# THE STRUCTURE OF THE BENZENEBORONATE OF PENTANE-1,3,5-TRIOL\*

EDWARD J. BOURNE, IAN R. MCKINLEY, AND HELMUT WEIGEL

Department of Chemistry, Royal Holloway College (University of London), Englefield Green, Surrey (Great Britain)

(Received December 13th, 1973; accepted for publication, January 28th, 1974)

### ABSTRACT

The relative ease of formation of five-, six-, seven-, and eight-membered cyclic benzeneboronates is discussed. Pentane-1,3,5-triol forms, by interaction with benzeneboronic anhydride, exclusively DL-4-(2-hydroxyethyl)-2-phenyl-1,3,2-dioxaborinane. It is suggested that, in this compound, the oxygen atom of the hydroxyl group is intramolecularly co-ordinated with the boron atom.

#### INTRODUCTION

Cyclic benzeneboronates possessing five, six, and seven ring-atoms, and which are derived from 1,2-, 1,3-, and 1,4-diols, are well known and thermodynamic properties of some of these have been investigated  $^{1-4}$ . Benzeneboronates possessing eight or more ring-atoms, however, have not been reported. Sugihara and Bowman<sup>5</sup> attempted the synthesis of the benzeneboronate of pentane-1,5-diol, but the liquid product could not be distilled below 300°, and the authors concluded that it was polymeric. As part of our studies of benzeneboronates of carbohydrates and related compounds, we have examined the relative ease of formation of benzeneboronates of acyclic 1,3-, 1,4-, 1,5-, and 1,6-diols, *i.e.*, rings possessing six, seven, eight, and nine atoms, respectively. We now report some of our results.

#### **RESULTS AND DISCUSSION**

The mass spectra of separate reaction mixtures formed from benzeneboronic anhydride and propane-1,3-, butane-1,4-, and pentane-1,5-diols, bis(hydroxyethyl) ether, and hexane-1,6-diol showed peaks corresponding to the molecular ions of the cyclic benzeneboronate of these diols, *i.e.*, respectively,  $C_9H_{11}BO_2^+$  (*m/e* 162),  $C_{10}H_{13}BO_2^+$  (*m/e* 176),  $C_{11}H_{15}BO_2^+$  (*m/e* 190),  $C_{10}H_{13}BO_3^+$  (*m/e* 192), and  $C_{12}H_{17}BO_2^+$  (*m/e* 204). Apart from the molecular ion of unreacted benzeneboronic

<sup>\*</sup>Dedicated to Dr. Horace S. Isbell, in honour of his 75th birthday.

anhydride,  $C_{18}H_{15}B_3O_3^{\dagger}$  (*m/e* 312), and its ionic fragments, ions with *m/e* greater than those given above could not be detected.

These results demonstrate that compounds with structures 1 and 2 are formed under the conditions employed here. However, a quantitative assessment of the relative ease of formation of the benzeneboronates 1 and 2, employing g.l.c., was unsuccessful as either the peaks showed extensive tailing (e.g., 1c) or the benzeneboronates underwent decomposition on the g.l.c. column (e.g., 1d). Nevertheless, g.l.c. of reaction mixtures obtained by competitive reactions between benzeneboronic anhydride, propane-1,3-diol, and one of the other diols mentioned above, and in the molecular ratios 0.33:1:1, always revealed the benzeneboronate of propane-1,3-diol (1a) as the major product.

In view of the unsatisfactory behaviour of the benzeneboronates of the higher diols in g.l.c., we have investigated the interaction between benzeneboronic anhydride and pentane-1,3,5-triol, where the product could be either a six- (3) and/or an eightmembered cyclic benzeneboronate (4). The method of analysis of the product, which was as described in detail for benzeneboronates of other triols<sup>6</sup>, involved (a) methylation of the hydroxyl group, (b) hydrolysis of the benzeneboronate ring, and (c) acetylation of the hydroxyl groups generated in step b. The diacetoxy-methoxy-pentane thus obtained was analysed by g.l.c.-m.s.



The diacetoxy-methoxypentane obtained as described was chromatographically homogeneous and, thus, was likely<sup>6</sup> to be a single compound. This inference was confirmed by m.s. The mass spectrum contained a peak with m/e 45, expected from DL-1,3-diacetoxy-5-methoxypentane (5). A peak corresponding to a fragment with m/e 131, expected from 1,5-diacetoxy-3-methoxypentane (6) could not be detected. Thus, we conclude that pentane-1,3,5-triol forms exclusively the six-membered benzeneboronate 3, *i.e.*, DL-4-(2-hydroxyethyl)-2-phenyl-1,3,2-dioxaborinane.

We have already reported<sup>6</sup> the ratios of the products of the reaction between benzeneboronic anhydride and such triols as glycerol and butane-1,2,4-triol. These and the present results show (Table I) that, although seven-, eight-, and ninemembered cyclic benzeneboronates are formed in separate reactions, in competitive reactions where the products may be five-, six-, seven-, or eight-membered cyclic benzeneboronates, the seven- and eight-membered rings are not formed.

# TABLE I

BENZENEBORONATES OBTAINED FROM TRIOLS

Triol	Mole fra Number				
	5	6	7	8	
Glycerol	0.31	0.69			
Butane-1,2,4-triol	0.10	0.90	0	_	
Pentane-1.3,5-triol	—	1.00		0	

As the benzeneboronate of pentane-1,3,5-triol proved to be a single compound (3), in contrast<sup>6</sup> to those of several other triols, supplementary evidence for the assignment of structure by m.s. was sought. The fragmentation modes of molecular ions of cyclic benzeneboronates have already been reported<sup>7</sup>. The low-resolution mass spectrum of the benzeneboronate of pentane-1,3,5-triol is shown in Fig. 1. Precise masses of the ions produced from the benzeneboronate and precursors of ions in the m.s. of the benzeneboronate are shown in Tables II and III, respectively. It is appreciated that the fragmentation of the molecular ion proceeds by competitive reactions.

# TABLE II

PRECISE MASSES OF IONS PRODUCE	FROM THE BENZENEBORONATE	OF PENTANE-1,3,5,-TRIOL
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Ion	Measured mass (m/e)	Possible formula	Calculated mass (m/e)	Multiplet intensity ratio
26	178.07814	C <sub>9</sub> H <sub>11</sub> BO <sub>3</sub>	178.0801"	····
27	177.0717	C <sub>9</sub> H <sub>10</sub> BO <sub>3</sub>	177.0723	
30	122.0537	C <sub>6</sub> H <sub>7</sub> BO <sub>2</sub>	122.0539	
(30)	121.0574	C <sub>6</sub> H <sub>7</sub> <sup>10</sup> BO <sub>2</sub>	121.0575	
13	105.0508	C <sub>6</sub> H <sub>6</sub> BO	105.0512	
(13)	104.0545	C <sub>6</sub> H <sub>6</sub> <sup>10</sup> BO	104.0548	
		0 0		1/3
22	104.0431	CeHaBO	104.0433	•
(22)	103.0466	C <sub>6</sub> H <sub>5</sub> <sup>10</sup> BO	103.0469	
•				2/1
	103.0352	C <sub>6</sub> H <sub>4</sub> BO	103.0355	
28	101.0409	C <sub>3</sub> H <sub>6</sub> BO <sub>3</sub>	101.0410	
(28)	100.0447	C <sub>3</sub> H <sub>6</sub> <sup>10</sup> BO <sub>3</sub>	100.0448	
()				1/1
29	100.0331	C3H4BO3	100.0332	
20. 21	84.0574	C <sub>5</sub> H <sub>8</sub> O	84.0575	

The relatively large difference between measured and calculated mass (11 p.p.m.) is due to  $^{13}$  C interference from m/e 177.

Deduced from defocussing experiment		Deduced from m/e of metastable ion					
.' <i>'a. "II</i> (m <u>.</u> /e)	Daughter (m <sub>2</sub> /e)	Voltage ratio (V <sub>1</sub> /V)	Parent (m <sub>1</sub> /e)	Daughter (m2/e)	Metastable ion (m/e)		Assignment
					Found.	Calc.	-
			206	188	171.5	171.6	7b→ 17, 18
			206	178	153.8	153.8	<b>25</b> → <b>26</b>
205.2	122	1.690					7a, 7b, 25 → 30
			206	101	49.3	49.5	$25 \rightarrow 28$
206.2	100	2.062					$25 \rightarrow 29$
205.8	84	2.450	206	84	34.3	34.3	$7a \rightarrow 20, 21$
			188	159	134.4	134.5	$17, 18 \rightarrow 23, 24$
187.8	105	1.789				-	$17, 18 \rightarrow 13$
187.8	104	1.804	188	104	57.6	57.5	$17, 18 \rightarrow 22$
187.8	84	2.236	188	84	37.4	37.5	$17, 18 \rightarrow 20, 21$
			178	177	176.0	176.0	$26 \rightarrow 27$
177.4	100	1.774	177	100	56.7	56.5	$27 \rightarrow 29$
			161	91	51.5	51.4	9→11

## TABLE III

PRECURSORS OF IONS IN M.S. OF BENZENEBORONATE OF PENTANE-1,3,5-TRIOL



Fig. 1. Mass spectrum of the benzeneboronate of pentane-1,3,5-triol.

The ion  $CH_3O^+$  (8, *m/e* 31), characteristically produced from primary alcohols (cf. 7a), supports the structure (3) already assigned. In addition, fission of the exocyclic C–C bond in the molecular ion 7a (mode B of ref. 7) produces an oxonium ion 9, which, in turn, fragments in a manner<sup>7</sup> similar to that produced from the molecular ion of the benzeneboronate (10) of butane-1,3-diol. Thus, skeletal rearrangement of 9 gives rise to the hydrocarbon ion  $C_7H_7^+$  (11), whereas consecutive

elimination of  $CH_2O$  and  $C_2H_2$  gives the ions  $[C_2H_3OBPh]^+$  (12) and  $[PhBOH]^+$  (13), respectively.



Previously, we have reported<sup>7</sup> that the mode of fragmentation under electron impact, characteristic of six-membered benzeneboronate rings, is a double elimination (mode D of ref. 7). Accordingly, the molecular ion of the benzeneboronate of pentane-1,3,5-triol would be expected to give ions with m/e 28, 30, 72, 74, and/or 104, as shown in Fig. 2ab. Of these, only the ion [PhBO]<sup>†</sup> (m/e 104) could be detected. However, defocussing experiments have revealed that the parent ion of [PhBO]<sup>†</sup> is not the molecular ion 7a, but the M—H<sub>2</sub>O ion, [C<sub>5</sub>H<sub>8</sub>BO<sub>2</sub>Ph]<sup>†</sup>.



Fig. 2. Fragmentation by double elimination.

Dehydration of the molecular ion 7a might be envisaged to give the ion 14 by a 1,2-elimination. However, evidence for fragmentation of such an ion by double elimination (cf. Fig. 2cd) could not be obtained. On the other hand, dehydration by 1,4-elimination, *i.e.*,  $7b \rightarrow 15$ , could produce the ions 16, 17, and/or 18, the formation



of 17 and 18 involving rearrangement. Fragmentation of the ions 16, 17, and 18 by "double elimination" would give the ion  $[C_5H_8O]^{\ddagger}$  (*m/e* 84), the formation of which is indeed indicated by defocussing experiments and a metastable ion. The ion  $[C_5H_8O]^{\ddagger}$  might have structure 19 (from 16), 20 (from 17), and/or 21 (from 18). However, the M—H<sub>2</sub>O ion also gives the ion  $[C_3H_3O_2BPh]^+$  (*m/e* 159), *i.e.*, by loss of  $C_2H_5$ . It is thus more likely that the M—H<sub>2</sub>O ion has structure 17 and/or 18, which, by cleavage of the exocyclic C–C bond, give the oxonium ions 23 and/or 24, respectively. The formation of 17 and/or 18 is a further demonstration that electron-impact induced dehydration does not proceed by a 1,2-elimination, but is likely to proceed by a 1,4-elimination, involving a six-membered ring transition<sup>8,9</sup> (as shown in structure 7b) and rearrangement of hydrogen atoms.

In addition, simultaneous elimination of  $H_2O$  and PhBO from the molecular ion 7a also produced the ion 20 and/or 21.

An unusual feature of the fragmentation of the molecular ion of the benzeneboronate of pentane-1,3,5-triol was the formation of the ions  $[C_9H_{11}BO_3]^{\ddagger}$  (*m/e* 178),  $[C_3H_6BO_3]^+$  (*m/e* 101), and  $[C_3H_5BO_3]^{\ddagger}$  (*m/e* 100). They were formed by, respectively, elimination of  $C_2H_4$ ,  $C_8H_9$ , and  $C_8H_{10}$ . The ion  $[C_3H_5BO_3]^{\ddagger}$  (*m/e* 100) was also produced by consecutive elimination of  $C_2H_4$ , H<sup>-</sup>, and  $C_6H_5^-$ ; the ions  $[C_9H_{11}BO_3]^{\ddagger}$  (*m/e* 178) and  $[C_9H_{10}BO_3]^+$  (*m/e* 177) being the respective intermediates. The facts that (*a*)  $C_2H_4$  cannot be eliminated from the aromatic portion of the molecular ion, and (*b*) the ions  $[C_3H_6BO_3]^+$  and  $[C_3H_5BO_3]^{\ddagger}$  possessed only three carbon atoms yet all the three oxygen atoms of the original pentane-1,3,5-triol suggested that this fragmentation mode was due to a particular structure adopted by the benzeneboronate.

Boron is strongly electrophilic. Consequently, the properties of many boron compounds have been explained by postulating intramolecular co-ordination of an



electron-donating atom with boron<sup>10-12</sup>. We suggest that such intramolecular co-ordination occurs in the benzeneboronate of pentane-1,3,5-triol, as shown for the molecular ion 25. The fragmentation sequences  $25 \rightarrow 26 \rightarrow 27 \rightarrow 29$ ,  $25 \rightarrow 28$ , and  $25 \rightarrow 29$  are compatible with such a structure. Thus, it is likely that DL-4-(2-hydroxy-ethyl)-2-phenyl-1,3,2-dioxaborinane (3) and its intramolecularly co-ordinated form are in equilibrium.

Cleavage of a B-Ph bond has previously been observed to occur only with formation of hydrocarbon ions,  $cf. 9 \rightarrow 11$ . It is likely that the weakening of the B-Ph bond in the benzeneboronate of pentane-1,3,5-triol is a consequence of the donation of electrons from the oxygen atom of the primary hydroxyl group to the boron atom. It has yet to be ascertained whether such a fragmentation mode can be regarded as a diagnosis for the presence of a dative bond.

## EXPERIMENTAL

G.l.c.-mass spectrometry. — The procedure used was as described before<sup>6</sup>.

Formation of benzeneboronates of diols. — A solution of the diol (~30 mg) and benzeneboronic anhydride [(PhBO)<sub>3</sub>, 0.4 mol.] in dry 1,2-dimethoxyethane (3 ml) was allowed to stand for 30 min. A portion (~1  $\mu$ l) was transferred to a silica dipper and evaporated with an air blast. The residue was inserted directly on a probe into a Hitachi RMS-4 mass spectrometer. The temperature of the probe and the ion source were 120° and 200°, respectively. For results, see Results and Discussion.

Benzeneboronate of pentane-1,3,5-triol (3). — Pentane-1,3,5-triol<sup>13</sup> (8 g) and benzeneboronic anhydride (6.9 g) were heated in boiling toluene (100 ml) for 6 h. Water was removed by azeotropic distillation. The residue obtained by evaporation of the solvent was distilled to give the title compound (13.2 g), b.p. 125–128°/ 0.03 mmHg (Found: m/e, 206.1110; B, 5.20. C<sub>11</sub>H<sub>15</sub>BO<sub>3</sub> calc.: m/e 206.1114; B, 5.24%).

Preparation of diacetoxy-methoxypentane. — The method used was as described before<sup>6</sup>. G.l.c. of the product showed a single peak with a retention volume, relative to that of tri-O-acetylglycerol, of 0.46. M.s. showed an ion with m/e 45.

Mass spectrometry of the benzeneboronate of pentane-1,3,5-triol. — An A.E.I. MS-902 spectrometer operating at 70 eV was used. The low-resolution spectrum, the precise masses, and the data of the defocussing experiments were obtained by directly inserting the sample into the ion source maintained at  $200^{\circ}$ .

## ACKNOWLEDGMENTS

The authors thank the authorities of Royal Holloway College, Ranks Hovis McDougall (Research) Ltd., and British Petroleum Ltd., for financial support; they are greatly indebted to Mr. M. J. Nicholson and Mr. T. Sargent of A.W.R.E., Aldermaston, for carrying out precise mass measurements and defocussing experiments.

#### REFERENCES

- 1 R. A. BOWIE AND O. C. MUSGRAVE, J. Chem. Soc., (1963) 3945.
- 2 A. FINCH, P. J. GARDNER, AND E. J. PEARN, Trans. Faraday Soc., 62 (1966) 1072.
- 3 J. C. LOCKHART, J. Chem. Soc., A, (1968) 869.
- 4 A. FINCH, P. J. GARDNER, P. M. MCNAMARA, AND G. R. WELLUM, J. Chem. Soc., A, (1970) 3339.
- 5 J. M. SUGIHARA AND C. M. BOWMAN, J. Amer. Chem. Soc., 80 (1958) 2443.
- 6 I. R. MCKINLEY AND H. WEIGEL, Carbohyd. Res., 31 (1973) 17.
- 7 I. R. MCKINLEY AND H. WEIGEL, Chem. Commun., (1972) 1051.
- 8 W. H. MCFADDEN, D. R. BLACK, AND J. W. CORSE, J. Phys. Chem., 67 (1963) 1517.
- 9 C. G. McDonald, J. S. SHANON, AND G. SUGOWDZ, Tetrahedron Lett., (1963) 807.
- 10 R. L. LETSINGER AND I. SKOOG, J. Amer. Chem. Soc., 77 (1955) 2491.
- 11 W. GERRARD, M. F. LAPPERT, AND R. SHAFFERMAN, J. Chem. Soc., (1958) 3648.
- 12 E. J. BOURNE, E. M. LEES, AND H. WEIGEL, J. Chem. Soc., (1965) 3798.
- 13 R. PAUL AND S. TCHELITCHEFF, Bull. Soc. Chim. Fr., (1951) 550.