PREPARATION OF *O*-, *S*- AND *N*-BENZYL DERIVATIVES OF 1,6-ANHYDRO-β-D-HEXOPYRANOSES *via* AZIRIDINE RING OPENING

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The aziridine ring opening of *N*-tosylepimino carbohydrates **1**–**6** having D-*allo*, D-*manno*, D-*galacto* and D-*talo* configurations with benzyl alcohol, benzylamine and phenylmethanethiol afforded 2-, 3- and 4-*O*-benzyl-, benzylsulfanyl and benzylamino derivatives of 1,6-anhydro-β-D-hexopyranoses of D-*gluco*, D-*galacto* and D-*manno* configurations **7**–**23** in 44–99% yields. Hexenopyranoses **24**–**26** were prepared from tosylepimino carbohydrates **1**, **4** and **5** by intramolecular rearrangement of the aziridine ring.

Keywords: Carbohydrates; Ring opening reactions; Stereospecific synthesis; NMR spectroscopy; Aziridines; Amino sugars; Anhydro sugars; Nucleophilic additions.

Epimino derivatives of 1,6-anhydro-β-D-hexopyranoses constitute an important class of compounds potentially useful as starting compounds for the preparation of substituted amino derivatives of 1,6-anhydrohexoses and the corresponding hexoses. In the present paper, we performed opening reactions of the aziridine ring of *N*-tosylated epimino derivatives of 1,6-anhydro-β-D-hexopyranoses with benzyl nucleophiles (BnOH, BnSH, $BnNH_2$) exploiting the temporary protective function of the benzyl group.

The benzyl group is frequently used for protection of OH, SH and NH_2 groups, especially in carbohydrate chemistry[1–3]. Deprotection of the benzyl group can be preferentially effected by hydrogenolysis over palladium catalysts[1,2] or by reduction with sodium in liquid ammonia[4,5]. In some cases, selective deprotection of OBn or NBn group is also possible (hydrogenation under acidic conditions[6] and treatment with diisopropyl azodicarboxylate[7] favours *N*-debenzylation). Thus, the orthogonal protection by benzyl group

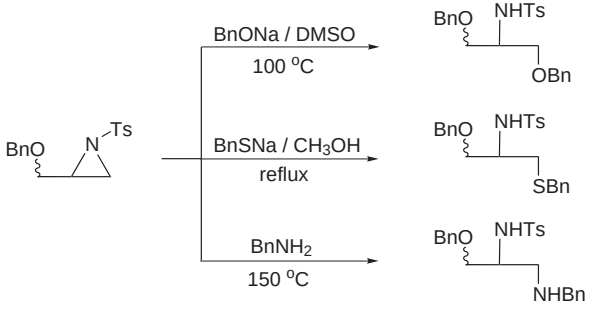
is applicable[8,9]. Benzylamine, benzyl alcohol and phenylmethanethiol are better nucleophiles than ammonia, water and hydrogensulfide, due to their enhanced reactivity even under milder reaction conditions, in the ring opening of oxiranes[10–14] and aziridines[15–17]. Moreover, the products thus obtained are more stable, *e.g.* towards oxidation.

The opening of the aziridine ring is a common method extensively used for non-sugar aziridines (*cf.* refs[18,19]), but sporadically for the derivatives of epimino carbohydrates[20]. The main reason is much lower reactivity and poor regioselectivity of the ring opening of the latter compounds. The development of new procedures is, therefore, still needed.

For these reasons we decided to prepare *O*-, *S*- and *N*-benzyl protected 1,6-anhydro-β-D-hexopyranoses of the D-*gluco*, D-*galacto* and D-*manno* configurations *via* aziridine ring opening in *N*-tosylepimino carbohydrates **1**–**6** having a rigid structure. *N*-Tosyl group was used to enhance low ring-reactivity of unsubstituted epimino compounds. Recently we have found out that *N*-tosylepimino carbohydrates react with halides by *trans*-diaxial cleavage with high regioselectivity[21] in contrast to other sugar aziridines[22].

RESULTS AND DISCUSSION

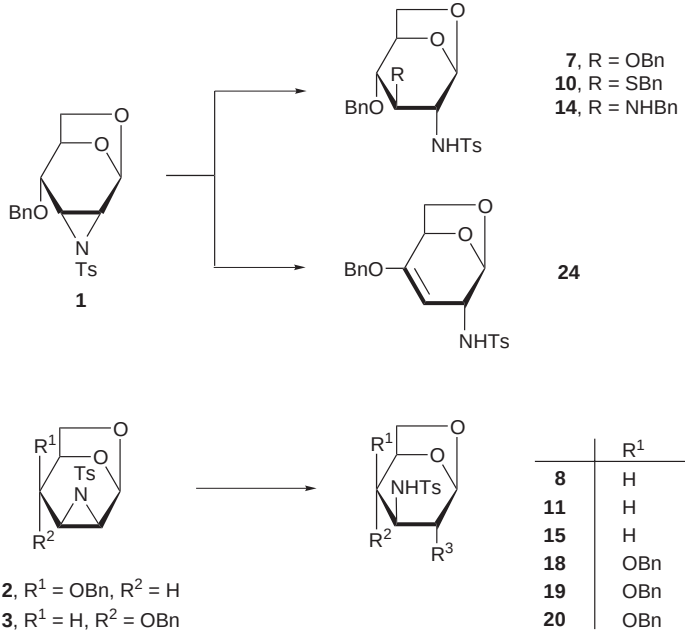
The epimino derivatives **1**–**6** were prepared by lithium aluminium hydride reduction of vicinal azidotosylates and subsequent tosylation following literature procedures[21,23]. *O*-Benzyl and *S*-benzyl derivatives were obtained by the reaction of tosylepimino carbohydrates **1**–**6** with BnONa in DMSO at 100 °C and with BnSNa in refluxing methanol, respectively. The reaction of tosylepimino carbohydrates with neat benzylamine at 150 °C was used for the introduction of NHBn group (Scheme 1). All performed cleavage reactions were optimised with respect to a particular nucleophile. The opening of the aziridine ring catalysed by Lewis acids ($BF_3 \cdot OEt_2$ or titanium isopropoxide) in reactions of tosylepimino carbohydrates with BnSH and



SCHEME 1

BnOH in toluene or with BnONa in BnOH at 150 °C afforded mainly unidentifiable products.

The epimino derivatives **1**, **3**, **4** and **6** when reacted with BnONa, BnSNa and $BnNH_2$ gave the corresponding di-*O*-benzyl derivatives **7**–**9** (both epimino derivatives **3** and **6** afforded the same product **8** by the action of BnONa) in 58–74% yields, benzylsulfanyl derivatives **10**–**13** in 62–97% yields and benzylamino derivatives **14**–**17** in 44–99% yields, respectively. Compounds **7**–**17** were of D-*gluco* configuration. The D-*talo* epimino derivatives **2** and **5** afforded D-*galacto* derivatives **18**–**20** and D-*manno* derivatives **21**–**23**, respectively. Yields were 91 and 80% for the di-*O*-benzyl derivatives **18** and **21**, 70 and 71.5% for the benzylsulfanyl derivatives **19** and **22**, and 76 and 96% for the benzylamines **20** and **23**, respectively. The ring opening of the epimino derivatives proceeded with 100% regioselectivity and followed the Fürst–Plattner rule[24] (*trans*-diaxial aziridine ring opening).

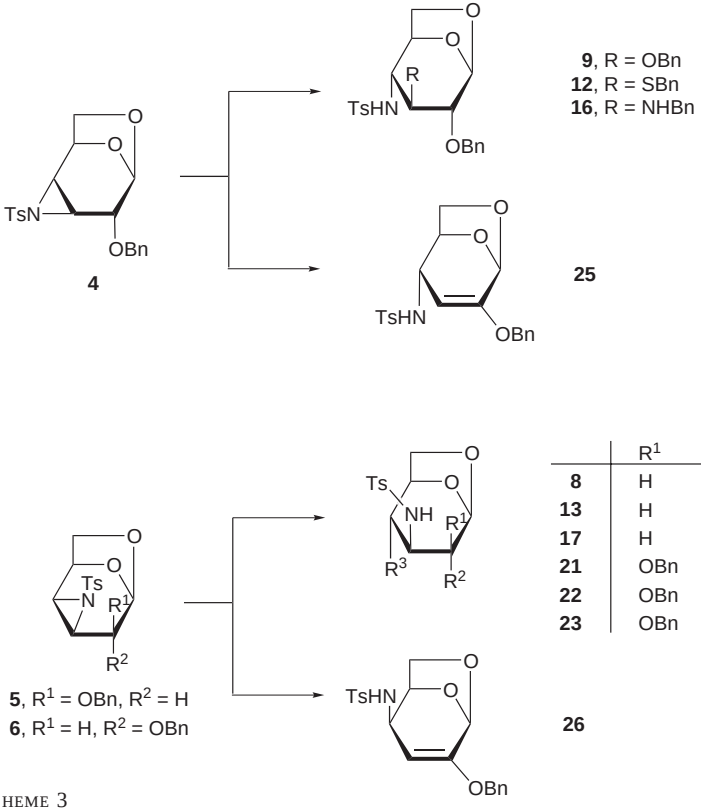


	R^1	R^2	R^3
8	H	OBn	OBn
11	H	OBn	SBn
15	H	OBn	NHBn
18	OBn	H	OBn
19	OBn	H	SBn
20	OBn	H	NHBn

SCHEME 2

The reactions of epimino derivatives **4** and **5** with BnONa in DMSO gave a mixture of benzyl derivatives **9** and **21** together with unsaturated tosylamines **25** and **26**, from which **9** and **21** could not be separated in pure form by column chromatography on silica gel. Pure compounds **9** and

21 were prepared by alternative reactions of tosylepimino carbohydrates **4** and **5** with BnONa in benzyl alcohol. Under these conditions, the unsaturated derivatives were not formed. Tosylepimino carbohydrates **1**, **4**, and **5** with the *cis* arrangement of the aziridine ring and neighbouring *O*-benzyl group gave rise to unsaturated tosylamines (compounds **24**–**26**) when treated with a base. Their formation was dependent on the base and the solvent used. The best yields *viz*. 57, 44 and 35% for **24**, **25** and **26**, respectively, were obtained when the appropriate tosylamine was treated with potassium *tert*-butoxide in THF at room temperature. When sodium hydride in DMSO was used, then no unsaturated, but only unidentifiable products were formed.

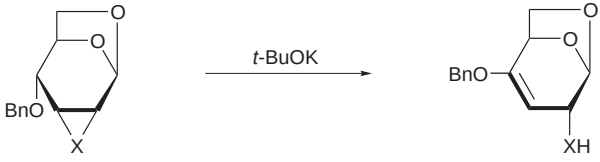


	R^1	R^2	R^3
8	H	OBn	OBn
13	H	OBn	SBn
17	H	OBn	NHBn
21	OBn	H	OBn
22	OBn	H	SBn
23	OBn	H	NHBn

SCHEME 3

The 2,3-epimino compound **2** yielded only polymeric products and the corresponding unsaturated tosylamine was not isolated. Other epimino derivatives (**3** and **6**) did not react with potassium *tert*-butoxide at all. We assume that the formation of unsaturated tosylamines requires base-catalysed

abstraction of the hydrogen atom, which is *trans* oriented to the aziridine ring. Molecular modelling (MM2+) of the epimino derivative **1** predicted the dihedral angle H(4)–C(4)–C(3)–N of *ca* 169°. The E2 elimination is, therefore, sterically favoured. The mechanism is analogous to the rearrangement of the dianhydro derivative **27** into the allylic alcohol **28** (Scheme 4) by the reaction with potassium *tert*-butoxide in 2-methylpropan-2-ol[25], but cannot account for the smooth elimination alone (*cf.* *N*-benzylated or unsubstituted epimino derivatives with appropriate configuration did not provide the corresponding unsaturated amines). Thus, the presence of *N*-tosyl substituent likely plays the dominant role.



1, X = NTs
27, X = O

24
28

SCHEME 4

The structure of prepared compounds has been determined from ^{1}H and ^{13}C NMR spectra (Tables I–III). The D-*gluco* configuration in compounds **7**–**17** is confirmed by small vicinal couplings *J*(1,2), *J*(2,3), *J*(3,4) and *J*(4,5) in the range 1.1–2.4 Hz in accordance with equatorial positions of all corresponding protons. The D-*galacto* configuration in derivatives **18**–**20** is manifested by relatively large values of couplings *J*(3,4) ≈ 6.15–6.6 and *J*(4,5) ≈ 4.0–4.3 Hz and by long-range coupling *J*(4,6*ex*) ≈ 1.0–1.1 Hz. The D-*manno* configuration in derivatives **21**–**23** is evidenced by large values of coupling *J*(2,3) ≈ 6.15–6.5 Hz whilst other couplings *J*(1,2), *J*(3,4) and *J*(4,5) are relatively small (1.4–1.8 Hz). The structure of unsaturated tosylamines **24**–**26** was deduced on the basis of ^{13}C NMR data – chemical shifts of the olefinic carbon atoms in –CH=C(–OBn)– fragment appeared in the range δ 89.1–90.1 ppm (C-3) and δ 156.3–157.6 ppm (C-4 in **24** and C-2 in **25**–**26**).

CONCLUSION

Ring-opening reactions of *N*-tosylepimino derivatives of 1,6-anhydro-β-D-hexopyranoses with benzyl nucleophiles *viz*. BnOH, BnSH, $BnNH_2$ were elaborated with respect to the formation of a single isomer of the product. Its configuration could be predicted using the Fürst–Plattner rule[24]. An un-

TABLE I

Proton NMR data of compounds **2**, **5**, **7**–**9**, **11**, **14**–**26** (500 MHz) and **10**, **12**, **13** (400 MHz) in $CDCl_3$

	Chemical shifts (δ, ppm)/signal multiplicity													
	H-1	H-2	H-3	H-4	H-5	H-6*en*	H-6*ex*	X**CH$_2$**C$_6$H$_5$[a]		O**CH$_2$**C$_6$H$_5$		C$_6$H$_5$	C$_6$H$_4$	NHTs	CH$_3$
2	5.63 d	3.48 dd	3.18 m	4.01 dd	4.37 m	4.12 ddd	3.54 dd	–	–	4.60 d	4.42 d	7.18–7.34 m	7.88, 7.29 m	–	2.38 s
5	5.29 dd	3.62 dd	3.10 m	3.67 dd	44.78 dd	3.95 d	3.52 dd	–	–	4.49 d	4.38 d	7.28–7.32 m	7.90, 7.19 m	–	2.40 s
7	5.18 dt	3.51 dm	3.50 m	3.26 m	4.50 m	4.12 dd	3.67 dd	4.53 d	4.24 d	4.46 d	4.39 d	7.26–7.41 m	7.72, 7.27 m	5.26 d	2.43 s
8	5.34 m	2.93 m	3.57 dm	3.51 m	4.53 m	4.00 dd	3.65 dd	4.74 d	4.61 d	4.35 d	3.92 d	7.02–7.39 m	7.74, 7.34 m	5.07 d	2.46 s
9	5.36 m	3.26 m	3.41 p	3.52 dm	4.30 m	4.19 dd	3.64 dd	4.41 d	4.30 d	4.39 d	4.27 d	7.18–7.37 m	7.72, 7.27 m	5.52 d	2.43 s
10	5.21 bt	3.69 dm	3.10 m	2.70 q	4.40 dm	4.27 dd	3.63 dd	3.59 d	3.44 d	4.12 d	4.06 d	7.15–7.38 m	7.76, 7.33 m	5.39 d	2.45 s
11	5.14 m	2.26 m	3.81 dm	3.50 m	4.47 m	4.02 dd	3.61 dd	3.46 d	3.25 d	4.79 d	4.55 d	7.01–7.36 m	7.77, 7.36 m	5.34 d	2.44 s
12	5.29 dt	3.31 ddt	2.89 dp	3.66 dm	4.25 dm	4.48 dd	3.60 dd	3.65 d	3.60 d	4.23 d	4.01 d	7.10–7.34 m	7.76, 7.26 m	5.65 d	2.43 s
13	5.30 dt	2.91 dm	3.76 dm	2.93 dm	4.33 dm	4.06 d	3.61 dd	3.88 d	3.83 d	4.42 d	3.85 d	7.03–7.39 m	7.76, 7.22 m	5.34 d	2.46 s
14	5.29 t	3.41 bd	2.61 p	3.26 m	4.49 m	4.13 dd	3.67 dd	3.68 d	3.45 d	4.37 d	4.29 d	7.16–7.36 m	7.71, 7.24 m	5.38 d	2.42 s
15	5.41 m	2.24 m	3.67 dp	3.62 m	4.52 dt	4.16 dd	3.70 dd	3.51 d	3.08 d	4.70 d	4.65 d	6.98–7.36 m	7.76, 7.36 m	5.29 d	2.44 s
16	5.38 m	3.08 m	2.69 p	3.46 dm	4.38 dt	4.28 dd	3.62 dd	3.60 d	3.44 d	4.40 d	4.27 d	7.20–7.36 m	7.70, 7.25 m	5.57 d	2.42 s
17	5.34 bt	3.02 m	3.72 m	2.69 m	4.55 dt	4.08 dd	3.68 dd	3.84 d	3.76 d	4.32 d	4.07 d	7.07–7.29 m	7.78, 7.31 m	5.32 d	2.43 s
18	5.24 dd	3.52 t	3.82 m	3.89 ddd	4.35 m	4.13 dd	3.59 ddd	4.56 d	4.39 d	4.44 d	4.24 d	7.16–7.38 m	7.75, 7.24 m	5.25 d	2.41 s
19	5.23 dd	2.98 m	4.05 m	3.94 m	4.33 bt	4.20 bd	3.59 ddd	3.68 d	3.63 d	4.44 d	4.27 d	7.23–7.35 m	7.77, 7.18 m	5.43 d	2.40 s
20	5.23 dd	2.69 t	3.88 m	3.74 ddd	4.32 bt	4.22 bd	3.58 ddd	3.67 d	3.51 d	4.60 d	4.32 d	7.18–7.37 m	7.75, 7.24 m	5.31 d	2.39 s
21	5.34 t	3.58 ddd	3.66 m	3.92 bt	4.45 m	4.31 dd	3.68 dd	4.73 d	4.69 d	4.01 d	3.97 d	7.24–7.41 m	7.66, 7.18 m	5.57 d	2.39 s
22	5.32 bs	3.70 dd	3.80 m	3.35 t	4.42 m	4.42 dd	3.66 dd	3.95 d	3.87 d	4.03 d	3.99 d	7.00–7.42 m	7.65, 7.17 m	5.77 d	2.39 s
23	5.31 bt	3.48 dd	3.65 m	3.21 t	4.40 m	4.39 dd	3.70 dd	3.93 d	3.90 d	4.04 d	3.99 d	7.00–7.36 m	7.65, 7.17 m	5.78 d	2.38 s
24	5.30 t	3.68 ddd	4.29 dt	–	4.53 dd	3.80 d	3.68 dd	–	–	4.68 d	4.60 d	7.26–7.39 m	7.88, 7.33 m	4.63 d	2.44 s
25	5.32 d	–	4.27 dt	3.64 ddd	4.52 m	3.48 dd	3.85 dd	–	–	4.63 d	4.59 d	7.18–7.38 m	7.77, 7.33 m	4.88 d	2.44 s
26	5.30 m	–	4.05 dt	4.45 dddd	4.60 m	4.01 ddd	3.81 ddd	–	–	4.61 d	4.58 d	7.24–7.41 m	7.78, 7.34 m	4.81 d	2.44 s

[a] X = O, S, NH.

TABLE II

Coupling constants from ^{1}H NMR spectra of compounds **2**, **5**, **7**–**9**, **11**, **14**–**26** (500 MHz) and **10**, **12**, **13** (400 MHz) in $CDCl_3$

Compound	Coupling constants (*J*, Hz)												
	1,2	2,3	3,4	4,5	5,6*en*	5,6*ex*	6*en*,6*ex*	1,3	2,4	3,5	X-C**H**$_2$[a]	O-C**H**$_2$	N**H**,C**H**
2	3.8	7.2	4.4	6.2	1.7	6.2	7.4	–	–	1.0	–	11.4	–
5	3.6	4.7	7.5	5.8	≈0	4.5	6.8	1.0	–	–	–	12.0	–
7[b]	2.0	1.4	2.3	1.4	1.1	5.9	7.2	1.9	1.4	1.9	12.0	12.1	10.7
8[c]	1.7	1.6	1.4	2.0	0.8	5.2	7.9	1.45	1.2	1.3	12.6	12.4	8.5
9	2.0	1.5	1.9	1.5	1.0	5.7	7.3	1.7	1.4	1.3	12.1	12.1	10.6
10	2.4	1.5	1.2	1.5	0.8	5.3	7.85	1.2	1.4	1.2	13.5	11.8	10.8
11[d]	2.1	1.1	1.5	1.2	0.6	5.2	7.9	1.3	1.9	1.5	13.5	12.4	8.5
12	2.4	1.2	1.2	1.2	<1	5.2	7.9	1.2	1.2	1.2	13.9	11.9	10.4
13[e]	1.5	1.2	1.3	1.2	<1	5.0	8.1	1.2	1.2	1.2	13.7	12.4	8.4
14[f]	2.1	1.5	1.5	2.1	0.8	5.4	7.5	1.6	1.2	1.4	13.3	12.2	9.0
15[e]	2.2	1.55	1.5	1.8	0.7	5.1	7.8	1.4	1.6	1.2	13.2	12.0	8.1
16[g]	2.3	1.6	1.9	2.0	0.7	5.3	7.5	1.5	1.4	1.5	13.5	12.0	10.1
17[h]	2.0	1.8	1.5	1.6	0.6	5.0	7.8	1.5	1.3	1.5	13.3	11.9	–
18[i]	1.9	1.6	6.6	4.0	0.4	4.75	8.0	1.2	–	1.0	12.2	11.7	6.2
19[j]	1.8	1.2	6.15	4.1	0.5	4.7	7.95	1.2	0.5	1.2	13.4	11.7	6.9
20[k]	1.95	1.8	6.2	4.3	0.6	4.7	7.9	1.2	<0.3	1.0	13.5	11.7	7.9
21	1.4	6.4	1.8	1.8	0.8	5.5	7.5	1.1	0.3	1.6	12.3	12.0	3.9
22[l]	1.45	6.15	1.7	1.6	0.6	5.25	7.6	1.2	–	1.45	13.75	11.9	4.0
23[l]	1.5	6.5	1.65	1.75	0.7	5.4	7.3	1.2	<0.3	1.65	13.5	12.1	3.9
24	1.4	4.5	–	–	≈0	3.9	6.8	1.3	–	–	–	11.4	10.0
25	–	–	5.0	1.4	2.0	6.3	7.9	1.6	–	1.5	–	11.6	9.7
26[m]	–	–	2.5	4.6	1.8	5.9	8.4	1.6	–	1.4	–	11.5	7.6

[a] X = O, S, NH. [b] $J(1,4) = 0.8$, $J(2,5) = 0.65$, $J(1,6ex) \leq 0.3$. [c] $J(1,4) = 0.8$, $J(1,5) \leq 0.3$, $J(1,6ex) \leq 0.3$, $J(1,6en) \leq 0.3$, $J(2,5) = 0.8$. [d] $J(1,4) = 0.6$, $J(1,6ex) = 0.3$. [e] $J(1,4) = 0.6$. [f] $J(1,4) = 0.6$, $J(1,5) \leq 0.3$. [g] $J(1,4) = 1.1$. [h] $J(1,4) = 0.8$. [i] $J(4,6ex) = 1.0$. [j] $J(1,5) < 0.2$, $J(1,6ex) < 0.3$, $J(1,6en) < 0.3$, $J(2,5) < 0.5$, $J(4,6ex) = 1.1$. [k] $J(1,6ex) < 0.3$, $J(1,6en) < 0.3$, $J(4,6ex) = 1.1$. [l] $J(1,4) < 0.3$, $J(1,5) < 0.3$, $J(1,6ex) < 0.3$, $J(1,6en) < 0.3$. [m] $J(1,6en) = 0.6$, $J(4,6ex) = 1.1$.

TABLE III

Carbon-13 chemical shifts (δ, ppm) for compounds **2**, **5**, **7**–**9**, **11**, **14**–**26** (125.7 MHz) and **10**, **12**, **13** (100 MHz) in $CDCl_3$

Compound	C-1	C-2	C-3	C-4	C-5	C-6	$XCH_2C_6H_5$[a]	$OCH_2C_6H_5$	CH_3	$C_6H_{5(4)}$
2	95.70	35.06	45.67	69.30	69.37	63.21	–	70.30	21.62	144.72, 137.20, 134.83, 129.68(2), 128.40(2), 127.92, 127.79(2), 127.69(2)
5	97.02	70.73	43.47	35.99	70.22	65.76	–	70.44	21.65	144.94, 137.13, 134.45, 129.78(2), 128.40(2), 128.01(2), 127.91, 127.81(2)
7	100.82	51.56	75.75	75.06	73.66	65.11	71.80	71.11	21.53	143.56, 138.10, 137.51, 137.13, 129.80(2), 128.61(2), 128.46(2), 128.12, 127.88, 127.79(2), 127.60(2), 127.04(2)
8	100.44	75.30	50.14	76.50	75.23	65.25	71.24	71.24	21.56	143.93, 137.88, 137.18, 137.12, 129.99(2), 128.40(2), 128.35(2), 128.03(2), 127.86, 127.76, 127.59(2), 127.27(2)
9	100.11	73.92	75.46	52.29	75.20	65.42	71.82	71.75	21.54	143.52, 137.32, 137.06, 129.80(2), 128.58(2), 128.47(2), 128.14, 127.87(2), 127.64(2), 127.49(2), 126.97(2)
10	101.06	55.81	43.72	77.72	74.18	65.75	39.68	70.89	21.55	143.59, 138.15, 137.66, 137.17, 129.84(2), 128.98(2), 128.64(2), 128.52(2), 128.04, 127.62(2), 127.35, 127.20(2)
11	102.00	47.26	53.44	76.34	75.65	65.51	36.97	71.06	21.52	143.90, 137.62, 137.46, 137.36, 129.37(2), 128.64(2), 128.53(2), 128.44, 128.39(2), 128.04(2), 127.97, 127.17(2)
12	100.39	77.22	42.75	54.39	75.97	65.87	37.55	71.34	21.54	143.65, 138.33, 137.54, 136.98, 129.86(2), 129.24(2), 128.59(2), 128.51(2), 128.07, 128.02(2), 127.35, 126.99(2)
13	100.81	76.14	52.78	47.23	75.05	67.31	36.99	71.11	21.55	143.93, 138.05, 137.11, 136.97, 129.99(2), 129.38, 129.00(2), 128.55(2), 128.45, 128.35(2), 127.88, 127.64, 127.39, 127.25(2)
14	101.58	53.35	57.40	76.60	74.41	65.53	52.37	70.66	21.52	143.41, 139.68, 138.27, 137.40, 129.75(2), 128.38(2), 128.08(2), 127.97, 127.65(2), 127.13, 127.00(2)
15	102.55	58.61	48.94	77.33	74.72	65.37	50.47	71.52	21.56	143.81, 139.50, 137.56, 137.20, 129.95(2), 128.52(2), 128.28(2), 127.94, 127.89(2), 127.78(2), 127.17(2), 126.95

TABLE III
(*Continued*)

Compound	C-1	C-2	C-3	C-4	C-5	C-6	X**C**H$_2$C$_6$H$_5$[a]	O**C**H$_2$C$_6$H$_5$	CH$_3$	C$_6$H$_{5(4)}$
16	100.51	76.09	57.51	53.33	76.22	65.89	52.28	71.49	21.53	143.37, 139.70, 138.38, 137.20, 129.76(2), 128.59(2), 128.48(2), 128.11, 127.92(2), 127.81(2), 127.20, 127.00(2)
17	100.40	75.98	49.71	57.81	75.98	66.12	50.46	71.53	21.50	143.73, 139.93, 137.32, 136.95, 129.88(2), 128.42(2), 128.30(2), 128.03(2), 127.96, 127.56(2), 127.24(2), 126.88
18	100.62	77.58	51.29	69.47	72.91	63.82	72.02	71.18	21.51	143.57, 137.52, 137.18, 136.96, 129.69(2), 128.50(2), 128.44(2), 128.10, 127.92, 127.76(2), 127.71(2), 127.32(2)
19	102.21	50.04	54.55	69.51	73.63	64.47	36.80	71.25	21.53	143.57, 137.70, 137.52, 137.11, 129.70(2), 128.82(2), 128.62(2), 128.50(2), 128.07, 127.68(2), 127.34(2), 127.30
20	102.14	61.00	51.79	69.55	73.54	64.00	51.50	71.04	21.52	143.40, 139.87, 137.81, 137.29, 129.68(2), 128.52(2), 128.47(2), 128.04, 127.87(2), 127.80(2), 127.25(2), 127.16
21	99.82	71.74	51.81	78.13	75.17	65.32	71.84	70.41	21.57	143.56, 137.88, 136.08, 137.29, 129.69(2), 128.55(2), 128.48(2), 128.00, 127.93(2), 127.88(2), 127.33(2), 127.17
22	100.33	71.67	54.95	49.36	76.77	67.48	36.70	70.56	21.53	143.53, 138.26, 136.83, 136.22, 129.70(2), 128.97(2), 128.62(2), 128.40(2), 127.97, 127.36(2), 127.24(2), 127.22
23	100.11	71.67	52.78	60.02	75.87	66.28	51.67	70.25	21.50	143.36, 140.22, 136.86, 136.38, 129.61(2), 128.50(2), 128.39(2), 128.00(2), 127.94, 127.41(2), 127.28(2), 127.14
24	102.06	52.33	89.77	157.57	72.32	69.54	–	70.18	21.54	143.64, 138.04, 135.51, 129.68(2), 128.64(2), 128.41, 127.68(2), 127.00(2)
25	97.57	156.34	89.10	51.77	76.22	64.53	–	69.47	21.53	143.66, 138.22, 135.42, 129.87(2), 128.55(2), 128.26, 127.49(2), 126.90(2)
26	97.60	156.68	90.07	51.70	74.71	63.29	–	69.56	21.56	144.03, 137.10, 135.39, 129.98(2), 128.54(2), 128.26, 127.52(2), 127.10(2)

[a] X = O, S, NH.

usual rearrangement of tosylepimino carbohydrates into hexenopyranoses was also observed.

EXPERIMENTAL

Melting points were determined on a Boëtius melting-point microapparatus and are uncorrected. The optical rotations were measured on an Autopol III (Rudolph Research, Flanders, NJ, U.S.A.) polarimeter at 23 °C; $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. The ^{1}H and ^{13}C NMR spectra were measured on a Varian INOVA-400 (^{1}H at 400 MHz and ^{13}C at 100 MHz) or on a Varian UNITY-500 (^{1}H at 500 MHz and ^{13}C at 125.7 MHz) instrument in $CDCl_3$ (TMS reference for ^{1}H and the chloroform signal at δ 77.0 ppm for ^{13}C) at 25 °C. Chemical shifts are given in ppm (δ-scale), coupling constants (*J*) in Hz. The ^{1}H-^{1}H-COSY and ^{1}H-^{13}C-HMQC techniques were used for the structural assignments. High-resolution mass spectra were recorded on a ZAB-EQ (VG Analytical, U.K.) instrument using the FAB method (Xe ionisation). TLC was carried out on MERCK DC Alufolien with Kiesegel F_{254} with the following solvent systems: S1, hexane–ethyl acetate 3:2; S2, hexane–ethyl acetate 1:1; S3, hexane–ethyl acetate 3:1. TLC plates were visualised by UV detection at 254 nm, iodine vapours and anisaldehyde solution in sulfuric acid. Column chromatography was performed on silica gel 60 MERCK (70–230 mesh ASTM) with hexane–ethyl acetate gradient elution. The solvents were evaporated on a vacuum rotary evaporator at 40 °C (unless stated otherwise). Toluene and diethyl ether were dried over sodium, methanol and ethanol over magnesium. Petroleum ether refers to the 40–60 °C distillation fraction. DMF and DMSO were purchased from Aldrich and were used as supplied. All other chemicals were of common grade and were used without further purification. Reactions were carried out under argon atmosphere. The ^{1}H NMR spectral parameters are given in Tables I and II, and those of ^{13}C NMR spectra in Table III. For preparation of tosylepimino carbohydrates **1**, **3**, **4** and **6**, see ref.[21]

Preparation of Tosylepimino Carbohydrates **2** and **5**

The tosylepimino carbohydrates **2** and **5** were prepared by tosylation of free epimino derivatives according to the literature procedures[21,23].

1,6-Anhydro-4-O-benzyl-2,3-dideoxy-2,3-(N-tosylepimino)-β-D-*talopyranose* (**2**). Prepared from 1,6-anhydro-3-azido-4-*O*-benzyl-3-deoxy-2-*O*-tosyl-β-D-galactopyranose[23] (1.053 g, 2.44 mmol), $LiAlH_4$ (433 mg, 11.41 mmol) and tosyl chloride (1.147 g, 6.01 mmol). Yield 0.746 g (79%), m.p. 189–190 °C, $[\alpha]_D$ –123.4 (*c* 0.28, $CHCl_3$). For $C_{20}H_{21}NO_5S$ (387.5) calculated: 62.00% C, 5.46% H, 3.62% N, 8.28% S; found: 61.93% C, 5.38% H, 3.61% N, 8.14% S.

1,6-Anhydro-2-O-benzyl-3,4-dideoxy-3,4-(N-tosylepimino)-β-D-*talopyranose* (**5**). Prepared from 1,6-anhydro-3-azido-2-*O*-benzyl-3-deoxy-4-*O*-tosyl-β-D-mannopyranose[23] (0.928 g, 2.15 mmol), $LiAlH_4$ (163 mg, 4.30 mmol) and tosyl chloride (0.546 g, 2.86 mmol). Yield 0.397 g (48%), m.p. 156–157 °C, $[\alpha]_D$ +103.1 (*c* 0.26, $CHCl_3$). For $C_{20}H_{21}NO_5S$ (387.5) calculated: 62.00% C, 5.46% H, 3.62% N, 8.28% S; found: 61.87% C, 5.46% H, 3.65% N, 8.26% S.

Reaction of Tosylepimino Carbohydrates with Benzyl alcohol. General Procedure

Benzyl alcohol (140 µl, 1.35 mmol) was successively added into a suspension of sodium hydride (50 mg of 60% oil-suspension, 1.25 mmol) in DMSO (4 ml) under argon. The mixture

was stirred at room temperature for 1 h and gave a clear yellow solution of benzyl alcoholate. To this, a solution of tosylepimino carbohydrate (100 mg, 0.258 mmol) in DMSO (1–2 ml) was added and the mixture was heated to 100 °C while stirred. After consumption of starting epimino derivative, the mixture was poured onto crushed ice and the resulting suspension was extracted with dichloromethane (3 × 20 ml). The organic layer was washed with water, dried over anhydrous Na_2SO_4 and evaporated to dryness. Residue (oil or solid) was further purified by column chromatography and/or crystallized to afford the di-*O*-benzyl derivatives (**7**–**9**, **18**, **21**).

1,6-Anhydro-3,4-di-O-benzyl-2-deoxy-2-(N-tosylamino)-β-D-*glucopyranose* (**7**). Prepared from **1** following the general procedure (24 h heating). Chromatography on silica gel (50 g, eluent S2) gave an oil (103 mg, 80.5%), which was crystallized from an ethanol–diethyl ether–petroleum ether mixture. Yield 74.3 mg (58%), m.p. 65–66 °C, $[\alpha]_D$ –30 (*c* 0.29, $CHCl_3$). For $C_{27}H_{29}NO_6S$ (495.6) calculated: 65.44% C, 5.90% H, 2.83% N, 6.47% S; found: 65.34% C, 5.95% H, 2.89% N, 6.48% S.

1,6-Anhydro-2,4-di-O-benzyl-3-deoxy-3-(N-tosylamino)-β-D-*glucopyranose* (**8**)

Method A. Prepared from **3** following the general procedure (2 h heating). It was then purified on silica gel (25 g, eluent S3) and crystallized from an ethanol–diethyl ether–petroleum ether mixture. Yield 90 mg (70%), m.p. 134–135 °C, $[\alpha]_D$ +31.5 (*c* 0.25, $CHCl_3$). For $C_{27}H_{29}NO_6S$ (495.6) calculated: 65.44% C, 5.90% H, 2.83% N, 6.47% S; found: 65.41% C, 6.02% H, 2.82% N, 6.35% S.

Method B. Prepared from **6** following the general procedure (2 h heating). Purification on silica gel (25 g, eluent S3) and crystallization from an ethanol–diethyl ether–petroleum ether mixture yielded **8** (92 mg, 72%), m.p. 136–136.5 °C, which was identical with the sample prepared from **3**.

1,6-Anhydro-2,3-di-O-benzyl-4-deoxy-4-(N-tosylamino)-β-D-*glucopyranose* (**9**)

Method A. Prepared from **4** following the general procedure (2 h heating). The oil was purified on silica gel (25 g, eluent S3) and crystallized from an ethanol–diethyl ether–petroleum ether mixture. Yield 104 mg (81%) of impure **9**, m.p. 112–115 °C. The main impurity was the unsaturated tosylamine **25** (40%, based on ^{1}H NMR spectrum by integration of H-1 signals).

Method B. Tosylepimino carbohydrate **4** (100 mg, 0.258 mmol) was mixed with a 0.1 M solution of sodium benzyloxide in benzyl alcohol (2.5 ml, 0.25 mmol) and heated with stirring at 150 °C for 33 h. After this time, the starting epimino derivative was nearly consumed. Acetic acid (0.5 ml) and water (50 ml) were added and the reaction mixture was distilled to collect *ca* 50 ml of distillate. The residue was then evaporated to dryness and chromatographed on silica gel (25 g, eluent S1) to afford pure **9**, which was crystallized from an ethanol–diethyl ether–petroleum ether mixture. Yield 95 mg (74%), m.p. 115–116 °C, $[\alpha]_D$ +21.3 (*c* 0.30, $CHCl_3$). For $C_{27}H_{29}NO_6S$ (495.6) calculated: 65.44% C, 5.90% H, 2.83% N, 6.47% S; found: 65.31% C, 6.00% H, 2.85% N, 6.39% S.

1,6-Anhydro-2,4-di-O-benzyl-3-deoxy-3-(N-tosylamino)-β-D-*galactopyranose* (**18**). Prepared from **2** (2 h heating). The oil obtained was then purified on silica gel (25 g, eluent S1). Yield 117 mg (91%), $[\alpha]_D$ –48.2 (*c* 0.54, $CHCl_3$). HRMS (FAB), *m/z*: found 495.1803 (M^+); $C_{27}H_{29}NO_6S$ requires 495.1716.

1,6-Anhydro-2,4-di-O-benzyl-3-deoxy-3-(N-tosylamino)-β-D-*mannopyranose* (**21**)

Method A. Prepared from **5** following the general procedure (2 h heating). The oil was purified on silica gel (25 g, eluent S1) and crystallized from an ethanol–diethyl ether–petroleum ether mixture. Yield 102 mg (80%) of impure **21**, m.p. 48–51 °C. The main impu-

rity was the unsaturated tosylamine **26** (60%, based on ^{1}H NMR spectrum by the integration of H-1 signals).

Method B. Tosylepimino carbohydrate **5** (100 mg, 0.258 mmol) was mixed with a 0.1 M solution of sodium benzyloxide in benzyl alcohol (2.5 ml, 0.25 mmol) and heated under stirring at 150 °C for 24 h. After this time, the starting epimino derivative was all consumed. Acetic acid (0.5 ml) and water (50 ml) were added, and the reaction mixture was distilled to collect *ca* 50 ml of distillate. The residue was evaporated to dryness and chromatographed on silica gel (25 g, eluent S1) to afford pure **21**, which was crystallized from an ethanol–diethyl ether–petroleum ether mixture. Yield 89 mg (69%), m.p. 99–100 °C, $[\alpha]_D$ +94.8 (*c* 0.27, $CHCl_3$). For $C_{27}H_{29}NO_6S$ (495.6) calculated: 65.44% C, 5.90% H, 2.83% N, 6.47% S; found: 65.42% C, 5.88% H, 2.71% N, 6.45% S.

Reaction of Tosylepimino Carbohydrates with Phenylmethanethiol. General Procedure

A 1 M solution of sodium methoxide in methanol (500 µl, 0.5 mmol) was added into the mixture of tosylepimino carbohydrate (100 mg, 0.258 mmol), phenylmethanethiol (61 µl, 0.52 mmol) and methanol (8 ml) and the resulting solution was refluxed for a given time. After consumption of tosylepimino carbohydrate, the mixture was poured onto crushed ice and extracted with dichloromethane (3 × 20 ml). The organic layer was washed with water, dried over anhydrous Na_2SO_4 and stirred with charcoal. After filtration, the solution was evaporated to obtain oil (coevaporation with toluene was necessary to remove the thiol). Benzylsulfanyl derivatives (**10**–**13**, **19**, **22**) were obtained as colourless oils (dried over P_2O_5 under vaccum) or as crystals (from an ethanol–diethyl ether–petroleum ether mixture).

1,6-Anhydro-4-O-benzyl-3-benzylsulfanyl-2-deoxy-2-(N-tosylamino)-β-*D-glucopyranose* (**10**). Prepared from **1** following the general procedure (reflux 23 h). Yield 82 mg (62%), m.p. 126–128 °C, $[\alpha]_D$ –188 (*c* 0.31, $CHCl_3$). For $C_{27}H_{29}NO_5S_2$ (511.7) calculated: 63.38% C, 5.71% H, 2.74% N, 12.53% S; found: 63.25% C, 5.56% H, 2.68% N, 12.33% S.

1,6-Anhydro-4-O-benzyl-2-benzylsulfanyl-3-deoxy-3-(N-tosylamino)-β-*D-glucopyranose* (**11**). Prepared from **3** following the general procedure (reflux 22.5 h). Yield 104 mg (78%) of oily **11**, $[\alpha]_D$ –28 (*c* 0.72, $CHCl_3$). HRMS (FAB), *m/z*: found 511.1409 (M^+); $C_{27}H_{29}NO_5S_2$ requires 511.1487.

1,6-Anhydro-2-O-benzyl-3-benzylsulfanyl-4-deoxy-4-(N-tosylamino)-β-*D-glucopyranose* (**12**). Prepared from **4** following the general procedure (reflux 20 h). Yield 115 mg (87%), m.p. 114–115 °C, $[\alpha]_D$ +102 (*c* 0.20, $CHCl_3$). For $C_{27}H_{29}NO_5S_2$ (511.7) calculated: 63.38% C, 5.71% H, 2.74% N, 12.53% S; found: 63.23% C, 5.76% H, 2.69% N, 12.42% S.

1,6-Anhydro-2-O-benzyl-4-benzylsulfanyl-3-deoxy-3-(N-tosylamino)-β-*D-glucopyranose* (**13**). Prepared from **6** following the general procedure (reflux 25 h). Yield 129 mg (97%) of oily **13**, $[\alpha]_D$ +91.6 (*c* 0.95, $CHCl_3$). HRMS (FAB), *m/z*: found 511.1385 (M^+); $C_{27}H_{29}NO_5S_2$ requires 511.1487.

1,6-Anhydro-4-O-benzyl-2-benzylsulfanyl-3-deoxy-3-(N-tosylamino)-β-*D-galactopyranose* (**19**). Prepared from **2** following the general procedure (reflux 18 h). Yield 91 mg (70%) after recrystallization from an ethyl acetate–petroleum ether mixture, m.p. 41–43 °C (dec.), $[\alpha]_D$ –102.5 (*c* 0.08, $CHCl_3$). For $C_{27}H_{29}NO_5S_2$ (511.7) calculated: 63.38% C, 5.71% H, 2.74% N, 12.53% S; found: 63.17% C, 5.69% H, 2.66% N, 12.25% S.

1,6-Anhydro-2-O-benzyl-4-benzylsulfanyl-3-deoxy-3-(N-tosylamino)-β-*D-mannopyranose* (**22**). Prepared from **5** following the general procedure (reflux 18 h). Yield 93 mg (71.5%) after recrystallization from an ethyl acetate–petroleum ether mixture, m.p. 48–50 °C (dec.), $[\alpha]_D$

+212.2 (*c* 0.28, $CHCl_3$). For $C_{27}H_{29}NO_5S_2$ (511.7) calculated: 63.38% C, 5.71% H, 2.74% N, 12.53% S; found: 63.15% C, 5.66% H, 2.72% N, 12.52% S.

Reaction of Tosylepimino Carbohydrates with Benzylamine. General Procedure

Tosylepimino carbohydrate and benzylamine were mixed and heated at 150 °C for a given time. After consuming the starting epimino derivative, the mixture was cooled to –18 °C yielding crystals, if not then mixture was chromatographed on silica gel (25–50 g, eluent S2) to remove excess benzylamine. Benzylamino derivatives (**14**–**17**, **20**, **23**) were obtained as colourless oils (dried over P_2O_5 under vaccum) or crystals (from an ethanol–diethyl ether–petroleum ether mixture).

1,6-Anhydro-4-O-benzyl-3-(benzylamino)-2,3-dideoxy-2-(N-tosylamino)-β-D-*glucopyranose* (**14**). Prepared from **1** (100 mg, 0.258 mmol) and benzylamine (300 μl, 2.7 mmol) following the general procedure (23 h heating). Yield 87 mg (69%), m.p. 135–136 °C, $[\alpha]_D$ –45.5 (*c* 0.22, $CHCl_3$). For $C_{27}H_{30}N_2O_5S$ (494.6) calculated: 65.57% C, 6.11% H, 5.66% N, 6.48% S; found: 65.68% C, 6.23% H, 5.57% N, 6.36% S.

1,6-Anhydro-4-O-benzyl-2-(benzylamino)-2,3-dideoxy-3-(N-tosylamino)-β-D-*glucopyranose* (**15**). Prepared from **3** (100 mg, 0.258 mmol) and benzylamine (600 μl, 5.4 mmol) following the general procedure (64 h heating). Yield 55.4 mg (44%, after recrystallization 30 mg, 24%), m.p. 49–52 °C, $[\alpha]_D$ +71.4 (*c* 0.15, $CHCl_3$). For $C_{27}H_{30}N_2O_5S$ (494.6) calculated: 65.57% C, 6.11% H, 5.66% N, 6.48% S; found: 65.51% C, 6.29% H, 5.46% N, 6.49% S.

1,6-Anhydro-2-O-benzyl-3-(benzylamino)-3,4-dideoxy-4-(N-tosylamino)-β-D-*glucopyranose* (**16**). Prepared from **4** (100 mg, 0.258 mmol) and benzylamine (700 μl, 6.3 mmol) following the general procedure (50 h heating). Yield 110 mg (99%, after recrystallization 74 mg, 57%), m.p. 83–85 °C, $[\alpha]_D$ –5 (*c* 0.12, $CHCl_3$). For $C_{27}H_{30}N_2O_5S$ (494.6) calculated: 65.57% C, 6.11% H, 5.66% N, 6.48% S; found: 65.56% C, 6.08% H, 5.56% N, 6.39% S.

1,6-Anhydro-2-O-benzyl-4-(benzylamino)-3,4-dideoxy-3-(N-tosylamino)-β-D-*glucopyranose* (**17**). Prepared from **6** (200 mg, 0.516 mmol) and benzylamine (1 ml, 9.2 mmol) following the general procedure (64 h heating). Yield 247 mg (97%) of oily **17**, $[\alpha]_D$ +6.6 (*c* 1.57, $CHCl_3$). HRMS (FAB), *m/z*: found 495.1806 ($M^+ + H$); $C_{27}H_{31}N_2O_5S$ requires 495.1954.

1,6-Anhydro-4-O-benzyl-2-(benzylamino)-2,3-dideoxy-3-(N-tosylamino)-β-D-*galactopyranose* (**20**). Prepared from **2** (100 mg, 0.258 mmol) and benzylamine (300 μl, 2.7 mmol) following the general procedure (reflux 10 h). Yield 97 mg (76%, after crystallization from a methanol–diethyl ether–petroleum ether mixture), m.p. 109–111 °C, $[\alpha]_D$ +16.4 (*c* 0.28, $CHCl_3$). For $C_{27}H_{30}N_2O_5S$ (494.6) calculated: 65.57% C, 6.11% H, 5.66% N, 6.48% S; found: 65.47% C, 6.23% H, 5.62% N, 6.65% S.

1,6-Anhydro-2-O-benzyl-4-(benzylamino)-3,4-dideoxy-3-(N-tosylamino)-β-D-*mannopyranose* (**23**). Prepared from **5** (100 mg, 0.258 mmol) and benzylamine (300 μl, 2.7 mmol) following the general procedure (14 h heating). Yield 123 mg (96%, after recrystallization 100 mg, 78%), m.p. 126.5–127 °C, $[\alpha]_D$ +62.6 (*c* 0.31, $CHCl_3$). For $C_{27}H_{30}N_2O_5S$ (494.6) calculated: 65.57% C, 6.11% H, 5.66% N, 6.48% S; found: 65.34% C, 6.35% H, 5.52% N, 6.65% S.

Preparation of Unsaturated Tosylamines. General Procedure

A solution of tosylepimino carbohydrate (100 mg, 0.258 mmol) in THF (5 ml) was added to a stirred suspension of potassium *tert*-butoxide (140 mg, 1.25 mmol) in THF (5 ml). During the addition, potassium *tert*-butoxide gradually dissolved and the reaction mixture turned yellow. The reaction mixture was stirred at room temperature for a given time. After con-

suming the starting epimino derivative, Dowex 50X8 (H-cycle, air-dried) and ethyl acetate (50 ml) was added to adjust pH to 6. The resulting suspension was filtered and the filtrate evaporated. The residue was dissolved in the solvent system S1 (30 ml) and the solution passed through silica gel (2 g) to remove polymeric impurities. Silica gel was further eluted with another portion of solvent system S1 (50 ml). Combined eluates were evaporated and the solid was crystallized from an ethyl acetate–diethyl ether–petroleum ether mixture to obtain pure product.

1,6-Anhydro-4-O-benzyl-2,3-dideoxy-2-(N-tosylamino)-β-D-*erythro-hex-3-enopyranose* (**24**). Prepared from **1** following the general procedure (7 h). Yield 57 mg (57%), m.p. 175–177 °C, $[\alpha]_D$ –77.9 (*c* 0.23, $CHCl_3$). For $C_{20}H_{21}NO_5S$ (387.5) calculated: 62.00% C, 5.46% H, 3.62% N, 8.28% S; found: 61.72% C, 5.55% H, 3.53% N, 8.02% S.

1,6-Anhydro-2-O-benzyl-3,4-dideoxy-4-(N-tosylamino)-β-D-*erythro-hex-2-enopyranose* (**25**). Prepared from **4** following the general procedure (48 h). Yield 44 mg (44%), m.p. 118–119 °C, $[\alpha]_D$ +60.4 (*c* 0.30, $CHCl_3$). For $C_{20}H_{21}NO_5S$ (387.5) calculated: 62.00% C, 5.46% H, 3.62% N, 8.28% S; found: 62.01% C, 5.58% H, 3.55% N, 8.39% S.

1,6-Anhydro-2-O-benzyl-3,4-dideoxy-4-(N-tosylamino)-β-D-*threo-hex-2-enopyranose* (**26**). Prepared from **5** (95 mg, 0.245 mmol) following the general procedure (13 h). Yield 33 mg (35%), m.p. 124–126 °C, $[\alpha]_D$ –32.7 (*c* 0.31, $CHCl_3$). For $C_{20}H_{21}NO_5S$ (387.5) calculated: 62.00% C, 5.46% H, 3.62% N, 8.28% S; found: 61.96% C, 5.66% H, 3.88% N, 8.01% S.

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