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THE SYNTHESIS AND SOLVOLYSIS OF SOME FULLY ACETYLATED GLYCOPYRANOSYLULOSE CHLORIDES

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ABSTRACT

Several partially acetylated aldopyranosyl chlorides with an unprotected hydroxyl group at C-2 have been synthesised and some have been oxidised with ruthenium tetraoxide In this way, fully acetylated pyranosylulose chlorides having the α-D-*arabino*-hexo, α-D-*lyxo*-hexo, and β-L-*erythro*-pento structures have been prepared Their rates of methanolysis have been determined Key intermediates in the synthetic sequences were the per-*O*-acetyl-2-*O*-trichloroacetylglycopyranosyl chlorides, of which the α- and β-D-*galacto*, α- and β-L-*arabino*, and α- and β-D-*xylo* compounds were hitherto unknown The β-D-*xylo* derivative exists in the conformation in which all the ring substituents are axially disposed, whereas the α-L-*arabino* compound is a rare example of an acylated pentopyranosyl chloride that adopts, preponderantly, a chair conformation that places the halogen in an equatorial orientation

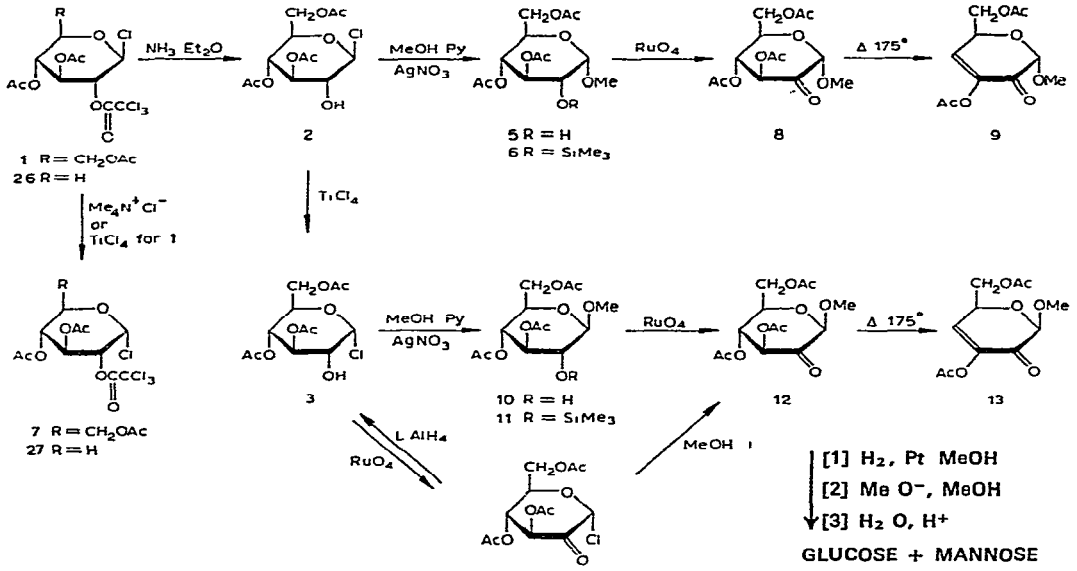
INTRODUCTION

In recent years, there has been growing interest[1] in glycopyranosyl halides possessing a blocking group at C-2 that does not participate in displacement reactions at the anomeric centre We now report on a new class of glycopyranosyl chlorides, which possess a carbonyl function at C-2 This study developed from our interests in glycosyl halides[2] and glycopyranosiduloses[3]

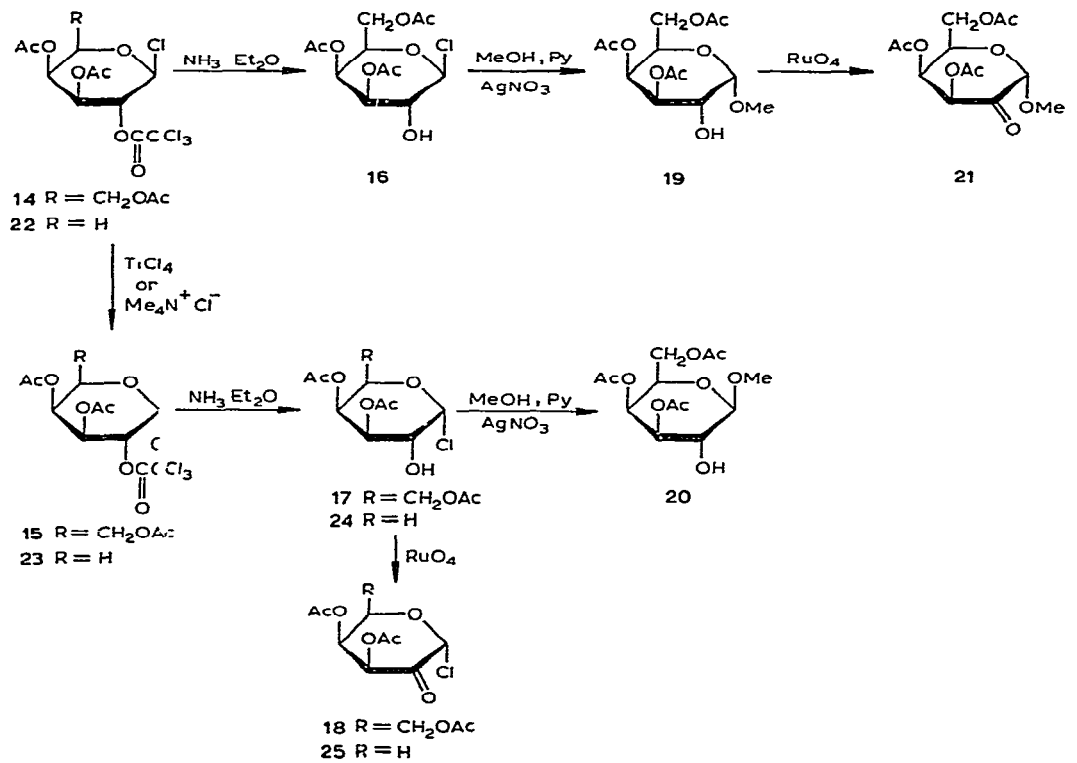
RESULTS AND DISCUSSION

Either chlorination of a suitable pyranosyl-2-ulose derivative or oxidation of a partially acylated 2-hydroxyglycopyranosyl chloride seemed to be possible routes to the fully acylated glycopyranosylulose chlorides The latter route was selected since methods for obtaining such precursors were already well-established for the *gluco* compound

β-D-Glucose penta-acetate is readily converted[4] into 3,4,6-tri-*O*-acetyl-2-*O*-trichloroacetyl-β-D-glucopyranosyl chloride, and the blocking group at C-2 may be preferentially removed by aminolysis We have used this two-step synthesis, in



Scheme 1



Scheme 2.

slightly modified form, to convert the peracetates of galactopyranose, xylopyranose, and arabinopyranose into the corresponding, partially acetylated, 2-hydroxy derivatives (see Schemes 1 and 2)

Pilot experiments showed that the best yield of trichloroacetylglucosyl chloride, from per-*O*-acetyl-β-D-glucopyranose, could be obtained by heating the latter with phosphorus pentachloride under reflux for 1 5–1 8 h Similar treatment of the thermodynamically less-stable anomers of peracetylated galactopyranose, xylopyranose, and arabinopyranose gave the corresponding per-*O*-acetyl-2-*O*-trichloroacetyl-glycopyranosyl chlorides (**14**, **26**, and **22**), with retention of configuration at C-1, in yields of 51, 24, and 38%, respectively.

The crystalline *galacto* derivative **14**, so obtained, differed markedly from the material claimed by Russian workers[5] to have this structure Chlorination of D-galactose penta-acetate, under the conditions employed by these authors, also failed, in our hands, to give any material corresponding to the desired product.

The β-D-*gluco*, β-D-*galacto*, and α-L-*arabino* trichloroacetates (**1**, **14**, and **22**) were smoothly anomerised with either titanium tetrachloride in chloroform or tetramethylammonium chloride in acetonitrile to give, respectively, compounds **7**, **15**, and **23** The β-D-*xylo* trichloroacetate (**26**) could not be anomerised with titanium tetrachloride but inversion at C-1 was achieved with tetramethylammonium chloride Titanium tetrachloride probably fails to bring about this anomerisation because the β-D-*xylo* derivative adopts the $^1C_4$ conformation (see below)

The structures of the six new trichloroacetates (**14**, **15**, **22**, **23**, **26**, and **27**) follow from their mode of preparation, their reactions, and their spectroscopic properties The configurations at C-1 were established from the anomerisation experiments and the n m r. data for pairs of anomers (see Table I).

TABLE I

N M R DATA AND OPTICAL ROTATIONS FOR SOME PER-*O*-ACETYL-2-*O*-TRICHLOROACETYLPYRANOSYL CHLORIDES

Chloride	D-gluco		D-galacto		D-xylo		L-arabino	
	α-(7)	β-(1)	α-(15)	β-(14)	α-(27)	β-(26)	α-(22)	β-(23)
$J_{1\,2}$[a] (Hz)	4 0	8 0[b]	3 5	8 5[c]	4 0	≤2 5	6 2	3 5
$[\alpha]_D$ (degrees)[d]		+1	+132	+14		−15	+36	+166

[a]First-order values, measured in $CDCl_3$ [b]Measured in $(CD_3)_2CO$ This compound behaved differently in $CDCl_3$ and C_6D_6, possibly undergoing conformational change [c]Measured in C_6D_6 [d]Measured in $CHCl_3$.

The chlorides **22** and **26**, which both possess the less-common anomeric configuration, were of particular interest following the striking observation[6] that tri-*O*-acetyl-β-D-xylopyranosyl chloride adopted preponderantly the $^1C_4$ conformation. Thus, the anomeric effect[7] of the chlorine atom appeared to outweigh the

combined steric interactions of four axially disposed ring-substituents Similar observations have been made with a xylosyl fluoride derivative[8] and a chlorosulphated xylosyl derivative[9] Consequently, the n m r spectra of compounds **22** and **26** in solution in deuteriochloroform were studied in greater detail at field strengths of 100 and 220 MHz. and the parameters obtained are recorded in Table II A comparison of these two compounds seemed worthwhile, although Durette and Horton[10] had studied the n m r spectra of the tetra-*O*-acetylpyranoses having the β-D-*xylo* and α-D-*arabino* structures, this pair of compounds was of less interest because the anomeric effect exerted by an acetoxy group is not large enough to cause the *xylo* isomer to adopt the $^1C_4$ conformation

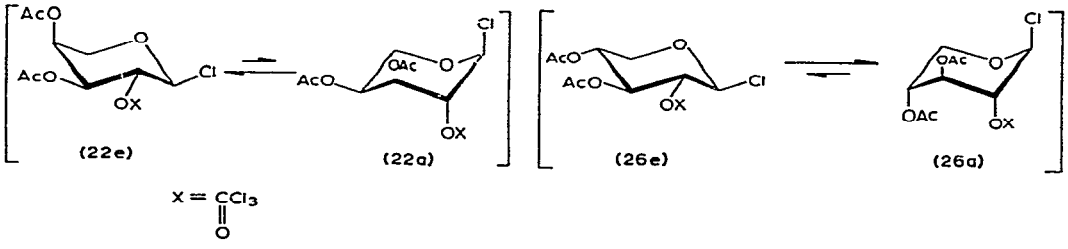
TABLE II

N M R. PARAMETERS[a] FOR 3,4-DI-*O*-ACETYL-2-*O*-TRICHLOROACETYLPENTOPYRANOSYL CHLORIDES WITH THE β-D-*xylo* AND α-L-*arabino* STRUCTURES

Chloride	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-5'*
26	~4 8	4 13(*t*)[b]	~4 8	5 05(*m*)	5 62(*q*)	6 20(*q*)
		J 1 8 and 2 5		$J_{4\,5}$ 2 9	$J_{5\,5}$ 12 8	$J_{5',4}$ 4 2
22[c]	4 32(*d*)	4 5(*q*)	4 65	4 56(*m*)	5 72(*q*)	6 08(*q*)
	$J_{1\,2}$ 6 2	$J_{2\,3}$ 8 0	$J_{3\,4}$ 3 5	$J_{4\,5}$ 5 4	$J_{5\,5}$ 13 0	$J_{5\,4}$ 2 7
22[d]	5 16(*d*)	4 52(*q*)	4 98(*q*)	4 85(*sex*)	6 33(*q*)	7 07(*q*)
	$J_{1,2}$ 7 0	$J_{2,3}$ 8 5	$J_{3,4}$ 3 5	$J_{4,5}$ 4 0	$J_{5,5}$ 13 0	$J_{5\,4}$ 2 0

[a]In $CDCl_3$ at 100 MHz and 37° [b]A definite assignment of these signals to H-1 or H-2 cannot be made, *cf* Ref 13 [c]Measured at 220 MHz [d]Measured in C_6D_6

Analysis[11] of the average spin-couplings*, obtained from the H-4, H-5, and H-5' ABX[12] spin system observed in the spectrum of the β-D-xylosyl chloride **26**, indicated that the pyranosyl ring was ~80% in the $^1C_4$ conformation as depicted in (**26a**), and the observed, small $J_{1\,2}$ value was in agreement with this conclusion. This result was not surprising in view of the earlier work[6,8,9] referred to above, and it led to the expectation that the α-L-arabinosyl chloride **22** would also adopt the $^1C_4$ conformation **22a** because it is the C-4 epimer of the *xylo* derivative **26** and consequently would suffer only one *syn*-diaxial interaction If this were so, a small coupling



*Values for $J_{ax\,ax}$ and $J_{eq\,eq}$ were taken from Ref 13

between H-1 and H-2 would be expected, and a large coupling between the axial protons at C-4 and C-5 However, neither of these features was observed in the spectrum Instead, $J_{1,2}$ was quite large (6 2 Hz), and $J_{4,5}$ and $J_{4,5}$ were both small These observations suggest that the α-L-arabinosyl compound adopts preponderantly the $^4C_1$ conformation **22e**, and this preference was calculated to be ~80% from the coupling between H-4 and H-5

Thus, removal of the *syn*-diaxial interaction from the *xylo* compound **26a** (which is achieved with the *arabino* derivative **22a**) caused the $^1C_4$ conformation to be disfavoured

This result supports the general conclusion[13] that conformations can be predicted only in the broadest sense with the currently used, empirical treatment based upon the summation of the polar contribution from the substituent at C-1 and steric interactions from all the other ring substituents There are, however, other contributions that can influence the conformation of pentopyranosyl chlorides For example, polar groups occupying 1,4-related positions on six-membered rings are known[14] to prefer a *trans*-diaxial relationship rather than a diequatorial one Furthermore, it has been suggested[13,15] that 1,3-*cis*-diaxially disposed acyl groups might exert an attractive force upon each other Either or both of those phenomena could account for the observation that **26a** is preferred to **26e** whereas **22e** is preferred to **22a**

Of the eight structurally related tri-*O*-acylpentopyranosyl chlorides that have been studied, the α- and β-D-*xylo*, β-D-*arabino*, α-D-*lyxo*[13], and the α-[16] and β-D-*ribo* derivatives[13] appear to exist preponderantly in the conformation in which the chloro substituent at C-1 is axial, whereas the α-L-(and presumably the α-D-)arabinosyl chloride **22** appears to provide the first example of the preponderant existence of such a derivative in the conformation in which the chloro group at C-1 is equatorial In contrast, however, 2,3,4-tri-*O*-acetyl-α-D-arabinosyl fluoride[17] adopts the $^4C_1$ conformation

Acylated β-D-lyxosyl chlorides have not been studied Such an investigation would be worthwhile since, in the $^1C_4$ conformation, this compound would also have only one 1,3-diaxial interaction, namely that between the chlorine atom and the C-3 acetoxy residue (*cf.* the *α-arabino* isomer) The report[9] that an analogous tris(chlorosulphate) with this structure adopts the $^1C_4$ conformation could be significant, but whether comparisons between acyl derivatives and chlorosulphates are valid is not known

Preparation of pure samples of the required 2-hydroxy compounds by selective removal of the 2-*O*-trichloroacetyl groups was difficult to accomplish with all of the new trichloroacetates (**14**, **15**, **22**, **23**, **26**, and **27**) Unlike the β-D-*gluco* chloride **2**, which was crystalline, the new 2-hydroxy products were non-crystalline It is noteworthy that selective deacylation at C-2 was less difficult with the thermodynamically more-stable *galacto* (**15**), *arabino* (**23**), and *xylo* (**27**) anomers

Compounds **2**, **3**, **14**, and **15** were converted into their methyl glycoside triacetates with methanol in the presence of pyridine and silver nitrate[18]. Under these

conditions, the 2-*O*-trichloroacetyl group was also removed, and displacements at the anomeric centres occurred mainly with inversion of configuration The isomer distribution was estimated by n m r. spectral analysis of the crude product and, in the case of the *gluco* compounds, confirmed by g l c analysis of the trimethylsilylated derivatives **6** and **11** The methyl α- and β-D-glycosides were obtained in the ratio 3 7 from the α-D-*gluco* (**3**) and α-D-*galacto* (**15**) chlorides, and in the ratio 9 1 from the β-D-*gluco* (**2**) and β-D-*galacto* (**14**) chlorides

In studies of oxidations with ruthenium tetraoxide, we reported[19] that methyl α-D-glucopyranoside 3,4,6-tribenzoate gave the corresponding glycopyranosidulose Similar treatment of the analogous acetate **5** yielded methyl 3,4,6-tri-*O*-acetyl-α-D-*arabino*-hexopyranosidulose (**8**), the structure of which was inferred from its elemental analysis and spectral properties The n m r spectrum was very similar to that reported previously for the corresponding tribenzoate, and the compound also exhibited a similar tendency to eliminate a carboxylic acid, to produce an enone This was revealed when g l c (SE 30, 175°) of crude **8** revealed extensive conversion into methyl 3,6-di-*O*-acetyl-α-D-*glycero*-hex-3-enopyranosidulose (**9**), which was isolated The n m r spectral parameters of **9** closely resembled those of the structurally related benzoyl enone[19] Others[20] have also noted the facile elimination from ulose derivatives, and this property appears to be general for any ulose possessing an ester function at a position β to the carbonyl group

Anomeric integrity was shown to be preserved during the oxidation by treating the β-D analogue (**10**) of glycoside **5** with ruthenium tetraoxide under similar conditions This afforded a ketonic product, the n m r spectrum of which contained signals that integrated correctly for a pyranosid-2-ulose derivative, but differed from the spectrum of the α-D ketone **8** Consequently, this product was assigned the β-D structure **12** This pyranosid-2-ulose also was thermally unstable on a g l c column, affording ~80% of a more-mobile material that was assumed to be the enone **13**

The methyl α-D-galactopyranoside triacetate (**19**) was oxidised likewise to afford methyl 3,4,6-tri-*O*-acetyl-α-D-*lyxo*-hexopyranosidulose (**21**) The n m r spectrum of **21** was very similar to that of its C-4 epimer (**8**), but it differed in the expected way, exhibiting a low value for $J_{3,4}$ (4 0 Hz, *cf* $J_{3,4}$ 10 0 Hz for **8**), thus showing that isomerisation at C-3 did not occur during this oxidation

Oxidation of HO-2 in the acetylpyranosyl chlorides **2**, **3**, and **24** was more difficult than for the glycosides, since these halides are highly reactive However, treatment of 3,4,6-tri-*O*-acetyl-α-D-glucopyranosyl chloride (**3**) with ruthenium tetraoxide gave crystalline tri-*O*-acetyl-α-D-*arabino*-hexopyranosyl-2-ulose chloride (**4**) Treatment of the β-D anomer **2** under similar conditions gave the identical product Thus, either the β-chloro-2-ulose rapidly anomerised under the oxidation conditions, or the rate of oxidation of the β-chloride **2** was slow compared with its rate of anomerisation

The structure of the ulose chloride **4** was deduced from the method of preparation, elemental analysis, and n m r spectrum (see Table III), which exhibited signals attributable to three acetoxy groups, an anomeric proton (singlet), H-3 (doublet),

TABLE III

N M R. PARAMETERS[a] (τ AND J IN Hz) FOR ACETYLPYRANOSYLULOSE CHLORIDES

Chloride	*H-1*	*H-3*	*H-4*	*H-5*	*H-6*	*H-6'*	*Ac*
4 ($CDCl_3$)	3 97(*s*)	4 06(*d*) $J_{3,4}$ 10 0	4 54(*t*) $J_{4,5}$ 10 0	← 5 2–6 0(*m*) →			7 83(*s*) 7 91(*s*) 7 91(*s*)
18 (C_6D_6)	4 05(*s*)	3 93(*d*) $J_{3,4}$ 4 0	4 32(*bd*) $J_{4,5}$ 0 5	5 38(broad *t*) $J_{5,6}$ 6 5 $J_{5,6}$ 7 5	← 5 6–6 2(*m*) →		8 17(*s*) 8 24(*s*) 8 30(*s*)
25 ($CDCl_3$)	3 92(*s*)	3 89(*d*) $J_{3,4}$ 4 0	4 36(*oct*) $J_{4,5}$ 1 0	5 41(*q*) $J_{5,5}$ 13 0		5 90(*q*)[b] $J_{5,4}$ 2 5	7 85(*s*) 7 91(*s*)

[a]Measured at 60 MHz [b]H-5'

H-4 (triplet), and three other protons The presence of the ketone group in compound **4** was suggested by the absence of a hydroxyl absorption in the i r spectrum, this deduction was confirmed by reduction of the carbonyl group Catalytic hydrogenation of the halide **4** in methanol gave, after deacetylation and hydrolysis, a mixture of D-glucose and D-mannose Reduction with lithium aluminium hydride converted **4** into its precursor, the hydroxy-chloroacetate **3** The last result also corroborates the anomeric configuration assigned to compound **4**

The arabinosyl chloride **24** and its C-5 acetoxymethyl analogue, the galactosyl chloride **17**, were oxidised in like fashion to give the pentopyranosyl-2-ulose chloride **25** and hexopyranosyl-2-ulose chloride **18**, respectively The structures of these compounds are based on spectroscopic evidence Their n m r spectra (see Table III) exhibited very similar splitting patterns for the H-1, H-3, and H-4 resonances

The rates of methanolysis of the three pyranosyl-2-ulose chlorides **4**, **18**, and **25** were determined at 27 5° (titration with standard alkali) The rate coefficients (calculated from the integrated first-order rate equation) showed a slight, initial decrease, with increasing time, followed by an increase The minima occurred after ~28% of the chlorides **18** and **25** had undergone reaction Relative rates ($\times 10^5$) of 3 3, 7 8, and 13 3 sec^{-1} for compounds **4**, **18**, and **25**, respectively, were obtained from the mean of the values at 28 and 63% reaction

For glycopyranosyl halides, the titrimetric method produces results[2] that critically indicate the quality of the pyranosyl derivative, material of low quality always afforded rate coefficients that decreased with reaction time Moreover, the liberated acid increases the rate of the reaction by increasing the ionic strength of the medium The change in rate coefficients with time observed for the pyranosylulose chlorides noted above probably results from a combination of these two features, since the chlorides could not be obtained in the high state of purity that we achieved with the pyranosyl halides in our earlier work[2]

An alternative explanation for the initial decrease in the rate coefficients, involving protonation of the ketone group in the pyranosylulose chloride by the

acid liberated, was excluded, since the rate coefficients obtained for compound **4** showed a minimum even in the presence of added hydrogen chloride Under these conditions, any protonation of the ketone function would be complete at the commencement of the reaction Thus, the initial decrease would not be expected to arise

Another possible cause of the initial rate decrease might be a slow addition of methanol to the carbonyl group at C-2 to give a hemiacetal (*cf* Ref 21)

Pyranosyl halides are believed to be solvolysed *via* a glycosyl carbonium ion by an S_Ni process[2,22] A similar mechanism appears to be operating with the pyranosylulose chlorides, since the rate of hydrolysis of the halide **4** was unchanged in the presence of 8mM sodium hydroxide Methanolysis, presumably, occurs by the same mechanism Tests, such as the addition of methoxide ions to the methanol solutions, were unreliable because extensive deacetylation occurred

Product analysis by g l c was attempted with the methanolysate obtained from the chloride **4** Unfortunately, **4** was thermally degraded and gave no detectable products Furthermore, the anomeric methyl pyranosiduloses **8** and **12**, which were the anticipated products, had identical T values and also underwent thermal elimination, being converted into the corresponding enones (**9** and **13**) This transformation, however, could be utilised to ascertain the anomeric composition, since the enones were separable by g l c The ratio for the anomeric products was thus estimated to be **12** : **8** = 7.3.

It is known that α-chloroketones react slower by a unimolecular mechanism than the corresponding saturated deoxy compounds[23], but comparisons have not been made with α-hydroxy chlorides For this reason, the 3,4,6-tri-*O*-acetyl-α-D-glucopyranosyl chloride (**3**), which is structurally related to the ulose chloride **4**, was methanolysed under the same conditions The rate of this reaction increased with increasing time, and the initial rate ($3\,6 \times 10^{-5}$ sec^{-1}) was determined by extrapolation[2] For the purpose of comparison, however, the average rate co-efficient between 28 and 63% reaction was calculated and found to be $9\,3 \times 10^{-5}$ sec^{-1} Thus, the chloroketone is a little less reactive than the hydroxy chloride in this series of compounds

The relative rates of methanolysis of the three 2-ulose chlorides **4**, **18**, and **25** were 1 0, 2 4, and 4 0, respectively, which may be compared with the relative rates of 1 0, 2 7, and 30 0 for the hydrolysis of the structurally related (*i e* , *gluco*, *galacto*, and *arabino*) pyranosyl bromides studied previously[2] The trend of each set of figures is similar and probably can be explained in terms of the changes in non-bonded interactions that occur on passing from the ground-state chair conformation of the pyranosyl chloride to the half-chair conformation adopted by the carbonium ion intermediates

EXPERIMENTAL

Unless stated otherwise, optical rotations were measured on chloroformic solutions with a Bellingham and Stanley polarimeter, ultraviolet spectra were determined with a Unicam S P. 700 spectrophotometer, infrared spectra were measured

on solid samples dispersed in potassium bromide with a Perkin–Elmer Infracord (model 137), and n m r spectra were measured with Varian A-60D, HA-100D, or HR 220 instruments The n m r spectra measured at 100 and 220 MHz were determined by the P C M U at Harwell

Silica gel G was used for t l c , and silica gel (0 05–0 2 mm) for column chromatography The following solvent systems were used (*a*) benzene–ethyl acetate (5 1), (*b*) benzene–ethyl acetate (1 1), (*c*) ethyl acetate For g l c , a Varian Aerograph model 202, fitted with either column *A* [5 ft × 0 25 in ; SE 30 (10%) on 60–80 mesh Chromosorb W], column *B* [10 ft, but otherwise as for *A*], or column *C* [10 ft × 0 25 in ; SE52 (10%) on 60–80 mesh Chromosorb W], was used, with hydrogen as carrier gas and a thermal-conductivity detector

Preparation of derivatives from D-*glucose*

*3,4,6-Tri-*O*-acetyl-2-*O*-trichloroacetyl-β-*D*-glucopyranosyl chloride* (**1**) — Penta-*O*-acetyl-β-D-glucopyranose (10 g, 0 026 mol.) and phosphorus pentachloride (30 g, 0 14 mol) were heated together[24] for 2 h under reflux at ~125° The volatile by-products were evaporated and a solution of the residual syrup in methylene chloride was worked up in the usual way to give a gum Crystallisation from ethyl ether (30 ml) at −10° gave the trichloroacetate **1** (5 8 g, 48%), R_F 0 47 (solvent *a*), which, after recrystallisation had m p 140–141°, $[\alpha]_D$ +1° (*c* 7 0, benzene), lit [4] m p 142°, $[\alpha]_D$ +3° N m r data (C_6D_6) τ 4 60–5 50 (*m*, H-1 to H-4), 5 80 (*q*, $J_{6,5}$ 5 0, $J_{6,6}$ 13 0 Hz), 6 08 (*q*, $J_{6,5}$ 3 0 Hz), 6 77 (*m*, H-5); 8 28, 8 32, 8 34 (3*s*, 3OAc)

*3,4,6-Tri-*O*-acetyl-2-*O*-trichloroacetyl-α-*D*-glucopyranosyl chloride* (**7**) — The β-trichloroacetate **1** (2 5 g) was anomerised[25] with titanium tetrachloride (15 ml) in chloroform (120 ml) to give the α-trichloroacetate **7** as a syrup (2 3 g, 92%) N m r data ($CDCl_3$) τ 3 61 (*d*, $J_{1,2}$ 4 0 Hz); 4 87 (*q*, $J_{2,3}$ 9 0 Hz), 4 25 (*t*, $J_{3,4}$ 9 0 Hz), 4 79 (*t*, $J_{4,5}$ 9 0 Hz), 5 4–6 0 (H-5,6,6'), 7 90, 7 93, 7 99 (3*s*. 3OAc)

*3,4,6-Tri-*O*-acetyl-β-*D*-glucopyranosyl chloride* (**2**) — The trichloroacetate **1** (10 g) was finely powdered and rapidly dissolved at 0° in ethyl ether (200 ml) that had been saturated with ammonia The mixture was vigorously agitated for 8 min and the precipitate that formed was collected (6 7 g, 97%); m p 122–124° Six recrystallisations from ethyl acetate gave **2**, m p 154–156°, $[\alpha]_D$ +38° (*c* 1 0), lit [4] m p 158°, $[\alpha]_D$ +25° acetic acid), ν_{max} 3350 (OH) and 1745 cm^{-1} (ester CO) N m r data (acetone-d_6) τ 4 56 (*d*, $J_{1,2}$ 8 5 Hz), 4 60–5 20 (*m*, H-3,4), 5 60–6 60 (*m*, H-2,5,6,6'), 7 20 (broad *s*, OH), and three acetoxy methyl signals obscured by solvent The resolution of this spectrum was not improved when $CDCl_3$ was used as solvent

*3,4,6-Tri-*O*-acetyl-α-*D*-glucopyranosyl chloride* (**3**) — The β-D-glucosyl chloride **2** (5 g) was anomerised[25] with titanium tetrachloride in chloroform Crystallisation of the product from ethyl acetate–light petroleum (b p 40–60°) gave the α anomer **3** (4 0 g, 80%), m p 93–94°, $[\alpha]_D$ +190° (*c* 1 0), lit.[25] m p 89–91°, $[\alpha]_D$ +181° N m r. data (C_6D_6) τ 3 94 (*d*, $J_{1,2}$ 4 0 Hz), 6 20 (*sex*, $J_{2,1}$ 4 0, $J_{2,OH}$ 9 5 Hz); 4 40 (*t*, $J_{3,2}$ 9 0, $J_{3,4}$ 9 0 Hz), 4 76 (*t*, $J_{4,5}$ 9 5 Hz), 6 80 (*d*, OH, when exchanged with D_2O, the signal at 6 20 collapsed to a quartet), 5 50–5 95 (*m*, H-5,6,6'), 8 12, 8 19 (2*s*, 2OAc)

3,4,6-Tri-O-*acetyl*-α-D-arabino-*hexosyl-2-ulose chloride* (**4**). — The α-D-glucosyl chloride **3** (4 g) in dry dichloromethane (35 ml) was treated[19] with ruthenium tetraoxide (from 2 g of ruthenium dioxide) in carbon tetrachloride (40 ml) for 2 5 h at room temperature The usual work-up gave a colourless syrup (2.9 g, 73%), which was distilled at 130°/10^{-5} × 133 Nm^{-2} to give a pale-yellow gum. Crystallisation from ethyl ether at −10° during 2 months gave the 2-ulose chloride **4**, m p 85–86°, $[\alpha]_D$ +179° (*c* 1 0), ν_{max} 3500 (very weak), 1750 cm^{-1} (intense) (ester and ketone CO) N m r data ($CDCl_3$) τ 3 97 (*s*, H-1), 4 06 (*d*, $J_{3,4}$ 10 Hz), 4 54 (*t*, $J_{4,5}$ 10 Hz), 5 20–6 00 (*m*, H-5,6,6'), 7 83 (*s*, OAc), 7 91 (*s*, 2OAc)

Anal Calc for $C_{12}H_{15}ClO_8$· C, 44 7, H, 4 7, Cl, 11 0 Found C, 44 5, H, 4 9; Cl, 10 9

A similar oxidation (48 h) of the β-D-glucosyl chloride **2** (5 g) in dichloromethane (250 ml) with ruthenium tetraoxide, prepared from the dioxide (4 g), gave the same 2-ulose chloride **4** (3 g, 60%)

Reduction of 3,4,6-tri-O-*acetyl*-α-D-arabino-*hexosylulose chloride* (**4**) *with lithium aluminium hydride* — The chloride **4** (0 4 g) was added to a suspension of lithium aluminium hydride (0 1 g) in anhydrous ethyl ether (10 ml) and stirred for 8 min at room temperature Water was then added and the product was isolated in the usual manner to give a syrup composed of at least two compounds having R_F 0 0 and 0 58 (solvent *b*) The mobile component, isolated by column chromatography, was the α-D-glucosyl chloride **3** (0 12 g), m p 91–93° (undepressed when mixed with authentic material)

Methyl 3,4,6-tri-O-*acetyl*-α-D-*glucopyranoside* (**5**) *and its 2-trimethylsilyl ether* (**6**) — The β-D-glucosyl chloride **2** (2 g) was heated for 2 h under reflux in anhydrous methanol (60 ml) containing pyridine (0 5 ml) and silver nitrate (1 05 g) (*cf* Ref. 26) The solution was filtered and evaporated to give a syrup that was homogeneous on t l c (R_F 0 7, solvent *c*), but n m r spectroscopy showed it to be a 9 1 anomeric mixture

The crude material (0 3 g) was treated[27] with hexamethyldisilazane (0 7 ml) and trimethylsilyl chloride (0 3 ml) in anhydrous pyridine (1 0 ml) for 18 h Separation of the two-component product mixture by preparative g l c (column *B* at 225°) gave the β-D-glucoside derivative **11**, *T* 6 5 min, 13% (see below for physical constants), and **6**, *T* 7 0 min, 87% Mass spectrum *m/e* 392 (M^+), 377 (M^+ − Me), 361 (M^+ − OMe) N m r data (CCl_4) τ 5 46 (*d*, $J_{1,2}$ 4 0 Hz), 6 30 (*q*, $J_{2,3}$ 9 0 Hz), 4 83 (*t*, $J_{3,4}$ 9 0 Hz), 5 19 (*t*, $J_{4,5}$ 9 0 Hz), 5 70–6 20 (H-5), 5 77 (*q*, $J_{6,5}$ 5 0, $J_{6,6}$ 12 0 Hz), 6 08 (*q*, $J_{6,5}$ 2 0 Hz), 6 57 (*s*, OMe), 7 98 (*s*, OAc), 8 03 (*s*, 2OAc), 9 89 (*s*, Me_3Si)

Anal Calc for $C_{16}H_{28}O_9Si$· C, 49 0, H, 7 2 Found C, 48.85, H, 7 0

The trimethylsilyl ether **6** was hydrolysed during 30 min in aqueous methanol at ~70° to give, after solvent evaporation, the glucoside **5** as a syrup, ν_{max} 3300 and 1760 cm^{-1} (OH and ester CO). N m r. data (C_6D_6) τ 5 47 (*d*, $J_{1,2}$ 4 0 Hz), 6 40 (*q*, $J_{2,3}$ 9 0 Hz), 4 48 (*t*, $J_{3,4}$ 9.0 Hz), 4 79 (*t*, $J_{4,5}$ 9 5 Hz), 6 0–6 4 (*m*, H-5), 5 66 (*q*,

$J_{6,6}$ 12 0, $J_{6,5}$ 4 0 Hz), 5 91 (*q*, $J_{6',5}$ 2 5 Hz), 6 99 (*s*, OMe), 7 75 (*s*, exchangeable with D_2O; OH), 8 19, 8 23, 8 27 (3*s*, 3OAc)

*Methyl 3,4,6-tri-*O*-acetyl-α-*D-arabino*-hexopyranosidulose* (**8**) — The α-D-glucoside triacetate (**5**) (140 mg) in carbon tetrachloride (10 ml) was oxidised during 5 h in the usual manner with ruthenium tetraoxide (derived from 0 3 g of the dioxide) to give **8** as a colourless syrup (89 mg, 64%); ν_{max} 1750 cm^{-1} (CO), no OH absorption N m r data (C_6D_6) τ 5 39 (*s*, H-1), 4 11 (*d*, $J_{3,4}$ 10 0 Hz); 4 44 (*sex*, $J_{4,5}$ 10 0, $J_{4,6}$ 1 8 Hz), 5 50–6 10 (*m*, H-5,6,6'), 7 05 (*s*, OMe), 8 20, 8 25, 8 30 (3*s*, 3OAc)

Anal Calc for $C_{13}H_{18}O_9$ C, 49 0; H, 5 7 Found C, 48 5; H, 5 7.

The sample for elemental analysis was purified by g l c (column *A* at 175°, *T* 9 5 min) It was accompanied by a thermal decomposition product, methyl 3,6-di-*O*-acetyl-4-deoxy-α-D-*glycero*-hex-3-enopyranosidulose (**9**) (60 mg), *T* 5 25 min, ν_{max} 1650 cm^{-1} (conj CO), λ_{max} 230 and 266 nm N m r data (C_6D_6) τ 5 21 (*s*, H-1), 3 82 (*d*, $J_{4,5}$ 2 0 Hz); 5 15 (*sex*, $J_{5,6}$ 5 0 Hz); 5 85 (*q*, $J_{6,6}$ 11 5 Hz), 6 10 (*q*, $J_{6',5}$ 5 0 Hz), 6 88 (*s*, OMe); 8 20, 8 29 (2*s*, 2OAc)

Anal Calc for $C_{11}H_{14}O_7$: C, 51 2, H, 5 5 Found C, 50 2, H, 5 55

*Methyl 3,4,6-tri-*O*-acetyl-β-*D*-glucopyranoside* (**10**) *and its 2-trimethylsilyl ether* (**11**) — The α-D-glucosyl chloride (**3**) (2 g) was treated as described above for the β-chloride The crude, syrupy product [1 6 g, 80% after crystallisation twice from ethyl ether–light petroleum (b p 40–60°)] gave **10**, m p 95–96°, $[\alpha]_D$ +17° (*c* 0 8), lit [28] m p 95–97°, $[\alpha]_D$ +19° (ethanol) N m r data (acetone-d_6) τ 5 60 (*d*, $J_{1,2}$ 8 0 Hz), 5.0 (*m*, H-3,4), 5 40–6 40 (*m*, H-2,5,6,6'), 6 50 (*s*, OMe), 8 00 (*s*, OAc), 8 05 (*s*, 2OAc), OH exchanged with solvent

Anal Calc for $C_{13}H_{20}O_9$: C, 48 75, H, 6 3 Found C, 48 7, H, 6 0.

Trimethylsilylation of **10** (0 2 g), as described above, gave, after three recrystallisations from ethyl ether–pentane, the ether **11**, *T* 6 5 min (column *B* at 225°), m p 139–140°, $[\alpha]_D$ +3 2° (*c* 1 0) Mass spectrum *m/e* 392 (M^+), 377 ($M^+ - Me$), 361 ($M^+ - OMe$) N m r data (C_6D_6) τ 6 02 (*d*, $J_{1,2}$ 7 5 Hz); 4 50–5 05 (*m*, H-3,4); 5 50–6 20 (*m*, H-6,6'); 6 20–6 85 (m, H-2,5); 6 78 (*s*, OMe); 8 21, 8 28, 8 30 (3*s*, 3OAc), 9 89 (*s*, $SiMe_3$)

Anal Calc for $C_{16}H_{28}O_9Si$ C, 49 0, H, 7 2 Found C, 49 0, H, 7 1

*Methyl 3,4,6-tri-*O*-acetyl-β-*D*-arabino-hexopyranosidulose* (**12**) — The β-D-glucoside triacetate (**10**) (0 3 g), dissolved in a mixture of carbon tetrachloride (40 ml) and dichloromethane (10 ml), was oxidised with ruthenium tetraoxide (from 0 2 g of the dioxide) After 12 h, t l c showed that oxidation was incomplete and so the mixture was treated with more oxidant (from 0 3 g of the dioxide) for 3 h The crude, syrupy β-D-pyranosid-2-ulose **12** had $[\alpha]_D$ +179°, ν_{max} 3300 cm^{-1} (very weak) N m r data (C_6D_6). τ 4 10–4 45 (*m*, 2-H), 5 25–5 90 (*m*, 4-H), 6 48 (*s*, OMe); 8 23, 8 31, 8 37 (3*s*, 3OAc) On g l c, **12** (*T* 9 5 min) was accompanied by what was assumed to be methyl 3,6-di-*O*-acetyl-4-deoxy-β-D-*glycero*-hex-3-enopyranosidulose (**13**), *T* 6 0 min

*Reduction of methyl 3,4,6-tri-*O*-acetyl-β-*D*-arabino-hexopyranosidulose* (**12**) — A methanolic solution (50 ml) of the hexosylulose chloride **4** (0 3 g) was neutralised

after 12 h at room temperature and evaporated to a syrup This was dissolved in ethanol (10 ml) and shaken in an atmosphere of hydrogen in the presence of platinum oxide (80 mg) The product was deacetylated and then hydrolysed in 2M hydrochloric acid for 10 h at 95° Paper-chromatographic analysis of the reaction product revealed glucose and mannose

Preparation of derivatives from D-*galactose*

3,4,6-Tri-O-*acetyl-2*-O-*trichloroacetyl-β*-D-*galactopyranosyl chloride* (**14**). — Penta-*O*-acetyl-*β*-D-galactopyranose (10 g) was treated as described above for the *gluco* compound This gave the trichloroacetate **14** (51%; 3 5 g by direct crystallisation and 2 5 g by column chromatography) Recrystallisation from ethyl ether–light petroleum (b p 60–80°) gave, depending upon the amount of petroleum used, needles or plates of **14**, m p 120–121°, $[\alpha]_D$ +14° (*c* 1 0) N m r data (C_6D_6) τ 5 25 (*d* $J_{1,2}$ 8 5 Hz), 4 41 (*q*, $J_{2\ 3}$ 10 0 Hz); 4 98 (*q*, $J_{3,4}$ 3 3 Hz), 4 59 (*q*, $J_{4,5}$ 1 0 Hz), 6 57 (*sep*, $J_{5,6}$ 5 8, $J_{5,6}$ 7 3 Hz); 5 97 (broadened doublet split by 6 5 Hz, H-6,6′), 8 34, 8 37, 8 41 (3*s*, 3OAc)

Anal Calc for $C_{14}H_{16}Cl_4O_9$· C, 35 8; H, 3 4; Cl, 30 15 Found. C, 35 7, H, 3 6, Cl, 30 15

Treatment of D-galactose penta-acetate (20 g), by the procedure described in the Russian literature[5], gave a gum composed of three compounds having R_F 0 80, 0 51, and 0 45 (solvent *a*). Fractionation of the crude syrup (2 g) by column chromatography gave a bis(trichloroacetate) (0 25 g), [R_F 0 80, the n m r spectra in C_6D_6 and $CDCl_3$ were identical with those for triacetate **14** in these solvents, except that **14** gives three acetate signals, whereas the former compound exhibits only two], the trichloroacetate **14** (0 4 g, R_F 0 51, m p 120°), and tetra-*O*-acetyl-α-D-galactopyranosyl chloride (0 1 g, R_F 0 45, m p 76–77°, lit [29] m p 77–78°)

3,4,6-Tri-O-*acetyl-2*-O-*trichloroacetyl-α*-D-*galactopyranosyl chloride* (**15**) — The *β*-D-galactosyl chloride **14** (5 0 g) was anomerised[25] with titanium tetrachloride (30 ml) in chloroform (250 ml) to give the α-D-galactosyl chloride (**15**) as a colourless syrup (4 6 g, 91%), $[\alpha]_D$ +132° (*c* 1 0), R_F 0 54 (solvent *a*) N m r data ($CDCl_3$)· τ 3 60 (*d*, $J_{1,2}$ 3 5 Hz), 4 20–4 85 (*m*, H-2,3,4), 5 42 (*m*, H-5), 5 75–6 00 (*m*, H-6,6′); 7 84, 7 95, 8 02 (3*s*, 3OAc)

The *β*-D-galactosyl chloride **14** (0 62 g) was also anomerised[30] with tetramethylammonium chloride (40 mg) in acetonitrile to give a syrup (0 58 g, 94%), identical with the α-D-anomer obtained above

3,4,6-Tri-O-*acetyl-β*-D-*galactopyranosyl chloride* (**16**) — The trichloroacetate **14** (2 0 g) was treated for 20 min with ammonia dissolved in ether, as described for the *gluco* analogue The usual work-up afforded a syrup, from which trichloroacetamide was separated by dissolving the product in chloroform The crude *β*-D-galactosyl chloride **16** was an oil. N m r. data ($CDCl_3$) τ 4 76 (*d*, $J_{1,2}$ 9 0 Hz), 4 08 (*q*, $J_{2\ 3}$ 10 0 Hz), 5 03 (*q*, $J_{3,4}$ 3 5 Hz), 4 60 (*d*, $J_{4,5}$ ~0 5 Hz), 5 6–6 0 (*m*, H-5,6,6′), 6 43 (*s*, OH), 7.85 (*s*, OAc), 7 95 (*s*, 2OAc)

3,4,6-Tri-O-*acetyl-α*-D-*galactopyranosyl chloride* (**17**) — The trichloroacetate

15 (3 g) was deacylated at position 2 with ammonia, as described above, to give the α-D-galactosyl chloride **17** (1.9 g, 94%), $[\alpha]_D$ +157° (*c* 1 0), ν_{max} 3500 cm^{-1} (OH) N m r data ($CDCl_3$)· τ 3 72 (*d*, $J_{1\,2}$ 4 0 Hz), 5 82 (*q*, $J_{2\,3}$ 10 0 Hz), 4 79 (*q*, $J_{3\,4}$ 3 0 Hz), 4 54 (*q*, $J_{4,5}$ 1 0 Hz), 5 48 (broad *t*, $J_{5,6}$ 6 0, $J_{5,6}$ 7 0 Hz), 5 8–6 2 (*m*, H-6,6'), 7 25 (*s*, OH), 7 86 (*s*, OAc), 7 96 (*s*, 2OAc)

3,4,6-Tri-O-acetyl-α-D-lyxo-hexosylulose chloride (**18**) — The α-D-galactosyl chloride **17** (1 g) was oxidised, as described for the *gluco* analogue, to give **18** (0 59 g, 59%) The crude gum was purified by distillation ($10^{-5} \times 133$ Nm^{-2}), $[\alpha]_D$ +238° (*c* 1 0) N m r data (C_6D_6) τ 4 05 (*s*, H-1), 3 93 (*d*, $J_{3\,4}$ 4 0 Hz), 4 32 (broad *d*, $J_{4,5}$ ~0 5 Hz), 5 38 (broad *t*, $J_{5,6}$ 6 5, $J_{5,6'}$ 7 5 Hz); 5 6–6 2 (*m*, H-6,6'), 8 17, 8 24, 8 30 (3*s*, 3OAc)

Methyl 3,4,6-tri-O-acetyl-α-D-galactopyranoside (**19**) — The β-D-galactosyl chloride **14** (3 8 g) in methanol (80 ml) containing pyridine (0 68 ml) was heated under reflux with silver nitrate (1 44 g) for 1 h Work-up gave **19** as a syrup (2 3 g, 88%), $[\alpha]_D$ +143° (*c* 1 0), ν_{max} 3500 cm^{-1} (OH) N m r data ($CDCl_3$) τ 5 12 (*d*, $J_{1,2}$ 4 0 Hz), 6 05 (*q*, $J_{2,3}$ 10 5 Hz), 4 85 (*q*, $J_{3,4}$ 3 5 Hz), 4 59 (broad *d*, $J_{4\,5}$ ~0 5 Hz), 5 6–6 1 (*m*, H-5,6,6'), 7 72 (broad *s*, exchangeable with D_2O, OH), 6 52 (*s*, OMe), 7 88 (*s*, OAc), 7 96 (*s*, 2OAc) A weak singlet at τ 6 40 (OMe) indicated the presence of ~10% of the β-D anomer This was confirmed by g l c analysis of the trimethylsilyl derivative (10 mg) on column *C* at 185° Two peaks were observed having *T* 7 8 min (11%) and 9 0 min (89%)

The α-D-galactosyl chloride **15** (2 8 g) was methanolysed, as described for the β-D chloride, to give a mixture of the α-D-galactoside triacetate **19** and the β-D anomer **20** in the ratio 3 7 (inferred from the relative intensities of the OMe signals at τ 6 51 and 6 40) This was confirmed by g l c analysis of the trimethylsilyl derivatives on column *C* at 185°, which showed peaks at *T* 7 8 min (72%) and 90 min (28%)

Methyl 3,4,6-tri-O-acetyl-α-D-lyxo-hexopyranosidulose (**21**) — The crude methyl galactoside **19** (90% of α-D anomer, 0 4 g) in carbon tetrachloride (20 ml) was oxidised during 5 h with ruthenium tetraoxide (prepared from 0 3 g of dioxide) Crystallisation of the product from ethyl ether–hexane gave the pyranosidulose **21** (0 27 g, 67%), m p 102–103°, $[\alpha]_D$ +138° (*c* 1 0) N m r data ($CDCl_3$) τ 5 20 (*s*, H-1), 4 15 (*d*, $J_{3,4}$ 4 0 Hz), 4 26 (broad *d*, $J_{4,5}$ ~0 5 Hz), 5 32 (broad *t*, $J_{5,6}$ 6 0, $J_{5\,6'}$ 5 5 Hz), 5 6–6 0 (H-6,6'), 6 48 (*s*, OMe), 7.93 (*s*, OAc), 7 93 (*s*, 2OAc)

Anal Calc for $C_{13}H_{18}O_9$. C, 49 1; H, 5 7 Found. C, 49 0, H, 5 8

Preparation of derivatives from L-*arabinose*

3,4-Di-O-acetyl-2-O-trichloroacetyl-α-L-arabinopyranosyl chloride (**22**) — Tetra-*O*-acetyl-α-L-arabinopyranose (5 g) was chlorinated as described above for the *gluco* compound The crude, syrupy product (5 65 g) was composed of two compounds having R_F 0 81 and 0 75 (solvent *a*) The less-mobile component crystallised and was shown to be 2,3,4-tri-*O*-acetyl-β-L-arabinosyl chloride (0.9 g, 20%), m p 145–147°, lit [31] m.p 146–147°. N m r data (C_6D_6) τ 3 61 (*d*, $J_{1,2}$ 4 0 Hz), 4 20–4 60

(*m*, H-2,3), 4 67 (*m*, H-4), 6.14 (*q*, $J_{5,5'}$ 13.5, $J_{5\,4}$ ~1.0 Hz), 6 55 (*q*, $J_{5',4}$ 2 0 Hz), 8 25 (*s*, OAc), 8 35 (*s*, 2OAc)

The syrupy mother liquors were fractionated by column chromatography to give the trichloroacetate **22** (2 4 g, 38%), $[\alpha]_D$ +36° (*c* 1 0) N m r data (220 MHz, $CDCl_3$)· τ 4 32 (*d*, $J_{1\,2}$ 6 2 Hz), ~4 5 (*q*, $J_{2,3}$ 8 0 Hz), 4.65 (*q*, $J_{3,4}$ 3 5 Hz), 4 56 (*m*, H-4), 5 72 (*q*, $J_{5,4}$ 5 4, $J_{5,5'}$ 13.0 Hz), 6 08 (*q*, $J_{5',4}$ 2 7 Hz), 7 81 (*s*, OAc), 7 91 (*s*, OAc), at 100 MHz (C_6D_6) 5 16 (*d*, $J_{1,2}$ 7 0 Hz), 4 52 (*q*, $J_{2,3}$ 8 5 Hz), 4 98 (*q*, $J_{3,4}$ 3 5 Hz), 4 85 (*sex*, $J_{4,5}$ 4 0 Hz), 6 33 (*q*, $J_{5,5}$ 13 0 Hz), 7 07 (*q*, $J_{5',4}$ 2 0 Hz), 8 35 (*s*, OAc), 8 42 (*s*, OAc).

3,4-Di-O-acetyl-2-O-trichloroacetyl-β-L-arabinopyranosyl chloride (**23**) — The α-L-trichloroacetate **22** was anomerised either with titanium tetrachloride in chloroform or with tetramethylammonium chloride in acetonitrile, by the methods described for the *galacto* analogue, to give the β-L trichloroacetate **23** as a syrup, $[\alpha]_D$ +166° (*c* 1 0) N m r data (100 MHz, C_6D_6). τ 4 03 (*d*, $J_{1,2}$ 3 5 Hz), 4 63 (*q*, $J_{2,3}$ 10 0 Hz), 4 38 (*q*, $J_{3\,4}$ 3.0 Hz), 4 8 (*m*, H-4), 6 35 (*q*, $J_{5,4}$ 1 0, $J_{5,5}$ 13 0 Hz), 6 70 (*q*, $J_{5',4}$ 2 0 Hz), 8 33 (*s*, OAc), 8 4 (*s*, OAc) Irradiation of the H-4 multiplet caused H-3, H-5, and H-5′ to appear as doublets, and irradiation of H-1 caused H-2 to become a doublet

3,4-Di-O-acetyl-β-L-arabinopyranosyl chloride (**24**) — The β-L-trichloroacetate **23** (8 g) was deacylated at position 2 in 4 min at 0° by the usual procedure This gave the chloride **24** as an unstable syrup, R_F 0 54 (solvent *a*) N m r. data ($CDCl_3$). τ 3 65 (*d*, $J_{1,2}$ 4 0 Hz), 4 5–5 0 (*m*, H-3,4), 5 5–6 3 (*m*, H-2,5,5′), 6 78 (broad *s*, OH), 7.88 (*s*, OAc), 7 94 (*s*, OAc)

3,4-Di-O-acetyl-β-L-erythro-pentosylulose chloride (**25**) — The arabinosyl chloride **24** (0 6 g) was oxidised in the usual way with ruthenium tetraoxide (prepared from 0 4 g of the dioxide) during 4 h The crude product was distilled ($10^{-5} \times 133$ Nm^{-2}) to give **25** as a gum (0 3 g, 50%) N m r. data ($CDCl_3$) τ 3 92 (*s*, H-1), 3 89 (*d*, $J_{3\,4}$ 4 0 Hz), 4 36 (*o*, H-4), 5 41 (*q*, $J_{5,4}$ 1 0, $J_{5,5}$ 13 0 Hz), 5 90 (*q*, $J_{5\,,4}$ 2 5 Hz), 7 85 (*s*, OAc), 7.91 (*s*, OAc), in C_6D_6 τ 4 03 (*s*, H-1), 3 95 (d, $J_{3,4}$ 4 0 Hz), 4 58 (*o*, H-4), 5 85 (*q*, $J_{5,4}$ 1 0, $J_{5\,5'}$ 13.0 Hz), 6 25 (*q*, $J_{5',4}$ 2 5 Hz), 8 13 (*s*, OAc), 8 28 (*s*, OAc).

Preparation of derivatives from D-*xylose*

3,4-Di-O-acetyl-2-O-trichloroacetyl-β-D-xylopyranosyl chloride (**26**). — Tetra-*O*-acetyl-β-D-xylopyranose (5 g) was chlorinated as for the *gluco* compound The crude product, after chromatography, gave **26** (1 5 g, 24%) as a colourless oil N m r. data (100 MHz, $CDCl_3$) τ 4 8–4 9 (*d*, H-1), 4 16 (*t*, $J_{2,1}$ 1 8, $J_{2,3}$ 2 5 Hz), 4 8–4 9 (*m*, H-3), 5 09 (*m*, H-4), 5 62 (*q*, $J_{5,4}$ 2 9, $J_{5,5}$ 12.8 Hz), 6 20 (*q*, $J_{5',4}$ 4 2 Hz), 7.88 (*s*, OAc), 7.91 (*s*, OAc)

3,4-Di-O-acetyl-2-O-trichloroacetyl-α-D-xylopyranosyl chloride (**27**) — The β-trichloroacetate **26** (1.0 g) was anomerised in acetonitrile (20 ml) with tetramethylammonium chloride (50 mg) during 8 h at ~80°, as described for the *galacto* analogue. The α-trichloroacetate **27** was isolated as a colourless syrup (0 8 g). N m r. data

($CDCl_3$) τ 3.70 (*d*, $J_{1,2}$ 4 0 Hz), 4 8–5 2 (*m*, H-2,4), 4 28 (*t*, $J_{3,2}$ 9.0, $J_{3,4}$ 9.0 Hz), 6 0 (*m*, H-5,5'), 7 96 (*s*, 2OAc)

Attempts to anomerise the β-trichloroacetate **26** with titanium tetrachloride in chloroform, as described for the *galacto* analogue, led to no reaction under the usual conditions, or to decomposition when a large excess of the titanium chloride was used.

Solvolysis experiments. — To samples of the ulose chlorides (150–250 mg) in tubes fitted with serum caps, dry methanol (5 ml) at 27 5° was added The solutions were thermostatted at 27 50° and, at intervals, aliquots (200 μl) were withdrawn and quenched by rapid mixing with pure acetone (2 ml) at −50°. The free hydrogen chloride in these samples was then titrated at this temperature against 30mM tetrabutylammonium hydroxide with Lacmoid (B D H , Ltd) as indicator. The results were calculated by using the integrated first-order rate equation.

In some experiments, the reaction products were monitored by g l c analysis The chloride (0 9 g) was dissolved in methanol (15 ml), and aliquots (1 ml) were removed at intervals and diluted with cold benzene (20 ml) The solvent was rapidly evaporated, and the residue was treated with hexamethyldisilazane (3 3 ml) and trimethylsilyl chloride (1 7 ml) in pyridine (0 25 ml) The resulting solutions were analysed by g l c on column *B* at 185°.

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