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ORGANOBORON COMPOUNDS

XXVI *. A MASS SPECTRAL STUDY OF SOME 2-PHENYL-1,3,2-DIAZABORACYCLOALKANES

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Summary

The mass spectra of the 2-phenyl-1,3,2-diazaboracycloalkanes contain peaks at *m/e* 91, 89, 65 and 63 which we assign to the tropylium, boratropylium, cyclopentadienyl and boracyclopentadienyl ions.

Introduction

For some time we have been investigating the mass spectra of organometallic compounds. Our initial studies, in which we observed election-impact rearrangements resulting in the formation of hydrocarbon ions in the mass spectrum of 2-phenyl-1,3,2-dioxaborolan, attracted some interest [2–7]. We have reported the results of our mass spectral studies on 2-phenyl-1,3,2-oxazaborolans [8], 2-substituted-4-methyl-1,3,2-dithiaborolans [9], 2-substituted 1,3,2-oxathiaborinans [10] and 2-phenyl-1,3,2-dioxaborinans [11]. We now present our observations concerning the mass spectra of some 2-phenyl-1,3,2-diazaboracycloalkanes. With the exception of a brief description of general features the fragmentation of 2-phenyl-1,3,2-diazaboracycloalkanes [12] and our communication [13], no detailed mass spectral information on these compounds has previously been published.

The mass spectrum of 2-phenyl-1,3,2-diazaborolan is discussed in detail and the general features of the mass spectra of 2-phenyl-1,3,2-diazaboracycloalkanes are commented on. The ions of importance are given in Table 1.

2-Phenyl-1,3,2-diazaborolan (Scheme 1) was observed to fragment via cleavage of one of four bonds.

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* For part XXV see ref. 15.

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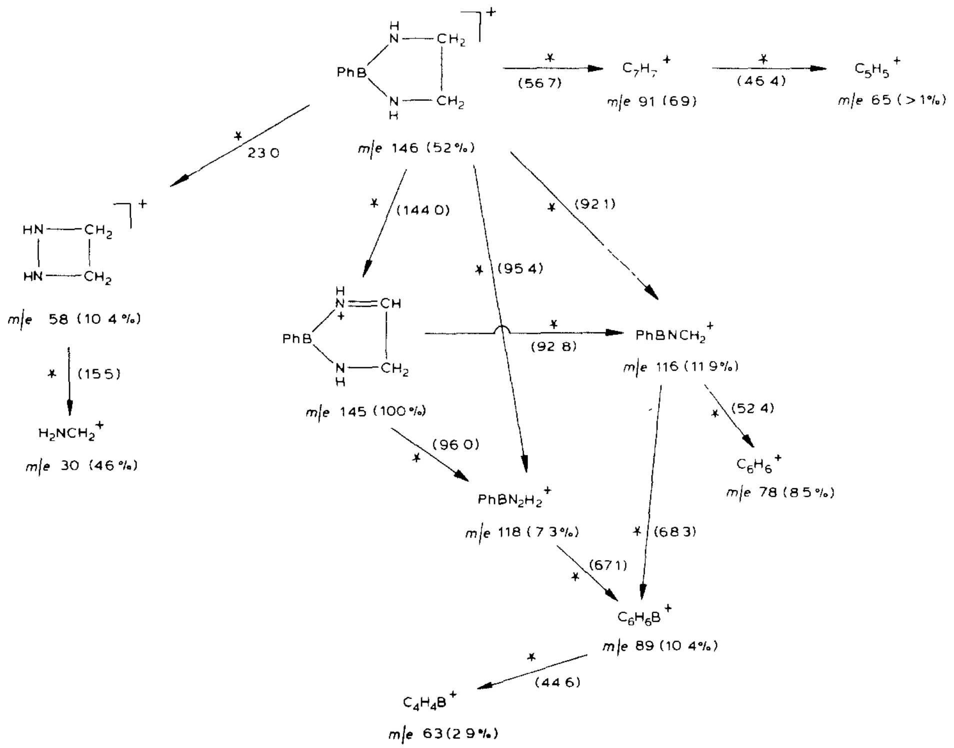
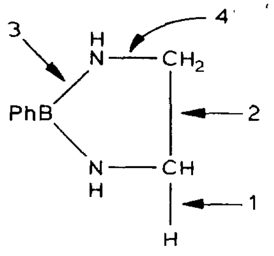


SCHEME 1. Proposed fragmentation pathway for 2-phenyl-1,3,2-diazaboracyclopentane (relative intensity as a percentage of base peak), ★ indicates metastable observed.



Process 1 involves the loss of an annular carbon-hydrogen atom which allowed one of the annular nitrogen atoms to take the charge by double N=C bond formation. Process 2 resulted in the formation of the $PhBNCH_2^+$ ion or the tropylium ion. Process 3 appeared to involve B–N bond fission followed by formation of a four-membered ring:

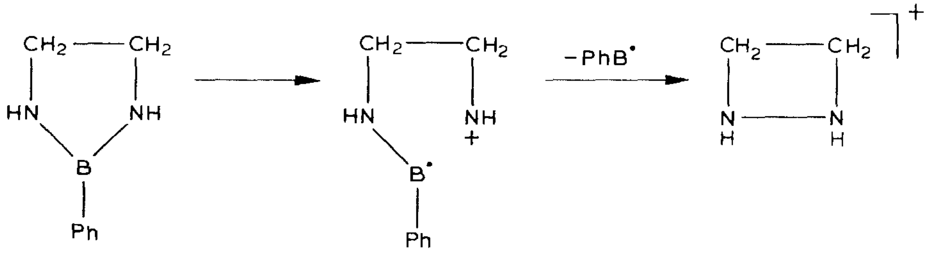
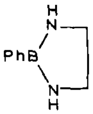
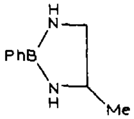
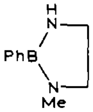
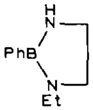
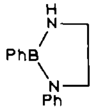
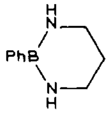
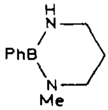
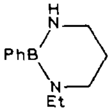
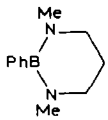
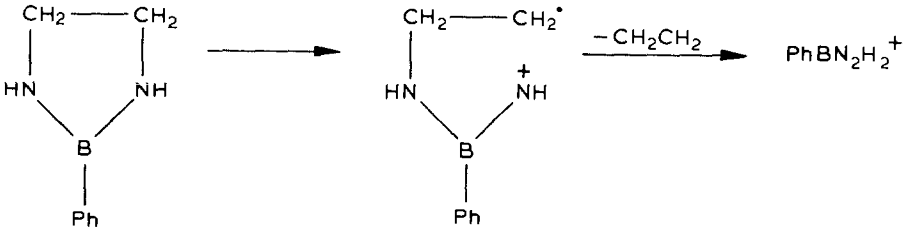


TABLE 1

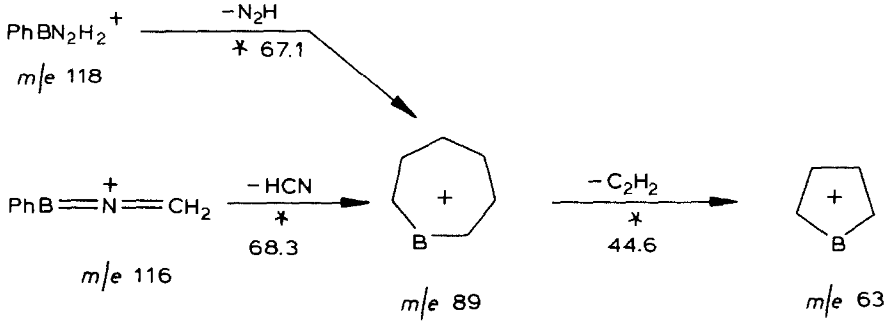
PRINCIPAL IONS OF INTEREST IN THE MASS SPECTRA OF 2-PHENYL-1,3,2-DIAZABORACYCLOALKANES (*m/e* values based on ^{11}B; relative intensities as a percentage of base peak)

Compound	Parent *m/e* (%)	Relative intensity (%)						
		P–H	C_8H_9 (*m/e* 105)	C_7H_7 (*m/e* 91)	C_6H_6B (*m/e* 89)	C_5H_5 (*m/e* 65)	C_4H_4B (*m/e* 63)	base
	146 (52)	100		6.9	10.4	>1	2.9	P–H
	160 (16.7)	9.4	1.7	5.3	10.0	1.1	3.3	P–15
	160 (56.7)	100	–	6.8	16.7	>1	4.3	P–H
	174 (22.7)	9.1	2.7	6.8	22.7	>1	5.9	P–15
	220 (100)	58.3	–	12.0	9.5	3.7	2.3	P
	160 (80.65)	100	5.8	5.5	6.8	2.4	2.4	P–H
	174 (80.6)	100	3.7	7.4	14.2	>1	3.5	P–H
	188 (25.6)	11.3	2.4	6.1	13.0	>1	3.0	P–15
	188 (80.6)	100	2.3	6.5	13.9	>1	3.2	P–H

Process 4 led to the formation of the $PhBN_2H_2^+$ ion resulting from the elimination of ethylene.



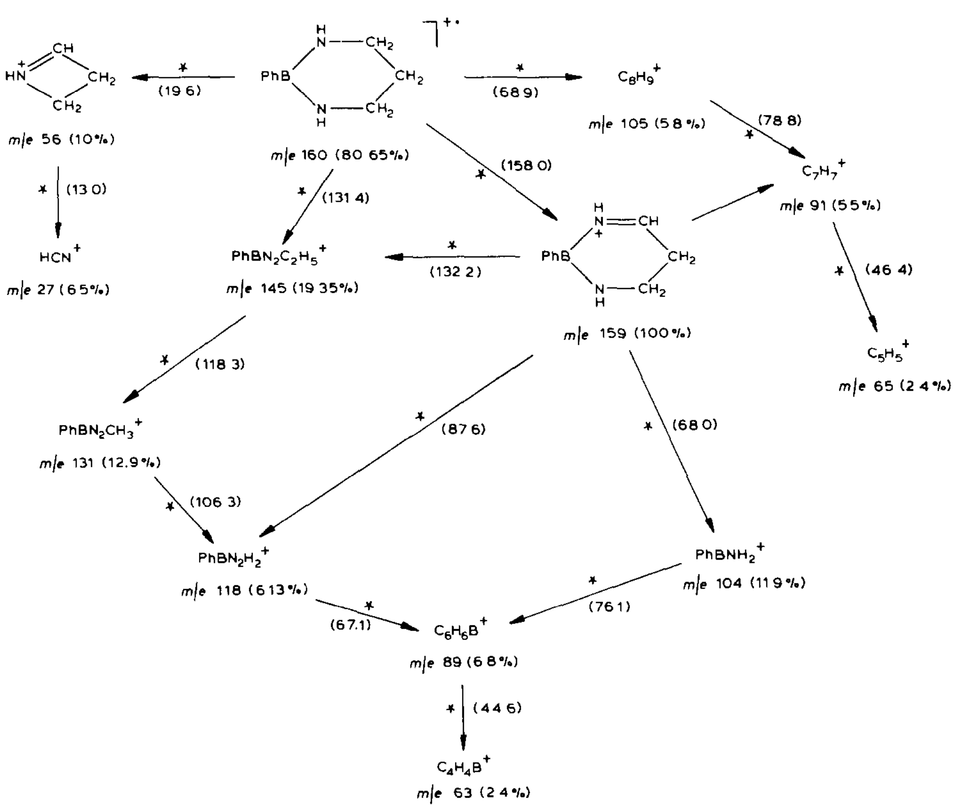
The $PhBNCH_2^+$ and $PhBN_2H_2^+$ ions fragmented further by loss of HCN or N_2H respectively to give an ion m/e 89 which further fragmented by loss of acetylene to give an ion m/e 63, the process characterised by a metastable at 44.6. Precise mass determinations of these ions showed them to have the formulation C_6H_6B and C_4H_4B.



The spectrum also contained ions at *m/e* 91 and 65 and these two ions are identified as the tropylium and cyclopentadienyl ions by precise mass determination and an accompanying metastable at 46.4 for the *m/e* 91/65 process. We therefore suggest that the ions at *m/e* 89 and 63 are the analogous boratropylium and boracyclopentadienyl ions. The borotropylium ion has previously been reported for three compounds [5,14] and the results support our suggestion that the formation of the boratropylium and boracyclopentadienyl ions is a general process observed in the mass spectra of heterocyclic organoboranes containing at least one boron–nitrogen bond [13].

We observed that the basic fragmentation pathway for 2-phenyl-1,3,2-diazaborinan was similar to that for 2-phenyl-1,3,2-diazaborolan (Scheme 2). Carbon–carbon bond cleavage resulted in the formation of the tropylium and methyltropylium ions, loss of a hydrogen atom from an annular carbon atom adjacent to a nitrogen atom and elimination of a four-membered heterocycles from the parent after N–C bond fission were observed. In addition loss of a methyl radical followed by CH_2 and CH (the ions involved being identified by precise mass determination) were also observed as well as the elimination of a propyl group from the $(P-H)^+$ ion resulting in the formation of the $PhBN_2H_2^+$ ion.

An examination of the mass spectra of the compounds listed in Table 1 enables the following comments to be made concerning the fragmentation pathways of 2-phenyl-1,3,2-diazaboracyloalkanes: (1) Loss of an annular carbon hydrogen atom



SCHEME 2. Proposed fragmentation pathway for 2-phenyl-1,3,2-diazaborinan (relative intensity as a percentage of base peak), ★ indicates metastable observed.

adjacent to a nitrogen atom or loss of a carbon substituent (eg. CH_3).

(2) Formation of a tropylium ion by rearrangement and phenyl ring expansion.

(3) Loss of alkyl or alkene groups to form the $PhBN_2H_2^+$ which is an intermediate in the formation of the boratropylium ion although higher ions, including the parent ions, were observed to fragment directly to the boratropylium ion to a small extent.

Experimental

General procedures

All the 2-phenyl-1,3,2-diazaboracycloalkanes were prepared by established methods [12]. 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 near liquids or solids using an unheated direct-insertion probe.

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