ACTA CHEMICA SCANDINAVICA 27 (1973) 2701–2709

Reaction of Sugar Esters with Hydrogen Fluoride

XI. Preparation of 1,6-Anhydro-β-D-altropyranose from Methyl Tetra-*O*-benzoyl-α-D-glucopyranoside

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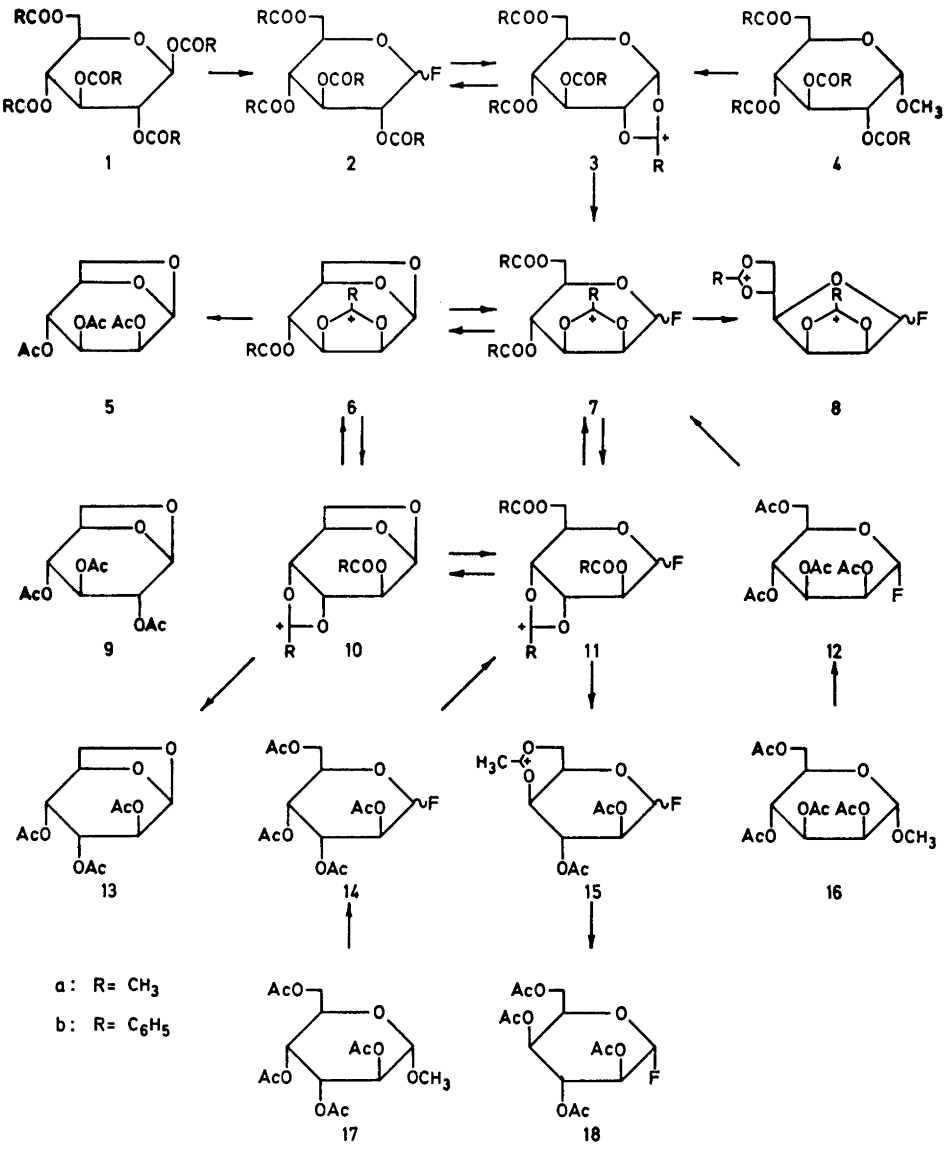
Treatment of the pentaacetates of D-glucopyranose, D-mannopyranose, and D-altropyranose with anhydrous hydrogen fluoride gave complicated mixtures of products. Among these were found derivatives of 1,6-anhydro-β-D-altropyranose and 1,6-anhydro-β-D-mannopyranose. When the tetraacetates of methyl α-D-glucopyranoside, methyl α-D-mannopyranoside, and methyl α-D-altropyranoside were reacted with hydrogen fluoride larger amounts of 1,6-anhydrides were formed. The mechanisms of these reactions are discussed. Treatment of methyl tetra-*O*-benzoyl-α-D-glucopyranoside with hydrogen fluoride gave a 45 % yield of 1,6-anhydro-β-D-altropyranose and 8 % of 1,6-anhydro-β-D-mannopyranose, the latter isolated as its triacetate.

In a previous paper it was shown that treatment of penta-*O*-acetyl-β-D-glucopyranose with anhydrous hydrogen fluoride gave derivatives of D-mannose and D-altrose.[1] The products were isolated as methyl α-D-mannopyranoside and 1,6-anhydro-β-D-altropyranose after treatment of the crude product with methanolic sodium methoxide. The same products were obtained when penta-*O*-acetyl-D-mannopyranose was treated with hydrogen fluoride.[2] These reactions and the reaction of other derivatives of glucose, mannose, and altrose with hydrogen fluoride have now been investigated more closely using NMR technique.

When penta-*O*-acetyl-β-D-glucopyranose (*1a*) was dissolved in anhydrous hydrogen fluoride at 0°C the α-fluoride (α-*2a*) was formed immediately as seen from an NMR spectrum of the solution. The spectrum showed signals at 2.30 and 2.40 ppm corresponding to 12 acetoxy-protons and a signal at 2.57, corresponding to one equivalent of acetic acid. The remaining part of the spectrum was very similar to that of (α-*2a*) in deuteriochloroform.[3] In agreement herewith (α-*2a*) may be isolated at this stage.[1] When the hydrogen fluoride solution was kept at room temperature further changes took place and after 24 h



the reaction was completed. An NMR spectrum obtained at this stage was complex and showed that several compounds were present. Thus the signals of the acetoxonium ion (*10a*), derived from 1,6-anhydro-β-D-altropyranose, were seen (see below). Small amounts of the diacetoxonium ion (*8a*) were also present as seen from signals at 6.15, 6.34, 2.90, and 2.81 ppm. The NMR spectrum of the latter ion in hydrogen fluoride was known from previous

work.[4] Work up of this hydrogen fluoride solution and acetylation gave a crude product, which was a complicated mixture of compounds. Chromatography and NMR spectroscopy showed that the mixture contained the tetraacetates of α- and β-D-glucopyranosyl fluoride (α- and *β-2*), α-D-mannopyranosyl fluoride (*12*), α- and β-D-altropyranosyl fluoride (α- and *β-14*), and α-D-idopyranosyl fluoride (*18*). Besides, the triacetates of 1,6-anhydro-β-D-altro-

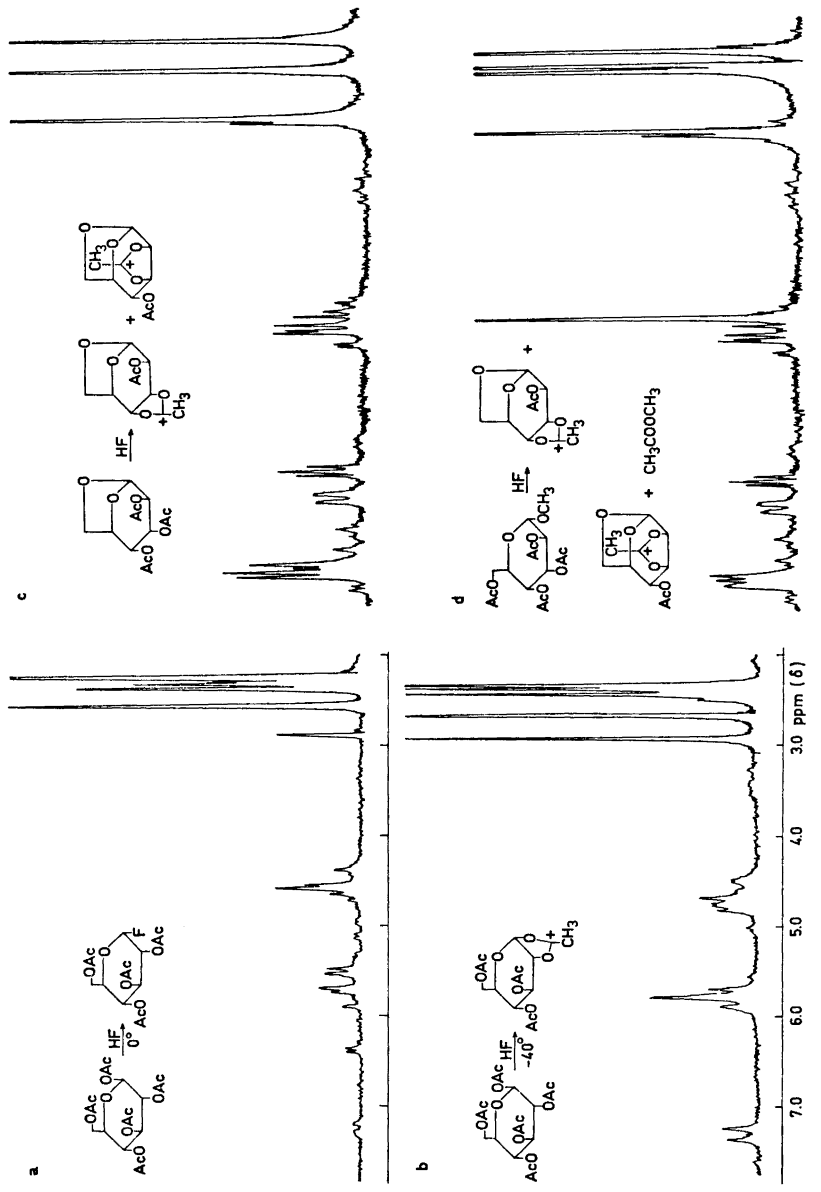


Fig. 1. a. 60 MHz. *b.* 60 MHz. *c.* 100 MHz, 0°C. *d.* 100 MHz, 0°C.

pyranose (*13*) and 1,6-anhydro-β-D-mannopyranose (*5*) were isolated from the mixture. These results thus show that 1,6-anhydrides are formed directly in the hydrogen fluoride solution and not, as assumed previously,[2] in a secondary reaction by treatment of the crude fluoride with sodium methoxide.

The pentaacetate (*1a*) gave the fluoride (α-*2a*) when dissolved in hydrogen fluoride at 0°C (Fig. 1a). When this hydrogen fluoride solution was prepared at −40°C the NMR spectrum changed completely, and it showed that at this temperature the acetoxonium ion (*3a*) (Fig. 1b) was formed. When the temperature was raised to 0°C the fluoride (α-*2a*) was reformed. In other cases dioxolanylium ions are observed when acylated carbohydrates are dissolved in hydrogen fluoride at 0°C. Thus penta-*O*-benzoyl-β-D-glucopyranose (*1b*) gives the benzoxonium ion (*3b*) as the only detectable product in hydrogen fluoride and the fluoride (*2b*) is not formed until the solution is hydrolyzed (see below). In general, it may be assumed that when an acylated carbohydrate is dissolved in hydrogen fluoride the acyloxy-group at C-1 is cleaved off at once, and an equilibrium is established between the fluoride and the 1,2-dioxolanylium ion, *e.g.* between (*2*) and (*3*). With acetylated pyranoses the equilibrium is generally shifted towards the fluoride at 0°C. This was found when the tetraacetates of arabinopyranose or ribopyranose were treated with hydrogen fluoride. With benzoylated pyranoses, and with both acetylated and benzoylated furanoses, the equilibrium is shifted towards the 1,2-dioxolanylium ion, and the fluorides can usually not be observed in the NMR spectra of the hydrogen fluoride solutions.[4–6]

The acetoxonium ion (*3a*) can, by further reaction with hydrogen fluoride, rearrange to the mannose-ion (*7a*) with loss of acetic acid and introduction of fluorine at C-1. The latter ion is in equilibrium with the altrose-ion (*11a*) and both these ions are in equilibrium with the corresponding 1,6-anhydrides (*6a*) and (*10a*), respectively. The spectrum shown in Fig. 1c is essentially an equilibrium mixture of the latter two ions with the altrose-ion (*10a*) predominating. As mentioned above, a small amount of the furanose derivative (*8a*) is also present. This is probably formed from the mannose-ion (*7a*) by ring contraction and loss of acetic acid in analogy to the pyranose-furanose rearrangements observed in other cases.[5,7]

When penta-*O*-acetyl-α-D-mannopyranose was dissolved in hydrogen fluoride the α-fluoride (*12*) was formed at once. The NMR spectrum showed signals of 4-acetoxy groups at 2.25, 2.33, 2.40, and 2.45 ppm and a signal at 2.59 ppm corresponding to one equivalent of acetic acid. The remaining part of the spectrum was identical with that of tetra-*O*-acetyl-α-D-mannopyranosyl fluoride (*12*) in deuteriochloroform.[3] After 24 h at room temperature the spectrum was identical with that obtained from glucose pentaacetate, in agreement with previous results.[2] The fluoride (*12*) contains a pair of *cis*-oriented acetoxy groups and it probably forms the acetoxonium ion (*7a*) by the mechanism by which *cis*-1,2-diacetoxycyclohexane reacts with hydrogen fluoride.[8]

Penta-*O*-acetyl-α-D-altropyranose gave the fluorides (*14*) at once when dissolved in hydrogen fluoride at 0°C, as seen from an NMR spectrum. Treatment of the pentaacetate with hydrogen fluoride at −70°C gave a mixture of the anomeric fluorides (*14*);[3] the pure fluoride (α-*14*) was obtained by chro-

matography. When penta-*O*-acetyl-α-D-altropyranose was kept in hydrogen fluoride for 24 h at room temperature an NMR spectrum showed that the ion (*10a*) was formed together with (*6a*) and other products. The furanose derivative (*8a*) could not be detected in the spectrum. Work up of the solution at this stage and acetylation of the crude product gave a complicated mixture of glycosyl fluorides. Besides, the acetates of 1,6-anhydro-β-D-altropyranose (*13*) and 1,6-anhydro-β-D-mannose (*5*) were isolated.

The initially formed tetra-*O*-acetyl-D-altropyranosyl fluorides (*14*) have the acetoxy-groups at C-3 and C-4 *cis*-oriented and they can therefore form the acetoxonium ions (*10a*) or (*11a*) by further reaction with hydrogen fluoride. Whether the 1,6-anhydride formation takes place prior to the acetoxonium ion formation or not could not be decided.

In analogy with the rearrangement of arabinose tetraacetate to ribose-derivatives [5] it might be expected that the altrosyl fluorides (*14*) should rearrange to D-allose derivatives by reaction with hydrogen fluoride. This was not observed; but it has been found that penta-*O*-benzoyl-D-altropyranose yields allose derivatives by treatment with hydrogen fluoride. These results will be described in a forthcoming paper.

Since 1,6-anhydrides were formed in hydrogen fluoride it was decided to study the reaction of tri-*O*-acetyl-1,6-anhydro-β-D-glucopyranose (*9*) and of the corresponding altrose derivative (*13*) with hydrogen fluoride.

The triacetate (*9*) reacted immediately with hydrogen fluoride to give a complicated mixture of products. In the course of *ca.* 48 h at room temperature the reaction was finished and rather large amounts of the acetoxonium ion (*10a*), derived from 1,6-anhydro-β-D-altropyranose, was formed together with the corresponding mannose derivative (*6a*). Appreciable amounts of the diacetoxonium ion (*8a*) and small amounts of other compounds were also present. Apparently (*9*) gives the same products as those obtained from glucose- and mannose-pentaacetate, but in a different ratio, larger amounts of the 1,6-anhydro-derivatives (*6a*) and (*10a*) being formed.

If an equilibrium exists between the fluorides (*7a*) and (*11a*) and the 1,6-anhydrides (*6a*) and (*10a*), respectively, then this equilibrium should be affected by the amount of acetic acid present in the hydrogen fluoride solution. It is therefore reasonable that the triacetate (*9*) should give more of the anhydro-ions (*6a*) and (*10a*) than glucose- or mannose-pentaacetate since the latter two compounds will liberate more acetic in hydrogen fluoride solution.

Tri-*O*-acetyl-1,6-anhydro-β-D-altropyranose (*13*), when kept in hydrogen fluoride solution at room temperature, was almost completely transformed into a mixture of the ions (*6a*) and (*10a*) in the course of 24 h. No other products could be seen in the NMR spectrum (Fig. 1c). Work up and acetylation gave the acetylated anhydrides (*5*) and (*13*) and small amounts of the fluorides (*12*) and (α- and β-*14*).

It was found previously that methanol and acetic acid react rapidly in hydrogen fluoride to give methyl acetate.[8] It might therefore be expected that tetraacetylated methyl glycosides should give the same products as those obtained from the triacetylated anhydrides since the methanol, which is initially liberated, should capture one equivalent of acetic acid.

This was actually found to be the case. When methyl tetra-*O*-acetyl-α-D-glucopyranoside (*4a*) was kept in hydrogen fluoride for *ca.* 48 h one equivalent of methyl acetate was formed as seen from the signals at 4.2 and 2.5 ppm. The remaining part of the spectrum was identical with that obtained from tri-*O*-acetyl-1,6-anhydro-β-D-glucopyranose and showed that the ions (*6a*) and (*10a*) were the main products together with (*8a*). The same result was obtained when methyl tetra-*O*-acetyl-α-D-mannopyranoside (*16*) was treated with hydrogen fluoride. Methyl tetra-*O*-acetyl-α-D-altropyranoside (*17*) gave the acetoxonium ions (*6a*) and (*10a*) and one equivalent of methyl acetate as the only products, that could be detected in the hydrogen fluoride solution (Fig. 1d).

Paulsen *et al.*[9,10] found that treatment of acetylated hexoses with antimony pentachloride gave acetoxonium ions, which rearranged in a manner similar to the one described above. However, whereas Paulsen [9] found that considerable amounts of a D-idose derivative was formed when tetra-*O*-acetyl-β-D-glucopyranosyl chloride was treated with antimony pentachloride the reaction with hydrogen fluoride gives only traces of idose derivatives. An idose derivative (*15*) would be formed by further rearrangement of the altrosyl fluoride (*11a*), but since it has now been found that this fluoride is largely converted to the 1,6-anhydride (*10a*) in hydrogen fluoride it is understandable that idose derivatives are only formed to a small extent. With antimony pentachloride 1,6-anhydrides are not formed.

The reactions described above with acetylated sugars are of little preparative value since low yields are obtained. This is probably due to the fact that partially acetylated products, which are formed by hydrolysis of the acetoxonium ions, are somewhat soluble in water, and therefore may be lost when the reaction mixtures are washed during the isolation. The reaction of some benzoylated compounds with hydrogen fluoride was therefore investigated.

The NMR spectrum, which was obtained from a solution of penta-*O*-benzoyl-β-D-glucopyranose (*1b*) in hydrogen fluoride, was not well resolved and the signal of the anomeric proton was hidden by the benzoyl group signals. It was, however, obvious that a fluoride was not present in the initial stage of the reaction. The spectrum probably represents the 1,2-benzoxonium ion (*3b*). When this solution was poured on ice tetra-*O*-benzoyl-β-D-glucopyranosyl fluoride (*β-2b*) was formed as the main product. Treatment of a dioxolanylium ion with water would be expected to give a hydroxy-compound. It has, however, been observed in several cases, that when hydrogen fluoride solutions of 1,2-benzoxonium ions, or 1,2-acetoxonium ions, are hydrolyzed then glycosyl fluorides are formed as the main products, usually with *trans*-opening of the dioxolanylium ring.[5,6]

Prolonged reaction of (*1b*) wih hydrogen fluoride gave a complicated mixture of products which was not investigated further. When methyl tetra-*O*-benzoyl-α-D-glucopyranoside (*4b*) was kept in hydrogen fluoride for *ca.* 72 h the ion (*10b*) was formed as the main product, as seen from NMR spectra. Besides, smaller amounts of (*6b*) and other products were present. The dibenzoxonium ion (*8b*) was not formed at all, in contrast to the result obtained with the corresponding acetate. Presumably, the ring-contraction of (*7*) to (*8*) is rather slow in the benzoate series.[5] When the hydrogen fluoride solution

was hydrolyzed and worked up a product was obtained which contained large amounts (50 – 60 %) of dibenzoylated 1,6-anhydro-β-D-altropyranose, smaller amounts of dibenzoylated 1,6-anhydro-β-D-mannopyranose, and a number of partially benzoylated glycosyl fluorides. These products were formed by hydrolysis of the benzoxonium ions, which were present in the hydrogen fluoride solution. Treatment of the crude reaction product with aqueous sodium hydroxide removed the benzoyl groups and destroyed the glycosyl fluorides and, after deionization, 1,6-anhydro-β-D-altropyranose could be isolated in 45 % yield. Besides, 8 % of 1,6-anhydro-β-D-mannopyranose was obtained, isolated as the triacetate (*5*). Thus the reaction of methyl tetra-*O*-benzoyl-α-D-glucopyranoside with hydrogen fluoride provides a convenient method for the preparation of 1,6-anhydro-β-D-altropyranose.

EXPERIMENTAL

Melting points are uncorrected. NMR spectra were obtained on Varian A-60 and HA-100 instruments. NMR spectra in anhydrous hydrogen fluoride were measured in Teflon sample tubes. Positions of signals in hydrogen fluoride are given in ppm relative to $(CH_3)_3SiCH_2CH_2CH_2SO_3Na$. ^{19}F spectra were measured at 94.1 MHz. Positions of signals (ΦF) are given in ppm relative to internal methyl trifluoroacetate. 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. Zones were visualized under UV light or by charring with a hot wire.

Penta-O-acetyl-β-D-glucopyranose (1.06 g) was dissolved in anhydrous hydrogen fluoride (3 ml) and the solution was kept for 24 h at room temperature. It was then diluted with chloroform and poured on ice. The organic phase was washed with aqueous sodium hydrogencarbonate and dried with magnesium sulfate. The solvent was evaporated and the residue was acetylated by treatment with acetic anhydride (3 ml) in pyridine (10 ml) at room temperature over night. Work up in the usual way gave 594 mg of crude product. This was separated into four fractions by preparative TLC using ether-pentane (3:1) as eluent.

The fastest moving fraction (274 mg, 29 %) was a mixture of tetra-*O*-acetyl-α- and β-D-glucopyranosyl fluoride (α- and *β-2a*), tetra-*O*-acetyl-α- and β-D-altropyranosyl fluoride (α- and *β-14*), and tetra-*O*-acetyl-α-D-mannopyranosyl fluoride (*12*) in a ratio of 30:12:58. The next fraction (85 mg, 9 %) was a mixture of (*12*) and tetra-*O*-acetyl-α-D-idopyranosyl fluoride (*18*) in a 1:1 ratio. The fluorides were identified by comparing the proton and ^{19}F NMR spectra with those of authentic samples of the pure fluorides. Spectra of all these fluorides have been published [3] except that of tetra-*O*-acetyl-α-D-idopyranosyl fluoride, which is described below.

The third fraction gave 103 mg (13 %) of tri-*O*-acetyl-1,6-anhydro-β-D-altropyranose (*13*), m.p. 98 – 100°C, $[\alpha]_D^{20}$ −163° (*c* 1.8, $CHCl_3$) (reported [11] m.p. 100 – 101°C, $[\alpha]_D$ −172°). An NMR spectrum was identical with that of an authentic sample.[12] The last fraction gave 30 mg (4 %) of tri-*O*-acetyl-1,6-anhydro-β-D-mannopyranose (*5*), which was not quite pure, m.p. 75 – 80°C (reported [13] m.p. 90 – 91°). An NMR spectrum was identical with that of an authentic sample.[12]

Penta-O-acetyl-α-D-idopyranose [9] (550 mg) was kept in anhydrous hydrogen fluoride (1 ml) for 15 min at 0°C. Work up as described above gave 454 mg of crude product which was separated into two fractions by preparative TLC (ether-pentane 3:1). The fast moving fraction gave 210 mg (43 %) of tetra-*O*-acetyl-α-D-idopyranosyl fluoride (*18*) which was not quite pure. The product was further purified by preparative TLC, first with benzene-ether (1:1) as eluent and then with ether-pentane (3:1). This gave 80 mg of pure (*18*) as a syrup, $[\alpha]_D^{24}$ +15.8° (*c* 1.5, $CHCl_3$). (Found: C 48.24; H 5.44. Calc. for $C_{14}H_{19}FO_9$: C 48.00; H 5.47).

An NMR spectrum in deuteriochloroform gave the following δ-values: H-1 5.88; H-2 5.9 – 6.0; H-3 5.06; H-4 5.9 – 6.0; H-5 4.59; H-6 4.1 – 4.2. A ^{19}F-spectrum using

methyl trifluoroacetate as internal reference gave the fluorine signal at −58.2 ppm in good agreement with the value predicted by Hall *et al.*,[3] $J_{1F} = 48.0$ Hz, $J_{2F} = 4.9$ Hz.

Penta-O-*acetyl*-α-D-altropyranose (562 mg) was kept in hydrogen fluoride (1.5 ml) for 1 h at −70°C. Work up as described above gave 570 mg of a product which was purified by preparative TLC using ether-pentane (2:1) as eluent. This gave 456 mg (80 %) of a mixture of tetra-*O*-acetyl-α- and β-D-altropyranosyl fluoride (α- and *β-14*) in a 10:1 ratio as seen from an NMR spectrum.[3] Repeated chromatography gave pure (*α-14*) as a syrup, $[\alpha]_D^{20}$ +35.9° (*c* 4.3, $CHCl_3$). (Found: C 47.97; H 5.42. Calc. for $C_{14}H_{19}FO_9$: C 48.00; H 5.47). NMR data in deuteriochloroform: H-1 5.50 δ; H-2 5.05; H-3 5.35; H-4 5.20; H-5 4.48; H-6 4.1−4.4. J_{1F} 49.0; J_{12} 1.0; J_{13} 0.7; J_{2F} 2.7; H_{23} 3.0; J_{34} 3.2; J_{45} 10.0. Fluorine chemical shifts are in agreement with those described.[3]

Penta-O-*acetyl*-α-D-*altropyranose* (1.02 g) was kept in hydrogen fluoride (2 ml) for 24 h at room temperature. The solution was then worked up and the product was acetylated as described above. The product thus obtained (530 mg) was separated into 3 fractions by preparative TLC with ether-pentane (3:1) as eluent. The fastest moving fraction gave 280 mg of a mixture of the tetraacetates of α-D-altropyranosyl fluoride (*α-14*), β-D-altropyranosyl fluoride (*β-14*), α-D-mannopyranosyl fluoride (*12*), and α-D-idopyranosyl fluoride (*18*) in a ratio of 2:1:4:1 as seen from proton and ^{19}F spectra. The next fraction gave 160 mg (22 %) of tri-*O*-acetyl-1,6-anhydro-β-D-altropyranose (*13*), m.p. 97−99°C, $[\alpha]_D^{20}$ −164° (*c* 1.6, $CHCl_3$). An NMR spectrum was identical with that of an authentic sample. The last fraction gave 35 mg (5 %) of tri-*O*-acetyl-1,6-anhydro-β-D-mannopyranose (*5*), m.p. 76−79°C. The product was characterized through its NMR spectrum.[12]

Tri-O-*acetyl*-*1,6-anhydro*-β-D-*altropyranose* (*13*) (538 mg) was dissolved in hydrogen fluoride (1.5 ml) and the solution was kept at room temperature for 24 h. Work up and acetylation as described above gave 370 mg of a product which was separated into 3 fractions by preparative TLC with ether-pentane (3:1). The fast moving fraction gave 76 mg (10 %) of a mixture of the fluorides (*12*) and (α- and *β-14*) in a ratio of 4:2:1 as seen from NMR spectra. The next fraction gave 188 mg (36 %) of (*13*), m.p. 98−100°C, $[\alpha]_D^{24}$ −165° (*c* 0.9, $CHCl_3$). The last fraction gave 46 mg (8 %) of (*5*), m.p. 83−86°C. The latter two products were further identified through their NMR spectra.

Methyl tetra-O-*acetyl*-α-D-*altropyranoside* (*17*) (1.03 g) was kept in hydrogen fluoride (2.5 ml) for 24 h at room temperature. Work up and acetylation gave a product (700 mg) which was separated into 3 fractions by preparative TLC with ether-pentane (3:1). The fast moving fraction gave 62 mg (6 %) of a mixture of (α- and *β-14*) and (*12*) in a ratio of 2:1:4, identified through proton and ^{19}F spectra. The next fraction gave 420 mg (50 %) of (*13*), m.p. 98−100°C, $[\alpha]_D^{24}$ −163° (*c* 2.3, $CHCl_3$). The last fraction gave 55 mg (7 %) of (*5*), m.p. 85−86°C, $[\alpha]_D^{24}$ −121° (*c* 0.9, $CHCl_3$).

Penta-O-*benzoyl*-β-D-*glucopyranose* (*1b*) (2.0 g) was dissolved in anhydrous hydrogen fluoride (4 ml) and the solution was kept at −10°C for 30 min. It was then diluted with dichloromethane and poured on ice. The dichloromethane solution was washed with aqueous sodium hydrogen carbonate and water, dried and evaporated. The residue (1.70 g) was crystallized from ether-pentane to give 950 mg (55 %) of tetra-*O*-benzoyl-β-D-glucopyranosyl fluoride (*β-2b*), m.p. 147−149°C. An additional recrystallization from ethanol gave the pure product, m.p. 147−149°C, $[\alpha]_D^{21}$ +54° (*c* 1.2, $CHCl_3$), in agreement with the reported values.[14] An NMR spectrum of the material in the mother liquors indicated that it was a mixture of (*β-2b*) and the corresponding α-fluoride.

Methyl tetra-O-*benzoyl*-α-D-*glucopyranoside* (*4b*) (50 g) was dissolved in anhydrous hydrogen fluoride (100 ml) with cooling in dry ice-acetone and the solution was kept at room temperature for 72 h. It was then cooled in dry ice-acetone, diluted with dichloromethane, and poured on ice. The organic phase was washed with aqueous sodium hydrogen carbonate, dried and evaporated. The residue (38.0 g) was boiled with water (200 ml) and sodium hydroxide (20 g) for 3 h. The solution was then acidified with hydrochloric acid and the benzoic acid was extracted with ether. The aqueous phase was deionized by passage through columns of Amberlite IR-120 and IR-4B. The solution was then evaporated and the residue was dissolved in ethanol and filtered through activated carbon. Evaporation gave 9.0 g of a syrup which was crystallized from ethanol (20 ml) to give 6.0 g (45 %) of 1,6-anhydro-β-D-altropyranose, m.p. 130−135°C, $[\alpha]_D^{22}$ −200° (*c* 2.3, H_2O). An additional recrystallization from ethanol gave 5.4 g, m.p. 133−134°C, $[\alpha]_D^{22}$ −208° (*c* 2.3, H_2O). (Reported [15] m.p. 134−135°C, $[\alpha]_D$ −211°).

The material in the mother liquors was separated into two fractions by chromatography on a column of silica gel (150 g) using butanone-2 saturated with water as eluent. The fast moving fraction (1.96 g) was acetylated with acetic anhydride in pyridine, and the product (2.56 g) was crystallized from ether-pentane to give 1.9 g (8 %) of tri-*O*-acetyl-1,6-anhydro-β-D-mannopyranose (*5*), m.p. 82 – 84°C. An additional recrystallization gave a product with m.p. 84 – 86°C, $[\alpha]_D^{22}$ −119° (*c* 2, $CHCl_3$). (Reported [13] m.p. 90 – 91°C, $[\alpha]_D$ −123°).

The second fraction (502 mg) was crystallized from ethanol to give 300 mg of 1,6-anhydro-β-D-altropyranose, m.p. 120 – 130°C.

Microanalyses were performed by Dr. A. Bernhardt.

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Received March 23, 1973.