

ELECTRON-IMPACT INDUCED FRAGMENTATIONS AND STRUCTURES OF BENZENEBORONATES OF ACYCLIC TETRAOLS

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ABSTRACT

The isomeric 4,4'-bi-2-phenyl-1,3,2-dioxaborolanes and 2,7-diphenyl-1,3,6,8-tetraoxa-2,7-diborabicyclo[4.4.0]decanes have been distinguished by their electron-impact induced fragmentation. The bisbenzeneboronates of erythritol, L-threitol, 1-deoxy-D-arabinitol, 1-deoxy-D-lyxitol, 1-deoxy-D-ribitol, 1-deoxy-D-xylitol, 1,6-dideoxygalactitol, and 1,6-dideoxy-L-mannitol are likely to be mixtures of structural isomers.

INTRODUCTION

Previously^{1,2}, structures have been assigned to the benzeneboronates of glycerol, DL-butane-1,2,4-triol, L-erythro-butane-1,2,3-triol, L-arabino-, ribo-, and xylo-pentane-2,3,4-triols, and pentane-1,3,5-triol. All, except the benzeneboronates of xylo-pentane-2,3,4-triol and pentane-1,3,5-triol, are mixtures of structural isomers, i.e., 2-phenyl-1,3,2-dioxaborolanes and 2-phenyl-1,3,2-dioxaborinanes. The method of their analysis involved methylation of the unsubstituted hydroxyl group, hydrolysis of the boronate ring, acetylation of the two hydroxyl groups thus generated, and g.l.c. followed by e.i.-mass spectrometry. The abundance of the isomers has been related to conformational effects. We now report on the bisbenzeneboronates of eight acyclic tetraols, namely, erythritol, L-threitol, 1-deoxy-D-arabinitol, 1-deoxy-D-lyxitol, 1-deoxy-D-ribitol, 1-deoxy-D-xylitol, 1,6-dideoxygalactitol, and 1,6-dideoxy-L-mannitol. For reasons already reported¹, no attempt was made to recrystallise the crude bisbenzeneboronates. In contrast to allied fields, e.g., dialkylidene compounds, the assignment of structure to bis- and tris-benzeneboronates of alditols is sometimes hindered by the failure to obtain the pure products of graded hydrolysis. On the other hand, the molecular ions (M^+), produced by electron impact (e.i.), of 2-phenyl-1,3,2-dioxaborolanes and 2-phenyl-1,3,2-dioxaborinanes are moderately stable and the mass spectra of these compounds often contain few peaks. Consequently, we have used e.i.-m.s. for the assignment of structure to the aforementioned compounds.

RESULTS AND DISCUSSION

E.i.-mass spectrometry of cyclic benzeneboronates of acyclic 1,2- 1,3- and 1,4-diols has revealed³ four fragmentation modes of the molecular ions (**1**; $n = 0, 1$, or 2). Elimination of an oxo-compound from each molecular ion produces ion **2** (mode A). Fission of an exocyclic C-C bond in ion **1** produces the oxonium ion **3** (mode B). Skeletal rearrangement may give rise to a series of hydrocarbon ions containing 7 and/or more carbon atoms (mode C). The fourth fragmentation mode (mode D) was exhibited only by the derivatives of 1,3-diols and is thus characteristic of 2-phenyl-1,3,2-dioxaborinanes ($n = 1$). Double elimination gives either the hydrocarbon ion **4** (and R^5R^6CO and $PhBO$) or the ion **5** (and $R^3R^4CCR^1R^2$ and R^5R^6CO). In the e.i.-mass spectrum of 5,5-dimethyl-2-phenyl-1,3,2-dioxaborinane (corresponding to **1a**; $R^1 = R^2 = R^5 = R^6 = H$, $R^3 = R^4 = Me$), the most abundant ion ($\% \Sigma_{40} 21.8$) is in fact the ion **4a** ($R^1 = R^2 = H$, $R^3 = R^4 = Me$). It is likely⁴ that the fragment having m/e 58, and arising from the molecular ions of 5-hydroxy-4,6-dimethyl-2-phenyl-1,3,2-dioxaborinanes (**1b**, $R^1 = R^5 = Me$, $R^3 = OH$, $R^2 = R^4 = R^6 = H$), has structure **6**.

The molecular ions of 2,7-diphenyl-1,3,6,8-tetraoxa-2,7-diborabicyclo[4.4.0]-decanes, *e.g.*, **7** (hereafter called tetraoxadiborabicyclodecane), therefore fragment as shown in Scheme 1, to give the characteristic D-ions (arising by mode D) **8** and thence **9**. Based on the formation of these D-ions, it has already been suggested that the benzeneboronate preparations of several alditols contain components that possess the tetraoxadiborabicyclodecane structure³.

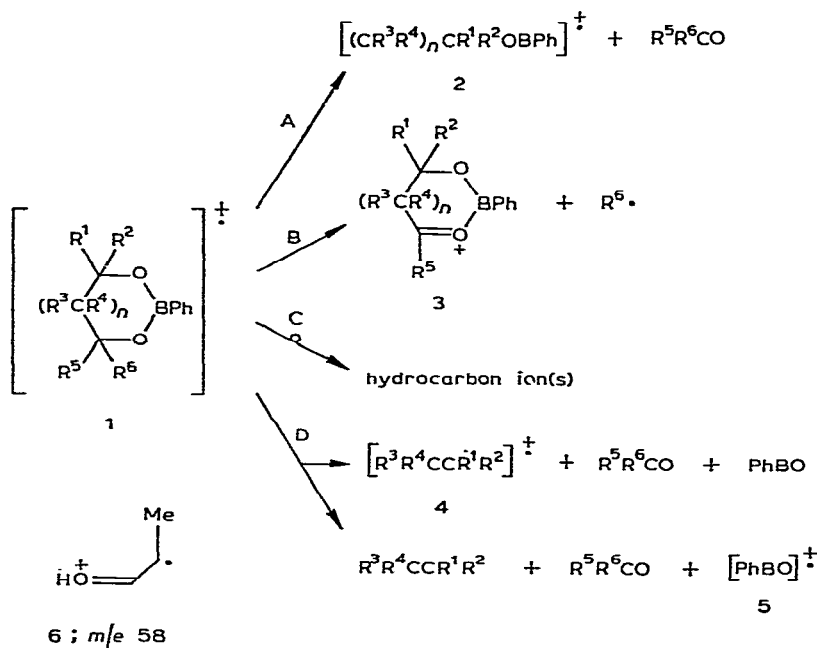
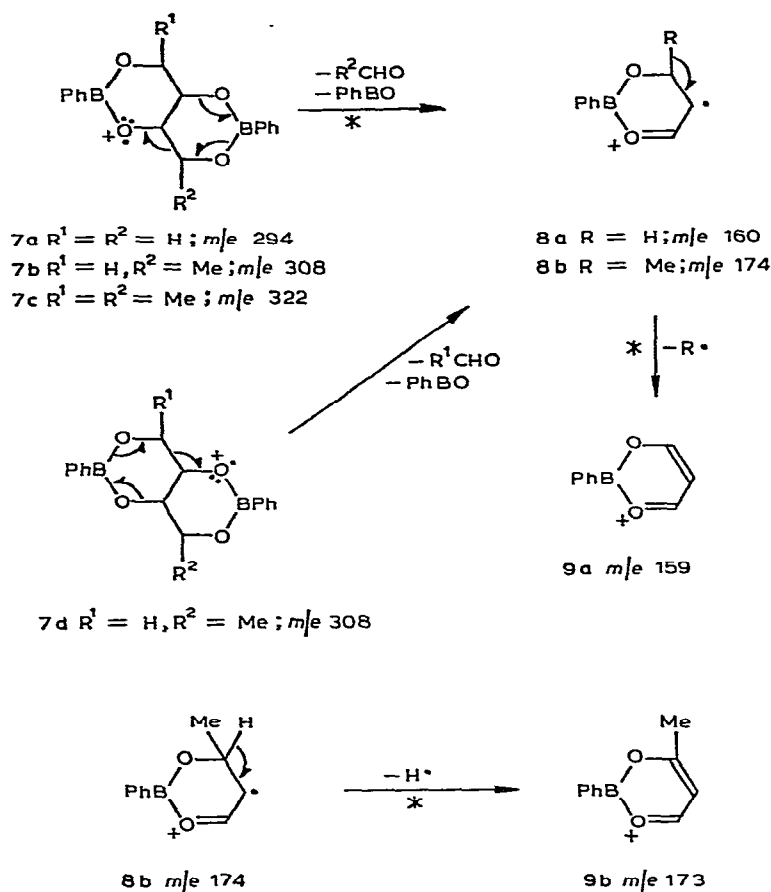


TABLE I

SIGNIFICANT IONS PRODUCED FROM BENZENE BORONATES OF TETRAOLS

Parent tetraol	Abundances of ions (% Σ_{40})						% ΣD -ions / % ΣB -ions		Structure of boronate
	m/e 147	m/e 159	m/e 160	m/e 161	m/e 173	m/e 174	M ⁺ b		
Erythritol (18)	11.7 ^a	6.1	6.8	—	—	—	7.4 (294)	1.0 ^c	19, 20
L-Threitol (21)	16.2 ^a	9.6	7.1	—	—	—	7.0 (294)	0.9	22, 23
1-Deoxy-D-arabinitol (24)	7.2	6.6	8.0 ^a	8.0 ^a	3.6	0.8	7.1 (308)	1.0	25, 26
1-Deoxy-D-lyxitol (27)	1.3	14.9	15.6 ^a	4.5	0.8	0.5	12.8 (308)	4.7	29 > 28
1-Deoxy-D-ribitol (30)	3.8	7.6	8.0 ^a	7.3	1.3	0.5	7.2 (308)	1.3	32, 31
1-Deoxy-D-xylitol (33)	3.1	9.0	18.0 ^a	12.2	1.6	0.2	8.6 (308)	1.4	35, 34
1,6-Dideoxygalactitol (36)	—	3.0	8.4	17.5 ^a	2.2	0.8	2.2 (322)	0.5	37 > 38
1,6-Dideoxy-L-mannitol (39)	—	13.2 ^a	2.1	1.4	3.8	5.2	2.3 (322)	15.9	41 > 40

^aMost abundant ion. ^bThe m/e value is given in parentheses. ^cAll values calculated for species containing ¹¹B only.

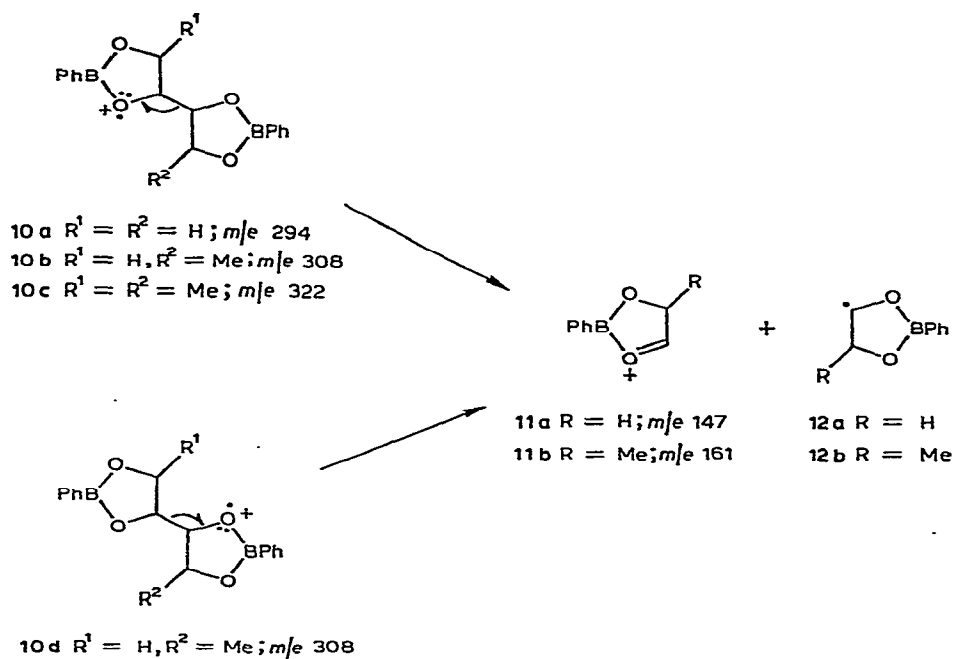


Scheme 1. Fragmentation of molecular ions of 2,7-diphenyl-1,3,6,8-tetraoxa-2,7-diborabicyclo[4.4.0]decanes (D-ions): *, transition evidenced by metastable ion.

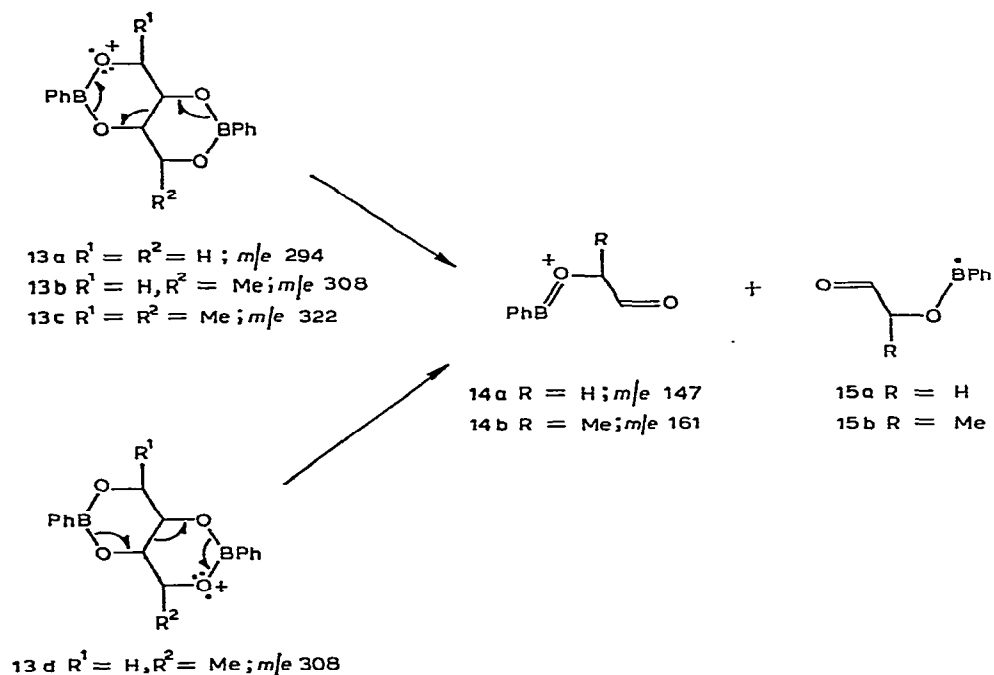
The significant ions produced from the eight benzeneboronate preparations are shown in Table I.

The spectrum of the 1,6-dideoxy-L-mannitol bisbenzeneboronate largely resembles that expected from the ion 7c, which fragments by mode D (Scheme 1); the D-ion with m/e 159 (9a) has the largest abundance. Therefore, the major component of this preparation is probably 1,6-dideoxy-L-mannitol 2,4:3,5-bis(benzeneboronate) (41).

On the other hand, the most abundant ion (m/e 161) formed from the 1,6-dideoxygalactitol bisbenzeneboronate preparation is not a D-ion and must arise either from a 4,4'-bi-2-phenyl-1,3,2-dioxaborolane (corresponding to 10) (it is known that 2-phenyl-1,3,2-dioxaborolanes and 2-phenyl-1,3,2-dioxaborinanes are formed in preference to 2-phenyl-1,3,2-dioxaborepanes²) or from an alternative fragmentation of a molecular ion of the tetraoxadiborabicyclodecane. Fragmentation of the molecular ions of 4,4'-bi-2-phenyl-1,3,2-dioxaborolanes by mode B will give the B-ions



Scheme 2. Fragmentations of molecular ions of 4,4'-bi-2-phenyl-1,3,2-dioxaborolanes (B-ions).



Scheme 3. Fragmentations of molecular ions of 2,7-diphenyl-1,3,6,8-tetraoxa-2,7-diborabicyclo[4.4.0]decanes by "half rupture".

shown in Scheme 2. The most abundant ion (m/e 161) in the spectrum of the bisbenzeneboronate preparation of 1,6-dideoxygalactitol could therefore be the B-ion **11b** arising from the molecular ion **10c**. An ion with m/e 161 (**14b**) could also arise from an alternative fragmentation, namely "half-rupture" of the molecular ion **13c** of the tetraoxadiborabicyclodecane (Scheme 3). This behaviour would be analogous to the "half-rupture" encountered in the e.i.-induced fragmentation of 1,3,6,8-tetraoxabicyclo[4.4.0]decane⁵. However, the very low abundance (% Σ_{40} 1.4) of the ion with m/e 161 in the spectrum of the bisbenzeneboronate preparation of 1,6-dideoxy-L-mannitol, already shown to be mainly the tetraoxadiborabicyclodecane **41**, indicates that "half-rupture" of tetraoxadiborabicyclodecanes is not a dominant feature, if it occurs at all. As recognition of chirality is generally not achieved by e.i.-induced fragmentation, it is unlikely that the major route for the formation of the ion with m/e 161 in the spectrum of the bisbenzeneboronate preparation of 1,6-dideoxygalactitol is the "half-rupture" of Scheme 3. We thus believe that the ion with m/e 161 is mainly the B-ion **11b** and, consequently, that 1,6-dideoxygalactitol 2,3:4,5-bis(benzeneboronate) (**37**) is indeed the major component of the aforementioned preparation. These results show that 4,4'-bi-2-phenyl-1,3,2-dioxaborolanes can be recognised by the formation of the B-ions **11** with m/e ($146 + R$), where $R = H$ or Me.

Table I shows the abundance of the significant ions produced by e.i.-induced fragmentation, together with the molecular ions, of the bisbenzeneboronate preparations of the tetraols examined. Table I also shows the ratios of the abundances of the D-ions to those of the B-ions. Where appropriate, allowances have been made for isotopic species containing the ^{10}B isotope. From these data, the following conclusions are drawn. The tetraols examined form only bisbenzeneboronates (*cf.* M^+). Molecular ions corresponding to monobenzeneboronates could not be detected. As suspected, under the conditions of analysis described here, the preparations of bisbenzeneboronates proved to be mixtures of structural isomers.

It is not always realistic to draw quantitative conclusions from abundances of fragment ions, particularly when they arise through multiple fragmentations and also fragment further. Nevertheless, the results shown in Table I indicate that only 1-deoxy-D-lyxitol, 1,6-dideoxygalactitol, and 1,6-dideoxy-L-mannitol exhibited any significant preference for the formation of one of the likely isomers. The formation of the bisbenzeneboronates of these tetraols follows a pattern analogous to that revealed for the formation of benzeneboronates of acyclic triols, namely, the major product is a tetraoxadiborabicyclodecane derivative when the methyl groups can be equatorially disposed [*cf.* the bisbenzeneboronates of 1-deoxy-D-lyxitol (**29**) and 1,6-dideoxy-L-mannitol (**41**)]. When the methyl groups can only be axially disposed, the 4,4'-bi-2-phenyl-1,3,2-dioxaborolane becomes the major product [*cf.* the bisbenzeneboronate of 1,6-dideoxygalactitol (**37**)]. The differences between the abundances of the B- and D-ions from the diboronates of 1-deoxy-D-arabinitol, 1-deoxy-D-ribitol, and 1-deoxy-D-xylitol were not significant enough to allow further conclusions.

The bisbenzeneboronates of the 1-deoxypentitols gave a characteristic ion

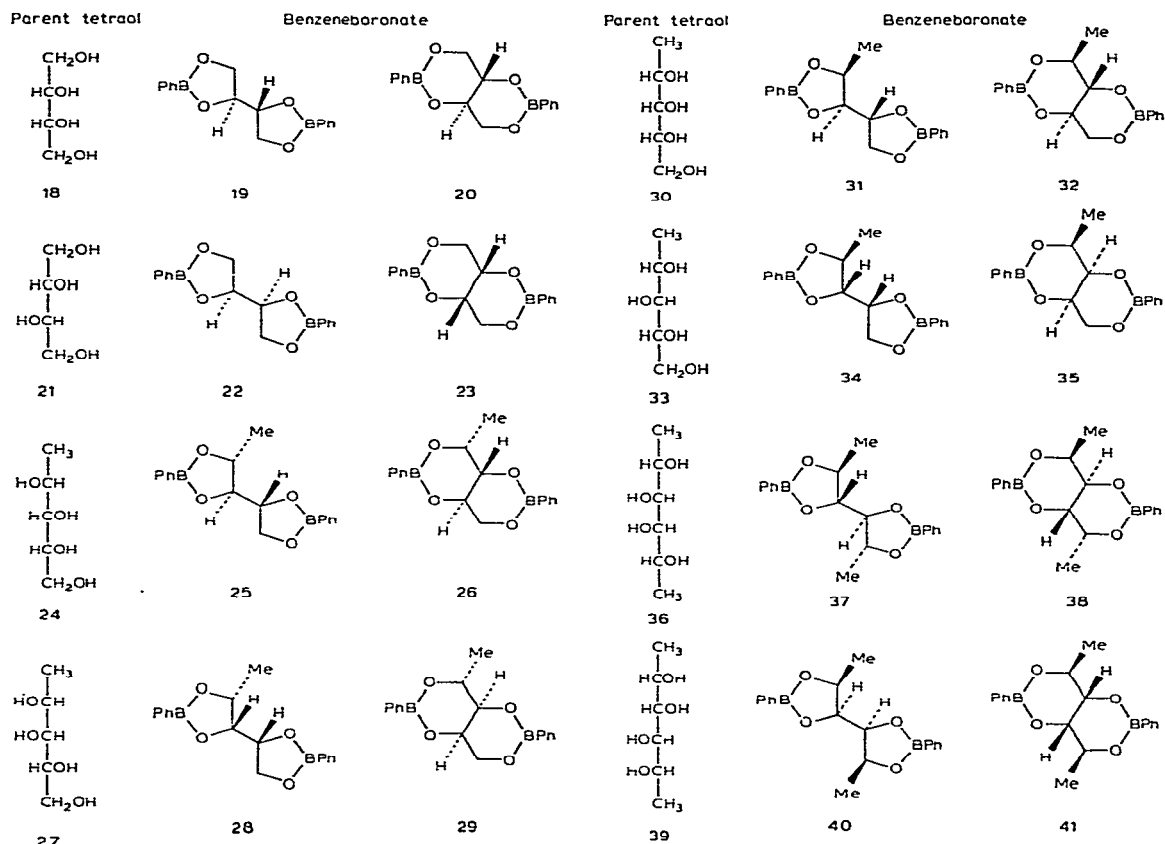
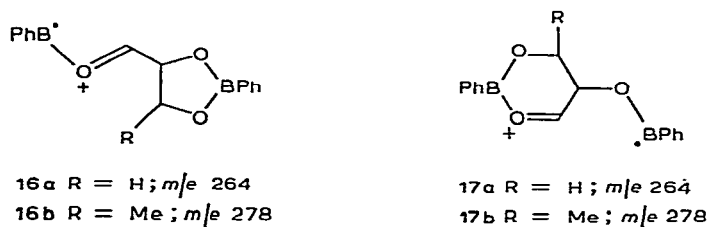


Fig. 1. Possible structures of benzeneboronates of tetraols.

having *m/e* 186. Its precise mass corresponded to $C_9H_8B_2O_3$, and a metastable ion with *m/e* 131.0 showed that it is produced from the ion having *m/e* 264 (**16a** or **17a**, produced from the molecular ion by mode A) by loss of C_6H_6 , probably through a six-membered, cyclic transition-state. The corresponding ion, but of lower abundance, from the bisbenzeneboronate of 1,6-dideoxy-L-mannitol had *m/e* 200 and was produced by both simultaneous and consecutive elimination of CH_3CO and C_6H_6 . In general, the abundances of the ions from these fragmentations were too low to affect significantly the conclusion drawn above.

EXPERIMENTAL

Bisbenzeneboronates of tetraols. — The tetraols (~ 0.5 g) were separately dissolved in dry 2-methoxyethanol (10 cm^3) together with benzeneboronic anhydride (0.66 molar equivalent), and the solution was heated, with the exclusion of moisture, at $\sim 90^\circ$ for 1 h. Removal of the solvent yielded a white, crystalline mass. Traces of water were removed by dissolution in dry toluene and evaporation under reduced pressure.

Mass spectrometry. — The low-resolution spectra and the precise masses were obtained by using an A.E.I. MS-92 mass spectrometer operating at 70 eV, with a trap current of $100 \mu\text{A}$ and an ion-source temperature of 200° . A direct-insertion method was used. Elemental compositions of ions were confirmed by high-resolution experiments.

REFERENCES

- 1 I. R. MCKINLEY AND H. WEIGEL, *Carbohydr. Res.*, 31 (1973) 17–26.
- 2 E. J. BOURNE, I. R. MCKINLEY, AND H. WEIGEL, *Carbohydr. Res.*, 35 (1974) 141–149.
- 3 I. R. MCKINLEY AND H. WEIGEL, *Chem. Commun.*, (1972) 1051–1052.
- 4 I. R. MCKINLEY, Ph.D. Thesis, University of London, 1972.
- 5 O. S. CHIZHOV, L. S. GOLOVKINA, AND N. S. WULFSON, *Carbohydr. Res.*, 6 (1968) 138–142.