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Unusually Easy Carbalumination of 1-*C*-Vinyl-substituted Benzylated D-Glucopyranoses

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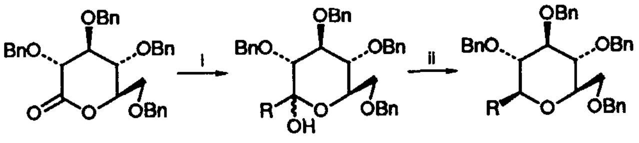
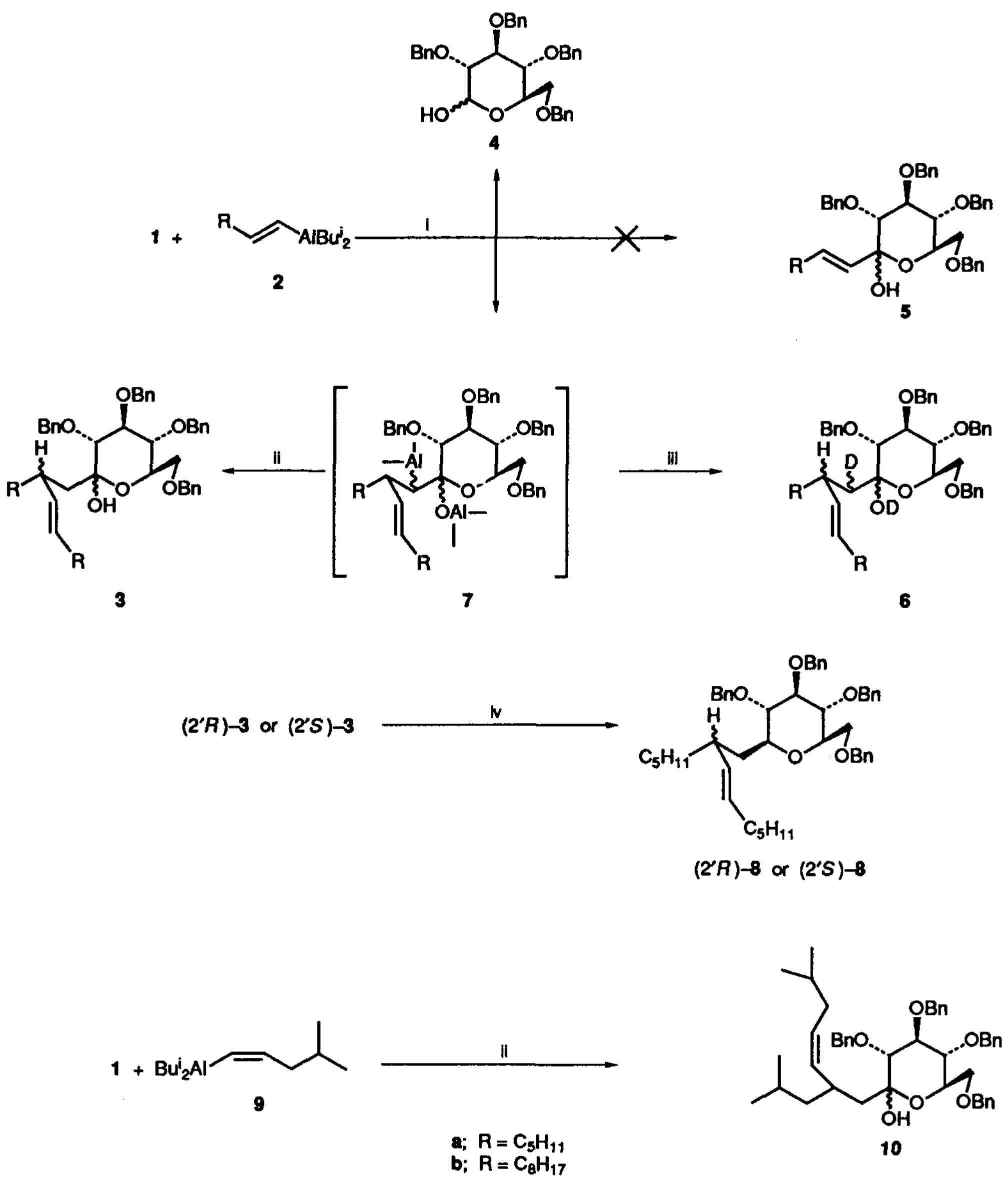
1-*C*-Vinyl-substituted benzylated D-glucopyranoses react with vinylaluminiums in carbalumination under unusually mild conditions.

In continuation of our study of the reactivity of organoaluminium compounds compared with that of Li- and Mg-organic reagents,[1,2] we turned to the reaction of vinylaluminium compounds with 2, 3, 4, 6-tetra-*O*-benzyl-D-glucopyranolactone **1**. According to refs. 3–5, the interaction of lactone **1** with organolithium compounds and Grignard reagents forms lactols, the reduction ($Et_3SiH–BF_3{\cdot}OEt_2$) of which leads to β-*C*-glucosides (Scheme 1).



Scheme 1 *Reagents and conditions*: i, RLi, tetrahydrofuran (THF), −78 °C, ii, $Et_3SiH–BF_3{\cdot}OEt_2$, CH_2Cl_2, −78 °C

In our case, the reaction of lactone **1** with vinylaluminium compounds **2a,b** after hydrolysis of the reaction mixture led to unexpected products. Hemiketals **3a,b**, containing a hydrocarbon substituent of dimer structure at the anomeric position, were obtained in yields of 59–61%. Along with compounds **3a,b**, benzylated pyranose **4** is also formed. The expected hemiketals **5a,b** were not observed, even in the form of admixtures. Deuteriolysis of the reaction mixture led to lactols **6a,b**, deuteriated in the side chain (C^1-D), providing evidence for the formation of novel organoaluminium compounds **7a,b** (Scheme 2) in the course of the reaction.



Scheme 2 *Reagents and conditions*: i, **2a,b** (2.5 equiv.), hexane–toluene, 20°C, 1 h; ii, H_2O, HCl 0.1 mol dm^{-3}; iii, D_2O; iv, $Et_2MeSiH–BF_3{\cdot}OEt_2$, CH_2Cl_2, −78°C

Lactols **3a,b** represented a mixture of two diastereoisomers in a ratio of 70:30, differing in the configuration of the substituents at carbon atom $C_2{}^1$ in the hydrocarbon aglycone.† The diastereoisomers were separated by column chromatography on SiO_2. β-*C*-Glycosides (2′*R*)-**8** and (2′*S*)-**8**‡ were isolated by reduction of each of the diastereoisomeric lactols (2′*R*)-**3a** and (2′*S*)-**3a** with $Et_2MeSiH–BF_3{\cdot}OEt_2$ under the conditions of ref. 2. The geometry of the double bond in the reaction products was observed to be retained during interaction with either *E*- or *Z*-isomers of vinylaluminium compounds. When *E*-**2a,b** were added to the reaction mixture, *E*-isomers of lactols **3a,b** were isolated. The interaction of lactone **1** with *Z*-diisobutylisohexenylaluminium **9** formed lactols **10** with a *Z*-geometry of the double bond. We surmised that one possible way to form organoaluminium compounds **7a,b** and, hence, hemiketals **3a,b** was *via* two successive transformations as follows. Reaction of gluconolactone **1** with the organometallic reagent, leading to alcoholates of vinyl-substituted lactols **5a,b**, and regioselective carbalumination of the double bonds of the alcoholates under the influence of the vinylaluminium compound. In order to verify this supposition, hemiketal **5a** was formed by reaction of gluconolactone **1** with *E*-heptenyllithium **11** (Scheme 3). Its exposure to the reaction conditions led to the formation of a diastereoisomeric mixture of compounds (2′*R*)-**3a** and (2′*S*)-**3a** in a 2:1 ratio in a yield of 33%, confirming our assumption. We tried to isolate intermediates **5a**, stopping the reactions of compounds **1** and **2a** at room temperature after 10 min and at −10°C after 15 min. A practically complete transformation of the lactones into hemiketals **3a** was observed. Compounds **5a** were absent in the reaction mixture. The rates of the reaction of

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† The configuration of the substituents at the anomeric centre in the lactols and the anomeric composition of the mixtures were not observed.

‡ *NMR spectral data* for compounds (2′*R*)-**8** and (2′*S*)-**8** [^{1}H NMR: 300 MHz, $CDCl_3$, Me_4Si; ^{13}C NMR: 75.5 MHz, $CDCl_3$]. First diastereoisomer: ^{1}H NMR δ = 0.90 (m, SH,Me), 1.20 (m, 14H, CH_2), 1.35 (m, $H_1{}^1$), 1.55 (dd, *J* 14.7, 11.7 Hz, $H_1{}^1$) 1.87 (m, 2H, $CH_2C{=}C$), 2.22 (m, 1H, CHC=C), 4.95 (dd, *J* 15.5, 8.0 Hz, $H_1{}^3$), 5.78 (dt, *J* 15.5, 6.6 Hz, $H_1{}^4$), pyranose cycle protons, 3.20 (m, H_1), 3.20, 3.60 (m, 6H, H_2–H_6), 4.50, 4.75 (m, 8H, OCH_2), 7.21 (m, 20H, Ph); ^{13}C NMR carbon atoms in aglycone, δ − 14.02, 14.12, 22.25, 22.69, 29.58, 31.64, 32.01, 32.33, 35.94, 37.53, 38.85, 131.42, 133.71; carbon atoms of pyranose cycle, δ − 69.27, 73.43, 74.93, 75.25, 75.58, 77.19, 78.96, 83.04, 87.56, 127.54–138.85. Second diastereoisomer: ^{1}H NMR δ − 0.88 (m, 6H, Me), 1.30 (m, 14H, CH_2), 1.45 (m, $H_1{}^1$), 1.79 (dd, *J* 14.5, 10.0 Hz, $H_1{}^3$), 2.0 (m, 2H, $2CH_2C{=}C$), 2.27 (m, 1H, CHC=C), 5.21 (dd, *J* 15.5, 8.0 Hz, $H_3{}^1$), 5.35 (dt, *J* 15.5, 6.6 Hz, $H_1{}^4$) pyranose cycle protons, 3.30 (m, H_1), 3.30, 3.70 (m, 6H, H_2–H_6), 4.50–4.90 (m, 8H, OCH_2) 7.30 (m, 20H, Ph); ^{13}C NMR carbon atoms in aglycone, δ − 37.90, 38.97, 129.67, 135.03, carbon atoms of pyranose cycle, δ − 69.22, 73.50, 74.90, 75.28, 75.57, 77.47, 78.81, 79.03, 83.08, 87.59, 127.54–138.85.

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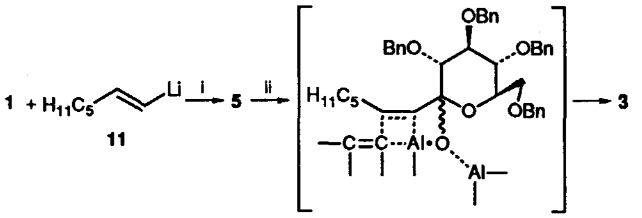

Scheme 3 *Reagents and conditions*: i, Et_2O, $-78\,°C$; ii, **2a** (2 equiv.), conditions similar to Scheme 2; iii, H_2O, HCl 0.1 mol dm^{-3}

gluconolactone **1** with the vinylaluminium and those of carbalumination proved to be comparable. As a rule,[6] organoaluminium compounds add to double bonds in alkenes under very harsh conditions (pressure, 100–200 °C). The extremely mild conditions of carbaluminium by vinylaluminium compounds of substituted pyranoses **5a,b** are apparently caused by a mutual reagent activity due to coordination of the aluminium atom by an oxygen atom of the hemiketal hydroxyl. The coordination of vinylaluminium with other oxygen-containing functions of the substrate next to the reaction centre may be expected.

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