Formation of Hydrocarbon Ions from Phenylboronates of Diols under Electron Impact

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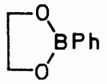
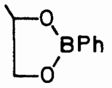
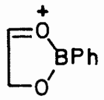
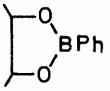
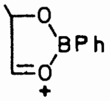
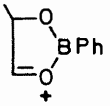
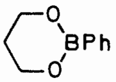
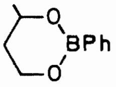
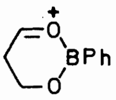
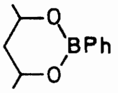
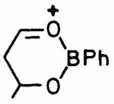
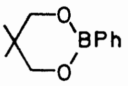
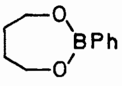
Summary Rearrangement under electron impact seems to be a general property of phenylboronates of diols: depending on the structure of the ester the products of rearrangement are hydrocarbon ions containing 7, 8, 9, and/or 10 carbon atoms.

THE report by Cragg and Todd[1] that the tropylium ion is formed by a rearrangement process from the phenylboronate of ethylene glycol (I) under electron impact prompts us to report that, in our experience, this type of rearrangement seems to be a more general property of cyclic esters of phenylboronic acid.

The Table shows the hydrocarbon ions produced from phenylboronates of diols in an A.E.I. M.S.902 spectrometer

Hydrocarbon ions formed from cyclic esters of phenylboronic acid

	Compound	Abundance of hydrocarbon ions (%Σ25)					Metastable peaks	
		$C_7H_7^{+}$ m/e 91	$C_8H_8^{+}$ m/e 104	$C_8H_9^{+}$ m/e 105	$C_9H_{11}^{+}$ m/e 119	$C_{10}H_{12}^{+}$ m/e 132	Obs. (m/e)	Assignment[a]
(I)		14·5	–	–	–	–	56·1	$(\mathrm{I})^{+} \longrightarrow C_7H_7^{+}$
							70·2	$PhBOCH_2^{+} \longrightarrow C_7H_7^{+}$
(II)		6·5	1·9	2·2	–	–	56·3	 $\longrightarrow C_7H_7^{+}$
							70·2	$PhBOCH_2^{+} \longrightarrow C_7H_7^{+}$
(III)		1·5	5·8	2·6	–	–	61·5	$(\mathrm{III})^{+} \longrightarrow C_8H_8^{+}$
							51·5	 $\longrightarrow C_7H_7^{+}$
							68·6	 $\longrightarrow C_8H_9^{+}$
(IV)		4·6	–	–	–	–	51·1	$(\mathrm{IV})^{+} \longrightarrow C_7H_7^{+}$
(V)		6·6	1·0	1·3	–	–	51·4	 $\longrightarrow C_7H_7^{+}$
(VI)		1·0	2·7	11·3	–	–	63·1	 $\longrightarrow C_8H_9^{+}$
(VII)		2·3	–	–	1·3	0·9	91·8	$(\mathrm{VII})^{+} \longrightarrow C_{10}H_{12}^{+}$
							70·2	$PhBOCH_2^{+} \longrightarrow C_7H_7^{+}$
(VIII)		2·0	3·5	–	–	–	47·1	$(\mathrm{VIII})^{+} \longrightarrow C_7H_7^{+}$
							61·5	$(\mathrm{VIII})^{+} \longrightarrow C_8H_8^{+}$

[a] Calculated using ^{11}B.

operating at 70 ev. In each case, assignment of structure was made from precise mass determinations. From the metastable peaks present in the mass spectra it is deduced that the hydrocarbon ions may arise from rearrangements of (i) the molecular ions, (ii) the resonance stabilised oxonium ions produced on removal of alkyl groups attached to the boronate ring system, and (iii) the ion $PhBOCH_2^+$. Details of the mass spectra of the listed phenylboronates and those of polyhydric alcohols will be published elsewhere.

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