SYNTHESIS OF 1,6-ANHYDRO-2,3,4-TRIDEOXY-2,3-EPIMINO- AND 1,6-ANHYDRO-2,3,4-TRIDEOXY-3,4-EPIMINO-β-D-HEXOPYRANOSES AND THEIR NMR AND INFRARED SPECTRA

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Dedicated to Professor Miloslav Černý on the occasion of his 75th birthday.

A complete series of 2,3,4-trideoxy-2,3-epimino and 2,3,4-trideoxy-3,4-epimino derivatives of 1,6-anhydro-β-D-hexopyranoses were prepared by lithium aluminium hydride reduction of vicinal *trans* azido tosylates. Unusual formation of the aziridine ring from precursors with the *trans*-diequatorial arrangement of the reacting groups was observed. NMR and infrared spectra of the aziridines are discussed.

Keywords: Anhydrosugars; 1,6-Anhydro-β-D-hexopyranoses; Azides; Aziridines; NMR spectroscopy; Infrared spectroscopy; Pyramidal inversion; Carbohydrates; Aminosugars.

During the recent years our interest in aziridine derivatives of carbohydrates[1–5] (called also epimines) as useful chiral synthons led us to the synthesis of the complete series of aziridine derivatives of 1,6-anhydro-β-D-hexopyranoses. The synthesis involved the reductive cyclization[2,6–8] of suitable vicinal *trans* azido tosylates using lithium aluminium hydride or the Mitsunobu reaction[1,9] of suitable vicinal *trans* benzylamino hydroxy derivatives as the key steps of the synthesis. Now we wish to report an extension of the former method to the synthesis of 1,6-anhydro-2,3,4-trideoxy-2,3-epimino- and 1,6-anhydro-2,3,4-trideoxy-3,4-epimino-β-D-hexopyranoses as the complete series of four configurational isomers.

Our approach can be characterized as the transformation of an oxirane derivative into the aziridine derivative through the change of configuration on both carbon atoms of the oxirane ring (Scheme 1).

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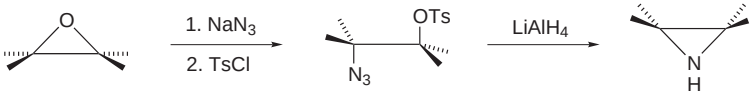
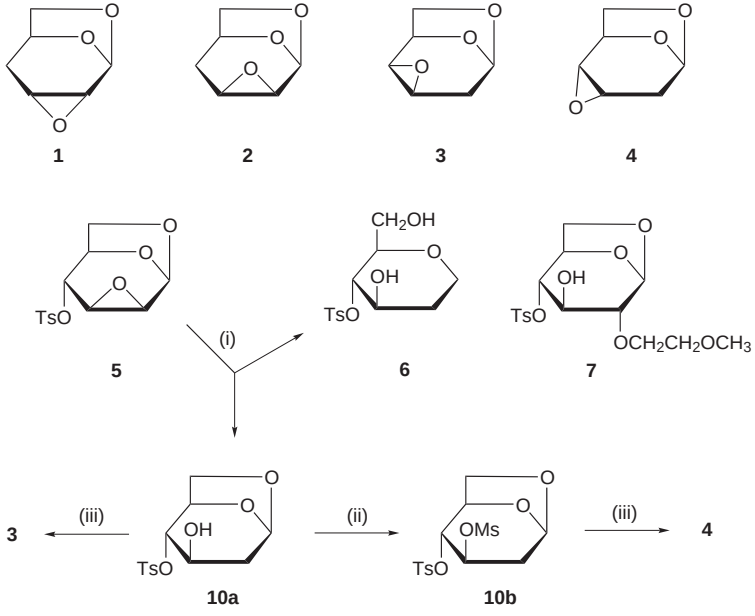


SCHEME 1

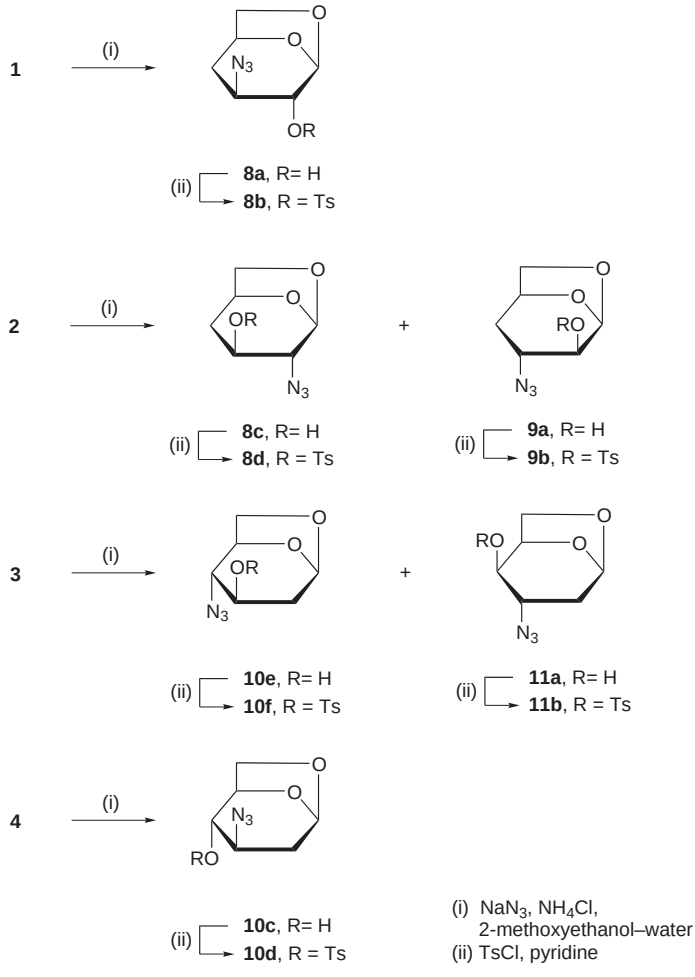
Starting dianhydro derivatives **1** and **2** were prepared according to the procedures described in literature[10,11]. Since procedures reported[12] in literature for the preparation of dianhydro derivatives **3** and **4** are tedious and afford low yields, we decided to prepare these compounds by an alternative reaction sequence from dianhydro derivative **5**. Reduction of compound **5** with diborane generated in situ from sodium borohydride and boron trifluoride etherate afforded tosylate **10a** in 57% yield together with 30% of the starting dianhydride **5** and 9% of the dihydroxy derivative **6**. A prolonged reaction time resulted in accumulation of compound **6**, which was formed most likely from tosylate **10a** by reductive cleavage of 1,6-anhydro bridge at carbon C-1. When excess of boron trifluoride etherate in 1,2-dimethoxyethane was used, compound **7**, formed by participation of the solvent, was isolated as the main product. In the next step, mesylation of **10a** yielded mesylate **10b**. Sulfonates **10a** and **10b** reacted with sodium methanolate to give dianhydrides **3** and **4**, respectively (Scheme 2).



(i) $NaBH_4$, $BF_3{\cdot}Et_2O$, 1,2-dimethoxyethane; (ii) MsCl, pyridine; (iii) CH_3ONa, CH_3OH–CH_2Cl_2

SCHEME 2

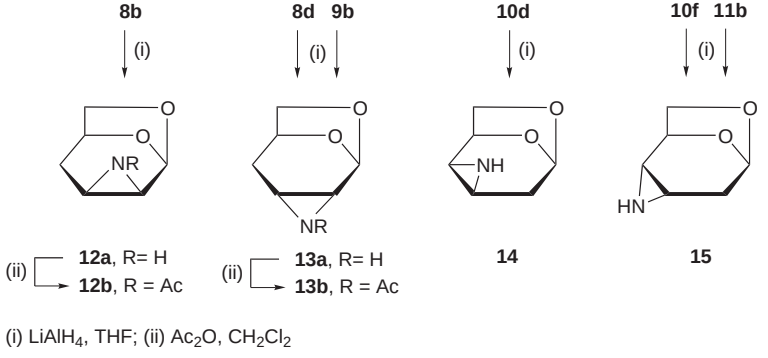
Dianhydrides **1** and **4** reacted regioselectively with sodium azide in 2-methoxyethanol–water mixture[13] under the diaxial splitting of the oxirane ring affording azides **8a** and **10c**, respectively, which were converted to azido tosylates **8b** and **10d** (Scheme 3). In contrast, azidolysis of dianhydrides **2** and **3** under the same conditions provided in addition to products of diaxial splitting **8c** and **10e**, respectively, also products **9a** and **11a**, respectively, formed by "anomalous" diequatorial splitting of the oxirane ring. Azides **10e** and **11a** were separated by column chromatography and converted to tosylates **10f** and **11b**. Azides **8c** and **9a** could be separated by column chromatography after their conversion to tosylates **8d**



SCHEME 3

and **9b**. The nonselective stereochemical course of the nucleophilic cleavage of dianhydrides **2** and **3** was already observed for other nucleophiles and was interpreted as the result of antagonistic influence of steric and polar effects[12] on the cleavage. Steric effect favours formation of diaxial products, while polar effect causes the cleavage of the oxirane ring at the carbon atom, which is located further from the acetal (dianhydrides **1** and **2**) or ether (dianhydride **3** and **4**) moiety. In the case of dianhydrides **1** and **4**, both effects are synergistic while in the case of dianhydrides **2** and **3** the effects are antagonistic giving rise to a mixture of regioisomers. Dianhydrides **1** and **4** with *exo*-oriented oxirane ring also needed a significantly shorter reaction time to complete the azidolysis than dianhydrides **2** and **3** with *endo*-oriented oxirane ring. This is in contrast with the low reactivity of *O*-benzylated 1,6:2,3- and 1,6:3,4-dianhydro-β-D-hexopyranoses with *exo*-oriented oxirane ring towards azidolysis[2]. The structure of all deoxy derivatives **6**, **8**–**11** was proved by ^{1}H and ^{13}C NMR spectra. The presence of tosyl, mesyl and in most cases also of the OH group is manifested by characteristic signals in ^{1}H and ^{13}C NMR spectra (see Tables I–III). The presence and position of the azido group was detected only indirectly from the upfield position of corresponding carbon signal (δ 55–62 ppm). The CH_2 group in tetrahydropyran ring provides characteristic upfield ^{13}C and ^{1}H signals (at δ 29–38 and 1.60–2.40 ppm, respectively). Vicinal proton couplings of CH_2 protons to H-1 and/or H-5 can distinguish between 2- and 4-deoxy derivatives. The all observed vicinal proton couplings of tetrahydropyran ring (Table II) suggest that it adopts $^1C_4$ (D) conformation in derivatives **8**–**11** with *xylo* and *arabino* configurations.

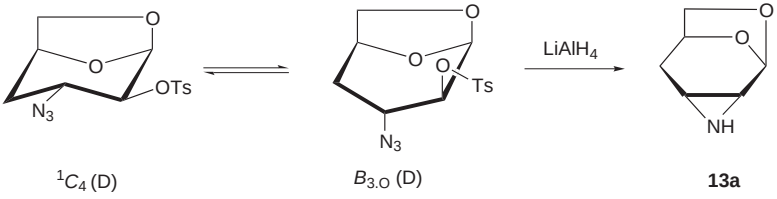
Reduction of azido tosylates **8b**, **8d**, **10d**, and **10f** with lithium aluminium hydride in tetrahydrofuran provided aziridine derivatives **12a**, **13a**, **14**, and **15**, respectively (Scheme 4). The reactions proceeded at room tem-



SCHEME 4

perature giving moderate yields in the range 55–72%. Epimine **13a** was found to slowly decompose and therefore was converted to stable *N*-acetyl derivative **13b** for characterization. Epimine **12a** was also converted to *N*-acetate **12b** for characterization purposes. Epimines **14** and **15** were stable crystalline compounds.

Azido tosylates **9b** and **11b** reacted with lithium aluminium hydride to aziridines **13a** and **15**, respectively. Reductive cyclization of these azido tosylates into the corresponding epimines is an unexpected result considering the diequatorial arrangement of the participating groups on a relatively rigid bicyclic skeleton . To our knowledge, this is the first reported case of a three-membered ring closure from a diequatorial precursor in the 1,6-anhydro-β-D-hexopyranose series. This reaction most likely involves the change of conformation from $^1C_4$ (D) into the energetically disadvantageous $B_{3,O}$ (D) conformation, in which the reacting azido and tosyloxy groups assume *trans*-diaxial relationship indispensable for SN2 intramolecular substitution (Scheme 5).



SCHEME 5

Structure of aziridine derivatives **12**–**15** was demonstrated by ^{1}H and ^{13}C NMR spectra. NMR spectra of epimines **12a**, **13a**, **14**, and **15** with a free amino group showed two sets of signals due to a slow inversion at nitrogen atom (for details, see lit.[14]). The observed ratios of isomers in $CDCl_3$ were 79:21 (**12a**), 86:14 (**13a**), 64:36 (**14**) and 88:12 (**15**). The isomer ratio can be influenced by the solvent – for **13a** in CD_3OD we have found the ratio 91:9. The structure assignment of signals belonging to the epimine isomer with *endo*- and *exo*-oriented NH hydrogen is very difficult since neither separate NH signals nor NH–CH couplings are observed. The inspection of models indicates a possible intramolecular H-bonding between NH and oxygen atom C(6)–O–C(1) in epimines **12a** and **14** or oxygen atom C(5)–O–C(1) in aziridines **13a** and **15**. The NH region of the IR spectra in CCl_4 showed indeed two bands belonging to free NH and intramolecularly H-bonded imino group for epimines **12a** and **13a** (see Table IV) with higher intensities of H-bonded bands. In epimine **15** only the band of H-bonded NH at 3295 cm^{-1} is clearly detected and a weak shoulder on higher-frequency side

may indicate a small amount of free NH form. On the contrary the IR spectrum of epimine **14** shows only broad band of free NH at 3321 cm^{-1}. This observation could be explained by a larger distance N···O (3.05 Å) in comparison with three previously discussed epimines (≈2.8 Å). Theoretical calculations using the MM+ method resulted in a slightly lower energy for *endo*-NH isomer in all epimines **12a**, **13a**, **14**, and **15**. From all the above discussed information we believe that prevailing isomer is the *endo*-NH.

The addition of a trace amount of CD_3COOD to the $CDCl_3$ solution leads for all epimines (**12a**, **13a**, **14**, and **15**) to the observation of only one set of signals due to protonation of nitrogen atom. The measurement of temperature dependence of ^1H NMR spectrum of aziridine **12a** in DMSO in the range 20–100 °C showed only narrowing of signals of one isomer but the coalescence temperature must be much higher than 100 °C. The *N*-acetylation of aziridines is known to decrease a coalescence temperature dramatically[15] as confirm the NMR spectra of compounds **12b** and **13b** containing only one set of signals in $CDCl_3$ already at room temperature.

EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. The optical rotations were measured on an Autopol III (Rudolf Research, Flanders, NJ) polarimeter at 23 °C and are given in 10^{-1} deg cm^2 g^{-1}. Infrared spectra of epimines **12a**, **13a**, **14**, and **15** were recorded on a PE684 in tetrachloromethane solution at concentrations lower than 4.0×10^{-3} mol dm^{-3} to avoid intramolecular associations. Wavenumbers and relative intensities of the absorption bands of the imino group are given in Table IV. NMR spectra were measured on FT NMR spectrometers Varian UNITY-500 and Bruker AVANCE-500 (^1H at 500 MHz, ^{13}C at 125.7 MHz). Chemical shifts (in ppm, δ-scale) were referenced to tetramethylsilane as internal standard; coupling constants (*J*) are given in Hz. Structure assignment of protons and carbon atoms was achieved using correlated homonuclear 2D-COSY and heteronuclear ^1H, ^{13}C-2D-HMQC spectra. The long-range couplings were identified with selective decoupling experiments in 1D ^1H NMR spectra. TLC was carried out on Merck DC Alufolien with Kiesegel F_{254} using two solvent systems: toluene–acetone 5:1 (S_1) and acetone (S_2). TLC plates were visualized by UV detection at 254 nm and with an anisaldehyde solution in H_2SO_4. Column chromatography was performed on silica gel 60 Merck (70–230 mesh ASTM). The solvents were evaporated on a vacuum rotary evaporator at 40 °C. Anhydrous sodium sulfate was used for drying solutions. The ^1H NMR spectral parameters of compounds **8**–**15** are given in Tables I and II, and those of ^{13}C NMR spectra in Table III.

1,6-Anhydro-2-deoxy-4-*O*-tosyl-β-D-*arabino*-hexopyranose (**10a**) and 1,2-Dideoxy-4-*O*-tosyl-β-D-*arabino*-hexopyranose (**6**)

To a suspension of 1,6:2,3-dianhydro-4-*O*-tosyl-β-D-mannopyranose[16] (**5**; 7.765 g, 26.0 mmol) and a finely ground $NaBH_4$ (3.060 g, 80.9 mmol) in 1,2-dimethoxyethane (90 ml), $BF_3 \cdot OEt_2$ (10.5 ml, 83.6 mmol) was added dropwise under cooling and stirring. The reaction course

TABLE I
^{1}H NMR chemical shifts of compounds **8–15** in $CDCl_3$

Compound	H-1	H-2ex	H-2en	H-3	H-4ex	H-4en	H-5	H-6en	H-6ex	Other protons
8a	5.42 m	–	3.64 m	3.78 m	2.37 m	1.67 m	4.52 m	4.14 m	3.75 ddd	OH: 2.66 b
8b	5.27 m	–	4.15 m	3.81 m	2.36 m	1.63 dm	4.51 m	4.04 dd	3.67 dddd	OTs: 2.47 bs (3H), 7.83 m (2H), 7.39 m (2H)
8d	5.41 m	–	3.24 m	4.62 m	2.37 m	1.94 dm	4.54 ddd	4.15 dd	3.74 dddd	OTs: 2.46 bs (3H), 7.81 m (2H), 7.38 m (2H)
9b	5.52 d	4.23 dd	–	3.75 ddd	1.81 dddd	2.06 bddd	4.59 m	3.84 dd	3.81 ddd	OTs: 2.46 bs (3H), 7.86 m (2H), 7.37 m (2H)
10a	5.63 m	2.13 ddd	1.82 dm	3.81 m	–	4.45 m	4.57 dm	4.21 dd	3.70 dd	OTs: 2.46 bs (3H), 7.83 m (2H), 7.37 m (2H)
10b	5.57 m	2.25 ddd	2.00 dm	4.76 m	–	4.58 m	4.57 m	4.10 dd	3.75 dd	OTs: 2.47 bs (3H), 7.85 m (2H), 7.38 m (2H), OMs: 3.03 s (3H)
10c	5.56 m	2.14 dddd	1.89 dm	3.78 m	–	3.60 m	4.48 m	4.26 bdd	3.77 bdd	OH: 2.74 b
10d	5.56 m	2.16 dddd	1.81 dm	3.76 m	–	4.26 m	4.52 dm	4.12 dd	3.70 ddd	OTs: 2.47 bs (3H), 7.83 m (2H), 7.38 m (2H)
10e	5.67 m	2.15 ddd	1.92 dm	3.94 m	–	3.48 m	4.64 m	4.31 dd	3.80 dd	OH: not observed
10f	5.52 m	2.05 ddd	1.83 dm	4.57 m	–	3.59 m	4.60 m	4.22 dd	3.81 ddd	OTs: 2.46 bs (3H), 7.80 m (2H), 7.37 m (2H)
11a	5.53 bt	1.66 m	2.22 dddt	3.65 dddd	3.79 bdt	–	4.44 bt	4.12 dd	3.71 bdd	OH: 2.42 bd
11b	5.50 t	1.60 ddd	2.22 m	3.71 ddd	4.36 ddd	–	4.75 bt	4.13 dd	3.76 ddd	OTs: 2.47 bs (3H), 7.86 m (2H), 7.39 m (2H)
12a NH-*endo* (79%)	5.78 dd	2.54 bt	–	2.11 um	2.28 bdt	1.81 dm	4.42	3.62	4.42 ddt	–
12a NH-*exo* (21%)	5.64 dd	2.41 dd	–	1.90 ddd	2.09 m	1.59 dt	4.36	3.71 ddd	3.63 m	–

TABLE I
(*Continued*)

Compound	H-1	H-2ex	H-2en	H-3	H-4ex	H-4en	H-5	H-6en	H-6ex	Other protons
12a + AcOD	5.82 dd	2.77 bdd	–	2.32 bt	2.40 m	1.88 dm	4.47 m	3.61 m	3.61 m	–
12b	5.47 ddd	2.50 dd	–	2.20 m	1.76 m	1.45 dm	3.96 m	3.40 ddd	3.38 dddd	NAc: 1.82 s (3H)
13a + NH-*endo* (86%)	5.61 bs	–	2.11 um	2.11 um	2.32 ddm	1.74 m	4.39 m	3.81 dd	3.94 ddd	–
13a + NH-*exo* (14%)	5.48 bs	–	2.01 dd	2.09 bt	2.13 bdd	1.64 bdd	4.34 m	3.75 dd	3.88 ddd	–
13a + AcOD	5.66 bs	–	2.47 bd	2.51 bt	2.42 bdd	1.84 dd	4.45 tt	3.84 dd	3.97 ddd	–
13b	5.67 bs	–	2.64 dd	2.72 tm	2.52 ddm	1.77 ddt	4.44 m	3.82 dd	3.96 ddd	NAc: 2.15 s (3H)
14 + NH-*endo* (64%)	5.41 dt	1.88 ddd	1.93 dq	2.19 m	2.78 bt	–	4.82 m	4.08 bd	3.46 ddd	–
14 + NH-*exo* (36%)	5.38 dt	1.81 ddd	1.68 dt	1.90 m	2.60 dd	–	4.75 m	4.00 bd	3.42 ddd	–
14 + AcOD	5.48 dt	2.00 ddd	2.05 dq	2.52 m	3.10 t	–	4.92 bdd	4.02 bd	3.54 dd	–
15 + NH-*endo* (88%)	5.38 dd	2.03	1.90 bdd	1.99 bt	–	2.12 bd	4.64 m	4.11 dd	3.84 dd	–
15 + NH-*exo* (12%)	5.35 um	?	?	1.95 tt	–	2.09 dd	4.51 dm	4.00 dd	3.72 dd	–
15 + AcOD	5.40 dd	2.08 dm	1.95 ddt	2.20 bt	–	2.36 dm	4.67 dm	4.14 dd	3.86 dd	–

TABLE II
^{1}H NMR coupling constants of compounds **8**–**15** in $CDCl_3$

Compound	1,2ex	1,2en	2ex,2en	2ex,3	2en,3	3,4ex	3,4en	4ex,4en	4ex,5	4en,5	5,6en	5,6ex	6en,6ex
8a[a]	–	2.1	–	–	1.9	6.0	1.8	15.1	4.2	1.8	0.9	5.2	7.1
8b[b]	–	1.9	–	–	1.9	6.4	1.9	15.0	4.4	2.0	0.9	5.2	7.2
8d[c]	–	1.2	–	–	1.9	5.6	1.5	15.8	4.1	1.6	0.9	5.2	7.2
9b[d]	1.6	–	–	8.8	–	11.5	6.6	13.8	3.6	1.9	1.1	4.8	7.6
10a[e]	1.7	2.2	15.1	5.5	1.2	–	2.6	–	–	1.8	0.8	5.5	7.9
10b[f]	2.2	1.8	15.6	6.0	3.0	–	2.1	–	–	*	1.1	5.6	8.3
10c[g]	1.9	1.5	15.3	6.1	1.7	–	1.7	–	–	2.3	1.0	5.8	7.6
10d[h]	2.3	1.4	15.1	6.5	2.4	–	2.5	–	–	2.5	1.0	5.8	7.9
10e[i]	1.6	1.7	15.3	5.2	3.2	–	1.4	–	–	2.7	0.8	5.3	7.7
10f[j]	1.9	1.9	15.6	5.8	1.7	–	2.6	–	–	1.7	1.0	5.7	7.8
11a[k]	1.4	2.1	13.3	10.9	6.5	9.0	–	–	4.0	–	0.8	5.1	7.8
11b[l]	2.0	1.3	13.5	10.8	6.8	9.1	–	–	4.1	–	0.8	5.0	8.3
12a[m] + AcOD	4.0	–	–	6.1	–	5.9	<1	15.4	6.8	<1	*	*	*
12b[n]	3.8	–	–	6.2	–	4.9	1.0	14.7	6.1	~0	2.1	5.7	6.8
13a[o] + AcOD	–	≤1.5	–	–	6.0	≤1.5	6.6	15.5	5.3	~0	1.9	6.2	7.7
13b[p]	–	1.3	–	–	6.0	0.7	6.7	15.0	5.2	0.7	2.0	6.2	7.7
14[t] + AcOD	3.2	~1.0	15.2	5.0	0.8	6.9	–	–	6.4	–	≤0.3	4.4	7.4
15[u] +AcOD	3.2	0.6	15.5	0.8	6.3	–	5.8	–	–	1.7	0.7	4.4	7.2

* *J*-value could not be determined.

Additional coupling constants: [a] $J(1,3) = 1.2$, $J(1,4ex) \leq 0.3$, $J(1,4en) = 1.0$, $J(1,6ex) = 0.5$, $J(1,6en) \leq 0.2$, $J(2en,4ex) = 0.6$, $J(2en,4en) = 1.1$, $J(2en,5) = 0.5$, $J(3,5) = 1.0$, $J(4ex,6ex) = 1.6$; [b] $J(1,3) = 1.2$, $J(1,4ex) \leq 0.3$, $J(1,4en) = 0.9$, $J(1,6ex) = 0.4$, $J(1,6en) \leq 0.2$, $J(2en,4ex) = 0.5$, $J(2en,4en) = 1.1$, $J(2en,5) = 0.6$, $J(3,5) = 1.0$, $J(4ex,6ex) = 1.5$; [c] $J(1,3) = 1.9$, $J(1,4en) = 1.0$, $J(1,6ex) = 0.4$, $J(2en,4en) = 1.5$, $J(3,5) = 1.7$, $J(4ex,6ex) = 1.6$; [d] $J(4ex,6ex) = 1.7$; [e] $J(1,3) = 1.4$, $J(1,4en) = 0.8$, $J(1,6ex) \leq 0.3$, $J(2en,4en) = 1.2$, $J(2en,5) = 1.2$, $J(3,5) = 1.6$, $J(3,OH) = 7.7$; [f] $J(1,3) \approx 1.0$, $J(2en,4en) = 1.0$, $J(3,5) \approx 1.0$; [g] $J(1,3) = 1.1$, $J(1,4en) = 0.8$, $J(1,6en) \leq 0.2$, $J(1,6ex) \leq 0.3$, $J(2ex,4en) = 0.5$, $J(2en,4en) = 1.2$, $J(2en,5) = 0.7$, $J(3,5) = 1.5$; [h] $J(1,3) = 0.9$, $J(1,4en) = 0.9$, $J(1,6ex) = 0.5$, $J(2ex,4en) = 0.5$, $J(2en,4en) = 0.9$, $J(2en,5) = 0.8$; [i] $J(1,3) = 1.3$, $J(2en,4ex) = 0.8$, $J(3,5) = 1.7$; [j] $J(1,3) = 1.0$, $J(1,4en) < 0.3$, $J(1,6ex) = 0.4$, $J(2en,4en) = 0.8$, $J(2en,5) = 1.0$, $J(3,5) = 1.5$; [k] $J(1,6ex) \approx 0.5$, $J(2en,4ex) \approx 0.6$, $J(2en,5) \approx 0.4$, $J(2en,4ex) \leq 0.5$, $J(2ex,5) \leq 0.4$, $J(4,OH) = 3.8$; [l] $J(2en,4ex) \approx 0.4$, $J(2en,5) = 0.7$, $J(4ex,6ex) = 1.2$; [m] $J(1,3) = 1.1$; [n] $J(1,3) = 0.4$, $J(1,4en) = 1.0$, $J(1,6en) = 0.6$, $J(1,6ex) = 0.5$, $J(4ex,6ex) = 1.1$; [o] $J(3,5) = 1.5$, $J(4ex,6ex) = 1.5$; [p] $J(1,4en) \approx 0.5$, $J(3,5) = 1.4$, $J(4ex,6ex) = 1.3$; [r] $J(1,3) = 0.8$, $J(1,6ex) = 0.5$, $J(2en,4ex) = 0.9$; [s] $J(1,5) \leq 0.3$, $J(1,6en) \leq 0.5$, $J(1,6ex) = 0.5$, $J(3,5) \approx 0.9$; [t] $J(1,3) = 1.1$, $J(2en,4ex) = 0.9$; [u] $J(1,5) = 0.7$, $J(1,3) = 1.9$, $J(2ex,4en) = 0.8$, $J(2en,4en) = 0.6$, $J(3,5) = 1.1$.

was monitored by TLC (S_1). The cooling bath was removed after 1 h and stirring continued for additional 1.5 h. The reaction mixture was carefully mixed with water, neutralized with 5% aqueous HCl and a crystal of compound **5** was added to induce precipitation. The precipitate was filtered off and dried to afford 2.335 g (30%) of the starting dianhydride **5**. The filtrate was extracted with dichloromethane (5×), organic layer was dried and concentrated to afford product **10a** (3.867 g, 49.5%), m.p. 104–105 °C (ethanol–hexane), $[\alpha]_D$ –64 (*c* 0.3, $CHCl_3$). For $C_{13}H_{16}O_6S$ (300.3) calculated: 51.99% C, 5.37% H, 10.68% S; found: 52.14% C,

TABLE III
^{13}C NMR chemical shifts of compounds **8**–**15** in $CDCl_3$

Compound	C-1	C-2	C-3	C-4	C-5	C-6	Other carbons
8a	101.10	68.42	56.66	29.63	71.45	67.17	–
8b	96.95	74.52	55.75	29.73	74.19	70.70	OTs: 145.62, 132.88, 130.20(2), 127.98(2), 21.66
8d	99.67	59.62	74.62	31.86	70.86	67.35	OTs: 145.44, 133.32, 130.16(2), 127.77(2), 21.65
9b	99.80	80.92	56.48	34.71	72.49	68.57	OTs: 145.37, 133.08, 129.93(2), 128.05(2), 21.66
10a	100.73	35.18	66.72	78.50	74.33	64.99	OTs: 145.27, 133.40, 130.05(2), 127.77(2), 21.67
10b	98.95	33.70	73.30	76.17	73.91	6.76	OTs: 145.74, 132.74, 130.18(2), 127.96(2), 21.71
10c	99.72	30.87	57.37	69.51	75.94	64.90	–
10d	99.13	31.34	55.21	77.38	74.24	65.17	OTs: 145.56, 133.18, 130.15(2), 127.86(2), 21.68
10e	101.10	35.95	67.20	62.14	74.62	65.91	–
10f	99.25	33.57	74.33	60.46	73.66	65.56	OTs: 145.41, 133.16, 130.12(2), 127.78(2), 21.67
11a	100.31	36.81	59.63	71.15	75.19	64.92	–
11b	100.09	37.84	56.49	78.18	73.60	65.19	OTs: 145.62, 133.47, 129.98(2), 128.11(2), 21.72
12a NH-*endo* (79%)	98.79	34.29	22.73	29.19	67.37	68.26	–
12a NH-*exo* (21%)	99.03	35.89	24.86	29.45	67.61	68.20	–
12b	97.05	39.22	29.11	28.25	67.16	67.55	NAc: 180.77, 22.69
13a NH-*endo* (86%)	98.00	30.93	25.43	30.05	71.63	68.70	–
13a NH-*exo* (14%)	98.16	31.87	25.99	30.40	70.88	68.43	–
13b	96.89	35.33	30.88	28.66	71.08	68.90	NAc: 181.14, 23.68
14 NH-*endo* (64%)	97.62	31.12	23.30	32.34	72.49	64.71	–
14 NH-*exo* (36%)	97.36	31.01	25.19	33.53	72.32	64.88	–
15 NH-*endo* (88%)	99.98	31.55	24.07	31.84	69.60	68.06	–
15 NH-*exo* (12%)	98.41	31.90	23.80	32.47	70.24	67.56	–

5.35% H, 10.47% S. Chromatography of the mother liquor on silica gel (60 g) in toluene–acetone 10:1 mixture afforded additional product **10a** (0.589 g, 7.5%). Further elution with toluene–acetone 4:1 gave tosylate **6** (0.672 g, 8.5%), m.p. 87–89 °C (ethyl acetate–diethyl ether–hexane), $[\alpha]_D$ +22 (*c* 0.3, $CHCl_3$). ^{1}H NMR ($CDCl_3$): 1.75 dddd, 1 H, *J*(2β,1α) = 12.8, *J*(2β,1β) = 5.1, *J*(2β,2α) = 13.5, *J*(2β,3) = 11.4 (H-2β); 2.47 bs, 3 H (CH_3 (OTs)); 2.07 ddt, 1 H, *J*(2α,1α) = 2.1, *J*(2α,1β) = 1.7, *J*(2α,2β) = 13.5, *J*(2α,3) = 5.4 (H-2α); 3.26 ddd, 1 H, *J*(5,4) = 9.6, *J*(5,6a) = 4.6, *J*(5,6b) = 2.4 (H-5); 3.43 ddd, 1 H, *J*(1α,1β) = 11.8, *J*(1α,2α) = 2.1, *J*(1α,2β) = 12.8 (H-1α); 3.56 ddd, 1 H, *J*(6a,5) = 4.6, *J*(6a,6b) = 12.3, *J*(6a,OH) = 6.1 (H-6a); 3.71 ddd, 1 H, *J*(6b,5) = 2.4, *J*(6b,6a) = 12.3, *J*(6b,OH) = 7.6 (H-6b); 3.85 m, 1 H, *J*(3,2α) = 5.4, *J*(3,2β) = 11.4, *J*(3,OH) = 2.9, *J*(3,4) = 8.7 (H-3); 3.99 ddd, 1 H, *J*(1β,1α) = 11.8, *J*(1β,2α) = 1.7, *J*(2β,2β) = 5.1 (H-1β); 4.43 dd, 1 H, *J*(4,3) = 8.7, *J*(4,5) = 9.6 (H-3); 7.38 m, 2 H and 7.85 m, 2 H (C_6H_4 (OTs)). ^{13}C NMR ($CDCl_3$): 21.72 (CH_3 (OTs)); 33.93 (C-2); 61.50 (C-6); 65.49 (C-1); 70.71 (C-3); 77.78 (C-5); 80.94 (C-4); 128.03 (2 C); 130.02 (2 C); 132.59 and 145.69 (C_6H_4 (OTs)). For $C_{13}H_{18}O_6S$ (302.3) calculated: 51.64% C, 6.00% H, 10.61% S; found: 51.66% C, 6.02% H, 10.58% S.

1,6-Anhydro-2-*O*-(2-methoxyethoxy)-4-*O*-tosyl-β-D-glucopyranose (**7**)

To a suspension of 1,6:2,3-dianhydro-4-*O*-tosyl-β-D-mannopyranose[14] (**5**; 0.538 g, 1.8 mmol) and a finely ground $NaBH_4$ (0.255 g, 6.7 mmol) in 1,2-dimethoxyethane (9 ml), $BF_3{\cdot}OEt_2$ (2.0 ml, 15.8 mmol) was added dropwise under cooling and stirring and the reaction mixture was left to stand at room temperature overnight. It was then diluted with water, neutralized with sodium hydrogencarbonate and extracted with dichloromethane (5×). The extract was concentrated and chromatography on silica gel (30 g) in S_1 gave compound **7** (0.359 g, 53%), m.p. 84–86 °C (ethyl acetate–diethyl ether), $[\alpha]_D$ –46 (*c* 0.3, $CHCl_3$). ^{1}H NMR ($CDCl_3$): 2.45 bs, 3 H (CH_3 (OTs)); 3.02 d, 1 H, *J*(OH,3) = 2.9 (OH-3); 3.18 dd, 1 H, *J*(2,1) = 0.9, *J*(2,3) = 4.9 (H-2); 3.36 s, 3 H (OCH_3); 3.52 ddd, 1 H, *J*(gem) = 10.8, *J*(vic) = 5.3 and 3.8; 3.54 ddd, 1 H, *J*(gem) = 10.8, *J*(vic) = 5.9 and 3.4; 3.71 ddd, 1 H, *J*(gem) = 11.5, *J*(vic) = 5.9 and 3.8; 3.80 ddd,

TABLE IV
Bands in IR spectra and geometry parameter of epimines **12a**, **13a**, **14**, and **15** in CCl_4

Parameter	**12a**	**13a**	**14**	**15**
	Wavenumber, cm^{-1} (relative intensity, %)			
Free NH	3324 (24)	3319 (10)	3321 (~100)	[a]
Intramol. H-bonded NH	3305 (76)	3294 (90)	–	3295
	Geometry parameter of H-bond			
N···O, Å[b]	2.76	2.80	3.05	2.80

[a] The accurate position and intensity could not be determined; [b] distances were obtained from the energetically minimized conformations calculated by MM+ method (using HYPERCHEM software package).

1 H, *J*(gem) = 11.5, *J*(vic) = 5.3 and 3.4 (O-CH_2-CH_2-O); 3.67 dd, 1 H, *J*(6ex,6en) = 7.8, *J*(6ex,5) = 5.3 (H-6ex); 3.82 tt, 1 H, *J*(3,2) = 4.9, *J*(3,4) = 5.4, *J*(3,1) ≈ 0.7, *J*(3,5) ≈ 1.0 (H-3); 3.87 dd, 1 H, *J*(6en,6ex) = 7.8, *J*(6en,5) = 1.0; 4.30 dd, 1 H, *J*(4,3) = 5.4, *J*(4,5) = 1.2 (H-4); 4.62 dq, 1 H, *J*(5,6ex) = 5.3, *J*(5,6en) = 1.0, *J*(5,4) = 1.2, *J*(5,3) ≈ 1.0 (H-5); 5.42 bs, 1 H (H-1); 7.35 m, 2 H and 7.83 m, 2 H (C_6H_4 (OTs)). ^{13}C NMR ($CDCl_3$): 21.66 (CH_3 (OTs)); 59.00 (OCH_3); 66.79 (C-6); 70.36 and 72.30 (O-CH_2-CH_2-O); 70.48 (C-3); 75.44 (C-4); 81.96 (C-5); 82.03 (C-2); 101.95 (C-1); 127.95 (2 C); 129.88 (2 C); 133.36 and 145.14 (C_6H_4 (OTs)). For $C_{16}H_{22}O_8S$ (374.4) calculated: 51.33% C, 5.92% H, 8.56% S; found: 51.55% C, 5.87% H, 8.55% S.

1,6:3,4-Dianhydro-2-deoxy-β-D-*lyxo*-hexopyranose (**3**)

To a solution of tosylate **10a** (2.427 g, 8.1 mmol) in dichloromethane (80 ml) a methanol (16 ml) solution of sodium (0.70 g, 30.4 mmol) was added dropwise under stirring and cooling (ice–water) and the reaction mixture was allowed to stand at room temperature for 3 h. It was then neutralized with 5% HCl, diluted with concentrated solution of NaCl and extracted with dichloromethane (4×). The extract was dried and concentrated (under pressure > 90 mbar, otherwise the product rapidly volatilizes) to afford crude **3** (0.984 g, 95%), which was used without further purification for azidolysis.

1,6-Anhydro-2-deoxy-3-*O*-mesyl-4-*O*-tosyl-β-D-*arabino*-hexopyranose (**10b**)

To a solution of tosylate **10a** (0.765 g, 2.55 mmol) in pyridine (10 ml), methanesulfonyl chloride (0.500 ml, 6.27 mmol) was added under stirring and cooling (ice–NaCl–water). The cooling bath was removed after 2 h and the reaction mixture was allowed to stand at 4 °C overnight. It was then diluted with water, extracted with dichloromethane, the extract was dried, filtered through a layer of silica gel and concentrated to afford product **10b** (0.726 g, 75%), m.p. 129 °C (dec., acetone–diethyl ether), $[\alpha]_D$ –61 (*c* 0.3, $CHCl_3$). For $C_{14}H_{18}O_8S_2$ (378.4) calculated: 44.43% C, 4.79% H, 16.94% S; found: 44.50% C, 4.83% H, 16.84% S.

1,6:3,4-Dianhydro-2-deoxy-β-D-*ribo*-hexopyranose (**4**)

The reaction was performed as described for the preparation of dianhydride **3** using a solution of tosylate **10b** (1.609 g, 4.25 mmol) in dichloromethane (70 ml) and methanol (18 ml) containing dissolved sodium (0.67 g, 29.1 mmol). The reaction mixture was allowed to stand at room temperature overnight. It was then processed as described for compound **3** to afford crude **4** (0.548 g, ca. 100%), which contained about 5% of its *lyxo*-isomer **3** according to GC-MS analysis. Crude **4** was used for azidolysis without futher purification.

General Procedure for the Preparation of Azido Tosylates **8b**, **8d**, **9b**, **10d**, **10f**, and **11b**

A solution of dianhydro derivatives **1**–**4**, sodium azide and ammonium chloride in a mixture of 2-methoxyethanol and water was heated to 100 °C until the starting compound disappeared (TLC, S_1). The reaction mixture was then worked up as described below for individual compounds to afford vicinal hydroxy azides, which were characterized as azido tosylates. Tosylation was carried out by mixing a solution of tosyl chloride and hydroxyazide in pyridine and keeping it at a given temperature for a given time. The pyridine solution was then poured onto crushed ice. If the azido tosylate precipitated, it was filtered off and re-

crystallized. If not, it was extracted with dichloromethane, the dichloromethane solution was dried, filtered through a layer of silica gel, decolorized with charcoal, if necessary, and concentrated.

1,6-Anhydro-3-azido-3,4-dideoxy-2-*O*-tosyl-β-D-*xylo*-hexopyranose (**8b**)

Dianhydride **1** (3.844 g, 30.0 mmol), sodium azide (5.0 g, 76.9 mmol), ammonium chloride (5.0 g, 93.5 mmol), 2-methoxyethanol (100 ml) and water (20 ml) were heated to 100 °C for 11 h. The reaction mixture was then concentrated to a thick suspension, diluted with acetone and filtered. The filtrate was concentrated to afford syrupy **8a** (4.809 g, 94%), $[\alpha]_D$ –12 (*c* 0.5, $CHCl_3$). Tosylation of product **8a** (4.754 g, 27.8 mmol) with tosyl chloride (13 g, 68.2 mmol) in pyridine (60 ml) at 4 °C for 3 days afforded tosylate **8b** (8.371 g, 93%), m.p. 99–101 °C (diethyl ether), $[\alpha]_D$ –46 (*c* 0.3, $CHCl_3$). For $C_{13}H_{15}N_3O_5S$ (325.3) calculated: 47.99% C, 4.65% H, 12.92% N, 9.86% S; found: 47.97% C, 4.76% H, 12.79% N, 9.61% S.

1,6-Anhydro-2-azido-2,4-dideoxy-3-*O*-tosyl-β-D-*xylo*-hexopyranose (**8d**) and
1,6-Anhydro-3-azido-3,4-dideoxy-2-*O*-tosyl-β-D-*arabino*-hexopyranose (**9b**)

Dianhydride **2** (2.30 g, 18.0 mmol), sodium azide (2.3 g, 35.4 mmol), ammonium chloride (2.3 g, 43.0 mmol), 2-methoxyethanol (40 ml) and water (10 ml) were heated to 100 °C for 80 h. After 30 h and 60 h, sodium azide (0.7 g, 10.8 mmol) and ammonium chloride (1.0 g, 18.7 mmol) were added. The reaction mixture was then concentrated to dryness, the residue was codistilled with toluene (3×) and extracted with dichloromethane. The dichloromethane solution was filtered through a layer of silica gel and concentrated to afford a mixture of azides **8c** and **9a** (2.52 g, 82%) in the 28:72 ratio according to ^{1}H NMR spectrum (H-1, δ 5.37 and 5.55 in $CDCl_3$). Tosylation of the product mixture (2.55 g, 14.9 mmol) with tosyl chloride (10.5 g, 55.1 mmol) in pyridine (60 ml) at 110 °C for 10 h afforded tosylate **9b** (2.52 g, 52%), m.p. 97–99 °C (acetone–diethyl ether), $[\alpha]_D$ –54 (*c* 0.5, $CHCl_3$). For $C_{13}H_{15}N_3O_5S$ (325.3) calculated: 47.99% C, 4.65% H, 12.92% N, 9.86% S; found: 48.12% C, 4.52% H, 13.26% N, 9.77% S. Chromatography of concentrated mother liquor on silica gel (200 g) in light petroleum–ethyl acetate 10:3 gave (in the following order):

1. azido tosylate **8d** (0.976 g, 20%), m.p. 52–54 °C (diethyl ether–light petroleum), $[\alpha]_D$ +56 (*c* 0.6, $CHCl_3$). For $C_{13}H_{15}N_3O_5S$ (325.3) calculated: 47.99% C, 4.65% H, 12.92% N, 9.86% S; found: 48.12% C, 4.60% H, 13.16% N, 9.78% S.

2. additional azido tosylate **9b** (0.215 g, 4%).

1,6-Anhydro-3-azido-2,3-dideoxy-4-*O*-tosyl-β-D-*arabino*-hexopyranose (**10d**)

Dianhydride **4** (0.548 g, 4.3 mmol), sodium azide (1.0 g, 15.4 mmol), ammonium chloride (1.0 g, 18.7 mmol), 2-methoxyethanol (20 ml) and water (5 ml) were heated to 100 °C for 7 h. The reaction mixture was then diluted with acetone, filtered and the filtrate concentrated. Chromatography on silica gel (30 g) in toluene–acetone 10:1 afforded syrupy **10c** (0.515 g, 70%), $[\alpha]_D$ –139 (*c* 0.3, $CHCl_3$). Tosylation of the product **10c** (0.482 g, 2.8 mmol) with tosyl chloride (2.30 g, 12.1 mmol) in pyridine (25 ml) at room temperature overnight afforded **10d** (0.587 g, 64%), m.p. 74–75 °C (ethyl acetate–diethyl ether–hexane), $[\alpha]_D$ –59 (*c* 0.2, $CHCl_3$). For $C_{13}H_{15}N_3O_5S$ (325.3) calculated: 47.99% C, 4.65% H, 12.92% N, 9.86% S; found: 47.80% C, 4.77% H, 12.65% N, 9.89% S.

1,6-Anhydro-4-azido-2,4-dideoxy-3-*O*-tosyl-β-D-*arabino*-hexopyranose (**10f**) and 1,6-Anhydro-3-azido-2,3-dideoxy-4-*O*-tosyl-β-D-*xylo*-hexopyranose (**11b**)

Dianhydride **3** (0.937 g, 7.31 mmol), sodium azide (1.5 g, 23.1 mmol), ammonium chloride (1.5 g, 28.0 mmol), 2-methoxyethanol (30 ml) and water (7 ml) were heated to 100 °C for 27 h. The reaction mixture was then diluted with acetone, filtered, concentrated, the residue codistilled with toluene, diluted with dichloromethane, dried, filtered and concentrated. Chromatography on silica gel (60 g) in toluene–acetone 9:1 afforded (in the following order):

1. syrupy *xylo* derivative **11a** (0.288 g, 23%), $[\alpha]_D$ –46 (*c* 0.25, $CHCl_3$). Tosylation of azide **11a** (0.262 g, 1.5 mmol) with tosyl chloride (3.06 g, 16.05 mmol) in pyridine (25 ml) at 80 °C for 26 h afforded product **11b** (0.313 g, 63%), m.p. 59–61 °C (diethyl ether–hexane), $[\alpha]_D$ –52 (*c* 0.3, $CHCl_3$). For $C_{13}H_{15}N_3O_5S$ (325.3) calculated: 47.99% C, 4.65% H, 12.92% N, 9.86% S; found: 47.83% C, 4.76% H, 12.54% N, 9.87% S.

2. *arabino* derivative **10e** (0.636 g, 51%), m.p. 88–90 °C (acetone–diethyl ether), $[\alpha]_D$ –26 (*c* 0.3, $CHCl_3$). For $C_6H_9N_3O_3$ (171.2) calculated: 42.11% C, 5.30% H, 24.55% N; found: 42.09% C, 5.30% H, 24.28% N. Tosylation of azide **10e** (0.625 g, 3.65 mmol) with tosyl chloride (3.794 g, 19.9 mmol) in pyridine (25 ml) at room temperature for 4 days afforded product **10f** (0.966 g, 81%), m.p. 110–112 °C (diethyl ether), $[\alpha]_D$ –76 (*c* 0.3, $CHCl_3$). For $C_{13}H_{15}N_3O_5S$ (325.3) calculated: 47.99% C, 4.65% H, 12.92% N, 9.86% S; found: 47.96% C, 4.66% H, 12.98% N, 9.89% S.

General Procedure for the Preparation of Epimines **12a**, **13a**, **14**, and **15**

To a suspension of lithium aluminium hydride in tetrahydrofuran, a solution of starting azido tosylate in tetrahydrofuran (3–5 ml) was added under cooling (ice–NaCl–water, temperature from –15 to –10 °C) and stirring. The cooling bath was removed after 2 h and the reaction mixture was allowed to stand at room temperature overnight. The amounts of the reactants and the volume of tetrahydrofuran are given for the individual compounds. The unreacted lithium aluminium hydride was then decomposed by addition of moist diethyl ether; water (1 ml) was added in the end to complete the decomposition. The precipitate was filtered off and washed with ethyl acetate. Combined filtrates were concentrated and chromatography of the residue on silica gel in S_1 afforded the products. Epimines **12a** and **13a** were converted to *N*-acetyl derivatives **12b** and **13b** for characterization purposes.

1,6-Anhydro-2,3,4-trideoxy-2,3-epimino-β-D-*lyxo*-hexopyranose (**12a**)

Azido tosylate **8b** (0.500 g, 1.54 mmol), lithium aluminium hydride (0.175 g, 4.6 mmol), tetrahydrofuran (18 ml). Chromatography afforded epimine **12a** (0.136 g, 70%), m.p. 102–110 °C (75 °C sublim., diethyl ether), $[\alpha]_D$ –52 (*c* 0.3, $CHCl_3$). For $C_6H_9NO_2$ (127.1) calculated: 56.68% C, 7.14% H, 11.02% N; found: 56.85% C, 7.27% H, 10.72% N.

2,3-(*N*-Acetylepimino)-1,6-anhydro-2,3,4-trideoxy-β-D-*lyxo*-hexopyranose (**12b**)

A solution of epimine **12a** (0.100 g, 0.79 mmol) and acetic anhydride (80 µl, 0.85 mmol) in dichloromethane (2 ml) was allowed to stand at room temperature for 1 h. It was then concentrated and codistilled with toluene (2×) to afford *N*-acetylepimine **12b** (0.094 g, 71%),

m.p. 82–83 °C (diethyl ether), $[\alpha]_D$ –26 (*c* 0.24, $CHCl_3$). For $C_8H_{11}NO_3$ (169.2) calculated: 56.80% C, 6.56% H, 8.28% N; found: 56.86% C, 6.75% H, 8.24% N.

1,6-Anhydro-2,3,4-trideoxy-2,3-epimino-β-D-*ribo*-hexopyranose (**13a**)

A. From azido tosylate **8d**. Azido tosylate **8d** (0.430 g, 1.32 mmol), lithium aluminium hydride (0.252 g, 6.64 mmol), tetrahydrofuran (20 ml). Chromatography afforded epimine **13a** (0.132 g, 79%) as hygroscopic crystalline substance, which slowly melted in air and became contaminated with traces of decomposition products after storing in a refrigerator.

B. From azido tosylate **9b**. Azido tosylate **9b** (0.700 g, 2.15 mmol), lithium aluminium hydride (0.410, 10.8 mmol), tetrahydrofuran (38 ml). Chromatography afforded epimine **13a** (0.172 g, 63%) identical with the product prepared under *A*.

2,3-(*N*-Acetylepimino)-1,6-anhydro-2,3,4-trideoxy-β-D-*ribo*-hexopyranose (**13b**)

It was prepared as described for compound **12b** from epimine **13a** (0.125 g, 0.98 mmol) and acetic anhydride (99 µl, 1.05 mmol). The work-up afforded *N*-acetylepimine **13b** (0.035 g, 48%), m.p. 70–72 °C (diethyl ether), $[\alpha]_D$ +7 (*c* 0.5, $CHCl_3$). For $C_8H_{11}NO_3$ (169.2) calculated: 56.80% C, 6.56% H, 8.28% N; found: 56.79% C, 6.56% H, 7.95% N.

1,6-Anhydro-2,3,4-trideoxy-3,4-epimino-β-D-*lyxo*-hexopyranose (**14**)

Azido tosylate **10d** (0.300 g, 0.92 mmol), lithium aluminium hydride (0.111 g, 2.92 mmol), tetrahydrofuran (12 ml). Chromatography afforded epimine **14** (0.136 g, 70%), m.p. 90–102 °C (60 °C sublim., diethyl ether), $[\alpha]_D$ –119 (*c* 0.2, $CHCl_3$). For $C_6H_9NO_2$ (127.1) calculated: 56.68% C, 7.14% H, 11.02% N; found: 56.61% C, 7.33% H, 10.78% N.

1,6-Anhydro-2,3,4-trideoxy-3,4-epimino-β-D-*ribo*-hexopyranose (**15**)

A. From azido tosylate **10f**. Azido tosylate **10f** (0.500 g, 1.54 mmol), lithium aluminium hydride (0.175 g, 4.6 mmol), tetrahydrofuran (18 ml). Chromatography afforded epimine **15** (0.107 g, 55%), m.p. 73–76 °C (65 °C sublim., diethyl ether), $[\alpha]_D$ –122 (*c* 0.25, $CHCl_3$). For $C_6H_9NO_2$ (127.1) calculated: 56.68% C, 7.14% H, 11.02% N; found: 56.38% C, 7.34% H, 10.70% N.

B. From azido tosylate **11b**. Azido tosylate **11b** (0.310 g, 0.95 mmol), lithium aluminium hydride (0.109 g, 2.9 mmol), tetrahydrofuran (11 ml). Chromatography afforded epimine **15** (0.070 g, 58%), m.p. 74–76 °C (65 °C sublim., diethyl ether), identical with the product prepared under *A*.

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