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BEHAVIOUR OF THE PRIMARY NITRO GROUP UNDER DENITRATION CONDITIONS

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ABSTRACT

Treatment of per-O-acetylated or acetalated glycosylnitromethanes derived from the common hexoses and pentoses with tributyltin hydride and a catalytic amount of a radical initiator [1,1'-azobis(cyclohexanecarbonitrile)] in refluxing benzene easily afforded the corresponding glycosylmethanal oximes in 84-97% yields. Per-O-acetylated C- β -glycopyranosylmethanal oximes were employed for synthesis of versatile C- β glycopyranosyl cyanides of the β -D-gluco, β -D-manno, β -D-galacto, β -D-xylo, and β -Lrhamno configurations.

INTRODUCTION

The utility of the aliphatic nitro group is firmly established, both for the manifold transformations of the functional group and for the creation of new carbon-carbon bonds under extremely mild conditions. However, application of nitro derivatives could be further extended if efficient and selective methods for replacing the nitro group by a hydrogen atom or for converting it into other functional groups become available. In 1981, Ono^1 discovered that the nitro group in tertiary nitro compounds is replaced by a hydrogen atom on treatment with tributyltin hydride (TBTH) in the presence of the radical initiator azoisobutyronitrile (AIBN). Under more drastic conditions and using a large excess of TBTH, this reaction can also be used for denitration of secondary nitro compounds.^{2,3} However, initially, primary nitro groups were considered to be inert to this procedure.³ Later, Witczak and Li⁴ reported denitration of compounds with primary nitro groups effected by reaction with TBTH in the presence of the radical initiator 1,1'-azobis(cyclohexanecarbonitrile) (ABCN). Therefore, as questions remained about the scope of the reaction we decided to focus our attention on the behavior of primary nitro groups of *C*-glycopyranosylnitromethanes under denitration conditions.⁵ Here, we introduce a one-step conversion of easily available *C*-glycosylnitromethanes derived from common hexoses and pentoses to the corresponding oximes under denitration conditions.

RESULTS AND DISCUSSION

effect denitration per-O-acetylated attempts of C-β-In our to glycopyranosylnitromethanes⁶ (2,6-anhydro-1-deoxy-1-nitroalditols) 1-4 in refluxing benzene with TBTH in the presence of ABCN, we found that the nitro group was not replaced by a hydrogen atom but underwent a reduction to give $C-\beta$ glycopyranosylmethanal oximes 9-12 in 85-97% yields (Scheme 1). The reduction products 9-12 (C-β-D-glucopyranosyl-, 9; C-β-D-mannopyranosyl-, 10; C-B-Dgalactopyranosyl-, 11; C- β -D-xylopyranosyl-, 12; methanal oximes) were readily separated from tin compounds in good yields by passing the reaction mixture through silica gel using ethyl acetate and hexane. The same reduction products were formed using AIBN instead of ABCN under otherwise identical reaction conditions. The 2-amino-2-deoxy-B-Dtransformation also occurred with per-O-acetylated glucopyranosylnitromethane (5),^{6g} β -L-rhamnopyranosylnitromethane (6),⁷ α -D-ribofuranosylnitromethane (7),⁸ and 2,3:4,6-di-O-isopropylidene-β-D-mannopyranosylnitromethane (8).⁹ In the all cases, the desired respective products 13-16 were obtained in high vields.

At the reflux temperature of benzene, the reaction provided only one isomer of the desired products 9-16, which were detected by TLC. After cooling and standing at rt, the compounds in solution easily isomerised to the mixture of E/Z oximes 9-16 and gradually decomposed to the corresponding aldehydes. To avoid the latter problem, the oxime group of compounds 9-16 was acetylated with a mixture of acetic anhydride and pyridine



9-13 X = H 17-21 X = Ac







Sc	he	m	е	1
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Compd.	R ¹	R ²	R ³	R ⁴	R ⁵	Yield ^{a)} (%)	E/Z
9	н	OAc	OAc	Н	CH ₂ -OAc	90	8:1
10	OAc	Н	OAc	Н	CH ₂ -OAc	85	1:1
11	н	OAc	Н	OAc	CH ₂ -OAc	92	9:1
12	н	OAc	OAc	Н	Н	97	5:3
13	н	NHAc	OAc	Н	CH ₂ -OAc	88	3:1
14	b)	b)	b)	b)	b)	84	3:2
15	b)	b)	b)	b)	b)	84	2:1
16	b)	b)	b)	b)	b)	90	3:2

a) Yield of isolated E/Z isomers; b) See Scheme 1.



at rt. Acetylation products 17-24 were obtained in very good yields. The crystalline oximes 9-14 and 16 could be stored at rt for several weeks without decomposition. To confirm the structure of the oximes obtained, compound 17 was also prepared from the previously described C- β -D-glucopyranosylmethanal¹⁰ (2,6-anhydro-D-glycero-D-gulo-heptose) by its reaction with hydroxylamine according to the Vasella methodology¹¹ followed by the aforementioned base-catalyzed acetylation (Scheme 2).

The structural assignment of prepared compounds was mainly established by ¹H and ¹³C NMR (including DEPT, COSY and HETCOR) spectral analyses. Especially diagnostic is the appearance of a signal CH=N-OH at $\delta \approx 146-148$ in the ¹³C NMR spectrum (Table 2) of compounds 9-16.^{11,12} The ¹³C chemical shifts for CH=N-OAc in compounds 17-24 (Table 4) appear 19 ppm downfield to those for CH=N-OH in the corresponding compounds 9-16. The ¹H NMR spectra of all compounds 9-14 and 16-22 showed H-H coupling constants corresponding to the ⁴C₁ conformations of the monosaccharide units of 9-13, 16-21 and to the ¹C₄ conformations of 14 and 22, and confirming their β -configuration.¹³

Structures of *E* and *Z* isomers were also confirmed on the basis of ¹H NMR spectra.^{11,12} The proton chemical-shift values of the CH=N signal of *E*-isomers of 9-16 were observed at $\delta \approx 7.2$ -7.4, while those of the corresponding *Z* isomers appeared at higher field ($\delta \approx 6.5$ -6.7). As shown in Scheme 1, the ratio of *E/Z* isomers of *C*- β -glycopyranosylmethanal oximes derived from hexoses is dependent on configuration of their substituent at position 3. When the oxime derivatives possessed a 2,3-threo-configuration, a 3:1 to 9:1 ratio of *E/Z* isomers was observed. However, when derivatives 10, 14, 16 with an axial substituent at position C-3 were examined, smaller *E/Z* ratios

Table 1. ¹H chemical shifts of oximes 9-16

Compd.	1-11	H-2	I-I-3	H-4	H-5	H-6a	ч9-Н	Н-7а	H-7b	Others
(E)-9	7.25 d	4.24 dd	5.06 dd	5.35 dd	5.04 dd	3.97 ddd		4.20 dd	4.10 dd	·10.40 (s, 1H, OH); 2.01, 2.00,
	J _{1,2} 7.1	J _{2,3} 9.9	J _{3,4} 9.6	J _{4,5} 9.3	J _{5,6} 10.1	J _{6,7a} 5.2,	J _{6,7b} 2.4	J _{7a,7b} 12.4		1.96, 1.93 (4s, 12H, 4Me)
(E)-10	7.29 d	4.57 dd	5.46 d	5.22 d	5.19 m	3.93 m		4.23 dd	4.10 dd	10.40 (s, 1H, OH); 2.13, 2.10,
	J _{1,2} 6.0	J _{2,3} 1.3		J _{4,5} 9.8		J _{6,7a} 5.4,	, J _{6,7b} 2.4	J _{7a,7b} 12.3		1.97, 1.92 (4s, 12H, 4Me)
(Z)-10	6.63 d	5.09 dd	5.80 d	5.20 —	5.15 m	3.90 m		4.21 dd	4.10 dd	10.70 (s, 1H, OH); 2.13; 2.10
	J _{1,2} 4.4	J _{2,3} 1.4				J _{6,7a} 5.3,	J _{6,7b} 2.4	J _{7a,7b} 12.3		1.95, 1.90 (4s, 12H, 4Me)
(E)-11	7.26 d	4.22 m	5.24	5.18 m	5.46 dd	4.18 m		4.12 dd	4.09 dd	10.35 (s, 1H, OH); 2.14, 1.98,
	J _{1,2} 7.3			J _{4,5} 1.2	$J_{5,6} < 0.5$	J _{6,7a} 5.7,	J _{6,7b} 7.0	J _{7a,7b} 11.2	2	1.96, 1.93 (4s, 12H, 4Me)
(E)-12	7.23 d	4.08 m	4.98 dd	5.30 t	4.90 m	4.06 m	3.55 dd			10.34 (s, 1H, OH); 2.01, 1.96,
	J _{1,2} 7.1	J _{2,3} 9.7	$J_{3,4}$ 9.5	J _{4,5} 9.5			J _{5,6b} 4.9,	J _{6a,6b} 10.9		1.93 (3s, 9H, 3Me)
(Z)-12	6.58 d	4.95 — 4	4.85 m	5.31 t	4.90 m	4.08 m	3.52 dd			10.51 (s, 1H, OH); 2.02; 1.95
	J _{1,2} 6.3		J _{3,4} 9.3	J _{4,5} 9.3			J _{5,6b} 4.9,	J _{6a,6b} 10.6		1.93 (3s, 9H, 3Me)
(E)-13	7.25 d	4.25	4.12 m	5.25 dd	5.00 dd	3.84 ddd		4.18 m	4.07 dd	10.24 (s, 1H, OH); 6.97 (d,
	J _{1,2} 7.2		J _{3,4} 9.8	J _{4,5} 9.4	J _{5,6} 10.1	$J_{6,7a}5.1,$	J _{6,7b} 2.4	J _{7a,7b} 12.4		J _{3,NH} 8.6, NH); 2.06, 2.01,
							•			1.94, 1.80 (4s, 12H, 4Me)

BEHAVIOR OF THE PRIMARY NITRO GROUP

(continued)

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Table 1. ¹H chemical shifts of oximes 9-16 (continued)

Compd.	I-H	H-2	11-3	H-4	H-5	H-6a	H-6b	H-7a	H-7b	Others
(E)-14	7.26 d	4.50 dd	5.44 dd	5.15 dd	5.00 t	3.75 m		1.20 d, 31	H	10.35 (s, 1H, OH); 2.13,
	J _{1,2} 6.0	$J_{2.3} 1.3$	J _{3,4} 3.4	$J_{4.5} 10.1$	$J_{5,6} 10.1$	J _{6,7} 6.7				2.08, 1.92 (3s, 9H, 3Me)
(Z)-14	6.60 d	5.02 dd	5.80 dd	5.17 dd	4.96 t	3.75 m		1.22 d, 31	H	10.65 (s, 1H, OH); 2.12,
	J _{1,2} 4.5	J _{2,3} 1.4	J _{3,4} 3.5	$J_{4,5} 10.1$	J _{5,6} 10.1	J _{6,7} 6.7	İ			2.09, 1.90 (3s, 9H, 3Me)
(E)-15	7.39 d	4.82 dd	5.53 t	5.38 m	4.30	4.1	0 m			10.30 (s, 1H, OH); 2.10,
	J _{1,2} 7.8	J _{2,3} 4.7	J _{3,4} 4.8							2.03, 1.97 (3s, 9H, 3Me)
(Z)-15	6.74 d	5.33 m	5.77 dd	5.38 m	4.30	4.1	0 m			10.43 (s, 1H, OH); 2.10,
	J _{1,2} 4.4	J _{2,3} 4.4	J _{3,4} 4.8							2.03, 1.97 (3s, 9H, 3Me)
(E)-16	7.40 d	4.49 dd	4.28 dd	4.11 dd	3.75 m	3.24 ddd		3.82 m	3.68 dd	10.28 (s, 1H, OH); 1.48, 1.46
	J _{1.2} 7.3	$J_{2,3} 2.7$	$J_{3,4} 5.3$	$J_{4,5} 7.9$	$J_{5,6} 10.0$	J _{6.7b} 10.2		$J_{7a,7b}$ 10.	۲.	1.34, 1.32 (4s, 12H, 4Me)
(Z)-16	6.68 d	5.11 dd	4.58 dd	4.09 dd	3.74 dd	3.23 ddd		3.83 dd	3.70 dd	10.57 (s, 1H, OH); 1.49, 1.45
	J _{1,2} 4.8	J _{2,3} 2.7	J _{3,4} 5.3	J _{4,5} 7.8	J _{5,6} 10.0	J _{6,7a} 5.7,	J _{6,7b} 10.2	J _{7a,7b} 10.	7	1.33, 1.30 (4s, 12H, 4Me)

Table 2. ¹³C chemical shifts of oximes 9-16

Compd.	C-I	C-2	C-3	C-4	C-5	C-6	C-7	Me, C=O, C acetal
(E)-9	146.7	76.4	70.6	74.1	69.4	75.3	63.1	20.6 (4×), 170.7, 1.70.3, 170.0, 169.9
(E)-10	146.4	75.2	70.5	72.5	66.6	76.7	63.1	20.6 (4×), 170.7, 170.6, 170.2 (2×)
(Z)-10	147.3	72.3	67.4	71.9	66.6	76.5	63.1	20.6 (4×), 170.7, 170.4, 170.2 (2×)
(E)-11	146.9	76.9	67.9	72.0	68.7	74.9	62.6	20.6 (4×), 170.6 (2×), 170.2 (2×)
(E)-12	146.9	77.0	70.7	73.6	69.8	6.99		20.6 (3×), 170.2 (3×)
(Z)-12	146.9	73.5	70.4	70.9	69.8	60.9		20.6 (3×), 170.2 (3×)
(E)-13	147.5	77.5	52.5	74.3	70.8	76.3	63.2	22.9, 20.6 (3×), 170.7 (2×), 170.0 (2×)
(E)-14	146.7	74.9	71.2	72.5	70.8	75.1	18.0	20.5 (3×), 170.3 (3×)
(Z)-14	147.7	72.3	71.2	71.8	69.3	74.6	18.0	20.7 (3×), 170.5 (3×)
(E)-15	146.8	77.8	73.2	73.6	79.1	64.4		20.4 (3×), 170.1, 170.0 (2×)
(Z)-15	148.2	74.4	72.7	73.0	78.3	64.3		20.6 (3×), 170.7 (3×)
(E)-16	147.5	76.7	76.7	75.1	73.5	70.2	62.3	28.5 (2×), 26.1, 19.1, 110.0, 109.7, 99.9
(Z)-16	148.0	71.4	76.5	74.4	73.4	70.0	61.9	28.5 (2×), 27.3, 19.3, 111.0, 109.7, 99.9

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7.12 (d, J_{3,NII} 8.6, NII); 2.14, 2.10, 2.09, 1.97, 2.12, 1.51, 1.50, 1.33, 2.10, 2.08, 2.05, 2.01, 2.07, 2.02, 1.98, 1.97 2.13, 2.11, 2.05, 1.92 2.13, 2.10, 2.07, 2.04 2.14, 2.11, 1.99, 1.98, 1.94 (5s, 1511, 5Mc) 2.10, 2.04, 2.01, 1.81 1.92 (5s, 1511, 5Me) I.32 (5s, 1511, 5Mc) 1.97 (5s, 1511, 5Mc) (4s, 12H, 4Mc) (4s, 1211, 4Me) (4s, 12H, 4Me) Others 4.24 dd 4.11 dd 4.24 dd 4.16 dd 4.13 dd 4.08 dd 4.26 dd 4.12 dd 3.72 m 97-11 1.23 d, 3H $J_{6,7a}$ 5.7, $J_{6,7b}$ 2.4 $J_{7a,7b}$ 12.4 $J_{2,3}$ 9.3 $J_{3,4}$ 10.2 $J_{4,5}$ 3.2 $J_{5,6}$ 1.2 $J_{6,7a}$ 5.7, $J_{6,7b}$ 7.0 $J_{7a,7b}$ 11.4 $J_{2,3}$ 9.9 $J_{3,4}$ 9.5 $J_{4,5}$ 9.5 $J_{5,6}$ 9.9 $J_{6,7a}$ 5.2, $J_{6,7b}$ 2.4 $J_{7a,7b}$ 12.4 $J_{1,2}$ 7.1 $J_{2,3}$ 10.2 $J_{3,4}$ 9.6 $J_{4,5}$ 9.6 $J_{5,6}$ 9.9 $J_{6,7a}$ 5.2, $J_{6,7h}$ 2.4 $J_{7a,7b}$ 12.4 3.87 dd 11-7a $J_{1,2}$ 6.9 $J_{2,3}$ 9.8 $J_{3,4}$ 9.6 $J_{4,5}$ 9.5 $J_{5,6b}$ 10.6 $J_{5,6a}$ 5.6 $J_{6a,6b}$ 11.2 J_{6,7a} 5.7, J_{7a,7b} 11.5 4.30 dd 5.04 dd 5.35 dd 4.98 ddd 4.12 dd 3.60 dd 4.20 — 4.35 m 11-6b 5.03 dd 3.93 ddd 4.07 ddd $J_{2,3} 1.0 J_{3,4} 2.5 J_{4,5} 10.2 J_{5,6} 9.8 J_{6,7} 6.2$ 4.42 dd 5.22 dd 5.28 dd 5.49 dd 4.34 m 4.02 m 3.30 dt 4.72 dd 5.53 dd 5.18 dd 5.03 dd 3.85 m 11-6a 5.21 m 4.30 m 3.78 m 5.09 t <u>11-5</u> 4.80 dd 5.55 dd 5.24 m 4.24 dd 4.23 m 5.28 t 5.43 t 4.17 dd J4,5 7.7 5.07 dd 5.39 t J_{2,3} 5.2 J_{3,4} 5.1 J_{4,5} 5.1 I-1-4 4.71 dd 4.38 dd J_{3,4} 5.3 $J_{2,3} 1.3 J_{3,4} 3.0$ 5.00 dd 5.63 t II-3 4.42 dd J_{2,3} 2.8 H-2 J_{1,2} 5.4 J_{1,2} 7.1 J1,2 7.4 $J_{1,2} 7.0$ J_{1,2} 5.6 7.70 d $J_{1,2} 6.8$ 7.65 d 7.74 d 7.71 d 7.68 d 7.62 d 7.80 d 7.67 d H-1 Compd. 17 18 19 20 53 33 24 21

Table 3. ¹H chemical shifts of per-O-acetylated oximes 17-24

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Table 4. ¹³C chemical shifts of per-O-acetylated oximes 17-24

Compd.	C-1	C-2	C-3	C-4	C-5	C-6	C-7	Me, C=O, C acetal
(E)-17	155.4	75.6	70.2	73.7	69.1	76.5	62.9	20.6 (4×), 19.2; 170.7, 170.5, 170.2, 170.1; 168.1
(E)-18	1.55.1	74.8	70.0	72.3	66.5	77.1	63.2	20.6 (4×), 19.3; 170.7, 170.6, 170.2 (2×), 168.3
(E)-19	155.4	76.1	67.5	71.6	68.6	75.3	62.5	20.5 (4×), 19.2; 170.6 (3×), 170.1, 168.2
(E)-20	155.6	76.2	70.3	73.2	69.6	67.1		20.6 (3×), 19.3; 170.2 (4×)
(E)-21	155.6	77.5	52.3	73.8	69.6	76.6	63.0	22.8, 20.6 (3×), 19.2; 170.7 (5×)
(E)-22	155.2	74.5	70.2	72.2	68.3	75.2	18.0	20.6 (3×), 19.3; 170.6, 170.3 (2×), 168.4
(E)-23	155.4	76,9	73.0	73.4	80.1	64.2		20.6(3×), 19.4; 170.7, 170.1, 169.9, 168.4
(E)-24	155.7	76.8	76.4	74.4	73.2	70.4	62.3	19.3; 168.7; 29.4, 28.5, 26.7, 19.1; 110.4, 100.0



Figure 1

were obtained (3:2 to 1:1). This observation can be explained by a hydrogen bond between the oxime hydroxyl group and the axial oxygen atom at position C-3. As illustrated in Figure 1, the formation of the hydrogen bond stabilizes the less favored Z isomers; consequently the pertinent E/Z ratios were decreased. Occurrence of the hydrogen bond was also recognized by means of IR spectroscopy, and supported by the fact that only E isomers were obtained for derivatives 17-24 with an acetylated oxime moiety.

Under conditions whereby TBTH selectively reduces a primary nitro group to an oxime, other common functionalities such as ester, amide, acetal, amino, cyano, formyl, sulfinyl, and olefinic groups have been shown not to be affected.^{3,14} This selectivity could enhance the utility of the present reaction in organic synthesis. The high selectivity of the reaction suggests that it may be a free-radical chain reaction.^{1,14b} This suggestion is further confirmed by facts that (1) the reaction proceeds slowly in the absence of a radical initiator ABCN and (2) mixtures of primary nitro compounds and TBTH are almost completely unreactive at low temperatures (20-30 °C) in the presence or absence of ABCN. No occurrence of the initiation step at low temperatures suggests the possibility that tin hydride by itself cannot act as an electron-transfer reagent.¹⁵ However, it is also conceivable that the uninitiated reaction can be initiated thermally by homolysis of the small amounts of hexabutyldistannane that appear to be always present in the starting TBTH.¹⁵ The reduction reaction of glycosylnitromethanes by TBTH can be proposed to proceed *via* the following addition-elimination mechanism (Scheme 3).

The first step is the formation of the alkyl(trialkyltinoxy)nitroxyl radical, which is generated by an addition of the tributyltin radical to the nitro compound.^{16,17} The subsequent step is a cleavage of the alkyl(trialkyltinoxy)nitroxyl radical affording the trialkyltinoxyl radical and a nitroso compound, which easily isomerizes into the corresponding oxime. The selectivity of the reaction is derived from the strong electron-accepting power of the nitro group and the formation of the alkyl(trialkyltinoxy)nitroxyl radical shown in Scheme 3.



Scheme 3

The reason for inactivity of primary nitro compounds in the denitration reaction is not yet clear, but a possible reason is that their carbon-nitrogen bond is harder to break than that of tertiary and activated secondary nitro compounds (α -nitroketones, α -nitroesters or α -nitroalkenes).^{2a} The fact that inactivated secondary nitro groups are denitrated under more drastic conditions using a large excess of TBTH, also confirms the previous hypothesis.

The use of aforementioned per-O-acetylated C- β -glycopyranosylmethanal oximes for synthesis of versatile C- β -glycopyranosyl cyanides was also carried out. As shown in Scheme 4, treatment of per-O-acetylated C-glycopyranosylmethanal oximes 17-22 with sodium acetate in acetic acid at 90 °C for 2-4 h easily afforded high yields of the corresponding C-glycopyranosyl cyanides 25-30. The most widely used methods for the preparation of C-glycopyranosyl cyanides give the 1,2-*trans* (α -D) isomers.¹⁸ The transformation reported here provides C-glycopyranosyl cyanides with the 1,2-*cis* (β -D) configuration and is an alternative to their preparation from C-glycosylnitromethanes by treatment with PCl₃.¹⁹

In summary, the treatment of per-O-acetylated C-glycopyranosyl- and -furanosylnitromethanes with TBTH in the presence of a radical initiator provides a general and convenient one-step synthesis of C-glycopyranosyl- and -furanosylmethanal



a) The resulting formula depicts the D enantiomer of 30.

oximes. Owing to unreactivity of a series of common functionalities under the reaction conditions employed,^{3,14} the method seems to be applicable to compounds containing other functional groups. Since *C*- β -glycosylmethanal oximes are convenient synthons for a number of subsequent reactions including cycloadditions, hydrolysis to aldehydes, and other reactions with various donors to give more complex carbohydrate mimics, their easy availability offers interesting prospects for synthesis of *C*-disaccharides and other *C*- β -glycosyl compounds.

EXPERIMENTAL

General methods and materials. Melting points were measured on a Kofler stage. Optical rotations were measured with a Perkin-Elmer 141 polarimeter at 20 °C. Microanalyses were obtained using a Perkin-Elmer 240 instrument. NMR spectra were recorded at 295 °K on a Bruker AM 300 spectrometer (300.13 MHz for ¹H and 75.47 MHz for ¹³C). TLC was run on glass plates precoated with silica gel L (0.005–0.040 mm, Lachema, Brno, Czech Republic); detection was effected by spraying the chromatograms

with 10% ethanolic sulfuric acid and charring them on a hot plate. Flash chromatography was performing using silica gel (0.040–0.100 mm, Lachema).

Commercial TBTH, AIBN and ABCN (Aldrich) were used. β -D-glycosylnitromethanes 1-8 were obtained according to published procedures.⁶⁻⁹

General procedure for preparation of C-glycosylmethanal oximes. A mixture of per-O-acetylated C-glycosylnitromethane (1.28 mmol), TBTH (1.2 mL, 4.50 mmol), and ABCN (30 mg) in benzene (5 mL) was stirred at 80 °C for 2 h. After addition of another portion of ABCN (20 mg), reflux was continued for 1-4 h until no starting material could be detected (TLC, 3:2 petroleum ether-ethyl acetate). The reaction mixture was then cooled to room temperature and the solvent removed under reduced pressure. Flash column chromatography of the residue (silica gel) afforded C-glycosylmethanal oximes.

3,4,5,7-Tetra-O-acetyl-2,6-anhydro-D-glycero-D-gulo-heptose oxime (2,3,4,6-tetra-O-acetyl- β -D-glucopyranosylmethanal oxime, 9). Yield 432 mg (90%), mp 155-157 °C (from hexane-ethyl acetate), $[\alpha]_D$ +22.0° (c 1.0, acetone); ratio of E/Z isomers 8:1. IR spectrum (KBr) v (cm⁻¹): 3428 (OH).

Anal. Calcd for C₁₅H₂₁NO₁₀: C, 48.00; H, 5.64; N, 3.73. Found: C, 48.25; H, 5.50; N, 3.71.

3,4,5,7-Tetra-O-acetyl-2,6-anhydro-D-glycero-D-galacto-heptose oxime (2,3,4,6-tetra-O-acetyl- β -D-mannopyranosylmethanal oxime, 10). Yield 408 mg (85%), mp 152-154 °C (from hexane-ethyl acetate), $[\alpha]_D$ +35.0° (c 1.0, acetone); ratio of *E/Z* isomers 1:1. IR spectrum (KBr) v (cm⁻¹): 3423 (OH).

Anal. Calcd for C₁₅H₂₁NO₁₀: C, 48.00; H, 5.64; N, 3.73. Found: C, 48.20; H, 5.49; N, 3.73.

3,4,5,7-Tetra-O-acetyl-2,6-anhydro-D-glycero-L-manno-heptose oxime (2,3,4,6-tetra-O-acetyl- β -D-galactopyranosylmethanal oxime, 11). Yield 441 mg (92%), mp 170-172 °C (from hexane-ethyl acetate), $[\alpha]_D$ +39.0° (c 1.0, acetone); ratio of *E/Z* isomers 9:1. IR spectrum (KBr) v (cm⁻¹): 3332 (OH).

Anal. Calcd for C₁₅H₂₁NO₁₀: C, 48.00; H, 5.64; N, 3.73. Found: C, 48.12; H, 5.58; N, 3.67.

3,4,5-Tri-O-acetyl-2,6-anhydro-D-gulose oxime (2,3,4-tri-O-acetyl- β -D-xylopyranosylmethanal oxime, 12). Yield 376 mg (97%), mp 160-163 °C (from hexaneethyl acetate), [α]_D +23.1° (*c* 0.5, acetone); ratio of *E*/*Z* isomers 5:3. IR spectrum (KBr) v (cm⁻¹): 3365, 3271 (OH).

Anal. Calcd for C₁₂H₁₇NO₈: C, 47.53; H, 5.65; N, 4.62. Found: C, 47.64; H, 5.69; N, 4.57.

3,4,5-Tri-O-acetyl-2,6-anhydro-7-deoxy-L-*glycero-L-galacto-***heptose** oxime (2,3,4-tri-O-acetyl-β-L-rhamnopyranosylmethanal oxime, 14). Yield 340 mg (84%) as

a syrup, $[\alpha]_D -27.5^\circ$ (c 1.0, acetone); ratio of E/Z isomers 3:2. IR spectrum (KBr) v (cm⁻¹): 3341 (OH).

Anal. Calcd for $C_{13}H_{19}NO_8$: C, 49.21; H, 6.04; N, 4.41. Found: C, 49.33; H, 6.00; N, 4.32.

3,4,6-Tri-O-acetyl-2,5-anhydro-D-altrose oxime (2,3,5-tri-O-acetyl- α -D-ribofuranosylmethanal oxime, 15). Yield 325 mg (84%) as a syrup, $[\alpha]_D$ -4.5° (c 1.0, acetone); ratio of E/Z isomers 2:1.

Anal. Calcd for C₁₂H₁₇NO₈: C, 47.53; H, 5.65; N, 4.62. Found: C, 47.70; H, 5.79; N, 4.45.

2,6-Anhydro-3,4:5,7-di-*O*-isopropylidene-D-glycero-D-galacto-heptose oxime (2,3:4,6-di-*O*-isopropylidene- β -D-mannopyranosylmethanal oxime, 16). Yield 331 mg (90%), (ratio of *E/Z* isomers 3:2). Fractional crystallization provided *Z* isomer, mp 157-160 °C (from heptane-ethyl acetate); $[\alpha]_D$ +58.0° (*c* 1.0, acetone). IR spectrum (KBr) v (cm⁻¹): 3251 (OH).

Anal. Calcd for C₁₃H₂₁NO₆: C, 54.35; H, 7.37; N, 4.88. Found: C, 54.23; H, 7.51; N, 4.75.

3-Acetamido-4,5,7-tri-*O*-acetyl-2,6-anhydro-3-deoxy-D-glycero-D-gulo-heptose oxime (2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy- β -D-glucopyranosylmethanal oxime, 13). A mixture of per-*O*-acetyl-2-acetamido-2-deoxy- β -D-glucopyranosylnitromethane (195 mg, 0.5 mmol), TBTH (0.4 mL, 1.5 mmol), and ABCN (20 mg) in benzene (5 mL) was refluxed for 8 h. The reaction mixture was cooled to room temperature, and the solvent was removed under reduced pressure. Flash chromatography of the residue on silica gel (1:4 petroleum ether-ethyl acetate) afforded oxime 13 (yield 165 mg, 88%). Crystallization of 13 from a mixture of heptane-ethyl acetate (1:1) gave needles. Mp 201-204 °C (from heptane-ethyl acetate), $[\alpha]_D$ +29.0° (*c* 1.0, acetone); ratio of *E/Z* isomers 4:1. IR spectrum (KBr) v (cm⁻¹): 3328 (OH).

Anal. Calcd for $C_{105}H_{22}N_2O_9$: C, 48.13; H, 5.92; N, 7.48. Found: C, 48.18; H, 5.96; N, 7.29.

General procedure for acetylation of C-glycosylmethanal oximes. Acetic anhydride (0.5 mL) and pyridine (0.4 mL) were added to a solution of C-glycosylmethanal oximes 9-16 (0.4 mmol) in CHCl₃ (10 mL) at 0 °C. After 1 day standing at rt, cold aqueous M HCl (10 mL) was added. The organic phase was washed with a second portion of cold aqueous M HCl (10 mL) and then twice with saturated aqueous NaHCO₃ (10 mL) and water (10 mL) and then dried (Na₂SO₄). Removal of the solvent gave a syrup, which was crystallized by triturating it with a mixture of hexane and ethyl acetate. Collection by filtration and recrystallization from heptane-ethyl acetate afforded the per-O-acetylated Cglycosylmethanal oximes 17-24 in 88-95% yields. (E)-3,4,5,7-Tetra-O-acetyl-2,6-anhydro-D-glycero-D-gulo-heptose oxime acetate (N-acetoxy-2,3,4,6-tetra-O-acetyl- β -D-glucopyranosylmethanimine, 17). Yield 154 mg (92%), mp 151-153 °C; [α]_D +26.0° (c 1.0, acetone).

Anal. Calcd for C₁₇H₂₃NO₁₁: C, 48.92; H, 5.55; N, 3.36. Found: C, 48.78; H, 5.51; N, 3.34.

(E)-3,4,5,7-Tetra-O-acetyl-2,6-anhydro-D-glycero-D-galacto-heptose oxime acetate (N-acetoxy-2,3,4,6-tetra-O-acetyl- β -D-mannopyranosylmethanimine, 18). Yield 149 mg (89%) as a syrup, $[\alpha]_D$ +3.0° (c 1.0, acetone).

Anal. Calcd for C₁₇H₂₃NO₁₁: C, 48.92; H, 5.55; N, 3.36. Found: C, 48.99; H, 5.42; N, 3.24.

(E)-3,4,5,7-Tetra-O-acetyl-2,6-anhydro-D-glycero-L-manno-heptose oxime acetate (N-acetoxy-2,3,4,6-tetra-O-acetyl- β -D-galactopyranosylmethanimine, 19). yield 159 mg (95%), mp 139-140 °C; [α]_D +45.0° (c 1.0, acetone).

Anal. Calcd for C₁₇H₂₃NO₁₁: C, 48.92; H, 5.55; N, 3.36. Found: C, 48.83; H, 5.61; N, 3.19.

(E)-3,4,5,7-Tetra-O-acetyl-2,6-anhydro-D-gulose oxime acetate (N-acetoxy-2,3,4-tri-O-acetyl- β -D-xylopyranosylmethanimine, 20): yield 134 mg (97%), mp 139-141 °C; $[\alpha]_D$ +4.5° (c 1.0, acetone).

Anal. Calcd for C₁₄H₁₉NO₉: C, 48.70; H, 5.55; N, 4.06. Found: C, 48.69; H, 5.50; N, 3.95.

(*E*)-3-Acetamido-4,5,7-tri-*O*-acetyl-2,6-anhydro-3-deoxy-D-*glycero*-D-*gulo*-heptose oxime acetate (2-acetamido-*N*-acetoxy-3,4,6-tri-*O*-acetyl-2-deoxy- β -D-glucopyranosylmethanimine, 21). Yield 156 mg (94%), mp 177-179 °C; [α]_D +13.5° (*c* 1.0, acetone).

Anal. Calcd for C₁₇H₂₄N₂O₁₀: C, 49.04; H, 5.81; N, 6.73. Found: C, 49.18; H, 5.96: N, 6.59.

(E)-3,4,5-Tri-O-acetyl-2,6-anhydro-7-deoxy-L-glycero-L-galacto-heptose oxime acetate (N-acetoxy-2,3,4-tri-O-acetyl- β -L-rhamnopyranosylmethanimine, 22). Yield 135 mg (94%), mp 130-132 °C; [α]_D +3.4° (c 1.0, acetone).

Anal. Calcd for C₁₅H₂₁NO₉: C, 50.14; H, 5.89; N, 3.90. Found: C, 50.23; H, 6.00; N, 3.78.

(E)-3,4,6-Tri-O-acetyl-2,5-anhydro-D-altrose oxime acetate (N-acetoxy-2,3,5-tri-O-acetyl- α -D-ribofuranosylmethanimine, 23). Yield 134 mg (97%) as a syrup. [α]_D +41.0° (c 1.0, acetone).

Anal. Calcd for C₁₄H₁₉NO₉: C, 48.70; H, 5.55; N, 4.06. Found: C, 48.85; H, 5.67; N, 3.90.

(E)-2,6-anhydro-3,4:5,7-di-O-isopropylidene-D-glycero-D-galacto-heptose oxime acetate (N-acetoxy-2,3:4,6-di-O-isopropylidene-β-D-mannopyranosyl-methanimine, 24). Yield 121 mg (92%), mp 156-158 °C. [α]_D-30.5° (c 1.0, acetone).

Anal. Calcd for C₁₅H₂₃NO₇: C, 54.70; H, 7.04; N, 4.25. Found: C, 54.59; H, 7.21; N, 4.17.

Preparation of oxime 17 from β -D-glucopyranosylmethanal. To a stirred prepared solution of C- β -D-glucopyranosylmethanal, freshly from β-Dglucopyranosylnitromethane (669 mg, 3 mmol) by ozonolysis,¹⁰ in water (2 mL) was added hydroxylammonium hydrochloride (417 mg, 6 mmol) and a 0.5 M NaOMe/MeOH (8 mL). Stirring was continued for 5 h at 60 °C, then the reaction mixture was The residue was dissolved in anhydrous pyridine (5 mL) and added concentrated. dropwise to a mixture of pyridine (20 mL) and acetic anhydride (10 mL) at 0 °C. The reaction mixture was stirred overnight at rt, poured into 0.5 M HCl (50 mL), and the mixture was then extracted with chloroform (20 mL). The organic phase was washed with 0.5 M HCl (10 mL), saturated aqueous NaHCO₃ (2 × 10 mL) and water (30 mL), then dried (Na₂SO₄). Removal of the solvent gave a syrup, which was subjected to column chromatography (1:1 petroleum ether-ethyl acetate) affording 17 in an overall 20% yield (250 mg).

General procedure for preparation of C-glycopyranosyl cyanides. A mixture of a per-O-acetylated C-glycopyranosylmethanal oxime acetate (0.2 mmol) and sodium acetate (0.2 mmol) in acetic acid (4 mL) was heated at 100 °C for 2-5 h. After cooling to ambient temperature, a mixture of water (10 mL) and chloroform (20 mL) was added. The organic phase was separated, and the aqueous phase was extracted with chloroform (10 mL). The combined organic phase was washed with saturated aqueous NaHCO₃ (10 mL) and water (2 × 20 mL), and then dried (Na₂SO₄). Solvent was evaporated to give a syrup of a C-glycopyranosyl cyanide, which was crystallized from a mixture of diethyl ether and hexane. ¹H and ¹³C NMR spectra of the cyanides 25-27 were in agreement with the published data.^{19,20}

3,4,5,7-Tetra-O-acetyl-2,6-anhydro-D-glycero-D-gulo-heptononitrile (2.3,4,6-tetra-O-acetyl- β -D-glucopyranosyl cyanide, 25). Yield 64 mg (90%). mp 114-115 °C: Lit.¹⁹ 113-114 °C; Lit.²⁰ 114-115 °C; Lit.²¹ 116 °C.

3,4,5,7-Tetra-O-acetyl-2,6-anhydro-D-glycero-D-galacto-heptononitrile (2.3,4,6-tetra-O-acetyl- β -D-mannopyranosyl cyanide, 26). Yield 63 mg (88%). mp 139-141 °C: Lit.¹⁹ 141-142 °C; Lit.²⁰ 142-144 °C.

3,4,5,7-Tetra-O-acetyl-2,6-anhydro-D-*glycero-L-manno*-heptononitrile (2,3,4,6tetra-O-acetyl-β-D-galactopyranosyl cyanide, 27). Yield 66 mg (93%). mp 170-171 °C: Lit.¹⁹ 167-168 °C, Lit.²⁰ 169-170 °C.

3,4,5-Tri-O-acetyl-2,6-anhydro-D-*gulo*-hexononitrile (2,3,4-tri-O-acetyl-β-Dxylopyranosyl cyanide, 28). Yield 51 mg (89%), mp 130-132 °C; Lit.¹⁹ 132-133 °C: Lit.²² 133 °C. 3-Acetamido-4,5,7-tri-*O*-acetyl-2,6-anhydro-3-deoxy-D-glycero-D-gulo-heptononitrile (2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranosyl cyanide, 29). Yield 68 mg (95%). mp 184-186 °C. ¹³H NMR (acetone-d₆): δ 7.44 (d, 1H, $J_{3,NH}$ 8.8 Hz. NH); 5.31 (dd, 1H. $J_{3,4}$ 10.2 Hz. $J_{4,5}$ 9.5 Hz, H-4); 5.04 (dd, 1H. $J_{5,6}$ 10.1 Hz. H-5); 4.92 (d, 1H, $J_{2,3}$ 10.8 Hz. H-2); 4.29 (m. 1H, H-3); 4.23 (dd, 1H, $J_{6,7a}$ 5.1 Hz. $J_{7a,7b}$ 12.6 Hz. H-7a): 4.11 (dd, 1H. $J_{6,7b}$ 2.2 Hz, H-7b); 3.95 (ddd, 1H, H-6); 2.02, 1.99, 1.97, 1.89 (4s, 12H. 4 Me of Ac). ¹³C NMR (acetone-d₆): δ 170.7 (3×), 169.9 (4 CO of Ac); 116.6 (CN); 77.2 (C-6); 73.1 (C-4); 69.0 (C-5); 67.5 (C-2); 62.6 (C-7); 52.9 (C-3); 22.8, 20.6 (3×).

Anal. Calcd for C₁₅H₂₀N₂O₈: C, 50.56; H, 5.66; N, 7.86. Found: C, 50.71; H, 5.76; N, 7.69.

3,4,5-Tri-*O*-acetyl-2,6-anhydro-7-deoxy-L-*glycero*-L-*galacto*-heptononitrile (2,3,4tri-*O*-acetyl-β-L-rhamnopyranosyl cyanide, 30). Yield 55 mg (92%), mp 129-130°C. ¹H NMR (acetone-d₆): δ 5.64 (dd, 1H, $J_{2,3}$ 1.3 Hz, $J_{3,4}$ 3.5 Hz, H-3); 5.16 (dd, 1H, $J_{4,5}$ 10.1 Hz, H-4); 5.13 (d, 1H, H-2); 4.99 (t, 1H, $J_{5,6}$ 9.8 Hz, H-5); 3.71 (m, 1H, H-6); 2.20, 2.02, 1.94 (3s, 9H, 3 Me of Ac); 1.20 (d, 3H, $J_{6,7}$ 6.2 Hz, 3H-7). ¹³C NMR (acetone-d₆): δ 170.2, 170.1, 169.9 (3 CO of Ac); 115.6 (CN); 75.6 (C-6); 71.1 (C-4); 70.5 (C-3); 69.1 (C-5); 67.1 (C-2); 20.6, 20.4, 20.3 (3 Me of Ac); 17.8 (C-7).

Anal. Calcd for C₁₃H₁₇NO₇: C, 52.17; H, 5.73; N, 4.68. Found: C, 52.31; H, 5.86; N, 4.65.

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