Dioxolanylium Ions Derived from Carbohydrates. I. Reactions with Water and with Bromide Ions

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Treatment of 3,4-*O*-benzylidene derivatives of methyl *β*-D-arabinopyranoside with triphenyl-methyl fluoroborate gave benzoxonium ions which were stable in acetonitrile solution. Reaction of the benzoxonium ions with water gave hydroxy-benzoates with *cis*-opening of the dioxolanylium ring. Treatment with bromide ions lead to *trans*-opening and formation of bromo-deoxypentopyranosides. Similar results were obtained with methyl 4-*O*-benzoyl-2,3-*O*-benzylidene-*α*-D-lyxopyranoside and with methyl 5-*O*-benzoyl-2,3-*O*-benzylidene-*β*-D-ribofurano-side.

The preparation of dioxolanylium ions from aldehydic acetals by hydride abstraction with triphenylmethyl fluoroborate or similar reagents is well known.[1-3] Dioxolanylium ions derived from carbohydrates have been obtained in a few cases using this method.[3-5]

We have now investigated the reaction of a variety of carbohydrate benzylidene acetals with triphenylmethyl fluoroborate with the purpose of preparing 2-phenyl-dioxolanylium (benzoxonium) ions and studying their reactions with nucleophilic reagents. In the present paper the reactions of some pentose derivatives are described. A following paper will describe the behaviour of some hexose derivatives. When this work was almost completed a communication by Hanessian and Staub appeared in which closely related work is described.[6]
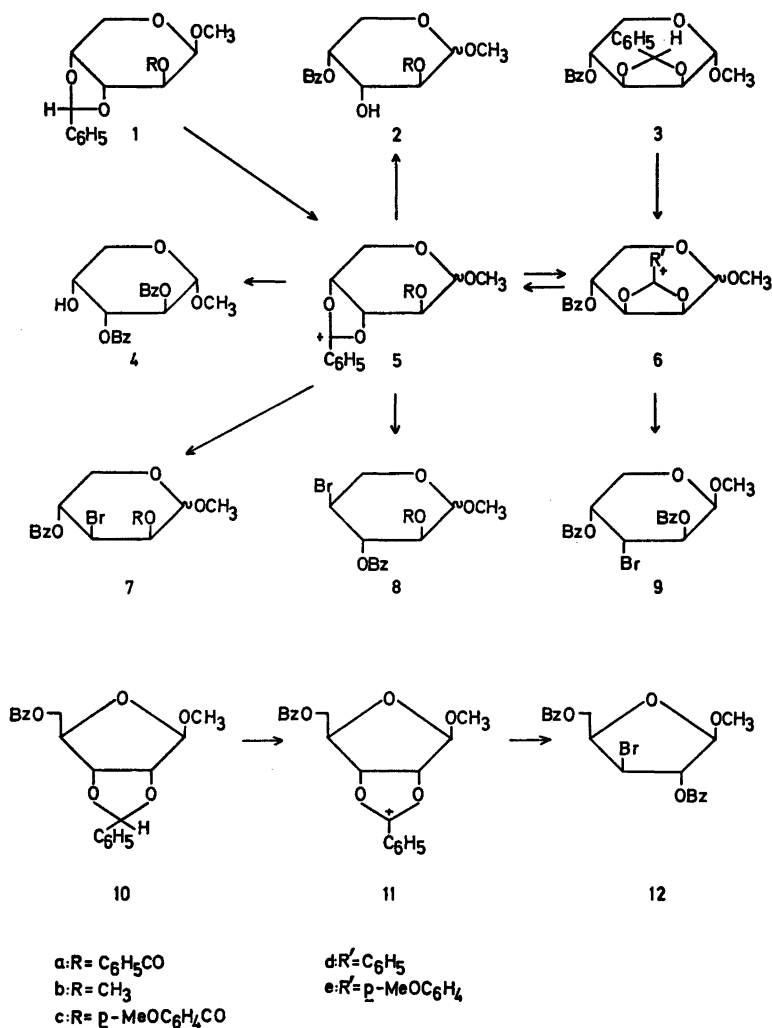
When methyl 2-*O*-benzoyl-3,4-*O*-benzylidene-*β*-D-arabinopyranoside (*1a*) was treated with triphenylmethyl fluoroborate in acetonitrile solution it was completely converted to a benzoxonium ion within a few hours and NMR spectra (Table 1) showed that it was the 3,4-benzoxonium ion (*β5a*) which was the main

product. When moisture was excluded the ion was stable in acetonitrile solution for several days except that anomerization took place to some extent. The ion *β5a* is in equilibrium with the 2,3-benzoxonium ion (*β6d*),[3,4,7] derived from methyl lyxoside. However, the spectra indicated that the equilibrium was almost completely shifted towards *β5a*. This was confirmed by the reaction of methyl 3,4-*O*-benzylidene-2-*O*-methyl-*β*-D-arabinopyranoside (*1b*) with triphenyl-methyl fluoroborate. This can of course only give the 3,4-benzoxonium ion (*β5b*) and the NMR spectrum (Table 1) of the ion formed was very similar to that of *β5a*.

A similar treatment of the lyxose derivative (*3*) would be expected to give initially the 2,3-benzoxonium ion (*α6d*), however, the product observed through NMR spectra was the 3,4-benzoxonium ion (*α5a*). Thus, the equilibrium between *5* and *6* is apparently largely shifted towards *5* in both anomers.

In order to get an NMR spectrum of a 2,3-benzoxonium ion methyl 3,4-*O*-benzylidene-2-*O*-*p*-methoxybenzoyl-*β*-D-arabinopyranoside (*1c*) was treated with triphenylmethyl fluoroborate. This gave a *p*-methoxybenzoxonium ion (*β6e*) in equilibrium with the 3,4-benzoxonium ion (*β5c*). Since a *p*-methoxy group stabilizes a benzoxonium ion[4] this equilibrium was shifted strongly towards *6* and only *ca.* 10 % of *5* was present. NMR data of both ions could be obtained from a spectrum of the mixture (Table 1) and the spectrum of *β6e* is quite different from that of *β5c* and from the spectra of the other 3,4-benzoxonium ions.

Treatment of the ribofuranose derivative *10* with triphenylmethyl fluoroborate gave the

OCH₃ ... RO ... H—C6H5 **1**

BzO ... OCH₃ ... OH **2**

C6H5 H ... BzO ... OCH₃ **3**

HO ... BzO ... OCH₃ ... OBz **4**

RO ... OCH₃ ... C6H5 **5**

BzO ... R' ... OCH₃ **6**

BzO ... Br ... RO ... OCH₃ **7**

Br ... RO ... OCH₃ ... OBz **8**

OCH₃ ... BzO ... BzO ... Br **9**

BzO ... OCH₃ ... C6H5 H **10**

BzO ... OCH₃ ... C6H5 **11**

BzO ... OCH₃ ... Br ... OBz **12**

a: R = C₆H₅CO
b: R = CH₃
c: R = p-MeOC₆H₄CO

d: R' = C₆H₅
e: R' = p-MeOC₆H₄

benzoxonium ion *11* as already described by Hanessian and Staub;[6] its NMR data are presented in Table 1.

It is well known that dioxolanylium ions react rapidly with water to give *cis*-hydroxy esters [2] and this reaction has been described for the benzoxonium ion (*11*).[6] Addition of water to a solution of β5a in acetonitrile gave methyl 2,4-di-*O*-benzoyl-β-D-arabinopyranoside (*β2a*) as the only detectable product. This is in agreement with the results of King and Allbutt [8] who found that hydrolysis of a benzoxonium ion gives predominantly the product which has the *O*-benzoyl group axially oriented. In *β2a*, which

preferentially adopts the $^{1}C_{4}$ conformation, the *O*-benzoyl group at C4 is axial. When α5a was hydrolysed, the main product was the 2,4-di-*O*-benzoate (*α2a*); but in this case a small amount of the 2,3-di-*O*-benzoate (*4*) was also isolated, possibly arising from acyl-migration. No products resulting from hydrolysis of *6* were found, indicating that the equilibrium between *5* and *6* is shifted strongly towards *5*, as also found from the NMR spectra. Hydrolysis of the 2-*O*-methylated ion (*β5b*) gave the 4-*O*-benzoate (*β2b*) as the only detectable product.

Reaction of benzoxonium ions with halide ions leads to *trans*-opening with formation of

Table 1. Proton NMR spectra of benzoxonium ions in deuterioacetonitrile. Chemical shifts are in ppm relative to TMS; coupling constants are in Hz.

Compound	H1	H2	H3	H4	H5	H5'	J_{12}	J_{23}	J_{34}	J_{45}	$J_{45'}$	$J_{55'}$	OCH$_3$	Conformation
β5a	5.17	5.63	6.27	6.15	4.53	4.35	4.2	6.0	8.4	~0	2.4		3.41	distorted $^1C_4$ or $^1H_0$
α5a	4.95	5.46	6.18–	6.20	4.70	4.44	4.3	~2		~0	1.8		3.27 3.43	$^{2,5}B$
β5b	5.04	3.90	5.85–	6.05	4.46	4.21	3.8	6.8		0	2.0	14.7	3.52 3.41	distorted $^1C_4$ or $^1H_0$
β6e	5.24	6.06	5.94	5.81	4.26	3.95	3.8	7.5	3.0	4.0	3.5	13.2	3.98 3.44	distorted $^1C_4$
β5c	5.18	5.60	6.27	6.16	4.55	4.35	4.0	6.0	8.5	~0	~2	~15.5	3.84	distorted $^1C_4$ or $^1H_0$
11	5.56	6.54 or 6.16		5.14	4.58	4.52	~0.5	6.8	0.6	6.3	6.7		3.38	

A ^{13}C NMR spectrum of β5a in deuterioacetonitrile gave the following chemical shifts (relative to TMS): C1, 94.7; C2, 67.6; C3 and C4, 87.1 and 84.3; C5, 55.6; C$_6$H$_5$C+, 181.5; –OCH$_3$, 55.2.

bromo-benzoates.[2,3] Treatment of the ions described above with tetraethylammonium bromide in acetonitrile proceeded in accordance herewith. The benzoxonium ions disappear within a few minutes when bromide is added, but the formation of the bromo-deoxy compounds requires ca. 2 h. This may indicate that intermediate orthoester bromides are formed rapidly and that they rearrange more slowly to the bromo-deoxy compounds.

Reaction of β5a with bromide ions gave two products in equal amounts. One was the 4-bromo-L-xylose derivative (α8a), resulting from attack of a bromide ion on C4 of β5a. The other product was the 3-bromo-arabinoside (9) which is probably formed by attack of bromide on C3 of β6d. The latter ion is only present to a small extent, as discussed above, but if its reaction with bromide is more rapid than that of 5 formation of rather large amounts of 9 would be possible.

Reaction of the 2-O-methylated ion (β5b) with bromide gave α8b as the main product and a small amount of the 3-bromo-lyxose derivative (β7b). Both can arise from β5b by substitution with bromide ions at C4 and C3, respectively. The same two bromo-compounds were obtained when 1b was treated with N-bromosuccinimide according to Hanessian and Plessas.[7] Reaction of 3 with triphenylmethyl fluoroborate followed by treatment with bromide ions gave α7a as the main product together with a small amount of β8a. Thus, in this case the ion α6d does not seem to be reactive enough, probably because the α-methoxy group at C1 exerts steric hindrance towards attack at C3 of α6. Similarly, the low reactivity of C3 of the β-anomer (β5a) may be explained through steric hindrance by the methoxy group at C1.

Treatment of the benzoxonium ion (11) with bromide ions gave a good yield of the 3-bromo-3-deoxy-D-xylofuranose derivative (12). Since anomerisation took place during the reaction with bromide a mixture of the two anomers of 12 was obtained. These were treated with hydrogen bromide and the furanosyl bromide thus obtained was reacted with methanol. This gave the pure β-anomer of 12.

The reactions of the benzoxonium ions described above with other nucleophiles will be discussed in a forthcoming paper.

EXPERIMENTAL

Thin layer chromatography (TLC) was performed on silica gel PF$_{254}$ (Merck); for preparative work 1 mm layers were used on 20 × 40 cm plates. NMR spectra were obtained on Varian A-60 or HA-100 instruments and on a Bruker WH-90 instrument.

BENZYLIDENE COMPOUNDS

Methyl 2-O-benzoyl-3,4-O-benzylidene-β-D-arabinopyranoside (1a). Finely powdered methyl β-D-arabinopyranoside (4.92 g), benzaldehyde (3.30 g), p-toluenesulfonic acid (100 mg), and chloroform (150 ml) were refluxed for 10 h with a Soxhlet extractor containing 30 g of 4 Å molecular sieves. The solution was then washed with aqueous sodium hydrogencarbonate and water and dried (MgSO$_4$). The solvent was evaporated and the residue was benzoylated with benzoyl chloride (4.2 ml) in pyridine (50 ml) to give a product which was crystallized from ether at − 20 °C. Decantation of the ether and recrystallization from ethyl acetate − pentane gave 5 − 7 g (47 − 65 %) of 1a as a mixture of diastereomers, m.p. 95 − 105 °C.[7,8]

Methyl 4-O-benzoyl-2,3-O-benzylidene-α-D-lyxopyranoside (3) was prepared in the same way from methyl α-D-lyxopyranoside (3.3 g) which gave 2.5 g (35 %) of a mixture of the diastereomeric benzylidene acetals. Fractional crystallization from ethyl acetate-cyclohexane yielded small amounts of pure exo and endo isomers of (3). The H-endo isomer had m.p. 101 − 103 °C, [α]$_D^{22}$ − 22.5° (c 1.0, CHCl$_3$). (Found: C 67.38; H 5.84. Calc. for C$_{20}$H$_{20}$O$_6$: C 67.40; H 5.66). The H-exo isomer had m.p. 93 − 94 °C, [α]$_D^{22}$ − 44.8° (c 1.5, CHCl$_3$). (Found: C 67.51; H 5.72).

Methyl-3,4-O-benzylidene-2-O-p-methoxybenzoyl-β-D-arabinopyranoside (1c). Crude methyl 3,4-O-benzylidene-β-D-arabinopyranoside (1.15 g) was treated with p-methoxybenzoyl chloride (1.27 g) in pyridine to give 1.7 g of a mixture of endo- and exo-H product. Preparative TLC (ether − pentane 1:1) gave two fractions. The fast moving component was the endo-H product (1c) (645 mg) which was crystallized from ethyl acetate − pentane to give 290 mg of pure material, m.p. 97 − 99 °C, [α]$_D^{21}$ − 161.7° (c 1.1, CHCl$_3$). (Found: C 65.28; H 5.70. Calc. for C$_{21}$H$_{22}$O$_7$: C 65.27; H 5.74). The slow moving fraction, obtained as a syrup, was the exo-H product contaminated with some of the endo-compound.

Methyl 5-O-benzoyl-2,3-O-benzylidene-β-D-ribofuranoside (10). A similar treatment of methyl β-D-ribofuranoside [10] (1.64 g) gave 3.3 g of crude 10 which was crystallized from ether (10 ml) − pentane (35 ml) to give 2.5 g (70 %) of the H-exo product, m.p. 70 − 72 °C. Further recrystallization from ether − pentane gave the

pure product, m.p. 73—75 °C, $[\alpha]_D^{27}$ —27.4° (c 2.4, CHCl$_3$). (Found: C 67.55; H 5.71. Calc. for C$_{20}$H$_{20}$O$_6$: C 67.40; H 5.66).

Conversion of benzylidene derivatives to hydroxy-benzoates

General procedure. The appropriate benzylidene derivative (1 part) was treated with a 10—25 % molar excess of triphenylmethyl fluoroborate in dry acetonitrile (10 parts) at room temp. for the time specified below. The solution was then poured into aqueous sodium hydrogencarbonate, the mixture was extracted with chloroform, and the chloroform solution was dried and evaporated. Preparative TLC with ether—pentane (2:1) as eluent gave triphenylmethane moving with the solvent front, closely followed by triphenylcarbinol and the product(s).

Methyl 2-O-benzoyl-3,4-O-benzylidene-β-D-arabinopyranoside (1a) (809 mg) was treated with triphenylmethyl fluoroborate for 5 h after which time it was completely converted to the ion *β5a* as seen from an NMR spectrum. Hydrolysis and chromatography as described above gave 569 mg (67 %) of methyl 2,4-di-O-benzoyl-β-D-arabinopyranoside (*β2a*), m.p. 143—146 °C. Recrystallization from ethyl acetate—pentane gave the pure product, m.p. 147—149 °C, $[\alpha]_D^{25}$ —240.4° (c 2.3, CHCl$_3$). (Found: C 64.36; H 5.23. Calc. for C$_{20}$H$_{20}$O$_7$: C 64.51; H 5.41). Acetylation with acetic anhydride in pyridine gave the known methyl 3-O-acetyl-2,4-di-O-benzoyl-β-D-arabinopyranoside, m.p. 86—88 °C (reported [11] m.p. 86—87 °C). A mixed melting point with an authentic sample gave no depression.

Direct crystallization of *β2a* from ethyl acetate-pentane without previous chromatographic separation gave a 40 % yield of a product with m.p. 140—146 °C.

Methyl 4-O-benzoyl-2,3-O-benzylidene-α-D-lyxopyranoside (3) (474 mg) was treated with triphenylmethyl fluoroborate for 7 h. Hydrolysis and chromatography gave two products. The fast moving compound was methyl 2,4-di-O-benzoyl-α-D-arabinopyranoside (*α2a*) (206 mg, 42 %). The slow moving fraction gave 41 mg (8 %) of methyl 2,3-di-O-benzoyl-α-D-arabinopyranoside (4). The products were identified through their NMR spectra (Table 2). On benzoylation they gave identical products as seen from NMR spectra. The two benzoylated products were mixed and recrystallized from methanol to give 191 mg of methyl tri-O-benzoyl-α-D-arabinopyranoside, m.p. 144—145 °C (reported [12] m.p. 146 °C). A mixed m.p. with an authentic sample gave no depression.

Methyl 3,4-O-benzylidene-2-O-methyl-β-D-arabinopyranoside (1b) [13] (560 mg) was treated with triphenylmethyl fluoroborate for 2 h. Hy-

drolysis and chromatography gave 274 mg (46 %) of methyl 4-O-benzoyl-2-O-methyl-β-D-arabinopyranoside (*β2b*) which slowly crystallized from pentane. Recrystallization from ethyl acetate—pentane gave the pure product, m.p. 107—108 °C, $[\alpha]_D^{21}$ —204.0° (c 0.9, CHCl$_3$). Benzoylation gave the known methyl 3,4-di-O-benzoyl-2-O-methyl-β-D-arabinopyranoside, m.p. 72—74 °C (reported [14] m.p. 75—77 °C). A mixed m.p. with an authentic sample gave no depression.

Conversion of benzylidene derivatives to bromo-deoxy compounds

General procedure. The benzoxonium ion was prepared as described above in acetonitrile solution. To this solution was added dry tetraethylammonium bromide (3 molar equiv.) and the mixture was stirred until it was homogeneous and then kept for 2 h at room temp. The solution was then stirred for 5 min with aqueous sodium hydrogencarbonate and extracted with chloroform. The chloroform solution was washed with water, dried and evaporated. Preparative TLC (ether—pentane 1:2) gave triphenylmethane, moving with the solvent front, and triphenylcarbinol, usually followed closely by the product(s).

Methyl 2-O-benzoyl-3,4-O-benzylidene-β-D-arabinopyranoside (1b) (935 mg) by this treatment gave two products. The fast moving fraction (380 mg, 33 %) was methyl 2,3-di-O-benzoyl-4-bromo-4-deoxy-α-L-xylopyranoside (*α8a*). Crystallization from cyclohexane gave the pure product, m.p. 109—110 °C, $[\alpha]_D^{25}$ —129.7° (c 1.1, CHCl$_3$). (Found: C 55.32; H 4.31; Br 18.50. Calc. for C$_{20}$H$_{19}$BrO$_6$: C 55.18; H 4.40; Br 18.36).

The slower moving product (351 mg, 31 %) was methyl 2,4-di-O-benzoyl-3-bromo-3-deoxy-β-D-arabinopyranoside (9) which crystallized slowly. Three recrystallizations from cyclohexane gave a product with m.p. 82—86 °C, $[\alpha]_D^{25}$ —267.8° (c 1.0, CHCl$_3$). (Found: C 55.34; H 4.37; Br 18.54). The structures of the two bromides were established from their NMR spectra (Table 2). Separation of the mixture of bromides described by Hanessian and Plessas [7] gave products identical with those described above.

In addition to *α8a* and *9* 135 mg (14 %) of *4* was also isolated.

Methyl 3,4-O-benzylidene-2-O-methyl-β-D-arabinopyranoside (1b) (925 mg) gave by the same treatment two products. The fast moving fraction (63 mg, 5 %) was methyl 4-O-benzoyl-3-bromo-3-deoxy-2-O-methyl-β-D-lyxopyranoside (*β7b*) as a syrup, $[\alpha]_D^{21}$ —33.7° (c 1.3, CHCl$_3$). (Found: C 48.78; H 4.97; Br 23.37. Calc. for C$_{14}$H$_{17}$BrO$_5$: C 48.71; H 4.97; Br 23.15). The slower moving fraction (494 mg, 41 %) was methyl 3-O-benzoyl-4-bromo-4-deoxy-2-O-

Table 2. Proton NMR spectra of benzylidene derivatives and products prepared from them. Chemical shifts are in ppm relative to tetramethylsilane; coupling constants in Hz.

Compound	Solvent	H1	H2	H3	H4	H5	H5'	OCH$_3$	J_{12}	J_{23}	J_{34}	J_{45}	$J_{45'}$	$J_{55'}$	Predominant conformation
1c endo-H	CDCl$_3$	5.04	5.30	4.80	4.30	4.10	3.97	3.82 3.40	3.4	8.2	5.3	~0.5	2.2	13.2	benzylidene H 6.26
1c exo-H	»	5.02	5.20	4.67	4.39	4.18	4.06	3.82 3.40	3.4	7.6	6.2	1.0	2.7	13.4	benzylidene H 5.93
3 endo-H	»	4.86	4.23	4.59	5.39	3.92	3.78	3.46	2.6	5.2	6.4	5.0	7.6	11.5	benzylidene H 6.26
3 exo-H	»	4.84	4.24	4.51	5.23	3.88	3.82	3.45	3.2	5.9	5.2	4.8	6.0	11.8	benzylidene H 5.94
10 exo-H	»	5.18	4.76	4.86	4.73	4.42	4.41	3.36	<0.5	6.3	<0.5	~6.4	~7.7		benzylidene H 5.80
α2a	»	4.64	5.35	4.18	5.42	4.15	3.78	3.50 3.41	4.9	7.0	3.2	6.2	3.3	12.5	
β2b	»	4.95	3.65	4.18	5.38	3.80		3.52	3.5	10.0	3.5	<2	<2		
4	»	4.58	5.62	5.39	4.32	4.10	3.75	3.50	5.8	8.3	3.2	4.5	2.3	12.4	
α7a	»	4.83	5.49	4.73	5.64	4.12	3.86	3.43 3.44	2.2	3.3	10.7	5.5	10.5	11.0	$^4C_1$
β7b	Benzene-d_6	4.72	3.57	4.53	5.45	4.06	3.65	3.55 2.95 3.44	2.6	3.2	9.8	4.9	9.0	10.8	$^4C_1$
α8a	»	5.11	5.25	6.31	3.53 – 3.90				3.5	9.8	9.9	7.5	9.3	11.6	$^1C_4$
α8b	Acetone-d_6	5.14	3.63	5.78	4.35	3.97	3.96	3.53	3.4	9.8	9.8	7.6	9.1	11.2	$^1C_4$
β8a	CDCl$_3$	4.61	5.32	5.72	3.7 – 4.4			3.50	7.6	9.3	~9				$^1C_4$
9	»	5.13	5.59	4.81	5.55	4.05	3.95	3.42	3.4	10.7	3.4	1.5	1.8	12.7	$^1C_4$
α12	»	5.40	5.56	4.3 – 4.9	4.4 – 4.9			3.40	4.5	5.5					
β12	Benzene-d_6	4.95	5.70	4.10	4.4 – 4.7			3.23	<0.5	1.6	5.2				
a	»	6.95	5.60	4.5 – 5.1					4.6	6.5					

[a] 2,5-Di-O-benzoyl-3-bromo-3-deoxy-α-D-xylofuranosyl bromide.

methyl-α-L-xylopyranoside (α8b), m.p. 72–74
°C. Two recrystallizations from ether-pentane
gave a product with m.p. 73–74 °C, $[\alpha]_D^{21}$
– 76.2° (c 1.3, CHCl$_3$). (Found: C 48.87; H
5.07; Br 23.02). The structures of the two
products were derived from their NMR spectra
(Table 2).

Methyl-2,3-O-benzylidene-4-O-benzoyl-α-D-lyxopyranoside (3) (587 mg) gave two products.
The fast moving material (351 mg, 49 %) was
methyl 2,4-di-*O*-benzoyl-3-bromo-3-deoxy-α-D-lyxopyranoside (α7a) which was crystallized
from ether–pentane, m.p. 103–105 °C, $[\alpha]_D^{25}$
– 125.4° (c 1.3, CHCl$_3$). (Found: C 55.26; H
4.25; Br 18.25. Calc. for C$_{20}$H$_{19}$BrO$_6$: C 55.18;
H 4.40; Br 18.36). The slower moving fraction
(44 mg, 6 %) was identified, after rechromatography, through its NMR spectrum as impure
methyl 2,3-di-*O*-benzoyl-4-bromo-4-deoxy-β-L-xylopyranoside (β8a).

Methyl 2,3-O-benzylidene-5-O-benzoyl-β-D-ribofuranoside (10) (576 mg) gave after treatment with triphenylmethyl fluoroborate followed by reaction with tetraethylammonium
bromide and chromatography 521 mg (74 %)
of methyl 2,5-di-*O*-benzoyl-3-bromo-3-deoxy-D-xylofuranoside as a mixture of anomers in an
α:β ratio of 3:2, as seen from an NMR spectrum.
Treatment with 30 % hydrogen bromide in
glacial acetic acid and work up in the usual
way gave 520 mg of 2,5-di-*O*-benzoyl-3-bromo-3-deoxy-α-D-xylofuranosyl bromide, characterized through its NMR spectrum. The bromide
was stirred over night with silver carbonate
(1.0 g) in methanol (10 ml) and the product
thus obtained was benzoylated with benzoyl
chloride (0.3 ml) in pyridine (10 ml). Preparative
TLC (ether–pentane 1:2) gave 276 mg (60 %)
of methyl 2,5-di-*O*-benzoyl-3-bromo-3-deoxy-β-D-xylofuranoside (12) as a syrup, $[\alpha]_D^{21}$ +31.8°
(c 3.0, CHCl$_3$). (Found: C 55.02; H 4.47; Br
18.54. Calc. for C$_{20}$H$_{19}$BrO$_6$: C 55.18; H 4.40; Br
18.36). Besides, 68 mg (12 %) of a mixture of
the anomeric 1,2,5-tri-*O*-benzoyl-3-bromo-3-deoxy-D-xylofuranoses was isolated. The products were characterized through their NMR
spectra.

Microanalyses were performed by Dr. A.
Bernhardt, Mikroanalytisches Laboratorium or
by Novo Microanalytical Laboratory.

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