

SYNTHESIS AND NMR SPECTRA OF 1,6-ANHYDRO-2,3-DIDEOXY-2,3-EPIMINO- AND 1,6-ANHYDRO-3,4-DIDEOXY-3,4-EPIMINO- β -D-HEXOPYRANOSSESJindřich KARBAN^{a,*}, Miloš BUDĚŠÍNSKÝ^b, Miloslav ČERNÝ^{c1} and Tomáš TRNKA^{c2}^a Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, 165 02 Prague 6, Czech Republic; e-mail: karban@icpf.cas.cz^b Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, 166 10 Prague 6, Czech Republic; e-mail: milos.budesinsky@uochb.cas.cz^c Department of Organic Chemistry, Charles University, 128 40 Prague 2, Czech Republic; e-mail: ¹ mila@mail.natur.cuni.cz, ² trnka@mail.natur.cuni.cz

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A complete series of 2,3-dideoxy-2,3-epimino- and 3,4-dideoxy-3,4-epimino-1,6-anhydro- β -D-hexopyranoses were prepared by lithium aluminum hydride reduction of the corresponding *trans*-azido tosylates or *trans*-azido epoxides of 1,6-anhydro- β -D-hexopyranoses. The structure of the epimino derivatives was confirmed by ¹H and ¹³C NMR spectra.

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

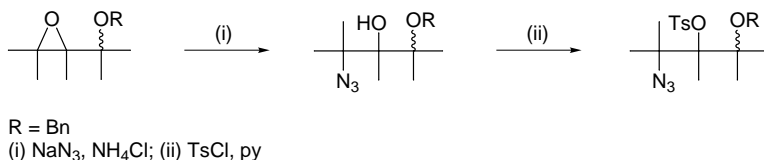
Recently, as a part of our programme focused on synthesis of epimino derivatives of 1,6-anhydro- β -D-aldohexopyranoses as versatile synthetic intermediates, we have reported¹ the synthesis of 1,6-anhydro-2,3-(*N*-benzylepimino)-2,3-dideoxy- β -D-hexopyranose of the *allo*-configuration and 1,6-anhydro-3,4-(*N*-benzylepimino)-3,4-dideoxy- β -D-hexopyranoses of the *allo*-, *talo*- and *galacto*-configuration. This synthesis employed the Mitsunobu reaction of 2-, 3- and 4-(benzylamino)-2-, 3- and 4-deoxy derivatives of 1,6-anhydro- β -D-hexopyranoses obtained by *trans*-diaxial cleavage of suitable 1,6:2,3- and 1,6:3,4-dianhydro- β -D-hexopyranoses with benzylamine. A major drawback of this procedure consists in the low reactivity of the dianhydro derivatives (having the oxirane ring *exo*-oriented) with benzylamine, which renders this method rather inconvenient for synthesis of all possible isomers. Therefore, we have examined the possibility of synthesising the complete series of 2,3-dideoxy-2,3-epimino and 3,4-dideoxy-3,4-epimino derivatives of 1,6-anhydro- β -D-hexopyranoses by lithium aluminum hydride reduction of the corresponding vicinal *trans*-azido tosylates or vicinal *trans*-azido epoxides of 1,6-anhydro- β -D-hexopyranoses. Format-

ion of the aziridine ring from azido tosylates by reaction of LiAlH_4 is a standard method in carbohydrate chemistry based on intramolecular substitution of tosyloxy group with amino group formed *in situ* from azido group². Formation of vicinal hydroxy epimines from azido epoxides on reaction with LiAlH_4 takes advantage of the known³ isomerisation of vicinal *trans*-amino epoxides into hydroxy epimines in alkaline solution.

RESULTS AND DISCUSSION

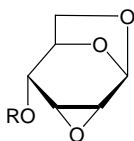
Azido tosylates and azido epoxides suitable for aziridine ring closure were prepared starting from 1,6:2,3-dianhydro derivatives **1a** (ref.⁴), **1b** (ref.⁴), **2a** (ref.⁵), **2b** (ref.⁵), **2c** (ref.^{3b}), **2d** (ref.⁶), **3a** (ref.⁷) and 1,6:3,4-dianhydro derivatives **4a** (ref.⁸), and **5a** (ref.⁹) of β -D-hexopyranoses. Benzylation of compounds **3a** and **4a** yielded *O*-benzyl derivatives **3b** and **4b**. Treatment of dianhydro derivatives **1a**, **1b**, **2a**, **3b**, **4b** and **5a** with sodium azide and ammonium chloride in 2-methoxyethanol- H_2O at 110–120 °C (see *e.g.* ref.¹⁰) gave azido derivatives **6a** (ref.¹¹), **6b**, **6c** (ref.¹²), **7a**, **8a** and **6d** (ref.¹³) in good yields, in most cases above 70%. The oxirane ring opening proceeded with high regio- and stereoselectivity affording products that have azido and hydroxy groups *trans*-diaxially oriented. This stereochemical course is in accordance with general stereochemical rules controlling reactivity of dianhydro derivatives with nucleophiles¹⁴. Dianhydro derivatives **3b** and **4b** reacted with sodium azide to give **7a** and **8a** more slowly than the other suggesting that the steric hindrance caused by the 1,6-anhydro bridge and benzyloxy group may play an important role in controlling the reaction rate.

Azido tosylates **6e** (ref.¹¹), **6f**, **6g**, **7b** and **8b** were obtained from compounds **6a**, **6c**, **6d**, **7a** and **8a** by treatment with tosyl chloride in pyridine. The tosylation of **6c** and **6d** required temperatures about 80–100 °C, which is consistent with the low reactivity of the axial hydroxy group^{14a} at C-3. Azido tosylate **6h** was prepared from azido derivative **6b** by reaction with benzyl bromide and sodium hydride in tetrahydrofuran. Azidolysis of epoxides **1a**, **2a**, **3b**, **4b** and **5a** and subsequent tosylation are shown in general Scheme 1.

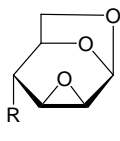


SCHEME 1

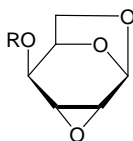
The structure of all azido derivatives was confirmed by ^1H and ^{13}C NMR spectra (see Tables I–III). The presence of azido group is indirectly manifested in ^{13}C NMR spectra by the observation of the upfield shifted signal of $>\text{CH}-\text{N}_3$ carbon in the range δ 58.9–62.8. Other substituents (OH, OBn and OTs) provide characteristic signals in ^1H NMR spectra (Table I) and last two substituents also in ^{13}C NMR spectra (Table III). The *gluco*-, *galacto*- and *manno*-configuration of azido derivatives **6**–**8** and the conformation of their pyranose ring is reflected by vicinal interproton coupling constants (Table II). In agreement with the chair form $^1\text{C}_4$ common for 1,6-anhydrohexopyranoses most of the *gluco*-derivatives **6** (with equatorial hydrogens in position 2, 3 and 4) show small values of $J(2,3)$ and $J(3,4)$ constants (≤ 2.5 Hz). Somewhat higher J -values ≈ 3.5 Hz in compounds **6c**, **6d** and **6k**



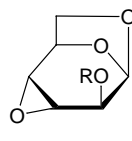
1a, R = Bn
1b, R = Ts



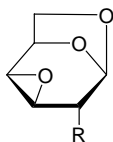
2a, R = OBn
2b, R = OH
2c, R = N_3
2d, R = OTs



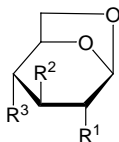
3a, R = H
3b, R = Bn



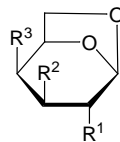
4a, R = H
4b, R = Bn



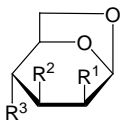
5a, R = OBn
5b, R = NH_2
5c, R = N_3



6	R ¹	R ²	R ³
a	OH	N_3	OBn
b	OH	N_3	OTs
c	N_3	OH	OBn
d	OBn	OH	N_3
e	OTs	N_3	OBn
f	N_3	OTs	OBn
g	OBn	OTs	N_3
h	OBn	N_3	OTs
i	NH_2	OH	OH
j	N_3	OH	OH
k	N_3	OH	OTs
l	N_3	OTs	OTs
m	N_3	OH	N_3



7	R ¹	R ²	R ³
a	OH	N_3	OBn
b	OTs	N_3	OBn



8	R ¹	R ²	R ³
a	OBn	N_3	OH
b	OBn	N_3	OTs

TABLE I
¹H NMR chemical shifts (ppm, δ-scale) of azido derivatives **6a–6h**, **6j–6l**, **7a**, **7b**, **8a**, **8b** in CDCl₃

Com- pound	H-1	H-2	H-3	H-4	H-5	H-6en	H-6ex	Other protons
6a	5.44 bt	3.59 dm	3.84 dq	3.31 ddt	4.58 dm	4.04 dd	3.74 ddd	Bn: 4.68 d, 4.65 d, 7.32–7.40 m (5 H); OH: 2.72 d
6b	5.42 t	3.52 vbd	3.63 m	4.24 m	4.65 m	4.04 dd	3.75 dd	Ts: 2.48 s (3 H), 7.84 m (2 H), 7.41 m (2 H); OH: ^a
6c	5.47 bt	3.23 dm	3.90 um	3.38 dm	4.62 dq	3.94 dd	3.70 dd	Bn: 4.70 d, 4.68 d, 7.30–7.40 m (5 H); OH: 2.45 bd
6d	5.49 bt	3.30 m	3.88 um	3.34 dm	4.59 dm	4.01 dd	3.75 dd	Bn: 4.70 d, 4.67 d, 7.30–7.39 m (5 H); OH: 2.41 bd
6e	5.37 bs	4.07 dd	3.71 tt	3.21 bdd	4.51 dm	3.70 bdd	3.59 ddd	Bn: 4.65 d, 4.60 d, 7.30–7.39 m (5 H); Ts: 2.46 s (3 H), 7.83 m (2 H), 7.36 m (2 H)
6f	5.44 t	3.06 q	4.60 p	3.49 q	4.56 dm	3.98 dd	3.71 dd	Bn: 4.72 d, 4.54 d, 7.31–7.38 m (5 H); Ts: 2.47 s (3 H), 7.80 m (2 H), 7.38 m (2 H)
6g	5.36 t	3.29 m	4.55 p	3.37 m	4.62 m	4.02 dd	3.77 dd	Bn: 4.55 d, 4.29 d, 7.20–7.35 m; Ts: 2.47 s (3 H), 7.79 m (2 H), 7.38 m (2 H)
6h	5.38 s	3.18 d	3.61 t	4.10 dd	4.68 dt	3.82 dd	3.67 dd	Bn: 4.65 d, 4.60 d, 7.30–7.38 m (5 H); Ts: 2.46 s (3 H), 7.82 m (2 H), 7.35 m (2 H)
6j	5.51 bt	3.52 m	3.89 dm	3.66 dm	4.58 dm	4.22 dd	3.80 bdd	3-OH: 2.45 d; 4-OH: 2.61 d
6k	5.44 bt	3.26 dm	3.91 tt	4.44 ddt	4.64 dq	4.06 dd	3.72 ddd	Ts: 2.46 s (3 H), 7.85 m (2 H), 7.38 m (2 H)
6l	5.44 m	3.13 m	4.53 dt	4.52 dd	4.63 m	4.07 dd	3.75 dd	2 × Ts: 2.48 s (3 H), 2.47 s (3 H), 7.83 m (2 H), 7.78 m (2 H), 7.39 m (4 H)
7a	5.31 t	3.76 bdt	4.00 dq	3.96 ddd	4.42 m	4.45 dd	3.67 ddd	Bn: 4.71 d, 4.63 d, 7.32–7.40 m (5 H); OH: 2.10 d
7b	5.81 um	4.28 t	≈3.98 m	≈3.98 m	4.40 m	4.38 bd	3.59 dd	Bn: 4.68 d, 4.60 d, 7.32–7.40 m (5 H); Ts: 2.47 s (3 H), 7.80 m (2 H), 7.38 m (2 H)
8a	5.43 t	3.71 ddd	3.97 dq	3.79 um	4.42 m	4.25 dd	3.77 dd	Bn: 4.71 d, 4.68 d, 7.30–7.40 m (5 H); OH: 2.39 d
8b	5.41 t	3.72 ddd	3.89 dq	4.42 bt	4.39 m	4.13 dd	3.70 dd	Bn: 4.66 d, 4.64 d, 7.30–7.37 m (5 H); Ts: 2.48 s (3 H), 7.80 m (2 H), 7.39 m (2 H)

^a Not observed.

indicate a certain population of boat form $B_{3,0}$ which becomes the preferred conformation in compounds **6e**, **6h** with bulky substituents OBn and OTs in position 2, 4 ($J(2,3) \approx J(3,4) = 5.0\text{--}6.6$ Hz). The higher values of $J(3,4) \approx 5.5$ Hz in *galacto* derivatives **7** and $J(2,3) \approx 5.5\text{--}5.9$ Hz in the *manno* derivatives **8** can be explained by the presence of axial hydrogen atoms in positions 4 and 2, respectively, in the preferred chair form 1C_4 . The presence of azido group in azido derivatives was also indicated in their IR spectra by the absorption band $\nu(\text{N}_3)$ at $2\ 106\text{--}2\ 121\ \text{cm}^{-1}$.

The azido tosylates **6e**, **6f**, **6g**, **6h**, **7b** and **8b** were converted into epimines **11**, **9a**, **13**, **15b**, **12a** and **16**, respectively, by the treatment with lithium aluminum hydride in tetrahydrofuran (see Scheme 2).

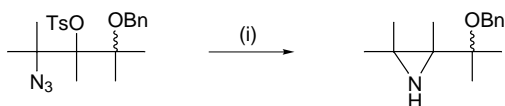
TABLE II
 ${}^1\text{H}$ NMR coupling constants (in Hz) of azido derivatives **6a–6h**, **6j–6l**, **7a**, **7b**, **8a** and **8b** in CDCl_3

Compound ^a	$J(1,2)$	$J(2,3)$	$J(3,4)$	$J(4,5)$	$J(5,6\text{en})$	$J(5,6\text{ex})$	$J(6\text{en},6\text{ex})$	$J(1,3)$	$J(2,4)$	$J(3,5)$
6a ^b	≈ 1.5	2.2	2.0	2.1	0.9	5.6	7.6	1.4	1.3	1.7
6b ^c	≈ 1.5	≈ 2.65	≈ 2.65	≈ 3.0	1.0	5.5	8.1	≈ 1.5	≈ 0.7	≈ 1.5
6c ^d	1.1	3.5	3.5	1.6	0.9	5.4	7.6	1.3	0.8	1.3
6d ^e	1.5	3.1	3.5	1.6	0.8	5.2	7.6	1.3	0.8	1.2
6e ^f	0.9	5.0	5.2	1.4	0.9	5.2	7.6	0.6	≈ 0.3	0.8
6f	≈ 1.6	≈ 1.5	≈ 1.5	≈ 2.1	1.1	5.7	7.8	≈ 1.6	≈ 1.5	≈ 1.5
6g ^g	1.6	1.5	1.5	1.5	1.0	5.6	7.8	1.2	1.4	1.4
6h	0	6.0	6.6	1.2	1.0	5.1	7.8	≈ 0	≈ 0	≈ 0
6j ^h	2.0	2.0	2.2	2.2	0.9	5.4	7.7	1.7	1.2	1.7
6k ⁱ	1.3	3.6	3.7	1.5	1.0	5.5	7.9	1.0	0.7	1.3
6l ^j	1.8	2.1	1.7	3.3	1.1	5.7	8.1	1.6	≈ 0	0.9
7a ^k	≈ 1.7	≈ 1.6	5.5	3.9	≈ 0.6	5.1	7.5	≈ 1.5	≈ 0	≈ 1.4
7b ^l	1.9	1.5	5.6	3.6	0.8	5.1	7.7	1.2	≈ 0	1.4
8a ^m	1.8	5.5	1.6	2.0	1.0	5.6	7.7	1.5	0.5	1.8
8b	1.8	5.9	1.6	2.0	1.0	5.6	8.0	1.4	0.4	1.8

^a Geminal coupling of benzyl protons appears in the range 11.8–12.4 Hz. Additional coupling constants: ^b $J(\text{OH},2) = 11.6$, $J(1,4) = 0.8$, $J(2,5) = 0.6$, $J(1,6\text{ex}) = 0.5$; ^c $J(2,\text{OH}) \approx 8.5$; ^d $J(1,4) = 0.4$, $J(1,6\text{en}) \approx 0.2$, $J(1,6\text{ex}) \approx 0.3$, $J(3,\text{OH}) \approx 8.5$; ^e $J(3,\text{OH}) \approx 4.8$, $J(2,5) = 0.5$, $J(1,4) = 0.5$, $J(1,5) < 0.3$; ^f $J(1,4) < 0.3$, $J(1,6\text{en}) \approx 0.2$, $J(1,6\text{ex}) = 0.4$; ^g $J(1,6\text{en}) \approx J(1,6\text{ex}) < 0.3$, $J(1,4) < 0.5$, $J(1,5) < 0.3$; ^h $J(3,\text{OH}) = 7.1$, $J(4,\text{OH}) = 10.4$, $J(2,5) = 0.6$, $J(1,4) = 0.7$, $J(1,6\text{ex}) = 0.3$; ⁱ $J(1,4) = 0.5$, $J(1,6\text{en}) = 0.2$, $J(1,6\text{ex}) = 0.4$, $J(2,5) = 0.5$; ^j $J(1,6\text{ex}) < 0.5$; ^k $J(2,\text{OH}) = 9.4$, $J(4,6\text{ex}) = 1.3$. ^l J -Values were obtained from $\text{CDCl}_3\text{--C}_6\text{D}_6$ (9 : 1): $J(4,6\text{ex}) = 1.0$, $J(1,6\text{en}) \approx J(1,6\text{ex}) < 0.3$, $J(1,5) < 0.5$; ^m $J(3,\text{OH}) = 9.2$.

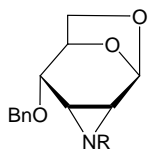
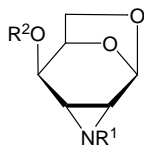
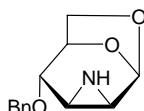
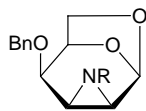
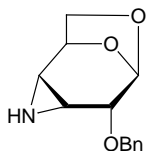
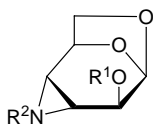
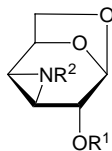
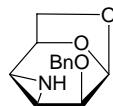
TABLE III
¹³C NMR chemical shifts (in ppm, δ-scale) of azido derivatives **6a–6h**, **6j–6l**, **7a**, **7b**, **8a** and **8b** in CDCl₃

Com- pound	C-1	C-2	C-3	C-4	C-5	C-6	Other carbons
6a	101.44	68.13	60.30	75.51	74.07	65.30	Bn: 136.74, 128.71 (2), 128.32 127.93 (2), 71.58
6b	101.50	68.94	61.20	76.95	74.79	65.55	Ts: 145.92, 132.72, 130.29 (2), 127.94 (2), 21.70
6c	101.05	62.76	70.45	78.59	75.03	66.26	Bn: 137.33, 128.60 (2), 128.10, 127.91 (2), 71.86
6d	101.19	77.80	70.12	62.44	74.85	66.89	Bn: 137.26, 128.60 (2), 128.13, 127.96 (2), 72.29
6e	100.02	77.76	60.37	77.76	75.10	66.67	Bn: 136.80, 128.67 (2), 128.29, 128.04 (2), 72.08; Ts: 145.48, 132.89, 130.02 (2), 128.07 (2), 21.69
6f	99.62	58.98	75.44	74.16	74.29	64.98	Bn: 136.88, 128.58 (2), 128.15, 127.90 (2), 71.52; Ts: 145.73, 132.91, 130.27 (2), 128.04 (2), 21.68
6g	100.10	73.42	75.31	59.33	73.76	65.66	Bn: 136.78, 128.52 (2), 128.12, 127.84 (2), 71.96; Ts: 145.68, 132.92, 130.24 (2), 127.96 (2), 21.68
6h	101.02	79.04	60.74	80.05	75.56	67.06	Bn: 136.76, 128.61 (2), 128.26, 128.01 (2), 72.49; Ts: 145.59, 132.85, 130.03 (2), 128.08 (2), 21.70
6j	100.42	61.88	71.74	70.86	76.74	65.64	
6k	100.94	62.45	70.10	79.46	74.92	66.02	Ts: 145.56, 132.95, 130.05 (2), 127.84 (2), 21.66
6l	99.77	58.92	74.07	75.19	74.16	64.91	2 × Ts: 146.00, 145.70, 132.75, 132.22, 130.29 (2), 130.12 (2), 128.08 (2), 128.05 (2), 21.72 (2)
7a	100.71	70.93	61.28	71.68	72.96	64.13	Bn: 137.19, 128.69 (2), 128.32, 127.73 (2), 71.83
7b	98.54	76.36	59.29	71.63	72.33	64.18	Bn: 137.00, 128.69 (2), 128.36, 127.72 (2), 72.15; Ts: 145.80, 132.54, 130.24 (2), 127.98 (2), 21.67
8a	100.02	73.83	61.44	70.89	76.01	65.01	Bn: 137.19, 128.62 (2), 128.22, 127.88 (2), 71.92
8b	99.62	73.99	59.24	77.72	74.09	65.02	Bn: 136.99, 128.60 (2), 128.24, 127.84 (2), 72.23; Ts: 145.72, 132.89, 130.22 (2), 127.84 (2), 21.70

(i) LiAlH_4 , THF

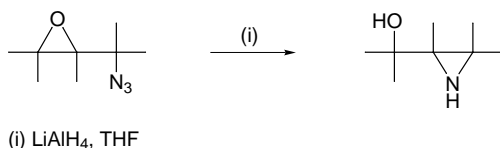
SCHEME 2

The reaction proceeded at room temperature and the yields of epimino derivatives were mostly in the narrow range 58–64% except epimino derivative **16** obtained in 81% yield. Epimino derivatives **11**, **13** and **16** were stable crystalline compounds, while derivatives **9a** and **12a** were isolated as slowly crystallising compounds which were characterised as the *N*-tosyl derivatives **9b** and **12b**, respectively. Epimino derivative **15b** was isolated as unstable syrupy substance which, after a few weeks of storing in a refrigerator at -20°C contained several products of decomposition according to TLC and NMR. Epimine **15b** was therefore characterised as stable crystalline *N*-tosyl derivative **15c**. Alternatively, unsubstituted epimine **15a** was obtained as a stable crystalline compound by lithium aluminum hydride reduction of azido derivative **6b**.

**9a**, $\text{R} = \text{H}$
9b, $\text{R} = \text{Ts}$ **10a**, $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{H}$
10b, $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Bn}$
10c, $\text{R}^1 = \text{Bn}$, $\text{R}^2 = \text{H}$
10d, $\text{R}^1 = \text{Bn}$, $\text{R}^2 = \text{Bn}$ **11****12a**, $\text{R} = \text{H}$
12b, $\text{R} = \text{Ts}$ **13****14a**, $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{H}$
14b, $\text{R}^1 = \text{Bn}$, $\text{R}^2 = \text{H}$
14c, $\text{R}^1 = \text{Bn}$, $\text{R}^2 = \text{Bn}$
14d, $\text{R}^1 = \text{Bn}$, $\text{R}^2 = \text{Ns}$ **15a**, $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{H}$
15b, $\text{R}^1 = \text{Bn}$, $\text{R}^2 = \text{H}$
15c, $\text{R}^1 = \text{Bn}$, $\text{R}^2 = \text{Ts}$ **16**

Bn, benzyl; Ns, 4-nitrobenzenesulfonyl; Ts, 4-methylbenzenesulfonyl

Epimino derivative **10a** has already been prepared¹⁵ by isomerisation of amino epoxide **5b** in 5% aqueous potassium hydroxide at 90–110 °C. However, this reaction is inconvenient for the preparation of epimine **10a** on a larger scale since the predominant product is amino sugar **6i** formed by hydrolysis of the oxirane ring¹⁵. Attempts to perform isomerisation of **5b** using potassium *tert*-butoxide in dioxan at 100 °C or potassium hydroxide in ethanol at 100 °C failed. Nevertheless, 68% yield of epimine **10a** was obtained by lithium aluminum hydride reduction of azido epoxide **5c** in tetrahydrofuran. This reaction likely involves reduction of the azido group followed by isomerisation (see Scheme 3). No products of reductive cleavage of the oxirane ring of **5c** were found in the reaction mixture.



SCHEME 3

Starting azido epoxide **5c** was prepared by the following reaction sequence: Dianhydro derivative⁵ **2b** reacted with sodium azide to give azido diol¹⁶ **6j** whose tosylation yielded monotosylate¹⁷ **6k** together with a small amount of ditosylate **6l**; monotosylate **6k** provided azido epoxide **5c** by the action of sodium methoxide in methanol–chloroform. No isomerisation of dianhydro derivative **2b** to *altro*-epoxide **4a** was observed during azidolysis of **2b**, despite the fact that compound **2b** is prone to isomerise in the presence of nucleophiles⁶. Attempts to prepare azido epoxide **5c** on a larger scale by azidolysis of **2d** followed by the oxirane ring closure at positions 3,4 according to the procedure described in literature¹⁷ failed due to rapid formation of compound **5c** during azidolysis and its further reaction with azide anion to give diazide¹⁷ **6m** as the main product of azidolysis.

Azido epoxide^{3b} **2c** reacted with lithium aluminum hydride in a similar way as azido epoxide **5c** and unsubstituted epimine¹⁸ **14a** was obtained in 38% yield. Treatment of epimines **10a** and **14a** with benzyl bromide in the presence of sodium hydride in tetrahydrofuran–*N,N*-dimethylformamide gave predominantly *O*-benzyl derivatives **10b** and **14b**. Only a small amount of *N,O*-dibenzyl derivative **14c** was isolated as a by-product after benzylation of **14a**; traces of *N*-benzyl derivative **10c** and *N,O*-dibenzyl derivative **10d** were detected by TLC in benzylation of **10b**. Preliminary experiments revealed that addition of tetrabutylammonium iodide to the

reaction mixture (see *e.g.* ref.¹⁹) significantly increased *N*-benzylation. Epimino derivative **10b** is a stable crystalline compound whereas isomer **14b** was obtained as a syrupy compound characterised as *N*-(4-nitrobenzenesulfonyl) derivative **14d**.

The structure of all epimino derivatives **9–16** was confirmed by ¹H and ¹³C NMR spectra (see Tables IV–VI). The presence of the aziridine ring is supported by characteristic upfield shifted signals for >CH–NR protons (δ 2.16–2.97 for R = H, δ 1.7–1.8 for R = Bn and δ 2.98–3.49 for R = Ts or Ns (4-nitrobenzenesulfonyl) – see Table IV) and also by >CH–NR carbons (δ 28.2–35.5 for R = H, δ 36.7–39.6 for R = Bn and δ 33.5–45.7 for R = Ts or Ns – see Table VI). Vicinal coupling constants of aziridine-ring protons appear in the range 5.0–6.6 Hz if R = H or Bn and 7.0–7.4 Hz if R = Ts or Ns (Table V) and they are significantly higher than the corresponding constants in epoxides ($J \approx 4$ Hz, *e.g.* compounds **3b**, **4b** – for data see Experimental). Conformation of the pyranose ring is determined by the aziridine ring leading to flattened half-chair conformation ⁵H_O(D) for 2,3-epimines and flattened half-chair conformation ¹H_O(D) for 3,4-epimines, respectively (MM2 calculated energy minimised conformations of epimines **9–16** showed variations of all pyranose ring torsion angles within 20°). The configuration at position 2 and 4 in the whole series of compounds **9–16** is clearly distinguished by *J*(1,2) and *J*(4,5) couplings: small values *J*(1,2) = 0.9–1.3 Hz and *J*(4,5) = 0.8–1.7 Hz indicate H2 β - and H4 β -configurations while higher values of *J*(1,2) = 2.9–4.0 Hz and *J*(4,5) = 5.2–6.9 Hz correspond to H2 α - and H4 α -configuration. We should still notice a characteristic difference between *J*(5,6en) and *J*(5,6ex) values in 2,3-epimines **9–12** (*J*(5,6en) = 1.2–2.2 Hz, *J*(5,6ex) = 5.4–6.9 Hz) and 3,4-epimines **13–16** (*J*(5,6en) = 0–0.5 Hz, *J*(5,6ex) = 4.2–4.6 Hz). This observation is in agreement with theoretically calculated torsion angles H5/H6en, H5/H6ex for epimines with aziridine ring 2,3-*exo*- (*ca* 114°, –13°), 2,3-*endo*-position (*ca* 103°, –23°) on one side and 3,4-*exo*- (*ca* 94°, –34°) and 3,4-*endo*-position (*ca* 90°, –37°) on the other side.

The structures of aziridine derivatives **9a**, **10a**, **11**, **12a**, **13**, **14a**, **15a** and **16** were also proved by X-ray analysis²⁰. IR spectra of unsubstituted epimines **10a**, **14a** and **15a** and *O*-benzyl epimines **9a**, **10b**, **11**, **12a**, **13**, **14b**, **15b** and **16** exhibit absorption in the 3 285–3 330 cm^{–1} region corresponding to the valence vibration of the imino group²¹.

TABLE IV
¹H NMR chemical shifts (in ppm, δ-scale) of epimino derivatives **9a**, **9b**, **10a**, **10b**, **11**, **12a**, **12b**, **13**, **14a–14d**, **15a–15c** and **16** in CDCl₃

Com- pound	H-1	H-2	H-3	H-4	H-5	H-6en	H-6ex	Other protons ^a
9a	5.63 bs	2.16 dd	2.33 m	3.52 dd	4.43 m	3.67 ddd	3.88 ddd	Bn: 4.86 d, 4.62 d, 7.30–7.42 m (5 H)
9b	5.55 bs	2.98 dd	3.23 m	3.48 dd	4.45 m	3.63 dd	3.88 dd	Bn: 4.57 d, 4.42 d, 7.27–7.34 m (5 H); Ts: 2.40 s (3 H), 7.91 m (2 H), 7.22 m (2 H)
10a ^b	5.61 um	2.32 dt	2.26 dd	4.29 dt	4.39 m	4.26 ddd	3.81 ddd	
10b ^c	5.50 bs	2.17 dt	2.19 ddd	3.85 dt	4.25 m	4.20 ddd	3.68 bdd	Bn: 4.63 d, 4.44 d, 7.24–7.33 m (5 H)
11 ^b	5.80 bd	2.75 dd	2.36 dd	3.61 bs	4.52 m	3.62 dd	3.64 dd	Bn: 4.74 d, 4.71 d, 7.29–7.40 m (5 H)
12a ^b	5.75 d	2.81 dd	2.42 t	4.19 dd	4.39 ddd	4.01 dd	3.45 dd	Bn: 4.84 d, 4.62 d, 7.30–7.39 m (5 H)
12b	5.63 d	3.48 bdd	3.19 bdd	4.02 dd	4.38 tm	4.12 dd	3.55 dd	Bn: 4.60 d, 4.42 d, 7.28–7.34 m (5 H); Ts: 2.39 s (3 H), 7.88 m (2 H), 7.19 m (2 H)
13	5.24 m	3.53 dd	2.24 m	2.16 dd	4.67 dm	3.96 dd	3.80 dd	Bn: 4.83 d, 4.60 d, 7.29–7.40 m (5 H)
14a ^b	5.30 dd	3.83 dd	2.16 ddd	2.38 dt	4.17 dm	4.12 dd	3.92 dd	
14b ^b	5.29 bdd	3.59 dd	2.20 bdd	2.33 dt	4.67 dm	4.19 dd	3.92 dd	Bn: 4.75 d, 4.64 d, 7.29–7.39 m (5 H)
14c	5.24 t	3.56 d	1.72 dd	1.80 dd	4.66 bd	4.05 d	3.80 dd	2 × Bn: 4.64 d, 4.52 d, 3.62 d, 3.46 d, 7.30–7.40 m (10 H)
14d	5.27 t	3.47 d	3.05 dd	3.14 dd	4.65 bd	4.16 d	3.86 dd	Bn: 4.64 d, 4.57 d, 7.32 m (3 H), 7.25 m (2 H); Ns: 8.11 m (2 H), 8.37 m (2 H)
15a ^b	5.24 t	3.78 bs	2.33 dd	2.88 t	4.84 dd	4.01 d	3.50 dd	
15b	5.29 t	3.50 d	2.30 bd	2.83 bt	4.82 dd	4.01 d	3.44 dd	Bn: 4.71 d, 4.68 d, 7.27–7.39 m (5 H)
15c	5.26 dd	3.37 bs	2.93 dd	3.49 dd	4.81 dd	3.78 d	3.41 dd	Bn: 4.67 d, 4.59 d, 7.27–7.36 m (5 H); Ts: 2.47 s (3 H), 7.76 m (2 H), 7.30 m (2 H)
16 ^b	5.24 dd	3.69 dd	2.44 ddd	2.97 t	4.81 dd	3.98 d	3.54 dd	Bn: 4.80 d, 4.72 d, 7.28–7.42 m (5 H)

^a Signals of NH and OH protons appear as broad singlets in the δ range of 0.8–1.7; ^b data obtained after addition of 2–3 drops of CD₃COOD; ^c data obtained after addition of 2–3 drops of CD₃COOD + 10% C₆D₆.

EXPERIMENTAL

The melting points were determined with a Boëtius melting point microapparatus and were not corrected. The optical rotations were measured with a Bendix-Ericsson ETL-143 A polarimeter at 21 °C, $[\alpha]_D$ values are given in $10^{-1} \text{ deg cm}^2 \text{ g}^{-1}$. The ^1H and ^{13}C NMR spectra were measured with a Varian-UNITY-500 apparatus (^1H at 500 MHz, ^{13}C at 125.7 MHz) in CDCl_3 solutions at 20 °C. Homonuclear 2D-COSY spectra were used for the assignment of protons. Proton 1D spectra with a selective decoupling of H-1 allowed to determine small long-range couplings. The signals of proton bearing carbons were structurally assigned from 2D- ^1H , ^{13}C -HMQC spectra. Chemical shifts are given in ppm (δ -scale), coupling constants (J) in Hz. Mass spectra were recorded on a VG-7070E spectrometer using electron ionisation (70 eV, trap current 50 μA , accelerating voltage 6 kV, ion source temperature 150 °C). Infrared spectra (wavenumbers in cm^{-1}) were recorded on a PE684 in chloroform solution. Infrared spectra of epimino derivatives were measured in tetrachloromethane at concentrations lower than $4.2 \cdot 10^{-3} \text{ mol dm}^{-3}$ in order to avoid intermolecular associations. Preparative

TABLE V
 ^1H NMR coupling constants (Hz) of epimino derivatives **9a**, **9b**, **10a**, **10b**, **11**, **12a**, **12b**, **13**, **14a–14d**, **15a–15c**, **16** in CDCl_3

Compound ^a	$J(1,2)$	$J(2,3)$	$J(3,4)$	$J(4,5)$	$J(5,6\text{en})$	$J(5,6\text{ex})$	$J(6\text{en},6\text{ex})$	$J(1,3)$	$J(2,4)$	$J(3,5)$
9a^b	1.3	5.0	5.8	0.8	2.2	6.8	7.9	0.9	≈ 0	1.6
9b	1.1	7.0	5.7	0.8	2.2	6.9	8.2	0.6	≈ 0	1.2
10a^{c,d}	1.3	5.6	≈ 0	5.5	2.1	6.3	8.2	< 0.3	0.9	1.7
10b^{e,f}	1.3	6.6	≈ 0	5.2	2.1	6.3	8.1	0.6	0.9	1.7
11^d	4.0	6.0	≈ 0.5	≈ 1	1.8	5.9	7.7	< 1	≈ 0	1.4
12a^d	3.8	5.8	5.0	6.9	1.2	5.4	7.7	≈ 0	≈ 0	≈ 0
12b	3.7	7.2	4.4	6.1	1.7	6.1	7.3	< 0.5	≈ 0	< 1
13^g	0.9	5.5	5.2	1.7	0.5	4.4	7.0	1.8	≈ 0	0.9
14a^d	3.4	≈ 0	5.6	1.6	0.5	4.4	7.3	2.0	1.0	0.6
14b^{d,h}	3.0	≈ 0	5.7	1.2	0.5	4.3	7.2	2.0	0.9	< 0.5
14c	2.9	≈ 0	6.5	1.0	≈ 0	4.2	7.2	1.8	≈ 0	≈ 0
14dⁱ	2.9	≈ 0	7.1	1.3	≈ 0	4.2	7.7	1.9	≈ 0	≈ 0
15a^d	0.9	≈ 0	6.4	6.3	≈ 0	4.4	6.8	1.6	≈ 0	≈ 0
15b	1.2	≈ 0.6	6.5	6.2	≈ 0	4.6	6.2	1.1	≈ 0	≈ 0
15c	1.0	≈ 0	7.4	6.1	≈ 0	4.6	6.6	1.5	≈ 0	≈ 0
16^d	3.6	4.8	6.4	6.1	≈ 0	4.3	7.0	1.0	≈ 0	≈ 0

^a Geminal coupling of *O*-benzyl protons appears in the range 11.5–12.3 Hz; $J(\text{gem})$ of *N*-benzyl protons in **14c** is 13.6 Hz. Additional coupling constants: ^b $J(1,5) = 0.2$, $J(1,6\text{en}) = 0.5$, $J(1,6\text{ex}) = 0.4$; ^c $J(1,5) < 0.3$, $J(1,6\text{en}) = 0.6$, $J(1,6\text{ex}) < 0.3$, $J(4,6\text{ex}) = 0.8$; ^e $J(1,5) < 0.2$, $J(1,6\text{ex}) < 0.3$, $J(4,6\text{ex}) = 0.7$; ^g $J(1,5) \approx 0.7$, $J(1,6\text{ex}) < 0.5$; ^h $J(1,5) \approx 0.5$; ⁱ $J(1,5) < 0.5$ Hz; ^d data obtained after addition of 2–3 drops of CD_3COOD ; ^f data obtained after addition of 2–3 drops of $\text{CD}_3\text{COOD} + 10\% \text{ C}_6\text{D}_6$.

TABLE VI
¹³C NMR chemical shift (in ppm, δ-scale) of epimino derivatives **9a**, **9b**, **10a**, **10b**, **11**, **12a**, **12b**, **13**, **14a–14d**, **15a–15c** and **16** in CDCl₃

Com- pound	C-1	C-2	C-3	C-4	C-5	C-6	Other carbons
9a	97.99	31.13	28.16	71.89	76.28	65.44	Bn: 137.40, 128.52 (2), 127.95 (3), 70.27
9b	96.29	36.58	35.10	70.78	75.21	65.64	Bn: 137.05, 128.39 (2), 128.33 (2), 127.86, 69.90; Ts: 145.07, 134.40, 129.80 (2), 127.81 (2), 21.70
10a	97.75	30.97	32.96	64.50	73.52	62.82	
10b	98.05	30.74 ^a	30.66 ^a	71.66	72.24	63.27	Bn: 137.56, 128.55 (2), 128.03, 127.63 (2), 71.49
11	98.53	34.51	26.96	74.50	72.02	65.80	Bn: 137.68, 128.53 (2), 127.92, 127.74 (2), 71.55
12a	97.88	38.77	26.53	71.48	69.11	62.74	Bn: 137.82, 128.52 (2), 127.97, 127.80 (2), 70.43
12b	95.72	45.68	35.05	69.29	69.37	63.22	Bn: 137.22, 128.43 (2), 127.96, 127.82 (2), 70.31; Ts: 144.75, 134.85, 128.71 (2), 127.72 (2), 21.62
13	101.45	71.33	27.23	31.28	69.56	67.15	Bn: 137.52, 128.50 (2), 127.98, 127.95 (2), 70.70
14a	99.44	65.64	31.32	31.32	70.30	68.87	
14b	98.49	72.90	29.10	31.40	70.44	69.04	Bn: 137.45, 128.52 (2), 128.01 (3), 71.58
14c	98.05	73.31	36.71	39.60	70.69	68.77	2 × Bn: 138.30, 137.43, 128.44 (2), 128.41 (2), 128.16 (2), 127.95, 127.88 (2), 127.20, 71.40, 62.75
14d	97.94	71.54	38.54	39.34	69.53	68.29	Bn: 136.57, 128.66 (2), 128.37, 128.06 (2), 71.83; Ns: 150.74, 143.70, 129.13 (2), 124.41 (2)
15a	100.85	66.28	29.69	31.96	72.31	65.60	
15b	99.04	73.12	27.52	32.04	72.04	65.06	Bn: 137.67, 128.51, 128.48 (2), 127.90 (2), 72.32
15c	99.14	71.27	35.57	40.46	69.76	65.51	Bn: 136.89, 128.59 (2), 128.17, 127.92 (2), 72.49; Ts: 144.99, 134.18, 129.88 (2), 128.00 (2), 21.65
16	97.07	72.95	27.78	35.46	72.34	65.02	Bn: 137.50, 128.43 (2), 128.04 (2), 127.86, 70.88

^a The assignment of signals may be mutually interchanged.

column chromatography was carried out on Kieselgel 60 (Merck, 60–230 mesh). Thin layer chromatography was carried out on TLC aluminium sheets (Merck) with Kieselgel 60 F₂₅₄ and layer thickness 0.2 mm. Detection was performed by spraying with 50% sulfuric acid and heating. UV detection was also employed when appropriate. Preparative thin-layer chromatography was performed on plates 20 × 20 cm with Kieselgel GF₂₅₄ (Merck). Solvent systems used for chromatography were benzene–acetone 10 : 1 (S₁), chloroform–methanol 10 : 1 (S₂), cyclohexane–acetone 1 : 1 (S₃), unless stated otherwise. Solutions were dried with anhydrous Na₂SO₄ and concentrated under reduced pressure and temperatures below 50 °C if not stated otherwise. The term “standard workup” refers to extracting with dichloromethane, washing the dichloromethane solution with water, drying and concentrating. Tetrahydrofuran was dried with LiAlH₄. Sodium hydride dispersion (60% in mineral oil) and 98% benzyl bromide, both purchased from Sigma-Aldrich, Czech Republic, were used for benzylation. If not stated otherwise, ice–NaCl was used as an external cooling mixture (ca –15 °C). Starting dianhydro derivatives **1a** (ref.⁴), **1b** (ref.⁴), **2a** (ref.⁵), **2b** (ref.⁵), **2c** (ref.^{3b}), **2d** (ref.⁶), **3a** (ref.⁷), **4a** (ref.⁸) and **5a** (ref.⁹) were prepared using procedures described in literature.

General Procedure for Tosylation

A solution of starting compound and tosyl chloride in pyridine was allowed to stand for a given time at room temperature unless stated otherwise. The reaction mixture was then diluted with water. The amounts of reactants, the volume of pyridine and further workup are given for the individual compounds.

General Procedure for Benzylation

Sodium hydride dispersion (60% in mineral oil) was added under cooling and stirring to a solution of starting compound in tetrahydrofuran–*N,N*-dimethylformamide and the mixture was cooled and stirred for 1–2 h. Tetrabutylammonium iodide (except synthesis of compound **10b** and **14b**) and benzyl bromide was then added. After additional stirring and cooling for 1.5–2 h, the cooling bath was removed and stirring continued overnight at room temperature. Amounts of reactants, volumes of solvents and further workup are given for individual compounds.

1,6:2,3-Dianhydro-4-*O*-benzyl-β-D-gulopyranose (**3b**)

Sodium hydride dispersion (2.54 g, 64 mmol), dianhydro derivative⁷ **3a** (4.61 g, 32 mmol), tetrahydrofuran (80 ml), *N,N*-dimethylformamide (30 ml), tetrabutylammonium iodide (20 mg, 0.05 mmol), benzyl bromide (5.10 ml, 42 mmol). According to TLC (S₁) two compounds having *R_F* 0.49 (major product **3b**) and *R_F* 0.34 (by-product **5a**) were present. The reaction mixture was diluted with water and neutralised with 5% HCl. Standard workup yielded **3b** (4.70 g; 63%), m.p. 64–65 °C (ether–petroleum ether), [α]_D –10 (c 0.4, CHCl₃). ¹H NMR: 7.30–7.39 m (5 H, C₆H₅); 5.57 bs (1 H, H-1); 4.73 d and 4.58 d (2 H, CH₂ (Bn), *J*(gem) = 11.9); 4.37 m (1 H, H-5, *J*(5,3) = 2.1, *J*(5,4) = 5.1, *J*(5,6en) = 2.1, *J*(5,6ex) = 6.2); 4.17 ddd (1 H, H-6en, *J*(6en,1) = 0.5, *J*(6en,5) = 2.1, *J*(6en,6ex) = 8.1); 3.97 dt (1 H, H-4, *J*(4,2) = 1.0, *J*(4,3) ≈ 0, *J*(4,5) = 5.1, *J*(4,6ex) = 0.8); 3.75 ddd (1 H, H-6ex, *J*(6ex,4) = 0.8, *J*(6ex,5) = 6.2, *J*(6ex,6en) = 8.1); 3.12 ddd (1 H, H-3, *J*(3,1) = 0.6, *J*(3,2) = 3.9, *J*(3,4) ≈ 0, *J*(3,5) = 2.1); 3.02 dt (1 H, H-2, *J*(2,1) = 1.2, *J*(2,3) = 3.9, *J*(2,4) = 1.0). ¹³C NMR: 137.24, 128.62 (2), 128.20, 127.72

(2) (C_6H_5); 97.06 (C-1); 71.98 (C-5); 71.94 (CH_2 (Bn)); 70.46 (C-4); 63.52 (C-6); 50.98 (C-3); 48.50 (C-2). For $\text{C}_{13}\text{H}_{14}\text{O}_4$ (234.3) calculated: 66.65% C, 6.02% H; found: 66.63% C, 6.12% H.

In preliminary experiments the reaction was carried out with 280 mg of the starting dianhydro derivative **3a**. Preparative TLC of the mother liquor on silica gel (15 g) in benzene–cyclohexane–acetone (10 : 9 : 1) gave 37 mg (8%) of 1,6:3,4-dianhydro-4-*O*-benzyl- β -D-galactopyranose (**5a**) identical with the authentic sample⁹ according to TLC, IR and m.p. 47–49 °C (authentic sample m.p. 48–49 °C).

1,6:3,4-Dianhydro-2-*O*-benzyl- β -D-altropyranose (**4b**)

Sodium hydride dispersion (1.03 g, 26 mmol), dianhydro derivative⁸ **4a** (3.50 g, 24 mmol), tetrahydrofuran (47 ml), *N,N*-dimethylformamide (35 ml), tetrabutylammonium iodide (14 mg, 0.04 mmol), benzyl bromide (3.10 ml, 25.5 mmol). The reaction mixture was diluted with water and neutralised with 5% HCl. Standard workup gave oil residue, which was twice codistilled with toluene to yield **4b** (3.81 g; 67%), m.p. 80–82 °C (ether), $[\alpha]_{\text{D}} -66$ (*c* 0.6, CHCl_3) in agreement with the authentic sample²² (m.p. 80–81 °C, $[\alpha]_{\text{D}} -68$ (*c* 1.5, CHCl_3)). ¹H NMR: 7.29–7.38 m (5 H, C_6H_5); 5.32 t (1 H, H-1, $J(1,2) = 2.8$, $J(1,3) = 2.4$); 4.74 d and 4.66 d (2 H, CH_2 (Bn), $J(\text{gem}) = 12.1$); 4.69 m (1 H, H-5, $J(5,3) = 0.6$, $J(5,4) = 1.5$, $J(5,6\text{en}) = 0.6$, $J(5,6\text{ex}) = 4.3$); 4.13 bd (1 H, H-6en, $J(6\text{en},5) = 0.6$, $J(6\text{en},6\text{ex}) = 7.5$); 3.87 dd (1 H, H-6ex, $J(6\text{ex},5) = 4.3$, $J(6\text{ex},6\text{en}) = 7.5$); 3.64 dd (1 H, H-2, $J(2,1) = 2.8$, $J(2,3) \approx 0$, $J(2,4) = 1.0$); 3.13 dt (1 H, H-4, $J(4,2) = 1.0$, $J(4,3) = 4.0$, $J(4,5) = 1.5$); 3.06 ddd (1 H, H-3, $J(3,1) = 2.4$, $J(3,2) \approx 0$, $J(3,4) = 4.0$, $J(3,5) = 0.6$). ¹³C NMR: 137.14, 128.59 (2), 128.17, 128.08 (2) (C_6H_5); 98.21 (C-1); 72.13 (C-2); 72.02 (CH_2 (Bn)); 69.97 (C-5); 67.38 (C-6); 50.16 (C-4); 49.66 (C-3).

1,6:3,4-Dianhydro-2-azido-2-deoxy- β -D-galactopyranose (**5c**)

To a solution of azide **6k** (1.292 g, 3.79 mmol) in chloroform (30 ml) a solution of sodium (0.27 g, 12 mmol) in methanol (9 ml) was added dropwise under cooling. After 40 min the cooling bath was removed and the reaction mixture was allowed to stand at room temperature for 24 h. The reaction mixture was then diluted with water. Standard workup gave **5c** (388 mg; 61%), m.p. 79–81 °C (ether–petroleum ether), $[\alpha]_{\text{D}} -87$ (*c* 0.4, CHCl_3), identical with the authentic compound **5c** prepared according to literature^{17a} (ref.^{17a} gives m.p. 76.5–78 °C, $[\alpha]_{\text{D}} -93$ (*c* 2, CHCl_3)).

General Procedure for Preparation of Azido Derivatives **6a–6d**, **7a** and **8a**

Dianhydro derivatives **1a**, **1b**, **2a**, **3b**, **4b** and **5a**, sodium azide and ammonium chloride were heated in a mixture of 2-methoxyethanol and water at 110–120 °C for a given time. The reaction was monitored by TLC (S_1). After cooling to room temperature the reaction mixture was concentrated almost to dryness. The residue was diluted with water, extracted with dichloromethane, the extract was washed with water, dried, decolorised with charcoal and concentrated. Further workup is described for individual compounds. For the workup of **6a** see ref.¹¹. For NMR data of azido derivatives see Tables I–III.

1,6-Anhydro-3-azido-4-*O*-benzyl-3-deoxy- β -D-glucopyranose (**6a**)

Preparation of the title compound from **1a** is described in ref.¹¹, m.p. 74–76 °C (ethanol–water), $[\alpha]_{\text{D}} -15$ (*c* 0.6, CHCl_3); ref.¹¹ gives m.p. 74–76.5 °C, $[\alpha]_{\text{D}} -13$ (*c* 2.6, CHCl_3).

1,6-Anhydro-3-azido-3-deoxy-4-*O*-tosyl- β -D-glucopyranose (**6b**)

Dianhydro derivative⁴ **1b** (5.60 g, 18.8 mmol), sodium azide (5.0 g, 77 mmol), ammonium chloride (6.0 g, 112 mmol), 2-methoxyethanol (80 ml) and water (20 ml) were heated at 110–120 °C for 30 h. The reaction mixture was worked up as described in General procedure to give **6b** (3.96 g; 62%), m.p. 85–91 °C (ethanol–water) with traces of a polar compound according to TLC (S_1), but pure enough to be used for further reactions. Preparative TLC of 70 mg of the product **6b** on silica gel (10 g) in S_1 afforded 46 mg of pure **6b**, m.p. 93–95 °C (ethanol–water), $[\alpha]_D$ –27 (c 0.7, CHCl_3). IR: 3 562 (OH); 2 111 (N_3); 1 375, 1 177 (SO_2). For $\text{C}_{13}\text{H}_{15}\text{N}_3\text{O}_6\text{S}$ (341.3) calculated: 45.74% C, 4.43% H, 12.31% N, 9.39% S; found: 46.08% C, 4.45% H, 12.63% N, 9.69% S.

1,6-Anhydro-2-azido-4-*O*-benzyl-2-deoxy- β -D-glucopyranose (**6c**)

Dianhydro derivative⁵ **2a** (4.000 g, 17.1 mmol), sodium azide (4.0 g, 61.5 mmol), ammonium chloride (4.0 g, 75 mmol), 2-methoxyethanol (40 ml) and water (20 ml) were heated at 110–120 °C for 30 h. The reaction mixture was worked up as described in General procedure to give **6c** (3.361 g; 71%), m.p. 102–105 °C (methanol–water), $[\alpha]_D$ –7 (c 0.4, CHCl_3); ref.¹² gives m.p. 101–103 °C, $[\alpha]_D$ –7 (EtOH).

1,6-Anhydro-4-azido-2-*O*-benzyl-4-deoxy- β -D-glucopyranose (**6d**)

Dianhydro derivative⁹ **5a** (790 mg, 3.37 mmol), sodium azide (0.8 g, 12.3 mmol), ammonium chloride (1.4 g, 26 mmol), 2-methoxyethanol (15 ml) and water (5 ml) were heated at 110–120 °C for 25 h. The reaction mixture was worked up as described in General procedure to give **6d** (676 mg; 72%), m.p. 76–78 °C (ether–petroleum ether), $[\alpha]_D$ –82 (c 0.4, CHCl_3); ref.¹³ gives $[\alpha]_D$ –71 (c 1.0, CHCl_3), m.p. not given.

1,6-Anhydro-3-azido-4-*O*-benzyl-3-deoxy- β -D-galactopyranose (**7a**)

Dianhydro derivative **3b** (3.800 g, 16.2 mmol), sodium azide (3.8 g, 58.4 mmol), ammonium chloride (4.8 g, 90 mmol), 2-methoxyethanol (105 ml) and water (30 ml) were heated at 110–120 °C. Every 25 h, ammonium chloride (0.5 g, 9 mmol) and sodium azide (0.5 g, 8 mmol) were added into the reaction mixture. After 210 h the reaction was stopped. The reaction mixture was worked up as described in General procedure. Chromatography of oil residue (4.4 g) on silica gel (200 g) in toluene–acetone (50 : 1) gave unreacted **3b** (774 mg; 20%). Elution with toluene–acetone (5 : 1) gave syrupy **7a** (3.392 g; 75%), $[\alpha]_D$ –22 (c 0.5, CHCl_3). IR: 3 569 (OH); 2 111 (N_3).

1,6-Anhydro-3-azido-2-*O*-benzyl-3-deoxy- β -D-mannopyranose (**8a**)

Dianhydro derivative **4b** (3.015 g, 12.9 mmol), sodium azide (4.0 g, 61.5 mmol), ammonium chloride (9.0 g, 168 mmol), 2-methoxyethanol (65 ml) and water (35 ml) were heated at 110–120 °C. Every 25 h, ammonium chloride (0.5 g, 9 mmol) and sodium azide (0.5 g, 8 mmol) were added into the reaction mixture. After 150 h the starting compound **4a** had disappeared (TLC). The reaction mixture was worked up as described in General procedure to give syrupy **8a** (3.076 g; 86%), $[\alpha]_D$ –62 (c 0.6, CHCl_3). IR: 3 571 (OH); 2 113 (N_3).

1,6-Anhydro-2-azido-4-*O*-benzyl-2-deoxy-3-*O*-tosyl- β -D-glucopyranose (**6f**)

Azido derivative **6c** (1.000 g, 3.6 mmol), tosyl chloride (3.5 g, 18.4 mmol) and pyridine (12 ml) were heated at 80 °C. Compound **6c** disappeared after 10 h according to TLC (S_1). The reaction mixture was poured into water, the separated product was filtered off and dissolved in acetone. The acetone solution was decolorised with charcoal and concentrated to yield **6f** (1.35 g; 87%), m.p. 101–102.5 °C (methanol), $[\alpha]_D^{+121}$ (c 0.5, CHCl₃). IR: 2 108 (N₃); 1 374, 1 178 (SO₂). For C₂₀H₂₁N₃O₆S (431.5) calculated: 55.67% C, 4.91% H, 9.74% N, 7.43% S; found: 55.67% C, 4.82% H, 9.35% N, 7.31% S.

1,6-Anhydro-4-azido-2-*O*-benzyl-4-deoxy-3-*O*-tosyl- β -D-glucopyranose (**6g**)

Azido derivative **6d** (637 mg, 2.3 mmol), tosyl chloride (3.2 g, 16.8 mmol) and pyridine (12 ml) were heated at 100 °C. Starting **6d** had disappeared after 6 h according to TLC (S_1). Standard workup (the dichloromethane solution was decolorised with charcoal) gave **6g** (844 mg; 85%), m.p. 85.5–87 °C (methanol-water), $[\alpha]_D^{-117}$ (c 0.5, CHCl₃). IR: 2 106 (N₃); 1 374, 1 177 (SO₂). For C₂₀H₂₁N₃O₆S (431.5) calculated: 55.67% C, 4.91% H, 9.74% N, 7.43% S; found 55.78% C, 4.89% H, 9.32% N, 7.41% S.

1,6-Anhydro-3-azido-2-*O*-benzyl-3-deoxy-4-*O*-tosyl- β -D-glucopyranose (**6h**)

Sodium hydride dispersion (130 mg, 3.25 mmol), azido tosylate **6b** (500 mg, 1.46 mmol), tetrahydrofuran (11 ml), tetrabutylammonium iodide (10 mg, 0.03 mmol), benzyl bromide (300 μ l, 2.52 mmol). The unreacted sodium hydride was decomposed by addition of ethanol. The reaction mixture was diluted with water. Standard workup gave **6h** (438 mg; 69%), m.p. 73–75 °C (ether–petroleum ether), $[\alpha]_D^{-117}$ (c 0.6, CHCl₃). IR: 2 113 (N₃); 1 370, 1 177 (SO₂). For C₂₀H₂₁N₃O₆S (431.5) calculated: 55.67% C, 4.91% H, 9.74% N, 7.43% S; found: 55.74% C, 4.84% H, 9.86% N, 7.39% S.

1,6-Anhydro-2-azido-2-deoxy-4-*O*-tosyl- β -D-glucopyranose (**6k**)and 1,6-Anhydro-2-azido-2-deoxy-3,4-di-*O*-tosyl- β -D-glucopyranose (**6l**)

Azide¹⁶ **6j** (963 mg, 5.14 mmol), tosyl chloride (1.0 g, 5.24 mmol) and pyridine (15 ml) were allowed to stand for 5 days. According to TLC (S_1) the reaction mixture contained small amount of starting **6j** and two products: R_F 0.35 (major product **6k**) and R_F 0.72 (by-product **6l**). Standard workup followed by chromatography on silica gel (30 g) in benzene–acetone (20 : 1) gave the following products (in order).

1,6-Anhydro-2-azido-2-deoxy-3,4-di-*O*-tosyl- β -D-glucopyranose (**6l**) (231 mg; 9%), m.p. 148–150 °C (ethanol–acetone), $[\alpha]_D^{+43}$ (c 0.6, CHCl₃). IR: 2 107 (N₃); 1 376, 1 177 (SO₂). For C₂₀H₂₁N₃O₈S₂ (495.5) calculated: 48.47% C, 4.27% H, 8.48% N, 12.94% S; found: 48.58% C, 4.34% H, 7.94% N, 12.61% S.

1,6-Anhydro-2-azido-2-deoxy-4-*O*-tosyl- β -D-glucopyranose¹⁷ (**6k**) (1.389 g; 79%), syrup, $[\alpha]_D^{-22}$ (c 0.8, CHCl₃). IR: 3 605 (OH); 2 109 (N₃); 1 371, 1 177 (SO₂).

1,6-Anhydro-3-azido-4-*O*-benzyl-3-deoxy-2-*O*-tosyl- β -D-galactopyranose (**7b**)

Azide **7a** (3.33 g, 12.0 mmol), tosyl chloride (4.50 g, 23.6 mmol) and pyridine (58 ml) were allowed to stand for 42 h. Standard workup yielded **7b** (4.42 g; 85%), m.p. 77–82 °C (ether–petroleum ether), $[\alpha]_D^{-79}$ (c 0.5, CHCl₃). IR: 2 113 (N₃); 1 373, 1 178 (SO₂). For

$C_{20}H_{21}N_3O_6S$ (431.5) calculated: 55.67% C, 4.91% H, 9.74% N, 7.43% S; found: 55.70% C, 5.14% H, 9.55% N, 7.15% S.

1,6-Anhydro-3-azido-2-*O*-benzyl-3-deoxy-4-*O*-tosyl- β -D-mannopyranose (**8b**)

Azide **8a** (500 mg, 1.80 mmol), tosyl chloride (1.9 g, 10.0 mmol) and pyridine (9 ml) were allowed to stand for 18 h. Standard workup yielded **8b** (619 mg; 80%), m.p. 79–81 °C (ether–petroleum ether), $[\alpha]_D -13$ (c 0.5, $CHCl_3$). IR: 2 121 (N_3); 1 371, 1 177 (SO_2). For $C_{20}H_{21}N_3O_6S$ (431.5) calculated: 55.67% C, 4.91% H, 9.74% N, 7.43% S; found: 55.63% C, 4.94% H, 9.62% N, 7.29% S.

General Procedure for Preparation of Epimino Derivatives **9a**, **10a**, **11**, **12a**, **13**, **14a**, **15a**, **15b** and **16**

A solution of starting azido tosylate or azido epoxide in tetrahydrofuran was added dropwise to a suspension of lithium aluminum hydride in tetrahydrofuran under cooling and stirring. The cooling bath was removed after given time and the reaction mixture was allowed to stand at room temperature overnight until stated otherwise. The amount of starting compound, lithium aluminum hydride, the volume of tetrahydrofuran and the time of cooling are given for the individual compounds. The reaction was monitored by TLC in S_1 and S_3 . Unreacted lithium aluminum hydride was decomposed by dropwise addition of moist ether; 0.5–2 ml of ethanol was added to complete the decomposition. The precipitate was removed either by filtration through a short column of silica gel (3 g), by centrifugation or by decantation. Combined filtrates or supernatants were concentrated. Details of the workup are given for the individual compounds.

1,6-Anhydro-4-*O*-benzyl-2,3-dideoxy-2,3-epimino- β -D-allopyranose (**9a**)

Azido tosylate **6f** (700 mg, 1.62 mmol) in tetrahydrofuran (3 ml); lithium aluminum hydride (246 mg, 6.48 mmol) in tetrahydrofuran (29 ml). The cooling bath was removed after 2 h. After decomposition of the unreacted lithium aluminum hydride, the reaction mixture was filtered through a short column of silica gel and the column was washed with ether and ethyl acetate. Chromatography on silica gel (30 g) in toluene–propan-2-ol (10 : 1) gave 330 mg of **9a** with traces of impurities according to TLC. The product was dissolved in ethanol and the solution was decolorised with charcoal and concentrated. Chromatography on silica gel (30 g) in ethyl acetate gave **9a** (224 mg; 59%), m.p. 50–56 °C (ether), $[\alpha]_D +139$ (c 0.6, $CHCl_3$). IR: 3 301, 3 285 (NH).

1,6-Anhydro-2,3-dideoxy-2,3-epimino- β -D-gulopyranose (**10a**)

Azido epoxide **5c** (531 mg, 3.14 mmol) in tetrahydrofuran (2 ml); lithium aluminum hydride (265 mg, 6.98 mmol) in tetrahydrofuran (30 ml). The cooling bath (ice-water) was removed after 20 min. After decomposition of unreacted lithium aluminum hydride the precipitate was separated by decantation, washed twice with tetrahydrofuran and then applied on a short column of silica gel and washed with ethyl acetate–ethanol (10 : 1). Chromatography on silica gel (50 g) in acetone gave **10a** (305 mg; 68%), m.p. 146–148 °C (methanol–ether, at 90–100 °C crystals changed shape and transparency), $[\alpha]_D +23$ (c 0.5, H_2O); ref.¹⁵ gives m.p. 143–145 °C, $[\alpha]_D +27$ (c 0.45, H_2O). IR: 3 636 (OH); 3 321, 3 293 (NH).

1,6-Anhydro-4-*O*-benzyl-2,3-dideoxy-2,3-epimino- β -D-mannopyranose (**11**)

Azido tosylate¹¹ **6e** (700 mg, 1.62 mmol) in tetrahydrofuran (3 ml); lithium aluminum hydride (246 mg, 6.48 mmol) in tetrahydrofuran (29 ml). The cooling bath was removed after 2 h. After decomposition of unreacted lithium aluminum hydride the reaction mixture was filtered through a short column of silica gel and the column was washed with dichloromethane. Concentration gave **11** (227 mg; 60%), m.p. 99–100.5 °C (acetone–ether), $[\alpha]_D -45$ (c 0.5, CHCl₃). The product was identical with the authentic sample¹¹ (m.p. 98–99 °C, $[\alpha]_D -45$ (c 0.8, CHCl₃)).

1,6-Anhydro-4-*O*-benzyl-2,3-dideoxy-2,3-epimino- β -D-talopyranose (**12a**)

Azido tosylate **7b** (700 mg, 1.62 mmol) in tetrahydrofuran (3 ml); lithium aluminum hydride (246 mg, 6.48 mmol) in tetrahydrofuran (29 ml). The cooling bath was removed after 2 h. After decomposition of unreacted lithium aluminum hydride the reaction mixture was filtered through a short column of silica gel, the column was washed with ether and ethyl acetate. Chromatography on silica gel (30 g) in toluene–acetone (2 : 1) gave **12a** (235 mg; 62%), m.p. 45–50 °C (ether), $[\alpha]_D -138$ (c 0.5, CHCl₃). IR: 3 322, 3 309 (NH).

1,6-Anhydro-2-*O*-benzyl-3,4-dideoxy-3,4-epimino- β -D-allopyranose (**13**)

Azido tosylate **6g** (600 mg, 1.39 mmol) in tetrahydrofuran (3 ml); lithium aluminum hydride (120 mg, 3.16 mmol) in tetrahydrofuran (18 ml). The cooling bath was removed after 3 h and the reaction mixture was allowed to stand at room temperature overnight. According to TLC (S₃) the reaction mixture contained in addition to product **13** (*R_F* 0.20) another compound (*R_F* 0.32). Therefore, lithium aluminum hydride (18 mg, 0.47 mmol) was added and the reaction mixture was heated at 45–50 °C for 3 h and then allowed to stand at room temperature for 3 days. Only epimine **13** was present (TLC). After decomposition of unreacted lithium aluminum hydride the precipitate was separated by centrifugation and washed with tetrahydrofuran and ether–acetone (4 : 1). Combined supernatants were filtered through celite, concentrated to 2 ml and diluted with dichloromethane. Dichloromethane solution was washed with water, dried, decolorised with charcoal and concentrated. Chromatography on silica gel (35 g) in S₃ gave **13** (208 mg; 64%), m.p. 63–65 °C (ether–petroleum ether), $[\alpha]_D -178$ (c 0.6, CHCl₃). IR: 3 302, 3 288 (NH). For C₁₃H₁₅NO₃ (233.3) calculated: 66.93% C, 6.48% H, 6.01% N; found: 67.22% C, 6.65% H, 6.15% N.

1,6-Anhydro-3,4-dideoxy-3,4-epimino- β -D-altropyranose (**14a**)

Azido tosylate^{3b} **2c** (700 mg, 4.14 mmol) in tetrahydrofuran (3 ml); lithium aluminum hydride 350 mg (9.22 mmol) in tetrahydrofuran (36 ml). The cooling bath was removed after 1 h. After decomposition of unreacted lithium aluminum hydride the precipitate was separated by decantation, washed twice with tetrahydrofuran and combined supernatants were filtered through celite and concentrated to yield **14a** (222 mg; 38%), m.p. 146–148 °C (methanol–ether), $[\alpha]_D -119$ (c 0.6, H₂O), identical with the authentic sample¹⁸ (m.p. 147–148 °C, $[\alpha]_D -119$ (c 0.6, H₂O)). IR: 3 568 (OH); 3 326, 3 295 (NH).

1,6-Anhydro-3,4-dideoxy-3,4-epimino- β -D-galactopyranose (**15a**)

Azido tosylate **6b** (600 mg, 1.76 mmol) in tetrahydrofuran (3 ml); lithium aluminum hydride (240 mg, 6.32 mmol) in tetrahydrofuran (20 ml). The cooling bath was removed after 2 h. After decomposition of unreacted lithium aluminum hydride the precipitate was separated by centrifugation and washed with tetrahydrofuran–acetone (1 : 1), ether–acetone (1 : 1) and acetone. Combined supernatants were filtered through celite. Chromatography on silica gel (50 g) in ethyl acetate–acetone (2 : 1) gave **15a** (140 mg; 56%), m.p. 115–118 °C (ethanol–ether), $[\alpha]_D -67$ (c 0.5, H₂O). IR: 3 629, 3 585 (OH); 3 327 (NH). For C₆H₉NO₃ (143.1) calculated: 50.34% C, 6.34% H, 9.79% N; found: 50.07% C, 6.27% H, 9.81% N.

1,6-Anhydro-2-O-benzyl-3,4-dideoxy-3,4-epimino- β -D-galactopyranose (**15b**)

Azido tosylate **6b** (230 mg, 0.53 mmol) in tetrahydrofuran (2 ml); lithium aluminum hydride (80 mg, 2.11 mmol) in tetrahydrofuran (8 ml). The cooling bath was removed after 2.5 h and the reaction mixture was allowed to stand at room temperature for 4 h and then at 4 °C for 18 h. Unreacted lithium aluminum hydride was decomposed under cooling (ice-water). The precipitate was separated by centrifugation and washed twice with tetrahydrofuran. Combined supernatants were concentrated at room temperature to 20 ml and diluted with excess of dichloromethane. Dichloromethane solution was washed with water, dried, decolorised with charcoal and concentrated at room temperature. Preparative TLC on silica gel (20 g) in ethyl acetate–acetone (5 : 1) gave syrupy **15b** (72 mg; 58%), only one product was present according to TLC (S₃ and ethyl acetate–acetone (4 : 1)). After a few weeks of storing at –20 °C at least five products of decomposition were detected by TLC (S₃) in addition to epimine **15b**. IR: 3 325 (NH). EI MS, *m/z* (rel.%): 233 (0.05, M⁺), 204 (11.38, C₁₂H₁₄NO₂), 190 (0.84), 158 (8.29, C₁₁H₁₂N), 142 (19.87, C₆H₈NO₃), 96 (59.70, C₅H₆NO), 91 (100.00, C₇H₇).

1,6-Anhydro-2-O-benzyl-3,4-dideoxy-3,4-epimino- β -D-talopyranose (**16**)

Azido tosylate **8b** (700 mg, 1.62 mmol) in tetrahydrofuran (3 ml); lithium aluminum hydride (246 mg, 6.48 mmol) in tetrahydrofuran (29 ml). The cooling bath was removed after 2 h. After decomposition of unreacted lithium aluminum hydride the reaction mixture was filtered through a short column of silica gel, the column was washed with ether and ethyl acetate and combined filtrates concentrated to yield **16** (306 mg; 81%); m.p. 164–166 °C (ether, 150 °C sublimation), $[\alpha]_D +15$ (c 0.5, CHCl₃). IR: 3 322, 3 309 (NH). For C₁₃H₁₅NO₃ (233.3) calculated: 66.93% C, 6.48% H, 6.01% N; found: 66.87% C, 6.47% H, 5.86% N.

1,6-Anhydro-4-O-benzyl-2,3-dideoxy-2,3-(tosylepimino)- β -D-allopyranose (**9b**)

Epimine **9a** (40 mg, 0.17 mmol), tosyl chloride (77 mg, 0.40 mmol) and pyridine (0.4 ml) were allowed to stand overnight. The precipitated **9b** was filtered off to give 44 mg (67%), m.p. 204–206 °C (acetone–ether), $[\alpha]_D +130$ (c 0.4, CHCl₃). IR: 1 332, 1 162 (SO₂). For C₂₀H₂₁NO₅S (387.5) calculated: 62.00% C, 5.46% H, 3.62% N; found: 61.92% C, 5.44% H, 3.52% N.

1,6-Anhydro-4-*O*-benzyl-2,3-dideoxy-2,3-epimino- β -D-gulopyranose (**10b**)

Sodium hydride dispersion (36 mg, 0.90 mmol), epimine **10a** (120 mg, 0.84 mmol), tetrahydrofuran (2 ml), *N,N*-dimethylformamide (1.2 ml), benzyl bromide (100 μ l, 0.82 mmol). The reaction mixture contained according to TLC (S_3) compound with R_F 0.28 (main product) and traces of two compounds with R_F 0.39 and 0.61. The reaction mixture was diluted with water. Standard workup followed by chromatography on silica gel (30 g) in ethyl acetate–acetone (4 : 1) gave **10b** (65 mg; 33%), m.p. 81–83 °C (ether–petroleum ether), $[\alpha]_D^{25}$ –5 (c 0.5, CHCl_3). IR: 3 323, 3 289 (NH). For $\text{C}_{13}\text{H}_{15}\text{NO}_3$ (233.3) calculated: 66.93% C, 6.48% H, 6.01% N; found: 66.74% C, 6.42% H, 5.92% N.

1,6-Anhydro-4-*O*-benzyl-2,3-dideoxy-2,3-(tosylepimino)- β -D-talopyranose (**12b**)

Epimine **12a** (40 mg, 0.17 mmol), tosyl chloride (120 mg, 0.63 mmol) and pyridine (1 ml) were left to stand overnight. The precipitated product was filtered off, dissolved in dichloromethane, decolorised with charcoal and concentrated. Preparative TLC on silica gel (10 g) in toluene–acetone (15 : 1) gave **12b** (39 mg; 59%), m.p. 192–193.5 °C (acetone–ether), $[\alpha]_D^{25}$ –132 (c 0.5, CHCl_3). IR: 1 329, 1 161 (SO_2). For $\text{C}_{20}\text{H}_{21}\text{NO}_5\text{S}$ (387.5) calculated: 62.00% C, 5.46% H, 3.62% N, 8.28% S; found: 61.90% C, 5.50% H, 3.48% N, 8.09% S.

1,6-Anhydro-2-*O*-benzyl-3,4-dideoxy-3,4-epimino- β -D-altropyranose (**14b**)

Sodium hydride dispersion (60 mg, 1.50 mmol), epimine **14a** (200 mg, 1.40 mmol), tetrahydrofuran (2.5 ml), *N,N*-dimethylformamide (3.5 ml), benzyl bromide (173 μ l, 1.43 mmol). The reaction mixture was diluted with ethanol, concentrated and the residue was codistilled twice with toluene. Standard workup followed by chromatography on silica gel (40 g) in ethyl acetate–acetone (2 : 1) gave the following compounds (in order).

A) Syrupy *N,O*-dibenzyl derivative **14c** (48 mg; 11%);

B) Syrupy epimino derivative **14b** (160 mg; 49%). IR: 3 326, 3 294 (NH).

1,6-Anhydro-2-*O*-benzyl-3,4-dideoxy-3,4-[(4-nitrobenzenesulfonyl)epimino]- β -D-altropyranose (**14d**)

Epimine **14b** (50 mg, 0.21 mmol) and 4-nitrobenzenesulfonyl chloride (100 mg, 0.45 mmol) in pyridine (2 ml) were allowed to stand overnight. The reaction mixture was then diluted with water, the precipitated product was separated and dissolved in acetone. The acetone solution was decolorised with charcoal, filtered through a short column of celite and concentrated to give **14d** (59 mg; 66%), m.p. 139–141 °C (ether), $[\alpha]_D^{25}$ –51 (c 0.6, CHCl_3). IR: 1 537 (NO_2); 1 167 (SO_2). For $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_7\text{S}$ (418.4) calculated: 54.54% C, 4.34% H, 6.67% N, 7.66% S; found: 54.59% C, 4.27% H, 6.65% N, 7.70% S.

1,6-Anhydro-2-*O*-benzyl-3,4-dideoxy-3,4-(tosylepimino)- β -D-galactopyranose (**15c**)

Epimine **15b** (56 mg, 0.24 mmol), tosyl chloride (150 mg, 0.79 mmol) and pyridine (1.5 ml) were left to stand overnight. The reaction mixture was worked up as described for **14d** to give **15c** (55 mg; 59%), m.p. 152–152.5 °C (ether–petroleum ether), $[\alpha]_D^{25}$ –6 (c 0.6, CHCl_3). IR: 1 332, 1 163 (SO_2). For $\text{C}_{20}\text{H}_{21}\text{NO}_5\text{S}$ (387.5) calculated: 62.00% C, 5.46% H, 3.62% N, 8.28% S; found: 61.78% C, 5.47% H, 3.70% N, 8.04% S.

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