ELSEVIER

Carbohydrate Research 280 (1996) 277–286

CARBOHYDRATE RESEARCH

A method for the synthesis of *C*-(2-deoxy-β-glycosyl)arenes

Abu T. Khan, Wasim Ahmed, Richard R. Schmidt *

Fakultät für Chemie, Universität Konstanz, Postfach 5560 M 725, D-78434 Konstanz, Germany

Received 8 February 1995; accepted 29 August 1995

Abstract

2,3:4,5-Di-*O*-isopropylidene-*aldehydo*-D-arabinose (**2**) was converted by a Wittig reaction into a mixture of (*E*/*Z*)-1-aryl-1,2-dideoxy-3,4:5,6-di-*O*-isopropylidene-D-*arabino*-hex-1-enitols (**4**,**5**). Selective deprotection of the 5,6-*O*-isopropylidene group in compounds **4** and **5** followed by selective silylation at position 6 afforded the separable (*Z*)-1-aryl-6-*O*-(*tert*-butyldimethylsilyl)-1,2-dideoxy-3,4-*O*-isopropylidene-D-*arabino*-hex-1-enitols **8a–d** and the corresponding *E*-isomers (**9a–d**). Iodonium-ion-induced cyclization of compounds **8c** and **9a–c** furnished stereoselectively the 6-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-2-iodo-3,4-*O*-isopropylidene-β-D-glucopyranosylarenes **10a–c**. Full deprotection of compounds **10a–c** and then *O*-acetylation led to compounds **11a–c**, which on treatment with tributyltin hydride–azobisisobutyronitrile yielded the title compounds (**12a–c**).

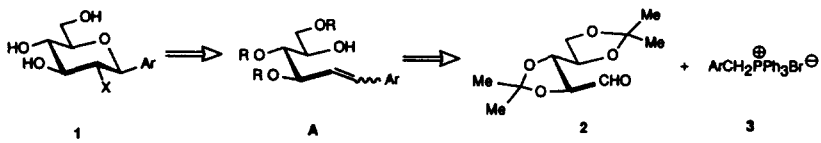
Keywords: *C*-Glycosides; *C*-Glycosylarenes; *C*-(2-Deoxy-β-D-*arabino*-hexopyranosyl)arenes; Di-*O*-isopropylidene-*aldehydo*-D-arabinose; Wittig reaction; Cyclization; *N*-Iodosuccinimide

1. Introduction

C-Glycosylarenes as well as *C*-(2-deoxy-β-glycosyl)arenes are widely found in Nature [1,2]. There has been continuing interest [3,4] in the synthesis of these compounds largely on account of their biological activities. A few years ago, from our laboratory, the synthesis of *C*-(2-deoxy-β-glycosyl)arenes was devised [5] by employing an inverse-type hetero-Diels–Alder reaction using 1-oxa-1,3-dienes as diene and substituted styrenes as dienophile. Various other synthetic methodologies have been developed to synthesize these compounds, involving normal hetero-Diels–Alder cycloadditions [6],

* Corresponding author.

SSDI 0008-6215(95)00321-5

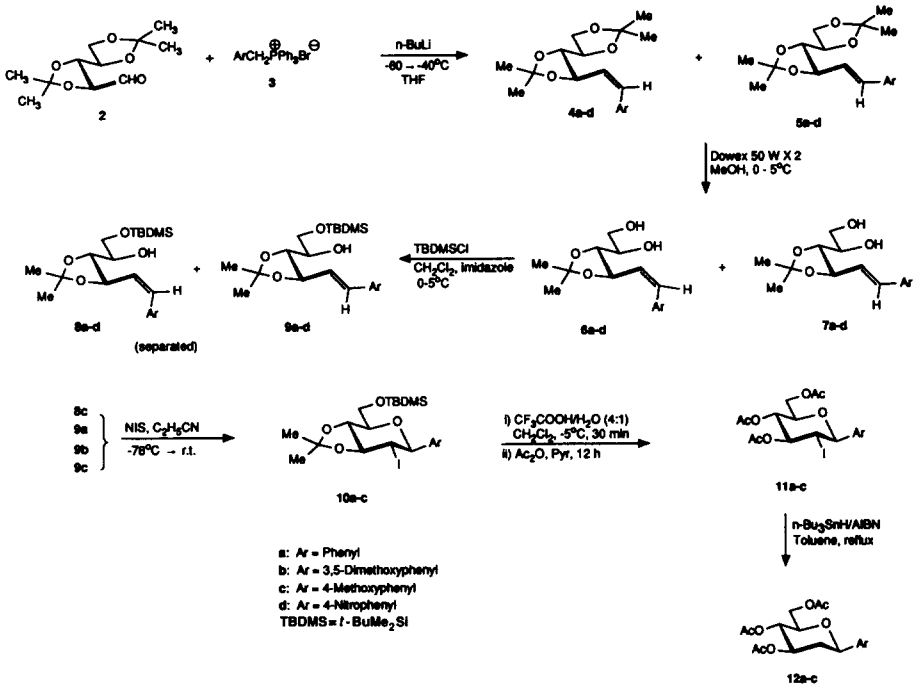


Scheme 1.

direct glycosylation of C-nucleophiles [7] (including the use of 1,2-epoxides [8]), reaction of C-nucleophiles with sugar lactones [9], reaction of C-1-lithiated glycals with C-electrophiles [10], and palladium-mediated glycal reactions [11]. An important approach is also condensation of CH-acidic compounds with sugar aldehydes followed by base-catalyzed ring closure by Michael addition [12]. Electrophile-induced ring closure of arylalkenols for the synthesis of *C*-(2-deoxy-*β*-glycosyl)arenes has been reported for a special case [13]; however, quite a few papers have reported the electrophile-induced cyclization of carbohydrate-derived alkenols [13–15], leading to *C*-glycosylalkanes, for which a different behavior in terms of regio- and diastereo-control can be expected. In this paper we report a simple and convenient approach for the synthesis of *C*-(2-deoxy-*β*-glycosyl)arenes based on electrophile-induced cyclization of carbohydrate-derived arylalkenols. The retrosynthetic analysis is shown in Scheme 1.

2. Results and discussion

The required 2,3:4,5-di-*O*-isopropylidene-*aldehydo*-D-arabinose (**2**) was prepared from D-arabinose [16]. The Wittig salts (**3**) were made according to literature procedures [17]. Wittig reaction of **2** in dry tetrahydrofuran with compounds **3a–d**, using butyllithium as the base, provided mixtures of **4a–d** and **5a–d** (Scheme 2) with *cis*-selectivity. The configurational assignments are based on ^{1}H NMR data (**4a–d**: J_{cis} 11.4 Hz, **5a–d**: J_{trans} 15.9 Hz). The *cis*/*trans* ratio was determined with the help of ^{1}H NMR by integration of the H-2 signals at δ 6.10–6.45 (dd, J_{trans} 15.9 Hz) and 5.60–5.85 (dd, J_{cis} 11.4 Hz). Next, the 5,6-*O*-isopropylidene group of compounds **4a–d** and **5a–d** was selectively removed using an acidic ion-exchange resin (Dowex 50W-X2, H^+ form) in methanol at 0–5 °C; migration of the 3,4-*O*-isopropylidene group was not observed, presumably because it spans a *threo*-diol moiety. 5,6-*O*-Deisopropylidenation was followed by regioselective silylation of position 6 to afford compounds **8a–d** and **9a–d**. At this stage, both isomers are well separated in TLC and were therefore isolated by flash chromatography. The electrophile-induced cyclization of the individual compounds **8a–d** and **9a–d** with *N*-iodosuccinimide (NIS) was then studied; the results are shown in Table 1. The cyclized products **10a–c** were fully characterized by ^{1}H NMR. The ^{1}H NMR spectra showed disappearance of the olefinic proton signals at δ 6.68–6.75 and 5.61–5.85 in the *cis* isomer. The *trans* isomer also showed disappearance of olefinic signals at δ 6.64–6.79 and 6.10–6.48. The new signal for the H-1 proton appears at δ 4.40–4.47 with a coupling constant of J 9.8 Hz, thus indicating the *β*-D configuration of the aryl group. Attempts to study the electrophile-induced cyclization with PhSeCl



Scheme 2.

and PhSeOTf [13,18] were unsuccessful. Compounds **10a–c** were converted into the acetyl derivatives **11a–c** by complete deprotection using aqueous trifluoroacetic acid (4:1) followed by acetylation with acetic anhydride in pyridine. Finally, removal of iodine with tributyltin hydride–azobisisobutyronitrile, by refluxing in dry toluene, furnished the title compounds **12a–c** in good yield. All compounds were characterized on the basis of ^{1}H NMR and ^{13}C NMR data, and elemental analyses. Compound **12a** had ^{1}H NMR data in agreement with those reported by Czernecki and co-workers [19].

Table 1
Electrophilic cyclization with *N*-iodosuccinimide (NIS)

Compound	Reaction conditions	Reaction time (h)	Product	Yield (%)	$\alpha:\beta$ Ratio
8a	NIS, C_2H_5CN, −78 °C → r.t. [a]	12	No reaction	–	–
9a	NIS, C_2H_5CN, −0 °C	10	**10a**	90	0:100
8b	NIS, C_2H_5CN, −78 °C → r.t.	10	No reaction	–	–
9b	NIS, C_2H_5CN, r.t.	72	**10b**	70	0:100
8c	NIS, C_2H_5CN, −78 °C	2	**10c**	80	0:100
9c	NIS, C_2H_5CN, −78 °C	10 min	**10c**	78	0:100
8d	NIS, C_2H_5CN, −78 °C → r.t.	40	No reaction	–	–
9d	NIS, C_2H_5CN, −78 °C → r.t.	40	No reaction	–	–

[a] r.t., Room temperature.

The results can be explained by the initial reversible formation of a π-complex of the iodonium ion with the CC-double bond [*Si*-face attack at C-2 (and C-1) in the *trans* isomers **9a–c**] and then, due to conformational proximity, fast attack of HO-5 at C-1 will directly lead to **10a–c** with the *β-gluco* configuration. Due to the unfavorable 1,3-interaction in the *cis* isomers **8a,b**, leading to a greater distance between C-1 and HO-5, reversible NIS attack at the CC-double bond (*Si*-face of C-2, *Re*-face of C-1) does not result in ring closure with HO-5; in the more electron-rich **8c** this problem is overcome by generating a *p*-methoxybenzyl cation after iodonium addition (σ-complex formation); the rotation of this group then leads to the thermodynamically stable **10c**.

In conclusion, this methodology is applicable for the synthesis of *C*-(2-deoxy-*β*-glycosyl)arenes where direct *C*-glycosylation at the anomeric position is not possible. The *trans* isomers **9a–c** are favoured in the cyclization reaction. In the case of the *cis* isomers, cyclization is favoured when electron-donating groups are present in the aromatic ring. Electron-withdrawing groups at the aromatic ring prevent cyclization.

3. Experimental

Melting points were recorded in a metal-bath and are uncorrected. Optical rotations were determined with a Perkin–Elmer 241 MC polarimeter for solutions in $CHCl_3$ at 20 °C, unless noted otherwise. ^1H NMR spectra and ^{13}C NMR spectra were recorded for solutions in $CDCl_3$ with $SiMe_4$ as internal standard on a Bruker Ac 250 cryospec instrument. R_f values refer to TLC performed on Silica Gel 60 F_{254} (Merck). Column chromatography was performed using flash silica gel (230–400 mesh ASTM). Elemental analyses were performed on a Heraeus CHN-analyser.

*(Z)- and (E)-1-Aryl-1,2-dideoxy-3,4:5,6-di-*O*-isopropylidene-*D-arabino*-hex-1-enitols* (**4a–d** *and* **5a–d**).—*General procedure.* To the appropriate Wittig salt **3a–d** (10 mmol) in dry THF (50 mL) under N_2 atmosphere at −60 to −40 °C was added slowly butyllithium (6.25 mL, 10 mmol) and immediately an orange solution of the phosphorane was produced. After stirring for 15 min, 2,3:4,5-di-*O*-isopropylidene-*aldehydo*-D-arabinose (**2**) (2.3 g, 10 mmol) in dry THF (20 mL) was added dropwise and the orange color disappeared slowly. Then the reaction mixture was stirred at room temperature for 4 h, poured into aq NH_4Cl, and extracted with ether (2 × 100 mL). The combined extracts were dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography of the residue afforded the corresponding *cis* and *trans* Wittig-product mixture **4a–d** and **5a–d**.

Compounds **4a** and **5a**: liquid; yield 2.86 g (94%); R_f 0.42 (4:1 light petroleum–EtOAc); $[\alpha]_D$ +43.3° (*c* 1, $CHCl_3$); *cis*:*trans* 2:1; ^1H NMR (250 MHz, $CDCl_3$): δ 1.30, 1.34, 1.39, 1.42, 1.44, 1.46 [s, 12 H, $(CH_3)_2C$], 3.79–4.20 (m, 4 H, H-4,5,6a,6b), 4.54 (dd, 0.33 H, $J_{2,3} = J_{3,4} = 7.4$ Hz, H-3), 4.75 (dd, 0.67 H, $J_{2,3}$ 9.3, $J_{3,4}$ 8.3 Hz, H-3), 5.70 (dd, 0.67 H, J_{cis} 11.4, $J_{2,3}$ 9.3 Hz, H-2), 6.22 (dd, 0.33 H, J_{trans} 15.9, $J_{2,3}$ 7.4 Hz, H-2), 6.75 (d, 0.33 H, J_{trans} 15.9 Hz, H-1), 6.77 (d, 0.67 H, J_{cis} 11.4 Hz, H-1), 7.25–7.44 (m, 5 H, Ph). Anal. Calcd for $C_{18}H_{24}O_4$: C, 71.02; H 7.95. Found: C, 70.60; H, 7.89.

Compounds **4b** and **5b**: liquid; yield 2.37 g (65%); R_f 0.58 (4:1 light petroleum–EtOAc); $[\alpha]_D$ +11.9° (*c* 1, $CHCl_3$); *cis*:*trans* 3:2; ^1H NMR (250 MHz, $CDCl_3$): δ

1.25, 1.29, 1.30, 1.34, 1.35, 1.45, 1.46 [s, 12 H, $(CH_3)_2C$], 3.76 (s, 3 H, OCH_3), 3.77 (s, 3 H, OCH_3), 3.75–4.20 (m, 4 H, H-4,5,6a,6b), 4.50 (dd, 0.4 H, $J_{2,3} = J_{3,4} = 7.4$ Hz, H-3), 4.75 (dd, 0.6 H, $J_{2,3}$ 9.3, $J_{3,4}$ 8.4 Hz, H-3), 5.65 (dd, 0.6 H, J_{cis} 11.5, $J_{2,3}$ 9.3 Hz, H-2), 6.20 (dd, 0.4 H, J_{trans} 15.9, $J_{2,3}$ 7.4 Hz, H-2), 6.35–6.38 (m, 1 H, Ar), 6.52 (d, 1 H, J 2.3 Hz, Ar), 6.58 (d, 1 H, J 2.3 Hz, Ar), 6.65 (d, 0.4 H, J_{trans} 15.9 Hz, H-1), 6.70 (d, 0.6 H, J_{cis} 11.5 Hz, H-1). Anal. Calcd for $C_{20}H_{28}O_6$: C, 65.91; H, 7.74. Found: C, 65.92; H, 7.76.

Compounds **4c** and **5c**: liquid; yield 2.51 g (75%); R_f 0.6 (3:1 light petroleum–EtOAc); $[\alpha]_D$ +68.6° (*c* 1, $CHCl_3$); *cis*:*trans* 3:2; ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.30, 1.34, 1.39, 1.42, 1.44, 1.46 [s, 12 H, $(CH_3)_2C$], 3.79 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3), 3.77–4.20 (m, 4 H, H-4,5,6a,6b), 4.51 (dd, 0.4 H, $J_{2,3} = J_{3,4} = 6.8$ Hz, H-3), 4.74 (dd, 0.6 H, $J_{2,3}$ 9.3, $J_{3,4}$ 8.3 Hz, H-3), 5.60 (dd, 0.6 H, J_{cis} 11.4, $J_{2,3}$ 9.3 Hz, H-2), 6.10 (dd, 0.4 H, J_{trans} 15.9, $J_{2,3}$ 6.8 Hz, H-2), 6.66 (d, 0.4 H, J_{trans} 15.9 Hz, H-1), 6.70 (d, 0.6 H, J_{cis} 11.4 Hz, H-1), 6.83–6.89 (m, 2 H, Ar), 7.26–7.39 (m, 2 H, Ar). Anal. Calcd for $C_{19}H_{26}O_5$: C, 68.24; H, 7.84. Found: C, 68.05; H, 7.81.

Compounds **4d** and **5d**: liquid; yield 2.02 g (58%); R_f 0.5 (4:1 light petroleum–EtOAc); $[\alpha]_D$ +6.5° (*c* 1, $CHCl_3$); *cis*:*trans* 8.5:1.5; ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.27, 1.28, 1.32, 1.37, 1.42, 1.44 [s, 12 H, $(CH_3)_2C$], 3.70–4.20 (m, 4 H, H-4,5,6a,6b), 4.59 (dd, 0.15 H, $J_{2,3} = J_{3,4} = 7.0$ Hz, H-3), 4.62 (dd, 0.85 H, $J_{2,3}$ 9.3, $J_{3,4}$ 8.3 Hz, H-3), 5.85 (dd, 0.85 H, J_{cis} 11.6, $J_{2,3}$ 9.3 Hz, H-2), 6.45 (dd, 0.15 H, J_{trans} 15.9, $J_{2,3}$ 7.0 Hz, H-2), 6.75 (d, 0.85 H, J_{cis} 11.6 Hz, H-1), 6.80 (d, 0.15 H, J_{trans} 15.9 Hz, H-1), 7.56–7.59 (m, 2 H, Ar), 8.16–8.19 (m, 2 H, Ar). Anal. Calcd for $C_{18}H_{23}NO_6$: C, 61.88; H, 6.63; N, 4.00. Found: C, 61.84; H, 6.63; N, 4.12.

(Z)- and (E)-1-Aryl-1,2-dideoxy-3,4-O-isopropylidene-D-arabino-*hex-1-enitols* (**6a–d** *and* **7a–d**).—The *cis* and *trans* mixtures **4a–d** and **5a–d** (1 g) were each dissolved in MeOH (50 mL) and Dowex 50W-X2 resin (1 g, H^+ form) was added. The mixture was stirred at 5 °C for 12–16 h. Then the resin was filtered off and washed with methanol (20 mL). Methanol was removed, and the residue was passed through a small silica gel column. The products **6a–d** and **7a–d** were obtained in 85–90% yield and were used for the next step without characterization.

*(Z)- and (E)-1-Aryl-6-O-(*tert*-butyldimethylsilyl)-1,2-dideoxy-3,4-O-isopropylidene*-D-arabino-*hex-1-enitols* (**8a–d** *and* **9a–d**).—To a solution of each mixture **6a–d** and **7a–d** (1 mmol) and imidazole (82 mg, 1.2 mmol) in dry CH_2Cl_2 (15 mL) was added *t*-$BuMe_2SiCl$ (166 mg, 1.1 mmol). The solution was stirred at 5 °C for 12–18 h and the reaction was monitored by TLC. The solution was extracted with excess of CH_2Cl_2 (2 × 50 mL), washed with water, and dried ($MgSO_4$). The *cis* and *trans* isomers were separable in TLC. The solvent was removed in vacuo and the crude mixture was purified by flash chromatography. Both isomers **8a–d** and **9a–d** were isolated in each case. The overall yield was 88–90% after purification.

Compound **8a**: liquid; R_f 0.58 (4:1 light petroleum–EtOAc); $[\alpha]_D$ +47° (*c* 1, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.03 (s, 6 H, $SiCH_3$), 0.86 [s, 9 H, $SiC(CH_3)_3$], 1.40 [s, 3 H, $(CH_3)_2C$], 1.44 [s, 3 H, $(CH_3)_2C$], 2.47 (d, 1 H, J 4.1 Hz, D_2O exchangeable, OH), 3.58–3.79 (m, 3 H, H-5,6a,6b), 3.79 (dd, 1 H, $J_{3,4}$ 7.3, $J_{4,5}$ 6.7 Hz, H-4), 4.82 (dd, 1 H, $J_{2,3}$ 9.3, $J_{3,4}$ 7.3 Hz, H-3), 5.75 (dd, $J_{1,2}$ 11.4, $J_{2,3}$ 9.3 Hz, H-2), 6.75 (d, 1 H, $J_{1,2}$ 11.4 Hz, H-1), 7.25–7.44 (m, 5 H, Ph); ^{13}C NMR (62.5 MHz,

$CDCl_3$): δ 18.25, 25.84, 26.98, 27.33, 64.03, 72.17, 74.68, 80.94, 109.09, 127.48, 128.24, 128.44, 128.95, 135.02, 136.11. Anal. Calcd for $C_{21}H_{34}O_4Si$: C, 66.63; H, 9.05. Found C, 66.51; H, 8.90.

Compound **9a**: liquid; R_f 0.55 (4:1 light petroleum–EtOAc); $[\alpha]_D$ −2.9° (*c* 1, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$): δ 0.01 (s, 6 H, $SiCH_3$), 0.83 [s, 9 H, $SiC(CH_3)_3$], 1.39 [s, 3 H, $(CH_3)_2C$], 1.40 [s, 3 H, $(CH_3)_2C$], 2.60 (bs, 1 H, D_2O exchangeable, OH), 3.67–3.77 (m, 4 H, H-4,5,6a,6b), 4.60 (dd, 1 H, $J_{2,3} = J_{3,4} = 6.6$ Hz, H-3), 6.20 (dd, 1 H, $J_{1,2}$ 15.8, $J_{2,3}$ 6.6 Hz, H-2), 6.68 (d, 1 H, $J_{1,2}$ 15.8 Hz, H-1), 7.15–7.35 (m, 5 H, Ph); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 18.15, 25.74, 26.90, 26.92, 63.95, 72.59, 79.67, 80.30, 109.00, 126.50, 127.36, 127.59, 128.33, 132.25, 136.49. Anal. Calcd for $C_{21}H_{34}O_4Si$: C, 66.63; H, 9.05. Found: C, 66.67; H, 9.09.

Compound **8b**: liquid; R_f 0.5 (4:1 light petroleum–EtOAc); $[\alpha]_D$ +73.5° (*c* 1, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$): δ 0.05 (s, 6 H, $SiCH_3$), 0.88 [s, 9 H, $SiC(CH_3)_3$], 1.40 [s, 3 H, $(CH_3)_2C$], 1.45 [s, 3 H, $(CH_3)_2C$], 2.52 (d, 1 H, *J* 4.2 Hz, D_2O exchangeable, OH), 3.60–3.80 (m, 4 H, H-4,5,6a,6b), 3.75 (s, 6 H, OCH_3), 4.85 (dd, 1 H, $J_{2,3}$ 9.2, $J_{3,4}$ 8.7 Hz, H-3), 5.65 (dd, 1 H, $J_{1,2}$ 11.5, $J_{2,3}$ 9.2 Hz, H-2), 6.35 (t, 1 H, *J* 2.3 Hz, Ar), 6.65 (d, 2 H, *J* 2.3 Hz, Ar), 6.70 (d, 1 H, $J_{1,2}$ 11.5 Hz, H-1); ^{13}C NMR (62.5 MHz $CDCl_3$): δ 18.24, 25.82, 27.05, 27.29, 55.30, 64.03, 72.24, 74.89, 80.84, 100.33, 106.89, 109.03, 128.65, 135.09, 137.99, 160.61. Anal. Calcd for $C_{23}H_{38}O_6Si$: C, 62.98; H, 8.73. Found: C, 63.08; H, 8.80.

Compound **9b**: liquid; R_f 0.47 (4:1 light petroleum–EtOAc); $[\alpha]_D$ −5.5° (*c* 1, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$): δ 0.04 (s, 3 H, $SiCH_3$), 0.05 (s, 3 H, $SiCH_3$), 0.87 [s, 9 H, $SiC(CH_3)_3$], 1.42 [s, 3 H, $(CH_3)_2C$], 1.43 [s, 3 H, $(CH_3)_2C$], 2.49 (d, 1 H, *J* 4.0 Hz, D_2O exchangeable, OH), 3.70–3.77 (m, 4 H, H-4,5,6a,6b), 3.77 (s, 6 H, OCH_3), 4.60 (dd, 1 H, $J_{2,3} = J_{3,4} = 6.5$ Hz, H-3), 6.20 (dd, 1 H, $J_{1,2}$ 15.8, $J_{2,3}$ 6.5 Hz, H-2), 6.35 (t, 1 H, *J* 2.2 Hz, Ar), 6.53 (d, 2 H, *J* 2.2 Hz, Ar), 6.64 (d, 1 H, $J_{1,2}$ 15.8 Hz, H-1). Anal. Calcd for $C_{23}H_{38}O_6Si$: C, 62.98; H, 8.73. Found: C, 62.94; H, 8.81.

Compound **8c**: liquid; R_f 0.58 (4:1 light petroleum–EtOAc); $[\alpha]_D$ +88.5° (*c* 1, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$): δ 0.03 (s, 6 H, $SiCH_3$), 0.86 [s, 9 H, $SiC(CH_3)_3$], 1.41 [s, 3 H, $(CH_3)_2C$], 1.44 [s, 3 H, $(CH_3)_2C$], 2.49 (d, 1 H, *J* 4.0 Hz, D_2O exchangeable, OH), 3.76–3.58 (m, 4 H, H-4,5,6a,6b), 3.79 (s, 3 H, OCH_3), 4.80 (dd, 1 H, $J_{2,3}$ 9.2, $J_{3,4}$ 7.2 Hz, H-3), 5.61 (dd, 1 H, $J_{1,2}$ 11.4, $J_{2,3}$ 9.3 Hz, H-2), 6.68 (d, 1 H, $J_{1,2}$ 11.4 Hz, H-1), 6.85 (mc, 2 H, Ar), 7.37 (mc, 2 H, Ar); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 18.25, 25.63, 26.98, 27.34, 55.20, 64.04, 72.10, 74.68, 81.00, 108.97, 113.70, 126.79, 128.77, 130.30, 134.64, 159.09. Anal. Calcd for $C_{22}H_{36}O_5Si$: C, 64.66; H, 8.88. Found: C, 64.43; H, 8.87.

Compound **9c**: liquid; R_f 0.55 (4:1 light petroleum–EtOAc); $[\alpha]_D$ −1.1° (*c* 1, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$): δ 0.03 (s, 3 H, $SiCH_3$), 0.04 (s, 3 H, $SiCH_3$), 0.86 [s, 9 H, $SiC(CH_3)_3$], 1.42 [s, 3 H, $(CH_3)_2C$], 1.43 [s, 3 H, $(CH_3)_2C$], 2.51 (d, 1 H, *J* 4.0 Hz, D_2O exchangeable, OH), 3.53–3.77 (m, 4 H, H-4,5,6a,6b), 3.77 (s, 3 H, OCH_3), 4.60 (dd, 1 H, $J_{2,3} = J_{3,4} = 7.0$ Hz, H-3), 6.10 (dd, 1 H, $J_{1,2}$ 15.8, $J_{2,3}$ 7.0 Hz, H-2), 6.65 (d, 1 H, $J_{1,2}$ 15.9 Hz, H-1), 6.80–6.83 (m, 2 H, Ar), 7.28–7.33 (m, 2 H, Ar); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 18.26, 25.83, 27.01, 55.23, 64.01, 72.69, 79.98, 80.41, 109.03, 113.91, 125.06, 127.85, 129.37, 132.31, 159.40. Anal. Calcd for $C_{22}H_{36}O_5Si$: C, 64.66; H, 8.88. Found: C, 64.60; H, 8.81.

Compound **8d**: liquid; R_f 0.5 (4:1 light petroleum–EtOAc); $[\alpha]_D$ +15.3° (*c* 0.25, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$): δ 0.04 (s, 6 H, $SiCH_3$), 0.87 [s, 9 H, $SiC(CH_3)_3$], 1.38 [s, 3 H, $(CH_3)_2C$], 1.42 [s, 3 H, $(CH_3)_2C$], 2.50 (d, 1 H, *J* 4.4 Hz, D_2O exchangeable, OH), 3.59–3.82 (m, 4 H, H-4,5,6a,6b), 4.70 (dd, 1 H, $J_{2,3}$ 9.3, $J_{3,4}$ 7.8 Hz, H-3), 5.85 (dd, 1 H, $J_{1,2}$ 11.6, $J_{2,3}$ 9.4 Hz, H-2), 6.75 (d, 1 H, $J_{1,2}$ 11.6 Hz, H-1), 7.60 (mc, 2 H, Ar), 8.18 (mc, 2 H, Ar); ^{13}C NMR (62.50 MHz, $CDCl_3$): δ 18.25, 25.81, 27.00, 27.24, 64.07, 72.40, 74.83, 80.72, 109.60, 123.49, 129.77, 132.20, 132.37, 142.77, 147.03. Anal. Calcd for $C_{21}H_{33}NO_6Si$: C, 59.54; H, 7.85; N, 3.31. Found: C, 59.41; H, 7.91; N, 3.4.

Compound **9d**: liquid; R_f 0.45 (4:1 light petroleum–EtOAc); $[\alpha]_D$ −21.5° (*c* 1, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$): δ 0.05 (s, 3 H, $SiCH_3$), 0.06 (s, 3 H, $SiCH_3$), 0.87 [s, 9 H, $SiC(CH_3)_3$], 1.43 [s, 6 H, $(CH_3)_2C$], 2.55 (d, 1 H, *J* 4.0 Hz, D_2O exchangeable, OH), 3.64–3.81 (m, 4 H, H-4,5,6a,6b), 4.64 (dd, 1 H, $J_{2,3} = J_{3,4} = 5.8$ Hz, H-3), 6.48 (dd, 1 H, $J_{1,2}$ 1.6, $J_{2,3}$ 5.8 Hz, H-2), 6.79 (dd, 1 H, $J_{1,2}$ 15.9 Hz, H-1), 7.50 (mc, 2 H, Ar), 8.15 (mc, 2 H, Ar); ^{13}C NMR: δ 18.18, 25.73, 26.80, 26.91, 64.02, 72.88, 79.68, 80.22, 109.56, 123.84, 127.02, 129.27, 132.57, 143.10, 146.98. Anal. Calcd for $C_{21}H_{33}NO_6Si$: C, 59.54; H, 7.85; N, 3.31. Found: C, 59.54; H, 7.83; N, 3.4.

*General procedure for the synthesis of 6-*O*-tert-butyldimethylsilyl-2-deoxy-2-iodo-3,4-*O*-isopropylidene-β-*D*-glucopyranosylarenes* (**10a–c**).—A solution of compound **8** or **9** (1 mmol) in dry EtCN (20 mL) was cooled to −78 °C under N_2 atmosphere. Then *N*-iodosuccinimide (292 mg, 1.3 mmol) was added. When the reaction was complete (TLC), the solution was extracted with EtOAc (2 × 50 mL), and washed successsively with aq 5% $Na_2S_2O_3$ (2 × 25 mL) and saturated aq NaCl (10 mL). The organic solution was dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by flash chromatography. The product was obtained in 70–90% yield after purification.

Compound **10a**: liquid; R_f 0.50 (9:1 light petroleum–EtOAc); $[\alpha]_D$ +81.1° (*c* 1, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$): δ 0.02 (s, 6 H, $SiCH_3$), 0.84 [s, 9 H, $SiC(CH_3)_3$], 1.48 [s, 6 H, $(CH_3)_2C$], 3.55 (dd, 1 H, $J_{3,4}$ 8.9, $J_{4,5}$ 8.7 Hz, H-4), 3.72–3.86 (m, 4 H, H-3,5,6a,6b), 4.02 (dd, 1 H, *J* 9.9, *J* 10.6 Hz, H-2), 4.47 (d, 1 H, $J_{1,2}$ 9.9 Hz, H-1), 7.30–7.40 (m, 5 H, Ph); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 18.32, 25.81, 26.58, 26.72, 29.98, 63.07, 75.71, 80.16, 84.54, 84.67, 110.08, 128.07, 128.12, 128.74, 137.90. Anal. Calcd for $C_{21}H_{33}IO_4Si$: C, 49.49; H, 6.59. Found: C, 50.12; H, 6.66.

Compound **10b**: liquid; R_f 0.5 (4:1 light petroleum–EtOAc); $[\alpha]_D$ +92.1° (*c* 1, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$): δ −0.05 (s, 3 H, $SiCH_3$), 0.00 (s, 3 H, $SiCH_3$), 0.85 [s, 9 H, $Si(CH_3)_3$], 1.48 [s, 6 H, $(CH_3)_2C$], 3.55 (dd, 1 H, $J_{3,4}$ 8.9, $J_{4,5}$ 8.7 Hz, H-4), 3.77 (s, 6 H, OCH_3), 3.68–3.89 (m, 4 H, H-3,5,6a,6b), 3.99 (dd, 1 H, $J_{1,2}$ 9.8, $J_{2,3}$ 10.9 Hz, H-2), 4.40 (d, 1 H, $J_{1,2}$ 9.8 Hz, H-1), 6.40 (t, 1 H, *J* 2.3 Hz, Ar), 6.50 (d, 2 H, *J* 2.3 Hz, Ar); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 18.24, 25.73, 26.49, 26.63, 29.57, 55.26, 62.87, 75.50, 80.02, 84.49, 84.54, 100.81, 106.16, 109.98, 139.89, 160.38. Anal. Calcd for $C_{23}H_{37}IO_6Si$: C, 48.93; H, 6.60. Found: C, 48.68; H, 6.67.

Compound **10c**: liquid; R_f 0.5 (9:1 light petroleum–EtOAc); $[\alpha]_D$ +79.4° (*c* 1, $CHCl_3$); ^1H NMR (250 MHz, $CDCl_3$): δ −0.02 (s, 6 H, $SiCH_3$), 0.84 [s, 9 H, $SiC(CH_3)_3$], 1.48 [s, 6 H, $(CH_3)_2C$], 3.53 (dd, 1 H, $J_{3,4}$ 8.9, $J_{4,5}$ 8.7 Hz, H-4), 3.79 (s, 3 H, OCH_3), 3.73–3.84 (m, 4 H, H-3,5,6a,6b), 3.97 (dd, 1 H, $J_{1,2}$ 9.8, $J_{2,3}$ 10.9 Hz,

H-2), 4.44 (d, 1 H, $J_{1,2}$ 9.8 Hz, H-1), 6.84–6.87 (m, 2 H, Ar), 7.24–7.27 (m, 2 H, Ar); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 18.35, 25.83, 26.59, 26.74, 30.52, 55.22, 63.12, 75.74, 80.03, 84.14, 84.76, 110.09, 113.54, 129.20, 130.25, 159.84. Anal. Calcd for $C_{22}H_{35}IO_5Si$: C, 49.43; H, 6.60. Found: C, 49.50; H, 6.61.

*General procedure for the synthesis of 3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo-β-*D*-gluco-pyranosylarenes* (**11a–c**).—To a solution of compound **10a–c** (0.7 mmol) in CH_2Cl_2 (15 mL) was added a solution of trifluoroacetic acid in water (4:1, 5 mL) at −5 °C. The reaction mixture was stirred for 30 min, then toluene (50 mL) was added and the solvent was evaporated. This process was repeated twice. A solution of the residue in dry pyridine (5 mL) and Ac_2O (3 mL) was stirred at room temperature for 12 h. Then excess of pyridine and Ac_2O were removed by coevaporation with toluene (2 × 50 mL). Finally the residue was purified by flash column chromatography. The product was obtained in 80–90% yield after purification.

Compound **11a**: mp 145 °C, R_f 0.5 (3:2 light petroleum–EtOAc); $[\alpha]_D$ +83.3° (*c* 1, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.04 (s, 3 H, $COCH_3$), 2.06 (s, 3 H, $COCH_3$), 2.10 (s, 3 H, $COCH_3$), 3.88 (ddd, 1 H, $J_{5,6a}$ 4.6, $J_{5,6b}$ 2.2, $J_{4,5}$ 10.0 Hz, H-5), 4.10 (dd, 1 H, $J_{6a,6b}$ 12.4 Hz, H-6b), 4.14 (dd, 1 H, $J_{1,2}$ 10.8, $J_{2,3}$ 10.7 Hz, H-2), 4.30 (dd, 1 H, H-6a), 4.62 (d, 1 H, H-1), 5.13 (dd, 1 H, $J_{3,4}$ 9.3 Hz, H-4), 5.45 (dd, 1 H, H-3), 7.37–7.38 (m, 5 H, Ph); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 20.61, 20.72, 20.82, 31.69, 62.41, 69.32, 76.41, 77.05, 84.30, 127.71, 128.45, 129.22, 137.85, 169.64, 169.66, 170.83. Anal. Calcd for $C_{18}H_{21}IO_7$: C, 45.38; H, 4.44. Found: C, 45.69; H, 4.50.

Compound **11b**: mp 149–150 °C, R_f 0.50 (1:1 light petroleum–EtOAc); $[\alpha]_D$ +30.4° (*c* 0.5, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.04 (s, 3 H, $COCH_3$), 2.06 (s, 3 H, $COCH_3$), 2.10 (s, 3 H, $COCH_3$), 3.81 (s, 6 H, OCH_3), 3.87 (ddd, 1 H, $J_{5,6a}$ 4.7, $J_{5,6b}$ 2.2, $J_{4,5}$ 10 Hz, H-5), 4.09 (dd, 1 H, $J_{6a,6b}$ 12.3 Hz, H-6b), 4.10 (dd, 1 H, $J_{1,2} = J_{2,3} = 10.7$ Hz, H-2), 4.28 (dd, 1 H, H-6a), 4.53 (d, 1 H, H-1), 5.12 (dd, 1 H, $J_{3,4}$ 9.2, H-4), 5.42 (dd, 1 H, H-3), 6.44 (t, 1 H, *J* 2.2 Hz, Ar), 6.50 (d, 2 H, *J* 2.2 Hz, Ar); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 20.61, 20.73, 20.81, 31.21, 55.40, 62.41, 69.30, 76.38, 77.21, 84.34, 100.93, 105.98, 139.83, 160.72, 169.65, 170.62. Anal. Calcd for $C_{20}H_{25}IO_9$: C, 44.78; H, 4.70. Found: C, 44.63; H, 4.77.

Compound **11c**: mp 164–165 °C, R_f 0.5 (1:1 light petroleum–EtOAc); $[\alpha]_D$ +94.5° (*c* 1, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.03 (s, 3 H, $COCH_3$), 2.04 (s, 3 H, $COCH_3$), 2.09 (s, 3 H, $COCH_3$), 3.80 (s, 3 H, OCH_3), 3.88 (ddd, 1 H, $J_{5,6b}$ 2.2, $J_{5,6a}$ 4.7, $J_{4,5}$ 10 Hz, H-5), 4.09 (dd, 1 H, $J_{6a,6b}$ 12.2 Hz, H-6b), 4.12 (dd, 1 H, $J_{1,2} = J_{2,3} =$ 10.7 Hz, H-2), 4.28 (dd, 1 H, H-6a), 4.58 (d, 1 H, H-1), 5.11 (dd, 1 H, $J_{3,4}$ 9.4 Hz, H-4), 5.44 (dd, 1 H, H-3), 6.90 (mc, 2 H, Ar), 7.28 (mc, 2 H, Ph); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 20.56, 20.66, 20.77, 32.21, 55.22, 62.41, 69.31, 76.25, 77.07, 83.82, 113.80, 128.82, 130.14, 160.13, 169.58, 170.55. Anal. Calcd for: C, 45.07; H, 4.58. Found: C, 45.00; H, 4.58.

*General procedure for the synthesis of 3,4,6-tri-*O*-acetyl-2-deoxy-β-*D*-arabino-hexopyranosylarenes* (**12a–c**).—To a solution of compound **11a–c** (0.3 mmol) in dry toluene (15 mL) was added tributyl hydride (175 mg, 0.6 mmol) and azobisisobutyronitrile (5 mg, 0.03 mmol) under N_2 atmosphere. The reaction mixture was refluxed for 2–3 h. The solution was extracted with toluene (50 mL), washed with water (3 × 10 mL), and dried ($MgSO_4$). Removal of solvent in vacuo gave an oily residue which was

purified by flash chromatography. The compound **12a–c** was obtained in 80–85% yield after purification.

Compound **12a**: liquid; R_f 0.50 (3:2 light petroleum–EtOAc); $[\alpha]_D$ −5.6° (*c* 1, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.84 (ddd, $J_{1,2ax}$ 11.4, $J_{2ax,3}$ 9.5, $J_{2ax,2eq}$ 13.0 Hz, H-2ax), 2.07 (s, 3 H, $COCH_3$), 2.09 (s, 3 H, $COCH_3$), 2.40 (ddd, 1 H, $J_{1,2eq}$ 2.1, $J_{2eq,3}$ 4.8 Hz, H-2eq), 3.78 (ddd, $J_{5,6b}$ 2.2, $J_{5,6a}$ 4.8, $J_{4,5}$ 9.5 Hz, H-5), 4.16 (dd, 1 H, $J_{6a,6b}$ 12.3 Hz, H-6b), 4.31 (dd, 1 H, H-6a), 4.57 (dd, 1 H, H-1), 5.10 (dd, $J_{3,4}$ 9.5 Hz, H-4), 5.16 (ddd, 1 H, H-3), 7.26–7.36 (m, 5 H, Ph); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 20.70, 20.75, 20.88, 38.42, 62.87, 69.32, 72.45, 76.17, 77.26, 125.72, 127.97, 128.45, 140.05, 169.84, 170.33, 170.74. Anal. Calcd for $C_{18}H_{22}O_7$: C, 61.70; H, 6.33. Found: C, 61.44; H, 6.49.

Compound **12b**: liquid; R_f 0.5 (7:3 light petroleum–EtOAc); $[\alpha]_D$ −6.1° (*c* 0.5, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.80 (ddd, $J_{1,2ax}$ 11.6, $J_{2ax,3}$ 9.4, $J_{2ax,2eq}$ 13.1 Hz, H-2ax), 2.03 (s, 3 H, $COCH_3$), 2.07 (s, 3 H, $COCH_3$), 2.08 (s, 3 H, $COCH_3$), 2.37 (ddd, 1 H, $J_{1,2eq}$ 2.1, $J_{2eq,3}$ 4.8 Hz, H-2eq), 3.75 (ddd, 1 H, $J_{5,6b}$ 2.2, $J_{5,6a}$ 4.9, $J_{4,5}$ 9.4 Hz, H-5), 3.78 (s, 6 H, OCH_3), 4.16 (dd, 1 H, $J_{6a,6b}$ 12.2 Hz, H-6b), 4.30 (dd, 1 H, H-6a), 4.50 (dd, 1 H, H-1), 5.08 (dd, 1 H, $J_{3,4}$ 9.4 Hz, H-4), 5.12 (ddd, 1 H, H-3), 6.38 (t, 1 H, *J* 2.2 Hz, Ar), 6.49 (d, 2 H, *J* 2.2 Hz, Ar); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 20.74, 20.79, 20.92, 38.40, 55.34, 62.89, 69.34, 72.42, 76.15, 77.21, 99.89, 103.85, 142.41, 160.91, 169.88, 170.38, 170.78. Mass spectrum. Calcd for $C_{20}H_{26}O_9$: 410. Found: *m/z* 410 (M^+), 230, 165 (base peak).

Compound **12c**: mp 106–107 °C; R_f 0.58 (3:2 light petroleum–EtOAc); $[\alpha]_D$ −6.3° (*c* 1, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.86 (ddd, 1 H, $J_{1,2ax}$ 11.7, $J_{2ax,3}$ 9.4, $J_{2ax,2eq}$ 13.1 Hz, H-2ax), 2.07 (s, 3 H, $COCH_3$), 2.08 (s, 3 H, $COCH_3$), 2.35 (ddd, 1 H, $J_{1,2eq}$ 2.0, $J_{2eq,3}$ 4.6 Hz, H-2eq), 3.75 (ddd, 1 H, $J_{5,6b}$ 2.2, $J_{5,6a}$ 4.8, $J_{4,5}$ 9.4 Hz, H-5), 3.79 (s, 3 H, OCH_3), 4.14 (dd, 1 H, $J_{6a,6b}$ 12.3 Hz, H-6b), 4.30 (dd, 1 H, H-6a), 4.51 (dd, 1 H, H-1), 5.08 (dd, 1 H, $J_{3,4}$ 9.4 Hz, H-4), 5.14 (ddd, 1 H, H-3), 6.88 (mc, 2 H, Ar), 7.28 (mc, 2 H, Ph); ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 20.73, 20.77, 20.91, 38.29, 55.28, 62.94, 69.41, 72.51, 76.16, 77.22, 113.90, 127.15, 132.23, 159.43, 169.88, 170.36, 170.77. Anal. Calcd for $C_{19}H_{24}O_8$: C, 59.99; H, 6.36. Found: C, 60.10; H, 6.45.

Acknowledgements

The authors thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support. A.T.K. is grateful for a stipend from the Alexander von Humboldt Foundation, and W.A. for a stipend from the Deutscher Akademischer Austauschdienst.

References

[1] L.J. Haynes, *Adv. Carbohydr. Chem.*, 20 (1965) 357–369; S.R. James, *J. Carbohydr. Nucleosides Nucleotides*, 6 (1979) 417–465; J. Asakawa, *Prog. Chem. Org. Nat. Prod.*, 42 (1982) 154; U. Hacksell and G.D. Daves, Jr., *Prog. Med. Chem.*, 22 (1985) 1–65; R.R. Schmidt, *Conference Proceedings*, 5th In-

Conf. Chem. Biotechnol. Biol. Active Nat. Prod., 18–23 September, 1989, Varna, Bulgaria, Bulgarian Acad. Sci., Sofia, 1989, Vol. 3, pp 560–575.
[2] B.W. Bycroft, *Dictionary of Antibiotics and Related Substances*, Chapman and Hall, London, 1988.
[3] C. Jaramillo and S. Knapp, *Synthesis*, (1994) 1–20.
[4] M.H.D. Postema, *Tetrahedron Lett.*, 48 (1992) 8545–8599.
[5] R.R. Schmidt, W. Frick, B. Haag-Zeino, and S. Apparao, *Tetrahedron Lett.*, 28 (1987) 4045–4048; R.R. Schmidt, *ACS Symp. Ser.*, 386 (1989) 182–196.
[6] S.J. Danishefsky, B.J. Uang, and G. Quallich, *J. Am. Chem. Soc.*, 107 (1985) 1285–1293.
[7] K. Suzuki, *Pure Appl. Chem.*, 66 (1994) 2175–2178; K. Toshima, G. Matsuo, and M. Nakata, *J. Chem. Soc., Chem. Commun.*, (1994) 997–998; F.L. Andrews and D.S. Larsen, *Tetrahedron Lett.*, 35 (1994) 8693–8694; J.A. Mahling and R.R. Schmidt, *Synthesis*, (1993) 325–328.
[8] V. Bellosta and S. Czernecki, *Carbohydr. Res.*, 244 (1993) 275–284.
[9] V.A. Boyd, B.E. Drake, and G.A. Sulikowski, *J. Org. Chem.*, 58 (1993) 3191–3193; K. Tatsuta, H. Ozeki, M. Yamaguchi, M. Tanaka, and T. Okui, *Tetrahedron Lett.*, 31 (1990) 5495–5498.
[10] K.A. Parker, *Pure Appl. Chem.*, 66 (1994) 2135–2138; R.R. Schmidt, R. Preuss, and R. Betz, *Tetrahedron Lett.*, 28 (1987) 6591–6594.
[11] R.N. Farr, R.A. Outten, J.C.-J. Cheng, and G.D. Daves, Jr., *Organometallics*, 9 (1990) 3151–3156; V. Bellosta, S. Czernecki, D. Avenel, S. El Bahij, and H. Gillier-Pandrand, *Can. J. Chem.*, 68 (1990) 1364–1368; M.A. Tius, J. Gomez-Galeno, X.-q. Gu, and J.H. Zaidi, *J. Am. Chem. Soc.*, 113 (1991) 5775–5783; E. Dubois and J.-M. Beau, *Carbohydr. Res.*, 223 (1992) 157–167.
[12] M. Yamaguchi, A. Horiguchi, C. Ikeura, and T. Minami, *J. Chem. Soc., Chem. Commun.*, (1992) 434–436; F. Nicotra, G. Russo, F. Ronchetti, and L. Toma, *Carbohydr. Res.*, 124 (1983) C5–C7.
[13] D.J. Hart, V. Leroy, G.H. Merriman, and D.G.J. Young, *J. Org. Chem.*, 57 (1992) 5670–5680, and references therein.
[14] R.W. Armstrong and B.R. Teegarden, *J. Org. Chem.*, 57 (1992) 915–922; A.B. Reitz, S.O. Nortey, and B.E. Maryanoff, *ibid.*, 52 (1987) 4191–4202; J.R. Pougny, M.A.M. Nassr, and P. Sinaÿ, *J. Chem. Soc., Chem. Commun.*, (1981) 375–376; K. Suzuki and T. Mukaiyama, *Chem. Lett.*, (1982) 683–686; F. Freeman and K.D. Robarge, *Tetrahedron Lett.*, 26 (1985) 1943–1946; F. Nicotra, F. Ronchetti, and G. Russo, *J. Chem. Soc., Chem. Commun.*, (1982) 470–471.
[15] P.A. Bartlett, in J.D. Morrison (Ed.), *Asymmetric Synthesis*, Vol. 3, Academic, New York, 1984, pp 411–454.
[16] H. Zinner and G. Rembarz, *Chem. Ber.*, 92 (1959) 1614–1617.
[17] F. Kröhnke, *Chem. Ber.*, 83 (1950) 291–296; E. Reimann, *Arch. Pharm.*, 312 (1979) 772–776.
[18] S. Murata and R. Suzuki, *Chem. Lett.*, (1987) 849–852.
[19] R. Benhaddon, S. Czernecki, and G. Ville, *J. Org. Chem.*, 57 (1992) 4612–4616.