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SYNTHESIS OF MONOSACCHARIDES WITH THE AID OF A NEW SYNTHETIC EQUIVALENT FOR THE GLYCOLALDEHYDE ANION*

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ABSTRACT

The synthesis and characterization of previously unknown *B*-aryl- and *B*-alkyl-1,3,2-dioxaboroles is reported. These compounds can act as synthetic equivalents for the glycolaldehyde anion, because they undergo an aldol-type reaction with aldehydes yielding mono, and large amounts of multiple, addition products. By immobilizing the 1,3,2-dioxaboroles on a polymeric support, which accomplishes the site separation of the enediolate intermediates, further addition beyond the primary stage could be inhibited. As a first example of a synthetic application, the synthesis of the otherwise arduously accessible L-ribose was undertaken. 2,3-*O*-Cyclohexylidene-L-glyceraldehyde reacted with polymer-bound 1,3,2-dioxaborole to give a mixture of pentoses in good yield, from which 54% of enantiomerically pure L-ribose could be isolated. This work provides a general methodology for the lengthening of sugar chains by two C-atoms, thus furnishing a novel route for the synthesis of rare sugars.

INTRODUCTION

A very general problem existent in carbohydrate chemistry since the time of Emil Fischer, the teacher of Burckhardt Helferich, has been the synthesis of monosaccharides, mostly carried out by elongation of available sugar aldehydes. Following the classical cyanhydrin synthesis[1], many other possibilities were investigated[2]. Newer approaches to sugar synthesis make use of the Diels–Alder reaction[3], aldol addition[4], addition of allylboronic acids[5], addition of 2-trimethyl-

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*Dedicated to Burckhardt Helferich in commemoration of the hundredth anniversary of his birth.

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[‡] Personal note by G.W.: During the period 1960 to 1979, when Burckhardt Helferich had already retired but was still quite active in research most of the time, I worked at the same institute of Bonn University. I enjoyed many fruitful discussions with him on various general aspects of the history of chemistry and, in particular, on special topics involving carbohydrate chemistry. I admired his great scientific accomplishments, his broad interests in chemistry as well as in humanities and most of all his noble and strong personality.

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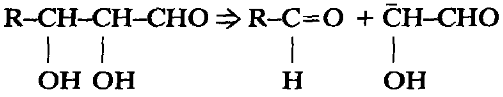
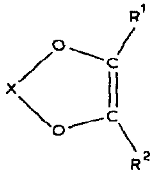
silylthiazole[6], or the formation of allyl alcohols followed by osmium tetroxide hydroxylation[7] or an asymmetric, titanium(IV)-catalyzed epoxidation[8].

Another attractive possibility for elongation by two carbon atoms would involve an aldol reaction as shown in the following retrosynthetic scheme.



$$\mathrm{R{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CHO} \Rightarrow \mathrm{R{-}\underset{\displaystyle H}{\underset{|}{C}}{=}O} + \mathrm{\underset{\displaystyle OH}{\underset{|}{\bar{C}H}}{-}CHO}$$

The problem of implementing this scheme is then one of obtaining a suitable synthetic equivalent for the glycolaldehyde anion. Glycolaldehyde cannot be used directly because it equilibrates with cyclic dimers, *etc.*[9] in nonaqueous solutions, and under basic conditions generates a number of undesired materials such as polycondensation products and α,β-unsaturated carbonyl compounds[10].

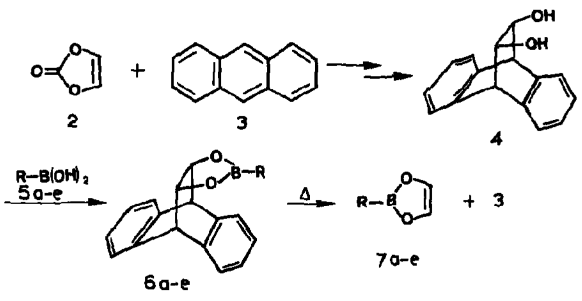


1a $X = P(OMe)_3$ (ref. 11)
1b $X = B{-}Ph$ (ref 12)
$X = B{-}Et$ (ref. 13)
1c $X = Sn$ (refs. 14, 15)
1d $X = ZrCp_2$ (ref 16)

R^1 = alkyl, aryl
R^2 = H, alkyl, aryl

The cyclic enediolates **1**, $R^1 = R^2 = H$, would appear to be suitable synthetic equivalents for glycolaldehyde, although only their 4- and 4,5-substituted derivatives have proven to be useful from a preparative point of view. Ramirez and coworkers[11] were able to prepare α,β-dihydroxyketones by the reaction of 1,3,2-dioxaphospholes (**1a**) with aldehydes and ketones. The reactions with aldehydes of the compound having no substituents at the 4- and 5-positions (obtainable from glyoxal and trimethyl phosphite[11]) are not described. Tin(II) and tin(IV) 1,3,2-dioxastannoles[14] (**1c**) having substituents at the 4- or 4,5-positions have also been used in a similar manner. In this case an asymmetric induction was observed in the presence of optically active amines[15]. The zirconium compound **1d** has been prepared recently[16] but its synthetic applications have not so far been reported. Mukaiyama and Yamaguchi[12] and Köster[13] investigated the reactions of 4- and 4,5-substituted 1,3,2-dioxaboroles (**1b**). Upon reacting these with aldehydes they obtained α,β-dihydroxy ketones having *threo*:*erythro* ratios of 3:1 to 7:1.

We have been specifically interested in the synthetic applications of the previously unknown 1,3,2-dioxaboroles possessing substituents only in the 2-position. These compounds would function as synthetic equivalents of the anion of glycolaldehyde, and their reactions with aldehydes would result in syntheses of aldoses. In the present paper we describe our results on the preparation and properties of 1,3,2-dioxaboroles as well as their application to the synthesis of pentoses. Some of these results have already been reported in a short communication[17].



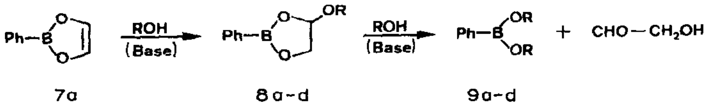
Series: a, R = phenyl ; b, R = 2-methylphenyl ;
c, R = 2,6-dimethylphenyl ; d, R = cyclohexyl ;
e, R = methoxy

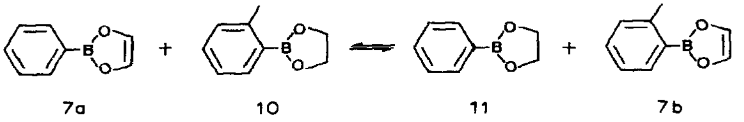
RESULTS

Synthesis of 2-substituted 1,3,2-dioxaboroles. — 4- And 4,5-substituted 1,3,2-dioxaboroles (**1b**) have been prepared by the reaction of boronic acids with acyloins[18]. The use of glycolaldehyde in this approach failed to give the desired product, and the reaction of lithium enediolate[19] (prepared from glycolaldehyde) with alkyl or aryl dichloroboranes or with alkyl or aryl boronic acids also did not meet with any success. Our consistent failures to obtain these compounds by standard methods forced us to look for new synthetic routes, and, by a properly designed synthetic scheme, it was possible to generate the 1,3,2-dioxaboroles in excellent yields. The starting material was the well known diol **4**, easily obtained by the Diels–Alder reaction of vinylene carbonate (**2**) and anthracene with subsequent hydrolysis[20]. Diol **4** reacted with boronic acids **5a–e** to yield esters **6a–e**. These esters were sublimable at 160–220°/10 Pa and on thermolysis in the gas phase at 550°/10 Pa underwent a quantitative retro-Diels–Alder reaction to give the formerly unknown 1,3,2-dioxaboroles **7a–e** and anthracene. The retro-Diels–Alder reactions of other derivatives of diol **4** have been studied previously[21]. The two reaction products could easily be separated at the outlet of the thermolyser by fractional condensation, thus producing the 1,3,2-dioxaboroles directly in analytically pure form. The total yields with respect to vinylene carbonate were over 80% for all the products **7a–e**.

The newly synthesized dioxaboroles are liquids at room temperature, they can be handled in air, and are stable for months when stored at −20°. The 1,3,2-dioxaboroles are actually aromatic heterocycles, as has been discussed by Dewar[22] for some derivatives of this type of compound. The question of the aromaticity of our novel parent members of this series is a subject for future discussion.

Chemical properties of the 1,3,2-dioxaboroles **7a–e**. — The addition of bromine to the double bond of the 1,3,2-dioxaborole **7a** yields a single diastereomer of 4,5-dibromo-2-phenyl-1,3,2-dioxaborolane. All dioxaboroles **7a–e** tend to polymerize when exposed to light, and these reactions can be systematically investigated using free radical initiators[23]. Like the 4- and 4,5-substituted compounds, **7a–e** also possess relatively high hydrolytic and alcoholytic stabilities[18]. Upon treatment of **7a** with equimolar amounts of alcohol or water in $CDCl_3/CD_3CN$ (1:1) no reaction could be detected by ^{1}H-n.m.r., even after several hours. Furthermore, a solution of **7a** in pure CD_3OD did not show any transformation for many days, thus confirming its resistance to alcoholysis and hydrolysis. In contrast, in the presence of bases a spontaneous reaction with water and alcohols took place. After the addition of 0.1–1.0 mol. equiv. of triethylamine to a mixture of **7a** and water, the **7a** quickly disappeared, by a relatively complex reaction, according to the ^{1}H-n.m.r. results. With alcohols a quantitative reaction yielding the alkoxy derivative **8** occurs in presence of base. A further reaction yielding the phenyl dialkoxy boranes **9** is much slower and requires an excess of alcohol.





Formulas 8 and 9 : a,R = methyl ; b,R = ethyl ; c,R = isopropyl ;
d,R = trideuteromethyl

It is well known that the kinetics of transesterifications between phenyl-1,3,2-dioxa-borolanes (and -borinanes) and 1,2- or 1,3-diols are greatly enhanced both inter- and intra-molecularly by certain bases[24]. Transesterifications between two cyclic esters of aryl boronic acids have also been reported[25]. It was of particular interest to observe whether aryl 1,3,2-dioxaboroles, too, show an exchange reaction with aryl 1,3,2-dioxaborolanes. The reaction between **7a** and the dioxaborolane **10** was observed by monitoring the variation of the areas of the ^{1}H-n.m.r. signals of the ortho methyl groups in **7b** and **10** at 2.62 and 2.55 p.p.m., respectively. In the absence of base a slow reaction ($t_{1/2}$ = 2–4 h) occurred, and on addition of triethylamine a significant acceleration in the rate of reaction took place (with 0.5 mol. equiv. $t_{1/2}$ = 157 sec, and with 1.5 mol. equiv. $t_{1/2}$ = 57 sec) (see Fig. 1). The equilibrium constant for this reaction is close to unity. Triethylamine possesses stronger catalytic power than quinuclidine, which is contrary to observations on transesterifications of **11** with ethylene glycol[26]. Similar transesterifications were observed in the systems shown in Scheme 1. It is thus a very general reaction

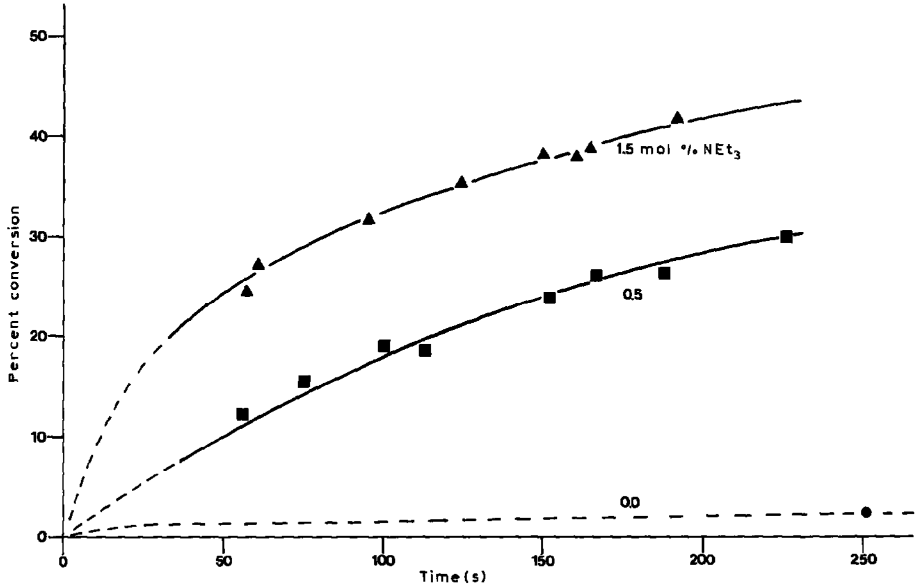
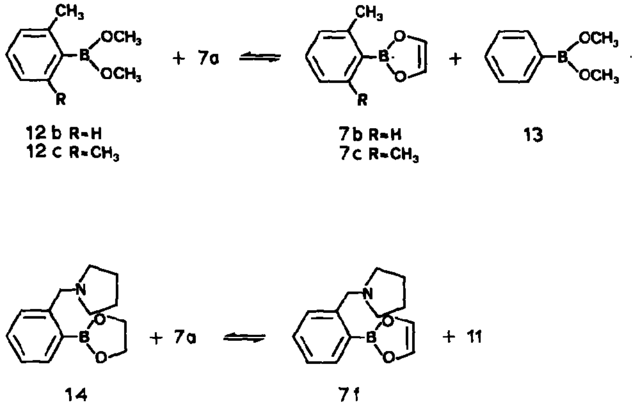


Fig. 1. Kinetics of exchange of **7a** with **10**. Initial concentrations 0.2M in benzene. The exchange yielding **11** and **7b** was followed by ^{1}H-n.m.r. measurement.

providing a novel route to various 1,3,2-dioxaboroles that are not volatile enough to be obtained by thermolysis.

Reactions of 2-phenyl-1,3,2-dioxaborole (**7a**) *with aldehydes involving C–C bond formation.* — Substituted 1,3,2-dioxaboroles **1b** have been reported to undergo addition reactions with aldehydes[12,13]. Under similar conditions (in tetrahydrofuran at 0°) several simple aldehydes (**15**) were allowed to react with **7a**. In



Scheme 1

contrast to the reactions of **1b** (refs. 12, 13) the process in our case happened to be rather complex, and not confined to the formation of the monoaddition products **16** and **17**. Unlike the products obtained by Mukaiyama and Yamaguchi[12] and Köster[13] from **1b** and aldehydes, our compounds **16** and **17** contain an aldehyde group instead of a keto group, and it is susceptible to further reactions with **7a**, yielding diaddition products **18** and higher addition products. Despite the use of a large excess of the aldehyde (molar ratio **15**:**7a** = 7:1) monoaddition products were obtained to a maximum extent of 12–30% (see Table I). At a molar ratio of 2:1 the yield of monoaddition products dropped to as low as 6.8%. This feature of the reaction can be utilized for preparing oligomers and polymers in a controlled manner using an excess of **7a** in the presence of a small amount of aldehyde acting as the initiator for polymerization[23].

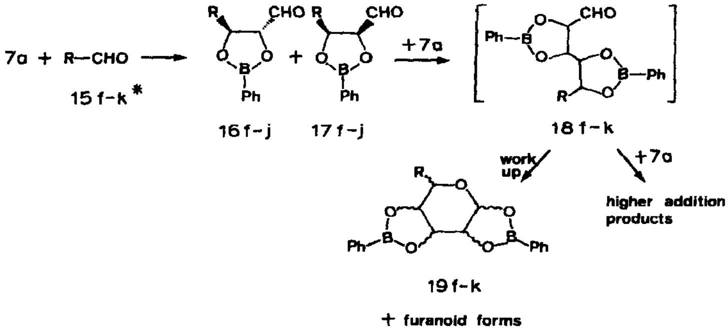


TABLE I

PRODUCTS OF THE ADDITION OF **7a** TO VARIOUS ALDEHYDES[a]

Aldehyde	*R*	*Yield of* **16** + **17** *(%)*	*B.p. at 0.1 Pa (°)*	*Proportions* *threo*	*erythro*	*Yield of* **19** *(%)*	*B.p. at 0.1 Pa (°)*
15f	methyl	29	113–117	37	63	36	180–190
15f	methyl	6.8[b]	113–117			39[b]	180–190
15g	ethyl	23	115–119	40	60	39	185–190
15h	isopropyl	22	83–84	27	73	33	140–160
15i	*tert*-butyl	12	108	24	76	8	185–195
15j	(*R*)-2,2-dimethyl-1,3-dioxolan-4-yl	24	175–188				
15k	phenyl	0	—	—	—	~90	

[a] Reaction in THF at 0° for several hours; ratio **7a**:**15** = 7:1. [b] Ratio **7a**:**15f** = 2:1.

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*For the identities of the R-groups designated by **f–k** in formulas **15–19**, see Table I and the text.

The mono- (**16** + **17**), di- (**18**), and higher addition products were separated by distillation *in vacuo* and obtained as mixtures of diastereoisomers. The *threo*:*erythro* ratio of the monoaddition products (**16**, **17**) lies between 1:2 and 1:3, which is inverse to that obtained with substituted 1,3,2-dioxaboroles **1b** (refs. 12, 13). The ratio of the isomers could be determined by ^{13}C n.m.r. spectroscopy, since there is a pronounced steric γ-effect[27] resulting in a 4 p.p.m. downfield shift for the γ-carbon of **16**.

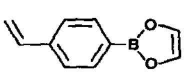
The primary diaddition products **18** were not isolated as such but were apparently transformed during the workup and distillation process, by transesterification and transacetalization, to pyranoid (and furanoid) isomers (**19**). Such transesterifications have already been observed during the synthesis of 2-deoxy-*aldehydo* hexose derivatives[28]. No attempts were made to separate the diastereoisomers of **19** or determine their relative ratios.

During the reaction of **7a** with benzaldehyde (**15k**) diaddition products (**19k**) were exclusively formed, leaving none of the monoaddition products **16k** and **17k**. In the case of the glyceraldehyde derivative (**15j**) the monoaddition products were obtained in four diastereoisomeric forms. The ratio was determined after splitting off the boronic acid and the isopropylidene groups with water and Dowex 50W X-4 respectively. Thus a mixture of four pentoses was obtained in the approximate ratio of D-ribose:D-lyxose:D-arabinose:D-xylose = 63:5:31:1. This ratio, however, varied to some extent for different sets of experiments, presumably because it does not necessarily represent the product ratio from the first reaction step. The initial products might undergo further transformations at varying rates. Therefore the compositional ratio of the diastereoisomers does not provide any insight towards the steric course of that first step.

Synthesis of pentoses on polymer-supported 1,3,2-dioxaboroles. — Our experiments demonstrated that lengthening of sugar aldehydes by two carbon atoms is possible in practice, but low yields due to undesired polyaddition reactions limit the general applicability of the procedure. In order to restrict the reaction to a single addition to aldehydes, and thus overcome this difficulty, **7a** was immobilized on a cross-linked polymer. This strategy for site separation[29] inhibits any further reaction of the primary addition products.

For the preparation of a suitable polymeric 1,3,2-dioxaborole the direct incorporation of compounds like **20** into a polymer is not possible due to the susceptibility of the dioxaborole moiety to radical polymerization. Therefore the transformation of polymeric boronic acids to polymeric dioxaboroles was called for.

Crosslinked polystyrene boronic esters can be prepared by the copolymerization of *e.g.* **21** (ref. 30) with cross-linkers, or by derivatization reactions on cross-linked polystyrene[31]. After optimizing the co-monomer compositions for the preparation of the support[23], good results were obtained with a styrene based polymer containing 0.1 mmol/g of 2-(4-vinylphenyl)-1,3,2-dioxaborolane (**21**) and 12% *m*-diisopropenylbenzene as cross-linker. The dioxaborole groupings were



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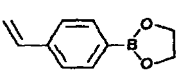

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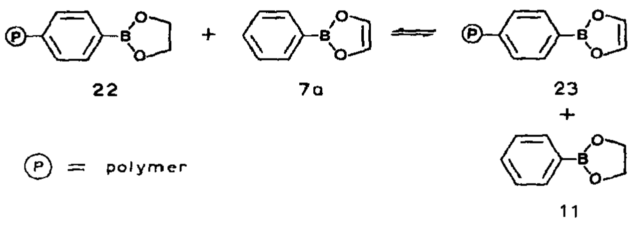


introduced by triethylamine-catalyzed ester-exchange reaction with **7a**. Repeated treatments with an excess of **7a** made it possible to shift the equilibrium quantitatively to the right side. At the end of this procedure no further ethylene glycol

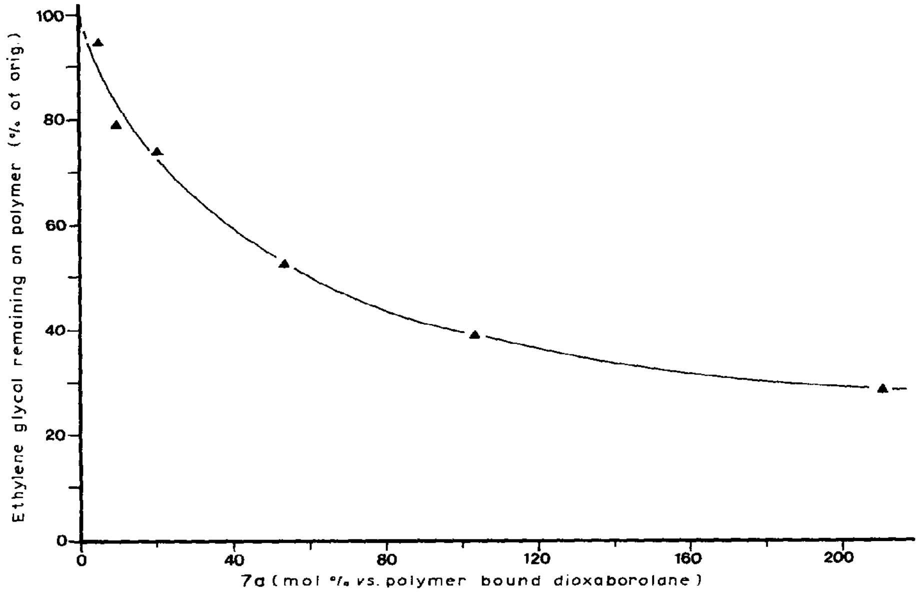
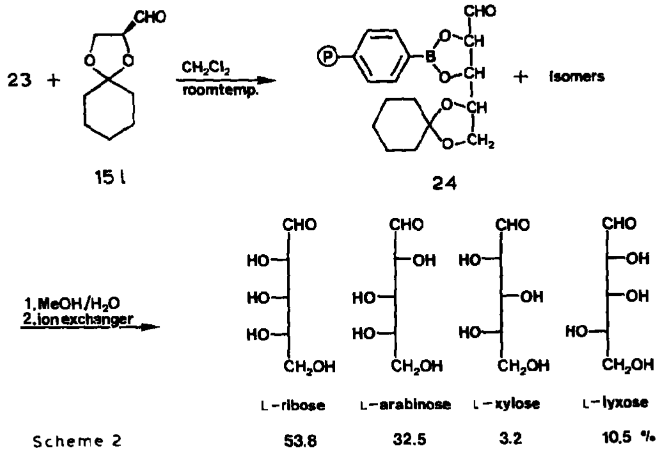


Fig. 2. Equilibrium of the exchange of **7a** with **22**. Batches (500 mg) of polymer **22** were equilibrated with different proportions of **7a** in the presence of triethylamine (5 mol% with respect to polymer-bound dioxaborolane). After 15 min all soluble exchange products were washed out, and the remaining ethylene glycol was removed from the polymer and estimated quantitatively by g.l.c. Points are measured values; the curve represents the calculated values for $K = 1.2$.

could be released from the polymer.

In order to investigate the accessibility of the polymeric dioxaborolane groups samples of the polymer were equilibrated for 15 min with different amounts of **7a**. Afterwards the samples were hydrolyzed and the amount of ethylene glycol still bound to the polymer was determined by g.l.c. analysis. The results of this study are depicted in Fig. 2. The apparent equilibrium constant, *K*, for the reaction is 1.2. The close agreement between the experimental and theoretical values in Fig. 2 suggests that the attainment of equilibrium is quick and complete and all the functional groups possess good accessibility. This implies that the loading of the polymer with dioxaborole functions can as well be achieved by the passing of a solution of **7a** and triethylamine through a column packed with polymer **22**.

2,3-*O*-Isopropylidene-(*R*)-glyceraldehyde (**15j**) (ref. 32) was allowed to react with the dioxaborole-containing polymer **23** in methylene chloride at room temperature. The addition products were isolated by treating the polymer with methanol–water. From the eluted 4,5-*O*-isopropylidene pentoses the protecting group could be directly removed by treatment with an acidic ion exchanger. The diastereomeric composition of the resulting mixture of aldopentoses was then determined quantitatively by g.l.c. of the acetylated aldononitriles[33], or by h.p.l.c.



Scheme 2

TABLE II

PRODUCTS OF THE REACTION OF POLYMER **23** WITH 2,3-*O*-ISOPROPYLIDENE-(*R*)-GLYCERALDEHYDE (**15j**)

Molar ratio **23**:**15j**	*Yield based on* **23** *(%)*	*Yield based on* **15j** (%)	*Ribose* (%)	*Lyxose* (%)	*Arabinose* (%)	*Xylose* (%)
0.5	35.7	75.8	56.2	5.6	35.7	2.3
1.1	64.3	—	58.8	4.5	35.0	1.4
2.0	96.1	—	54.5	4.5	38.4	2.5

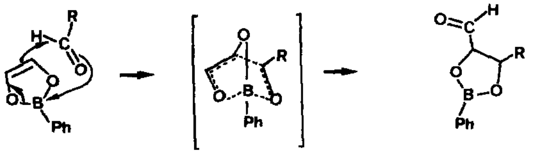
using a column filled with LiChrosorb–NH_2 (see Table II). The chemical yield, which was found to be dependent on the stoichiometric ratio of the reactants, could be increased up to 96% by using an excess of **15j**. This result shows that multiple additions have been completely eliminated, and thus, that at a functionalization of 0.3 mmol/g of polymer, there is still a large degree of site separation. When an excess of **23** was used the yield based on **15j** was 76%. Immobilized 1,3,2-dioxaboroles can therefore be successfully employed for the preparation of monosaccharides by elongation of the chain by two carbon atoms.

To demonstrate the potentiality of the procedure, the synthesis of the otherwise arduously accessible L-ribose (**25**) was performed. As starting material 2,3-*O*-cyclohexylidene-(*S*)-glyceraldehyde (**15l**, Scheme 2) (ref. 34) was used. Following the same strategy as in the case of the (*R*)-glyceraldehyde derivative, from 30 g of polymer **23** we were able to obtain 410 mg of the mixture of the L-aldopentoses in a similar diastereomeric ratio as in the case of **15j**. The mixture was separated by liquid chromatography (LiChrosorb–NH_2, 85:15 acetonitrile–water). The L-ribose isolated showed $[\alpha]_D^{20}$ +19.7° (*c* 0.22, H_2O) (lit.[35] $[\alpha]_D$ +18.8°), showing that the product was enantiomerically pure.

DISCUSSION

It was shown that immobilized 1,3,2-dioxaboroles act as excellent tools for the elongation of sugar aldehydes by two carbon atoms. The synthetic procedure furnishes the free sugars in only two reaction steps. A mixture of diastereoisomers is obtained which is 54–58% ribose, and this can be isolated in pure form by chromatography, which then constitutes a third step in the experimental procedure. Thus an overall yield of more than 40% based on the glyceraldehyde derivatives **15j** and **15l** was attainable. The method might be particularly suitable for the preparation of smaller quantities of rare sugars or for the preparation of isotopically labelled compounds.

At the present time our method gives predominantly products having the *ribo* configuration. Following standard procedures these can be epimerised almost quantitatively to compounds of the *arabino* configuration[36]. This means that after the epimerisation the *arabino* compound might be present in the reaction mixture to the extent of 90%. Thus, in syntheses of hexoses, one anticipates the predominant formation of D-allose, and after epimerisation D-altrose from D-erythrose derivatives, and of D-talose, and after epimerisation D-galactose, from D-threose



Scheme 3

derivatives. In an analogous manner, the L sugars could also be synthesized. The advantage of the method is thus the facile preparation of rare sugars which cannot be easily synthesized chemically or isolated from natural sources.

Other possibilities for the synthesis of ribose have recently been described by Masamune and Sharpless and their co-workers[8]. In an elegant work they started with **15j** as in our case, and obtained D-ribose in 42% yield through a six-step synthetic procedure. An epoxidation with high asymmetric induction constitutes the key step of their method. Another synthetic approach to a D-ribose derivative by two iterative one-carbon elongations, using 2-trimethylsilylthiazole and **15j** has also appeared recently[6].

The transition state of the reaction of 1,3,2-dioxaboroles with aldehydes should be analogous to that described by Zimmermann and Traxler[37] for other metal enolates. Due to the additional bridging by the oxygen atom, only a boat conformation (Scheme 3) is favourable. The stereochemical course of the reaction is rationalized as the result of influence by the following three different factors.

(1) The nucleophilic attack of the enediolate **23** at the aldehyde group of **15j** or **15l** is controlled *ul*-selectively (1,2-induction *ca.* 9:1) by the diastereofacial influence of the isopropylidene- or the cyclohexylidene-dioxy residue according to the Felkin–Anh model[38].

(2) Enantiofacial control (1,3-induction) was seldom observed.

(3) The influence of the optically active aldehydes **24** and **25** on the *threo:erythro* ratio at C-2 and C-3 was similar to that observed with achiral aldehydes **15f–i**.

EXPERIMENTAL

General methods. — U.v. spectra were obtained with a Perkin–Elmer model 554 spectrophotometer. ^{1}H-N.m.r. spectra were recorded with a Varian EM 390 spectrometer and ^{13}C-n.m.r. spectra with a Varian XL 100, for solutions in $CDCl_3$ containing tetramethylsilane as internal standard. Optical rotation measurements were made with a Perkin–Elmer 241 polarimeter. Elemental analyses were carried out at the Microanalytical Laboratory, Faculty of Natural Sciences of the University of Düsseldorf. Specific inner surface areas (BET) were measured with a Ströhlein Areameter II. Melting points were determined with the Büchi 510 apparatus. Gas chromatographic separations were performed with the Hewlett–Packard model 5840 gas chromatograph, or, when capillary columns were used, with the Carlo–Erba model 4160. H.p.l.c. separations were done on a Hewlett–Packard model 1084 B liquid chromatograph.

Starting materials. — The following substances were prepared according to literature procedures: phenylboroxine[39] (**5a**), 2-methylphenylboroxine[39] (**5b**), 2,6-dimethylphenylboroxine[39] (**5c**), cyclohexylboroxine[40] (**5d**), 2-(2-methylphenyl)-1,3,2-dioxaborolane[41] (**10**), 2-phenyl-1,3,2-dioxaborolane[42] (**11**), phenylboronic acid dimethyl ester[43] (**13**), (2-methylphenyl)-boronic acid dimethyl ester[43] (**12b**), 2-(4-vinylphenyl)-1,3,2-dioxaborolane[30] (**21**), 2,3-*O*-isopropylidene-D-glyceraldehyde[44,45] (**15j**), 2,3-*O*-cyclohexylidene-L-glyceraldehyde[34] (**15l**), 9,10-dihydro-9,10-ethanoanthracene-11,12-diol[20] (**4**).

Preparation of **6a–d**. — A mixture of **4** (100 mmol), the respective boronic acid **5a–d** (100 mmol) or the corresponding boroxine, and dry benzene (300 mL) was heated for 2–4 h under reflux, with azeotropic distillation of the formed water. When no more water separated, the benzene was removed under vacuum and the residue was purified by sublimation (160–220°/10 Pa). The products and their properties were as follows:

9,10-Dihydroanthraceno[*9,10*-d]*-2-phenyl-1,3,2-dioxaborolane* (**6a**). — The yield was 93.5%, m.p. 221.5°; ^{1}H-n.m.r. (DMSO-d_6): δ 4.63–4.74, 4.80–4.90 (4 H, C*H*), and 6.93–7.46 (12 H, Ph–H); m.s. (70 eV): *m*/*z* 324 (M^+), 178, and 160.

Anal. Calc. for $C_{22}H_{17}BO_2$ (324.18): C, 81.5; H, 5.3. Found: C, 81.6; H, 5.1.

9,10-Dihydroanthraceno[*9,10*-d]*-2-(2-methylphenyl)-1,3,2-dioxaborolane* (**6b**). — M.p. 183°; m.s. (70 eV): *m*/*z* 338 (M^+).

Anal. Calc. for $C_{23}H_{19}BO_2$ (338.21): C, 81.7; H, 5.7. Found: C, 81.7; H, 5.5.

9,10-Dihydroanthraceno[*9,10*-d]*-2-(2,6-dimethylphenyl)-1,3,2-dioxaborolane* (**6c**). — M.p. 244–245°; m.s. (70 eV): *m*/*z* 178 (no M^+).

Anal. Calc. for $C_{24}H_{21}BO_2$ (352.24): C, 81.9; H, 5.7. Found: C, 81.7; H, 5.7.

9,10-Dihydroanthraceno[*9,10*-d]*-2-cyclohexyl-1,3,2-dioxaborolane* (**6d**). — M.p. 181°; m.s. (70 eV): *m*/*z* 330 (M^+).

Anal. Calc. for $C_{22}H_{23}BO_2$ (330.23): C, 80.0; H, 7.0. Found: C, 80.2; H, 7.0.

9,10-Dihydroanthraceno[*9,10*-d]*-2-methoxy-1,3,2-dioxaborolane* (**6e**). — A mixture of **4** (2.38 g, 10 mmol), molecular sieves 4 A (7.0 g) and dry benzene (50 mL) was shaken for 1 h. After the addition of trimethylborate (2.06 g, 20 mmol) the shaking was continued for a further 2 h. The molecular sieves were removed by filtration (Büchner funnel without filter paper) and washed with dry benzene (30 mL). The solvent was removed under vacuum and the residue was purified by sublimation. The yield of **6e** was >90%; m.p. 177.0°; ^{1}H-n.m.r. ($CDCl_3$): δ 3.29 (s, 3 H, OCH_3), 4.45–4.68 (m, 4 H, C*H*, C*H*O), and 7.04–7.47 (m, 8 H, Ph–H); m.s. (70 eV): *m*/*z* 278 (M^+).

Anal. Calc. for $C_{17}H_{15}BO_3$ (278.11): C, 73.4; H, 5.4. Found: C, 73.3; H, 5.5.

Preparation of **7a–e**. — Compounds **6a–e** (2–20 g) were converted into vapor by sublimation (160–220°/10 Pa) in a quartz thermolysis apparatus[46], and thermolyzed by passage of the vapor through a quartz tube at 550°/10 Pa. The anthracene (**3**) formed during the thermolysis condensed in the cooler portion of the tube, while the 1,3,2-dioxaboroles **7a–e** were collected in a cold trap (yields >95%). The properties of these compounds were as follows:

2-Phenyl-1,3,2-dioxaborole (**7a**). — The yield was 97%; ^{1}H-n.m.r. ($CDCl_3$): δ 6.99 (s, 2 H, =C*H*O–), 7.20–7.48 (m, 3 H, Ph–H), and 7.82–8.00 (m, 2 H, Ph–H, *ortho*); ^{13}C-n.m.r. ($CDCl_3$): δ 127.93 (d, $^1J_{CH}$ 162 Hz, Ph–C, *meta*), 131.35 (d, $^1J_{CH}$ 160 Hz, $^3J_{CH}$ 20.3 Hz, Ph–C, *para*), 133.33 (d, $^1J_{CH}$ 205.9 Hz, $^2J_{CH}$ 20.3 Hz, =*C*HO–), and 134.18 (d, $^1J_{CH}$ 160 Hz, $^3J_{CH}$ 7 Hz, Ph–C, *ortho*); m.s. (70 eV): *m/z* 146 (M^+).

Anal. Calc. for $C_8H_7BO_2$ (145.95): C, 65.8; H, 4.8. Found: C, 65.8; H, 4.8.

2-(2-Methylphenyl)-1,3,2-dioxaborole (**7b**). — ^{1}H-N.m.r. ($CDCl_3$): δ 2.62 (s, 3 H, CH_3), 7.08 (s, 2 H, =CHO), 7.12–7.48 (m, 3 H, Ph–H), and 7.84–8.06 (m, 1 H, Ph–H, *ortho*); ^{13}C-n.m.r. ($CDCl_3$): δ 22.27 (q, CH_3), 124.92 (d, Ph–C, *meta* to C-B, *para* to CH_3), 129.92 (d, Ph–C, *meta* to C-B, *ortho* to CH_3), 131.13 (d, Ph–C, *para*), 133.14 (d, =CHO–), 135.77 (s, Ph–C, *ortho*), and 144.45 (s, CCH_3); m.s. (70 eV): *m/z* 160 (M^+).

Anal. Calc. for $C_9H_9BO_2$ (159.98): C, 67.6; H, 5.7. Found: C, 67.2; H, 5.6.

2-(2,6-Dimethylphenyl)-1,3,2-dioxaborole (**7c**). — ^{1}H-N.m.r. ($CDCl_3$): δ 2.45 (s, 6 H, CH_3), 6.90–7.20, and 7.06 (m, s, 5 H, Ph–H, =CHO–); ^{13}C-n.m.r. ($CDCl_3$): δ 22.87 (CH_3), 126.91 (Ph–C, *meta*), 127.00 (Ph–C, *para*), 133.01 (=CHO–), and 143.62 (Ph–CCH_3); m.s. (70 eV): *m/z* 174 (M^+).

Anal. Calc. for $C_{10}H_{11}BO_2$ (174.01): C, 69.0; H, 6.4. Found: C, 68.9; H, 6.4.

2-Cyclohexyl-1,3,2-dioxaborole (**7d**). — ^{1}H-N.m.r. ($CDCl_3$): δ 1.05–2.10 (m, 11 H, C_6H_{11}) and 6.93 (s, 2 H, =CHO–); ^{13}C-n.m.r. ($CDCl_3$): δ 26.70 (C-4 of C_6H_{11}), 27.09, 28.20 (C-2, C-3 of C_6H_{11}), and 132.75 (d, =CHO–); m.s. (70 eV): *m/z* 152 (M^+).

Anal. Calc. for $C_8H_{13}BO_2$ (156.00): C, 63.2; H, 8.6. Found: C, 62.7; H, 8.4.

2-Methoxy-1,3,2-dioxaborole (**7e**). — ^{1}H-N.m.r. ($CDCl_3$): δ 3.74 (s, 3 H, OCH_3) and 6.76 (s, broad, 2 H, =CHO–); ^{13}C-n.m.r. ($CDCl_3$): δ 53.28 (d, $^1J_{CH}$ 144.9 Hz, CH_3) and 132.57 (d, $^1J_{CH}$ 205.8 Hz, =CHO–); m.s. (70 eV): *m/z* 69 ($M^+ - 15$).

Anal. Calc. for $C_3H_5BO_2$ (83.88): C, 36.1; H, 5.1. Found: C, 36.5; H, 4.9.

2-[2-(Pyrrolidin-1-ylmethyl)-phenyl]-1,3,2-dioxaborolane (**14**). — A solution of 2-[(2-bromomethyl)phenyl]-1,3,2-dioxaborolane[41] (10 mmol) in abs. tetrahydrofuran (40 mL) (THF) was cooled to 0° and pyrrolidine (0.022 mol) was added dropwise over a period of 15 min. The reaction mixture was kept for 15 min at 0°, 30 min at room temperature, and 3 h at 50°. The mixture was then cooled to 10° and filtered and the solvent was removed under vacuum. The addition of 30 mL of *n*-pentane caused the formation of a yellow solid. The solid was extracted several times by refluxing in dry ether (20 mL) and decanting. The ether was evaporated, and after the addition of *n*-pentane (5 mL) the residue was stirred at room temperature until white crystals formed. The yield was 30–50%; ^{1}H-n.m.r. ($CDCl_3$): δ 2.1–2.3 (m, 4 H, $CH_2CH_2CH_2CH_2$), 2.8–3.3 (m, 4 H, CH_2NCH_2), 3.93 (s, 2 H, $ArCH_2N$), 4.65 (s, 4 H, OCH_2CH_2O), 6.9–7.25 (Ph–H), and 7.35–7.60 (m, 1 H, Ph–H, *ortho*).

Anal. Calc. for $C_{13}H_{18}BNO_2$ (231.10): C, 67.6; H, 7.8; N, 6.1. Found: C, 66.8; H, 8.2; N, 6.1.

4,5-Dibromo-2-phenyl-1,3,2-dioxaborolane. — To a cooled (−70°) and stirred mixture of 2-phenyl-1,3,2-dioxaborole (**7a**) (2.55 g, 17.5 mmol) and dry CH_2Cl_2 (70 mL) a solution of bromine (2.79 g, 17.5 mmol) in dry CH_2Cl_2 (70 mL) was added dropwise over a period of 6 h in such a manner that the colour from each drop of the halogen rapidly disappeared. At the end, the temperature was raised to −30°. After being stirred for 2 h at −30° the reaction mixture was kept at −30° overnight. The solvent was removed under vacuum and the residue was purified by distillation (Kugelrohr). The yield was 4.06 g (76%); b.p. 75°/80 Pa; m.p. 25.5–26.5°; ^{1}H-n.m.r. (CDCl$_3$): δ 6.73 (s, 2 H, OC*H*Br), 7.23–7.79 (m, 3 H, Ph–H), and 7.70–8.11 (m, 2 H, Ph–H, *ortho*); ^{13}C-n.m.r. (CDCl$_3$): δ 86.28 (d, O*C*HBr), 127.94 (d, Ph–CH, *meta*), 133.17 (d, Ph–C, *para*), and 135.38 (d, Ph–C, *ortho*); m.s. (70 eV): *m/z* 304/306 (M$^+$).

Anal. Calc. for $C_8H_7BBr_2O_2$ (305.76): C, 31.4; H, 2.3. Found: C, 31.5; H, 2.4.

4-Alkoxy-2-phenyl-1,3,2-dioxaborolanes (**8a–d**). — **7a** (10 mmol), the respective alcohol (10 mmol), and NEt$_3$ (0.3 mmol) were dissolved in dry THF or dry ether (20 mL). The solution was kept in an ice bath and stirred for 6–12 h. The solvent was removed and the residue was purified by distillation (Kugelrohr). The individual products had the following properties:

4-Methoxy-2-phenyl-1,3,2-dioxaborolane (**8a**). — The yield was 200 mg (58.5%); b.p. 58°/75 Pa (Kugelrohr); ^{1}H-n.m.r. (CDCl$_3$): δ 3.52 (s, 3 H, OC*H*$_3$), 4.10 (AB of ABX, 1 H, C*H*$_2$), 4.33 (AB of ABX, 1 H, C*H*$_2$), 5.50 (X of ABX, 1 H, CH of ring) ($^3J_{AX}$ 3.5, $^3J_{BX}$ 5.7, $^2J_{AB}$ 10.4 Hz), 7.21–7.63 (m, 3 H, Ph–H), and 7.70–7.99 (m, 1 H, Ph–H, *ortho*); ^{13}C-n.m.r. (CDCl$_3$): δ 55.30 (O*C*H$_3$), 71.50 (*C*H$_2$), 103.07 (*C*H), 127.66 (Ph–C, *meta*), 131.47 (Ph–C, *para*), and 134.76 (Ph–C, *ortho*); m.s. (70 eV): *m/z* 178 (M$^+$).

Anal. Calc. for $C_9H_{11}BO_3$ (177.99): C, 60.7; H, 6.2. Found: C, 60.8; H, 6.1.

4-Ethoxy-2-phenyl-1,3,2-dioxaborolane (**8b**). — The yield was 54%, b.p. 67–68°/80 Pa; m.s. (70 eV): *m/z* 192 (M$^+$).

Anal. Calc. for $C_{10}H_{13}BO_3$ (192.02): C, 62.6; H, 6.8. Found: C, 62.5; H, 7.0.

4-Isopropoxy-2-phenyl-1,3,2-dioxaborolane (**8c**). — The yield was 11%, b.p. 60°/80 Pa; m.s. (70 eV): *m/z* 206 (M$^+$).

Anal. Calc. for $C_{11}H_{15}BO_3$ (206.05): C, 64.1; H, 7.3. Found: C, 64.4; H, 7.4.

5-Deuterio-2-phenyl-4-trideuteriomethoxy-1,3,2-dioxaborolane (**8d**). — The yield was 33.5%, b.p. 55°/50 Pa; m.s. (70 eV): *m/z* 182 (M$^+$).

Anal. Calc. for $C_9H_7D_4BO_3$ (182.02): C, 59.4; H, 6.2. Found: C, 59.0; H, 6.2 (D calculated as H).

Preparation of compounds **16f–j/17f–j** *and* **19f–k**. — A solution of **7a** (1.46 g, 10 mmol) in dry THF (20 mL) was cooled to 0°. After the addition of freshly distilled aldehyde (**15**, 7 mmol) the reaction mixture was stirred for 2–12 h at 0°. The solvent was removed under vacuum and the residue distilled (Kugelrohr).

4-Formyl-5-methyl-2-phenyl-1,3,2-dioxaborolane (**16f/17f**). — The yield was 0.72 g (29%), b.p. 113–117°/0.1 Pa (Kugelrohr); ^{1}H-n.m.r. (CDCl$_3$): δ 1.30 (d, ^3J 6.25 Hz, C*H*$_3$, *anti*), 1.46 (d, ^3J 6.3 Hz, C*H*$_3$, *syn*), 4.21–5.20 (m, CH of ring), 7.18–7.58 (Ph–H), 7.65–8.02 (Ph–H, *ortho*), 9.77, and 9.80 (d, –C*H*O); ^{13}C-n.m.r. (CDCl$_3$): δ 18.14 (*C*H$_3$, *anti*, steric γ-effect), 22.20 (*C*H$_3$, *syn*, steric γ-effect), 75.19

($CHCH_3$, *syn*), 75.91 ($CHCH_3$, *anti*), 82.95 ($CHCH_3$, *anti*), 86.87 ($CHCH_3$), 127.77 (Ph–C, *meta*), 131.79 (Ph–CH, *para*), 134.87 (Ph–C, *ortho*), 200.42 (–CHO, *syn*), and 201.29 (–CHO, *anti*), diastereoisomeric ratio (*syn*:*anti*) 37:63; m.s. (70 eV): *m*/*z* 190 (M^+).

Anal. Calc. for $C_{10}H_{11}BO_3$ (190.00): C, 63.2; H, 5.8. Found: C, 63.3; H, 5.8.

5-Ethyl-4-formyl-2-phenyl-1,3,2-dioxaborolane (**16g/17g**). — The yield was 23%, b.p. 115–119°/0.1 Pa; m.s. (70 eV): *m*/*z* 204 (M^+).

Anal. Calc. for $C_{22}H_{13}BO_3$ (204.03): C, 64.8; H, 6.4. Found: C, 64.8; H, 6.6.

4-Formyl-5-isopropyl-2-phenyl-1,3,2-dioxaborolane (**16h/17h**). — The yield was 22%, b.p. 83–84°/0.1 Pa; m.s. (70 eV): *m*/*z* 218 (M^+).

Anal. Calc. for $C_{12}H_{15}BO_3$ (218.06): C, 66.1; H, 6.9. Found: C, 66.2; H, 6.9.

*5-*tert*-Butyl-4-formyl-2-phenyl-1,3,2-dioxaborolane* (**16i/17i**). — The yield was 12%, b.p. 108°/0.1 Pa; m.s. (70 eV): *m*/*z* 232 (M^+).

Anal. Calc. for $C_{13}H_{17}BO_3$ (232.08): C, 67.3; H, 7.4. Found: C, 67.1; H, 7.3.

*5-[(*R*)-2,2-Dimethyl-1,3-dioxolane-4-yl]-4-formyl-2-phenyl-1,3,2-dioxaborolane* (**16j/17j**). — The yield was 24%; b.p. 175–188°/0.1 Pa; m.s. (70 eV): *m*/*z* 261 (M^+).

Anal. Calc. for $C_{14}H_{17}BO_5$ (276.09): C, 60.9; H, 6.2. Found: C, 61.1; H, 6.4.

Diaddition product **19f** *of acetaldehyde.* — The yield was 36%; b.p. 180–190°/0.1 Pa; m.s. (70 eV): *m*/*z* 336 (M^+).

Anal. Calc. for $C_{18}H_{18}B_2O_5$ (335.96): C, 60.9; H, 6.2. Found: C, 61.1; H, 6.4.

Diaddition product **19g** *of propionaldehyde.* — The yield was 33%; b.p. 185–190°/0.1 Pa; m.s. (70 eV): *m*/*z* 350 (M^+).

Anal. Calc. for $C_{19}H_{20}B_2O_5$ (349.98): C, 65.2; H, 5.7. Found: C, 64.8; H, 5.9.

Diaddition product **19h** *of isobutyraldehyde.* — The yield was 29%; b.p. 140–160°/0.1 Pa; m.s. (70 eV): *m*/*z* 364 (M^+).

Anal. Calc. for $C_{20}H_{22}B_2O_5$ (364.01): C, 66.0; H, 6.1. Found: C, 66.0; H, 6.2.

Diaddition product **19i** *of 2,2-dimethylpropanal.* — The yield was 8%; b.p. 185–195°/0.1 Pa; m.s. (70 eV): *m*/*z* 378 (M^+).

Anal. Calc. for $C_{21}H_{24}B_2O_5$ (378.04): C, 66.7; H, 6.4. Found: C, 66.9; H, 6.3.

Diaddition product **19k** *of benzaldehyde.* — M.s. (70 eV): *m*/*z* 398 (M^+).

Anal. Calc. for $C_{23}H_{20}B_2O_5$ (398.03): C, 69.4; H, 5.1. Found: C, 69.7; H, 5.0.

Polymers. — Cross-linked polymers containing 1,3,2-dioxaborolane groups were prepared by copolymerization of a mixture of 50% monomers, 25% dry benzene, and 25% dry acetonitrile according to previously published procedures[47] in sealed tubes under reduced pressure for 12–36 h at 65°. The monomer mixture contained 12% *m*-diisopropenylbenzene, 82.8–86.3% styrene, 1.70–5.2% **21**, and 0.8% azobis(isobutyronitrile) (AIBN). The polymers were milled, sieved (250 μm), dried under vacuum (100 Pa/12–20 h), and stored under nitrogen. Functionalization with 1,3,2-dioxaborole groups was accomplished by treating a 1,3,2-dioxaborolane group-containing polymer with 4–5 mol. equiv. of **7a** (in dry CCl_4) in the presence of 3–5 mol% NEt_3 and subsequent removal of the reaction products by filtration. The procedure was repeated 3–4 times. Finally the polymer was carefully washed with dry CH_2Cl_2.

The concentration of accessible 1,3,2-dioxaborole groups on the polymer was determined by measuring the ethylene glycol split off by the same procedure as that used for the isolation of the aldehyde-addition products. The estimation procedure involved the addition of an internal standard (glycerol) to the isolated ethylene glycol solution, removal of the solvent (30°, vacuum), and acetylation (3:1 acetic anhydride–pyridine, 2 h, 60–90°) prior to g.l.c. analysis.

Reactions of the functionalized polymer with aldehydes. — To the dioxaborole-functionalized polymer dry CH_2Cl_2 was added dropwise until the suspension could be stirred. Aldehyde **15j** or **15k** was added by means of a syringe and the mixture was stirred under a nitrogen atmosphere for 12–36 h at room temperature.

Isolation of products. — The addition products were isolated by stirring the polymer with three successive portions of solvent mixture I and three successive portions of solvent mixture II. Stirring was continued for 1.5 h with each solvent portion, and the suspension was then filtered. Solvent mixture I was 20:5:1 CH_2Cl_2–CH_3OH–H_2O and solvent mixture II was 20:5:1 CH_3CN–CH_3OH–H_2O. The combined solvent washes were concentrated to dryness under vacuum at 30°. Then 200–250 mg of ion exchanger (Dowex 50W X-4) and nitrogen-flushed water (10 mL) were added to the residue, the mixture was heated for 2 h at 80°, cooled to room temperature, and filtered, and the ion exchanger washed with water. The filtrate and washings were concentrated under vacuum at 30°.

L-*Ribose.* — Polymer (30 g; 0.296 mmol functional groups per g polymer) was treated with 5 mol. equiv. of **15l**. On isolation of the products and removal of the protecting groups a mixture of aldopentoses (410 mg) was obtained. Enantiomerically pure L-ribose was separated by liquid chromatography (LiChrosorb–NH_2, 85:15 acetonitrile–water); $[\alpha]_D^{20}$ +19.7° (c 0.22, H_2O); lit.[35] $[\alpha]_D$ +18.8° (c 1.5, H_2O).

Derivatization of reaction products for g.l.c. analysis. — The conversion of the sugars into peracetylated aldononitriles was performed according to known procedures[33]. The reaction was carried out under a nitrogen atmosphere and the temperature was strictly maintained between 60 and 65°. The g.l.c. separation was performed on a packed column (OV17, W-HP, 80–100 mesh, 3 m) or a capillary column (OV17, 50 m) at 195°.

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