Gaseous Bivalent Borenium Cations

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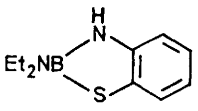
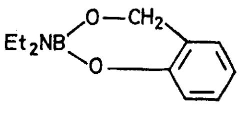
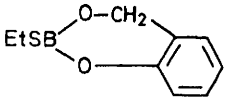
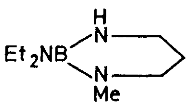
Summary A mass spectral study of a series of heterocyclic organoboranes shows that when the exocyclic group attached to boron is either an amino- or an alkylthio-group then the cyclic borenium ion can have considerable stability.

In our investigations of the mass-spectral fragmentation processes of main-group organometallic compounds, especially those of boron, two significant observations have been made. (*a*) In phenylorganoboranes hydrocarbon rearrangements occur to form, in the main, tropylium[1–3] ions and (*b*) in those compounds containing at least one boron–nitrogen bond boratropylium and boracyclopentadienyl ions can be identified.[4]


(I)


(II)


(III)


(IV)

There has been considerable interest recently concerning the structure of ions, in the gas phase, from organoboranes. One paper in particular provided evidence for the non-stability of borenium ions (BX_2^+) in the gas phase.[5] However the examples chosen, from a wide variety of compounds, invariably had phenyl or oxygen attached to boron in the exocyclic position. Both groups are strongly bonded to boron and hence the mass spectra of these compounds were devoid of borenium ions, presumably owing to the groups in the ring being more weakly bonded to boron than the exocyclic group.

We now report that where the exocyclic group, attached to boron, is weakly bonded (for example an NR_2 or SR group), then peaks in the 70 eV mass spectra which we assign to the borenium ion are of importance. Although in the compounds studied the BX_2^+ ion intensity is always less than that of the respective parent ion, a significant contribution has been observed from (I)—(IV) where the abundances relative to the base peaks (*m/e*—values in parentheses) are 15·5%(58), 15·3%(190), 20·0%(194), and 13·5%(154) respectively. Borenium ions are also observed but in lower yields, from five-membered cyclic compounds of the type $\overline{(\mathrm{CH_2})_2\text{—}\mathrm{Y}\text{—}\mathrm{BNEt_2}\text{—}\mathrm{X}}$, where X = Y = O or S and X = NH, Y = S, and from $\overline{(\mathrm{CH_2})_2\text{—}\mathrm{O}\text{—}\mathrm{BSEt}\text{—}\mathrm{S}}$.

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[1] R. H. Cragg and J. F. J. Todd, *Chem. Comm.*, 1970, 386.

[2] R. H. Cragg, D. A. Gallagher, J. P. N. Husband, G. Lawson, and J. F. J. Todd, *Chem. Comm.*, 1970, 1562.

[3] R. H. Cragg, G. Lawson, and J. F. J. Todd, *J.C.S. Dalton*, 1972, 878.

[4] R. H. Cragg, J. F. J. Todd, R. B. Turner, and A. F. Weston, *J.C.S. Chem. Comm.*, 1972, 206.

[5] J. C. Kotz, R. J. V. Zanden, and R. G. Cooks, *Chem. Comm.*, 1970, 923.