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Note

An abnormal deallylation reaction of an L-fucopyranoside

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Abstract

Deallylation of allyl 2,3,4-tri-*O*-benzyl-L-fucopyranoside in the presence of palladium chloride and cuprous chloride led to an unexpected result. Instead of the expected deallylated product, (2-oxopropyl)-2,3,4-tri-*O*-benzyl-L-fucopyranoside was obtained. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Allyl fucoside; Deallylation; Wacker–Hoechst reaction

The allyl group is a useful protective group for the synthesis of oligosaccharides because it can be readily introduced and removed. There are various methods for deallylation under different conditions [1–7]. In an attempt to prepare 2,3,4-tri-*O*-benzyl-L-fucopyranose (**4**), the allyl group was chosen to protect the hydroxyl group at the anomeric position of L-fucose, based on the consideration that the allyl group could be removed under very mild conditions as described by Mereyala et al. [7], whereas the common procedure for preparation of compound **4** via the methyl glycoside needs relatively more drastic conditions to remove the methyl group [8].

Allylation of L-fucose with acidified allyl alcohol under reflux for 1 h gave a mixture of the allyl α- and β-fucosides (**2α**, **2β**) in ~4:1 α/β ratio, detected by TLC, which was directly O-benzylated with benzyl bromide and sodium hydride to give compound **3** (also an α,β mixture). To compound **3** in 10:1 (v/v) tetrahydrofuran–water, were added the equivalent amount of palladium chloride and cuprous chloride to effect the modified Mereyala deallylation process [7]. The reaction mixture was exposed to air and stirred vigorously instead of oxygen bubbling according to Mereyala. This modification had proved effective in our previous work [9,10].

An unexpected compound **5** was obtained in 46% overall yield and some material decomposed (the α, β anomers, **5α** and **5β**, could be isolated by column chromatography with 8:1 cyclohexane–EtOAc as eluent, α:β ~ 2:1). No deallylated compound **4** was detected in these experiments even when the reaction time was extended.

The mechanism of the reaction seems to involve the addition of a water molecule to the carbon–carbon double bond, followed by oxidation by palladium chloride, a mechanism similar to the Wacker–Hoechst reaction [11].

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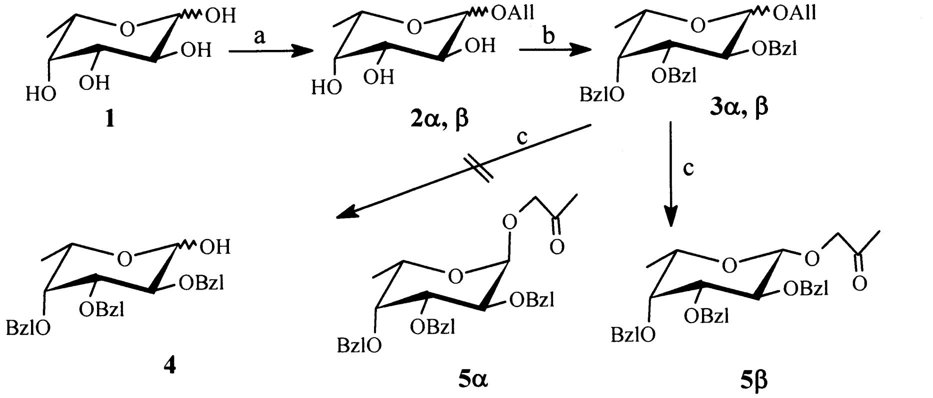

a. allyl alcohol/H^+, reflux, 1h. **b.** $PhCH_2Br$/NaH, DMF, rt. **c.** $PdCl_2$-CuCl/THF-H_2O.

Physical and spectroscopic data are recorded for compounds **5α** and **5β**. The α and β anomers could be discriminated by the chemical shifts and $^3J_{C-H}$ of C-1.

*2-Oxopropyl 2,3,4-tri-*O*-benzyl-α-*L*-fucopyranoside* (**5α**).—Colorless syrup, $[\alpha]_D - 7.8°$ (*c* 0.51, $CHCl_3$); IR: 3058, 3026, 2948, 1719, 1449, 1168 cm^{-1}; FABMS: *m*/*z* 497 $[M+Li]^+$, 513 $[M+Na]^+$; ^1H NMR (500 MHz, $CDCl_3$): δH (ppm) 1.10 (d, 3 H, *J* 6.4 Hz, H-6), 2.11 (s, 3 H, $COCH_3$), 3.66–5.00 (m, 13 H, H-1,2,3,4,5, $3 \times PhCH_2$–, CH_2COCH_3), 7.21–7.42 (m, 15 H, aromatic H); ^{13}C NMR (500 MHz, $CDCl_3$): δ_C (ppm) 16.72 (C-6), 26.53 (CH_3CO), 67.05, 72.10, 73.24, 73.42, 75.00, 76.21, 77.84, 79.09 (C-2,3,4,5, $3 \times PhCH_2$, CH_2COCH_3), 97.83 (C-1, $^3J_{C-H}$ 169.0 Hz), 127.60–139.02 (aromatic C), 205.81 (CH_3CO). Anal. Calcd for $C_{30}H_{34}O_6$: C,73.45; H, 6.99. Found: C, 73.78; H, 6.91.

*2-Oxopropyl 2,3,4-tri-*O*-benzyl-β-*L*-fucopyranoside* (**5β**).—Colorless syrup, $[\alpha]_D - 81.7°$(*c* 1.42, $CHCl_3$); IR: 3050, 3027, 2918, 1717, 1449, 1172 cm^{-1}; FABMS: *m*/*z*: 497 $(M+Li)^+$, 513 $(M+Na)^+$.^1H NMR (500 MHz, $CDCl_3$), δ_H (ppm) 1.15 (d, 3 H, *J* 6.40 Hz, H-6), 2.21 (s, 3 H, $COCH_3$), 3.34–5.00 (m, 13H, H-1,2,3,4,5, $3 \times PhCH_2$, CH_2COCH_3), 7.26–7.39 (m, 15 H, aromatic H); ^{13}C NMR (500 MHz, $CDCl_3$): δ_C (ppm) 16.87 (C-6), 27.07 (CH_3CO), 70.71, 73.28, 74.31, 74.75, 75.30, 76.20, 79.27, 82.52 (C-2,3,4,5, $3 \times PhCH_2$, CH_2COCH_3), 103.51 (C-1, $^3J_{C-H}$ 158.9 Hz), 127.69–138.77 (aromatic C), 207.31 (CH_3CO). Anal. Calcd for $C_{30}H_{34}O_6$: C, 73.45; H, 6.99. Found: C, 73.51; H, 6.77.

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