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Carbohydrate Research 323 (2000) 202–207

CARBOHYDRATE RESEARCH

Note

Stereoselective synthesis of *C*-[2-*S*-(*p*-tolyl)-2-thio-β-D-galactopyranosyl] compounds using the reaction of TolSCl adducts of D-galactal with *C*-nucleophiles

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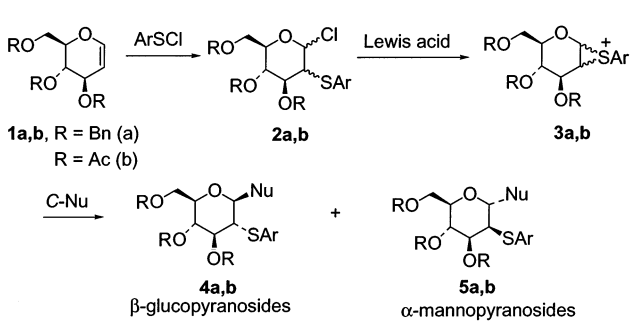
Received 20 July 1999; accepted 7 September 1999

Abstract

Pyranosyl chlorides prepared in situ from tri-*O*-benzyl-D-galactal and TolSCl react with silyl enol ethers, allyltrimethylsilane, and vinyl ethers to give a mixture of β-*C*-galacto and α-*C*-talopyranosides in a ratio of 19:1.

Keywords: β-*C*-Galactopyranosides; D-Galactal; Episulfonium ion; Pyranosyl chlorides

In the last two decades, the chemistry of *C*-glycosylic compounds ('*C*-glycosides') has attracted a great deal of attention because of their unique properties and applications [1–3]. Numerous methods of *C*-glycoside preparation have been proposed [1,2a]. The majority of them involve an electrophilic substitution at the anomeric center [1]. Due to the anomeric effect, the α-side nucleophilic attack is a more favored process. As a result, *C*-α-glycosides are more easily synthesized than the corresponding β isomers. Recently, we proposed a new method of stereoselective synthesis of *C*-(2-*S*-aryl-2-thio-β-D-glucopyranosyl) compounds [4]. Our approach is based on the reaction of different carbon nucleophiles (*C*-Nu, e.g., silyl enol ethers, allyltrimethylsilane, silyl ketene acetals, vinyl ethers, Grignard reagents, and TMSCN) with episulfonium-like intermediates (**3a,b**) generated from ArSCl adducts (**2a,b**) of a glucal (Scheme 1) [4b]. We found that the stereoselectivity of this reaction is greatly affected by the solvent polarity and the sugar structure [4a,b]. For example, the



Scheme 1.

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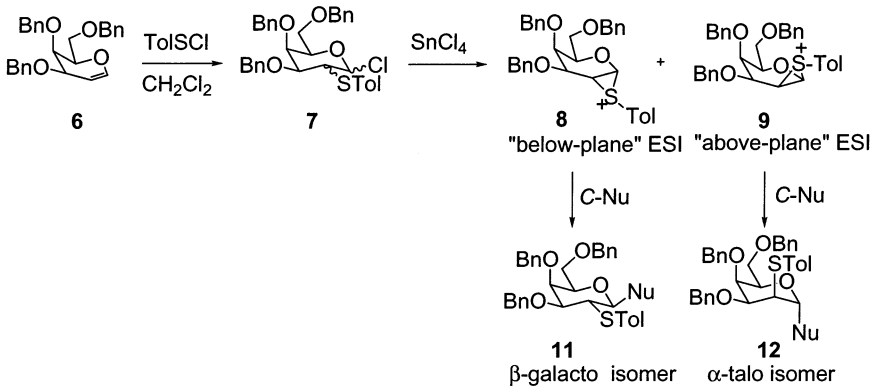
PII: S0008-6215(99)00256-6



Scheme 2.

reaction of TolSCl (Tol = *p*-tolyl) adducts of tri-*O*-benzyl- or tri-*O*-acetyl-D-glucal (**1a,b**) with 2-methyl-1-(trimethylsilyloxy)propene in CH_2Cl_2 and treated with $SnCl_4$ yields a mixture of β-gluco and α-manno isomeric *C*-glycosides (**4a,b** and **5a,b**) in the same ratio of 87:13 [4b]. However, the reaction of TolSCl adducts of 3,4-di-*O*-acetyl-6-deoxy-L-glucal with 2-methyl-1-(trimethylsilyloxy)propene affords a mixture of the two isomers in a ratio of 57:43 [4b]. In order to learn how the sugar structure affects the stereoselectivity of the reaction, we conducted the study of the reaction of carbon nucleophiles with episulfonium-like intermediates generated from D-galactal. Herein we report our results.

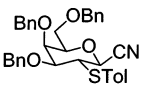
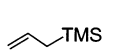
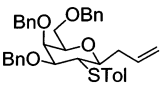
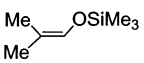
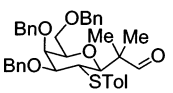
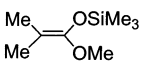
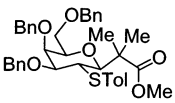
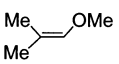
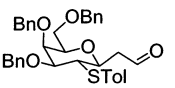
We found that tri-*O*-benzyl-D-galactal (**6**) reacts with TolSCl to give a mixture of isomeric 2-*S*-(*p*-tolyl)-2-thio-D-aldopyranosyl chlorides (**7**)[1]. Upon treatment with $SnCl_4$ or $ZnCl_2$, this mixture was transformed into intermediates, presumably, of the episulfonium ion structure (**8** and **9**). The latter were capable of reacting with different *C*-Nu (TMSCN, silyl enol ethers, allyltrimethylsilane, and vinyl ethers) to yield *C*-β-D-galactopyranosides **11a**–**e** with high stereoselectivity and in good yield (Scheme 2, Table 1). Along with *C*-β-D-galactopyranosides **11a**–**e**, a small amount of an isomeric *C*-glycoside (**12a**–**e**, 5%, ^{1}H NMR data) was formed in all the reactions. In the case of 2-methyl-1-(trimethylsilyloxy)propene as a *C*-Nu, the second isomer was isolated and identified as a *C*-α-D-talopyranoside (^{1}H NMR data).

The exclusive formation of *C*-glycosides corresponding to the trans addition of the TolS electrophile and *C*-Nu across the double bond of galactal **6** supports the suggestion that intermediates of this reaction are episulfonium-like species (i.e., **8** and **9**) [4a,b,5]. In the case of using vinyl ethers as *C*-Nu, the reaction takes place through the formation of an additional intermediate, the five-membered sulfonium salt (**10**, Scheme 3). Similar intermediates have been isolated [6] in the ArS-group mediated dimerization of vinyl ethers [4a,7].

So far, the reactions of nucleophiles with cyclic intermediates (episulfonium [4,8], episelenonium [9], and iodonium [10] ions) generated from carbohydrate derivatives have been studied mainly using protected D-glucals as starting compounds. Previously, it has been shown that pseudoaxial and axial groups in allal and galactal derivatives are effective directors [8a]. For example, the reaction of MeOH with the electrophilic species generated from D-galactal and phenylbis(phenylthio)-sulfonium salt led to a more stereoselective formation of *O*-β-D-galactopyranosides (β-galacto:α-talo 12:1), compared with a low stereoselectivity of glycosidation using D-glucal (β-gluco:α-manno 3.7:1) [8a]. Similar enhancement of stereoselectivity has been observed by Ito and Ogawa when sulfenate esters were used for the generation of cyclic intermediates from glycals [8b]. The re-

[1] The ^{1}H NMR spectrum of **7** taken 3 min after mixing tri-*O*-benzyl-D-galactal and TolSCl shows signals of α- and β-D-galactopyranosyl chlorides in a ratio of 53:47. After 3 h, only signals of the α-D-galacto isomer were present in the spectrum of the same sample. α-D-Galacto isomer: δ 6.27 (d, 1 H, $J_{1,2}$ 3, H-1); β-D-galacto chloride: δ 5.20 (d, 1 H, $J_{1,2}$ 9, H-1). In both spectra we were unable to identify any signals belonging to α,β-D-talopyranosyl chlorides.

Table 1
Reaction of TolSCl adducts of galactal **6** with carbon nucleophiles

Entry	C-Nu	C-β-D-Galactopyranoside		Yield, %[a]	Ratio β-galacto : α-talo
1	TMSCN		**11a**	46	95 : 5
2			**11b**	60	95 : 5
3			**11c**	56	95 : 5
4			**11d**	55	95 : 5
5		**11c**		79	95 : 5
6			**11e**	42	95 : 5

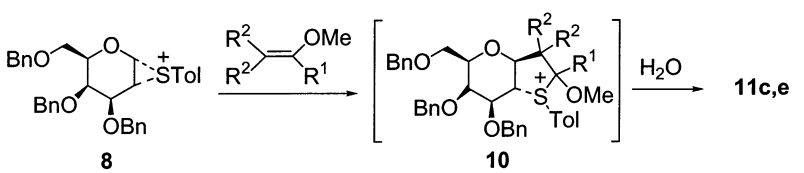
[a] Yields are given for the mixtures of two isomers after preparative TLC. Tol=*p*-tolyl.

action of a primary alcohol with the epoxide obtained from dimethyldioxirane and 1,5-anhydro-6-*O*-(*tert*-butyldiphenylsilyl)-2-deoxy-D-*lyxo*-hex-1-enopyranose 3,4-carbonate (a derivative of D-galactal) yielded exclusively a β-D-galactopyranoside [11]. Our experimental data for the reaction of *C*-Nu with episulfonium-like intermediates generated from D-glucal [4a,b] and D-galactal are in line with the observations for reactions of other cyclic intermediates with *O*-Nu [8a,b,11]. Thus, in CH_2Cl_2, the formation of a cyclic intermediate (e.g., **8**) with the 'above-plane' configuration of the three-membered ring followed by the formation of a 1,2-diaxial product is more favored in the case of axial position of a substituent (e.g., OBn group) at C-4 of a pyranose ring.

In summary, we have shown that stereoselectivity of the reaction of pyranosyl chlorides with carbon nucleophiles is increased from 87:13 (β-gluco:α-manno) to 95:5 (β-galacto:α-talo) in the case of using D-galactal instead of D-glucal as a starting carbohydrate derivative.

1. Experimental

Instrumentation and materials.—^1H and ^{13}C NMR spectra (300 and 75 MHz, respectively) of all compounds were recorded in $CDCl_3$ using TMS as a standard unless otherwise stated. Coupling constants, *J*, are given in Hz. Preparative thin-layer chromatography (TLC) was carried out using glass plates, 200 × 250 mm, with an unfixed layer of E. Merck Silica Gel 60, 230–400 mesh. Analytical TLC was performed on E. Merck precoated 0.2 mm plates of Silica Gel 60 F_{254}. IR spectra were recorded on an ATI Mattson Genesis Series



Scheme 3.

FTIR spectrometer. Optical rotations were measured on an Autopol III automatic polarimeter.

p-Tolylsulfenyl chloride was obtained from *p*-methyl thiophenol using SO_2Cl_2 [12]. 1-Methoxy-2-methyl-1-propene was synthesized from the corresponding acetal by pyrolysis using *p*-toluenesulfonic acid as a catalyst [13]. Other chemicals were commercially available (Aldrich Chemical Co.). All reactions were carried out under an atmosphere of dry nitrogen using oven-dried or flame-dried glassware and freshly distilled and dried solvents.

General procedure for synthesis of C-*[2*-S-*(*p-*tolyl)-2-thio-β-*D*-*galactopyranosyl] compounds*.—To a solution of 104 mg tri-*O*-benzyl-D-galactal (0.25 mmol) in CH_2Cl_2 (10 mL), 40 mg TolSCl (0.25 mmol) in CH_2Cl_2 (0.3 mL) was added dropwise at room temperature (the color changed from yellow to colorless). After 10 min, the mixture was cooled to −78 °C, and 0.3 mL of a 1.0 M solution of $SnCl_4$ (0.3 mmol) in CH_2Cl_2 was added, followed by the carbon nucleophile (0.3 mmol). The mixture was stirred for 1 h at −78 °C, quenched with a satd soln of $NaHCO_3$, extracted with ether, and dried over Na_2SO_4. Preparative TLC of the crude material after solvent removal in vacuum afforded a mixture of isomeric β-galacto and α-talo *C*-glycosides (see Table 1 for the exact ratios of the isomers for different *C*-Nu).

C-*[3,4,6-Tri*-O-*benzyl-2*-S-*(*p-*tolyl)-2-thio-β-*D*-*galactopyranosyl]carbonitrile* (**11a**).—R_f 0.43 (1:1 ether–hexane); $[\alpha]_D^{22}$ −14.60° (*c* 0.13, $CHCl_3$); IR ($CHCl_3$): *v* 2254 cm^{-1} (CN); ^1H NMR: δ 2.34 (s, 3 H, CH_3), 3.30 (dd, 1 H, $J_{2,3}$ 11.4, $J_{3,4}$ 2.4, H-3), 3.50 (m, 3 H, H-5, H-6a, H-6b), 3.59 (t, 1 H, $J_{2,3}$ 11.4, $J_{1,2}$ 11.4, H-2), 3.96 (d, 1 H, $J_{3,4}$ 2.4, H-4), 4.03 (d, 1 H, $J_{1,2}$ 11.4, H-1), 4.39, 4.46 (two d, 2 H, *J* 11.7, C*H*$_2$Ph), 4.55, 4.89 (two d, 2 H, *J* 11.3, C*H*$_2$Ph), 4.73, 4.82 (two d, 2 H, *J* 11.3, C*H*$_2$Ph), 7.30 (m, 19 H, H-Arom); ^{13}C NMR: δ 21.2 (CH_3), 49.6 (CS), 68.4, 69.7, 72.1, 72.5 (4 OCH_2 groups), 73.6, 74.7, 78.1, 79.9 (4 OCH groups), 116.3 (CN), 127.7, 127.8, 127.9, 127.9, 127.9, 128.0, 128.3, 128.4, 128.5, 128.9, 134.8, 137.4, 137.5, 138.1, 138.9 (C-Arom); HRMS: Calcd for $C_{35}H_{35}NSO_4$ 565.2289; Found: M^+ *m*/*z* 565.2271.

*1-*C-*[3,4,6-Tri*-O-*benzyl-2*-S-*(*p-*tolyl)-2-thio-β-*D*-*galactopyranosyl]-2-propene* (**11b**).—R_f 0.77 (1:1 ether–hexane); $[\alpha]_D^{22}$ +11.40° (*c* 0.55, $CHCl_3$); IR ($CHCl_3$): *v* 1641 cm^{-1} (C=C); ^1H NMR: δ 2.38 (s, 3 H, CH_3), 2.45 (m, 1 H, H-7a), 3.01 (m, 1 H, H-7b), 3.39 (m, 3 H, H-1, H-2, H-3), 3.49 (dd, 1 H, $J_{5,6a}$ 6.5, $J_{5,6b}$ 5.5, $J_{4,5} \approx 0$, H-5), 3.60 (m, 2 H, H-6a, H-6b), 4.01 (broad d, 1 H, $J_{3,4}$ 2, $J_{4,5} \approx 0$, H-4), 4.46, 4.52 (two d, 2 H, *J* 12, PhC*H*$_2$O), 4.64, 4.93 (two d, 2 H, *J* 11.5, PhC*H*$_2$O), 4.70, 4.81 (two d, 2 H, *J* 12, PhC*H*$_2$O), 5.09 (m, 2 H, =CH_2), 5.96 (m, 1 H, =CH), 7.30 (m, 19 H, H-Arom); ^{13}C NMR: 21.0 (CH_3), 37.0 (CH_2), 52.2 (CHS), 69.0, 72.3, 73.4, 74.2 (4 OCH_2 groups), 72.7, 76.8, 80.0, 82.0 (4 OCH groups), 11.7 (=CH_2), 127.4, 127.5, 127.6, 127.7, 127.8, 128.0, 128.1, 128.2, 128.3, 129.5, 129.7, 131.8, 132.8, 135.1, 137.0, 138.0, 138.1, 138.8 (C-Arom); HRMS: Calcd for $C_{37}H_{40}SO_4$ 580.2637; Found: M^+ *m*/*z* 580.2628.

*2-Methyl-2-*C-*[3,4,6-tri*-O-*benzyl-2*-S-*(*p-*tolyl)-2-thio-β-*D*-*galactopyranosyl]propionaldehyde* (**11c**).—R_f 0.60 (1:1 ether–hexane); $[\alpha]_D^{22}$ −14.60° (*c* 0.20, $CHCl_3$); IR ($CHCl_3$): *v* 1717 cm^{-1} (CHO); ^1H NMR: δ 0.98, 1.12 (two s, 6 H, C(CH_3)$_2$), 2.33 (s, 3 H, CH_3), 3.48 (t, 1 H, $J_{1,2} \approx J_{2,3}$ 11, H-2), 3.53 (d, 1 H, $J_{1,2}$ 11, H-1), 3.53 (dd, 1 H, $J_{2,3}$ 11, $J_{3,4}$ 3, H-3), 3.62 (m, 3 H, H-5, H-6a, H-6b), 4.01 (broad d, 1 H, $J_{3,4}$ 3, $J_{4,5} \approx 0$, H-4), 4.48, 4.53 (two d, 2 H, *J* 11.8, PhC*H*$_2$O), 4.62, 4.97 (two d, 2 H, *J* 11.5, PhC*H*$_2$O), 4.72, 4.80 (two d, 2 H, *J* 11.5, PhC*H*$_2$O), 7.30 (m, 19 H, H-Arom), 9.74 (s, 1 H, CHO). ^{13}C NMR: 15.8, 21.6, 21.9 (3 CH_3 groups), 29.7 (*C*(CH_3)$_2$), 50.7 (SCH), 69.0, 72.9, 73.5, 74.4 (4 OCH_2 groups), 73.2, 77.5, 82.1, 83.3 (4 OCH groups), 127.3, 127.5, 127.6, 127.7, 127.8, 128.1, 128.2, 128.4, 129.6, 130.6, 131.6, 136.6, 137.9, 139.0, 199.6 (C=O); HRMS: Calcd for $C_{38}H_{42}SO_5$ 610.2753; Found: M^+ *m*/*z* 610.2752.

*Methyl 2-methyl-2-*C-*[3,4,6-tri*-O-*benzyl-2*-S-*(*p-*tolyl)-2-thio-β-*D*-*galactopyranosyl]propionate* (**11d**).—R_f 0.42 (1:1 ether–hexane); $[\alpha]_D^{22.5}$ −10.91° (*c* 0.55, $CHCl_3$); IR ($CHCl_3$,): *v* 1725 cm^{-1} (ester); ^1H NMR: δ 1.17, 1.31 (2 s, 6 H, C(CH_3)$_2$), 2.33 (s, 3 H, CH_3), 3.60 (m, 5 H, H-1, H-2, H-5, H-6a, H-6b), 3.75 (s, 3 H, OCH_3), 3.94 (broad d, 1 H, $J_{2,3}$ 8.0, $J_{3,4}$ 0.5, H-3), 4.00 (broad s, 1 H, $J_{3,4}$ 0.5, $J_{4,5} \approx 0$, H-4), 4.47, 4.53 (two d, 2 H, *J* 11.7, OC*H*$_2$Ph),

4.60, 4.95 (two d, 2 H, *J* 11.4, OC*H*$_2$Ph), 4.66, 4.75 (two d, 2 H, *J* 11.6, OC*H*$_2$Ph), 7.27 (m, 19 H, H-Arom); ^{13}C NMR: δ 18.1, 21.1, 25.7 (3 CH_3 groups), 46.1 ($C(CH_3)_2$), 50.2 (CS), 51.8 (OCH_3), 69.2, 72.9, 73.5, 73.7 (4 OCH_2 groups), 74.5, 77.4, 82.5, 83.7 (4 OCH groups), 127.4, 127.6, 127.7, 127.8, 127.9, 128.2, 128.3, 128.5, 129.5, 131.3, 132.9, 136.3, 138.2, 139.2 (C-Arom), 177.3 ($COOCH_3$); HRMS: Calcd for $C_{39}H_{44}SO_6$ 640.2859; Found: M^+ *m*/*z* 640.2883.

*Methyl [2-methyl-2-*C*-[3,4,6-tri-*O*-benzyl-2-*S*-(p-tolyl)-2-thio-α-*D*-talopyranosyl]]propionate* (**12d**).—This isomer was separated from the mixture of two isomers using a Whatman PE Sil G/UV plate (H 20 cm, W 10 cm, 70:9 CCl_4–Et_2O). ^{1}H NMR: δ 1.19, 1.24 (two s, 6 H, $C(CH_3)_2$), 2.33 (s, 3 H, CH_3), 2.96 (dd, 1 H, $J_{1,2}$ 10.1, $J_{2,3}$ 2.3, H-2), 3.61 (m, 1 H, H-4), 3.67 (s, 3 H, OCH_3), 3.78 (dd, 1 H, $J_{6a,6b}$ 11.5, $J_{5,6}$ 2, H-6a), 3.94 (m, 1 H, H-3), 4.14 (dd, 1 H, $J_{6a,6b}$ 11.5, $J_{5,6b}$ 8.4, H-6b), 4.27 (d, 1 H, $J_{1,2}$ 10.1, H-1), 4.35 (m, 1 H, H-5), 4.46, 4.54 (two d, 2 H, *J* 11.8, OC*H*$_2$Ph), 4.56 (broad s, 2 H, OC*H*$_2$Ph), 4.77, 4.85 (two d, *J* 11.2, OC*H*$_2$Ph), 7.30 (m, 19 H, H-Arom).

*2-*C*-[3,4,6-Tri-*O*-benzyl-2-*S*-(p-tolyl)-2-thio-β-*D*-galactopyranosyl]acetaldehyde* (**11e**). —R_f 0.38 (1:1 ether–hexane); $[\alpha]_D^{22}$ −7.5° (*c* 0.20, $CHCl_3$); IR ($CHCl_3$): *v* 1714 cm^{-1} (CHO); ^{1}H NMR: δ 2.33 (s, 3 H, CH_3), 2.70 (ddd, 1 H, $J_{7a,7b}$ 16.3, $J_{1,7a}$ 8.7, $J_{8,7a}$ 2.3, H-7a), 3.22 (ddd, 1 H, $J_{7a,7b}$ 16.3, $J_{1,7b}$ 3.1, $J_{8,7b}$ 1.5, H-7b), 3.33 (t, 1 H, $J_{3,2}$ 10.5, $J_{2,1}$ 10.5, H-2), 3.43 (dd, 1 H, $J_{2,3}$ 10.5, $J_{3,4}$ 2.5, H-3), 3.53 (m, 3 H, H-5, H-6a, H-6b), 3.91 (ddd, 1 H, $J_{1,2}$ 10.5, $J_{1,7a}$ 8.7, $J_{1,7b}$ 3.1, H-1), 4.00 (d, 1 H, $J_{3,4}$ 2.5, $J_{4,5} \approx 0$, H-4), 4.40, 4.45 (two d, 2 H, *J* 11.8, C*H*$_2$Ph), 4.56, 4.90 (two d, 2 H, *J* 11.5, C*H*$_2$Ph), 4.69, 4.78 (two d, 2 H, *J* 11.5, C*H*$_2$Ph), 7.25 (m, 19 H, H-Arom), 9.77 (dd, 1 H, $J_{8,7a}$ 2.3, $J_{8,7b}$ 1.5, CHO); ^{13}C NMR: δ 21.3 (CH_3), 47.5 (CH_2CO), 52.8 (CS), 69.0, 72.7, 73.0, 73.7 (4 OCH_2 groups), 74.9, 76.1, 77.3, 81.8 (4 OCH groups), 127.8, 127.9, 128.0, 128.1, 128.3, 128.4, 128.5, 128.6, 128.7, 130.0, 130.6, 133.1, 137.8, 138.1, 138.2, 138.8 (C-Arom), 200.9 (C=O); HRMS: Calcd for $C_{36}H_{38}SO_5$ 582.2441; Found: M^+ *m*/*z* 582.2423.

Acknowledgements

The authors gratefully acknowledge the National Institute of General Medical Sciences (grant no. 1 R15 GM/OD55965-01) and ND EPSCoR (grant no. OSR-9452892) for financial support.

References

[1] (a) D.E. Levy, C. Tang, *The Chemistry of C-Glycosides*, *Tetrahedron Organic Chemistry Series*, Vol. 13, Elsevier Science Inc., Tarrytown, New York, 1995. (b) M.H.D. Postema, *C-Glycoside Synthesis*, CRC Press, Boca Raton, FL, 1995. (c) S. Hanessian, *Total Synthesis of Natural Products*: *The Chiron Approach*, Pergamon, Oxford, 1983.

[2] (a) C.B. Bertozzi, M.D. Bednarski, in S.H. Khan, R.A. O'Neill (Eds.), *Modern Methods in Carbohydrate Synthesis*, Hardwood Academic Publishers, Amsterdam, 1996, pp. 316–351. (b) J.W. Lown, *Chem. Soc. Rev.*, (1993) 165–176. (c) J. Rohr, R. Thiericke, *Nat. Prod. Rep.*, (1992) 103–137. (d) N.V. Murenetz, *Antibiot. Khimioter.*, 35 (1990) 47–50. (e) U. Hacksell, G.D. Daves, Jr., *Prog. Med. Chem.*, 22 (1985) 1–63.

[3] L. Kiss, L. Somsak, *Carbohydr. Res.*, 291 (1996) 43–52.

[4] (a) I.P. Smoliakova, M. Han, J. Gong, R. Caple, W.A. Smit, *Tetrahedron*, 55 (1999) 4559–4572. (b) I.P. Smoliakova, R. Caple, D. Gregory, W.A. Smit, A.S. Shashkov, O.S. Chizhov, *J. Org. Chem.*, 60 (1995) 1221–1227. (c) I.P. Smoliakova, R. Caple, J.W. Brenny, W.A. Smit, Y.K. Kryschenko, A.S. Shashkov, O.S. Chizhov, M.Z. Krimer, G.V. Morar, Y.B. Kalyan, *Synlett* (1995) 275–276. (d) I.P. Smoliakova, Y.H. Kim, M.J. Barnes, R. Caple, W.A. Smit, A.S. Shashkov, *Mendeleev Commun.*, (1995) 15–16.

[5] W.A. Smit, R. Caple, I.P. Smoliakova, *Chem. Rev.*, 94 (1994) 2359–2382.

[6] M.I. Lazareva, Y.K. Krychenko, A. Hayford, M. Lovdahl, R. Caple, W.A. Smit, *Tetrahedron Lett.*, 39 (1998) 1083–1086.

[7] (a) I.P. Smoliakova, W.A. Smit, A.I. Lutzenko, *Izv. Acad. Nauk SSSR, Ser. Khim.*, (1987) 119–125. (b) I.P. Smoliakova, R. Caple, V.R. Magnuson, V.R. Polyakov, W.A. Smit, A.S. Shashkov, B. Ohinov, *J. Chem. Soc., Perkin Trans. 1*, (1995) 1065–1069.

[8] (a) S. Ramesh, N. Kaila, G. Grewal, R.W. Franck, *J. Org. Chem.*, 55 (1990) 5–7. (b) Y. Ito, T. Ogawa, *Tetrahedron Lett.*, 28 (1987) 2723–2726. (c) S. Ramesh, R.W. Franck, *J. Chem. Soc., Chem. Commun.*, (1989) 960–962. (d) R. Preuss, R.R. Schmidt, *Synthesis* (1988) 694–696. (e) K.C. Nicolaou, C.W. Hummel, N.J. Bockovich, C.-H. Wong, *J. Chem. Soc., Chem. Commun.*, (1991) 870–872. (f) K.C. Nicolaou, T. Ladduwahetty, J.L. Randall, A. Chucholowski, *J. Am. Chem. Soc.*, 108 (1986) 2466–2467. (j) T. Kondo, H. Abe, T. Goto, *Chem. Lett.*, (1988) 1657–1660. (h) G. Grewal, N. Kaila, R.W. Frank, *J. Org. Chem.*, 57 (1992) 2084–2092. (i) D.P. Sebesta, W.R. Roush, *J. Org. Chem.*, 57 (1992) 4799–4802. (k) W.A. Roush, D.P. Sebesta, R.A. James, *Tetrahedron*, 53 (1997) 8837–8852. (l) W.R. Roush, X.F. Lin, *J. Org. Chem.*, 56 (1991) 5740–5742. (m) W.R. Roush, K. Briner, B.S.

Kesler, M. Murphy, D.J. Gustin, *J. Org. Chem.*, 61 (1996) 6098–1099.
[9] (a) G. Jaurand, J.-M. Beau, P. Sinaÿ, *J. Chem. Soc., Chem. Commun.*, (1981) 572–573. (b) M. Pérez, J.-M. Beau, *Tetrahedron Lett.*, 30 (1989) 75–78. (c) A. Kaye, S. Neidle, C.B. Reese, *Tetrahedron Lett.*, 29 (1988) 2711–2714.
[10] R.W. Friesen, S.J. Danishefsky, *J. Am. Chem. Soc.*, 111 (1989) 6656–6660.
[11] J. Gervay, J.M. Peterson, T. Oriyama, S.J. Danishefsky, *J. Org. Chem.*, 58 (1993) 5465–5468.
[12] M. Fieser, L.F. Fieser, *Reagents for Organic Synthesis*, Vol. 5, Wiley, New York, 1975, p. 523.
[13] H.B. Dukstra, *J. Am. Chem. Soc.*, 57 (1935) 2255–2259.