Boratropylium and Boracyclopentadienyl Ions in the Mass Spectra of Aminoboranes

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Summary Acyclic and cyclic derivatives of organoboranes, containing at least one boron–nitrogen bond, give peaks in their mass spectra assignable to the boratropylium and boracyclopentadienyl ions.

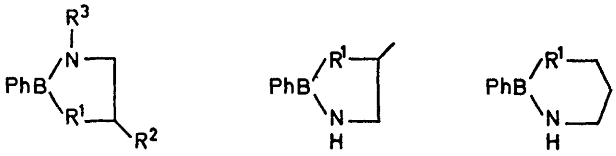
The formation of the tropylium ion, by electron impact, from 2-phenyl-1,3,2-dioxaborolane[1] has aroused considerable interest,[2–5] in the formation of hydrocarbon rearrangement ions (mainly the tropylium ion) from organophenylboranes under electron impact.

We now demonstrate that in the mass spectra of organoboranes containing at least one boron–nitrogen bond rearrangement, ions containing one boron atom are observed. The mass spectra of these compounds have at least four significant peaks *m/e* 91, *m/e* 65, *m/e* 89 and *m/e* 63.

Base peaks and relative intensities of the boratropylium and boracyclopentadienyl ion (^{11}B isotopic species only)

Compound	Base peak *m/e*	Relative intensities $C_6H_6B^+$	$C_4H_4B^+$
(I)	163	12·7	2·7
(II)	223	20·0	3·8
(III)	147	14·3	5·3
(IV)	146	19·0	4·8
(V)	327	14·0	4·0
(VI)	161	8·1	2·3
(VII)	145	12·0	4·0
(VIII)	145	10·0	3·3
(IX)	160	8·4	2·7
$PhB(NMe_2)_2$	58	13·1	4·6
$PhB(NEt_2)_2$	160	19·0	3·1
Ph_2BNEt_2	58	11·2	3·7

The first two peaks have been identified, as the tropylium and cyclopentadienyl ion, by precise mass measurement and accompanied by a metastable at 46·4 for the *m/e* 91→65 process.



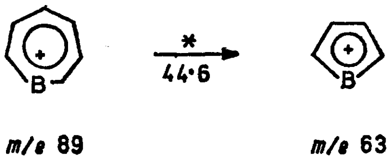
	R¹	R²	R³
(I)	S	H	H
(II)	O	Ph	H
(III)	O	H	H
(V)	O	H	CH_2Ph
(VII)	NH	H	H

	R¹
(IV)	O
(VIII)	NH

	R¹
(VI)	O
(IX)	NH

We find however that peaks at *m/e* 89 and *m/e* 63, by precise mass measurements and metastable scanning, are due to the analogous boratropylium (1) and boracyclopentadienyl (2) ions.

Although the boratropylium ion has been previously reported for three compounds[5,6] we demonstrate that it appears to be present in all the aminoboranes we have studied. However the most significant contributions we make are (i) the first identification of the boracylopentadienyl ion and (ii) the first example of the counterpart of the well known tropylium ion → cyclopentadienyl ion process[7] for a compound where the contributing carbon atom is not directly bonded to the phenyl group in the parent molecule.



(1) (2)

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[1] R. H. Cragg and J. F. J. Todd, *Chem. Comm.*, 1970, 386.
[2] I. R. McKinley and H. Weigel, *Chem. Comm.*, 1970, 1022.
[3] P. B. Brindley and R. Davis, *Chem. Comm.*, 1971, 1165.
[4] R. J. Bose and M. D. Peters, *Canad. J. Chem.*, 1971, **49**, 1766.
[5] C. Cone, M. J. S. Dewar, R. Golden, F. Maseles, and P. Rona, *Chem. Comm.*, 1971, 1522.
[6] C. J. W. Brooks, B. S. Middleditch, and G. M. Anthony, *Org. Mass Spectrometry*, 1969, **2**, 1023.
[7] K. R. Jennings, *Chem. Comm.*, 1966, 283.