Abundant Rearrangement Ions in the Mass Spectra of Benzeneboronic Acid Derivatives

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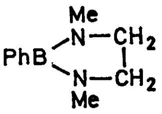
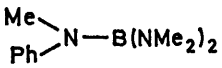
Summary Acyclic as well as cyclic derivatives of benzeneboronic acid give an intense peak in their mass spectra for tropylium ion.

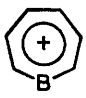
THERE has recently been a number of reports[1] on the formation of tropylium ion from cyclic phenylboranes in the mass spectrometer. We report that prominent peaks due to tropylium also appear in the spectra of acyclic esters of phenylboronic acid and in both acyclic and cyclic phenylbisaminoboranes. The compounds studied include bis(dimethylamino)phenylborane (I), 1,3-dimethyl-2-phenylborazolidine (II), and the diethyl (III) and di-n-butyl (IV) esters of benzeneboronic acid. The Table gives the relative intensities of the molecular ions (^{11}B isotope) and tropylium ion for these compounds. We have previously commented on the unusual abundance of the doubly charged molecular ions of the first two compounds.[2] Accurate mass measurements for compounds (I), (III), and (IV) confirm that the $C_7H_7^+$ ion gives rise to the major peak at *m/e* 91. It is of interest to note that in the high resolution mass spectrum of bis(dimethylamino)methyl(phenyl)aminoborane (V) there is no peak of significant intensity corresponding to $C_7H_7^+$.

TABLE

	Compound	Relative intensities (%) Molecular ion	$C_7H_7^+$
(I)	$PhB(NMe_2)_2$	74	76
(II)	.. ..	59	15
(III)	$PhB(OEt)_2$	15	42
(IV)	$PhB(OBu)_2$	11	36


(II)


(V)


(VI)

Although any specific mechanism drawn for the formation of tropylium ion from these compounds is somewhat conjectural it seems clear that four-membered transition states play an important role in their fragmentation. The formation of other ions involves migration of hydrogen through such transition states. One peak of particular interest in the spectrum of (I) is that at *m/e* 89. In the high resolution spectrum this peak is largely due to an ion with elemental composition C_6H_6B which seems to suggest formation of the boratropylium ion (VI). This same ion has also been noted in the mass spectra of 2-phenyl-1,3,2-oxazaborolidines.[3]

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[3] C. J. W. Brooks, B. S. Middleditch, and G. M. Anthony, *Org. Mass Spectrometry*, 1969, **2**, 1023.