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Chlorination of Tetra-*O*-benzoyl-1-deoxy-D-*arabino*-hex-1-enopyranose. Formation of an Orthoacid Chloride*

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Chlorination of tetra-*O*-benzoyl-1-deoxy-D-*arabino*-hex-1-enopyranose (*4*) gave tetra-*O*-benzoyl-2-chloro-α-D-mannopyranosyl chloride (*8*) and tetra-*O*-benzoyl-2-chloro-β-D-glucopyranosyl chloride (*6*). Similar results were obtained by chlorination of 2,4,6-tri-*O*-benzoyl-3-*O*-methyl-1-deoxy-D-*arabino*-hex-1-enopyranose (*16a*) and tetra-*O*-benzoyl-1-deoxy-D-*lyxo*-hex-1-enopyranose (*16b*). The structures of the dichlorosugars *6* and *8* are discussed using ^{1}H NMR and ^{13}C NMR spectroscopy.

Chlorination of *4*, at low temperature gave the orthoacid chloride *5*, which could be observed by NMR spectroscopy at −20 °C and which could be converted to the corresponding orthoester (*10*), orthoacid fluoride (*11*), and a benzylidene compound (*12*). Hydrolysis of *5* gave tetra-*O*-benzoyl-α-D-*arabino*-hexapyranosulose (*2*). At room temperature the orthoacid chloride (*5*) rearranges to the dichlorosugar (*6*).

In connection with previous work on the reactions of 1-deoxy-hex-1-eno-pyranoses with hydrogen halides [1,2] we became interested in the behaviour of these compounds towards halogen. In a series of papers Maurer *et al.*[3] described the reaction of acylated 1-deoxy-hex-1-enopyranoses with chlorine. When tetra-*O*-benzoyl-1-deoxy-D-*arabino*-hex-1-enopyranose (*4*) was treated with chlorine in benzene a crystalline dichloro-compound was obtained in 22 % yield.[3] No other compounds were isolated. When Maurer and Petsch [3] hydrolyzed the crude chlorination product they obtained a compound which they assumed was tetra-*O*-benzoyl-D-*arabino*-hexopyranosulose (*2*). We were, however, not able to obtain *2* by this procedure [4] and we therefore decided to reinvestigate the chlorination of *4*.

When *4* was treated with chlorine in carbon tetrachloride at room temperature a crystalline dichloro-compound (*8*), identical with that described by Maurer *et al.*, was isolated in *ca.* 25 % yield. The material in the mother liquor was an almost pure compound and chromatography gave a dichlorosugar (*6*), isomeric with *8*. Comparison of the ^{1}H NMR spectra of *6* and *8* (Table 1) shows that H1 and H5 of *8* are found 0.4 − 0.5 ppm downfield from those of *6*. This indicates that *8* is an α-chloride and *6* a β-chloride. The axial chlorine at C1 in *8*, which causes a downfield shift of H5, should also deshield H3. However, this proton is found at higher field than H3 of *6*. This may indicate that *6* and *8* have different configurations at C2.

Since *6* was assumed to be a β-chloride an anomerization with titanium tetrachloride was attempted. This gave a new, isomeric dichlorosugar (*9*). A ^{1}H NMR spectrum of *9* showed that the signals of H1 and H5 had moved downfield relative to those of *6*, thus confirming that an α-chloride had been formed. The ^{1}H NMR spectrum of *9* is quite similar to that of *8*, but the optical rotations and the ^{13}C NMR spectra (Table 2) are different. From this it is concluded that *8* and *9* are α-chlorides with different configuration at C2 and that *6* and *9* are a pair of anomers. Treatment of *8* with titanium tetrachloride gave no reaction. This confirms that *8* is an α-chloride and shows that isomerization does not take place at C2 by this treatment.

In order to get more information about the structures of *6*, *8*, and *9* their ^{13}C NMR spectra

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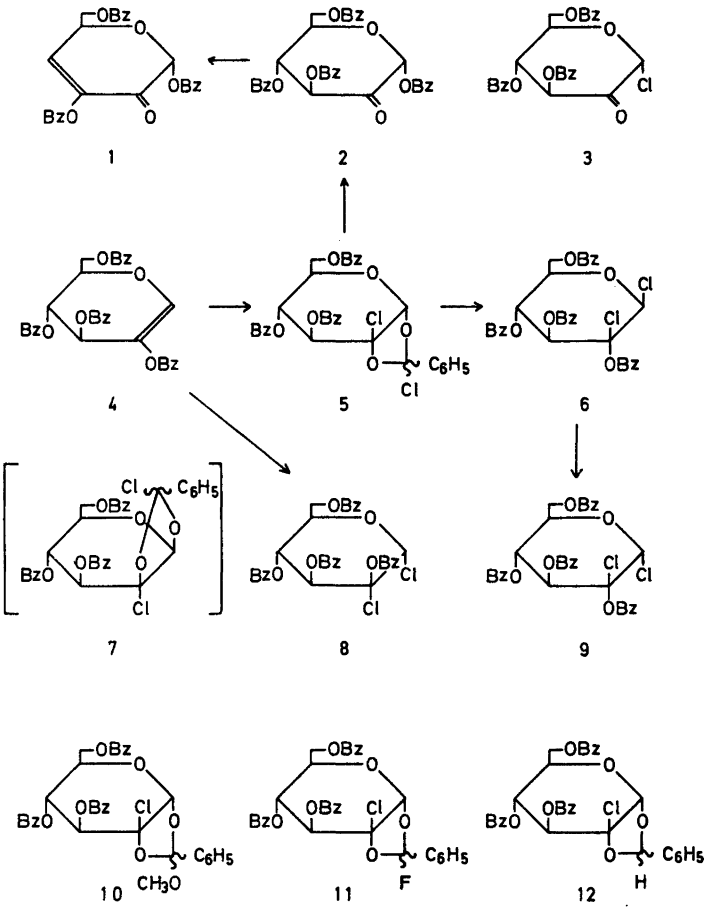


were measured (Table 2) and for comparison ^{13}C NMR spectra of the anomeric tri-*O*-acetyl-2-chloro-2-deoxy-D-gluco- (*13*) and -D-manno-pyranosyl chlorides (*14*) were also measured. These compounds were prepared according to Igarashi *et al.*[5] Besides, the anomeric tri-*O*-acetyl-2,2-dichloro-2-deoxy-D-*arabino*-hexo-pyranosyl chlorides (*15*) were prepared and their spectra were measured. Bradley and Buncel [5] obtained a crystalline product by addition of chlorine to tri-*O*-acetyl-1,5-anhydro-2-chloro-2-deoxy-D-*arabino*-hex-1-enopyranose and described it as the α-anomer (α-15). We isolated both a crystalline and a syrupy product from this reaction and found from ^{1}H NMR and ^{13}C NMR spectra that the crystalline product is the β-anomer (β-15) whereas the syrup is (α-15).

The ^{13}C chemical shifts of all the chloro-sugars shown in Table 2 were assigned by selective proton decoupling.[7] It is seen that the signal of C1 in an α-chloride is found at lower field than that of a β-chloride. This was also observed previously in case of the anomeric tetra-*O*-acetyl-D-glucopyranosyl chlorides [8] whereas in most other cases the signal of C1 is at lowest field in a β-pyranose derivative.[9] The signals of C3 and C5 in a β-chloride are shifted downfield compared to those of the corresponding α-chloride, in agreement with the γ-effect.[10] The chemical shifts of C4 and C6 are nearly independent of the anomeric configuration while C2 in compounds with an axial substituent at C1 (α-anomers) is at higher field than in β-anomers.

The ^{13}C chemical shifts of *6*, *8*, and *9* are in accordance with the structural assignments made from the proton spectra. Thus the β-

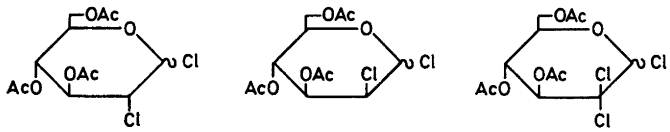
Table 1. Proton chemical shifts (δ) in deuteriochloroform and coupling constants (Hz) of 1,2-dichloro-sugars and some related compounds.

Compound	H1	H3	H4	H5	H6	H6′	J_{34}	J_{45}	J_{56}	$J_{66'}$	$J_{56'}$
8	7.50*a*	6.48	6.17	4.82	4.59	4.43	9.4	10.2	2.8	12.6	3.8
6	7.0	6.69	6.02	4.42	4.76	4.51	9.2	9.6	3.4	12.1	4.6
9	7.36*a*	6.55	6.17	4.78	4.7	4.54	9.6	10.0	2.8	12.6	4.6
17a	7.33*a*	4.34	5.92	4.64	4.53	4.34	9.4	10.2	2.6	12.4	4.2
18a	6.68	4.94	5.77	4.30	4.63	4.40	9.2	9.2	2.4	12.0	4.6
17b	7.52*a*	6.27	6.20	5.19	4.68	4.47	4.2	1.8	6.8	11.7	6.3
18b	6.93	6.81	6.14	4.67	4.35—4.9		4.5	1.8			
α15	6.24	5.88	5.37	4.46	4.2 —4.3		9.4	10.4	3.4		3.4
β15	5.58	5.52	5.25	3.95	4.2 —4.3		9.5	9.5	3.0		4.3
5	6.41	5.95	5.45	3.8	4.3 —4.6		1.2	7.8			
10	6.20	5.94	5.49	3.94	4.2 —4.6		1.2	7.8			
11	6.30	5.92	5.50	3.97	4.55—4.4		1.0	7.4	3.4	12.2	4.8
12[b]	6.50	6.05	5.61	4.37	4.60—4.43		1.0	7.6	4.0	13.0	4.6

[a] The signal was hidden by the signals of the aromatic protons. Its position was therefore determined through the ^{13}C NMR spectrum by selective proton decoupling, finding the proton frequency at which Cl collapses to a singlet.[7]
[b] Benzylidene proton δ 6.15.

chloride (*6*) has Cl at higher field than the α-chloride (*9*); C2, C3, and C5 of *6* are at lower field than those of *9* in agreement with the results described above. The α-chlorides *8* and *9* have rather similar spectra. The largest differences are in the shifts of Cl and C3, in agreement with the proposed structures in which only the configuration of C2 is different.

Undecoupled ^{13}C NMR spectra of a large number of carbohydrates have shown that hexopyranoses with an axial H1 have a $^1J[^{13}C-H(1)]$ value which is *ca.* 10 Hz lower than that of the corresponding compound with an equatorial H1.[8,11]



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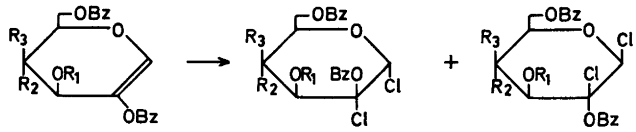

16 17 18

a: = R_1 = CH_3, R_2 = OBz, R_3 = H

b: = R_1 = Bz, R_2 = H, R_3 = OBz

Table 2. ^{13}C Chemical shifts (ppm relative to Me_4Si) and $^1J[^{13}C\text{-}H(1)]$ values (Hz) of 1,2-dichlorosugars and some related compounds.

Compound	C1	C2	C3	C4	C5	C6	$^1J[^{13}C\text{-}H(1)]$
8	90.7	96.2	73.0	67.6	70.8	61.6	190
6	88.8	102.0	72.3	68.0	76.6	62.0	174
9	92.0	96.7	71.0	67.0	71.3	61.8	193
17a	91.2	96.8	82.3	69.2	70.7	61.8	190
18a	87.2	103.9	81.2	70.5	76.5	62.7	171
17b	91.1	95.0	70.2	67.5	69.6	61.3	190
18b	88.5	100.5	69.5	67.6	76.3	61.7	172
α13	92.2	57.4	70.9	67.8	70.5	60.7	185
β13	89.5	61.0	73.8	67.6	75.0	61.0	171
α14	90.6	59.6	68.1	64.2	71.5	61.0	187
β14	86.8	61.8	71.7	64.2	76.5	61.8	166
α15	94.6	86.4	72.4	66.8	71.2	60.8	189
β15	91.9	87.8	76.4	66.7	76.4	61.4	173
5	106.4	97.4					≃190
10	105.2	98.0	71.0[a]	67.2	68.9[a]	63.3	188
11	105.2	97.2					190
12	104.8	100.7	71.4[a]	67.6	69.3[a]	63.9	185

[a] May be reversed.

This difference between $^1J[^{13}C-H(1)]$ values of a pair of anomers is also found in the dichlorides (*13*) with the *gluco*-configuration, although it is slightly bigger (14 Hz), while in the dichloro compounds with *manno*-configuration (*14*) the difference is unusually large (21 Hz) (Table 2). With two electronegative substituents at C2 such as in the trichlorides (*15*) the difference is 16 Hz. A similar large difference (19 Hz) is found between the anomeric pair *9* and *6*. Between *8* and *6* the difference is 16 Hz indicating that *8* is also an α-chloride.

Thus the ^1H NMR and ^{13}C NMR spectra indicate that *6* is tetra-*O*-benzoyl-2-chloro-β-D-glucopyranosyl chloride, *9* is the corresponding α-anomer, and *8* is tetra-*O*-benzoyl-2-chloro-α-D-mannopyranosyl chloride.

Despite the fact that the pure chlorides *6* and *8* are very resistant towards hydrolysis Maurer *et al.*[3] were able to obtain a hydrolysis product when they treated the crude chlorination mixture with aqueous sodium hydrogencarbonate. This seems to indicate that products other than *6* and *8* are present in the crude mixture.

To investigate this *4* was treated with chlorine in tetrachloro methane at −20 °C and a ^1H NMR spectrum was measured within a few minutes at −20 °C. This showed that a small amount (*ca.* 25 %) of *8* was present whereas the major product was a compound different from *6*. Spectra run at intervals showed that only small changes took place during 2 h at −20 °C; but at room temperature the major

product disappeared rapidly and *6* was formed instead. The amount of *8* remained unchanged. Thus chlorination of *4* yields *8* and an unstable intermediate which rearranges to *6* at room temperature. The intermediate is assumed to be an orthoacid chloride *5* on the basis of its ^{1}H NMR spectrum and reactions. Its spectrum (Table 1) showed a small coupling (1.2 Hz) between H3 and H4, indicating that it has a distorted chair conformation similar to that of 1,2-*O*-α-alkylidene derivatives.[12–14] Orthoacid chlorides have not been isolated, but they have been observed in solution at −60 °C.[15]

When a solution of *5*, prepared as described above, was treated with water it reacted immediately to give tetra-*O*-benzoyl-α-D-*arabino*-hexopyranosulose (*2*). Maurer and Petsch [3] hydrolyzed the crude chlorination product with aqueous sodium hydrogencarbonate in boiling benzene, and under these conditions *2* is unstable.[4] When *2* was subjected to this treatment it lost benzoic acid and gave *1* which is probably the product isolated by Maurer and Petsch. Treatment of crude *5* with methanol in pyridine gave a stable orthoester *10*. Reaction with silver fluoride yielded a rather unstable fluoride, which is probably *11*. Reduction of *5* with lithium borohydride gave a benzylidene derivative *12*. Proton and ^{13}C NMR spectra of *10*, *11*, and *12* are quite similar to those of *5*. The rather large $^1J[^{13}$C-H(1)] values (185 – 190) may indicate that all four compounds are α-anomers (Table 2).

The dichlorocompound *8* could be formed from *4* by direct *cis*-addition of chlorine or, possibly, *via* a very unstable orthoacid chloride *7*. The latter has not been observed.

The chlorination of two other compounds was also investigated. Treatment of tri-*O*-benzoyl-3-*O*-methyl-1-deoxy-D-*arabino*-hex-1-enopyranose (*16a*) with chlorine gave *17a* and *18a* in 67 % and 16 % yield, respectively. From the spectra (Tables 1 and 2) the structures were shown to be analogous to those of *8* and *6*. No intermediates analogous to *5* could be observed by chlorination at low temperature. Similar results were obtained when tetra-*O*-benzoyl-1-deoxy-D-*lyxo*-hex-1-enopyranose (*16b*) was chlorinated. No intermediates were observed at low temperature. Work up gave the compounds *17b* and *18b* the structures of which were derived from their spectra.

The dichlorosugars *6* and *8* are very unreactive. Hydrolysis or methanolysis gave only unchanged starting materials. Catalytic reduction using palladium on carbon did not affect any of the chlorine atoms. Treatment with pyridine converted both *6* and *8* into di-*O*-benzoyl-kojic acid.[3] With anhydrous hydrogen fluoride *6* was destroyed, but *8* gave tri-*O*-benzoyl-α-D-*arabino*-hexopyranosulosyl chloride (*3*).

EXPERIMENTAL

Melting points are uncorrected. For thin-layer chromatography (TLC) silica gel PF_{254} (Merck) was used; preparative TLC was conducted with 1 mm layers on 20 × 40 cm plates. ^{1}H NMR spectra were recorded with a Varian HA-100 and a Bruker HXE-90 instrument using tetramethylsilane as the internal reference. ^{13}C NMR spectra were measured as previously recorded.[11] Optical rotations were measured in chloroform solution.

*Chlorination of tetra-*O*-benzoyl-1-deoxy-*D*-arabino-hex-1-enopyranose (4).* 3.17 g of *4* was dissolved at 0 °C in carbon tetrachloride (*ca.* 10 ml) which was previously saturated with chlorine. The solution was kept for 15 min at 0 °C and for 15 min at room temperature. The solvent was evaporated and carbon tetrachloride was added and again evaporated. The residue (*ca.* 4 g) was crystallized from ethanol (40 ml) to give 1.03 g (29 %) of *8*, m.p. 153 – 155 °C. Recrystallization gave a product with m.p. 155.5 – 157 °C, $[\alpha]_D^{25}$ +10.1° (*c* 1) (reported [3] m.p. 156 °C, $[\alpha]_D$ +10.3°).

Evaporation of the mother liquor gave a syrup (2.5 g, 71 %) which was almost pure as seen from TLC and ^{1}H NMR spectra. A sample was purified by preparative TLC eluting twice with benzene. The fast moving fraction gave a trace of *8*. The main fraction gave *6* as a syrup, $[\alpha]_D^{25}$ +28.0° (*c* 3). (Found: C 63.07; H 4.06; Cl 10.87. Calc. for $C_{34}H_{26}Cl_2O_9$: C 62.87; H 4.04; Cl 10.92). The product could be crystallized with some difficulty from cyclohexane, m.p. 84 – 88 °C, $[\alpha]_D^{25}$ +24.4°. A ^{1}H NMR spectrum showed that this product contained *ca.* one equivalent of cyclohexane.

Treatment of 6 *with titanium tetrachloride.* Pure *6* (200 mg) was dissolved in dry chloroform (20 ml). 10 ml of the solvent was evaporated to remove moisture. To the solution was added titanium tetrachloride (0.1 ml). The mixture was heated to 85 °C and the reaction was monitored by TLC (benzene). After 2 h *6* was no longer present. The dark mixture was poured on ice and the product was extracted with chloroform. The extract was washed with aqueous sodium hydrogencarbonate, dried and evaporated to give a syrup (140 mg) which was

almost pure as seen from TLC and an NMR spectrum. The product was purified by preparative TLC (benzene) to give 100 mg (50 %) of *9* as a syrup, $[\alpha]_D^{25}$ +25.2° (*c* 3.4). (Found: C 63.16; H 4.23; Cl 10.94). No other products could be isolated.

A similar treatment of *8* with $TiCl_4$ led to recovery of 70 % unchanged *8*. No other products could be isolated.

Tetra-O-*benzoyl*-α-D-arabino-*hexopyranosulose* (*2*). The glycal *4* (160 mg) was treated with chlorine in carbon tetrachloride at 0 °C as described above. The solution was stirred at 0 °C for 5 min with water (0.5 ml) and sodium hydrogencarbonate (0.5 g). It was then filtered, dried ($MgSO_4$) and evaporated. The residue (200 mg) was separated into two fractions by preparative TLC (ether-pentane 2:1). The fast moving fraction gave 43 mg (24 %) of *8*. The next fraction gave 116 mg (71 %) of partly hydrated *2*, which was dried *in vacuo* over P_2O_5, $[\alpha]_D^{25}$ +38.6° (*c* 4.6). A ^1H NMR spectrum was identical with that of the product described previously.[4]

1,3,6-Tri-O-*benzoyl*-*4-deoxy*-α-D-glycero-*hex*-*3*-*enopyranosulose* (*1*). Chlorination of *4* (4.6 g) followed by hydrolysis as described above gave a crude product which was crystallized from ethanol (10 ml) to give 1.4 g (27 %) of *8*, m.p. 153–155 °C. Evaporation of the mother liquor gave 3.7 g of residue which was boiled for 1 h in benzene (20 ml) in the presence of water (0.5 ml) and sodium hydrogencarbonate (5 g). The mixture was then diluted with dichloromethane, dried (Na_2SO_4), filtered and evaporated. The residue (2.8 g) was crystallized from ethanol (15 ml) to give 1.2 g (32 %) of *1*, m.p. 122–124 °C (recorded [4] m.p. 126.5–127 °C). A ^1H NMR spectrum [4] further confirmed the structure.

Preparation of the orthoester (*10*). 2.0 g of *4* was treated with chlorine in carbon tetrachloride at 0 °C. A mixture of dry methanol (6 ml) and pyridin (6 ml) was cooled to 0 °C and added in one portion to the chlorination mixture. After 30 min at 0 °C the mixture was diluted with carbon tetrachloride and washed five times with ice-water. The organic phase was dried by pouring through filter paper and evaporated at room temperature. The residue was crystallized from ethanol to remove some *8*. The ethanol was evaporated and the residue was chromatographed on a column of silica gel (100 g) eluting with ether-pentane (1:1). The main fraction gave 1.06 g (47 %) of *10* as a syrup, $[\alpha]_D^{25}$ −12.4° (*c* 3). (Found: C 65.84; H 4.66. Calc. for $C_{35}H_{29}ClO_{10}$: C 65.15; H 4.53).

Preparation of the orthoacid fluoride (*11*). 2.0 g of *4* was chlorinated as described above. Silver fluoride (5 g) was suspended in dry acetonitrile (5 ml) and stirred with Siccon for 15 min at room temperature and then cooled to 0 °C. The carbon tetrachloride solution, containing the chlorinated sugar, was poured into the silver fluoride suspension at 0 °C and the mixture was stirred for 30 min. It was then filtered under dry air and the solid was washed with carbon tetrachloride. The combined filtrate was evaporated *in vacuo* at room temperature to give a syrupy product which contained some silver salts. Spectra were measured on a carbon tetrachloride solution. A ^{19}F NMR spectrum gave a singlet 50 ppm upfield from $CFCl_3$. The product was too unstable to be purified further.

Preparation of the benzylidene-derivative (*12*). A solution of chlorinated *4* (1.04 g) was added slowly with stirring to an excess of lithium borohydride suspended in ether, which was cooled in an ice-salt bath. The stirring was continued for 10 min at room temperature and the mixture was then diluted with dichloromethane. Water was then added with caution and the organic phase was washed twice with water, dried ($MgSO_4$) and evaporated to give a syrup (1.2 g). The product was purified by preparative TLC eluting twice with benzene. The fast moving fraction gave 266 mg (23 %) of *8*. The next fraction gave 546 mg (50 %) of the benzylidene-derivative *12*. A sample was rechromatographed (ether-pentane 1:1), $[\alpha]_D^{25}$ −52.7° (*c* 1.1). (Found: C 66.52; H 4.40; Cl 5.70. Calc. for $C_{34}H_{27}ClO_9$: C 66.40; H 4.42; Cl 5.76).

Treatment of 8 *with anhydrous hydrogen fluoride*. The dichlorocompound *8* (1.36 g) was dissolved in anhydrous hydrogen fluoride (3 ml) at −10 °C and the solution was kept at +5 °C for 24 h. It was then diluted with dichloromethane and poured on ice; the organic phase was washed with aqueous sodium hydrogencarbonate, dried and evaporated. The syrupy residue (1.03 g) was crystallized from ether to give 407 mg (38 %) of *3*, m.p. 161–163 °C. Recrystallization gave the pure product, m.p. 165–167 °C, $[\alpha]_D^{25}$ +137° (*c* 2). (Found: C 63.81; H 4.14; Cl 6.84. Calc. for $C_{27}H_{21}ClO_8$: C 63.71; H 4.16; Cl 6.97).

Tri-O-*acetyl*-*2,2-dichloro*-*2*-*deoxy*-α- *and* β-D-arabino-*hexopyranosyl chlorides* (*15*). Tri-*O*-acetyl-2-chloro-1,2-dideoxy-D-*arabino*-hex-1-enopyranose (5.0 g) was chlorinated as described by Brandley and Buncel [6] and worked up to give 667 mg (11 %) of a product with m.p. 161–163 °C, $[\alpha]_D^{25}$ −4.5° (*c* 6). A ^1H NMR spectrum was identical with that reported,[6] but showed that the product was the β-anomer (β-15).

The material in the mother liquor (4.2 g) was chromatographed on a column of silica gel (400 g) using benzene-ether (2:1) as eluent. The main fraction gave 1.76 g (29 %) of pure (α-15) as a syrup, $[\alpha]_D^{25}$ +113° (*c* 9). (Found: C 38.18; H 4.06; Cl 28.08. Calc. for $C_{13}H_{15}Cl_3O_7$: C 38.18; H 4.01; Cl 28.17).

Tri-O-*benzoyl*-*1,2-dideoxy*-*3*-O-*methyl*-D-arabino-*hex*-*1*-*enopyranose* (*16a*). Elimination of hydrogen bromide from tri-*O*-benzoyl-3-*O*-methyl-α-D-glucopyranosyl bromide (13 g) according to Ferrier [16] gave 11 g of crude *16a* as a syrup. Chromatography on a column of silica gel (500 g) using ether-pentane: (11) as eluent gave 7.8

g (70 %) of almost pure *16a*. Rechromatography with benzene-ether (19:1) as eluent gave 4 g (36 %) of pure *16a*, $[\alpha]_D^{25}$ −7.7° (*c* 6.8). (Found: C 68.53; H 4.96. Calc. for $C_{28}H_{24}O_8$: C 68.85; H 4.95).

Reaction of 16a *with chlorine.* Chlorination of *16a* (1.4 g) in carbon tetrachloride was performed as described above. Evaporation gave 1.34 g of a product which was crystallized from ethanol (10 ml) to give 931 mg (58 %) of tri-*O*-benzoyl-2-chloro-3-*O*-methyl-α-D-mannopyranosyl chloride (*17a*), m.p. 129 – 130 °C. Recrystallization gave the pure product, m.p. 131 – 132 °C, $[\alpha]_D^{25}$ +109.5° (*c* 4). (Found: C 60.05; H 4.36; Cl 12.34. Calc. for $C_{28}H_{24}Cl_2O_8$: C 60.12; H 4.33; Cl 12.68). The material in the mother liquor was separated into two fractions by preparative TLC (ethyl acetate-pentane 1:4). The first fraction gave 131 mg (8 %) of *17a*. The next fraction gave 259 mg (16 %) of tri-*O*-benzoyl-2-chloro-3-*O*-methyl-β-D-glucopyranosyl chloride (*18a*), which was crystallized from ether-pentane, m.p. 69 – 71 °C, $[\alpha]_D^{25}$ +16.8° (*c* 1.5). (Found: C 60.25; H 4.48; Cl 12.52).

*Tetra-O-benzoyl-1-deoxy-*D-lyxo-*hex-1-enopyranose* (16b) was prepared by the method of Ferrier [16] from tetra-*O*-benzoyl-α-D-galactopyranosyl bromide (9.5 g). The crude product (8.4 g) was purified by chromatography on a column of silica gel (500 g) eluting with ether-pentane (2:1). This gave a fraction containing 1.6 g (20 %) of pure *16b* as a syrup, $[\alpha]_D^{25}$ +16.9° (*c* 3). (Found: C 70.42; H 4.67. Calc. for $C_{34}H_{26}O_9$: C 70.58; H 4.53). Further elution of the column gave *16b* which was not quite pure.

Treatment of 16b *with chlorine.* Chlorination of *16b* (700 mg) in carbon tetrachloride as described above gave a product (771 mg) which was separated into two fractions by preparative TLC (benzene). The fast moving fraction gave 341 mg (44 %) of tetra-*O*-benzoyl-2-chloro-α-D-talopyranosyl chloride (*17b*) as a syrup, $[\alpha]_D^{25}$ +85.5° (*c* 8.5). (Found: C 63.04; H 4.21; Cl 10.66. Calc. for $C_{34}H_{26}Cl_2O_9$: C 62.87; H 4.04; Cl 10.92).

The next fraction gave 158 mg (20 %) of tetra-*O*-benzoyl-2-chloro-β-D-galactopyranosyl chloride (*18b*) as a syrup, $[\alpha]_D^{25}$ +93.6° (*c* 2.7). (Found: C 62.69; H 4.23; Cl 10.68).

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

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