C-GLYCOSIDES FROM HEXA-O-ACETYL-D-LACTAL

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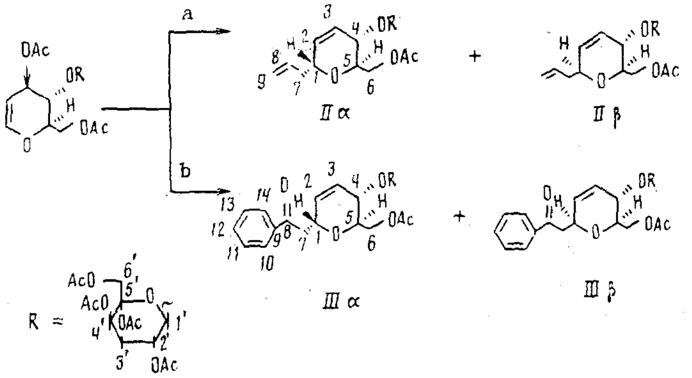
The reaction of allyltrimethylsilane and 1-trimethylsiloxystyrene catalyzed by Lewis acids has been described only for monosaccharides glycals [1, 2].

In a continuation of a study of the transformations of glycals from oligosaccharides [3, 4], we are the first to report that the reaction of hexa-O-acetyl-D-lactal (I) with a 1.5-molar excess of allyltrimethylsilane or 1-trimethylsiloxystyrene catalyzed by $BF_3 \cdot OEt_2$ leads to the corresponding C_1-glycosides (II) (88%) and (III) (80%) in a mixture of α/β-anomers. High-efficiency liquid chromatography gave the C_1-glycoside ratios: (IIα):(IIβ) = 20:1 and (IIIα):(IIIβ) = 5:1.



In pathway a, allyltrimethylsilane was used with $BF_3 \cdot OEt_2$ in CH_2Cl_2 upon warming from -50 to 0°C over 0.5 h. In pathway b, 1-trimethylsiloxystyrene was used with $BF_3 \cdot OEt_2$ in CH_2Cl_2 upon warming from -30 to 0°C over 1 h. The physical constants of the three pure isomers are given below.

(IIα): $[\alpha]_D^{20}$ +20.96° (c 2.29 $CHCl_3$). ^{13}C NMR spectrum (δ, ppm): 20.51, 20.71 q (5$\underline{C}H_3CO$), 37.44 t (C^7), 61.33 t ($C^{6'}$), 63.35 t (C^6), 67.0 d ($C^{4'}$), 68.86 d ($C^{2'}$), 69.2 d (C^5), 70.83 d ($C^{3'}$), 70.87 d ($C^{5'}$), 72.27 d, 73.02 d (C^1, C^4), 101.99 d ($C^{1'}$), 117.44 t (C^9), 126.66 d, 131.36 d (C^2, C^3), 134.14 d (C^8), 169.36, 169.91, 170.10, 170.22, 170.65 s (5$CH_3\underline{C}O$).

(IIIα): $[\alpha]_D^{20}$ +9.24°C (c 2.26 $CHCl_3$). ^{13}C NMR spectrum (δ, ppm): 20.50, 20.57, 20.95 q (5$\underline{C}H_3CO$), 41.44 t (C^7), 61.62 t ($C^{6'}$), 63.19 t (C^6), 66.96 d ($C^{4'}$), 68.86 d ($C^{2'}$), 69.8 d (C^1), 69.39 d (C^5), 70.83 d ($C^{3'}$, $C^{5'}$), 72.91 d (C^4), 102.14 d ($C^{1'}$), 127.03 d, 131.19 d (C^2, C^3), 128.14 d (C^{10}, C^{14}), 128.68 d (C^{11}, C^{13}), 133.34 d (C^{12}), 136.99 s (C^9), 169.35, 169.49, 169.96, 170.30, 170.68 s (5$CH_3\underline{C}O$), 197.15 s (C^8).

(IIIβ): $[\alpha]_D^{20}$ +64.6° (c 0.46 $CHCl_3$). ^{13}C NMR spectrum (δ, ppm): 20.69, 20.89 q (5$\underline{C}H_3CO$), 44.0 t (C^7), 61.43 t ($C^{6'}$), 63.58 t (C^6), 67.06 d ($C^{4'}$), 69.01 ($C^{2'}$), 70.92 d ($C^{5'}$), 71.01 d ($C^{3'}$), 71.76 d (C^5), 73.64 d (C^1), 75.20 d (C^4), 102.38 d ($C^{1'}$), 127.72, 131.71 d (C^2, C^3), 128.28 d (C^{10}, C^{14}), 128.66 d (C^{11}, C^{13}), 133.34 d (C^{12}), 137.14 s (C^9), 169.46, 170.11, 170.27, 170.39, 170.83 s (5$CH_3\underline{C}O$), 197.28 s (C^8).

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