

USE OF FERRIC CHLORIDE IN CARBOHYDRATE CHEMISTRY. I. A QUICK METHOD FOR THE PREPARATION OF Q-ISOPROPYLIDENE DERIVATIVES OF CARBOHYDRATES

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Isopropylidene derivatives are formed by the reaction of acetone with sugars or their derivatives in the presence of an acid catalyst. Although a large number of methods using different catalysts are available for this purpose¹, the known methods are generally time consuming. In addition, no single catalyst is suitable for all sugars. We have found that anhydrous ferric chloride is an excellent catalyst for the acetonation of sugars. The method using acetone-anhydrous ferric chloride is simple and gives excellent yields. We have prepared Q-isopropylidene derivatives of various sugars and D-mannitol with excellent results (Table). On the basis of these results, we feel that the method is of general application to carbohydrate and non-carbohydrate substances having a pair of suitably placed hydroxyl groups.

Various concentrations of reagents were tried and the following method was found to be most suitable. Finely powdered sugar (1.0 g), preferably dried, is suspended in dry acetone (50 ml) and anhydrous ferric chloride (0.3 g) is added. The mixture is stirred at room temp. ($\sim 36^{\circ}\text{C}$) and the reaction is monitored by TLC using chloroform-methanol (9:1 v/v). In most of the cases tried, the reaction is complete after the carbohydrate substance has dissolved. The reaction is terminated by addition of 10 ml of a 10% solution of potassium carbonate. A dark brown layer settles down. Without separation of this layer, acetone is removed on a vacuum evaporator. The brown syrup is extracted with chloroform (20 ml x 3) and the chloroform extract is washed with water (5 ml x 2), dried (Na_2SO_4), filtered and the filtrate is evaporated. D-galactose gave a colourless oil whereas D-glucose, D-mannose, D-mannitol, D-xylose and L-arabinose gave crystalline derivatives. Derivatization can be accelerated by carrying out the reaction at the reflux temperature of the mixture with good yields. The results are given in the table. In all cases, the crude product showed one spot on TLC. The reaction could be scaled up with 50 g. of D-glucose in good yields.

References

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TABLE
O-Isopropylidene Derivatives of Carbohydrates

Carbohydrate	Temperature*	Time	Derivative obtained	Yield(% Theory)		M. P. °C		Observed Reported	Observed Reported
				Crude	Recrystallized	Observed	Reported		
D-xyl ⁺	r. t.	5 hr.	1,2:3,5-di-O-isopropylidene- α -D-xylofuranose	87	27 ^c	41-42 ^o	44-45 ^{o2}	+12.4 ^o (H ₂ O)	+13 ^o (H ₂ O) ²
D-xyl ⁺	reflux	10min. b	"	80	-	-	-	-	-
L-arabinose ⁺	r. t.	6 hr.	1,2:3,4-di-O-isopropylidene- α -L-arabinopyranose	96	73	43 ^o	41.5-3 ^{o3}	+5.8 ^o (H ₂ O)	+5.4 ^o (H ₂ O) ³
L-arabinose ⁺	reflux	30min. b	"	88	67	43 ^o	-	-	-
D-glucose ⁺	r. t.	6 hr. a	1,2:5,6-di-O-isopropylidene- α -D-glucopyranose	83	70	110-111 ^o	110-111 ^{o1}	-12.5 ^o (HCl ₃)	-13.5 ^o (CHCl ₃) ¹
D-glucose ⁺	reflux	5 hr.	"	92	76	110-111 ^o	-	-	-
D-galactose ⁺	r. t.	12 hr. a	1,2:3,4-di-O-isopropylidene- α -D-galactopyranose	76	Colourless oil	-	-	-54.5 ^o (CHCl ₃)	-55 ^o (CHCl ₃) ¹
D-galactose ⁺	reflux	1 hr.	"	83	Slightly yellow oil	-	-	-	-
D-mannose ⁺	r. t.	1 hr.	2,3:5,6-di-O-isopropylidene- α -D-mannofuranose	90	76	121-122 ^o	122-123 ^{o1}	+18.3 ^o (acetone)	+17 ^o (acetone) ¹
D-mannose ⁺	reflux	30min. b	"	97	70	121-122 ^o	-	-	-
D-mannitol ⁺	r. t.	6 hr.	1,2:3,4:5,6-tri-O-isopropylidene-D-mannitol	88	63	70 ^o	70 ^{o4}	+13.2 ^o (EtOH)	+12.5 ^o (EtOH) ⁴
D-glucose ^d	r. t.	8 hr.	1,2:5,6-di-O-isopropylidene- α -D-glucopyranose	82	70	110 ^o	110-111 ^{o1}	-12.8 ^o (CHCl ₃)	-13.5 ^o (CHCl ₃) ¹
D-glucose ^d	reflux	4 hr.	"	88	74	110 ^o	-	-	-

⁺ One gram of sugar was taken for reaction.

* r. t. is room temperature (~36°C).

a Small amounts (~50 mg) of sugar remains undissolved.

b Starting material dissolves in less than 10 min.

c Due to high ambient temperature and humidity the compound had the tendency to soften during filtration and washing.

d Reaction was carried out with 50 g.