,2-*oxazaborolidine* (norephedrine phenylboronate) (Ib; R = Me, R′ = H, R″ = Ph) (Fig. 6) (see Table 1). Its formation can be represented as in II → III. The alternative loss of a hydrogen atom gives rise to a fairly intense ion at *m/e* [M − 1] (probably as IV) even when there is a methyl substituent in the 4-position.

* Kindly carried out by Dr A. McCormick, AWRE, Aldermaston, Berks, England.



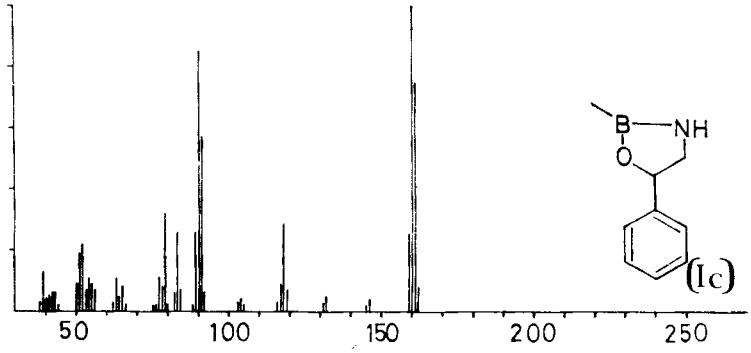


FIG. 1. Mass spectrum of 2-methyl-5-phenyl-1,3,2-oxazaborolidine.

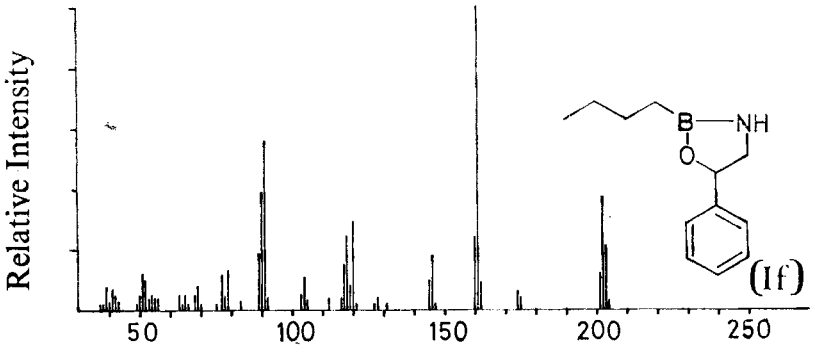


FIG. 2. Mass spectrum of 2-*n*-butyl-5-phenyl-1,3,2-oxazaborolidine.

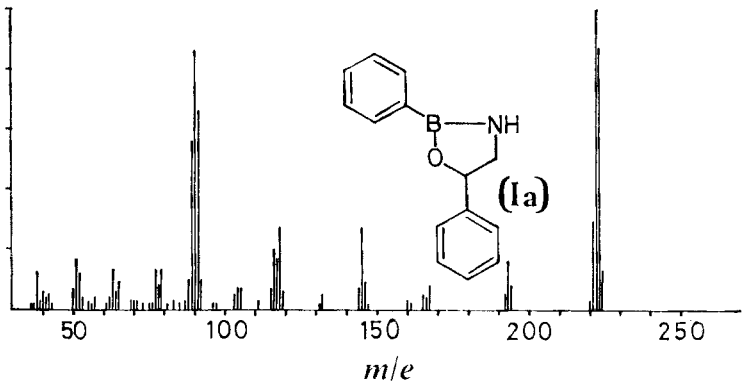


FIG. 3. Mass spectrum of 2,5-diphenyl-1,3,2-oxazaborolidine.

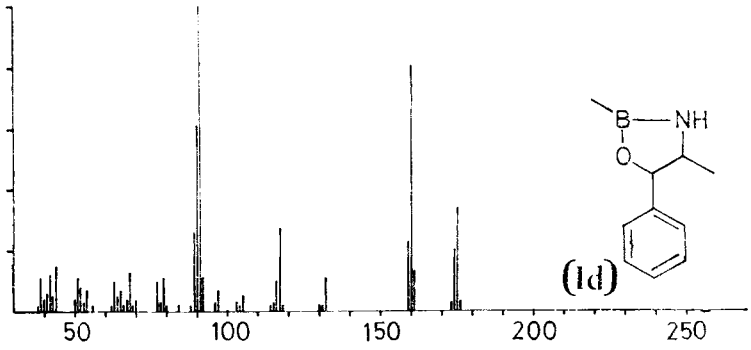


FIG. 4. Mass spectrum of 2,4-dimethyl-5-phenyl-1,3,2-oxazaborolidine.

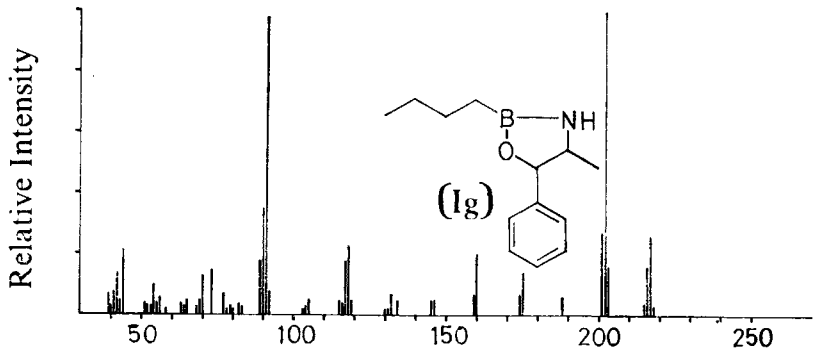


FIG. 5. Mass spectrum of 2-*n*-butyl-4-methyl-5-phenyl-1,3,2-oxazaborolidine.

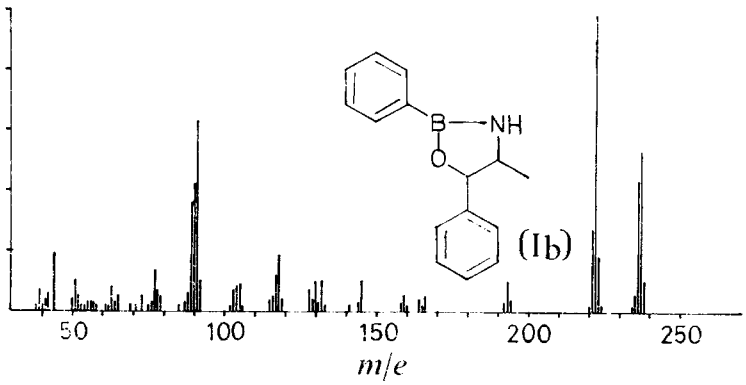


FIG. 6. Mass spectrum of 4-methyl-2,5-diphenyl-1,3,2-oxazaborolidine.

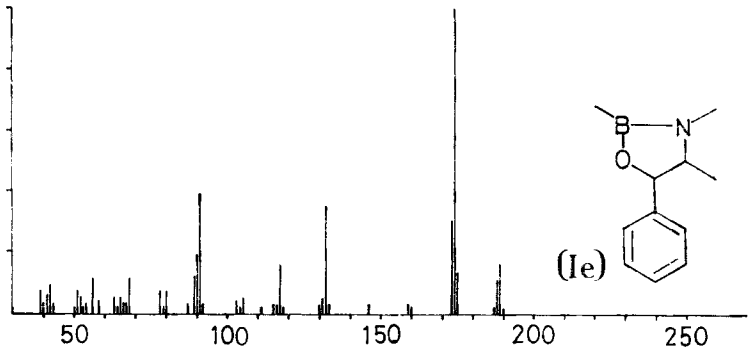


FIG. 7. Mass spectrum of 2,3,4-trimethyl-5-phenyl-1,3,2-oxazaborolidine.

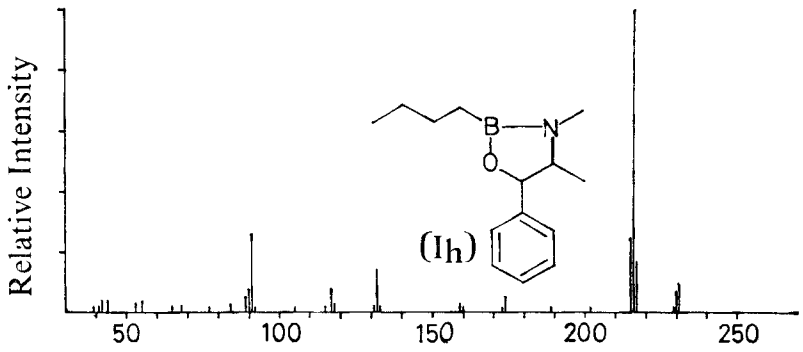


FIG. 8. Mass spectrum of 2-*n*-butyl-3,4-dimethyl-5-phenyl-1,3,2-oxazaborolidine.

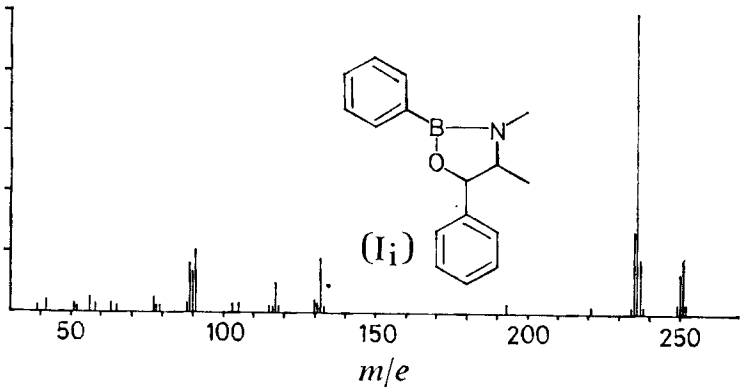


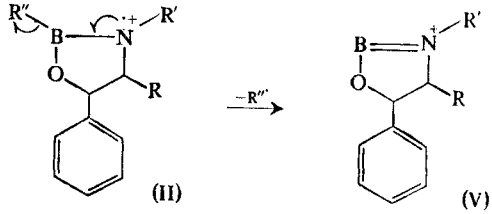
FIG. 9. Mass spectrum of 3,4-dimethyl-2,5-diphenyl-1,3,2-oxazaborolidine.

TABLE 1. SUBSTITUENT SHIFT CORRELATIONS FOR THE SPECTRA REPRESENTED IN FIGS. 1 TO 9

Fig.	Sample	$[M]^{+\cdot}$	$[M-1]^{+}$	$[M-R]^{+}$	$[M-R'']^{+}$	$[117+R']^{+}$	$[117+R'']^{+\cdot}$
1	2-Methyl-5-phenyl-1,3,2-oxazaborolidine	161	160	160	146	118	132
2	2-*n*-Butyl-5-phenyl-1,3,2-oxazaborolidine	203	202	202	146	118	174
3	2,5-Diphenyl-1,3,2-oxazaborolidine	223	222	222	146	118	194
4	2,4-Dimethyl-5-phenyl-1,3,2-oxazaborolidine	175	174	160	160	118	132
5	2-*n*-Butyl-4-methyl-5-phenyl-1,3,2-oxazaborolidine	217	216	202	160	118	174
6	4-Methyl-2,5-diphenyl-1,3,2-oxazaborolidine	237	236	222	160	118	194
7	2,3,4-Trimethyl-5-phenyl-1,3,2-oxazaborolidine	189	188	174	174	132	132
8	2-*n*-Butyl-3,4-dimethyl-5-phenyl-1,3,2-oxazaborolidine	231	230	216	174	132	174
9	3,4-Dimethyl-2,5-diphenyl-1,3,2-oxazaborolidine	251	250	236	174	132	194

Fragmentation directed by the 2-substituents: It can be seen from Figs. 1 to 9 and Table 1 that there is a tendency to lose the 2-substituent from the 1,3,2-oxazaborolidine ring (as in II → V) although this is less pronounced than the formation of the $[M - R]^+$ ion. There is also evidence for the fragmentation of the 2-butyl substituent.

The peak at *m/e* 146 in the spectrum (Fig. 1) of 2-*methyl*-5-*phenyl*-1,3,2-*oxazaborolidine* (Ic; R = R′ = H, R″ = Me) is presumably formed from the molecular ion by loss of the substituent methyl radical. This fragmentation is obscured in the spectra (Figs. 4 and 7) of 2,4-*dimethyl*-5-*phenyl*-1,3,2-*oxazaborolidine* (norephedrine



methylboronate) (Id; R = R″ = Me, R′ = H) and 2,3,4-*trimethyl*-5-*phenyl*-1,3,2-*oxazaborolidine* (ephedrine methylboronate) (Ie; R = R′ = R″ = Me) by the predominant loss of the 4-methyl substituents.

Peaks due to the [M − 57] ions in the spectra of 2-*n*-butyl-5-phenyl-1,3,2-oxazaborolidine (If; R = R′ = H, R″ = Bu^n) (Fig. 2), 2-*n*-butyl-4-methyl-5-phenyl-1,3,2-oxazaborolidine (norephedrine *n*-butylboronate) (Ig; R = Me, R′ = H, R″ = Bu^n) (Fig. 5) and 2-*n*-butyl-3,4-dimethyl-5-phenyl-1,3,2-oxazaborolidine (ephedrine *n*-butylboronate) (Ih; R = R′ = Me, R″ = Bu^n) (Fig. 8) are present at *m/e* 146, 160 and 174, respectively. In the last instance (*m/e* 174), accurate mass measurement confirmed the elemental composition expected for structure V (Table 2). The corresponding peaks in the spectra of the 2-phenyl derivatives are less intense, presumably because of the increased stability afforded by the charge delocalisation over an extra aromatic ring.

The 2-*n*-butyl derivatives apparently decompose to form ions [M − 29] and [M − 42]. For example, there are peaks at *m/e* 188 and 175 in the spectrum of Ig, but no corresponding peaks in the spectra of Id (at *m/e* 146 and 133) and Ib (at *m/e* 208 and 195). Two simple routes, both involving 4-membered cyclic rearrangements, can be envisaged for the formation of [M − 29] ions:

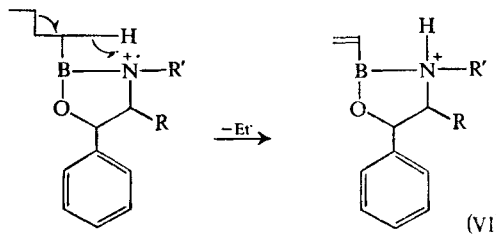
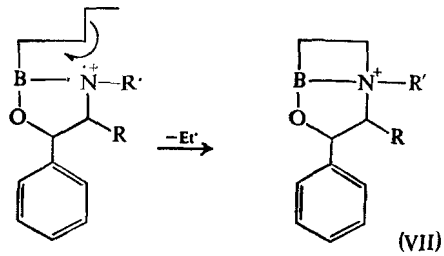


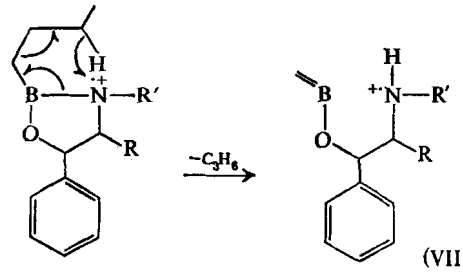
TABLE 2. ACCURATE MASS MEASUREMENTS

Sample	Peak	Measured mass	Possible formulae	Calculated mass	Intensity ratio
2-*n*-Butyl-3,4-dimethyl-5-phenyl-1,3,2-oxazaborolidine	174	174·1090	$[C_{10}H_{13}BNO]^+$	174·1090	Singlet
	117	117·0704	$[C_9H_9]^+$	117·0704	2
		117·0577	$[C_8H_7N]^{+\cdot}$	117·0578	2·9
		117·0511	$[C_7H_6BO]^+$	117·0512	1
3,4-Dimethyl-2,5-diphenyl-1,3,2-oxazaborolidine	117	117·0704	$[C_9H_9]^+$	117·0704	1
		117·0577	$[C_8H_7N]^{+\cdot}$	117·0578	4
2,5-Diphenyl-1,3,2-oxazaborolidine	90	90·0471	$[C_7H_6]^{+\cdot}$	90·0470	Singlet
	89	89·0392	$[C_7H_5]^+$	89·0391	2
		89·0560	$[C_6H_6B]^+$	89·0563	1



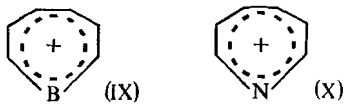
(VII)

The [M − 42] ion, on the other hand, is more likely to be formed *via* a six membered cyclic rearrangement, with the elimination of a neutral propylene molecule:



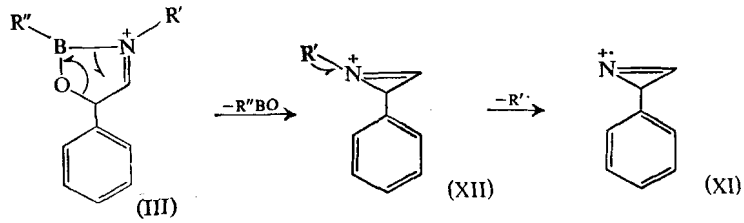
(VIII)

The 2-phenyl substituent does not appear to undergo extensive fragmentation, but it is of interest to note a possible incorporation of the boron atom into a tropylium-like ion (IX). High resolution mass measurement has shown (Table 2) that the peak in the spectrum of Ia at *m/e* 89 is due, in part, to the ion $[C_6H_6B]^+$. The existence of an analogous azatropylium ion (X) has been postulated in the spectrum of sulphathiazole.[9,10]



(IX) (X)

Fragmentations of the 1,3,2-*oxazaborolidine ring:* A study of the observed substituent shifts indicates that the ring undergoes extensive fragmentation, directed to some extent by the nature of the substituents. One of the most significant peaks in the low resolution spectra is that at *m/e* 117: this was further investigated by high resolution mass measurement (Table 2). For Ih it was found that the peak at *m/e* 117 was a triplet, the components of which were shown unequivocally to have the elemental compositions $[C_9H_9]^+$, $[C_8H_7N]^{+\cdot}$ and $[C_7H_6BO]^+$. The nitrogen-containing species is probably of the phenylazirine type (XI) and is likely to be produced via the ions III and XII. Ions corresponding to XII were observed, at *m/e* 118 and 132, for compounds with R′ = H and Me respectively (Table 1).



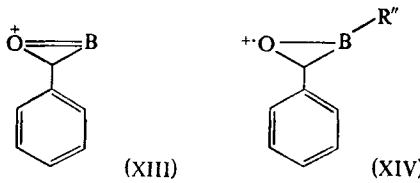
(III) (XII) (XI)

Ion XI is similar to the thiiren species postulated in the spectrum of thiophene.[11, 1] The ion $[C_7H_6BO]^+$ is probably formed in a similar way, and may be tentatively assigned the phenyloxaboriren structure (XIII). Ions retaining the group R″, and ascribable to the species XIV (117 + R″: Table 1) are prominent in the spectra (Figs. 1 to 9).

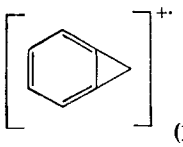
Alternatively, acyclic structures for both nitrogen- and boron-containing species may be postulated. Similarly, the $[C_9H_9]^+$ ion can be satisfactorily accounted for, from the 4-methyl-1,3,2-oxazaborolidines, as either a phenylcyclopropanyl or a phenylpropenyl species.

Hydrocarbon fragments: The peak at *m/e* 91 in all of the spectra is ascribed mainly to the tropylium ion formed by incorporation of the adjacent carbon atom into the 5-phenyl substituent, with hydrogen transfer probably from C-4.

The abundant fragments at *m/e* 89 and 90 have been shown by high resolution mass measurement to be mainly of the hydrocarbon type (Table 2). Similar peaks are not observed in the spectrum[13] of toluene, so it can be assumed that they do not arise from fragmentation of the tropylium ion, but rather from further breakdown of other fragment ions. Structures XV and XVI have been postulated for ions of *m/e* 90 and 89 observed for example, in the spectra of benzofuran derivatives[14] coumarin[15] and furanocoumarins.[16,17]



(XIII) (XIV)



(XV)

(XVI)

Metastable peaks: Metastable transitions were observed for all of the fragmentations proposed, either for the 5-phenyl derivatives described here, or other corresponding 5-aryl derivatives.[18]

CONCLUSIONS

Fragmentation patterns have been proposed for the formation of significant ions in the mass spectra of a series of substituted 1,3,2-oxazaborolidines. The value of a substituent shift technique has been demonstrated in this investigation. We describe elsewhere[18] the application of correlations outlined in this paper to the study of biologically active hydroxyamines as their cyclic boronate derivatives.

EXPERIMENTAL

All low resolution mass spectra were recorded on an LKB 9000 gas chromatograph-mass spectrometer under the following conditions: accelerating voltage, 3·5 kV; electron energy, 70 eV; trap current, 60 μA; ion source temperature, 290°C; molecular separator temperature, 275°C.

The following 1,3,2-oxazaborolidines were prepared by treatment of the hydroxy-amine (1 to 1·5 mg) with 1·5 molar equivalents of the appropriate boronic acid in pyridine (1 ml) at room temperature overnight: 2,5-diphenyl-, and 2-methyl-5-phenyl- (from β-hydroxy-β-phenylethylamine), 4-methyl-2,5-diphenyl- and 2,4-dimethyl-5-phenyl- (from norephedrine) and 2,3,4-trimethyl-5-phenyl- (from ephedrine). Aliquots of the reaction mixtures were injected directly on to the gas chromatography column (1% OV-17 on Gas Chrom Q (100 to 120 mesh), 10 ft × 4 mm I.D. silanised glass tubing).

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