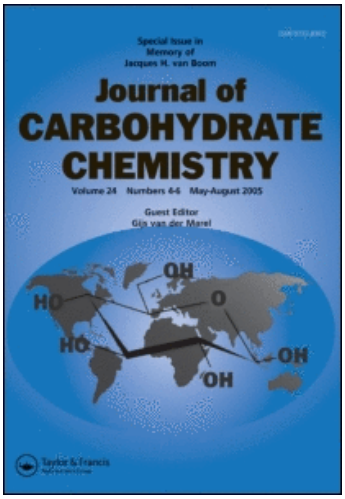

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AN EASY PREPARATION OF 2-DEOXY-2-PHTHALIMIDO-β-D-GLUCO- AND α-L-RHAMNOPYRANOSIDES

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ABSTRACT

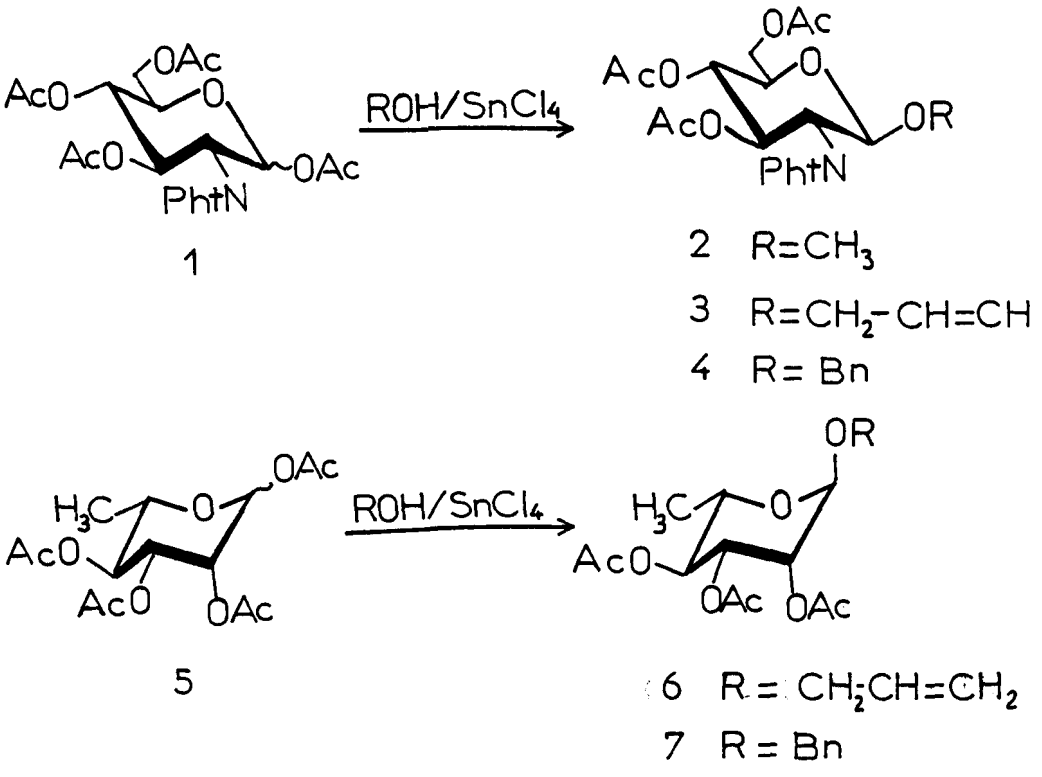
Benzyl and allyl glycosides are prepared directly from 1,3,4,6-tetra-O-acetyl-2-deoxy-2-phthalimido-α,β-D-glucopyranose and 1,2,3,4-tetra-O-acetyl-β-L-rhamnopyranose using stannic chloride as catalyst with solutions of the respective alcohols in methylene chloride.

INTRODUCTION

Stannic chloride as a promoter of glycosylation with acetylated sugars was first used by Lemieux and Shyluk[1] in 1953. Since that time, it has been frequently employed for the glycosylation of pyrimidines,[2] and nucleoside syntheses in general,[3] as well as for the synthesis of aryl,[4-8] alkyl[9,10] and other complex glycosides.[10] Sometimes tributylstannylation of the alcohol is required in order to enhance the nucleophilicity of the reactant.[10]

We have extensively studied this reaction and found that it is particularly suitable for 2-deoxy-2-phthalimido-β-D-glucopyranosides and α-L-rhamnopyranosides. The procedure is simple, and the yields are good to excellent.

SCHEME



EXPERIMENTAL

Melting points are uncorrected. Optical rotations were measured with a POLAMAT A automatic polarimeter (GDR) for 1% solutions in chloroform at 25 °C. NMR spectra were recorded with a JEOL JNM-FX90Q spectrometer in deuteriochloroform.

Methyl 3,4,6-Tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (2). A solution of 1,3,4,6-tetra-O-acetyl-2-deoxy-2-phthalimido-α,β-D-glucopyranose[7] (1, 200 mg, 0.42 mmol) and methanol (0.07 mL, 55.4 mg, 1.73 mmol) in dry dichloromethane (3 mL) was stirred under argon. Freshly distilled stannic chloride (0.2 mL, 440 mg, 1.69 mmol) was added dropwise. After 2 h, TLC (10:1 chloroform-acetone) showed the formation of a single compound with a slightly higher mobility. The solution was then added to a saturated solution of sodium hydrogen carbonate and

extracted with chloroform. The organic extract was washed with water, dried, and concentrated. Crystallization from methanol gave **2** (170 mg, 90%): mp 154-5 °C [lit.[12] mp 156-7 °C, lit.[13] mp 160 °C]; $[\alpha]_D$ +38° [lit.[12] $[\alpha]_D$ +46°, lit.[13] $[\alpha]_D$ +44°]; ^{13}C NMR: δ170.6, 170.1, 169.4, 167.6 (C=O); 134.3, 131.5, 123.6 (Ph); 99.1 (C-1), 71.9 (C-3), 70.9 (C-5), 69.2 (C-4), 62.1 (C-6), 56.9 (MeO), 54.6 (C-2), 20.7, 20.6, 20.4 (MeCO).

Allyl 3,4,6-Tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (3). As for the preparation of **2**, **1** (200 mg, 0.42 mmol) was stirred under argon in a solution of dichloromethane with allyl alcohol (0.11 mL, 97.6 mg, 4 equiv) and stannic chloride (0.2 mL, 440 mg, 4 equiv). After 5 h at room temperature, the reaction was treated as for **2**. Column chromatography of the crude product (10:1 chloroform:acetone) afforded pure **3** (160 mg, 80%): mp 107-9 °C (from methanol) [lit.[14] mp 108-9 °C]; $[\alpha]_D$ +43.5° [lit.[14] +36°]; ^{13}C NMR: δ170.4, 169.9, 169.3, 167.5 (C=O); 134.4, 131.5, 123.6 (Ph); 133.4, 117.6 (allyl); 97.2 (C-1), 71.9 (C-3), 70.8 (C-5), 69.2 (C-4), 62.1 (C-6), 54.7 (C-2); 20.6, 20.5, 20.3 (MeCO).

Benzyl 3,4,6-Tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (4). As for the preparation of **2** and **3**, a solution of **1** (200 mg, 0.42 mmol) in dichloromethane was stirred with benzyl alcohol (0.6 mL, 63 mg, 13 equiv) and stannic chloride (0.2 mL, 440 mg, 4 equiv) for 24 h at room temperature. After column chromatography of the crude product (2:1 toluene-ethyl acetate), pure **4** was obtained (117 mg, 53%): mp 102-4 °C (from ether) [Lit.[15] mp 106-7 °C]; $[\alpha]_D$ +5°, ^{13}C NMR: δ170.6, 170.0, 169.4, 167.5 (C=O); 134.2, 131.5, 123.5 (Ph); 97.3 (C-1), 71.9 (C-2), 70.8 (C-5), 69.2 (C-4), 62.1 (C-6), 54.8 (C-2), 71.3 (Bn); 20.7, 20.6, 20.4 (MeCO).

Allyl 2,3,4-tri-O-acetyl-α-L-rhamnopyranoside (6). A solution of 1,2,3,5-tetra-O-acetyl-α,β-L-rhamnopyranose[16] (5 g, 15 mmol) and allyl alcohol (1 mL, 854 mg, 14.7 mmol) in dry dichloromethane (20 mL) was cooled under argon. Freshly distilled stannic chloride (3 mL, 6.68 g,

25.6 mmol) was added dropwise, and the reaction was stirred at room temperature for 30 min. The mixture was diluted with chloroform, washed with ice-water, saturated sodium hydrogen carbonate, again with water, dried and concentrated to yield **6** (4.0g, 80%); $[\alpha]_D$ -73 °C; ^{1}H NMR: δ 5.80 (1H, m, CH=), 5.08 - 5.40 (2H, m, CH_2=), 4.78 (1H, d, H-1, J = 1.9 Hz), 2.16, 2.06, 2.00 (9H, 3s, MeCO), 1.53 (6H, d, Me, J = 6Hz). Anal. Calcd for $C_{15}H_{22}O_8$: C, 54.54; H, 6.71. Found: C, 54.54; H, 7.09.

Benzyl 2,3,4-tri-O-acetyl-α-L-rhamnopyranoside (7). Analogously to the preparation of **6** from acetate **5**, benzyl alcohol (1.5 mL, 1.58 g, 16.8 mmol) was used to prepare **6** (3.3g, 57%); mp 110 °C [Lit.[17] mp 110 °C]; $[\alpha]_D$ -60°; [Lit.[17] $[\alpha]_D$ -73°].

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16. Compound 5 was prepared from L-rhamnose and acetic anhydride in the presence of perchloric acid. [See method of M. L. Wolfrom and A. Thompson, Methods Carbohydr. Chem., 2, 211 - 215 (1963).] Continuous extraction with chloroform promotes excellent recovery of the acetate from water.

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