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Preliminary communication

Reaction of methyl pentofuranosides with sulfuryl chloride

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Although there exists considerable literature on the reaction of sulfuryl chloride (SO_2Cl_2) with carbohydrates[1], the only studies with a furanoid derivative that have been documented are those involving the fructose moiety of sucrose[2,3]. In the present Communication, preliminary results of an investigation of the reaction of sulfuryl chloride with methyl pentofuranosides are described. Under the particular conditions employed, the reaction provides a convenient method for the preparation of 5-chloro-5-deoxypentoses.

The experimental procedure for the reactions with sulfuryl chloride was as follows. To a cooled (Dry Ice–acetone) solution of the methyl pentofuranoside (1.7 g, 10 mmole) in dry pyridine (8 ml) and chloroform (20 ml) was added sulfuryl chloride (4 ml, 30 mmole) dropwise, with stirring. Cooling was continued for an additional 2 h, and then the reaction mixture was stirred for a further 1 h at 0°. The mixture was diluted with chloroform (150 ml), and the solution was washed successively with water, 3% hydrochloric acid, 5% sodium hydrogen carbonate solution, and water, dried (magnesium sulfate), and evaporated. The mixture of chlorosulfation products was resolved by chromatography on silica gel. The products were dechlorosulfated in the usual manner[4] by treatment of a solution of the carbohydrate chlorosulfate in methanol with sodium iodide in aqueous methanol.

The results with methyl α (and β)-D-ribofuranosides and methyl α (and β)-D-xylofuranosides are given in Table I. All of the products listed gave elemental analyses consistent with the assigned structures. It is noteworthy that, under the particular conditions employed, only 5-chloro-5-deoxy derivatives were obtained; the formation of dichlorodideoxy compounds was not observed.

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TABLE I

REACTION OF METHYL PENTOFURANOSIDES WITH SULFURYL CHLORIDE

Starting compound	*Chlorosulfation data*				*Methyl 5-chloro-5-deoxy-D-pentofuranosides*			
	Product	*Yield (%)*	*$[\alpha]_D$ (degrees)*[a]	*m.p. (degrees)*	*Compound*	*$[\alpha]_D$ (degrees)*	*m.p. (degrees)*	*b.p. (degrees)*[b]
Methyl α-D-ribofuranoside	methyl 5-chloro-5-deoxy-α-D-ribofuranoside 2,3-di(chlorosulfate)	59	+88	115–116	methyl 5-chloro-5-deoxy-α-D-ribofuranoside	−19		99–112/0.3 torr
	methyl α-D-ribofuranoside 2,3,5-tri(chlorosulfate)	6	+101	55–56				
Methyl β-D-ribofuranoside	methyl 5-chloro-5-deoxy-β-D-ribofuranoside 2,3-di(chlorosulfate)[c]	100	+36	78.5–79.5	methyl 5-chloro-5-deoxy-β-D-ribofuranoside	−65	69.5–70.5	
Methyl α-D-xylofuranoside	methyl 5-chloro-5-deoxy-α-D-xylofuranoside 2,3-di(chlorosulfate)	53	−15	73.5–74.5	methyl 5-chloro-5-deoxy-α-D-xylofuranoside	+24	73.5–74	
	methyl α-D-xylofuranoside 2,3,5-tri(chlorosulfate)	13	−51	113–114				
Methyl β-D-xylofuranoside[d]					methyl 5-chloro-5-deoxy-β-D-xylofuranoside	−102		115–118/0.3 torr

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[a] Optical rotations were measured with a Perkin–Elmer Model 141 polarimeter in chloroform ($c \sim 1$), except for that of methyl 5-chloro-5-deoxy-α-D-xylofuranoside, which was measured in methanol. [b] Microdistillations were performed with a Büchi heating block. [c] This product was isolated immediately after the reaction mixture had been kept for 2 h at −78°. [d] In this case, the mixture of chlorosulfation products was not resolved, but, on dechlorosulfation, methyl 5-chloro-5-deoxy-β-D-xylofuranoside was obtained in 27% yield (based on methyl β-D-xylofuranoside).

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