

Formation of Hydrocarbon Rearrangement Ions from 4,6-Dimethyl-2-phenoxy-1,3,2-dioxaborinan under Electron Impact

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Summary Massspectral studies on 4,6-dimethyl-2-phenoxy-1,3,2-dioxaborinan show that the electron impact-induced rearrangement to form hydrocarbon ions previously reported for phenylboronates of diols also takes place for this compound and this is rationalised in terms of the relative energies of the bonds involved

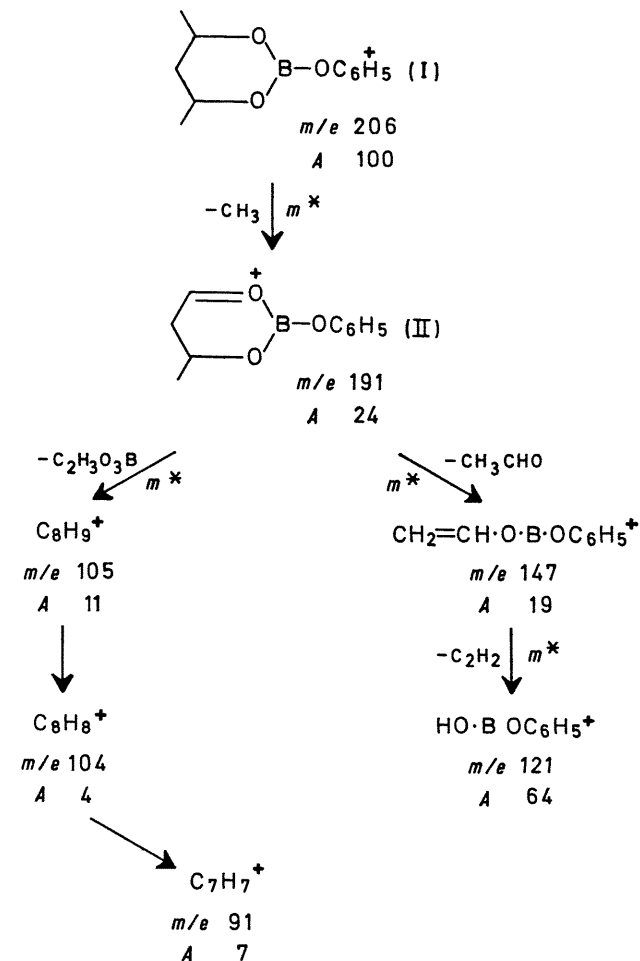
In the course of studies on derivatives of 4,6-dimethyl-1,3,2-dioxaborinans, a ring system selected for its high stability¹ we find that the 2-phenoxy-derivative under electron impact forms hydrocarbon ions by a rearrangement process. Although rearrangements of this type have been recently reported for the system C-O-B-Ph in the case of cyclic esters of phenylboronic acid and their analogues,²⁻⁴ our own observation extending to the C-O-B-OPh system would suggest that this is a rearrangement even more general than suggested by McKinley and Weigel³

The parent ion (I) of 4,6-dimethyl-2-phenoxy-1,3,2-dioxaborinan is observed as the base peak of the spectrum and this fragments *via* the resonance-stabilised oxonium ion (II) to the ion HO·B·OC₆H₅⁺. The details of this fragmentation are given in the Scheme. The ion C₆H₅OH⁺ (A = 25%) is also observed and has been characterised by accurate mass measurement and its expected fragmentation pattern⁵. A second mode of fragmentation has also been observed giving rise to the ions C₈H₉⁺, C₈H₈⁺, and C₇H₇⁺. Only one precursor of the C₈H₉⁺ ion has been definitely identified, that is the oxonium ion (II).

On the basis of these results it appears that hydrocarbon rearrangement ion formation from the compounds CH(CH₃)CH₂CH(CH₃)OBXO (X = Ph or OPh) is a more general process than has so far been reported and appears to reflect the relative strengths of the B-O bond (approx 500 kJ mol⁻¹) and the C-O bond (approx 360 kJ mol⁻¹)⁶ rather than the configuration of any transition state formed prior to rearrangement. However, on this basis the formation of the C₆H₅OH⁺ is not easily rationalised.

Further studies on this and similar compounds and their deuterium analogues are in progress and will be reported elsewhere.

All measurements were made on an A E I MS 9 spectrometer at 70 eV, special precautions being taken to prevent



hydrolysis of the ester. The purity and structure of the ester were confirmed by elemental analysis and n m r measure-

ments Elemental composition for all ions discussed was Mrs J Falla for assistance in obtaining mass spectra established by accurate mass measurements We thank

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¹ A Finch, P J Gardner, and E J Pearn, *Rec Trav chim*, 1965, **83**, 1314

² R H Cragg and J F J Todd, *Chem Comm*, 1970, 386

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

⁴ R H Cragg, D A Gallagher, J P N Husband, G Lawson, and J F J Todd, *Chem Comm*, 1970, 1562

⁵ H Budzikiewicz, C Djerassi and D H Williams "Mass Spectrometry of Organic Compounds", Holden-Day, San Francisco, 1967.

⁶ T L Cottrell, "The Strengths of Chemical Bonds", 2nd edn, Butterworths, London, 1958