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Note

A facile allyl β-glycosylation in the presence of a benzyl protecting group, using boron trifluoride etherate

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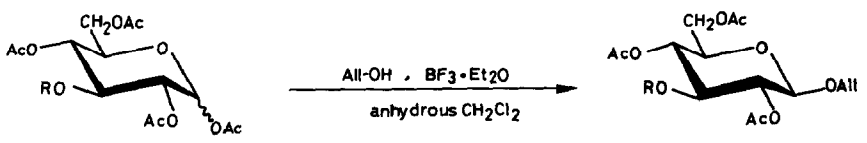
The allyl group is very useful as a temporary protective group at the anomeric position of sugars, because it is stable under a variety of conditions, and may be selectively removed readily by mild two-step reactions or by oxidative cleavage with selenium (IV) dioxide[1,2]. We reported that an *O*-benzyl substituent at the 3-position of the glycosyl acceptor is indispensable for obtaining a β-(1→4)-linked glycoside in high yield[3]. An allyl 3-*O*-benzyl-β-D-glucopyranoside derivative, such as compound **3**, is a very important intermediate in our cellulose analog synthesis.

The most important synthetic method for allyl β-D-glucopyranosides is the Koenigs–Knorr procedure whereby an acylglucosyl halide reacts with allyl alcohol in the presence of a suitable catalyst, such as silver carbonate[4] or mercuric cyanide[5]. However, this method requires the additional halogenation step before glycosylation. Furthermore, the 3-*O*-benzyl group was found to be partly removed under the halogenation reaction conditions.

This note describes a facile allyl β-glycosylation by a modified Magnusson method[6], which permits compound **3** to be prepared in high yield.

1,2,4,6-Tetra-*O*-acetyl-3-*O*-benzyl-α, β-D-glucopyranose[7] (**1**) (α/β = ~1:4) was treated with allyl alcohol–boron trifluoride etherate to afford allyl 2,4,6-tri-*O*-acetyl-3-*O*-benzyl-β-D-glucopyranoside (**3**) in 77.4% yield. The 3-*O*-benzyl group was stable under these conditions. In this modification of the original method, allyl alcohol and boron trifluoride etherate were used in excess (5.0 and 10.0 equiv., respectively) in order to make the reaction proceed to completion. Allyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (**4**) was also obtained from β-D-glucopyranose pentaacetate (**2**), (α:β = ~1:4) in 60.5% yield.



1 R = Bn
2 R = Ac

3 R = Bn
4 R = Ac

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This procedure is therefore a simple and highly stereoselective allyl β-glycosylation method in the presence of a benzyl protecting group.

EXPERIMENTAL

General methods. — Melting points are uncorrected. Optical rotations were determined with a Jasco DIP-181 polarimeter. ^{1}H-N.m.r. spectra were taken with a Varian XL-200 FT-NMR (200 MHz) spectrophotometer with Me_4Si as the internal standard in $CDCl_3$. Chemical shifts and coupling constants are given in δ-values and Hz, respectively. Anhydrous CH_2Cl_2 was distilled from P_2O_5.

*Allyl 2,4,6-tri-*O*-acetyl-3-*O*-benzyl-β-*D*-glucopyranoside* (**3**). — Compound **1** (1000 mg, 2.28 mmol) was dried over P_2O_5 in a vacuum desiccator. To a solution of compound **1** in anhydrous CH_2Cl_2 (10 mL) and allyl alcohol (0.78 mL, 11.4 mmol), $BF_3{\cdot}Et_2O$ (2.8 mL, 22.8 mmol) was added dropwise at 0°. The solution was kept for 4 h at 0°, and then diluted with EtOAc, washed with saturated aq. $NaHCO_3$ and with brine, and then dried over Na_2SO_4. The solvent was evaporated *in vacuo* to give a yellow oil. The product **3** crystallized from EtOH–*n*-hexane; yield 770 mg (77.4%); m.p. 76–77°, $[\alpha]_D^{20}$ – 25.4° (*c* 3.49, EtOH); ^{1}H-n.m.r.: 1.99 (s, 3 H, CH_3CO), 2.03 (s, 3 H, CH_3CO), 2.10 (s, 3 H, CH_3CO), 3.58 (ddd, 1 H, *J* 9.5, 5.0 and 2,5, H-5), 3.70 (t, 1 H, *J* 9.5, H-3), 4.07 (ddd, 1 H, *J* 13.5, 6.0 and 1.5, $-CH_2-C-C$), 4.11 (dd, 1 H, *J* 12.0 and 2.5, H-6_a), 4.22 (dd, 1 H, *J* 12.0 and 5.0, H-6_b), 4.33 (ddd, 1 H, *J* 13.5, 5.0 and 1.5, –CH_2–C–C), 4.46 (d, 1 H, *J* 8.0, H-1), 4.57 (d, 1 H, *J* 12.0, benzyl), 4.63 (d, 1 H, *J* 12.0, benzyl), 5.09 (dd, 1 H, *J* 9.5 and 8.0, H-2), 5.13 (t, 1 H, *J* 9.5, H-4), 5.18 (dd, 1 H, *J* 10.0 and 1.5, –C–C–CH*cis*), 5.26 (dd, 1 H, *J* 17.5 and 1.5, –C–C–CH*trans*), 5.84 (dddd, 1 H, *J* 17.5, 10.0, 6.0 and 5.0, –C–CH–C), and 7.20–7.40 (m, 5 H, phenyl).

Anal. Calc. for $C_{22}H_{28}O_9$: C, 60.55; H, 6.42. Found: C, 60.25; H, 6.42.

*Allyl 2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranoside* (**4**). — A solution of compound **2** (117 mg, 0.3 mmol) and allyl alcohol (0.1 mL, 1.5 mmol) in anhydrous CH_2Cl_2 (1.5 mL) was treated with $BF_3{\cdot}Et_2O$ (0.37 mL, 3 mmol) for 5 h at 0°. The solution was processed in the same way as for **3** to give a colorless oil. The product (**4**) crystallized from EtOH–*n*-hexane to yield 70 mg, (60.5%); m.p. 86–87° (Lee and Lee[5] reported 86°).

Anal. Calc. for $C_{17}H_{24}O_{10}$: C, 52.58; H, 6.19. Found: C, 52.33; H, 6.21.

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