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Reaction of 1,2-Dideoxy-glyc-1-enopyranoses and 2-Deoxyglycopyranoses with Hydrogen Fluoride. V *

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Treatment of tri-*O*-benzoyl-1,2-dideoxy-D-*lyxo*-hex-1-enopyranose (IIIb) with hydrogen fluoride at −70° gives the unstable 4,6-di-*O*-benzoyl-2,3-dideoxy-D-*threo*-hex-2-enopyranosyl fluoride (X), which was isolated as the corresponding methyl glycoside (XI). In addition, tri-*O*-benzoyl-2-deoxy-D-*lyxo*-hexopyranosyl fluoride (IV) and a disaccharide (XII) were obtained. Reaction of tetra-*O*-benzoyl-2-deoxy-D-*lyxo*-hexopyranose (I) with hydrogen fluoride at −70° gave the expected fluoride (IV). Treatment of (I), or of (IIIb), with hydrogen fluoride at −27° gave 4,6- and 3,6-di-*O*-benzoyl-2-deoxy-D-*lyxo*-hexopyranosyl fluorides, (V) and (VI), which were converted to the methyl glycoside (II). The mechanisms of the reactions are discussed, and experiments with deuterium fluoride showed that the deoxy-compound (I) is converted into (V) and (VI) *via* an unsaturated intermediate. Tetra-*O*-benzoyl-2-deoxy-D-*arabino*-hexopyranose(XIII) and deuterium fluoride gave, by elimination and addition of deuterium fluoride, the dioxolenium ion (XV). Hydrolysis and benzoylation of the latter yielded tri-*O*-benzoyl-2-deoxy-D-*ribo*-hexopyranosyl fluoride (XVII), which contained deuterium at C-2.

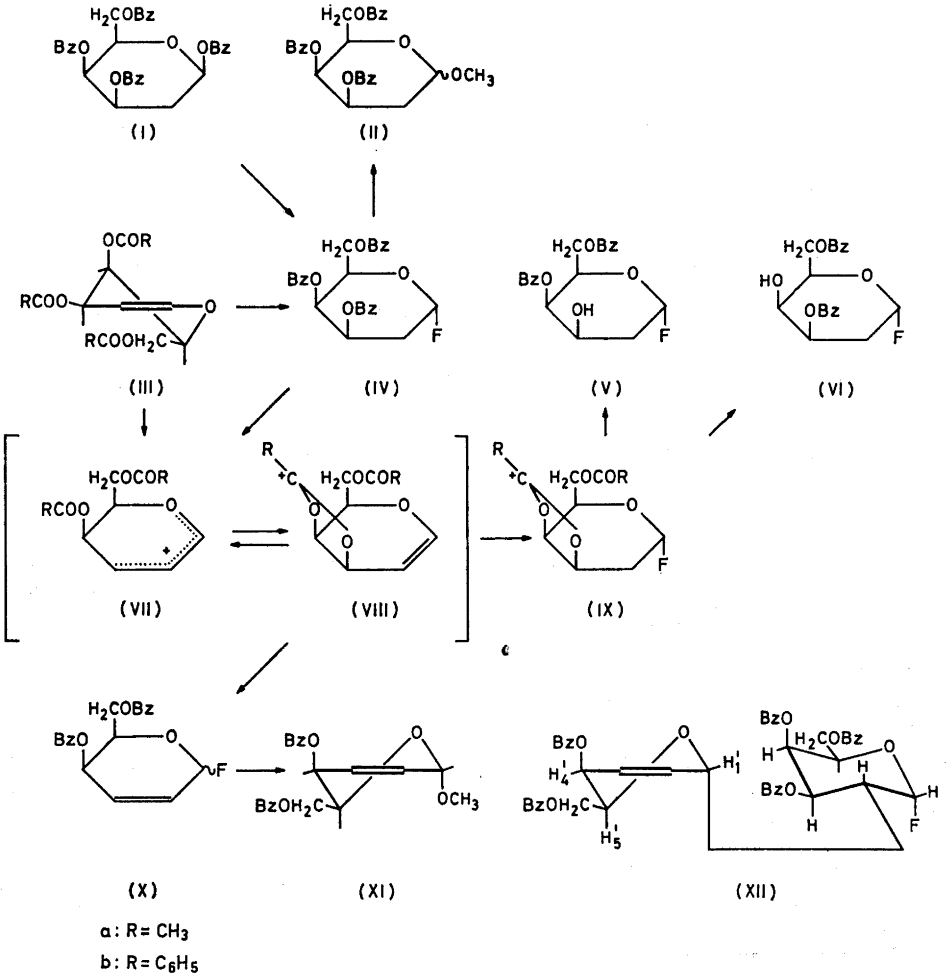
The reaction of tri-*O*-acyl-1,2-dideoxy-D-*arabino*-hex-1-eno-pyranose with hydrogen fluoride was previously shown to give a 1,2-unsaturated 3,4-dioxolenium ion as the initial product. Addition of hydrogen fluoride to the double bond of this ion subsequently gave a 3,4-dioxolenium ion, derived from 2-deoxy-D-*ribo*-hexopyranosyl fluoride.[1] The same ion was formed when tetra-*O*-acyl-2-deoxy-D-*arabino*-hexose was treated with hydrogen fluoride.[2] The driving force in these reactions is probably the formation of the 3,4-dioxolenium ion which is stable in hydrogen fluoride solution. 3,6-Di-*O*-benzoyl-4-*O*-methyl-1,2-dideoxy-D-*arabino*-hex-1-enopyranose cannot form a dioxolenium ion, and this compound gave an unstable 2,3-unsaturated fluoride with hydrogen fluoride.[3]

In the D-*arabino*-hex-1-enopyranose series, the substituents at C-3 and C-4 are *trans*-oriented, and the substituent at C-3 will probably be cleaved

* For previous papers in this series, see Refs. 1–3.

off rather easily with simultaneous formation of a 3,4-dioxolenium ion by anchimeric assistance from the acyloxy-group at C-4. It was of interest to see whether a 1,2-dideoxy-hex-1-enopyranose derivative, in which the acyloxy-groups at C-3 and C-4 are *cis*-oriented, would also form a 3,4-dioxolenium ion in hydrogen fluoride, or whether the reaction would take a different course. For this reason, we have now studied the reaction of tri-*O*-acyl-1,2-dideoxy-D-*lyxo*-hex-1-enopyranose (III) with hydrogen fluoride.

Treatment of the benzoate (IIIb) with anhydrous hydrogen fluoride for *ca.* 30 min at −70° gave an unstable product, which by chromatography yielded 17 % of tri-*O*-benzoyl-2-deoxy-α-D-*lyxo*-hexopyranosyl fluoride (IV) and 17 % of the disaccharide (XII). The structure of the latter will be discussed below. The reaction described above would be expected to give the unsaturated fluoride (X), based on previous results. This product would probably be too



a: R = CH_3

b: R = C_6H_5

unstable to be isolated, and the experiment was therefore repeated and the crude product was treated with methanol and boron trifluoride. This resulted in isolation of methyl 4,6-di-*O*-benzoyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside (XI) in 51 % yield, in addition to the anomeric glycosides (II) and the glycoside derived from the disaccharide (XII). Similar results were obtained when (IIIb) was treated with hydrogen fluoride in benzene at 0°.

When (IIIb) was treated with anhydrous hydrogen fluoride at −27° for 1 h, only 4 % of the tribenzoylated fluoride (IV) was isolated. Besides, the two di-*O*-benzoyl-2-deoxy-α-D-*lyxo*-hexopyranosyl fluorides (V) and (VI) were obtained in a total yield of 27 %. When the same experiment was carried out with benzoylation of the crude product, (IV) was isolated in 48 % yield. In addition, both experiments gave 10−20 % of the disaccharide (XII). Reaction of (IIIb) with hydrogen fluoride at −27° for 24 h gave the same results, except that the tribenzoylated fluoride (IV) was not present at all in the crude product.

The unsaturated methyl glycoside (XI) is undoubtedly formed from the fluoride (X). This fluoride could arise from the 1,2-unsaturated dioxolenium ion (VIIIb) since it was shown that the analogous ion, formed when 1,2-dideoxy-D-*arabino*-hex-1-enopyranose derivatives were dissolved in hydrogen fluoride, gave an unsaturated fluoride by work up of the hydrogen fluoride solution.[1] (VIIIb) would be expected to add hydrogen fluoride on further reaction to give the saturated ion (IX). Work up of a hydrogen fluoride solution, containing (IX), would result in formation of the dibenzoylated fluorides (V) and (VI), which were actually isolated when (IIIb) was treated with hydrogen fluoride at −27°. Thus the reaction of (IIIb) seems to be analogous to the reaction described previously.[1] However, treatment of (IIIb) with hydrogen fluoride at −70° gave a 15−20 % yield of the 2-deoxy-fluoride (IV), and this product must be formed directly from (IIIb) by addition of hydrogen fluoride to the double bond. A similar reaction was not observed when 1,2-dideoxy-D-*arabino*-hex-1-enopyranose derivatives were treated with hydrogen fluoride.[1,3] Ciment and Ferrier[4] have shown that acid catalyzed treatment of the acetate (IIIa) with alcohols gives mixtures of rearranged products and 2-deoxy-D-*lyxo*-hexopyranosides, the latter resulting from addition to the double bond of (IIIa).

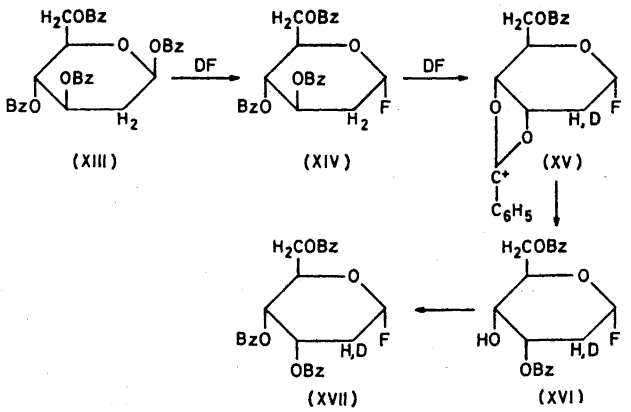
The reaction of (IIIb), and of the corresponding acetate (IIIa), with hydrogen fluoride was also studied by NMR spectroscopy. Spectra of (IIIa) or of (IIIb) in hydrogen fluoride at −70° showed that the compounds reacted very fast since no signals of the starting materials could be observed. In analogy with previous results[1] the hydrogen fluoride solutions should at this stage contain the unsaturated dioxolenium ions (VIIIa) or (VIIIb). Although the spectra were poorly resolved it was, however, obvious that (VIIIa or b) were not present. From the spectrum of the acetate (IIIa) in hydrogen fluoride it was seen that acetic acid was liberated at once, but no signal corresponding to an acetoxonium ion was present. It is possible that the unsaturated dioxolenium ion (VIII) is in equilibrium with an allylic carbonium ion (VII) and that the equilibrium is almost completely shifted towards (VII) in the present case. When the hydrogen fluoride solution is worked up (VII) will then give the unsaturated fluoride (X). When the solution of (IIIa) in hydrogen fluoride

was heated to $-27°$ a signal appeared rapidly at 2.9 δ, showing that an acetoxonium ion was formed. In the spectrum of the benzoate (IIIb) under the same conditions signals appeared at *ca.* 3 δ corresponding to deoxy-protons. This probably means that the initially formed ions (VII) or (VIII) add hydrogen fluoride and give the saturated dioxolenium ion (IX). Hydrolysis of the latter during work up gives the dibenzoylated fluorides (V) and (VI). As mentioned above, addition of hydrogen fluoride to the double bond of (IIIb) to give (IV) took place to some extent. The fluoride (IV) is, however, also converted into the ion (IX) by further reaction with hydrogen fluoride (see below).

3,4,5-Tri-*O*-benzoyl-2-*C*-(4′,6′-di-*O*-benzoyl-2′,3′-dideoxy-α-D-*threo*-hex-2′-enopyranosyl)-2-deoxy-α-D-galactopyranosyl fluoride (XII) is analogous to a product obtained by Ferrier and Prasad [5] from the reaction of tri-*O*-acetyl-1,2-dideoxy-D-*arabino*-hex-1-enopyranose with boron trifluoride. According to the mechanism proposed,[5] (XII) may be formed by a reaction between the allylic carbonium ion (VIIb) and unreacted (IIIb). Since (IIIb) disappears within a few minutes after it is dissolved in hydrogen fluoride, (XII) must be formed very rapidly. In agreement herewith the yield of (XII) was independent of the reaction times used. The structure of (XII) is seen from the NMR spectrum and from the composition (see Experimental). The coupling constants J_{12} (2.5 cps), J_{2F} (30), J_{23}(11.8), and J_{34} (2.2) reveal the stereochemistry at C-1, C-2, and C-3. A hydrogen-fluorine coupling of 30 cps is typical of a *trans*-diaxial configuration.[6]

The fluoride (IV) was also prepared by treating tetra-*O*-benzoyl-2-deoxy-β-D-*lyxo*-hexopyranose (I) with hydrogen fluoride for 10 min at $-70°$. When (I) was allowed to react with hydrogen fluoride for 20 h at $-27°$ (IV) was no longer present in the product, but the dibenzoylated fluorides (V) and (VI) were isolated. This indicates that the fluoride (IV) forms the dioxolenium ion (IX) on further reaction with hydrogen fluoride, and it is thus behaving analogous to the tri-*O*-benzoyl-2-deoxy-D-*arabino*-hexopyranosyl fluoride (XIV) studied previously.[2]

The reaction of (XIV) was assumed to take place *via* a 1,3-dioxolenium ion.[2] A similar mechanism would not explain the conversion of (IV) to (IX),



because the benzoyloxy-groups at C-3 and C-4 of (IV) are *cis*-oriented. A pair of *cis*-1,2-dibenzoyloxy-groups can form a benzoxonium ion directly in hydrogen fluoride, as found in the cyclohexane series.[7] This reaction is, however, rather slow and would probably not be completed within 20 h at $-27°$. In view of this and of the results obtained by treating methyl 3,4-di-*O*-acetyl-2-deoxy-D-*threo*-pentapyranoside with deuterium bromide,[8] it was decided to study the reaction of both (I) and (XIII) with deuterium fluoride.

Treatment of (I) with deuterium fluoride at $-27°$ for 28 h gave a mixture of (V) and (VI), which was immediately benzoylated. The product thus obtained yielded 59 % of the tribenzoylated fluoride (IV). An examination of this product by NMR spectroscopy showed that it contained 0.8 equiv. of deuterium at C-2, equally distributed between the axial and the equatorial position.[5] The fact that deuterium is incorporated at C-2 must mean that (IV), when it reacts with deuterium or hydrogen fluoride, undergoes elimination to an unsaturated intermediate before it forms the ion (IX). The fluoride (IV) may eliminate hydrogen fluoride to give (III), which then reacts *via* (VII) or (VIII) to (IX) as described above. Alternatively, (IV) may eliminate benzoic acid to give (VII) or (VIII) directly.

Similar treatment of (XIII) with deuterium fluoride gave (XVI)[2] which was benzoylated to give tri-*O*-benzoyl-2-deoxy-α-D-*ribo*-hexopyranosyl fluoride (XVII), identical with the product described previously,[1,2] except that it contained 0.8 equiv. of deuterium at C-2. This must mean that the conversion of the initially formed fluoride (XIV) to the ion (XV), which is the final product in hydrogen fluoride solution, must involve an unsaturated intermediate. The mechanism proposed previously,[2] in which the conversion of (XIV) to (XV) was assumed to take place *via* a 1,3-dioxolenium ion, must therefore be wrong.

EXPERIMENTAL

Melting points are uncorrected. For details of TLC and NMR spectra, see Ref. 1.

3,4,6-Tri-O-*benzoyl-1,2-dideoxy*-D-lyxo-*hex-1-enopyranose (IIIb).* 1,2-Dideoxy-D-*lyxo*-hex-1-enopyranose was benzoylated in the usual manner with benzoyl chloride in pyridine. The crude product was obtained in quantitative yield as a syrup which showed one spot on TLC, $[\alpha]_D^{23} = -106°$ (*c* 0.8, $CHCl_3$). (Found: C 70.74; H 4.46. Calc. for $C_{27}H_{22}O_7$: C 70.71; H 4.83.) NMR data are presented in Table 1, together with those of the acetate (IIIa).

Tetra-O-*benzoyl-2-deoxy-β*-D-lyxo-*hexopyranose (I).* A mixture of pyridine (5 ml) and benzoyl chloride (2.5 ml) was cooled to 0° and 2-deoxy-D-*lyxo*-hexose (562 mg) was added with stirring and cooling in ice in the course of 30 min. The mixture was kept overnight at room temperature and worked up in the usual manner. This gave 1.91 g (96 %) of (I) as a chromatographically homogeneous syrup, $[\alpha]_D^{23} = +14.8°$ (*c* 1.4, $CHCl_3$). (Found: C 70.50; H 4.96. Calc. for $C_{34}H_{28}O_9$: C 70.36; H 4.86.) The NMR spectrum (Table 1) showed that the product was the β-anomer only.

Reaction of 3,4,6-tri-*O*-benzoyl-1,2-dideoxy-D-*lyxo*-hex-1-eno-pyranose (IIIb) with hydrogen fluoride

In benzene solution. A solution of (IIIb) (230 mg) in benzene (10 ml) saturated with hydrogen fluoride was kept at 0° for 5 min. It was then diluted with methylene chloride and washed with ice-water and aqueous sodium hydrogen carbonate and dried. The

Table 1. δ-Values and coupling constants (cps) in deuteriochloroform of compounds given in Fig. 1.

Compound	H_1	H_2	H_3	H_4	H_5	H_6	H_6'	Conformation derived from spectrum
I[a]	6.10 $J_{12a}=9.2$ $J_{12e}=2.7$	2.0–2.6 $J_{2a3}=11.5$ $J_{2e3}=5.2$	5.33 $J_{34}=2.8$	5.86 $J_{45}=1.0$	3.85 $J_{56}=6.7$ $J_{56}'=6.7$	4.66 $J_{66}=11.2$	4.39	$^4C_1$
α-II	5.10 $J_{12a}=3.5$ $J_{12e}=1$	e a 2.16 2.38 $J_{e2a}=12.5$ $J_{2e3}=5.5$	5.70 $J_{2a3}=11.5$ $J_{34}=3.0$	5.87 $J_{45}=1$	4.3———4.7			$^4C_1$
β-II	4.68 $J_{12e}=3.2$ $J_{12a}=5.0$	2.0–2.4	5.41 $J_{34}=3.0$	5.82 $J_{45}=1$	4.15 $J_{56}=6.0$ $J_{56}'=6.0$	4.70 $J_{66}'=11.0$	4.42	$^4C_1$
IV	6.01 $J_{1F}=51$ $J_{12e}=2$	2.0–2.8 $J_{12a}=2.5$ $J_{2e3}=6$	5.76 $J_{2a3}=11.5$ $J_{34}=3$	6.0 $J_{45}=1$	4.75 $J_{56}=6$ $J_{56}'=6$	4.1–4.7		$^4C_1$
V	5.93 $J_{1F}=52$ $J_{12e}=2$	1.8–2.7 $J_{12a}=2$	4.2–4.7	5.68 $J_{34}=3.0$ $J_{45}=1$	4.2———4.7			$^4C_1$
VI	5.88 $J_{1F}=52$ $J_{12e}=2$	2.0–3.0 $J_{12a}=2$ $J_{2e3}=5.5$	5.5 $J_{34}=3$ $J_{2a3}=11.5$	4.2———4.8				$^4C_1$
IIIa	6.47 $J_{12}=6.2$	4.73 $J_{23}=2.6$	5.56 $J_{13}=1.7$	5.43 $J_{24}=1.6$ $J_{34}=4.7$	4.1———4.4			$^4H_5$
IIIb	6.63 $J_{12}=6.3$	4.99 $J_{23}=2.8$	5.9———6.1 $J_{13}=1.1$	 $J_{24}=1.8$	4.5–4.7	 $J_{66}'=12$	4.76 $J_{56}'=5.3$	$^4H_5$
XI	5.02 $J_{12}=2.8$	6.07 $J_{23}=10.0$	6.28 $J_{34}=5.0$	5.37 $J_{45}=1.2$	4.4———4.7			$^OH_5$

[a] In benzene-d_6

solution was concentrated at room temperature to *ca.* 2 ml, and 0.5 ml of a mixture of methylene chloride, methanol, and boron trifluoride etherate (17 : 2 : 1) was added. After 20 min at room temperature the solution was washed with aqueous sodium hydrogen carbonate, dried and evaporated. The product was separated into four fractions by preparative TLC, using ether : pentane (1 : 2) as eluent. The fastest running fraction gave 82 mg (44 %) of methyl 4,6-di-*O*-benzoyl-2,3-dideoxy-α-D-*threo*-hex-2-eno-pyranoside (XI). Recrystallization from ether : pentane gave the pure product, m.p. 99 – 100°, $[\alpha]_D^{23} = -186°$ (*c* 1, $CHCl_3$). (Found: C 68.65; H 5.60. Calc. for $C_{21}H_{20}O_6$: C 68.47; H 5.47.) The structure of (XI) is confirmed by the NMR spectrum (Table 1). The next fraction

gave 23 mg (10 %) of methyl 3,4,6-tri-*O*-benzoyl-2-deoxy-α-D-*lyxo*-hexopyranoside (α-II) as a syrup, $[\alpha]_D^{23} = +68.8°$ (*c* 2.8, $CHCl_3$). (Found: C 68.10; H 5.43. Calc. for $C_{28}H_{26}O_8$: C 68.57; H 5.34.) The third fraction consisted of the corresponding β-anomer (β-II), 16 mg (7 %), $[\alpha]_D^{23} = -38.0°$ (*c* 0.8, $CHCl_3$). (Found: C 68.38; H 5.43.) A fourth fraction gave 9 mg (4 %) of the methyl glycoside corresponding to (XII). Its structure was derived from an NMR spectrum and it was not investigated further.

The two methyl glycosides (α- and β-II) were also prepared by treating (IIIb) with hydrogen chloride in benzene for 40 min at 0°. This gave crude tri-*O*-benzoyl-2-deoxy-α-D-*lyxo*-hexopyranosyl chloride, as seen from the NMR spectrum. Treatment of this chloride with methanol gave the anomeric methyl glycosides which were separated by chromatography as described above, yielding 30 % of (α-II) and 45 % of (β-II). The products were identical with those described above. The anomeric structures are assigned on the basis of the NMR spectra (Table 1) and the optical rotations.

With anhydrous hydrogen fluoride at −70°. Compound (IIIb) (443 mg) was dissolved in anhydrous hydrogen fluoride (1 ml) at −70° and the solution was kept for 30 min. It was then diluted with cold methylene chloride and washed with ice-water and aqueous sodium hydrogen carbonate and dried. Evaporation gave 274 mg of crude product which was separated into several fractions by preparative TLC (ether : pentane 1 : 1). The fastest moving fraction gave 79 mg (17 %) of 3,4,6-tri-*O*-benzoyl-2-deoxy-α-D-*lyxo*-hexopyranosyl fluoride (IV) as a syrup, $[\alpha]_D^{23} = +26.8°$ (*c* 2.5, $CHCl_3$). (Found: C 67.90; H 4.99. Calc. for $C_{27}H_{23}FO_3$: C 67.77; H 4.85.)

In addition to several small fractions, a larger fraction (110 mg) was obtained. This was rechromatographed using benzene : methanol (96 : 4) as eluent, and thus gave 67 mg (17 %) of the disaccharide (XII) as a syrup, $[\alpha]_D^{23} = -66.8°$ (*c* 0.7, $CHCl_3$). (Found: C 69.25; H 5.00; F 2.22. Calc. for $C_{47}H_{39}FO_{12}$: C 69.29; H 4.82; F 2.33.) Molecular weight (Rast method) found: 772; calc.: 814. An NMR spectrum (100 Mc) in acetone solution gave the following δ-values and coupling constants (cps): H_1 (*ca.* 6.3); H_2 (3.34); H_3 (5.87); H_4 (6.0 − 6.2); $H_{2'}$ (6.28); $H_{3'}$ (6.14); $H_{4'}$ (5.50); $H_{1'}$, H_{5-6}, and $H_{5'-6'}$ gave a complex group of signals at 4.4 − 5.0. J_{12} (2.5); J_{23} (11.8); J_{34} (2.2); $J_{1'2'}$ (2.5); $J_{1'2'}$ (8.0); $J_{2'3'}$ (10.0); J_{2F} (30); J_{1F} (50.5).

In a separate experiment (IIIb) (410 mg) was treated with hydrogen fluoride for 15 min at −70°, as described above. The crude product was treated with methanol and boron trifluoride and worked up as described above. This gave 326 mg of a product which was separated into the following four fractions by preparative TLC (ether : pentane 1 : 2): 170 mg (52 %) of (XI), 34 mg (8 %) of (α-II), 12 mg (3 %) of (β-II), and 52 mg (14 %) of the methyl glycoside, corresponding to (XII). The purity and structure of the products were established by NMR spectroscopy.

With anhydrous hydrogen fluoride at −27°. Treatment of (IIIb) (572 mg) with anhydrous hydrogen fluoride (1 ml) at −27° for 1 h gave 415 mg of crude product, which was separated into three fractions by preparative TLC (ether : pentane 1 : 1). The fastest moving fraction gave 22.4 mg (3.7 %) of the tribenzoylated fluoride (IV). The two following fractions (193 mg and 71 mg) were each rechromatographed, using benzene : methanol (96 : 4) as eluent. Both of those fractions hereby gave the disaccharide (XII) in a total amount of 87 mg (17 %). Besides, the first fraction yielded 94 mg (20 %) of 3,6-di-*O*-benzoyl-2-deoxy-α-D-*lyxo*-hexopyranosyl fluoride (VI). The product was recrystallized from ether : pentane, m.p. 112 − 113° (decomp.), $[\alpha]_D^{23} = +11.5°$ (*c* 1.5), $CHCl_3$). (Found: C 63.90; H 5.23. Calc. for $C_{20}H_{19}FO_6$: C 64.15; H 5.11.) From the second fraction the isomeric 4,6-di-*O*-benzoyl-compound (V) was obtained as a syrup, 31 mg (6.6 %), $[\alpha]_D^{23} = -6.1°$ (*c* 1, $CHCl_3$). (Found: C 64.04; H 5.24.) The structures of (V) and (VI) were deduced from the NMR spectra (Table 1). The high field resonances of H-3 in (V) and of H-4 in (VI) proves the position of the benzoyl groups.

In a separate experiment the crude reaction product, resulting from treatment of (IIIb) (355 mg) with hydrogen fluoride for 1 h at −27°, was benzoylated with benzoyl chloride in pyridine. Preparative TLC (ether : pentane 1 : 2) gave 176 mg (48 %) of the tribenzoylated fluoride (IV) and 24 mg (9 %) of the disaccharide (XII).

When the reaction with hydrogen fluoride was allowed to proceed for 24 h similar results were obtained, except that the tribenzoyl fluoride (IV) was not present in the product prior to benzoylation.

Treatment of tetra-*O*-benzoyl-2-deoxy-D-*lyxo*-hexopyranose (I) with hydrogen fluoride

At −70°. The tetrabenzoate (I) (436 mg) was dissolved in anhydrous hydrogen fluoride (1 ml) at −70°. After *ca.* 10 min the solution was worked up as described above giving 330 mg (92 %) of the fluoride (IV). The product was virtually pure as seen from an NMR spectrum. Preparative TLC (ether : pentane 1 : 1) gave 289 mg (80 %) of pure product, identical with the material described above. The spectrum (Table 1) proves the structure of the product.

Treatment of (I) with hydrogen fluoride for 21 h at −70° gave the same result.

At −27°. Treatment of (I) (383 mg) with hydrogen fluoride (1 ml) for 20 h at −27° gave 290 mg of crude product which was separated into three fractions by preparative TLC (ether : pentane 1 : 1). The fastest running fraction gave the 3,6-di-*O*-benzoyl fluoride (VI), 91 mg (32 %), m.p. 110−112°. The second fraction gave 57 mg (23 %) of the 4,6-di-*O*-benzoyl fluoride (V). A third fraction consisted of 22 mg of an unidentified compound, possibly a disaccharide as seen from the NMR spectrum.

Preparation of deuterium fluoride.[9] Potassium hydrogen fluoride (20 g) was dissolved in deuterium oxide (10 ml). The deuterium oxide was then evaporated, first at 120°C, and then at 160°. This was repeated twice and the product was dried at 160° for 20 h. It was then transferred to a copper distillation apparatus and heated vigorously with a free flame. The deuterium fluoride distilled off in a few minutes and was collected in a polyethylene receiver which was cooled in dry ice-acetone. Yield 4.2 g. The product contained *ca.* 95 % deuterium as seen from an NMR spectrum.

Reactions with deuterium fluoride. A solution of (I) (266 mg) in deuterium fluoride (0.5 ml) was kept at −27° for 28 h. The solution was then worked up, as described above, to give a product which was shown by TLC to contain the two dibenzoylated fluorides (V) and (VI). The product was benzoylated with benzoyl chloride in pyridine, giving 241 mg of crude (IV). Purification by preparative TLC (ether : pentane 1 : 1) gave pure tri-*O*-benzoyl-2-deuterio-2-deoxy-α-D-*lyxo*-hexopyranosyl fluoride, 130 mg (59 %). Integrated NMR spectra showed that the product contained *ca.* 1.2 protium equiv. at C-2. Because of the 5 % protium fluoride present in the deuterium fluoride (see above) and the isotope effect the introduction of 1.0 equiv. of deuterium would not be expected.

Tetra-*O*-benzoyl-2-deoxy-β-D-*arabino*-hexopyranose (XIII) (444 mg) was dissolved in deuterium fluoride (0.5 ml) at −70°. After 24 h at −27° the solution was worked up, and the product was benzoylated with benzoyl chloride in pyridine. The product thus obtained was purified by preparative TLC (ether : pentane 1 : 1), giving tri-*O*-benzoyl-2-deuterio-2-deoxy-α-D-*ribo*-hexopyranosyl fluoride (XVII) (291 mg, 80 %). It was recrystallized from ether : pentane, m.p. 98.5−99°, $[\alpha]_D^{23} = +199°$ (*c* 1, $CHCl_3$). (Found: C 67.85; H+D 4.97. Calc. for $C_{27}H_{23}DFO_7$: C 67.63; H+D 5.04.) The NMR spectrum was identical with that of the product described previously,[2] except that only 1.2 equiv. of protium was present at C-2.

Microanalyses were performed by Dr. A. Bernhardt.

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