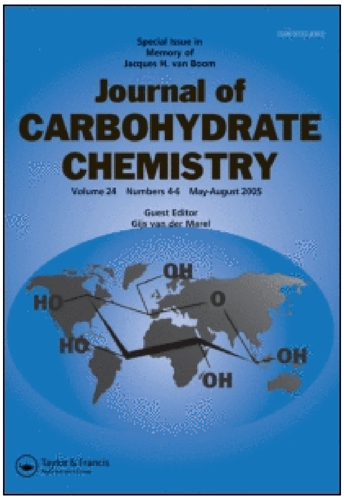

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Convenient Preparation of 2,3,4, 6-Tetra-O-methyl-α-D-glocopyranosyl Bromide

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Communication

CONVENIENT PREPARATION OF 2,3,4,6-TETRA-O-METHYL-α-D-GLUCOPYRANOSYL BROMIDE

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ABSTRACT

2,3,4,6-Tetra-O-methyl-α-D-glucopyranosyl bromide (3) is conveniently prepared by treatment of 2,3,4,6-tetra-O-methyl-D-glucose with HBr. This procedure is easier and produces higher yields than previously reported syntheses.

INTRODUCTION

As an exemplary glucopyranosyl halide with non-participating protecting groups, 2,3,4,6-tetra-O-methyl-α-D-glucopyranosyl bromide (3) has frequently been utilized as a substrate for nucleophilic substitution reactions [1-9] and a starting material for glycal preparation.[10] Originally 3 of questionable purity was prepared by reaction of 2,3,4,6-tetra-O-methyl-D-glucose (1) with phosphorus pentabromide.[4] In all subsequent syntheses, 2,3,4,6-tetra-O-methyl-D-glucose (1) was converted into 1-O-acetyl-2,3,4,6-tetra-O-methyl-D-glucopyranose (2) which was treated with HBr under various conditions to afford 3.[5-9]

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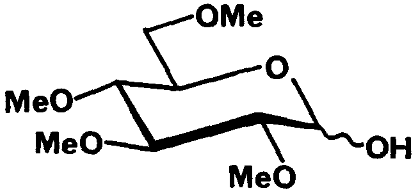
RESULTS AND DISCUSSION

We now report that 1 reacts directly with HBr to afford a good yield of 3. In our hands, this procedure is easier and produces higher yields than the previously reported syntheses of 3 which proceed via 2. Only the α-isomer was detected. In accord with previous reports, we observed that 3 decomposes quite rapidly, and therefore should be utilized directly after preparation.



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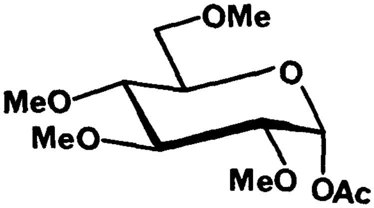

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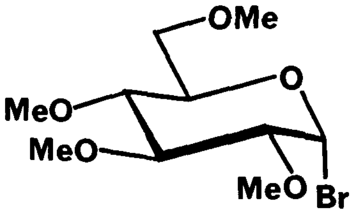

3

EXPERIMENTAL

2,3,4,6-Tetra-O-methyl-α-D-glucopyranosyl bromide (3). 1,2-Dichloroethane (8 mL) was saturated with HBr[11] in a flask fitted with a drying tube and then mixed with 2,3,4,6-tetra-O-methyl-D-glucopyranose[12] (1, 213 mg, 0.90 mmol). After 12 min at 20 °C, the reaction was quenched with cold water, rinsed with saturated $NaHCO_3$ and water, and dried over $CaCl_2$. Evaporation of the solvent afforded 3 as a syrup (217 mg, 81 % yield). Physical and spectral properties were in accord with literature.[5] ^1H NMR indicated only the α-isomer. A sealed sample stored at -15 °C for three weeks became dark and showed extensive decomposition.

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