Preliminary communication

Reactions of some glucofuranoid derivatives with sulphuryl chloride

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The reaction of sulphuryl chloride with carbohydrates has been extensively studied¹. However, the only reported studies with hexofuranoid derivatives are those involving the D-fructofuranosyl moiety of sucrose^{2,3} and 1,2:5,6-di-O-isopropylidene- α -D-glucofuranose⁴. Recently, Jones *et al.*⁵ have reported on the reaction of sulphuryl chloride with methyl α - and β -D-ribo- and -D-xylo-furanosides. We now describe the reaction of sulphuryl chloride with methyl β -D-glucofuranosidurono-6,3-lactone, 1,2-O-isopropylidene- α -D-glucofuranurono-6,3-lactone, and 1,2-O-isopropylidene- α -D-glucofuranose.

The experimental procedure used was as follows. To the cooled (below -40°) solution of the carbohydrate (10 g) in dry chloroform (80 ml) and dry pyridine (8 ml for every 5 ml of sulphuryl chloride required), sulphuryl chloride (5 ml for every hydroxyl group present) was added dropwise, with vigorous stirring. After storage for 2 h below -40° , the reaction mixture was stirred for a further 2 h at 0° , and then kept at room temperature until t.l.c. revealed the presence of a single, major compound, when it was diluted with chloroform and worked-up as previously described⁶. In another experiment, 1,2-O-isopropylidene- α -D-glucofuranose was treated as described above and the mixture was then heated for 16 h at 50° before being worked-up. The results of these reactions are given in Table I.

Compounds 1, 3, and 4 were dechlorosulphated with methanolic sodium iodide in the usual way. Table II lists the dechlorosulphated products and their physical constants. The n.m.r. spectra of 1, 2, and 5 all showed H-5 as a singlet, at τ 5.73 (CDCl₃), 5.88 [(CD₃)₂SO], and 5.73 (CDCl₃), respectively; in each case, $J_{4,5}$ was zero. These data indicate^{7,8} that 1, 2, and 5 have the L-*ido* configuration, and are consistent with the inversion of configuration that occurs when a chlorosulphate group is replaced by chloride. Furthermore, the n.m.r. data for 2 and 5 resemble closely those reported for the respective bromo analogues⁸. The structure of 6, and hence 3, follows from the conversion of 6 into the known 3,5-diacetate⁹, and from its conversion into 6-chloro-6-deoxy-Dglucose {m.p. 133-134°, [α]_D +102.8 (2 min) \rightarrow \div 52.8° (150 min) (c 1.0, water) }¹⁰. In addition, the n.m.r. data obtained for the diacetate coincide with those reported¹¹.

The n.m.r. spectrum (CDCl₃) of the dichloro derivative 7 contained doublets for H-1 and H-2 at τ 3.95 and 5.38, respectively ($J_{1,2}$ 4 Hz), signals for H-6 and H-6' at τ 5.95–6.1, and a 1-proton singlet (OH) at τ 7.28; the remaining resonances (H-3,4,5)

REACTION OF FURANOID DERIVATIVES V	WTH SULPHURYL CHLORIDE			
Starting compound	Product	Yield (%)	[α] ^a [degrees]	M.p. (degrees)
(a) At room temperature Methyl <i>p</i> -D-glucofuranosidurono-6,3-lactone	Methyl 5-chloro-5-deoxy-œ-L- idofuranosidurono-6,3-lactone	50-60	-11.0	102-104
1,2-O-Isopropylidene-a-D-glucofuranurono- 6,3-lactone	2-chlorosulphate (1) 5-Chloro-5-deoxy-1,2-O-iso- propylidene-&-L-idofuranurono-	70-80	+48.7	137-139
1,2.0 Iso propylidene-a-D-glucofuranose	6,3-lactone (2) 6-Chloro-6-deoxy-1,2-O-lso- propylidene-e-D-glucofuranose 3 S-difochterosulphete) (3)	75-85	-41.1	56- <i>5</i> 7.5
(b) At 50° 1,2-O Isopropylidene-æ-D-glucofuranose	9,0-uncontores transport 5,6-Dichloro-5,6-dideoxy-1,2- 0-isopropylidene-8-L-idofuranose 3-chlorosulphate (4) ^b			
a For solutions in chloroform. b This product wa	s contaminated with a small proportion c	of 3, and was is	olated in 70% y	ield as the

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TABLE I

4 Ļ crystalline, dechlorosulphated product. 4

C2

TABLE II

Starting compound	Product	[a]a (degrees)	M.p. (degrees)			
1	Methyl 5-chloro-5-deoxy- &L-idofuranosidurono-6,3- lactone (5)	-87.0	137139			
3	6-Chloro-6-deoxy-1,2-O-iso- propylidene-c-D-glucofuranose	-11.8 (6)	78- 79			
4	5,6-Dichloro-5,6-dideoxy- 1,2-O-isopropylidene-β-L- idofuranose ⁵ (7)	-18.7	112–114			

DECHLOROSULPHATION OF CHLOROSULPHATED FURANOID DERIVATIVES ·

^aFor solutions in methanol for 5 and 7, and chloroform for 6. ^bDecomposes slowly at room temperature, but is stable as the acetate, m.p. $93-94^{\circ}$.

were overlapped and occurred at τ 5.47–5.65. Addition of trichloroacetyl isocyanate to the solution resulted in the appearance of a 1-proton singlet at τ 1.1 due to the NH of the resulting carbamate. Furthermore, H-3 and H-4 gave a pair of coupled doublets at τ 4.6 and 5.4, respectively ($J_{3,4}$ 2.7 Hz). The deshielding of H-3 by ~0.9 p.p.m. indicates that the free hydroxyl group in 7 is located at C-3, and therefore that the second chloro group is attached to C-5. The assumed L-*ido* configuration for 7 is consistent with the inversion of configuration that occurs when a chlorosulphate group is replaced by chloride. All of the crystalline products listed gave elemental analyses consistent with the structures assigned. All of the dechlorosulphated products formed crystalline acetates.

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