Mass Spectral Studies of Organoboron Compounds. Part I. Facility of Hydrocarbon Ion Rearrangements in some Phenylborolans under Electron Impact

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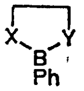
The mass spectra of phenyldioxa-, phenyloxathia-, and phenyldithia-borolans have been examined and a full analysis is reported. The formation of hydrocarbon ions, by electron impact-induced rearrangement, from these heterocycles is rationalised in terms of the relative bond-energies between the atoms in the heterocyclic ring.

THERE has been no systematic mass spectral study of the heterocyclic boron compounds and since our initial communication on the mass spectrum of phenyldioxaborolan,[1a] three further publications by other groups [2-5] have concerned the mass spectra of organoboron heterocycles.

The mass spectral study of heterocyclic boron compounds follows naturally from earlier synthetic work [6,7] and was undertaken to provide information on their stability as a function of the nature of groups attached to boron. We now report our results on some phenylborolans which are of interest because of the novel electron impact-induced rearrangements to form hydrocarbon ions, principally tropylium.

Although the occurrence of the tropylium rearrangement ion is characteristic in the mass spectral fragmentation patterns of aromatic hydrocarbons,[8,9] at the commencement of this present work the only example of this type of rearrangement in compounds where the contributing carbon atom is not directly bonded to the phenyl group in the parent molecule was in the case of alkylphenylphosphonates and related compounds.[10] Recently we have found that organoarsenic heterocycles also exhibit an electron-impact-induced rearrangement to form the tropylium ion.[11]

Mass Spectra.—The low-resolution mass spectra of the three boron heterocycles (I)—(III) are shown as



(I) X = Y = O
(II) X = O, Y = S
(III) X = Y = S

bar diagrams in Figure 1, together with the assignments of the principal ions. For compounds (I) and (II)

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[1] (*a*) R. H. Cragg and J. F. J. Todd, *Chem. Comm.*, 1970, 386; (*b*) R. H. Cragg, D. A. Gallagher, J. P. N. Husband, G. Lawson, and J. F. J. Todd, *Chem. Comm.*, 1970, 1562.

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

[3] I. R. McKinley and H. Weigel, *Chem. Comm.*, 1970, 1022.

[4] P. B. Brindley and R. Davis, *Chem. Comm.*, 1971, 1165.

[5] R. J. Bose and M. D. Peters, *Canad. J. Chem.*, 1971, **49**, 1766.

[6] R. H. Cragg, *J. Inorg. Nuclear Chem.*, 1968, **30**, 395.

[7] R. H. Cragg, *Chem. Comm.*, 1969, 832.

[8] H. Budzikiewicz, C. Djerassi, and D. H. Williams, 'Interpretation of Mass Spectra of Organic Compounds,' Holden Day Inc., San Francisco, California, 1964.

[9] H. M. Grubb and S. Meyerson, in 'Mass Spectrometry of Organic Ions,' ed. by F. W. McLafferty, Academic Press, New York, 1963, p. 435.

[10] H. Budzikiewicz and Z. Pelah, *Monatsh.*, 1965, **96**, 1739.

[11] R. H. Anderson, R. H. Cragg, and J. F. J. Todd, to be published.

ambiguities arise in the *m/e* 116—118 and 102—105 regions due to $^{11}B/^{10}BH$ doublets, and the proportions of the various isotopic ions were calculated from the naturally occurring $^{10}B:^{11}B$ ratio (taken as 1 : 4) and precise mass measurements. These calculations were found to be consistent when the ion intensities were large (116—118) but were less reliable for the weaker ions (102—105).

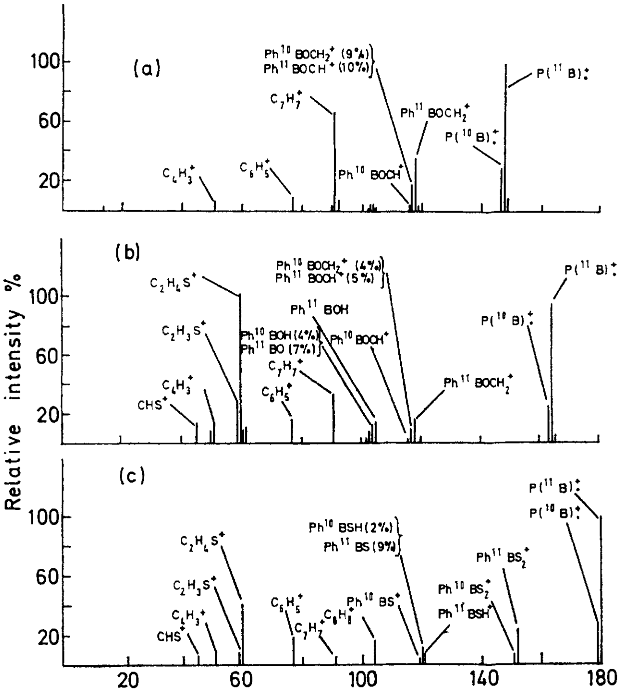
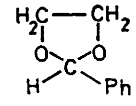


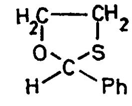
FIGURE 1 Bar diagrams showing the relative intensities (percentages) of principal peaks in the mass spectra of compounds (I)—(III). (a) Phenyldioxaborolan (I), *M* 148; (b) phenyloxathiaborolan (II), *M* 164; (c) phenyldithiaborolan (III), *M* 180

A common feature of the mass spectra of all three compounds is the exceptional stability of the parent molecule towards bombardment with 70 eV electrons. For compounds (I) and (III) the parent ion forms the base peak in the spectrum and for (II) it is only slightly less abundant than the ion with *m/e* 60, assigned as $C_2H_4S^{+\cdot}$. This behaviour contrasts markedly with that of aliphatic ethylene acetals where the total absence of molecular ions was noted [12] and of the acetal (IV) and thioacetal (V). The 70 eV mass spectrum of (IV) shows [13] a $P^{+\cdot}$ abundance of 37% relative to the $(P - 1)^+$ peak as base and (V) is even less stable [13] with $P^{+\cdot} = 0{\cdot}5\%$ and $(P - 1)^+ = 1{\cdot}6\%$ relative to *m/e* 121 as base.

Fragmentation Paths.—The decomposition ' maps ', which have been postulated on the basis of observed metastable ions coupled with metastable scanning, are shown for compounds (I)—(III) in Figure 2. Also indicated are the approximate percentages of the total ionisation appearing at the various values of *m/e*. A significant feature is the formation of hydrocarbon ions by rearrangement processes, and, as already indicated, for (I) and (II) that occurring at *m/e* 91 has been assigned as $C_7H_7^+$ (precise mass) and postulated to be the tropylium ion. This ion has been observed only in very low abundance in the mass spectrum of phenyldithiaboralan (III) (Table) whereas the species $C_8H_8^+$ (*m/e* 104, precise mass) is unique to this compound.



(IV)



(V)

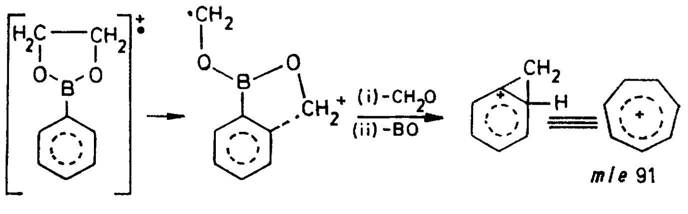
The mass spectrum of (II) is, in some senses, a hybrid of (I) and (III). Evidently the relative stability of the parent ion from (II) is somewhat reduced with a large part of the total charge residing on a species $C_2H_4S^{+\cdot}$ (*m/e* 60), which has the ethylene sulphide structure. Further ions containing C, H, and S at *m/e* 59 and 45 are also prominent.

The abundances of fragment ions from (II) containing B–S were exceedingly low and analogous pathways stemming from the ion $PhBOCH_2^+$ (*m/e* 118) were observed for both (I) and (II), although the distributions of charge between the various ions differed in the two systems. There was no evidence of the oxygen analogue of the ion $PhBS_2^+$ (*m/e* 152), formed in the spectrum of (III), occurring as a decomposition product of the dioxaborolane (I).

As previously reported [1a,b] and generalised by Cooks *et al.*,[2] the borenium ions corresponding to $(P^{+\cdot} - C_6H_5)$ were present only in very low abundance. This is not to be unexpected for cyclic structures where placing the positive charge on the boron atom precludes retention of trigonal hybridisation.[14]

DISCUSSION

Metastable ions in the mass spectrum of phenyldioxaborolan (I) indicate that $C_7H_7^+$ is formed both directly from the parent ion and indirectly *via* the species $PhBOCH_2^+$. This suggests that the primary scission occurs at the C–C bond in the heterocyclic ring:



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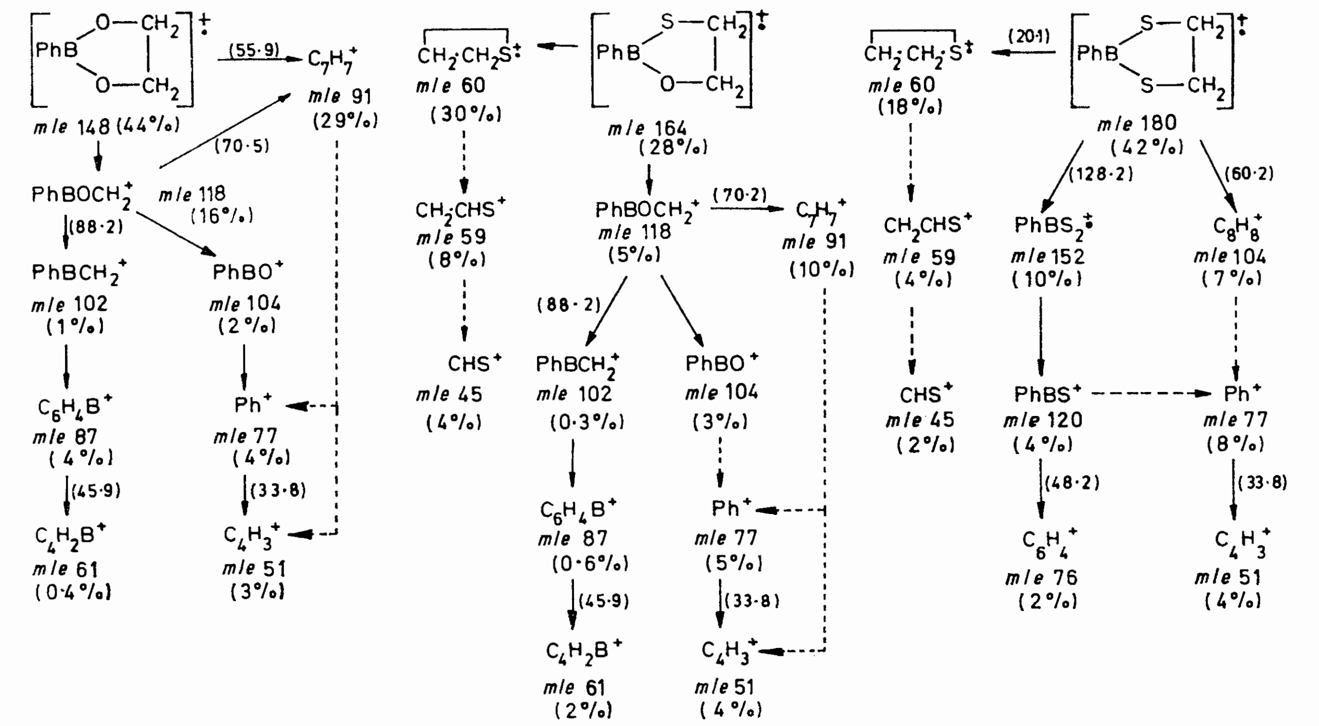
[12] R. G. Cooks, A. N. H. Yeo, and D. H. Williams, *Org. Mass Spectrometry*, 1969, **2**, 985.

[13] R. H. Cragg, G. Lawson, and J. F. J. Todd, unpublished work.

[14] Preliminary examination of the negative-ion spectra of these compounds suggests that the analogous borenide anion is also unstable.

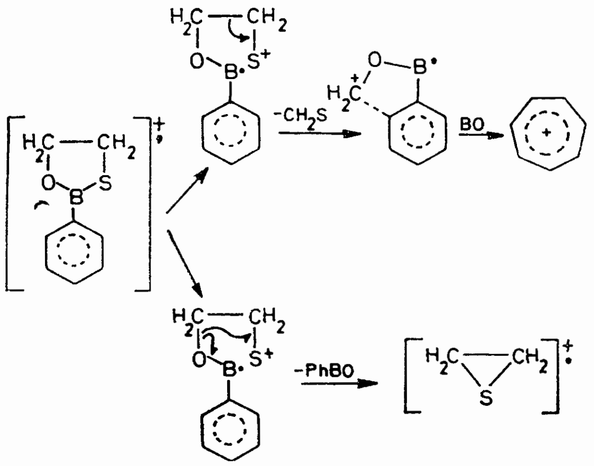
Deuterium-labelling studies which support this mechanism have recently been reported.[5]



(*a*) Phenyldioxaborolan (I) (*b*) Phenyloxathiaborolan (II) (*c*) Phenyldithiaborolan (III)

FIGURE 2 Postulated principal fragmentation paths (^{11}B species only). Heavy arrows indicate confirmation by observed metastable ions as shown, or metastable scanning. The quantities shown in parentheses are approximate percentages of the total ionisation arising from the ions in the respective diagrams

In the case of compound (II), where formation of $C_7H_7^+$ direct from the parent ion was not observed but only from $PhBOCH_2^+$, the primary scission would appear to be at the B–S bond followed by a competition involving either loss of CH_2S or formation of the $CH_2CH_2S^+$ ion, as represented by the tentative scheme:



These two primary modes of bond scission for compounds (I) and (II) are consistent with the hypothesis that the activation energies for the breaking of particular bonds are reflected in the relative bond energies for the ground-state molecule.[16] Thus in phenyldioxaborolan (I) the B–O bond energy (*ca.* 120 kcal mol^{-1}) [15] is considerably greater than that of the C–O bond (*ca.* 86 kcal mol^{-1}) [15] or the C–C bond (*ca.* 83 kcal mol^{-1}).[15] By contrast, in (II) the B–S bond (*ca.* 68 kcal mol^{-1}) [16] is weaker than the B–O and C–C bonds and is of the same order as the C–S bond (65—74 kcal mol^{-1}).[15] Further evidence in support of the proposed mechanisms lies in the virtual absence of (Ph–B–S)-type ions

Some ion abundances (percentages) in the 70 eV mass spectra

Compd.	Parent ion [a]	Base ion	$C_7H_7^+$ [c] *m/e* 91	$PhC_2H_5^+$ [c] *m/e* 104	$C_2H_4S^+$ *m/e* 60	$C_2H_4O^+$ *m/e* 44
(I)	100	Parent	66			1
(II)	93	$C_2H_4S^+$	32		100	*b*
(III)	100	Parent	4	16	42	

[a] Abundance of ions containing the ^{11}B isotope in the 70 eV mass spectra. [b] Abundance less than 1%. [c] Confirmed by precise mass measurements.

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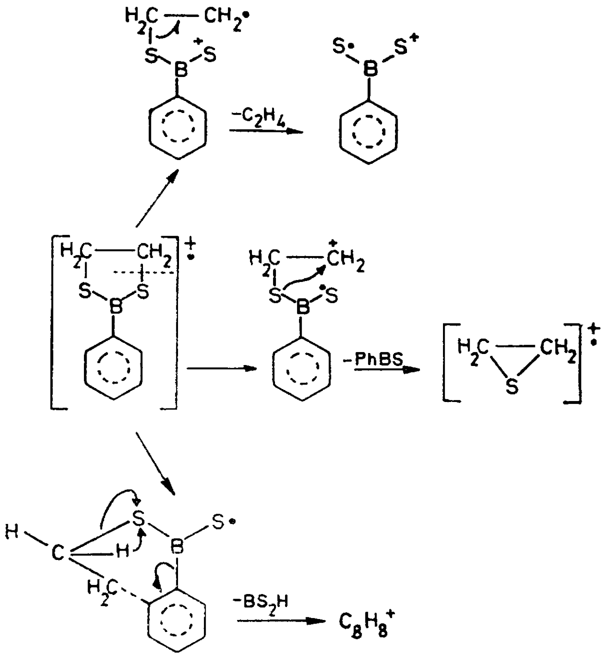
[15] T. L. Cottrell, 'The Strengths of Chemical Bonds,' 2nd edn., Butterworths, London, 1958.

[16] C. A. Brown and L. J. Schupp, Western Reserve University, Technical Research Report, Boron-Nitrogen Compounds, MCC-1023-TR-65, August 1954.

or the expulsion of CH_2O in the mass spectrum of (II) and the absence of $C_2H_4O^+$ ions in the spectra of both (I) and (II) (see Table).

The poor yield of $C_7H_7^+$ from the dithiaboralan (III) indicates that rearrangements of this specific type are not entirely general features of phenylborolans. Indeed at first sight it appears that at least one of the hetero-atoms joined to the boron atom must be oxygen for the formation of $C_7H_7^+$ to be ready. However the relatively high yield of tropylium ion (28%) from the dithioboronic ester[13] $(CH_3S)_2BPh$ (parent ion = 100%) contradicts this view.

It may therefore be suggested that the primary scission consequential upon ionisation of the phenyldithiaborolan molecule is a C–S bond leading to an intermediate species which decomposes by three competitive routes:



This interpretation is only tenable if it can be demonstrated that the relative bond strengths of B–S and C–S are reversed in the two compounds (II) and (III). At this stage detailed energetic information of this kind is not available, however the mass spectral results obtained in this work are consistent with the postulate that the B–S bond in the mixed heterocycle (II) is weaker than in the dithiaborolan (III).

Bonds between boron and atoms such as oxygen and sulphur are characterised by the back donation of π-electron density from the hetero-atom to the boron: it is to be expected that this will be greatest when the orbitals involved are of similar size. Thus the B–O bond is considerably stronger than the B–S bond. On the other hand the presence of one hetero-atom will inhibit back donation from a second atom. This means that replacing a B–S bond in (III) by a B–O bond to give (II) could profoundly reduce the extent of back donation between sulphur and boron, so labilising that bond.

Experimental support for this comes from the relative instability of the parent ion in the spectrum of (II) and the very high yield of the ethylene sulphide ion. Indeed on crude statistical grounds, according to the yield from (III), one might expect that only 9% of the total ionisation would be held by this species whereas the observed abundance is more than three times this figure.

EXPERIMENTAL

The mass spectra were recorded using an A.E.I. MS902 mass spectrometer at 70 eV. The source was maintained at 170 °C and the compounds were introduced as neat liquids using an unheated direct-insertion probe.

The phenylborolans (I)—(III) were prepared by the interaction of dichlorophenylborane with ethyleneglycol, 1,2-mercaptoethanol, and ethane-1,2-dithiol respectively.

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