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IODINE, A NOVEL CATALYST IN CARBOHYDRATE REACTIONS
I. O-ISOPROPYLIDINATION OF CARBOHYDRATES

K.P.R.KARTHA
Central Food Technological Research Institute (CFTRI)
Mysore-570 013 (India)

ABSTRACT. Iodine is found to serve as an excellent catalyst in the O-isopropylidination of sugars and sugar alcohols.

Iodine is known to interact with organic solvents such as acetone, carbon tetrachloride, etc. as well as molecules such as starch. However, its use as a reagent or catalyst has so far been limited to only certain classes of organic reactions[1]. It was felt that if in systems like iodine-acetone, iodine-acetic anhydride, etc. the interaction resulted in a favourable disposition of the electron density in the substrate it can be profitably employed in many carbohydrate reactions. It is now found that using iodine as catalyst O-isopropylidene derivatives of carbohydrates can be prepared in excellent yields with ease (Table). The present method is found to be superior to the conventional methods[2] with regard to reaction time, product yield and the conditions of handling the catalyst.

The following method was found to be optimal for most of the sugars. Iodine (300 mg) was dissolved in acetone (50 ml) and finely powdered sugar (1 g) was added and stirred at the ambient temperature (28°C). The reaction was monitored by TLC (irrigant, chloroform-methanol, 9.5:0.5, v/v), and was found to be complete when the sugar went into solution. Iodine was 'destroyed' by the addition of dilute aqueous sodium thiosulfate or hydroxide solution. The resulting solution would be colorless. The isopropylidene derivative was extracted with chloroform (20 ml x 3), chloroform extract was washed with water, dried (Na_2SO_4), and concentrated under vacuum. L-arabinose, D-xylose, D-glucose, D-mannose and D-mannitol gave colorless crystals, whereas D-galactose gave a colorless oil. By carrying out the reaction under reflux the reaction time could be considerably reduced, without, however, affecting the yield. The reaction was scaled up with 50 g D-glucose and the di-O-isopropylidene derivative was obtained in good yield.

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REFERENCES. 1. Pizey J.S., in "Synthetic Reagents", Vol.III, p. 227, Pizey J.S., ed., Ellis Horward Ltd., England (1977).

2. Singh P.P., et al.,Tetrahedron Letters No. 5, 439 (1977), and the references cited therein.

Table. Preparation of O-Isopropylidene Derivatives of Carbohydrates Using Iodine/acetone Reagent.

Starting* material	Derivative obtained	Reaction temperature	Reaction time	Yield** % theory	m.p., °C Observed	m.p., °C Reported[2]	$[\alpha]_D$ Observed	$[\alpha]_D$ Reported[2]
L-arabinose	1,2:3,4-di-O-isopropylidene-α-L-arabinopyranose	r.t.[+]	2 h.	85	42	43	+6.0 (H_2O)	+5.8 (H_2O)
		reflux	20 min.	85	42	43	--	--
D-xylose	1,2:3,5-di-O-isopropylidene-α-D-xylofuranose	r.t.	3 h.	75	44-46	41-42	+12.8 (H_2O)	+12.4 (H_2O)
		reflux	20 min.	75	44-46	--	--	--
D-galactose#	1,2:3,4-di-O-isopropylidene-α-D-galactopyranose	r.t.	16 h.	70	oil	--	-55.2 ($CHCl_3$)	-54.5 ($CHCl_3$)
		reflux	3 h.	70	oil	--	--	--
D-glucose #	1,2:5,6-di-O-isopropylidene-α-D-glucofuranose	r.t.	4 h.	80	109-110	110-111	-13.5 ($CHCl_3$)	-12.5 ($CHCl_3$)
		reflux	2 h.	80	--	--	--	--
		r.t.[++]	4.5 h.	75	109-110	110-111	--	--
D-mannose	2,3:5,6-di-O-isopropylidene-α-D-mannofuranose	r.t.	25 min.	85	121-122	121-122	+18.0 (acetone)	+18.3 (acetone)
		reflux	20 min.	85	121-122	121-122	--	--
D-mannitol	1,2:3,4:5,6-tri-O-isopropylidene-D-mannitol	reflux	30 min.	70	70	70	+13.5 (ethanol)	+13.2 (ethanol)

* 1 g. of the carbohydrate in 50 ml of the reagent.

** after recrystallization.

\# Traces of sugar remains undissolved.

\+ room temperature, 28°C.

++ reaction was carried out with 50 g. of D-glucose.

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