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Ring-Opening Reactions of Aziridines Fused to a Conformationally Locked Tetrahydropyran Ring

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Dedicated to Professor Jan Schraml on the occasion of his 70th birthday

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1,6-Anhydro-2,3,4-trideoxy-2,3-(tosylepimino)-β-D-hexopyranoses **1** and **2** underwent aziridine ring-opening reactions with halides and other heteroatom-centered nucleophiles. *Ribo*-epimine **1** provided *trans*-diaxial and *cis* products. The *lyxo*-epimine **2** gave *trans*-diaxial and *trans*-diequatorial products, depending upon the reaction conditions (acid cleavage versus base cleavage) and the nucleophile (hard nucleophiles versus soft ones). These results have been rationalized by assuming that both S_N2 and borderline S_N2 cleavage mechanisms are operative.

Introduction

Aziridines have found widespread use as synthetic intermediates in organic synthesis.[1–10] Their synthetic value is based predominantly upon their ability to undergo stereoselective ring-opening reactions. To facilitate nucleophilic ring opening, aziridines need to be activated by *N*-substitution with a strongly electron-withdrawing group such as an alkane/arenesulfonyl, acyl or alkoxycarbonyl group. Alternatively, Lewis-acid coordination, *N*-protonation or quarternization can be also used to enhance the reactivity of aziridines.

The stereoselectivity of the ring-opening reactions is usually determined by inversion of configuration at the attacked carbon, whereas regioselectivity presents a more complex issue, particularly for carbohydrate-based aziridines (epimines). Aziridines fused to a hexopyranose unit show regioselectivity dependent primarily upon the six-membered-ring conformation[11] (steric effect), but in analogy to similar oxiranes, we may expect that the simultaneous intervention of steric and electronic effects will play a significant role too.[12–17]

As predicted by the Fürst–Plattner rule, the preferential formation of the *trans*-diaxial stereoisomer is often observed.[11,18] The applicability of the Fürst–Plattner rule to the carbohydrate aziridines is, however, limited to cleavage reactions following the S_N2 mechanistic pathway. Moreover, the rule can be successfully applied only to aziridines that are fused to a six-membered ring with a fixed conformation.[11]

The unusual formation of *trans*-diequatorial isomers has also been observed[19–22] and rationalized by the postulation of an equilibrium between the unreacted aziridine and the *trans*-diaxial product.[19] To produce *trans*-diequatorial, ring-cleavage product the epimine probably reacts either through a twist conformation of the tetrahydropyran ring or through an ionic S_N1 mechanism.

Recently, we have published articles describing the reactivity of *N*-substituted epimines of 1,6-anhydro-β-D-hexopyranoses towards heteroatom-centered nucleophiles.[19,23–25] In this paper, we have extended the ring-cleavage reactions of epimines to 4-deoxy-derivatives of 1,6-anhydro-β-D-hexopyranoses in order to obtain deeper insight into the mechanisms actually involved in the aziridine cleavage. We have performed a series of nucleophilic ring-opening reactions on *N*-tosylaziridines **1** and **2** (Scheme 1) with selected nucleophiles. The tetrahydropyran ring of **1** and **2** is conformationally locked by the 1,6-anhydro bridge[26] and asymmetrically substituted (acetal oxygen versus hydrogen atoms) at the carbon atoms adjacent to the aziridine ring. This enabled us to assess the influence of the electron-with-

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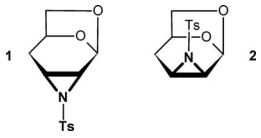
drawing properties of the acetal functionality in combination with steric effects on the regioisomeric outcome of the reaction. In addition, aziridine cleavage of **1** and **2** should provide various selectively substituted 2- or 3-amino-4-deoxyhexopyranoses, which are valuable chiral synthons.



Scheme 1.

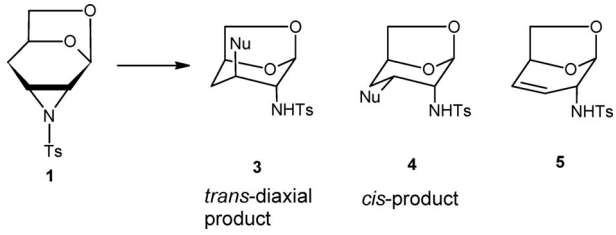
Results and Discussion

The reactions of 1,6-anhydro-2,3,4-trideoxy-2,3-(tosylepimino)-β-D-*ribo*-hexopyranose (**1**) provided solely the *trans*-diaxial products **3a**–**g** upon reaction with haloacids, azide, benzylamine, phenylmethanethiol and benzyl alcoholate (see Table 1, Entries 1–7). Only reactions with tetrabutylammonium halides (Table 1, Entries 8–10) gave a mixture of products **3**, **4** and **5**. We could not be separate product **3b** from **4b** or **3c** from **4c** (Nu = Br and I, respectively, Table 1, Entries 9 and 10) by column chromatography, and we determined their structures and ratios by NMR only. For Nu = Cl (Table 1, Entry 8), we estimated the composition of the mixture by GC/MS because **3a**, **4a**, **5** and unreacted **1** were completely inseparable by column chromatography. We could not properly identify **4a** in the mixture by NMR, and we tentatively assigned its structure by analogy with **4b** and **4c**.

We also obtained unsaturated tosylamino derivative **5** as a single product by the action of *t*BuOK upon **1** in THF (Table 1, Entry 11). The isomerization of **1** into **5** began with hydrogen abstraction from C-4, and the hydrogen had to be *trans* with respect to the aziridine.[23] We can explain the formation of **5** as a side product in the reaction with Bu_4NX by hydrogen abstraction from **1** by the strongly basic tosylamide anion formed during the cleavage.

The reactions of 1,6-anhydro-2,3,4-trideoxy-2,3-(tosylepimino)-β-D-*lyxo*-hexopyranose (**2**) are summarized in Table 2. *trans*-Diequatorial products formed by nucleophilic attack at C-3 predominated over *trans*-diaxial products in all reactions except for that with Bu_4NI and BnSH, in which case opening at C-2 prevailed (Table 2, Entries 6 and 9). Solely *trans*-diequatorial products **6a**–**c** formed in the reaction with haloacids in EtOH, along with minor *trans*-diequatorial solvolytic product **6h** (Table 2, Entries 1–3). We also obtained this *trans*-diequatorial ethoxy derivative (**6h**) upon reaction with EtOH under sulfuric-acid catalysis (Table 2, Entry 11), whereas we obtained both regioisomers **6h** and **7h** (Table 2, Entry 12) with sodium ethanolate. The unreacted epimine **2**, isolated after the workup of **6c** (Table 2, Entry 3), probably arose from back-cyclization, despite the *trans*-diequatorial disposition of the reacting groups. A similar aziridine closure has been observed for a *trans*-diequatorial azido tosylate upon reaction with $LiAlH_4$.[27] The regioselectivity of the cleavage of epimine **2** contrasts with that of the cleavage of 4-*O*-benzyl-1,6-anhydro-2,3-(tosylepimino)-2,3-dideoxy-β-D-mannopyranose, which provided only *trans*-diaxial stereoisomers upon reaction with the same nucleophiles.[19]

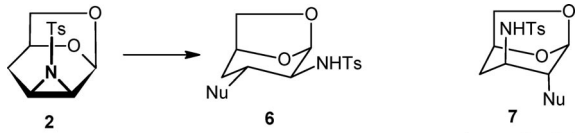
Table 1. The product distribution for reactions of **1** with nucleophiles.



Entry	Nu	Reagent	Solvent	Reaction time/temperature	Product yield [%] 3, *trans*-diaxial		4, *cis*		5	
1	Cl	HCl	EtOH	24 h/room temp.	**3a**	80	–		–	
2	Br	HBr	EtOH	12 h/room temp.	**3b**	70	–	–	–	–
3	I	HI	EtOH	3 h/room temp.	**3c**	63	–	–	–	–
4	N_3	NaN_3	$MeOCH_2CH_2OH/H_2O$	2.5 h/110 °C	**3d**	82	–	–	–	–
5	BnNH	$BnNH_2$	–	3 h/140 °C	**3e**	88	–	–	–	–
6	BnS	BnSH/MeONa	MeOH	3 h/70 °C	**3f**	94	–	–	–	–
7	BnO	BnONa	BnOH	7 h/105 °C	**3g**	72	–	–	–	–
8	Cl	Bu_4NCl, NH_4Cl	toluene	20 h/reflux	**3a**	62[a]	**4a**	9[a]	**5**	4[a]
9	Br	Bu_4NBr, NH_4Br	toluene	4 h/reflux	**3b**	15[b]	**4b**	39[b]	**5**	18
10	I	Bu_4NI, NH_4I	toluene	1.5 h/reflux	**3c**	7[c]	**4c**	67[c]	**5**	16
11	*t*BuO	*t*BuOK	THF	18 h/room temp.	–	–	–	–	**5**	52

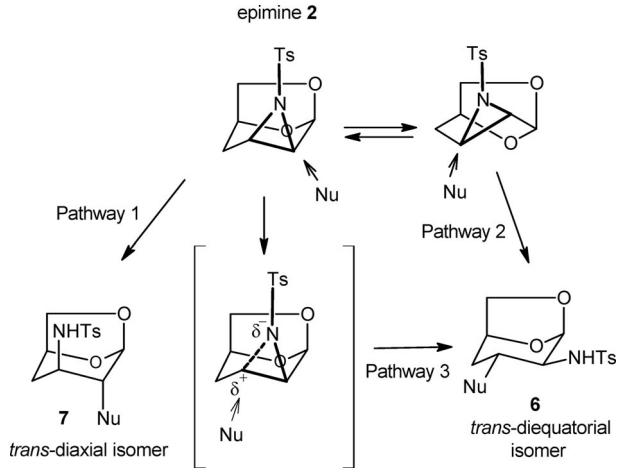
[a] **3a**, **4a** and **5** were inseparable by column chromatography; the total yield of 90% including 15% of regenerated **1** was determined by GC/MS, and the structure of **4a** was assigned tentatively by analogy with **4b** and **4c**. [b] Compounds **3b** and **4b** were inseparable by column chromatography, and the product distribution was determined by NMR. [c] Compounds **3c** and **4c** were inseparable by column chromatography, and the product distribution was determined by NMR spectroscopy.

Table 2. The product distribution for reactions of **2** with nucleophiles.

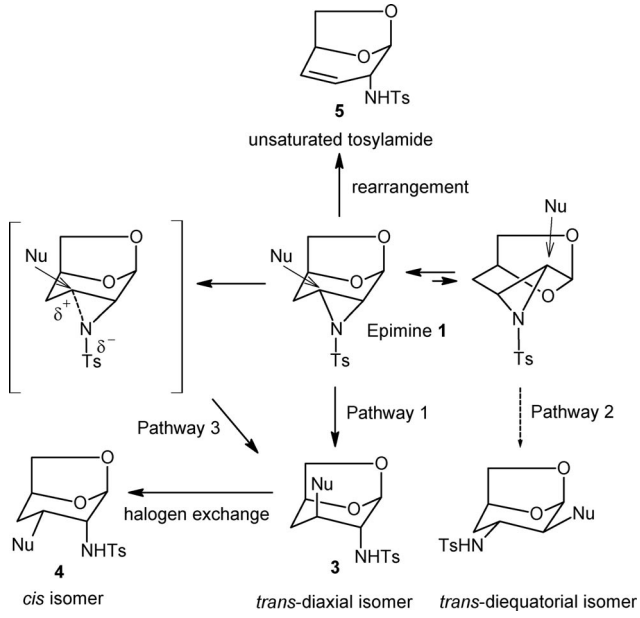


Entry	Nu	Reagent	Solvent	Reaction time/temperature	Product yield [%] **6**, *trans*-diequatorial		**7**, *trans*-diaxial	
1	Cl	HCl	EtOH	21 h/50 °C	**6a**	66 (+ 27% **6h**)	–	–
2	Br	HBr	EtOH	6 h/50 °C	**6b**	82 (+ 12% **6h**)	–	–
3	I	HI	EtOH	6 h/50 °C	**6c**	60 (+ 7% **6h**)[a]	–	–
4	Cl	Bu_4NCl, NH_4Cl	toluene	6 h/reflux	**6a**	80	**7a**	10[b]
5	Br	Bu_4NBr, NH_4Br	toluene	6 h/reflux	**6b**	61	**7b**	25
6	I	Bu_4NI, NH_4I	toluene	10 h/reflux	**6c**	31	**7c**	61
7	N_3	NaN_3	*i*PrOH/H_2O	14 h/reflux	**6d**	83	**7d**	17
8	BnNH	$BnNH_2$	–	3.5 h/140 °C	**6e**	55	**7e**	25
9	BnS	BnSH/MeONa	MeOH	18 h/50 °C	**6f**	35	**7f**	59
10	BnO	BnONa	BnOH	25 h/120 °C	**6g**	46	**7g**	36
11	EtO	EtOH/H_2SO_4	EtOH	14 d/room temp.	**6h**	78	–	–
12	EtO	EtONa	EtOH	12 h/reflux	**6h**	47	**7h**	47

[a] 23% of unreacted **2** was isolated after workup. [b] Compound **7a** contained 2% of unreacted **2** after workup.



Scheme 2.



Scheme 3.

To interpret these results, we propose three possible reaction pathways for the aziridine cleavage of epimines **1** and **2** (see Scheme 2 for epimine **2** and Scheme 3 for epimine **1**).

Pathway 1: S_N2 cleavage with the tetrahydropyran ring in approximately a half-chair conformation in the transition state. This is energetically the most favored cleavage pattern and produces *trans*-diaxial isomers.

Pathway 2: S_N2 cleavage with the tetrahydropyran ring in the energetically less-favored twist conformation in the transition state, which produces *trans*-diequatorial isomers (from the point of view of the product configuration, this cleavage is frequently termed as *trans*-diequatorial cleavage).

Pathway 3: Cleavage with a partially heterolyzed C–N aziridine bond (borderline S_N2), with the regioisomeric outcome determined by the electronic effects of the adjacent substituents. This pathway can produce either diaxial or diequatorial isomers.

Pathway 3 favors nucleophilic attack at C-3 for both D-*lyxo* and D-*ribo* epimines. The C-2 attack is disfavored because the transition state is destabilized by the inductive electron-withdrawing effect of the acetal group. Accordingly, *lyxo*-epimine **2** should afford the *trans*-diaxial products **7** in accordance with the Fürst–Plattner rule (pathway 1) and the *trans*-diequatorial products **6** by pathway 3 (see Scheme 2). In support of this explanation are two other observations. First, epimine **2** gave no C-2 *trans*-diaxial prod-

ucts under acidic conditions (reaction with HX or EtOH/H_2SO_4). Acidic conditions favor the opening that proceeds through the more stable, partially carbocationic species formed by protonation. Second, under non-acidic conditions, soft nucleophiles afforded more *trans*-diaxial product in comparison with hard nucleophiles and vice versa. For example, **2** gave 61% and 31% of C-2 and C-3 products, respectively, upon reaction with Bu_4NI but 10% and 80%, respectively, upon reaction with Bu_4NCl (Table 2, Entries 6 and 4). Similarly, the C-2 product/C-3 product ratio increased on going from N_3^- to BnSH upon reaction of **2** with the corresponding reagents (Table 2, Entries 7–9).

Soft nucleophiles are known[28] to exhibit more S_N2 behavior and greater sensitivity to steric effects than hard nucleophiles, in which case charge control and electrostatic interactions prevail. Consequently, under non-acidic conditions, the S_N2 mechanism is favored upon reaction of **2** with soft nucleophiles, giving rise predominantly to the C-2 product (**7**) by pathway 1, and the borderline S_N2 mechanism (pathway 3) is favored with hard nucleophiles, giving C-3 products (**6**). Under acidic conditions, the carbocationic species reacts quickly with any nucleophile present (either soft or hard) at C-3. Reactions with BnO^- and EtO^- (Table 2, Entries 10 and 12) appear to be exceptions with a significant amount of *trans*-diaxial products isolated.

The *trans*-diequatorial products **6** from *lyxo*-epimine **2** can also arise by reaction pathway 2. Under the given conditions, we cannot distinguish pathway 3 (borderline S_N2 cleavage) from pathway 2 (S_N2 cleavage through a twist conformation) by product analysis. The cleavage through the twist conformation, however, seems less likely, owing to the conformational rigidity of the tricyclic skeleton.[26]

The *ribo*-epimine **1** gave almost exclusively C-3 *trans*-diaxial products **3**. The unusual formation of C-3 *cis*-products **4a**–**c** in the reaction of **1** with NBu_4X/NH_4X most probably resulted from a consecutive halogen-exchange reaction with primarily formed *trans*-diaxial products **3**. In agreement with this explanation is an increasing amount of **4** going from X = Cl to X = I. An alternative explanation by *cis* opening of aziridine is extremely unlikely. An attempt to verify the halogen exchange by a direct halogen-exchange reaction from **3b** (Nu = Br) failed, because under the reaction conditions, **3b** is in equilibrium with aziridine **1**. The suggested reactions pathways for the ring cleavage of **1** are depicted in Scheme 3. Pathways 1 and 3 give the same *trans*-diaxial product, because steric and electronic effects are synergic. The S_N2 mechanism through a twist conformation (pathway 2) is not involved, because we isolated no *trans*-diequatorial product.

Structures and Configurations

We determined the structures of products **3a**–**7h** mainly from ^1H and ^{13}C NMR spectra. We measured the 2D-PFG-H,H-COSY and 2D-H,C-PFG-HSQC spectra for the structural assignment of ^1H and ^{13}C signals (see the Supporting Information for NMR spectroscopic data). We determined the position of the *N*-tosyl group by observing the *J* value of 8–10 Hz for the coupling of its NH proton to either H-2 (in **3a**–**6h**) or H-3 (in **7a**–**7h**). Small values of *J* for the equatorial H-2 and H-3 protons ($J_{2,1}$ = 1.7–2.3, $J_{2,3}$ = 1.3–2.2, $J_{3,4ax}$ = 4.0–7.2 and $J_{3,4eq}$ = 1.2–2.3 Hz) in **3a**–**3g** and **7a**–**7h** indicated the 2,3-*trans*-diaxial position of the substituents. The long-range couplings ($J_{1,3}$, $J_{2,4}$ and $J_{3,5}$) further supported the equatorial position of H-2 and H-3 in these compounds. On the other hand, large values of $J_{2,3}$ (8.7–10.3 Hz) and $J_{3,4ax}$ (10.4–12.2 Hz) indicated 2,3-*trans*-diequatorial substitution in **6a**–**6h**. In 2,3-*cis* substituted **4b**,**c**, the observed $J_{3,4ax}$ (12.7–13.2 Hz) and $J_{2,3}$ (ca. 5 Hz) required the axial H-3 and equatorial H-2 and, therefore, 2-axial-3-equatorial configuration of substituents. The different electronegativities of the substituents at C-2 or C-3 (Cl, Br, I, N_3, NBn, SBn or OBn) were obviously the main cause of the variations of $^3J_{H,H}$ inside each group of compounds with the same configuration of substituents; slight differences in the $^1C_4$ conformation of the pyranose ring contributed to these results minimally. The coupling constants $J_{5,6en}$ (0.16–1.5 Hz) and $J_{5,6ex}$ (4.1–5.1 Hz) observed throughout the whole series of **3a**–**7h** agreed approximately with an ^5E (in the atom sequence of C-1–O-2–C-6–C-5–O-1) conformation of the five-membered dioxolane ring. The -CH= signals in the ^1H (δ = 5.40 and 6.10 ppm) and ^{13}C (δ = 124.02 and 131.04 ppm) NMR spectra indicated the presence of a double bond in **5**.

In order to confirm the NMR assignment, we prepared a single crystal of **1**, **2**, **3g**, **3f**, **4c**, **5**, **6a** and **7c** and submitted them to X-ray crystallography. These compounds are representatives of each configuration discussed in this work. The results of the structural analysis verified the NMR assignment, and we assigned unequivocally the remaining derivatives on the basis of ^1H chemical shifts and spin-spin coupling patterns characteristic for each configuration.

The conformational analysis showed that the six-membered pyranose ring of the 4-deoxy-2,3-epimines **1** and **2** adopted the envelope conformation E_6 (in the atom sequence of C-1–C-2–C-3–C-4–C-5–O-1), thus falling in the range of other known 2,3-epimines (Figure 1).[26] The opening of the aziridine relieved the strain of the pyranose ring, and the resulting structures adopted conformations close to

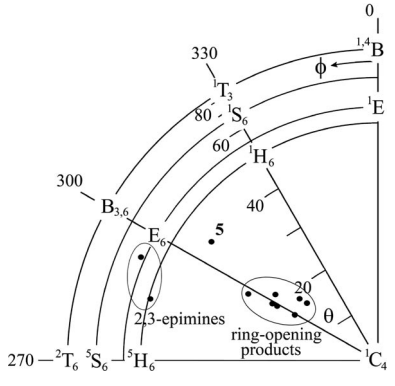


Figure 1. Projection of the ring-puckering parameters.

$^1C_4$. The ring-puckering parameters[29] of measured compounds are available in the Supporting Information, and their polar projection[30] is shown in Figure 1.

Conclusions

N-Tosylated aziridines with asymmetrical, vicinal substitution fused to a tetrahydropyran ring, whose conformation was locked by a 1,6-anhydro bridge, were shown to undergo ring cleavage with heteroatom-centered nucleophiles under appropriate conditions. The regioisomeric outcome depended primarily upon the configuration of the tricyclic skeleton but, to a significant degree, also upon the reaction conditions and the type of nucleophile. For D-*lyxo*-epimine **2**, the regioselectivity was controlled by electronic effects under acidic conditions or with hard nucleophiles, giving rise to predominantly C-3 cleavage products; whereas, under basic conditions with soft nucleophiles, C-2 cleavage products predominantly formed, in agreement with the Fürst–Plattner rule. D-*ribo*-Epimine **1** reacted at C-3 in all cases in accordance with the Fürst–Plattner rule. The ring-opening products represent 4-deoxy 2,3-disubstituted amino pyranoses, possessing a defined configuration and can serve as valuable intermediates for additional transformation. Further investigation into the aziridine cleavage mechanism is currently under way.

Experimental Section

General: The optical rotations were measured on an Autopol III (Rudolph Research, Flanders, NJ) polarimeter at 25 °C. The ^{1}H and ^{13}C NMR spectra were measured with a Varian UNITY-500 instrument (^{1}H at 500 MHz and ^{13}C at 125.7 MHz) in $CDCl_3$ (TMS was an internal reference for ^{1}H, and the chloroform signal at δ = 77.0 ppm was an internal reference for ^{13}C) at 25 °C. GC/MS analyses were carried out with a Hewlett–Packard HP 6890 gas chromatograph equipped with a DB-5MS column (30 m × 250 μm × 0.25 μm) and with a Hewlett–Packard HP 5973 mass-selective detector. TLC was carried out with Merck DC Alufolien with Kiesegel F_{254} and the following solvent systems: S^1 = hexane/ethyl acetate (1:1) and S^2 = dichloromethane/acetone (20:1); spots were detected with an anisaldehyde solution in H_2SO_4. UV detection at 254 nm was also used where appropriate. Column chromatography was performed with silica gel 60 (70–230 mesh, Merck), and the amount of silica gel is given in parentheses. The solvents were evaporated with a vacuum rotary evaporator at less than 40 °C. Anhydrous sodium sulfate was used to dry solutions during workup. The term "common workup" refers to extraction with dichloromethane followed by drying and concentration under reduced pressure. Toluene and diethyl ether were dried with sodium, methanol with magnesium, THF was dried with $LiAlH_4$ and absolute EtOH was of commercial grade (for synthesis, Merck). Ammonium halides were sublimed at 300 °C under water-aspirator vacuum, and tetraalkylammonium halides were purchased from Aldrich and used as supplied. Both ammonium halides and tetraalkylammonium halides were thoroughly pulverized immediately before use. All other chemicals were of reagent grade and were used without purification.

1,6-Anhydro-2,3,4-trideoxy-2,3-(tosylepimino)-β-D-*ribo*-hexopyranose (1): A solution of 4-toluenesulfonyl chloride (1.468 mg, 7.7 mmol) in dichloromethane (1.5 mL) was added dropwise to a solution of 1,6-anhydro-2,3,4-trideoxy-2,3-epimino-β-D-*ribo*-hexopyranose[27] (890 mg, 7.0 mmol) and pyridine (1.5 mL, 18.6 mmol) in dichloromethane (10 mL) under cooling (–15 °C) and stirring. Stirring and cooling continued for 30 min until the unreacted epimine was consumed (TLC in ethyl acetate). The reaction mixture was washed with cold water (ca. 0 °C), cold aq. HCl (2%) and cold water, dried and concentrated. Chromatography on silica gel (65 g) in ethyl acetate afforded **1** (1.365 g, 69%); m.p. 158–159.5 °C, $[a]_D^{25}$ = 0 (*c* = 0.2, $CHCl_3$). $C_{13}H_{15}NO_4S$ (281.33): calcd. C 55.50, H 5.37, N 4.98, S 11.40; found C 55.39, H 5.14, H 4.80, S 11.26.

1,6-Anhydro-2,3,4-trideoxy-2,3-(tosylepimino)-β-D-*lyxo*-hexopyranose (2): A solution of 4-toluenesulfonyl chloride (1.257 mg, 6.59 mmol) in dichloromethane (5 mL) was added dropwise to 1,6-anhydro-2,3,4-trideoxy-2,3-epimino-β-D-*lyxo*-hexopyranose[27] (762 mg, 6.0 mmol), pyridine (0.63 mL, 7.82 mmol) and triethylamine (1.67 mL, 12.0 mmol) in dichloromethane (10 mL) under cooling (–15 °C) and stirring. Stirring and cooling continued for 30 min until the unreacted epimine was consumed (TLC in S^2). The reaction mixture was poured into ice. The common workup followed by chromatography (50 g) in ethyl acetate/hexane (2:1) afforded **2** (1.248 g, 74%); m.p. 153–154.5 °C (sublimated, ethyl acetate/heptane), $[a]_D^{25}$ = –36 (*c* = 0.23, $CHCl_3$). $C_{13}H_{15}NO_4S$ (281.33): calcd. C 55.50, H 5.37, N 4.98, S 11.40; found C 55.79, H 5.32, N 4.97, S 11.03.

Reactions of 1 with Halo Acids: A mixture of the epimine **1** (100 mg, 0.355 mmol), EtOH (10 mL) and hydrohalogenic acid (3.41–3.62 mmol) was stirred for a given time at r.t. until **1** was consumed (TLC in S^1). The reaction mixture was poured into ice, and the crystalline precipitate was filtered off to afford the cleavage product. An attempt to isolate products **3b** and **3c** by solvent extraction with dichloromethane led to partial back-closure to epimine **1** according to TLC.

HCl: Reaction with HCl (35%, 320 μL, 3.62 mmol) for 24 h gave 1,6-anhydro-3-chloro-2,3,4-trideoxy-2-(tosylamino)-β-D-*xylo*-hexopyranose (**3a**, 90 mg, 80%); m.p. 158.5–161 °C (sublimated), $[a]_D^{25}$ = –69 (*c* = 0.25, $CHCl_3$). $C_{13}H_{16}ClNO_4S$ (317.79): calcd. C 49.13, H 5.07, N 4.41, S 10.09, Cl 11.16; found C 49.23, H 5.12, N 4.23, S 9.79, Cl 11.00.

HBr: Reaction with HBr (46%, 400 μL, 3.41 mmol) for 12 h gave 1,6-anhydro-3-bromo-2,3,4-trideoxy-2-(tosylamino)-β-D-*xylo*-hexopyranose (**3b**, 90 mg, 70%); m.p. 145–147.5 °C (decomposed), $[a]_D^{25}$ = –58 (*c* = 0.22, $CHCl_3$). $C_{13}H_{16}BrNO_4S$ (362.25): calcd. C 43.10, H 4.45, N 3.87, S 8.85, Br 22.06; found C 43.22, H 4.45, N 3.69, S 8.59, Br 21.94.

HI: Reaction with HI (57%, 465 μL, 3.52 mmol) for 3 h (the reaction mixture was decolorized with a few drops of aq. sodium thiosulfate before workup) gave 1,6-anhydro-3-iodo-2,3,4-trideoxy-2-(tosylamino)-β-D-*xylo*-hexopyranose (**3c**, 92 mg, 63%); m.p. 102–105 °C (sublimated), $[a]_D^{25}$ = –31 (*c* = 0.23, $CHCl_3$). $C_{13}H_{16}INO_4S$ (409.24): calcd. C 38.15, H 3.94, N 3.42, I 31.01; found C 38.53, H 3.97, N 3.17, I 31.21.

Reactions of 1 with Bu_4NX + NH_4X

X = Cl: A mixture of the epimine **1** (118 mg, 0.42 mmol), Bu_4NCl (232 mg, 0.83 mmol) NH_4Cl (304 mg, 5.68 mmol) and molecular sieves (4 Å) was refluxed in toluene (10 mL) for 20 h. The reaction mixture was then diluted with dichloromethane, filtered and concentrated. Chromatography (25 g) in dichloromethane/acetone (10:1) gave 117 mg (ca. 90%) of a mixture inseparable by column chromatography, whose composition was estimated by GC/MS by

means of comparison with authentic samples: 70% of **3a**, 15% of the unreacted **1**, 4% of the unsaturated tosylamino derivative **5** (see below) and 10% of an unidentified compound, probably chloride **4a**; the percentages in Table 1 are recalculated as yields from **1**. NMR analysis of the mixture confirmed this composition. Crystallization from anhydrous EtOH afforded **3a** (63 mg, 47%) in approximately 90% purity according to ^{1}H NMR and GC/MS.

X = Br: A mixture of the epimine **1** (100 mg, 0.355 mmol), Bu_4NBr (226 mg, 0.70 mmol) and NH_4Br (171 mg, 1.75 mmol) was refluxed in dry toluene (10 mL) for 4 h. The reaction mixture was worked up as described above for X = Cl. Chromatography (13 g) in heptane/ethyl acetate (12:5) gave: 1) 70 mg (54%) of an inseparable mixture of 1,6-anhydro-3-bromo-2,3,4-trideoxy-2-(tosylamino)-β-D-*ribo*-hexopyranose (**4b**) and 1,6-anhydro-3-bromo-2,3,4-trideoxy-2-(tosylamino)-β-D-*xylo*-hexopyranose (**3b**) in a 72:28 ratio (determined by ^{1}H NMR); the percentages in Table 1 were recalculated as yields from **1**, 2) 18 mg (18%) of 1,6-anhydro-2,3,4-trideoxy-2-(tosylamino)-β-D-*erythro*-hex-2-enopyranose (**5**), and 3) 13 mg of an unresolved mixture of **4b**, **3b** and **5**.

X = I: A mixture of epimine **1** (100 mg, 0.355 mmol), Bu_4NI (259 mg, 0.70 mmol) and NH_4I (254 mg, 1.75 mmol) was refluxed in dry toluene (10 mL) for 1.5 h. The reaction mixture was then concentrated to ca. 1 mL, diluted with ethyl acetate, washed with aq. sodium thiosulfate and concentrated. Chromatography (13 g) in heptane/ethyl acetate (2:1) gave: 1) 108 mg (74%) of a mixture of 1,6-anhydro-3-iodo-2,3,4-trideoxy-2-(tosylamino)-β-D-*ribo*-hexopyranose (**4c**) and 1,6-anhydro-3-iodo-2,3,4-trideoxy-2-(tosylamino)-β-D-*xylo*-hexopyranose (**3c**) in a 91:9 ratio (determined by ^{1}H NMR); recrystallization gave **4c** [15 mg, 10%, m.p. 179–182 °C (ethyl acetate/heptane) for X-ray analysis], 2) 16 mg (16%) of 1,6-anhydro-2,3,4-trideoxy-2-(tosylamino)-β-D-*erythro*-hex-2-enopyranose (**5**), and 3) 15 mg of an unresolved mixture of **4c**, **3c** and **5**.

Reaction of 1 with Azide: A mixture of the epimine **1** (100 mg, 0.355 mmol), sodium azide (100 mg, 1.54 mmol), 2-methoxyethanol (5 mL) and water (1 mL) was stirred for 2.5 h at 110 °C until **1** was consumed (TLC in S[1]). The reaction mixture was diluted with water, and the common workup afforded 1,6-anhydro-3-azido-2,3,4-trideoxy-2-(tosylamino)-β-D-*xylo*-hexopyranose (**3d**, 94 mg, 82%); m.p. 114–116 °C (ethyl acetate/heptane), $[\alpha]_D^{25}$ = –96 (c = 0.21, $CHCl_3$). $C_{13}H_{16}N_4O_4S$ (324.36): calcd. C 48.14, H 4.97, N 17.27, S 9.88; found C 48.05, H 4.95, N 17.13, S 9.96.

Reaction of 1 with Benzylamine: A solution of the epimine **1** (100 mg, 0.355 mmol) in benzylamine (600 μL, 5.69 mmol) was stirred for 3 h at 140 °C. The reaction mixture was then poured into ice, and the resulting crystalline precipitate was filtered off to afford 1,6-anhydro-3-benzylamino-2,3,4-trideoxy-2-(tosylamino)-β-D-*xylo*-hexopyranose (**3e**, 121 mg, 88%); m.p. 161–163 °C, $[\alpha]_D^{25}$ = –67 (c = 0.24, $CHCl_3$). $C_{20}H_{24}N_2O_4S$ (388.49): calcd. C 61.83, H 6.23, N 7.21, S 8.25; found C 62.31, H 6.21, N 7.11, S 8.40. HRMS: calcd. for $C_{20}H_{25}N_2O_4S$ $[M + H]^+$ 389.1529; found 389.1513.

Reaction of 1 with Phenylmethanethiol: Sodium methoxide (1 M in methanol, 0.3 mL, 0.3 mmol) was added to a solution of the epimine **1** (100 mg, 0.355 mmol) and phenylmethanethiol (80 μL, 0.68 mmol) in methanol (5 mL). The resulting solution was stirred at 70 °C for 3 h and then poured into ice. The crystalline precipitate was filtered off to afford 1,6-anhydro-3-benzylsulfanyl-2,3,4-trideoxy-2-(tosylamino)-β-D-*xylo*-hexopyranose (**3f**, 135 mg, 94%; 79% after recrystallization); m.p. 202–204 °C (ethyl acetate/methanol), $[\alpha]_D^{25}$ = –214 (c = 0.22, $CHCl_3$). $C_{20}H_{23}NO_4S_2$ (405.54): calcd. C 59.23, H 5.72, N 3.45, S 15.81; found C 59.27, H 5.70, N 3.43, S 16.08.

Reaction of 1 with Benzyl Alcohol: Sodium benzyl alcoholate (1.22 M in benzyl alcohol, 0.7 mL, 0.85 mmol) was added to a mixture of the epimine **1** (100 mg, 0.355 mmol) and benzyl alcohol (2 mL), and the resulting solution was stirred for 7 h at 105 °C. The reaction mixture was diluted with water and neutralized with aq. HCl (5%). The common workup afforded 1,6-anhydro-3-*O*-benzyl-2,4-dideoxy-2-(tosylamino)-β-D-*xylo*-hexopyranose (**3g**, 100 mg, 72%); m.p. 174–176 °C (methanol/water), $[\alpha]_D^{25}$ = –103 (c = 0.21, $CHCl_3$). $C_{20}H_{23}NO_5S$ (389.47): calcd. C 61.68, H 5.95, N 3.60, S 8.23; found C 61.45, H 5.93, N 3.55, S 8.53.

Reaction of 1 with Potassium *tert*-Butoxide: A solution of the epimine **1** (100 mg, 0.355 mmol) in THF (5 mL) was added to a suspension of potassium *tert*-butoxide (400 mg, 3.56 mmol) in THF (5 mL), and the resulting mixture was stirred for 18 h at r.t. The reaction mixture was worked up as described above for **3g**. Chromatography (10 g) in S[1] gave 1,6-anhydro-2,3,4-trideoxy-2-(tosylamino)-β-D-*erythro*-hex-2-enopyranose (**5**, 52 mg, 52%); m.p. 180–184 °C (acetone/heptane), $[\alpha]_D^{25}$ = –131 (c = 0.20, $CHCl_3$). $C_{13}H_{15}NO_4S$ (281.33): calcd. C 55.50, H 5.37, N 4.98, S 11.40; found C 55.46, H 5.37, N 4.89, S 11.02.

Reactions of 2 with Halo Acids: A mixture of the epimine **2** (100 mg, 0.355 mmol), EtOH (10 mL) and hydrohalogenic acid (320 μL, 3.41–3.62 mmol) was stirred at 50 °C for a given time until **2** was consumed (TLC in S[1]). The reaction mixture was diluted with brine, and the common workup followed by column chromatography afforded the ring-cleavage products.

HCl: Reaction with HCl (35%, 320 μL, 3.62 mmol) for 21 h. Chromatography (10 g) afforded: 1) 1,6-anhydro-3-chloro-2,3,4-trideoxy-2-(tosylamino)-β-D-*arabino*-hexopyranose (**6a**, 75 mg, 66%); m.p. 174–176 °C (EtOH), $[\alpha]_D^{25}$ = –107 (c = 0.21, $CHCl_3$), $C_{13}H_{16}ClNO_4S$ (317.79): calcd. C 49.13, H 5.07, N 4.41, Cl 11.16; found C 48.99, H 5.00, N 4.27, Cl 11.07 and 2) 1,6-anhydro-3-*O*-ethyl-2,4-dideoxy-2-(tosylamino)-β-D-*arabino*-hexopyranose (**6h**, 31 mg, 27%), identical to **6h** prepared by the ethanolysis of **2**.

HBr: Reaction with HBr (46%, 400 μL, 3.41 mmol) for 6 h. Chromatography (20 g) afforded: 1) 1,6-anhydro-3-bromo-2,3,4-trideoxy-2-(tosylamino)-β-D-*arabino*-hexopyranose (**6b**, 106 mg, 82%); m.p. 170–172 °C (EtOH), $[\alpha]_D^{25}$ = –104 (c = 0.21, $CHCl_3$); $C_{15}H_{22}BrNO_5S$ (408.31, M + EtOH): calcd. C 44.12, H 5.43, N 3.43, S 7.85; found C 43.81, H 5.47, N 3.37, S 7.60; HRMS: calcd. for $C_{13}H_{17}BrNO_4S$ $[M + H]^+$ 362.0056; found 362.0057 and 2) 1,6-anhydro-3-*O*-ethyl-2,4-dideoxy-2-(tosylamino)-β-D-*arabino*-hexopyranose (**6h**, 14 mg, 12%), identical to **6h** prepared by the ethanolysis of **2**.

HI: Reaction with HI (57%, 470 μL, 3.56 mmol) for 6 h. The reaction mixture was decolorized by the addition of aq. sodium thiosulfate before workup. Chromatography (20 g) afforded: 1) the epimine **2** (23 mg, 23%), formed by aziridine back-closure during workup according to TLC, 2) 1,6-anhydro-3-iodo-2,3,4-trideoxy-2-(tosylamino)-β-D-*arabino*-hexopyranose (**6c**, 88 mg, 60%); m.p. 176–181 °C (EtOH), $[\alpha]_D^{25}$ = –108 (c = 0.21, $CHCl_3$); $C_{13}H_{16}INO_4S$ (409.24): calcd. C 38.15, H 3.94, N 3.42, S 7.83, I 31.01; found C 38.14, H 3.97, N 3.29, S 7.66, I 30.87, and 3) 1,6-anhydro-3-*O*-ethyl-2,4-dideoxy-2-(tosylamino)-β-D-*arabino*-hexopyranose (**6h**, 7 mg, 7%), identical to **6h** prepared by the ethanolysis of **2**.

Reactions of 2 with Bu_4NX + NH_4X

X = Cl: A suspension of the epimine **2** (100 mg, 0.355 mmol), Bu_4NCl (195 mg, 0.70 mmol), NH_4Cl (264 mg, 4.93 mmol) and molecular sieves (4 Å) was refluxed in toluene (10 mL) for 6 h. The reaction mixture was then diluted with dichloromethane, filtered, washed with water, and the water was re-extracted with dichloro-

methane. The combined dichloromethane extracts were dried and concentrated. The residue was dissolved in dichloromethane/acetone (10:1) and filtered through silica gel (10 g). The filtrate was concentrated, and chromatography (20 g) in S^2 gave: 1) 13 mg of a mixture of 1,6-anhydro-2-chloro-2,3,4-trideoxy-3-(tosylamino)-β-D-*xylo*-hexopyranose (**7a**) and the unreacted epimine **2** in a 82:12 ratio, inseparable by column chromatography, whose composition was estimated by NMR; the percentage in Table 2 was recalculated as the yield from **2** and 2) 1,6-anhydro-3-chloro-2,3,4-trideoxy-2-(tosylamino)-β-D-*arabino*-hexopyranose (**6a**, 90 mg, 80%), identical to **6a** prepared by the reaction of **2** with HCl, described above.

X = Br: A suspension of the epimine **2** (100 mg, 0.355 mmol), Bu_4NBr (226 mg, 0.70 mmol) and NH_4Br (171 mg, 1.75 mmol) was refluxed in toluene (10 mL) for 6 h. The reaction mixture was then diluted with ethyl acetate, filtered and concentrated. Chromatography (20 g) in S^2 gave: 1) 1,6-anhydro-2-bromo-2,3,4-trideoxy-3-(tosylamino)-β-D-*xylo*-hexopyranose (**7b**, 32 mg, 25%); m.p. 128–131.5 °C (EtOH), $[\alpha]_D^{25}$ = +95 (*c* = 0.20, $CHCl_3$); HRMS: calcd. for $C_{13}H_{16}BrNO_4SNa$ $[M + Na]^+$ 383.9881; found 383.9875 and 2) 1,6-anhydro-3-bromo-2,3,4-trideoxy-2-(tosylamino)-β-D-*arabino*-hexopyranose (**6b**, 79 mg, 61%), identical to **6b** prepared by the reaction of **2** with HBr.

X = I: A suspension of the epimine **2** (100 mg, 0.355 mmol), Bu_4NI (259 mg, 0.70 mmol) and NH_4I (254 mg, 1.75 mmol) was refluxed in dry toluene (10 mL) for 10 h. The reaction mixture was decolorized by washing it with aq. sodium thiosulfate. The common workup followed by chromatography (20 g) in S^2 afforded: 1) 1,6-anhydro-2-iodo-2,3,4-trideoxy-3-(tosylamino)-β-D-*xylo*-hexopyranose (**7c**, 88 mg, 61%); m.p. 128–129 °C (EtOH), $[\alpha]_D^{25}$ = +145 (*c* = 0.20, $CHCl_3$); $C_{13}H_{16}INO_4S$ (409.24): calcd. C 38.15, H 3.94, N 3.42, S 7.83, I 31.01; found C 38.06, H 3.98, N 3.26, S 7.99, I 30.95 and 2) 1,6-anhydro-3-iodo-2,3,4-trideoxy-2-(tosylamino)-β-D-*arabino*-hexopyranose (**6c**, 45 mg, 31%), identical to **6c** prepared by the reaction of **2** with HI.

Reaction of 2 with Azide: A solution of the epimine **2** (100 mg, 0.355 mmol) and sodium azide (100 mg, 1.54 mmol) in 2-propanol (5 mL) and water (1 mL) was refluxed for 14 h until **2** was consumed (TLC in S^2). The reaction mixture was worked up as described above for the reaction of **1** with azide. Chromatography (20 g) in S^2 afforded: 1) 1,6-anhydro-2-azido-2,3,4-trideoxy-3-(tosylamino)-β-D-*xylo*-hexopyranose (**7d**, 20 mg, 17%); m.p. 103–105.5 °C (EtOH); HRMS: calcd. for $C_{13}H_{16}N_4SO_4Na$ $[M + Na]^+$ 347.0790; found 347.0784 and 2) 1,6-anhydro-3-azido-2,3,4-trideoxy-2-(tosylamino)-β-D-*arabino*-hexopyranose (**6d**, 95 mg, 83%); m.p. 136 °C (EtOH); $C_{13}H_{16}N_4O_4S$ (324.36): calcd. C 48.14, H 4.97, N 17.27, S 9.88; found C 47.93, H 5.04, N 17.14, S 10.22.

Reaction of 2 with Benzylamine: A solution of the epimine **2** (100 mg, 0.355 mmol) in benzylamine (600 μL, 5.69 mmol) was stirred for 3.5 h at 140 °C until the epimine **2** was consumed (TLC in S^2). The reaction mixture was poured into ice, and the resulting precipitate was filtered off and chromatographed (13 g) in S^2 to yield: 1) 1,6-anhydro-2-benzylamino-2,3,4-trideoxy-3-(tosylamino)-β-D-*xylo*-hexopyranose (**7e**, 35 mg, 25%); m.p. 152–154 °C, $[\alpha]_D^{25}$ = +22 (*c* = 0.18, $CHCl_3$); HRMS: calcd. for $C_{20}H_{25}N_2SO_4$ $[M + H]^+$ 389.1530; found 389.1529 and 2) 1,6-anhydro-3-benzylamino-2,3,4-trideoxy-2-(tosylamino)-β-D-*arabino*-hexopyranose (**6e**, 76 mg, 55%); m.p. 168 –169 °C (EtOH), $[\alpha]_D^{25}$ = –40 (*c* = 0.20, $CHCl_3$); $C_{20}H_{24}N_2O_4S$ (388.49): calcd. C 61.83, H 6.23, N 7.21, S 8.25; found C 61.67, H 6.31, N 7.14, S 8.34.

Reaction of 2 with Phenylmethanethiol: Sodium methoxide (1 M solution in methanol, 0.3 mL, 0.3 mmol) was added to a mixture of the epimine **2** (100 mg, 0.355 mmol), methanol (5 mL) and phenylmethanethiol (160 μL, 1.36 mmol). The resulting solution was stirred at 50 °C for 18 h and then poured into ice and neutralized with aq. HCl (5%). The common workup followed by chromatography (20 g) in S^2 afforded: 1) 1,6-anhydro-2-benzylsulfanyl-2,3,4-trideoxy-3-(tosylamino)-β-D-*xylo*-hexopyranose (**7f**, 85 mg, 59%); m.p. 142–143 °C (EtOH), $[\alpha]_D^{25}$ = –161 (*c* = 0.20, $CHCl_3$); $C_{20}H_{23}NO_4S^2$ (405.54): calcd. C 59.23, H 5.72, N 3.45, S 15.81; found C 59.10, H 5.80, N 3.35, S 15.78 and 2) 1,6-anhydro-3-benzylsulfanyl-2,3,4-trideoxy-2-(tosylamino)-β-D-*arabino*-hexopyranose (**6f**, 50 mg, 35%); m.p. 186 °C (EtOH), $[\alpha]_D^{25}$ = –22 (*c* = 0.20, $CHCl_3$); $C_{20}H_{23}NO_4S^2$ (405.54): calcd. C 59.23, H 5.72, N 3.45, S 15.81; found C 59.01, H 5.79, N 3.38, S 15.68.

Reaction of 2 with Benzyl Alcohol: Sodium benzyl alcoholate (1.0 M solution in benzyl alcohol, 1.4 mL, 1.4 mmol) was added to a mixture of the epimine **2** (100 mg, 0.355 mmol) and benzyl alcohol (1.6 mL), and the resulting solution was stirred for 25 h at 120 °C. The reaction mixture was diluted with water and neutralized with aq. HCl (5%). The common workup followed by chromatography (20 g) in S^2 afforded: 1) 1,6-anhydro-2-*O*-benzyl-3,4-trideoxy-3-(tosylamino)-β-D-*xylo*-hexopyranose (**7g**, 49 mg, 36%); m.p. 109–111 °C (EtOH), $[\alpha]_D^{25}$ = –40 (*c* = 0.18); $C_{20}H_{23}NO_5S$ (389.47): calcd. C 61.68, H 5.95, N 3.60, S 8.23; found C 61.43, H 6.02, N 3.56, S 7.99 and 2) 1,6-anhydro-3-*O*-benzyl-2,4-trideoxy-2-(tosylamino)-β-D-*arabino*-hexopyranose (**6g**, 64 mg, 46%); m.p. 177–178 °C (EtOH), $[\alpha]_D$ = –46 (*c* = 0.20); $C_{20}H_{23}NO_5S$ (389.47): calcd. C 61.68, H 5.95, N 3.60, S 8.23; found C 61.43, H 6.05, N 3.56, S 8.01.

Reaction of 2 with EtOH Under Acidic Conditions: A mixture of the epimine **2** (100 mg, 0.355 mmol), EtOH (10 mL) and concentrated H_2SO_4 (50 μL, 0.90 mmol) was stirred at room temperature for 14 d until the unreacted **2** was consumed (TLC in S^2). The reaction mixture was then diluted with water and neutralized with $NaHCO_3$. The common workup followed by chromatography (20 g) in S^1 afforded 1,6-anhydro-3-*O*-ethyl-2,4-trideoxy-2-(tosylamino)-β-D-*arabino*-hexopyranose (**6h**, 91 mg, 78%); m.p. 155 °C (ethyl acetate/heptane), $[\alpha]_D^{25}$ = –87 (*c* = 0.18, $CHCl_3$); $C_{15}H_{21}NO_5S$ (327.40): calcd. C 55.03, H 6.47, N 4.28, S 9.79; found C 54.88, H 6.66, N 3.97, S 9.45.

Reaction of 2 with EtOH Under Basic Conditions: The epimine **2** (100 mg, 0.355 mmol) was added to a solution of sodium ethanolate prepared by the reaction of sodium hydride (229 mg, 9.54 mmol) with anhydrous EtOH (10 mL), and the reaction mixture was refluxed for 12 h until **2** was consumed [TLC in dichloromethane/acetone (30:1)]. The reaction mixture was diluted with water and neutralized with aq. HCl (5%). The common workup followed by chromatography (20 g) in dichloromethane/acetone (30:1) afforded: 1) 1,6-anhydro-2-*O*-ethyl-3,4-trideoxy-3-(tosylamino)-β-D-*xylo*-hexopyranose (**7h**) as a colorless oil (54 mg, 47%); $[\alpha]_D^{25}$ = +4 (*c* = 0.21, $CHCl_3$), HRMS: calcd. for $C_{15}H_{21}NSO_5Na$ $[M + Na]^+$ 350.1033; found 350.1032 and 2) 1,6-anhydro-3-*O*-ethyl-2,4-trideoxy-2-(tosylamino)-β-D-*arabino*-hexopyranose (**6h**, 54 mg, 47%), identical to **6h** prepared by the reaction of **2** with EtOH under sulfuric-acid catalysis.

Supporting Information (see also the footnote on the first page of this article): NMR spectroscopic data, crystallographic data, ring puckering parameters, dihedral angles and ORTEP projections of the crystal structures.

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