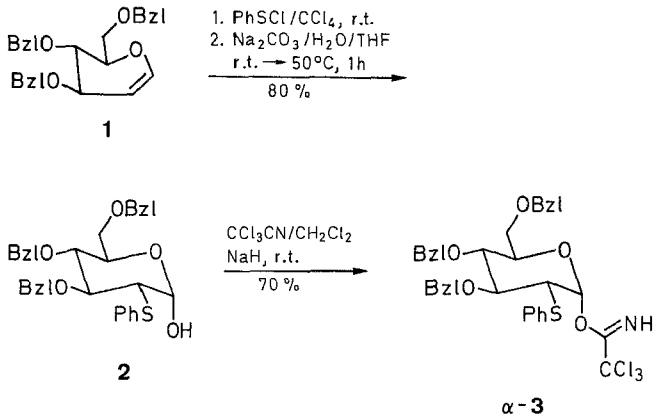
A Convenient Synthesis of 2-Deoxy-β-D-glucopyranosides[1]

Rainer Preuss, Richard R. Schmidt*

Fakultät Chemie, Universität Konstanz, D-7750 Konstanz, Federal Republic of Germany

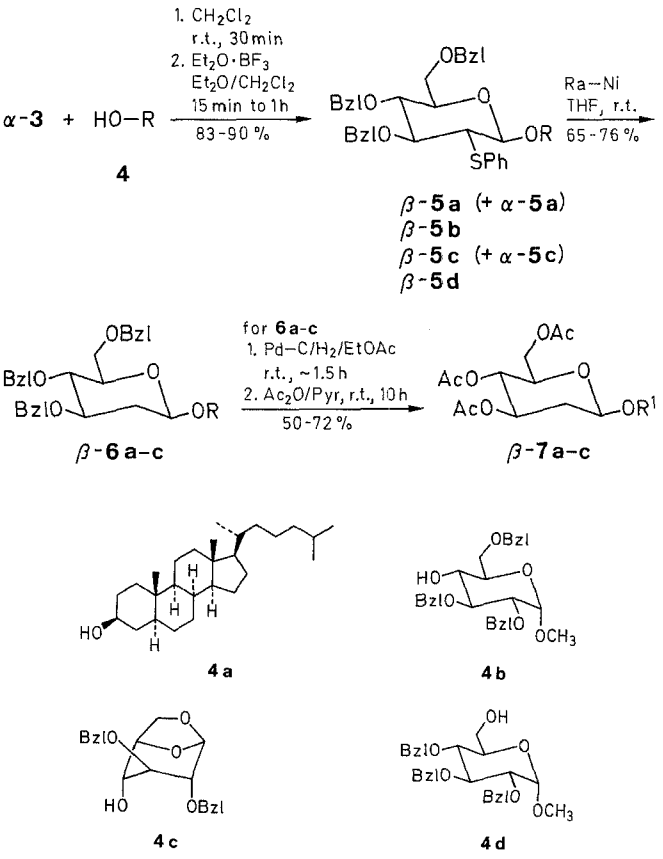
The *O*-(2-deoxy-2-phenylthio-α-D-glucopyranosyl) trichloroacetimidate α-**3** was obtained from 3,4,6-tri-*O*-benzyl-D-glucal (**1**) in a two-step procedure. This compound is a powerful glucopyranosyl donor, which with typical alcohol acceptors provided mainly the corresponding 2-phenylthio-substituted 2-deoxy-β-D-glucopyranosides β-**5a** to β-**5d**. These were converted by Raney nickel treatment to the desired 2-deoxy-β-D-glucopyranosides **6** in high yields.

The presence of the 2-deoxy-β-D-glucopyranoside moiety in natural products has led to different approaches for the selective synthesis of this glycosidic bond.[2-9] The recently introduced 2-phenylthio group as a neighboring group,[8,9] generating an episulfonium ion intermediate during glycoside bond formation, seems to be advantageous, because it is also readily removable by hydrogenation leaving behind the desired 2-deoxy sugar. In the method introduced by Nicolaou et al.[8] the required 2-deoxy-2-phenylthioglucopyranosyl fluoride was obtained from the corresponding mannopyranosyl-phenylsulfide via 1,2-migration with diethylaminosulfur trifluoride (DAST). Ogawa and coworkers added directly benzenesulfonate esters to D-glucal derivatives.[9] However, this reaction went only with moderate diastereoselectivity at the anomeric position. For the successful application of the trichloroacetimidate method[10] to this problem (i) a convenient synthesis of a 2-deoxy-2-phenylthio-D-glucose derivative, (ii) subsequently a stable α-trichloroacetimidate, and finally (iii) high diastereoselection in the glycosyl transfer was required. This could be accomplished starting from D-glucal as will be reported here.



1 **2** α-**3**

The readily available tri-*O*-benzyl-D-glucal **1** afforded with phenylsulfenyl chloride and subsequent hydrolysis with sodium carbonate in a one-pot reaction the required 3,4,6-tri-*O*-benzyl-2-deoxy-2-phenylthio-D-glucose **2**;[11] it was obtained as the α-anomer. Treatment with trichloroacetonitrile in the presence of sodium hydride as the base gave the *O*-(α-glucosyl)trichloroacetimidate α-**3** (containing only trace amounts of the β-anomer, < 5%) as a stable compound, which could be isolated.



4 β-**5a** (+ α-**5a**) β-**5b** β-**5c** (+ α-**5c**) β-**5d**

β-**6a-c** β-**7a-c**

4a **4b** **4c** **4d**

This compound is an extremely powerful glycosyl donor toward alcohol acceptors **4** on addition of catalytic amounts of ether–boron trifluoride complex. With cholestanol as acceptor in dichloromethane as solvent the β-glucoside β-**5a** was obtained in high yield and diastereoselectivity (β-**5a**/α-**5a**, 8:1; see Table 1). The β-isomer β-**5a** was separated and treated with Raney-Nickel[8] to provide the 2-deoxy-β-D-glucoside β-**6a** (Table 2); subsequent hydrogenolytic debenzylation and per-*O*-acetylation gave compound β-**7a** for which unequivocal structural proof was obtained through the ^{1}H-NMR data. The 4-*O*-unprotected methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside as an acceptor afforded with the donor α-**3** exclusively the β-anomer β-**5b** whose structure was again assigned through compound β-**7b** made available via compound β-**6b** as outlined above. The extraordinary high reactivity of the glycosyl donor α-**3**, was demonstrated in the reactions with 1,6-anhydro-2,3-*O*-benzyl-D-glucopyranose as an acceptor. When the reaction was carried out at temperature from 0 °C to − 80 °C it was completed within five to ten minutes with isolated product β/α-**5c** yields of always over 85 %. Only at a reaction temperature of − 95 °C the rate was noticeably decreased and it took about fifteen minutes to complete the reaction. Presumably due to the high rate in this case the anomer ratio was lower. It varied from β:α, 1.2:1 (0 °C) to 3:1 (− 95 °C). Clean separation of the anomers β/α-**5c** was possible after desulfurization to compounds β/α-**6c** and subsequent debenzylation and acetylation giving the isomers β-**7c** and α-**7c**, respectively, whose structures were verified through the ^{1}H-NMR data. As expected, the 6-*O*-unprotected methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside was a good acceptor for the donor α-**3** furnishing the disaccharide β-**5d** practically exclusively. The structure of compound β-**5d** was assigned through the data given previously.[9]

3,4,6-Tri-*O*-benzyl-2-deoxy-2-phenylthio-α-D-glucopyranose (2):
A solution of 3,4,6-tri-*O*-benzyl-D-glucal **(1)** (10 g, 24 mmol) and benzenesulfenyl chloride (6 g, 41 mmol) in dry CCl_4 (100 mL) is stirred at room temperature until **1** has totally disappeared (careful TLC monitoring with petroleum ether/EtOAc, 9:1 is required; **1**: $R_f = 0.34$). Then CCl_4 is evaporated and the residual orange oil is treated with THF/water (1:1, 200 mL) and 5 g solid Na_2CO_3. This mixture is stirred at room temperature for 0.5 h and finally warmed to 50 °C for 1 h to complete the formation of compound **2** (monitored by TLC with petroleum ether/EtOAc, 4:1; **2**: $R_f = 0.31$). The mixture is cooled to room temperature, water (100 mL) added, and then extracted with Et_2O (3 × 100 mL). The ether extract is concentrated, and the residue is purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc, 4:1) and for analytical purposes also by medium-pressure-chromatography (MPLC) on silica gel (eluent: petroleum ether/EtOAc, 3:1). After evaporation of the solvent the product crystallized; yield: 10.4 g (80%); mp 85.5–86 °C.

$C_{33}H_{34}O_5S$ (542.7) calc. C 73.03 H 6.31 found 72.68 6.20

^{1}H-NMR (250 MHz, $CDCl_3$/TMS): δ (*J* in Hz) = 3.15 (d, 1 H, *J* = 1.85, OH-1); 3.36 (dd, 1 H, *J* = 3.17, 10.99, H-2); 3.58 (dd, 1 H, *J* = 9.03, 9.04, H-4); 3.65–3.66 (m, 2 H, H-6a, H-6b); 4.03 (dd, 1 H, *J* = 9.03, 10.99, H-3); 4.12–4.16 (m, 1 H, H-5); 4.46–4.58 (m, 3 H, $C_6H_5C\underline{H}_2$); 4.80–4.85

Table 1. 3,4,6-Tri-*O*-benzyl-2-deoxy-2-phenylthio-D-glucopyranosides **5a–d** Prepared

Product	Reaction Temp. (°C)	Yield[a] (%)	Ratio β:α	mp[b] (°C)	R_f[c] (PE/EA)	Molecular Formula[d] Lit. mp (°C)	^{1}H-NMR ($CDCl_3$/TMS) δ, *J*(Hz)[e]
β-5a	20	90 (β + α)	8:1	oil	0.54 (9:1)	$C_{60}H_{80}O_5S$ (913.4)	0.59–1.98 (m, 46H, cholestane); 3.22 (dd, 1H, $J_{2',3'} = 10.38$, $J_{2',1'} = 8.85$, H-2'); 3.48–3.73 (m, 6H, H-3' to H-6b', H-1); 4.50 (d, 1H, $J_{1',2'} = 8.85$, H-1'); 4.53–4.63 (m, 3H, $C_6H_5C\underline{H}_2$); 4.81 (d, 1H, $J = 10.99$, $C_6H_5C\underline{H}_2$); 4.83 (d, 1H, $J = 10.38$, $C_6H_5C\underline{H}_2$); 5.02 (d, 1H, $J = 10.37$, $C_6H_5C\underline{H}_2$); 7.16–7.56 (m, 20H, H_{arom})
α-5a				oil	0.61 (9:1)		0.53–1.97 (m, 46H, cholestane); 3.46–3.58 (m, 1H, H-1); 3.69–3.91 (m, 5H, H-3' to H-6b'); 4.29 (dd, 1H, $J_{2',1'} = 4.88$, $J_{2',3'} = 8.24$, H-2'); 4.52 (d, 1H, $J_{1',2'} = 4.88$, H-1'); 4.47–4.64 (m, 3H, $C_6H_5C\underline{H}_2$); 4.70 (d, 1H, $J = 11.9$, $C_6H_5C\underline{H}_2$); 4.88 (d, 1H, $J = 10.68$, $C_6H_5C\underline{H}_2$); 7.14–7.48 (m, 20H, H_{arom})
β-5b	0	90	only β	oil	0.60 (2:1)	$C_{61}H_{64}O_{10}S$ (989.4)	3.14–4.18 (m, 15H, H-2 to H-6b, H-2' to H-6b', $C\underline{H}_3O$); 4.38–4.96 (m, 14H, $C_6H_5C\underline{H}_2$, H-1, H-1'); 7.16–7.43 (m, 35H, H_{arom})
β-5c	−95	85 (β + α)	3:1	oil	0.64 (2:1)	$C_{53}H_{54}O_9S$ (867.1)	3.21–3.93 (m, 12H, H-3 to H-6b, H-2' to H-6b'); 4.35–4.59 (m, 9H, $C_6H_5C\underline{H}_2$, H-2, H-1'); 4.81 (d, 1H, $J = 10.68$, $C_6H_5C\underline{H}_2$); 4.84 (d, 1H, $J = 10.07$, $C_6H_5C\underline{H}_2$); 5.03 (d, 1H, $J = 10.37$, $C_6H_5C\underline{H}_2$); 5.40 (s, 1H, H-1); 7.10–7.60 (m, 30H, H_{arom})
α-5c				98.5–101	0.71 (2:1)		–
β-5d	−40	83	only β	108–110	0.36 (3:1)	$C_{61}H_{64}O_{10}S$[9] (989.4)	3.29–4.16 (m, 15H, H-2 to H-6b, H-2' to H-6b'); 4.35 (d, 1H, $J_{1,2} = 9.0$, H-1'); 4.50–5.01 (m, 13H, $C_6H_5C\underline{H}_2$, H-1); 7.03–7.50 (m, 35H, H_{arom})

[a] Yield of pure, isolated product.
[b] Melting points are taken from samples purified for elemental analysis by MPLC; measured on a Büchi (Switzerland) melting point apparatus; uncorrected.
[c] The R_f values for all compounds are obtained on Merck Silica gel 60 F_{254}, 0.2 mm; petroleum ether (PE, bp 30–60 °C) and EtOAc (EA) are distilled.
[d] Satisfactory microanalyses obtained for compounds **β-5a**, **α-5a**, **β-5b**: C ± 0.33, H ± 0.03; except **β-5a** (C − 0.51) and **β-5b** (C − 0.44).
[e] Obtained on a Bruker WM 250 spectrometer at 250 MHz.

Table 2. 3,4,6-Tri-*O*-benzyl-2-deoxy-D-glucopyranosides **6a–c** Prepared

Product	Yield[a] (%)	mp (°C)	R_f[c] (PE/EA)	Molecular Formula[d]	^{1}H-NMR ($CDCl_3$/TMS) δ, *J*(Hz)[e]
β-6a	76	105.5–106	0.47	$C_{54}H_{76}O_5$ (8.05.2)	0.60–1.99 (m, 47H, Cholestane, H-2'$_{ax}$); 2.32 (dd, 1H, $J = 4.5$, 12, H-2'$_{eq}$); 3.42–3.80 (m, 6H, H-1, H-3' to H-6b'); 4.54–4.71 (m, 6H, $C_6H_5C\underline{H}_2$, H-1'); 4.91 (d, 1H, $J = 10.68$, $C_6H_5C\underline{H}_2$); 7.20–7.33 (m, 15H, H_{arom})
β-6b	65	oil	0.55 (2:1)	$C_{55}H_{60}O_{11}$ (897.1)	1.46–1.50 (m, 1H, $J > 10$, H-2'$_{ax}$); 2.16–2.23 (m, 1H, H-2'$_{eq}$); 3.26–3.92 (m, 14H, H-2 to H-6b, H-2'–H-6b', $C\underline{H}_3O$); 4.44–4.64 (m, 10H, $C_6H_5C\underline{H}_2$, H-1, H-1'); 4.73–4.87 (m, 3H, $C_6H_5C\underline{H}_2$); 5.03 (d, 1H, $J = 10.99$, $C_6H_5C\underline{H}_2$); 7.16–7.38 (m, 30H, H_{arom})
β-6c	75	62–63	0.23 (3:1)	$C_{47}H_{50}O_9$ (758.9)	1.83–1.70 (m, 1H, $J > 10$, H-2'$_{ax}$); 2.45–2.51 (m, 1H, H-2'$_{eq}$); 3.28–4.04 (m, 10H, H-2 to H-6b, H-2'–H-6b'); 4.03 (d, 1H, $J = 12.51$, $C_6H_5C\underline{H}_2$); 4.38–4.75 (m, 9H, $C_6H_5C\underline{H}_2$, H-1'); 4.93 (d, 1H, $J = 10.99$, $C_6H_5C\underline{H}_2$); 5.42 (s, 1H, H-1); 7.21–7.33 (m, 25H, H_{arom}) ^{13}C-NMR: 100.53 ppm (C-1); 98.63 ppm (C-1'); 36.63 ppm (C-2')
α-6c		62–63	0.44 (3:1)	$C_{47}H_{50}O_9$ (758.9)	1.68–1.79 (m, 1H, H-2'$_{ax}$); 2.27–2.34 (m, 1H, H-2'$_{eq}$); 3.34–5.04 (m, 22H, $C_6H_5C\underline{H}_2$, H-2 to H-6b, H-3'–H-6b'); 5.44 (s, 1H, H-1); 7.18–7.38 (m, 25H, H_{arom}) ^{13}C-NMR: 100.34, (C-1); 96.01, (C-1'); 35.67 (C-2')

[a–c] See Table 1.
[d] Satisfactory elemental analyses for compounds **β-6a**, **β-6c**, **α-6c**: C ± 0.30, H ± 0.13; except **β-6c** (C − 0.54) and **α-6c** (C − 0.52).
[e] Obtained on a Bruker WM 250 spectrometer at 250 MHz.

Table 3. 3,4,6-Tri-*O*-acetyl-2-deoxy-D-glucopyranosides **7a–c** Prepared

Product	Yield[a] (%)	mp[b] (°C)	R_f[c] (PE/EA)	Molecular Formula[d]	^{1}H-NMR ($CDCl_3$/TMS) δ, J(Hz)[e]
β-**7a**	72	143.5–144	0.28	$C_{39}H_{64}O_8$ (660.9)	0.55–2.28 (m, 48H, cholestane, H-2′$_{ax}$, H-2′$_{eq}$); 2.02 (s, 1H, C$\underline{H}_3$CO); 2.03 (s, 3H, C$\underline{H}_3$CO); 2.08 (s, 3H, C$\underline{H}_3$CO); 3.58–3.66 (m, 2H, H-3, H-5′); 4.09 (dd, 1H, J = 2.44, 12.21, H-6b′); 4.30 (dd, 1H, J = 4.7, 12.21, H-6a′); 4.69 (dd, 1H, J = 1.53, 9.46, H-1′); 4.93–5.03 (m, 2H, H-3′, H-4′)
β-**7b**	60	oil	0.44 (1:1)	$C_{25}H_{36}O_{16}$ (592.6)	1.63–1.78 (m, 1H, J > 9.7, H-2′$_{ax}$); 2.02–2.13 (6s, 18H, C$\underline{H}_3$CO); 2.22–2.29 (m, 1H, H-2′$_{eq}$); 3.39 (s, 3H, C$\underline{H}_3$O); 3.55 (m, 1H, H-5′); 3.77 (dd, 1H, J = 9.46, 9.76, H-4); 3.89–3.96 (m, 1H, H-5); 4.03 (dd, 1H, J = 2.3, 12.3, H-6b′); 4.19 (dd, 1H, J = 4.58, 12.21, H-6a′); 4.32–4.42 (m, 2H, H-6a, H-6b); 4.55 (dd, 1H, J = 1.83, 9.46, H-1′); 4.81–5.05 (m, 4H, H-1, H-2, H-3′, H-4′); 5.46 (dd, 1H, J = 9.15, 9.76, H-3)
β-**7c**	50	oil	0.51 (EA)	$C_{22}H_{30}O_{14}$ (518.5)	1.78–1.95 (m, 1H, J > 10, H-2′$_{ax}$); 2.04–2.13 (5s, 15H, C$\underline{H}_3$CO); 2.33–2.40 (m, 1H, H-2′$_{eq}$); 3.57 (s, 1H); 3.70 (m, 1H, H-5′); 3.82 (dd, 1H, J = 5.49, 7.93); 4.06 (dd, 1H, J = 2, 12.21, H-6b′); 4.24 (dd, 1H, J = 5.19, 12.21, H-6a′); 4.57 (s, 1H); 4.64 (bd, 1H, J = 4.9); 4.86–5.07 (m, 3H, H-1, H-3′, H-4′); 5.34 (s, 1H, H-2); 5.47 (s, 1H, H-1)
α-**7c**	50	oil	0.62 (EA)	$C_{22}H_{30}O_{14}$ (518.5)	1.88–1.95 (m, 1H, H-2′$_{ax}$); 2.02–2.18 (5s, 15H, C$\underline{H}_3$CO); 2.26–2.34 (m, 1H, J = 5.19, 13.43, H-2′$_{eq}$); 3.52 (s, 1H); 3.79 (dd, 1H, J = 5.80, 7.63); 4.01 (d, 1H, J = 7.63); 4.08–4.15 (m, 1H, H-6b′); 4.22–4.21 (m, 2H, H-5′, H-6a′); 4.59 (s, 1H); 4.74 (d, 1H, J = 5.49); 4.79 (bs, 1H); 5.01 (dd, 1H, J = 9.46, H-4′); 5.23 (bd, 1H, J = 2.47, H-1′); 5.34–5.45 (ddd, 1H, J = 5.18, 9.46, 11.60, H-3′); 5.47 (s, 1H, H-1)

[a–c] See Table 1.

[d] Satisfactory elemental analyses were obtained for compounds β-**7a**, β-**7b**, α-**7c**: C ±0.27, H ±0.34.

[e] Obtained on a Bruker WM 250 spectrometer at 250 MHz.

(m, 2H, $C_6H_5C\underline{H}_2$); 5.00 (d, 1H, J = 10.25, $C_6H_5C\underline{H}_2$); 5.31 (dd, 1H, J = 3.17, H-1); 7.13–7.50 (m, 20H, H_{arom}).

***O*-(3,4,6-Tri-*O*-benzyl-2-deoxy-2-phenylthio-α-D-glucopyranosyl)trichloroacetimidate (α-3):**

To a solution of compound **2** (500 mg, 0.95 mmol) and trichloroacetonitrile (0.42 mL, 4 mmol) in dry CH_2Cl_2 (10 mL) is added NaH (0.2 g, 8 mmol) at room temperature. While stirring the reaction is monitored by TLC with petroleum ether/EtOAc, 3:1; α-**3**: R_f = 0.64. After completion of the reaction the mixture is filtered through silica gel, and the silica gel is washed with dry CH_2Cl_2 (2 × 20 mL). The solvent is evaporated, and the residual dark yellow oil is purified by flash chromatography on silica gel (eluent: petroleum ether/EtOAc, 7:1 + 1% NEt_3). The resulting product is analytically pure; it is stable at −20 °C for several weeks; yield: 460 mg (70%); yellow oil.

$C_{35}H_{34}Cl_3NO_5S$ (687.1)	calc.	C 61.18	H 4.99	N 2.04
	found	61.21	5.09	2.00

^{1}H-NMR (250 MHz, $CDCl_3$/TMS): δ (J in Hz) = 3.49 (dd, 1H, J = 3.36, 10.99, H-2); 3.63–4.07 (m, 5H, H-3 to H-6b); 4.42–5.09 (m, 6H, $C_6H_5C\underline{H}_2$); 6.50 (d, 1H, J = 3.36, H-1); 7.13–7.57 (m, 20H, H_{arom}); 8.66 (s, 1H, N$\underline{H}$).

Formation of 2-Deoxy-2-phenylthio-D-glucopyranosides 5a–d; General Procedure:

A solution of donor α-**3** (1 mmol) and acceptor HOR (1.2 mmol) in dry CH_2Cl_2 (20 mL) is stirred for 30 min at room temperature in the presence of molecular sieves (4 Å, 0.5 g). After cooling to the given reaction temperature (**5a**: 20 °C; **5b**: −40 °C; **5c**: −60 °C; **5d**: −95 °C) a solution of ether-boron trifluoride complex (0.1–0.2 equiv, 0.1 M solution in Et_2O/CH_2Cl_2, 1:1) is added dropwise within 5 to 10 min. The reaction is monitored by TLC (see Table 1). When the reaction is completed (**5a**: ~1 h; **5b–d**: ~15 min), $NaHCO_3$ (0.5 g) is added and stirring continued for 10 min. The reaction mixture is filtered, and the solid material is washed with CH_2Cl_2 (2 × 10 mL). The solvent is removed *in vacuo*, and the residue thus obtained is purified, and the anomers are separated by flash-chromatography on silica gel using petroleum ether/EtOAc (ratios, see Table 1) as eluent. Compounds β/α-**5c** are not completely separated even by MPLC on silica gel using petroleum ether/EtOAc, 7:2, as eluent. For yields and physical data, see Table 1.

Formation of 2-Deoxy-D-glucopyranosides 6a–c; General Procedure:

To a solution of compounds **5a–c** (0.5 mmol) in dry THF (30 mL) was added Raney nickel (WII, ~4 g) at room temperature. The reaction is monitored by TLC (Table 2). When the reaction is completed the mixture is filtered, and the solid is washed with THF (3 × 10 mL). The solvent is removed *in vacuo*, and the colorless residue thus obtained is purified by flash-chromatography on silica gel using petroleum ether/EtOAc (ratios, see Table 2) as eluent. For yields and physical data, see Table 2.

Formation of 2-Deoxy-D-glucopyranosides 7a–c; General Procedure:

A solution of compounds **6a–c** (0.3 mmol) in dry EtOAc (10 mL) is hydrogenated in the presence of Pd–C (200 mg) at room temperature. After ~1.5 h the catalyst is filtered and carefully washed with CH_3OH; the solvents are evaporated *in vacuo*. The residue is dissolved in dry pyridine (1.5 mL) and Ac_2O (1.5 mL). After 10 h at room temperature the solution is concentrated *in vacuo*, and the residue thus obtained is purified by flash-chromatography on silica gel using petroleum ether/EtOAc β-**7a**, 3:1; β-**7b**, 1:1) and EtOAc (for the separation of β-**7c** and α-**7c**) as eluents. For yields and physical data, see Table 3.

The authors are indebted to the Deutsche Forschungsgemeinschaft and to the Fonds der Chemischen Industrie for financial support.

Received: 26 March 1988

(1) This is Part 38 on Glycosylimidates, for Part 37, see Eßwein, A., Schmidt, R.R. *Liebigs Ann. Chem.*, submitted.
(2) Tatsuta, K., Fujimoto, K., Kinoshita, M., Umezawa, S. *Carbohydr. Res.* **1977**, *54*, 85.
(3) Thiem, J., Karl, H., Schwentner, J. *Synthesis* **1978**, 696.
Thiem, J., Karl H. *Tetrahedron Lett.* **1978**, 4999.
Thiem, J., Gerken, M. *J. Carbohydr. Chem.* **1983**, *1*, 229.
(4) Bock, K., Pedersen, C., Thiem, J. *Carbohydr. Res.* **1979**, *73*, 85.
Thiem, J., Gerken, M., Bock, K. *Liebigs Ann. Chem.* **1983**, 462.
(5) Jaurand, G., Beau, J.-M., Sinay, P. *J. Chem. Soc. Chem. Commun* **1981**, 572.
(6) Gaegg, P.J., Köpper, S., Ossowski, P., Thiem, J. *J. Carbohydr Chem.* **1986**, *5*, 59.
(7) Bock, K., Lundt, I., Pedersen, C. *Carbohydr. Res.* **1984**, *130*, 125
(8) Nicolaou, K.C., Ladduwahetty, T., Randall, J.L., Chucholowski A. *J. Am. Chem. Soc.* **1986**, *108*, 2466.
(9) Ito, Y., Ogawa, T. *Tetrahedron Lett.* **1987**, *28*, 2723.

(10) Schmidt, R.R. *Angew. Chem.* **1986**, *98*, 213; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 212.
Schmidt, R.R., in: *Stereochemistry of Organic and Bioorganic Transformations*, Workshop Conferences Hoechst, Vol. 17, Bartmann, W., Sharpless, K.B. (eds.), VCH Verlagsgesellschaft, Weinheim, 1987, pp. 169–189.

(11) *Note added at proof:* The stereochemical outcome is not in accordance with previous results of phenylselenyl chloride addition.[5] However, very recently phenylselenyl chloride addition was reported to take place also from the α-face. Kaye, A., Neidle, S., Reese, C.B. *Tetrahedron Lett.* **1988**, *29*, 2711.