Mass Spectrometry of Cyclic Phenylboronates of Diols and Polyols

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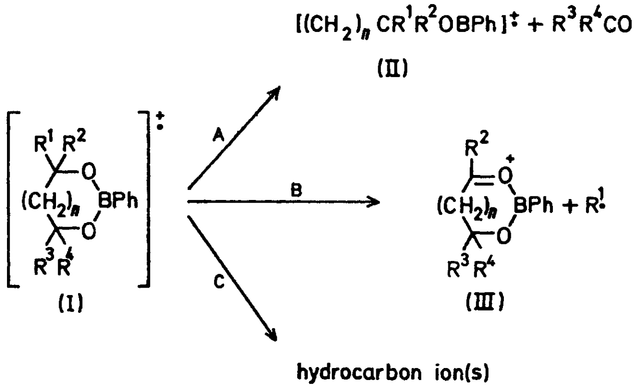
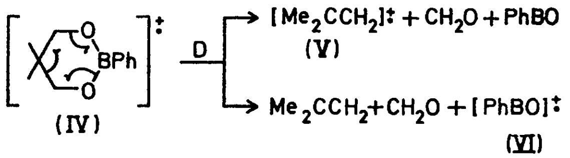
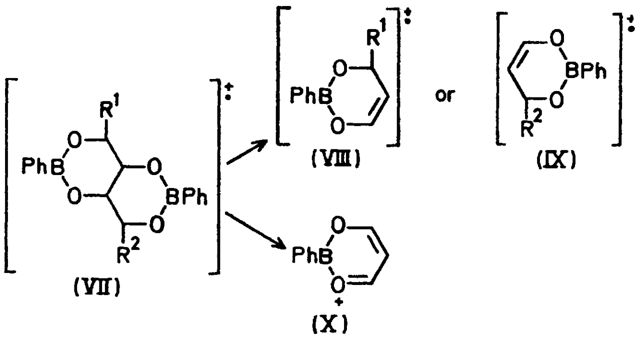
Summary Fragmentation modes of the molecular ions of 5-, 6-, and 7-membered cyclic phenylboronates are reported, one of them being exclusive to 6-membered-ring compounds.

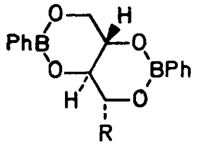
MASS SPECTROMETRY of cyclic phenylboronates of ethane-1,2-diol, propane-1,2-diol, butane-2,3-diol, 2,3-dimethylbutane-2,3-diol, propane-1,3-diol, butane-1,3-diol, pentane-2,4-diol, and butane-1,4-diol has revealed four fragmentation modes of their molecular ions (I; $n = 0$, 1, or 2). Elimination of an oxo-compound[1,2] from all molecular ions produces ion (II) (mode A). Fission of an exocyclic C–C bond in ion (I) produces the oxonium ion (III) (mode B). Skeletal rearrangement may give rise to a series of hydrocarbon ions containing 7, 8, 9, and/or 10 carbon atoms (mode C).[1] The fourth fragmentation mode (mode D), exemplified by the molecular ion of the phenylboronate of 2,2-dimethylpropane-1,3-diol (IV), was exhibited only by the derivatives of 1,3-diols and might thus be characteristic of 6-membered phenylboronate rings. Double elimination gives rise to either the hydrocarbon ion (V) (and CH_2O and PhBO) or the ion (VI) (and $Me_2C{:}CH_2$ and CH_2O). Two fused 6-membered rings, such as in ion (VII), might then be recognised by the ions (VIII), (IX), and/or (X).



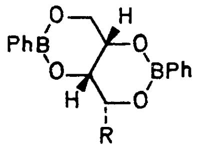




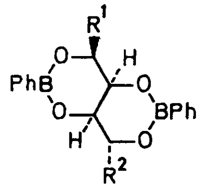
The findings have been applied in the assignment of structures to the bis-phenylboronates of erythritol, L-threitol, 1-deoxy-D-xylitol, D-arabinitol, ribitol, and xylitol and the tris-phenylboronates of galactitol and D-glucitol. Previous knowledge of the structures of these compounds is limited to the fact that the derivatives of the three pentitols possess a primary hydroxy-group.[3] In all cases, the mass spectra exhibited peaks corresponding to the ions (VIII; $R^1 = H$) and (X). The spectra of the tris-phenylboronates exhibited also peaks corresponding to the ion (IX; $R^2 = C_8H_8O_2B$). The combined abundance (% Σ_{40}) of the ions (VIII), (IX), and (X), ranged from 14 to 25. Mass spectrometry of phenylboronates of several triols does not modify ring size.[4] We thus believe that, on the evidence presented here, the above bis- and tris-phenylboronates contain two fused 6-membered rings and that the structure of the derivatives of erythritol (XIa), ribitol (XIb), L-threitol (XIIa), xylitol (XIIb), 1-deoxy-D-xylitol (XIIIa), and galactitol (XVa) are mainly, if not exclusively, those shown (only one enantiomer of each of the ribitol, xylitol, and galactitol derivatives is shown). Work is in progress to distinguish between the possible structures of the derivatives of D-arabinitol (XIIIb and XIVa) and D-glucitol (XIVb and XVb). The method did not detect a fused 6-membered ring system in D-mannitol tris-phenylboronate.



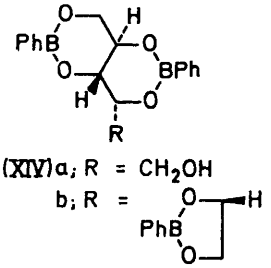
(XI)a; R = H
b; R = CH_2OH



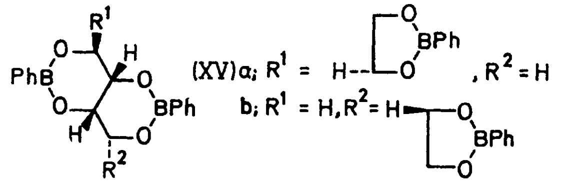
(XII)a; R = H
b; R = CH_2OH



(XIII)a; $R^1 = CH_3$, $R^2 = H$
b; $R^1 = H$; $R^2 = CH_2OH$



(XIV)a; R = CH_2OH
b; R =



(XV)a; R^1 = , R^2 = H
b; R^1 = H, R^2 =

All assignments of atomic composition of ions were deduced from precise mass measurements, and all fragmentation modes were assigned from metastable ions. The phenylboronates of diols, except those of 2,2-dimethylpropane-1,3-diol and butane-1,4-diol, were introduced into a A.E.I. M.S.902 mass spectrometer using an all-glass heated-inlet system. All other compounds were inserted directly on a probe. The temperature of the ion source ranged from 50° to 255° depending on the volatility of the compound.

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[2] R. H. Cragg and J. F. J. Todd, *Chem. Comm.*, 1970, 386.
[3] N. A. Sufi, Ph.D. Thesis, London, 1965.
[4] I. R. McKinley, Ph.D. Thesis, London, 1972.