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Preliminary communication

Carbohydrate triflates: reaction with nitrite, leading directly to epi-hydroxy compounds

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Following the reaction of a chiral, secondary sulfonate with potassium nitrite, Lattrell and Lohaus[1] isolated the corresponding alcohol with inverted configuration. The compatibility of ester groups with the reaction conditions, demonstrated[2] with steroid and prostaglandin derivatives, prompted a study of the scope of this reaction in the carbohydrate field and we now report findings with some derivatives of D-glucose.

TABLE I

PRODUCTS OBTAINED FROM TRIFLATES[a] BY TREATMENT WITH NITRITE ION

Starting compound	*Reagent*[b]	*Conditions*[c]	*Time (h)*	*Products*[d]	*Yields (%)*
Methyl 2,3,6-tri-*O*-acetyl-α-D-glucopyranoside[4]	$NaNO_2$	$HCONMe_2$/20°	1	Methyl 2,3,6-tri-*O*-acetyl-α-D-galactopyranoside[e]	78.6
Methyl 2-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranoside[5]	$NaNO_2$	$HCONMe_2$/60°	18	Methyl 2-*O*-acetyl-[6] (**1**) and 3-*O*-acetyl-4,6-*O*-benzylidene-α-D-allopyranoside[6] (**2**)	12.6 (**1**) 54.4 (**2**)
Methyl 3-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranoside[5]	Bu_4NNO_2	MeCN/reflux	6	Methyl 2-*O*-acetyl-[7] (**3**) and 3-*O*-acetyl-4,6-*O*-benzylidene-α-D-mannopyranoside[7] (**4**)	19.4 (**3**) 54.1 (**4**)
1,2-*O*-Isopropylidene-α-D-glucofuranurono-6,3-lactone[8]	$NaNO_2$ Bu_4NNO_2	$HCONMe_2$/20° CH_2Cl_2/20°	0.5 3	1,2-*O*-Isopropylidene-β-L-idofuranurono-6,3-lactone[9]	62.5 72.5

[a] Prepared by reaction of the starting material (10 mmol) with triflic anhydride (12 mmol) in dichloromethane (100 mL)/pyridine (5 mL) for 20 min at 0°. Pyridine and excess of reagent were removed by extraction, and the dried solution was concentrated to a syrup, which was used immediately for the displacement reaction. [b] 10 mol ($NaNO_2$), 3 mol (Bu_4NNO_2). [c] 5% Solutions were employed. [d] Isolated from the reaction mixture, after removal of the solvent *in vacuo*, by chromatography[10] on silica gel with toluene–ethyl acetate. The structure of the products, if not otherwise indicated, was proved by comparison with authentic samples. [e] Syrup, $[\alpha]_D^{20}$ +146° (*c* 1, chloroform); the ^{13}C-n.m.r. spectrum of the *O*-deacetylated product was identical with that of methyl α-D-galactopyranoside[11]. The position of the acetyl groups was proved by treatment of the triflate with acetate, which gave methyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside[12].

Although displacement of 4-chlorobenzenesulfonates and toluene-*p*-sulfonates has been described, we selected the trifluoromethanesulfonates (triflates) because of their reactivity in nucleophilic substitution reactions[3]. Details of the compounds studied and the conditions and products of reaction with sodium and/or tetrabutylammonium nitrite are shown in Table I.

Satisfactory yields of products formed by nucleophilic substitution with inversion of configuration were obtained when the reactions were performed at 20°. When more vigorous conditions were applied (>60°) in order to obtain reasonable rates of reaction, a mixture of products was obtained as a result of participation by a neighbouring acetyl group. Thus, methyl 2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-triflyl-α-D-glucopyranoside and, to a minor extent, methyl 3-*O*-acetyl-4,6-*O*-benzylidene-2-*O*-triflyl-α-D-glucopyranoside gave mixtures of the corresponding 2- and 3-acetates, with inversion of configuration at positions 3 and 2, respectively.

Further studies of triflate displacement reactions are in progress

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