Carbohydrate Research, 254 (1994) 317–324
Elsevier Science B.V., Amsterdam

Note

A synthesis in one reaction vessel of 2,4-diamino sugar precursors from 2,3-dideoxy-2-enopyranos-4-uloses *

Elias A. Couladouros [a], Violetta Constantinou-Kokotou [a], Minas P. Georgiadis [a,†] and George Kokotos [b]

[a] *Chemical Laboratories, Agricultural University of Athens, Iera Odos 75, Athens 11855 (Greece)*
[b] *Department of Chemistry, University of Athens, Panepistimiopolis, Zografou, Athens 15771 (Greece)*

(Received July 30th, 1992; accepted with revision September 8th, 1993)

2,4-Diaminosugars are components of several natural products, especially antibiotics such as kasugamycin[1], prumycin[2], and minosaminomycin[3]. Since their discovery a great number of analogues have been synthesized[4]. Amongst them, deoxygenated derivatives that lack centers for detoxification have shown improved antibiotic properties[5].

Our synthetic interest in aminodeoxy sugars[6,7] has stimulated us to develop a simple and general method for the synthesis of racemic, *N*-protected 2,4-diamino-2,3,4,-trideoxypentapyranosides. The 2,3-dideoxy-2-enopyranos-4-uloses **1–3** (ref 8) were the starting materials for our procedure, since they possess the carbohydrate skeleton, as well as a Michael center and a carbonyl function, which are the ideal entry points for the introduction of the amino functionalities.

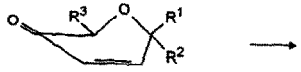
RESULTS AND DISCUSSION

Michael addition of nucleophiles on related enones has already been well studied[9,10]. When the nucleophile is the azide anion, the adduct is stabilized by a reduction in situ of the carbonyl moiety[6,7].

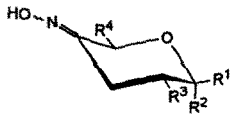
In the procedure presented herein, stabilization of the Michael addition adducts involves another amino functionality, resulting in a stable *N*-bifunctionalized pyran. According to the general Scheme, azide anion was added under acidic conditions to compounds **1–3**, yielding predominantly the thermodynamically preferred equatorial adduct, which by the addition at 0°C of a buffered solution of hydroxylamine hydrochloride afforded the respective oxime within 5 to 15 min. The starting materials **1–3** and their derivatives are racemic mixtures and, for the

* This paper is no. 24 in the series Products from Furans. For previous papers, see ref 8.
† Corresponding author.

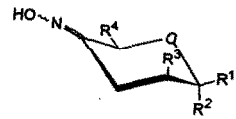
SSDI 0008-6215(93)E0327-W



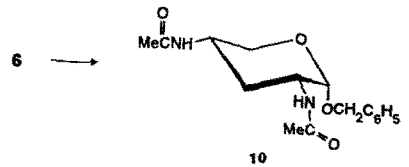
1 R^1 = H, R^2 = OCOMe, R^3 = Me
2 R^1 = OCOMe, R^2 = H, R^3 = Me
3 R^1 = R^3 = H, R^2 = $OCH_2C_6H_5$

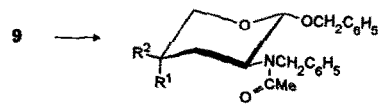


4(*E*) R^1 = H, R^2 = OCOMe, R^3 = N_3, R^4 = Me
5(*E*) R^1 = OCOMe, R^2 = H, R^3 = N_3, R^4 = Me
6(*E*) R^1 = R^4 = H, R^2 = $OCH_2C_6H_5$, R^3 = N_3
6(*Z*) R^1 = R^4 = H, R^2 = $OCH_2C_6H_5$, R^3 = N_3
7(*E*) R^1 = R^4 = H, R^2 = $OCH_2C_6H_5$, R^3 = $NHCH_2C_6H_5$
7(*Z*) R^1 = R^4 = H, R^2 = $OCH_2C_6H_5$, R^3 = $NHCH_2C_6H_5$



8(*E*) R^1 = H, R^2 = OCOMe, R^3 = N_3, R^4 = Me
9(*E*) R^1 = R^4 = H, R^2 = $OCH_2C_6H_5$, R^3 = $NHCH_2C_6H_5$
9(*Z*) R^1 = R^4 = H, R^2 = $OCH_2C_6H_5$, R^3 = $NHCH_2C_6H_5$





11 R^1 = NHCOMe, R^2 = H
12 R^1 = H, R^2 = NHCOMe

Scheme 1.

sake of simplicity, only the D enantiomer is depicted throughout the paper. Reference to α or β anomers refers to those of the D series as depicted in Scheme 1. The relative stereochemistry resulting from the above procedure on several hex-2-enopyranos-4-uloses is presented in the following.

1-*O*-Acetyl- (**1** and **2**) and 1-*O*-benzyl- (**3**) derivatives of 2-enopyranos-4-uloses were chosen as starting materials since they result in suitably protected sugars for further chemical transformations at the anomeric center. The two anomers of 1-*O*-acetyl-2,3,6-trideoxy-DL-hex-2-enopyranos-4-ulose (**1** and **2**) were treated according to the general procedure. The α anomer **1** gave in high yield a mixture of the two C-2 epimeric azido-4(*E*)-oximes **4** and **8** in a 3:1 ratio in accordance with the stereoelectronic effect which governs this kind of addition[11]. The conformation of the products was confirmed from the ^{1}H NMR coupling constants as well as their ^{13}C NMR spectra (see Tables I and II). The calculated coupling constants for H-2 ($J_{1,2}$ 3.2 and $J_{1,2}+J_{2,3a}+J_{2,3e}=13$ Hz) of compound **4** indicated an axial orientation of this proton. The lower values of the analogous coupling constants of

TABLE I

^{1}H NMR data in $CDCl_3$

Compound	Chemical shifts (in ppm)							Coupling constants (Hz)			
	H-1	H-2	H-3e	H-3a	H-5e	H-5a	Other	$J_{1,2}$	$J_{2,3e}$	$J_{2,3a}$	$J_{3e,3a}$
4 [a]	6.1	3.5	3.1	2.1		4.4	$OCOCH_3$ (2.2), CH_3 (1.3)	3.2	$\overset{b}{\longleftrightarrow}$		
5 [a]	5.6	3.5	3.2	1.8		4.3	$OCOCH_3$ (2.1), CH_3 (1.3)	7.6	$\overset{c}{\longleftrightarrow}$		
6(*E*) [d]	4.88	3.68	3.25	2.62	4.55	4.10	$OCH_2C_6H_5$ (4.82, 4.55)	3.0	4.5	5.0	15.0
6(*Z*) [d]	4.90	3.68	2.70	2.54	4.70	4.33	$OCH_2C_6H_5$ (4.80, 4.57)	3.0	4.5	7.0	15.0
7(*E*) [d]	4.98	2.85	3.60	2.10	4.28	3.95	$OCH_2C_6H_5$ (4.80, 4.55) $NHCH_2$ (3.82, 3.75)	3.0	5.0	12.0	15.0
7(*Z*) [d]	4.98	3.00	2.70	2.45	4.85	4.05	$OCH_2C_6H_5$ (4.80, 4.55) $NHCH_2$ (3.82, 3.75)	3.0	5.0	12.0	15.0
8 [a]	5.9	3.5	2.9	2.2		4.5	$OCOCH_3$ (2.1), CH_3 (1.3)	1.9	$\overset{e}{\longleftrightarrow}$		
9(*E*) [d]	4.85	3.00	3.15	2.70	4.35	4.05	$OCH_2C_6H_5$ (4.80, 4.55) $NHCH_2$ (3.92, 3.77)	3.5	4.5	5.0	15.0
9(*Z*) [d]	4.80	3.00	2.72	2.45	4.70	4.02	$OCH_2C_6H_5$ (4.80, 4.55) $NHCH_2$ (3.92, 3.77)	3.5	4.5	5.0	15.0
10 [f]	4.73	4.12	1.99	1.53	3.72	3.32	$OCH_2C_6H_5$ (4.72, 4.43), CH_3CO (1.92, 1.90) NHCO (5.64, 5.30), H-4 (4.12)	3.5	5.2	11.9	11.9

[a] Spectrum was determined at 60 MHz. [b] $J_{1,2} + J_{2,3e} + J_{2,3a} = 13$ Hz. [c] $J_{1,2} + J_{2,3e} + J_{2,3a} = 19$ Hz. [d] Spectrum was determined at 300 MHz. [e] $J_{1,2} + J_{2,3e} + J_{2,3a} = 11$ Hz. [f] $J_{5a,4}$ 10.7, $J_{5e,4}$ 4.7, $J_{5e,3e}$ 1.6 Hz.

TABLE II

^{13}C NMR chemical shifts in $CDCl_3$

Compound	C-1	C-2	C-3	C-4	C-5	$OCOCH_3$	$NHCH_2$	OCH_2	$COCH_3$	CH_3	$NHCOCH_3$
4	90.6	56.5	23.1	153.9	67.3	169.4			20.9	15.9	
5	94.4	58.4	25.9	153.6	72.6	169.2			20.9	16.2	
7(*E*)	96.7	50.3	25.0	154.2	55.1		60.6	69.5			
8	92.3	57.3	23.6	154.0	68.1	169.2			20.9	16.6	
10	95.1	47.1	31.2	44.5	61.3			69.2	23.2		169.5, 169.3

compound **8** ($J_{1,2}$ 1.9 and $J_{1,2}+J_{2,3a}+J_{2,3e}=11$ Hz) suggested an equatorial orientation of H-2. A γ-gauche interaction between C-5 and the axial acetoxy group for compounds **4** and **8** was also revealed by their ^{13}C NMR spectra. The observed difference between the chemical shifts of H-3e and H-3a of compounds **4** and **8** (1.0 and 0.7 ppm, respectively) suggested the formation of *E*-oximes. In addition, the selective formation of the *E*-oxime has also been reported in analogous cases[12].

The β anomer **2** selectively yielded the thermodynamically favored oxime **5** in good yield (70%), while a minor product decomposed during column chromatography. The repulsion between the entering anion and the electron-rich *p*-orbitals of the ring oxygen and the equatorially oriented anomeric oxygen are an additional factor which favors an equatorial attack. The equatorial orientation of the azido group was indicated by the characteristic resonance at 5.6 ppm (d, 1 H, $J_{1,2}$ 7.6 Hz).

Finally, application of the above procedure upon the pentenuloside **3** gave only one epimer at C-2, compound **6**, as a mixture of the *E*- and *Z*-oximes [**6**(*E*) and **6**(*Z*)].

The recorded values for the coupling constants $J_{1,2}$, $J_{2,3a}$, and $J_{2,3e}$ (3.0, 7.0, and 4.5 Hz, respectively) confirmed the equatorial orientation of the azido group. Furthermore, the greatest deviations between the *E*- and *Z*-isomers were observed for the chemical shifts of H-3e and H-5e. As shown in Table I, the H-3e signal of the *E*-isomer of **6** appeared 0.55 ppm downfield from the corresponding signal of the *Z*-form. The *cis* relationship between the oxime and C-5 was clearly discernible by the downfield shift of the H-5e resonance of the *Z*-isomer relative to the *E*-isomer[13]. Thus, benzyl α-pent-2-enuloside **3** and 1-*O*-acetyl-β-hex-2-enulose **1** yielded stereospecifically the equatorial azido derivative, while 1-*O*-acetyl-α-hex-2-enulose yielded both of the 2-epimers, with the equatorial adduct being the predominant one.

An alternative route for the formation of a C–N bond at the Michael center of substrates **1–3** involves the direct introduction of a suitably derivatized amine such as benzylamine. This procedure was applied on the α anomer of benzyl 2,3-dideoxy-DL-pent-2-enopyranosid-4-ulose (**3**), yielding two epimers at C-2, each a mixture of *E*- and *Z*-oximes, namely **7**(*E*) and (*Z*) and **9**(*E*) and (*Z*) derivatives. The

relatively low stereoselectivity (**7**:**9** 1:3) was improved by lowering the reaction temperature. Thus, at −20°C using a two-fold excess of benzylamine, the ratio **7**:**9** increased to **1**:**4**, while at −40°C the stereoselectivity was maximized to 1:10.

Determination of the configuration of compounds **7** and **9** was based on their ^{1}H and ^{13}C NMR spectra and correlation with previous compounds. The equatorial orientation of the amino substituent of compounds **7**(*E*) and **7**(*Z*) was obvious from the recorded values of the coupling constants $J_{2,3a}$ and $J_{2,3e}$ (12 and 5 Hz, respectively). The H-3e proton of the *E*-oxime resonated at lower field (0.90 ppm) than that of the *Z*-oxime, and the *H*-5e proton of the *Z*-oxime appeared further downfield (0.57 ppm) than that of the *E*-oxime[14]. The spin–spin splitting pattern of protons H-2, H-3a, and H-3e of compounds **9** [**9**(*E*) and **9**(*Z*)] suggested an axial position for the amino substituent ($J_{2,3a}$ 5 and $J_{2,3e}$ 4.5 Hz). Also deviations between the *Z*- and *E*-isomers were observed. Thus, the resonances at 3.15 and 4.35 ppm were assigned, respectively, to protons H-3e and H-5e of the *E*-isomer and those at 2.72 and 4.70 ppm were assigned to the corresponding protons of the *Z*-isomer.

The acetyl derivatives of oximes **6** and **9** were reduced using sodium borohydride in the presence of nickel(II) chloride in methanol and the mixture was quenched with acetic anhydride. Precursor **6** afforded only the α-DL-*erythro*-diaminopyranoside **10** in high yield (70% from **6**), while compound **9** afforded both **11** and **12** and a 6:4 ratio. Examination of the ^{1}H NMR spectrum of **10** revealed that the attack of the hydride anion is from the less hindered side. The spin–spin splitting pattern of protons H-1, H-3a, and H-5a confirmed the α-DL-*erythro* configuration. The recorded values for the coupling constants $J_{2,3a}$ $J_{4,3a}$, $J_{4,5a}$, and $J_{1,2}$ (11.9, 11.9, 10.7 and 3.5 Hz, respectively) were in agreement with a *trans*-diaxial orientation of H-2 and H-4. For compound **11** the recorded values $J_{5a,4}$ and $J_{1,2}$ (4.5 and 7.8 Hz) suggested an axial orientation of H-1 and H-2 and an equatorial orientation of H-4, while the corresponding values for **12** (8.0 and 8.1 Hz) suggested an axial orientation for H-1, H-2, and H-4.

In summary, the presented methodology leads to 2,4-*N*-bifunctionalized hexen- or penten-ulose derivatives and *N*-protected 2,4-diamino sugars with high relative stereoselectivity and may find many applications in the synthesis of 2,4-diamino sugars.

EXPERIMENTAL

General methods.—Melting points were determined on a Buchi micro melting-point apparatus and are uncorrected. NMR spectra were recorded on a Varian EM 360 (60 MHz) or on a Bruker AM 300 (300 MHz) spectrometer in deuteriochloroform containing tetramethylsilane as the internal reference. IR spectra were recorded with a Perkin–Elmer 283B spectrophotometer. Column chromatography was performed using silica gel. Elemental analyses were carried out at the University of Thessaloniki.

General procedure for the preparation of 2-azido-2,3-di- and 2,3,6-trideoxy-4-ulose oximes **4–6** *and* **8**.—To a solution of **1–3** (11 mmol, ref 8) in THF (50 mL) and acetic acid (20 mL) was added a solution of sodium azide (3.0 g, 46 mmol) in water (10 mL), in portions, at 0°C. An excess of a solution of hydroxylamine hydrochloride (4.0 g, 58 mmol) and sodium acetate (6.0 g, 73 mmol) in water (10 mL) (pH 4–5) was added in one portion. After completion of the reaction, the mixture was extracted with ether, washed successively with $NaHCO_3$ and water, dried ($MgSO_4$), and chromatographed using 30:70 ether–hexane as the eluant.

*1-O-Acetyl-2-azido-2,3,6-trideoxy-α-*D- *(and β-*L-*)* erythro-*hexopyranos-4-ulose (*E*)-oxime (***4***).*—White crystals (1.83 g, 71%); mp 70–71°C (from ether–hexane); ν_{max}^{KBr} 3440, 1260, 940 (=NOH), 2100 (N_3), 1755 cm^{-1} ($COCH_3$). Anal. Calcd for $C_8H_{12}N_4O_4$ (228.21): C, 42.11; H, 5.30; N, 24.55. Found: C 42.24; H, 5.17; N, 24.31.

*1-O-Acetyl-2-azido-2,3,6-trideoxy-α-*D- *(and β-*L-*)* threo-*hexopyranos-4-ulose (*E*)-oxime (***8***).*—White crystals (0.61 g, yield 24%); mp 74–75°C (from ether–hexane); ν_{max}^{KBr} 3250, 1270, 970 (=NOH), 2110 (N_3), 1770 cm^{-1} ($COCH_3$). Anal. Calcd for $C_8H_{12}N_4O_4$ (228.21): C, 42.11; H, 5.30; N, 24.55. Found: C, 42.35; H, 5.22; N, 24.39.

*1-O-Acetyl-2-azido-2,3,6-trideoxy-β-*D- *(and α-*L-*)* threo-*hexopyranos-4-ulose (*E*)-oxime (***5***).—White crystals (1.72 g, 70%); mp 82–83°C (from ether–hexane); ν_{max}^{KBr} 3250, 1270, 970 (=NOH), 2110 (N_3), 1770 cm^{-1} ($COCH_3$). Anal. Calcd for $C_8H_{12}N_4O_4$ (228.21): C, 42.11; H, 5.30; N, 24.55. Found: C, 42.29; H, 5.09; N, 24.42.*

*Benzyl 2-azido-2,3-dideoxy-α-*D- *(and β-*L-*)* erythro-*pentopyranosid-4-ulose (*E, Z*)-oxime (***6***).*—Compound **6** was prepared as a mixture of *E*- and *Z*-oximes from **3** (0.20 g, 0.1 mmol) following the general procedure described above. The product was obtained as a colorless oil (0.15 g, 65%), ν_{max}^{neat} 3250, 1270, 970 (=NOH), 2110 cm^{-1} (N_3). Anal. Calcd for $C_{12}H_{14}H_4O_3$ (262.27): C, 54.96; H, 5.38; N, 21.36. Found: C, 55.08; H, 5.14; N, 21.12.

*General procedure for the addition of benzylamine to benzyl 2,3-dideoxy-α-*D- *(and β-*L-*) pent-2-enopyranosid-4-ulose.*—To a stirred solution of **3** (0.40 g, 2 mmol) in THF (5 mL), was added benzylamine (0.45 mL, 4 mmol) at −5°C. After 5 min, a solution of hydroxylamine hydrochloride (0.24 g, 3.4 mmol) and sodium acetate (0.54 g, 3.9 mmol) (pH 4–5) in water (10 mL) was added in one portion. After completion of the reaction (confirmed by TLC), CH_2Cl_2 was added, and the organic layer was washed sequentially with $NaHCO_3$ and water, dried ($MgSO_4$), and chromatographed on a silica gel column (1:50) using 60:40 ether–hexane as the eluant.

*Benzyl 2-benzylamino-2,3-dideoxy-α-*D- *(and β-*L-*)* erythro-*pentopyranosid-4-ulose (*E*)-oxime (*7E*).*—White crystals (0.10 g, 16%); mp 70°C (from ether–hexane); ν_{max}^{KBr} 3400–3200, 1255, 940 (=NOH), 3310 cm^{-1} (NH). Anal. Calcd for $C_{19}H_{22}N_2O_3$ (326.40): C, 69.92; H, 6.79; N, 8.58. Found: C, 70.13; H, 6.69; N, 8.51.

*Benzyl 2-benzylamino-2,3-dideoxy-α-*D- *(and β-*L-*)* erythro-*pentopyranosid-4-ulose (*Z*)-oxime (*7Z*).*—White crystals (0.033 g, 5%); mp 68°C (from ether–hexane);

ν_{max}^{KBr} 3400–3200, 1260, 935 (=NOH), 3280 cm^{-1} (NH). Anal. Calcd for $C_{19}H_{22}N_2O_3$ (326.40): C, 69.92; H, 6.79; N, 8.58. Found: C, 70.19; H, 6.61; N, 8.50.

*Benzyl 2-benzylamino-2,3-dideoxy-α-*D*- (and β-*L*-)* threo*-pentopyranosid-4-ulose (*E*)-oxime (***9E***).*—Colorless oil (0.267 g, 41%); ν_{max}^{neat} 3400–3200, 1250, 930 (=NOH), 3270 cm^{-1} (NH). Anal. Calcd for $C_{19}H_{22}N_2O_3$ (326.40): C, 69.92; H, 6.79; N, 8.58. Found: C, 70.14; H, 6.54; N, 8.53.

*Benzyl 2-benzylamino-2,3-dideoxy-α-*D*- (and β-*L*-)* threo*-pentopyranosid-4-ulose (*Z*)-oxime (***9Z***).*—Colorless oil (0.143 g, 22%); ν_{max}^{neat} 3400–3200, 1260, 950 (=NOH), 3270 cm^{-1} (NH). Anal. Calcd for $C_{19}H_{22}N_2O_3$ (326.40): C, 69.92; H, 6.79; N, 8.58. Found: C, 70.16; H, 6.58; N, 8.44.

*Benzyl 2,4-diacetamido-2,3,4-trideoxy-α-*D*- (and β-*L*-)* erythro*-pentopyranoside (***10***).*—The pentopyranoside-4-ulose oxime **6** (0.26 g, 0.1 mmol) in CH_2Cl_2 (4 mL) was treated with Ac_2O (0.4 mmol) for 3 h at room temperature. The mixture was poured into 5% $NaHCO_3$ and extracted with EtOAc and dried ($MgSO_4$). The solvent was evaporated at reduced pressure. The residue was dissolved in MeOH (5 mL), and nickel(II) chloride (0.47, 0.2 mmol) was added at 0°C, followed by the addition of $NaBH_4$ (320 mg, 10 mmol) portionwise. The suspension was stirred for 3 h, then Ac_2O (5 mL) was added. The mixture was treated with $NaHCO_3$, extracted with EtOAc, and dried ($MgSO_4$). After evaporation of the solvent, compound **10** was obtained as white crystals (0.21 g, 70%); mp 194°C; ν_{max}^{KBr} 3300 (NH), 1650 cm^{-1} (NHCO). FABMS: 307 [39%, $(M + H)^+$], 199 (100%). Anal. Calcd for $C_{16}H_{22}N_2O_4$ (306.36): C, 62.73; H, 7.24; N, 9.14. Found: C, 62.98; H, 7.19; N, 9.07.

Products **11** and **12** were prepared by the same procedure as used for **10**.

*Benzyl 4-acetamido-2-(*N*-benzylacetamido)-2,3,4-trideoxy-α-*D*- (and β-*L*-) pentopyranoside (***11***).*—Oil (23 mg, 60%) FABMS: 419 [100%, $(M + 23)^+$], 397 [4%, $(M + H)^+$]. Anal. Calcd for $C_{23}H_{28}N_2O_4$ (396.48): C, 69.68; H, 7.12; N, 7.06. Found: C, 69.79; H, 6.94; N, 6.98.

*Benzyl 4-acetamido-2-(*N*-benzylacetamido)-2,3,4-trideoxy-α-*D*- (and β-*L*-) pentopyranoside (***12***).*—Oil (15 mg, 40%); FABMS: 419 [100%, $(M + 23)^+$], 397 [6%, $(M + H)^+$]. Anal. Calcd for $C_{23}H_{28}N_2O_4$ (396.48): C, 69.68; H, 7.12; N, 7.06. Found: C, 69.84; H, 6.92; N, 7.01.

ACKNOWLEDGMENT

We thank Professor W.A. Gibbons (University of London) for the FABMS spectra.

REFERENCES

1 Y. Suhara, K. Maeda, and H. Umezawa, *J. Antibiot. Ser. A*, 18 (1965) 182–183.
2 S. Ohmura, M. Katagiri, K. Atsumi, T. Hata, A.A. Jukubowski, E.B. Sprines, and M. Tishler, *J. Chem. Soc., Perkin Trans. 1*, (1974) 1627–1631.

3 K. Iinuma, S. Kondo, K. Maeda, and H. Umezawa, *J. Antibiot.*, 28 (1975) 613–615.
4 J.P.H. Verheyden, D.B. Repke, T.C. Tompkins, and J.G. Moffat, in K. Rinehart, Jr., and T. Suami (Eds.), *Aminocyclitol Antibiotics*, American Chemical Society, Washington, D.C., 1980, pp 209–245.
5 (a) S. Umezawa, T. Tsuchiya, R. Muto, and H. Umezawa, *J. Antibiot.*, 24 (1971) 274–275; (b) H. Hashimoto, K. Araki, K-I. Miyazawa, and J. Yoshimura, *Carbohydr. Res.*, 99 (1982) 59–69.
6 M.P. Georgiadis and E.A. Couladouros, *J. Heterocycl. Chem.*, 28 (1991) 1325–1337.
7 V. Constantinou-Kokotou, E.A. Couladouros, M.P. Georgiadis, G. Kokotos, and T. Georgiadis, *Carbohydr. Res.*, 222 (1991) 163–172.
8 M.P. Georgiadis, K.M. Albizati, and T.M. Georgiadis, *Org. Prep. Proced. Int.*, 24 (1992) 95–118.
9 (a) M.P. Georgiadis, *J. Med. Chem.*, 19 (1976) 346–349; (b) G. Grynkiewicz, O. Achmatowicz, Jr., and H. Barton, *Rocz. Chem.*, 51 (1977) 1663–1674.
10 J. Leboul, J. Cleophax, S.D. Gero, A. Rolland, and A. Forchioni, *Tetrahedron*, 33 (1977) 965–968.
11 (a) T. Sakakibara, and R. Sudoh, *J. Org. Chem.*, 42 (1977) 1746–1750; (b) R. Lemieux, T. Nagabhushan, and K. James, *Can. J. Chem.*, 51 (1973) 1–6.
12 J. Herscovici, M-J. Ergon, and K. Antonakis, *J. Chem. Soc., Perkin Trans. 1*, (1988) 1219–1226.
13 M. Rouillard, Y. Girault, M. Decouzon, and M. Azarro, *Org. Magn. Reson.*, 21 (1983) 357.
14 J. Snyder, *Carbohydr. Res.*, 198 (1990) 1–13.
15 J. Ipaktschi, *Chem. Ber.*, 117 (1984) 856.