Aziridine Ring Cleavage by Nucleophiles in Epimino Derivatives of 1,6-Anhydro-β-D-hexopyranoses

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The regioselectivity of aziridine ring cleavage by nucleophiles (Cl^-, Br^-, I^-, N_3^-, HBr) in a series of *N*-tosyl- and *N*-benzylepimino derivatives of 1,6-anhydro-β-D-hexopyranoses of D-*allo*, D-*manno* and D-*galacto* configurations has been studied. On treatment with halide anions, the tosylepimines **1**, **3**, **5** and **7** were opened *trans*-diaxially according to the Fürst–Plattner rule. The courses of the reactions of benzylepimines **2**, **4**, **6** and **8** depended strongly on the configuration of the epimine and partially on the type of nucleophile used. On treatment with bromide and iodide, *N*-benzylepimines of D-*allo* (compounds **2**, **4**) and D-*galacto* (compound **6**) configuration gave products of *trans*-diequatorial cleavage, while the *manno*-epimine **8** was opened *trans*-diaxially. In comparison, the reactions of all benzylepimines with azide and hydrobromic acid were independent of the configuration and proceeded *trans*-diaxially.

Introduction

Whereas the versatility of aliphatic aziridines in organic synthesis is well established,[1] examples of the successful utilization of sugar aziridines (epimines) are extremely sporadic in the literature (synthesis of D-kijanose[2]). This contrasts with the heavily exploited synthetic potential of sugar epoxides (such as 1,6:2,3-dianhydro- and 1,6:3,4-dianhydro-β-D-hexopyranoses[3]). The main reasons for this are the relatively low reactivity of the aziridine ring towards nucleophilic cleavage[4,5] and the complex stereochemistry[6] of the products formed. To enhance the reactivity of aziridines, protonation,[4,7] addition of a Lewis acid[8] or appropriate *N*-substitution[4,9] is necessary. The configuration of the products depends[4,5] mainly on the configuration (conformation) of the starting epimine, the nature of its *N*-substituent, and the type of nucleophile used. The Fürst−Plattner rule[10] (generally applied to sugar epoxides[3,11]) has limited predictive value for these reactions.[4−6] Usually, a mixture of diaxial and diequatorial isomers[12] is formed,[4,5,9a] but the diequatorial isomer may predominate completely[4,13] in special cases. Nevertheless, no satisfactory interpretation of the factors governing the regioselectivity of aziridine ring cleavage has yet been presented in the literature (cf. refs.[4,5]). Since we view epimines as prospective starting compounds in the synthesis of chiral natural and nonnatural amino compounds, we have investigated reactions of sterically rigid *N*-benzyl- and *N*-tosylepimino derivatives of 1,6-anhydro-β-D-hexopyranoses.[14,15]

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Results

The starting epimines **1**−**8** (Figure 1) were prepared from benzylamino and azidotosyl derivatives of 1,6-anhydro-β-D-glucopyranose by Mitsunobu reaction[16] or by reductive aziridine ring closure with lithium aluminium hydride and subsequent tosylation, respectively. The epimine **6** with a free hydroxy moiety was used instead of the unstable *O*-benzyl derivative.

The reactions between epimines **1**−**8** and azide, chloride, bromide and iodide anions, and also hydrobromic acid, were performed under conditions that gave maximum yields for the cleavage products **9**−**35** and only small amounts of degradation by-products. Consequently, some unchanged starting epimines were recovered.

N-Tosylepimines **1**, **3**, **5** and **7** were treated with a mixture of LiCl and NH_4Cl in DMSO to give the corresponding chloro derivatives **9**, **16**, **23** and **29** by *trans*-diaxial cleavage in 31−65% yields. For efficient cleavage by Br^- and I^-, a new procedure had to be developed, since under the conditions formerly reported in the literature[4] (ammonium halides in boiling DMF) epimines **1**−**8** were mainly decomposed. On treatment with $Bu_4NX + NH_4X$ (X = Br, I) mixtures in boiling toluene, *N*-tosylepimines **1**, **3**, **5** and **7** formed the bromo derivatives **10**, **17**, **24** and **30** and the iodo derivatives **11**, **18**, **25** and **31** by *trans*-diaxial cleavage

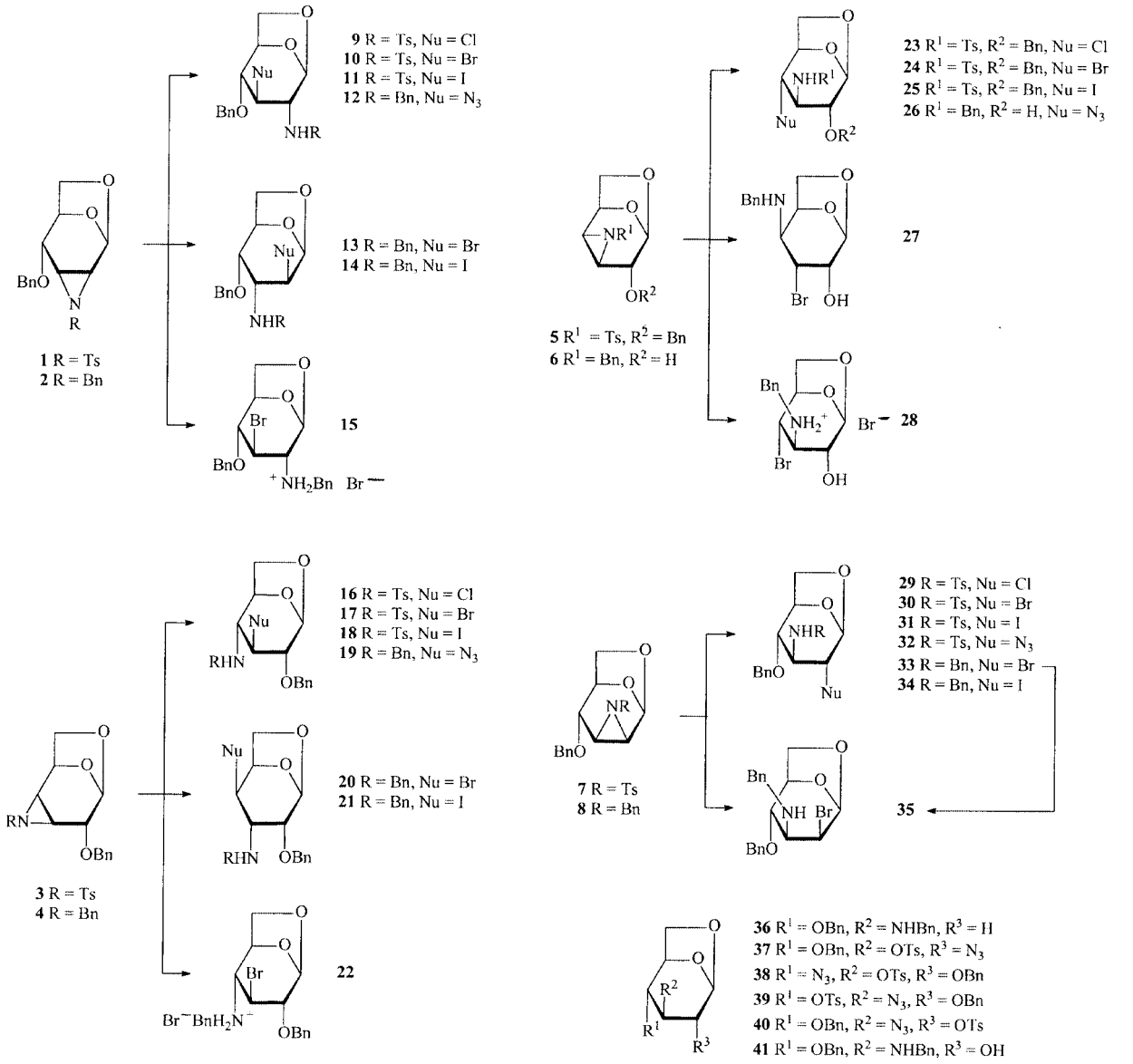

Figure 1. Starting epimines **1**−**8** and the products **9**−**41** of the reactions performed

in 51−72% and 74−95% yields, respectively. The cleavage of *N*-tosylepimines **1**, **3**, **5** and **7** by azide was performed under the standard reaction conditions (a mixture of sodium azide and ammonium chloride in 2-methoxyethanol and water) described for the azidolysis of sugar epoxides (ref.[3]), but did not provide pure azido derivatives. Instead, only mixtures of azido derivatives and by-products originating from the cleavage of the aziridine ring with 2-methoxyethanol and water were formed. However, the azido derivative **32** was prepared from the *N*-tosylepimine **7** in 87% yield by means of an alternative reaction with lithium azide and ammonium trifluoroacetate in DMSO.

The cleavage of *N*-benzylepimines **2**, **4**, **6** and **8** by Cl^- was unsuccessful both with a mixture of LiCl and NH_4Cl in DMSO and with Bu_4NCl and NH_4Cl in toluene, due to decomposition of starting epimines. The reactions between *N*-benzylepimines **2**, **4** and **6** (D-*allo* and D-*galacto* configuration) and Br^- and I^- were performed with mixtures of Bu_4NX and NH_4X (X = Br, I) in boiling toluene and gave the bromo derivatives **13**, **20** and **27** and the iodo derivatives **14** and **21** in 56−92% and 79−83% yields, respectively. The corresponding iodo derivative originating from epimine **6** was too unstable to be isolated. Under the same reaction conditions, the *N*-benzyl-*manno*-epimine **8** with Bu_4NBr and NH_4Br gave a mixture of two isomers, the bromo derivative **33** (29%) and the unexpected bromo derivative **35** (28%) of D-*manno* configuration. The structures of **33** and **35** were unambiguously verified by NMR spectroscopy and by their conversion into the dideoxy derivative **36** on hydrogenation over Raney nickel catalyst. Treatment of epimine **8** with Bu_4NI and NH_4I afforded only the iodo derivative **34**, in 68% yield.

Treatment of *N*-benzylepimines **2**, **4**, **6** and **8** with hydrobromic acid in boiling ethanol was also performed, and diaxial bromo derivatives were produced. Unfortunately, these were unstable and readily cyclized to form starting epimines again under the basic workup conditions. Thus, only the mixtures of bromo derivatives **15**, **22** and **28** and the corresponding epimines **2**, **4** and **6** could be isolated. In contrast, the bromo derivative **33** was quite a stable compound, showing no tendency towards aziridine ring closure.

Treatment of *N*-benzylepimines **2**, **4** and **6** with sodium azide proceeded *trans*-diaxially to afford the azido derivatives **12**, **19** and **26** in high yields (88−94%). The epimine **8** was almost unreactive, and gave only traces of azido derivative.

Except for the halo derivatives **16**−**18**, the tosylamino halogen sugars were reasonably stable crystalline compounds, while all the benzylamino derivatives were less stable oils.

The structures of all compounds described were determined by ^{1}H and ^{13}C NMR spectroscopy. The D-*gluco* configuration in compounds **9**−**12**, **15**−**19**, **22**−**26**, and **29**−**34** was confirmed by the small vicinal couplings J(1,2), J(2,3), J(3,4) and J(4,5) in the 1−3 Hz range, in accordance with equatorial orientations for all corresponding protons. The D-*altro* configuration in derivatives **13** and **14** was manifested in a set of relatively small couplings [J(1,2) ≈ 1.2, J(3,4) ≈ 4.3 and J(4,5) ≈ 2.3 Hz] and a large value for J(2,3) (ca. 10.5 Hz, due to a diaxial orientation of 2-H and 3-H). On the other hand, compounds **20**, **21**, **27**, with the D-*gulo* configuration, showed relatively small values of J(1,2) (ca. 2.2 Hz), J(2,3) (ca. 4.5 Hz) and J(4,5) (ca. 3.8 Hz), whilst the couplings between 3-H and 4-H, in axial relationships, were large [J(3,4) ≈ 11 Hz]. In the protonated bromo derivatives **28**, the tetrahydropyran ring adopted the boat $B_{O,3}$ conformation, as indicated by values of J(2,3) = 5.4 Hz and J(3,4) = 6.7 Hz. This corresponds to the known behaviour of other *N*-substituted 3-amino-1,6-anhydro-3-deoxy-β-D-glucopyranoses.[14,15,17] Some J values from the ^{1}H NMR spectrum of bromo derivative **15** could not be estimated due to the broadness of hydrogen signals of the nearby protonated benzylamino group. In this case, the D-*gluco* configuration was deduced by comparison of the chemical shifts of 2-H, 3-H and 4-H protons with those of analogous benzylamino derivatives.[14]

Discussion

To recapitulate: *N*-tosylepimines **1**, **3**, **5** and **7** were cleaved *trans*-diaxially regardless of their configuration and the nucleophile type. The *N*-benzylepimines **2**, **4** and **6** − with their aziridine rings in 2,3-*exo*- (**2**), 3,4-*exo*- (**4**) and 3,4-*endo* arrangements (**6**), respectively − were cleaved *trans*-diequatorially with Bu_4NX and NH_4X (X = Br, I), but *trans*-diaxially with sodium azide. On the other hand, the *N*-benzylepimine **8**, with a 2,3-*endo*-oriented aziridine ring, was opened *trans*-diaxially in all reactions. Except in one case (the reaction between *manno*-epimine **8** and bromide), only one isomer − originating either from *trans*-diaxial or from *trans*-diequatorial aziridine ring cleavage − was formed. We suggest that the formation of the diequatorial isomer crucially depends on the capability of the corresponding diaxial isomer to form an aziridine ring in a reversible reaction.

Great differences in the reactivities of 2-, 3- and 4-*O*-tosyl derivatives of 1,6-anhydro-β-D-glucopyranoses towards alkaline formation of oxirane rings have been reported in the literature.[18b] Epoxides with 2,3-*exo*-, 3,4-*exo*- and 3,4-*endo*-oriented rings were formed readily in comparison with the rather slow formation of the epoxide with a 2,3-*endo*-oriented oxirane ring. The formation of aziridine rings proceeded similarly; the bromo derivatives **15**, **22** and **28** readily formed the epimines **2**, **4** and **6**, respectively, while the bromo derivative **33** did not react to give epimine **8** when treated with a pyridine/triethylamine mixture. To account for these findings, a pathway from diaxial to diequatorial isomers via protonated *N*-benzylepimines (Figure 2) is suggested.

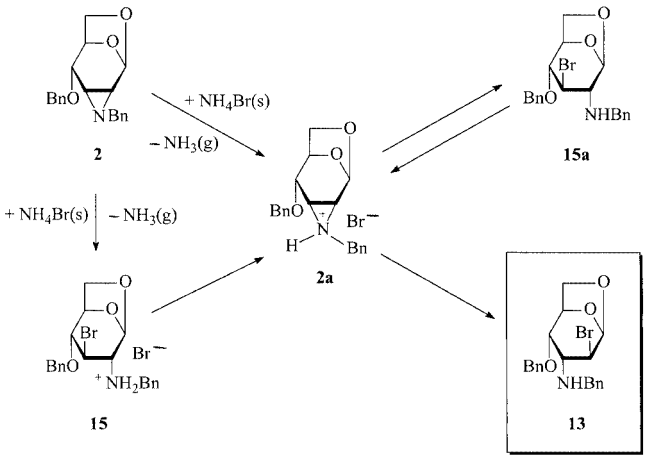

Figure 2. Reaction pathway for the formation of bromo derivative **13**

The bromo derivative **13** was the final cleavage product, and did not form the corresponding epimine **2** either with Bu_4NBr and NH_4Br in boiling toluene or with a pyridine/triethylamine mixture (cf. refs.[18a,18c] − 1,6-anhydro-2-*O*-tosyl-β-D-altropyranose treated with sodium methoxide also did not form the corresponding epoxide). To test the suggested pathway for the formation of diequatorial cleavage products, bromo derivatives **15**, **22**, **28** and **33** were treated with Bu_4NBr and NH_4Br in boiling toluene. The bromo derivatives **13**, **20**, **27**, **33** and **35**, together with corresponding *N*-benzylepimines **2**, **4**, **6** and **8**, were formed in yields similar to those of the direct aziridine ring cleavage (Table 1).

It could hence be deduced that the primary cleavage product was the diaxial stereoisomer. If an equilibrium between the diaxial isomer and the starting epimine was possible, then the corresponding diequatorial isomer was formed as the final cleavage product likely under thermodynamic control of the reaction (cf. Figure 2). This is sup-

Table 1. Yields of reactions between the bromo derivatives **15**, **22**, **28** and **33** and Bu_4NBr and NH_4Br

Reactant	Products			
	Bromo derivative	Yield (%)	*N*-Benzylepimine	Yield (%)
15	**13**	40	**2**	40
22	**20**	80	**4**	0
28	**27**	56	**6**	ca. 0
33	**33** + **35**	58 + 29	**8**	10

ported by the fact that the reactions of the *N*-benzylepimines (**2**, **4**, **6**) with sodium azide and all the reactions of *N*-tosylepimines (**1**, **3**, **5**, **7**) always proceeded *trans*-diaxially. The *trans*-diaxial cleavage was preferred due to the azide anion's poorer leaving group quality and because the benzylamino group was a much more powerful nucleophile than the tosylamino group. Moreover, the products formed by *trans*-diequatorial cleavage of the aziridine rings were also more stable than those of *trans*-diaxial cleavage (D-*altro* and D-*gulo* configurations vs. D-*gluco*: cf. ref.[3]). Similar equilibria between products of *trans*-diaxial cleavage and the starting epimines, giving rise to *trans*-diequatorial products, have been reported in the literature.[19]

The reasons for the formation of bromo derivative **35**, with the *cis*-oriented bromine atom and benzylamino group, in the reaction between epimine **8** and Bu_4NBr and NH_4Br in boiling toluene remains unclear. Bromo derivative **35** might be formed by *cis*-aziridine ring cleavage, but nucleophilic displacement of the bromine atom in **33**, resulting in **35**, seems much more likely. Moreover, an example of a similar displacement at a C-2 carbon atom in the 1,6-anhydro-β-D-glucopyranose skeleton, giving rise to the D-*manno* configuration, has been reported in the literature.[20]

Conclusion

Experimental conditions for an efficient and high-yielding aziridine ring cleavage in epimino derivatives of 1,6-anhydro-β-D-hexopyranoses by azide, chloride, bromide and iodide anions and by HBr are reported. The majority of epimines investigated were cleaved *trans*-diaxially to give single products. The diequatorial stereoisomers, which were formed in the reactions between the *N*-benzylepimines **2**, **4** and **6** and bromide and iodide anions presumably arose from thermodynamic control of the course of the reaction.

Experimental Section

General Remarks: Melting points were determined with a Boëtius melting point microapparatus and are uncorrected. The optical rotations were measured with a Bendix−Ericsson ETL-NPL 143 A polarimeter at 23 °C. The IR spectra were recorded with a Perkin−Elmer 490 spectrometer in $CHCl_3$ solutions at 23 °C. The ^1H and ^{13}C NMR spectra were measured with a Varian INOVA 400 (^1H at 400 MHz and ^{13}C at 100 MHz) and with a Varian UNITY 500 (^1H at 500 MHz and ^{13}C at 125.7 MHz) in $CDCl_3$ (reference TMS for ^1H and the signal of chloroform at δ = 77.0 ppm for ^{13}C) at 25 °C. The ^1H-^1H COSY and ^1H-^{13}C HMQC techniques were used for structural assignment. GC-MS analyses were carried out with a Hewlett−Packard HP 6890 gas chromatograph equipped with an HP5MS column (30 m long, inner diameter 250 μm, thickness of stationary phase 0.25 μm) and with a Hewlett−Packard HP 5973 mass-selective detector (with EI ionization, 70 eV). High-resolution mass spectra were recorded with a ZAB-EQ (VG Analytical, UK) instrument by the FAB method (Xe ionization). The accurate masses of molecular ions determined for bromo derivatives relate to the ^{79}Br isotope. However, the same elemental compositions were found for the ^{81}Br isotope. TLC was carried out on Merck DC Kieselgel F_{254} Alufolien with these solvent systems: S_1 = petroleum ether/ethyl acetate, 3:2; S_2 = petroleum ether/ethyl acetate, 1:1; S_3 = petroleum ether/ethyl acetate, 3:1; spots were detected with the aid of an anisaldehyde solution in sulfuric acid or of iodine vapour. UV detection at 254 nm was also used where appropriate. Column chromatography was performed on Merck 60 silica gel (70−230 mesh) with the TLC solvent systems. The solutions were concentrated in a vacuum rotary evaporator below 40 °C (if not stated otherwise). Toluene and diethyl ether were dried with sodium, methanol and ethanol with magnesium, and tetrahydrofuran with $LiAlH_4$. All solvents were distilled before use. Petroleum ether refers to the 40−60 °C distillation fraction. Ammonium halides were sublimed at 300 °C under water jet pump vacuum, lithium chloride was dried by heating under reflux with thionyl chloride in dry diethyl ether, tetrabutylammonium halides and DMSO were purchased from Aldrich and used as supplied. All other chemicals were of common grade and did not have to be additionally purified. All reactions (except the reactions with Bu_4NBr + NH_4Br and Bu_4NI + NH_4I in toluene) were carried out under argon.

The Preparation of *N*-Tosylepimines 1, 3, 5 and 7. General Procedure: The azido tosylate **37**−**40**, dissolved in THF (10 mL/2 g), was gradually added at −15 °C to a stirred suspension of $LiAlH_4$ (4−5 equiv.) in THF (20−30 mL). The reaction mixture was then allowed to warm up and stirred for 2 h at 0 °C and overnight at room temperature. TLC (S_1) showed no starting azide. The reaction mixture was again cooled to 0 °C, and excess $LiAlH_4$ was decomposed by careful addition of saturated sodium sulfate solution in water. After addition of ethyl acetate (50 mL), the suspension was filtered through a pad of Celite and repeatedly washed with ethyl acetate (total 100 mL). The combined filtrates were concentrated, and the resulting oil was dried in a vacuum dessicator over P_2O_5. The free epimine was subsequently dissolved in pyridine (20−40 mL), and solid tosyl chloride (3 equiv.) was added at −15 °C, in a few portions whilst stirring. Sufficient cooling was essential for satisfactory yields of tosylated epimine. After addition, the reaction mixture was allowed to warm, and was stirred overnight at room temperature. The resulting brown solution was poured onto crushed ice, and the precipitated tosylepimine was filtered off and washed with water. The air-dried product was further recrystallised from an acetone/diethyl ether/petroleum ether mixture to afford pure *N*-tosylepimines **1**, **3**, **5** and **7**.

1,6-Anhydro-4-*O*-benzyl-2,3-dideoxy-2,3-tosylepimino-β-D-allopyranose (1): This compound was prepared from 1,6-anhydro-2-azido-4-*O*-benzyl-2-deoxy-3-*O*-tosyl-β-D-glucopyranose[15] (**37**, 2.1 g, 4.9 mmol), $LiAlH_4$ (800 mg, 21 mmol) and tosyl chloride (3 g, 15.7 mmol). Yield 1.432 g (76%), m.p. 205−206 °C. $[\alpha]_D$ = +130 (c = 0.4, $CHCl_3$). Ref.[15] states m.p. 204−206 °C and $[\alpha]_D$ = +130 ($CHCl_3$).

1,6-Anhydro-2-*O*-benzyl-3,4-dideoxy-3,4-tosylepimino-β-D-allopyranose (3): This compound was prepared from 1,6-anhydro-4-azido-2-*O*-benzyl-4-deoxy-3-*O*-tosyl-β-D-glucopyranose[15] (**38**, 2.11 g, 4.9 mmol), $LiAlH_4$ (800 mg, 21 mmol) and tosyl chloride (2.5 g, 13.1 mmol). Yield 1.028 g (54%), m.p. 164−165 °C. $[\alpha]_D$ = −149 (*c* = 0.28; $CHCl_3$). The ^1H and ^{13}C NMR spectra are summarized in Tables 2 and 3. $C_{20}H_{21}NO_5S$ (387.45): calcd: C 62.00, H 5.46, N 3.62, S 8.28; found C 61.75, H 5.46, N 3.63, S 8.10.

1,6-Anhydro-2-*O*-benzyl-3,4-dideoxy-3,4-tosylepimino-β-D-galactopyranose (5): This compound was prepared from 1,6-anhydro-3-azido-2-*O*-benzyl-3-deoxy-4-*O*-tosyl-β-D-glucopyranose[15] (**39**, 1.534 g, 3.55 mmol), $LiAlH_4$ (600 mg, 15.5 mmol) and tosyl chloride (2.4 g, 12.5 mmol). Yield 925 mg (67%), m.p. 152−153 °C. $[\alpha]_D$ = −7 (*c* = 0.44, $CHCl_3$). Ref.[15] states m.p. 152−152.5 °C and $[\alpha]_D$ = −6 ($CHCl_3$).

1,6-Anhydro-4-*O*-benzyl-2,3-dideoxy-2,3-tosylepimino-β-D-mannopyranose (7): This compound was prepared from 1,6-anhydro-3-azido-4-*O*-benzyl-3-deoxy-2-*O*-tosyl-β-D-glucopyranose[21] (**40**, 1.675 g, 3.88 mmol), $LiAlH_4$ (750 mg, 19.3 mmol) and tosyl chloride (2.5 g, 13.1 mmol). Yield 918 mg (61%), m.p. 143−144 °C. $[\alpha]_D$ = −44.4 (*c* = 0.22, $CHCl_3$). The ^1H and ^{13}C NMR spectra are summarized in Tables 2 and 3. $C_{20}H_{21}NO_5S$ (387.45): calcd. C 62.00, H 5.46, N 3.62, S 8.28; found C 61.92, H 5.43, N 3.55, S 8.29.

The Preparation of *N*-Benzylepimino Derivatives 2, 4, 6 and 8. General Procedure: Epimines **2**, **4** and **6** were prepared according to ref.[14] by Mitsunobu reaction.[16]

1,6-Anhydro-4-*O*-benzyl-2,3-(*N*-benzylepimino)-2,3-dideoxy-β-D-mannopyranose (8): Diethyl azodicarboxylate (0.7 mL, 4.4 mmol) was added to a stirred solution of 1,6-anhydro-4-*O*-benzyl-3-benzylamino-3-deoxy-β-D-glucopyranose[6] (**41**, 0.5 g, 1.5 mmol) and triphenylphosphane (1.2 g, 4.5 mmol) in toluene (20 mL), and the orange solution was heated under argon at 50 °C for 29 h. The reaction was monitored by TLC (S_2) and, after consumption of benzylamine **41**, was concentrated. The yellow oil was chromatographed on silica gel (50 g) with mixture S_2. The mixture of epimine **8** and diethyl hydrazodicarboxylate was separated and hydrolysed with 4 M aqueous NaOH (10 mL) and ethanol (20 mL) for 48 h at 45 °C. After hydrolysis, the ethanol was removed in vacuo, the epimine **8** was extracted four times with dichloromethane (total 150 mL), and the organic layer was washed with water and dried with sodium sulfate. The solution was concentrated under reduced pressure, and the resulting oil (354 mg, 75%) was dried in a vacuum dessicator over P_2O_5, upon which it crystallised. After recrystallization from an ethanol/diethyl ether/petroleum ether mixture, pure **8** was obtained. Yield 304 mg (64%), m.p. 72−74 °C. $[\alpha]_D$ = −56.3 (*c* = 0.16, $CHCl_3$).). The ^1H and ^{13}C NMR spectra are summarized in Tables 2 and 3. $C_{20}H_{21}NO_3$ (323.2): calcd. C 74.28, H 6.55, N 4.33; found C 74.31, H 6.67, N 4.28.

General Procedure for Treatment of *N*-Tosylepimines 1, 3, 5 and 7 with Chloride: A mixture of tosylepimine **1**, **3**, **5** or **7**, lithium chloride and ammonium chloride in DMSO (5 mL) was heated under argon at 100 °C for the time given. The reaction was monitored by TLC (S_1) and stopped after consumption of the starting epimine. The mixture was poured onto crushed ice (50−100 mL), and the precipitated chloro derivative was filtered off or (if it did not precipitate) extracted three times with dichloromethane (total 60−80 mL), washed with water and dried with sodium sulfate. After evaporation of dichloromethane, the oily residue was chromatographed on silica gel (S_2) and the purified chloro derivative was recrystallised from an ethanol/diethyl ether/petroleum ether mixture. The ^1H and ^{13}C NMR spectra are summarized in Tables 4 and 5.

1,6-Anhydro-4-*O*-benzyl-3-chloro-2,3-dideoxy-2-tosylamino-β-D-glucopyranose (9): This compound was prepared from **1** (100 mg,

Table 2. Proton NMR spectroscopic data of epimines **3**, **7** and **8** in $CDCl_3$

Compound	Chemical shifts (ppm)/signal multiplicity											
	1-H	2-H	3-H	4-H	5-H	6-H_{ex}	6-H_{en}	O$CH_2C_6H_5$		N$CH_2C_6H_5$		$C_6H_{5(4)}$	CH_3
3[a]	5.26 dt	3.45 dd	3.16 ddd	3.05 dd	4.69 dd	3.70 dd	3.91 d	4.45 d	4.34 d	–		7.28−7.30 m, 7.91−7.93 m	2.39 s
7[b]	5.64 d	3.26 dd	3.07 dd	3.57 bs	4.50 m	3.65 d[c]	3.66 s[c]	4.74 d	4.65 d	–		7.32−7.37 m, 7.79−7.81 m	2.45 s
8[b]	5.75 dd	2.24 vbdd	1.90 vbd	3.60 b	4.48 dm	3.68 t	3.90 vbd	4.68 d	4.65 d	3.62 d	3.48 d	7.26−7.36 m	–
	Coupling constants (Hz)												
	1,2	2,3	3,4	4,5	5,6*ex*	5,6*en*	6*ex*,6*en*	1,3	3,5	N−CH_2		O−CH_2	
3[d]	0.8	5.6	7.0	1.2	4.3	< 1	7.5	1.7	< 1	–		11.9	
7	3.8	7.0	[c]	[c]	6.2	0.9	[c]	[c]	1.8	–		12.1	
8	4.0	6.1		1.8	6.8	1.0	7.0	0.75	1.7	13.9		12.2	

[a] At 400 MHz. [b] At 500 MHz. [c] Higher-order system of 6-H*ex* and 6-H*en*, some *J* values could not be estimated. [d] *J*(1,4) = 0.8 Hz.

Table 3. Carbon-13 chemical shifts of epimines **3**, **7** and **8** in $CDCl_3$

Compound	C-1	C-2	C-3	C-4	C-5	C-6	O$CH_2C_6H_5$	N$CH_2C_6H_5$	CH_3	$C_6H_{5(4)}$
3[a]	100.56	69.08	35.10	37.21	70.01	66.01	70.39	–	21.62	144.92, 137.07, 134.58, 129.73(2), 128.28(2), 128.23(2), 127.76, 127.68(2)
7[a]	96.02	42.88	34.16	72.65	72.31	65.66	71.83	–	21.64	144.82, 136.94, 134.37, 129.80 (2), 128.60(2), 128.13, 127.86(2), 127.68(2)
8[b]	97.90	43.12	35.48	73.45	72.06	65.79	71.51	62.54	–	137.56(2), 127.91, 128.51(2), 128.43(2), 127.83(2), 127.63(2), 127.20

[a] At 100 MHz. [b] At 125.7 MHz.

Table 4. Proton NMR spectroscopic data (500 MHz) of *N*-tosylamino derivatives **9**−**11**, **16**−**18**, **23**−**25** and **29**−**32** in $CDCl_3$ (um: unresolved multiplet; p: pentet; dp: double pentet)

Compound	Chemical shifts (ppm)/signal multiplicity												
	1-H	2-H	3-H	4-H	5-H	6-H$_{ex}$	6-H$_{en}$	O*CH*$_2$C$_6$H$_5$		NH*Ts*	C$_6$H$_5$	C$_6$H$_4$	CH$_3$
9	5.25 t	3.66 dm	3.85 m	3.51 m	4.53 m	3.72 dm	4.25 dd	4.58 d	4.46 d	5.29 d	7.28−7.40 m	7.31, 7.74 m	2.44 bs
10	5.28 t	3.77 dm	3.86 dq	3.63 m	4.52 m	3.73 dd	4.36 dd	4.57 d	4.43 d	5.29 d	7.26−7.41 m	7.31, 7.75 m	2.45 bs
11	5.33 t	3.82 vbd	3.95 dq	3.72 m	4.51 m	3.77 dd	4.47 dd	4.54 d	4.38 d	5.32 bd	7.26−7.41 m	7.32, 7.74 m	2.45 bs
16	5.39 bt	3.48 m	3.79 p	3.68 dm	4.39 m	3.69 dd	4.34 dd	4.54 d	4.40 d	5.55 d	7.26−7.39 m	7.31, 7.75 m	2.45 bs
17	5.39 bt	3.60 m	3.79 p	3.79 dm	4.41 m	3.71 dd	4.45 dd	4.52 d	4.38 d	5.57 d	7.25−7.38 m	7.32, 7.75 m	2.45 bs
18	5.40 bt	3.71 m	3.88 p	3.81 dm	4.44 m	3.75 dd	4.57 dd	4.50 d	4.34 d	5.59 d	7.24−7.38 m	7.32, 7.75 m	2.45 bs
23	5.40 um	2.98 m	3.74 dm	4.07 m	4.64 m	3.76 dd	4.17 dd	4.46 d	3.92 d	5.25 d	7.04−7.27 m	7.38, 7.80 m	2.47 bs
24	5.42 um	3.00 m	3.88 dp	4.15 m	4.70 m	3.73 dd	4.17 dd	4.48 d	3.92 d	5.31 d	7.06−7.34 m	7.39, 7.79 m	2.47 bs
25	5.43 um	3.04 m	3.94 dm	4.28 m	4.73 dm	3.59 dd	4.17 dd	4.51 d	3.92 d	5.44 d	7.08−7.28 m	7.39, 7.79 m	2.47 bs
29	5.43 t	3.30 m	3.88 dm	3.52 m	4.56 m	3.72 dd	4.04 dd	4.80 d	4.58 d	5.16 d	7.32−7.40 m	7.36, 7.75 m	2.46 bs
30	5.48 um	3.33 m	4.00 dm	3.53 m	4.57 m	3.70 dd	4.05 dd	4.82 d	4.57 d	5.23 d	7.31−7.41 m	7.36, 7.76 m	2.46 bs
31	5.53 um	3.42 m	4.02 dm	3.57 m	4.56 m	3.67 dd	4.10 dd	4.84 d	4.56 d	5.26 d	7.32−7.44 m	7.38, 7.76 m	2.47 bs
32	5.43 um	3.30 m	3.88 dp	3.52 m	4.57 bdt	3.72 dd	4.04 dd	4.81 d	4.58 d	5.16 d	7.30−7.46 m	7.35, 7.75 m	2.46 bs

	Coupling constants (Hz)											
	1,2	2,3	3,4	4,5	5,6*ex*	5,6*en*	6*ex*,6*en*	1,3	2,4	3,5	C*H*,NH*Ts*	O−CH$_2$
9[a]	2.0	1.3	1.2	2.0	5.5	0.8	7.8	1.6	1.2	1.8	11.0	11.9
10[b]	2.1	1.2	1.2	2.0	5.5	0.7	7.9	1.5	1.2	1.9	11.0	12.0
11[c]	2.4	2.0	1.2	2.0	5.4	0.8	8.1	1.3	1.0	1.9	10.3	11.9
16[d]	2.2	1.4	1.6	1.6	5.6	1.0	8.0	1.5	1.5	1.6	10.5	11.8
17[e]	2.0	1.6	1.7	1.7	5.6	0.9	8.0	1.5	1.2	1.5	10.7	11.8
18[f]	2.2	1.6	1.7	1.9	5.4	0.9	8.2	1.5	1.1	1.4	10.3	11.8
23[g]	2.4	1.2	1.2	1.3	5.1	0.7	8.1	1.4	1.8	1.6	8.2	12.3
24[h]	2.5	1.2	1.3	1.3	5.0	0.7	8.1	1.3	1.6	1.4	8.1	12.3
25[i]	2.4	1.3	1.2	1.3	5.0	0.6	8.0	1.4	1.6	1.2	8.2	12.2
29[j]	2.0	1.4	1.4	1.5	5.2	0.6	8.1	1.3	1.4	1.4	9.3	12.3
30[k]	2.0	1.4	1.3	1.5	5.1	0.7	8.1	1.2	1.4	1.3	9.3	12.3
31[l]	1.8	1.3	1.3	1.5	5.2	0.7	8.1	1.1	1.5	1.3	9.3	12.3
32[m]	2.0	1.8	1.5	1.8	5.2	0.8	8.0	1.3	1.2	1.2	9.3	12.3

[a] $J(1,4) = 0.8$ Hz, $J(1,5) \# 0.3$ Hz, $J(1,6ex) \# 0.3$ Hz, $J(2,5) = 0.7$ Hz. [b] $J(1,4) = 0.7$ Hz, $J(1,6ex) \# 0.3$ Hz, $J(2,5) = 0.7$ Hz. [c] $J(1,4) = 0.7$ Hz. [d] $J(1,4) = 0.8$ Hz, $J(1,6ex) = 0.3$ Hz. [e] $J(1,4) = 0.8$ Hz, $J(1,6ex) \# 0.3$ Hz. [f] $J(1,4) = 0.7$ Hz, $J(1,6ex) = 0.3$ Hz. [g] $J(1,4) = 0.8$ Hz, $J(1,6ex) = 0.5$ Hz. [h] $J(1,4) = 0.8$ Hz, $J(1,6ex) = 0.3$ Hz. [i] $J(1,4) = 0.8$ Hz, $J(1,6ex) < 0.5$ Hz. [j] − $J(1,4) = 0.6$ Hz. [k] − $J(1,4) = 0.$ Hz, $J(1,5) = 0.5$ Hz. [l] − $J(1,4) = 0.7$ Hz, $J(1,5) < 0.5$ Hz. [m] − $J(1,4) = 0.6$ Hz.

0.26 mmol), LiCl (25 mg, 0.59 mmol) and NH_4Cl (150 mg, 2.8 mmol), after 17 h of heating at 150 °C. The oily chloro derivative **9** (104 mg, 94%) crystallised after chromatographic purification to afford 60.4 mg (55.4%) of pure **9**, m.p. 136−137 °C. $[\alpha]_D = -49.3$ ($c = 0.13$, $CHCl_3$). $C_{20}H_{22}ClNO_5S$ (423.9): calcd. C 56.67, H 5.23, Cl 8.36, N 3.30, S 7.56; found C 56.52, H 5.25, Cl 8.54, N 3.20.

1,6-Anhydro-2-*O*-benzyl-3-chloro-3,4-dideoxy-4-tosylamino-β-D-glucopyranose (16): This compound was prepared from **3** (100 mg, 0.26 mmol), LiCl (50 mg, 1.2 mmol) and NH_4Cl (200 mg, 3.7 mmol), after 46 h of heating. The mixture of the chloro derivative **16** and the starting epimine **3** was chromatographically separated to afford unchanged epimine **3** (25 mg, 25%) and pure **16** (63 mg, 58%) as an uncrystallizable oil. $[\alpha]_D = -33.3$ ($c = 0.9$, $CHCl_3$). HR MS (FAB) analysis found $m/z = 423.0928$ [M^+], $C_{20}H_{22}ClNO_5S$ requires 423.0907.

1,6-Anhydro-2-*O*-benzyl-4-chloro-3,4-dideoxy-3-tosylamino-β-D-glucopyranose (23): This compound was prepared from **5** (100 mg, 0.26 mmol), LiCl (50 mg, 1.2 mmol) and NH_4Cl (200 mg, 3.7 mmol), after 23 h of heating. After workup, the precipitated crude chloro derivative **23** (78 mg, 71.5%) was dissolved in acetone, stirred with a small amount of charcoal and filtered, and the solvents were evaporated to dryness. The resulting solid residue was recrystallised from an ethanol/diethyl ether/petroleum ether mixture to afford pure **23** (33.5 mg, 31%), m.p. 48−52 °C (dec.). $[\alpha]_D = -61.1$ ($c = 0.11$, $CHCl_3$). $C_{20}H_{22}ClNO_5S$ (423.9): calcd. C 56.67, H 5.23, Cl 8.36, N 3.30, S 7.56; found C 56.69, H 5.28, N 3.20.

1,6-Anhydro-4-*O*-benzyl-2-chloro-2,3-dideoxy-3-tosylamino-β-D-glucopyranose (29): This compound was prepared from **7** (100 mg, 0.26 mmol), LiCl (50 mg, 1.2 mmol) and NH_4Cl (200 mg, 3.7 mmol), after 16 h of heating. After workup, the precipitated chloro derivative **29** (90 mg, 83%) was recrystallised from an ethanol/diethyl ether/petroleum ether mixture to afford pure **29** (71 mg, 65%), m.p. 150−151 °C. $[\alpha]_D = +154.1$ ($c = 0.17$, $CHCl_3$). $C_{20}H_{22}ClNO_5S$ (423.9): calcd. C 56.67, H 5.23, Cl 8.36, N 3.30, S 7.56; found C 56.60, H 5.23, N 3.26, Cl 8.04.

General Procedure for Treatment of Epimines 1−8 with Bromide and Iodide: A mixture of epimine **1**−**8** and thoroughly pulverized tetrabutylammonium and ammonium bromide or iodide in toluene (10−15 mL) was heated under reflux (the temperature of a silicon oil bath was maintained at 200 °C) with exclusion of water for given time. The reaction was monitored by TLC (S_1 or S_3) and stopped when no further progress was detected. The brown suspension was concentrated to dryness, and the solid residue was partitioned between water (5 mL) and dichloromethane (40 mL). The aqueous layer was extracted twice with dichloromethane (total 40

Table 5. Carbon-13 NMR chemical shifts (125.7 MHz) of *N*-tosylamino derivatives **9**−**11**, **16**−**18**, **23**−**25** and **29**−**32** in $CDCl_3$

Compound	C-1	C-2	C-3	C-4	C-5	C-6	$OCH_2C_6H_5$	$C_6H_{5(4)}$	CH_3
9	100.77	55.29	52.01	76.90	74.06	65.50	71.52	143.93, 137.64, 136.53, 129.98(2), 128.71(2), 128.36, 127.88(2), 126.98(2)	21.56
10	100.98	55.80	40.26	77.20	74.49	65.82	71.57	143.92, 137.79, 136.61, 130.00(2), 128.74(2), 128.38, 127.91(2), 127.05(2)	21.55
11	101.24	57.20	12.81	78.17	75.03	66.38	71.39	143.89, 137.82, 136.66, 130.04(2), 128.74(2), 128.36, 127.91(2), 127.05(2)	21.56
16	100.14	76.80	52.32	55.20	75.58	65.65	72.24	143.94, 137.77, 136.53, 130.00(2), 128.69(2), 128.37, 127.92(2), 126.94(2)	21.57
17	100.28	77.19	40.62	55.31	75.89	65.84	72.18	143.97, 137.74, 136.51, 130.03(2), 128.69(2), 128.37, 127.93(2), 126.94(2)	21.59
18	100.50	78.80	13.53	56.18	76.42	66.23	72.05	143.93, 137.78, 136.59, 130.06(2), 128.70(2), 128.36, 127.94(2), 126.97(2)	21.59
23	100.78	74.65	53.35	56.30	76.54	66.35	71.20	144.30, 136.85, 136.67, 130.14(2), 128.46(2), 128.07, 127.75(2), 127.28(2)	21.60
24	100.83	74.79	53.25	46.08	76.89	66.84	71.10	144.30, 136.72, 136.64, 130.14(2), 128.46(2), 128.07, 127.79(2), 127.26(2)	21.60
25	100.89	75.06	54.08	21.83	78.36	67.16	70.88	144.26, 136.58(2), 130.14(2), 128.45(2), 128.05, 127.85(2), 127.23(2)	21.60
29	101.20	53.95	53.95	76.05	75.62	65.76	71.12	144.27, 137.31, 136.94, 130.20(2), 128.50(2), 128.14(2), 127.97, 126.92(2)	21.60
30	101.38	43.54	53.84	76.29	75.60	65.84	71.00	144.26, 137.27, 136.94, 130.22(2), 128.47(2), 128.15(2), 127.94, 126.91(2)	21.60
31	102.79	19.78	54.55	76.76	75.59	66.07	70.85	144.25, 137.21, 137.02, 130.32(2), 128.48(2), 128.22(2), 127.94, 126.92(2)	21.62
32	101.21	53.96	53.96	76.08	75.62	65.76	71.13	144.27, 137.32, 136.95, 130.19(2), 128.50(2), 128.14(2), 127.96, 126.92(2)	21.60

mL) and the combined organic fractions were washed with water and dried with sodium sulfate. The dichloromethane solution was concentrated, and the residue was chromatographed on silica gel (40−50 g, solvent mixture S_2) to separate unchanged epimine and the bromo or iodo derivative. The separated halo derivatives were further recrystallised from ethanol/diethyl ether/petroleum ether mixtures to afford pure compounds. Uncrystallizable oils were dried in a vacuum dessicator over phosphorus pentoxide. The ^1H and ^{13}C NMR spectra are summarized in Tables 4 to 7.

1,6-Anhydro-4-*O*-benzyl-3-bromo-2,3-dideoxy-2-tosylamino-β-D-glucopyranose (10): This compound was prepared from **1** (100 mg, 0.26 mmol), Bu_4NBr (90 mg, 0.28 mmol) and NH_4Br (250 mg, 2.55 mmol), after 19.5 h of reflux. Yield 86 mg (72%, after recrystallization 58 mg, 48%), m.p. 142−144 °C. $[\alpha]_D = -41.3$ ($c = 0.1$, $CHCl_3$). $C_{20}H_{22}BrNO_5S$ (468.4): calcd. C 51.29, H 4.73, Br 17.06, N 2.99, S 6.85; found C 51.19, H 4.76, Br 17.02, N 2.87. In addition, 10 mg (10%) of unchanged starting epimine **1** was isolated.

1,6-Anhydro-4-*O*-benzyl-3-iodo-2,3-dideoxy-2-tosylamino-β-D-glucopyranose (11): This compound was prepared from **1** (100 mg, 0.26 mmol), Bu_4NI (100 mg, 0.27 mmol) and NH_4I (380 mg, 2.62 mmol), after 9 h of reflux. Yield 110 mg (83%, after recrystallization 93 mg, 70%), m.p. 144−146 °C. $[\alpha]_D = -38.3$ ($c = 0.23$, $CHCl_3$). $C_{20}H_{22}INO_5S$ (515.4): calcd. C 46.61, H 4.30, I 24.62, N 2.72, S 6.22; found C 46.69, H 4.33, I 24.83, N 2.56.

1,6-Anhydro-4-*O*-benzyl-3-benzylamino-2-bromo-2,3-dideoxy-β-D-altropyranose (13): This compound was prepared from **2** (100 mg, 0.26 mmol), Bu_4NBr (100 mg, 0.31 mmol) and NH_4Br (600 mg, 6.1 mmol), after 12.5 h of reflux. Yield 87 mg (69%) of colourless oil, $[\alpha]_D = +105$ ($c = 0.28$, $CHCl_3$). HR MS (FAB) analysis found $m/z = 404.0862$ [$M^+ + H$], $C_{20}H_{23}BrNO_3$ requires 404.0861.

1,6-Anhydro-4-*O*-benzyl-3-benzylamino-2-iodo-2,3-dideoxy-β-D-altropyranose (14): This compound was prepared from **2** (100 mg, 0.26 mmol), Bu_4NI (115 mg, 0.31 mmol) and NH_4I (500 mg, 3.45 mmol), after 12.5 h reflux. Yield 110 mg (79%) of colourless oil. $[\alpha]_D = +107$ ($c = 0.34$, $CHCl_3$). HR MS (FAB) analysis found $m/z = 452.0756$ [$M^+ + H$], $C_{20}H_{23}INO_3$ requires 452.0723.

1,6-Anhydro-2-*O*-benzyl-3-bromo-3,4-dideoxy-4-tosylamino-β-D-glucopyranose (17): This compound was prepared from **3** (100 mg, 0.26 mmol), Bu_4NBr (100 mg, 0.31 mmol) and NH_4Br (500 mg, 5.1 mmol), after 46 h of reflux. Yield 75 mg (**17**, 62%). $[\alpha]_D = -37.1$ ($c = 0.76$, $CHCl_3$). HR MS (FAB) analysis found $m/z = 467.0388$ [M^+], $C_{20}H_{22}BrNO_5S$ requires 467.0402. In addition, 37 mg (37%) of unchanged starting epimine **3** was isolated.

1,6-Anhydro-2-*O*-benzyl-3-iodo-3,4-dideoxy-4-tosylamino-β-D-glucopyranose (18): This compound was prepared from **3** (100 mg, 0.26 mmol), Bu_4NI (100 mg, 0.27 mmol) and NH_4I (400 mg, 2.75 mmol), after 46 h of reflux. Yield 95 mg (73.5%) **18**. $[\alpha]_D = -42.8$ ($c = 1.01$, $CHCl_3$). HR MS (FAB) analysis found $m/z = 515.0265$ [M^+], $C_{20}H_{22}INO_5S$ requires 515.0263. In addition, 23 mg (23%) of unchanged starting epimine **3** was isolated.

1,6-Anhydro-2-*O*-benzyl-3-benzylamino-4-bromo-3,4-dideoxy-β-D-gulopyranose (20): This compound was prepared from **4** (100 mg, 0.26 mmol), Bu_4NBr (200 mg, 0.6 mmol) and NH_4Br (600 mg, 6.1 mmol), after 20 h of reflux. Yield 115 mg (92%) of colourless oil. $[\alpha]_D = +118.5$ ($c = 0.54$, $CHCl_3$). HR MS (FAB) analysis found $m/z = 404.0812$ [$M^+ + H$], $C_{20}H_{23}BrNO_3$ requires 404.0861.

1,6-Anhydro-2-*O*-benzyl-3-benzylamino-4-iodo-3,4-dideoxy-β-D-gulopyranose (21): This compound was prepared from **4** (100 mg, 0.26 mmol), Bu_4NI (115 mg, 0.31 mmol) and NH_4I (500 mg, 3.45 mmol), after 3 h of reflux. Yield 115 mg (83%) of colourless

Table 6. Proton NMR spectroscopic data (400 MHz) of *N*-benzylamino derivatives **12**−**15**, **19**−**22**, **26**−**28** and **33**−**36** in $CDCl_3$

Compound	Chemical shifts (ppm)/signal multiplicity											
	1-H	2-H	3-H	4-H	5-H	6-H_{ex}	6-H_{en}	O$CH_2C_6H_5$		N$CH_2C_6H_5$		C_6H_5
12	5.49 d	2.66 m	3.78 m	3.30 m	4.55 dm	3.70 dd	3.97 dd	4.62 d	4.64 d	3.88 d	3.85 d	7.25−7.40 m
13	5.54 d	3.95 dd	3.03 dd	3.47 dd	4.72 bdd	3.79 dd	3.65 dd	4.76 d	4.51 d	3.78 d	3.72 d	7.23−7.43 m
14	5.67 bs	4.04 dd	3.00 dd	3.44 dd	4.78 dd	3.79 dd	3.67 dd	4.77 d	4.49 d	3.76 d	3.66 d	7.23−7.44 m
15[a]	5.72 vbs	3.72 vbm	4.03 bs	3.77 dd	4.60 bdt	3.77 dd	4.34 d	4.74 d	4.63 d	4.03(2) bs		7.24−7.45 m
19[b]	5.42 bt	3.35 m	3.76 m	2.52 m	4.56 dm	3.70 ddd	3.95 dd	4.65 d	4.63 d	3.88 d	3.84 d	7.26−7.37 m
20	5.52 d	3.56 dd	2.99 dd	4.12 ddd	4.60 bd	3.72 ddd	4.18 dd	4.67 d	4.54 d	3.75 d	3.67 d	7.23−7.38 m
21[b]	5.64 d	3.52 dd	2.95 dd	4.19 ddd	4.72 bd	3.75 ddd	4.27 dd	4.67 d	4.53 d	3.71 d	3.61 d	7.23−7.37 m
22[a]	5.49 bs	3.75 bt	4.38 bp	3.67 bs	4.97 bd	3.82 dd	4.42 d	4.72 d	4.61 d	4.26(2) bs		7.22−7.47 m
26[b]	5.42 um	3.53 m	2.86 m	3.58 m	4.53 dm	3.78 bdd	4.26 dd	−		3.92 d	3.87 d	7.26−7.37 m
27	5.43 d	3.82 dd	3.27 dd	4.15 ddd	4.45 dd	3.60 ddd	4.14 dd	−		3.85 d	3.83 d	7.25−7.36 m
28[a]	5.44 s	4.11 d	4.64 d	3.40 t	4.83 d	3.71 dd	4.17 d	−		4.49 d	4.41 d	7.32−7.63 m
33	5.65 bt	3.37 m	3.26 m	3.87 m	4.62 bdm	3.71 dd	4.03 dd	4.60 d	4.42 d	3.85 d	3.74 d	7.28−7.37 m
34	5.74 vb	3.43 m	3.31 m	4.03 m	4.61 dm	3.68 dd	4.09 dd	4.60 d	4.38 d	3.85 d	3.73 d	7.26−7.37 m
35[b]	5.50 t	4.50 dd	3.03 dq	3.54 bt	4.54 dm	3.69 dd	4.63 dd	4.45 d	4.30 d	3.86 d	3.68 d	7.21−7.36 m
36[b]	5.59 t	[c]	2.93 m	3.56 m	4.55 dm	3.68 dd	4.23 dd	4.58 d	4.52 d	3.85 d	3.80 d	7.25−7.37 m

	Coupling constants (Hz)											
	1,2	2,3	3,4	4,5	5,6*ex*	5,6*en*	6*ex*,6*en*	1,3	2,4	3,5	O−CH_2	N−CH_2
12	2.2	1.2	1.2	1.5	5.9	1.0	8.0	1.1	1.0	1.3	12.1	13.3
13	1.2	10.4	4.3	2.3	5.6	0.9	7.9	ca. 0	ca. 0	ca. 0	11.8	13.4
14	1.2	10.7	4.3	2.3	5.6	0.9	7.9	ca. 0	ca. 0	ca. 0	11.8	13.5
15[a]	[a]	[a]	[a]	2.9	5.3	<1	7.8	[a]	[a]	[a]	11.9	[a]
19[d]	1.7	2.9	3.0	1.8	5.5	1.0	7.3	1.0	1.0	1.4	12.0	13.2
20[e]	2.2	4.6	10.8	3.6	4.9	0.8	8.1	ca. 0	ca. 0	ca. 0	11.9	13.4
21[f]	2.2	4.4	11.3	3.3	5.0	# 0.5	8.1	ca. 0	ca. 0	ca. 0	11.9	13.2
22[a]	1.2−1.5	1.2−1.5	1.2−1.5	< 1	5.5	< 1	8.1	1.2−1.5	ca. 0	1.2−1.5	11.9	[a]
26[g]	1.6	2.2	1.9	2.1	5.5	0.9	7.6	1.3	1.0	1.8	−	13.1
27[h]	2.5	3.7	11.0	3.8	5.0	0.8	7.8	ca. 0	ca. 0	ca. 0	−	13.4
28[i]	0	5.4	6.7	0	5.5	< 1	8.5	ca. 0	ca. 0	ca. 0	−	13.3
33[j]	1.2	1.8	1.8	1.8	5.5	0.7	7.8	1.2	0.9	1.4	12.4	13.4
34[k]	1.2	1.8	1.7	1.8	5.5	0.7	7.7	1.2	0.9	1.5	12.5	13.3
35	1.2	6.2	1.9	2.0	5.5	0.9	7.0	1.2	ca. 0	1.6	12.3	13.2
36	[l]	[l]			5.6	1.0	7.3				12.2	13.8

[a] CD_3COOD (10% v/v) was added to the NMR tube, some *J* values could not be estimated due to peak broadness. [b] At 500 MHz. [c] 2-H_α: 1.70 dm; 2-H_β: 2.24 ddd. [d] $J(1,4) = 0.7$ Hz, $J(1,6ex) = 0.4$ Hz. [e] $J(4,6ex) = 1.3$ Hz. [f] $J(4,6ex) = 1.5$ Hz. [g] $J(1,6ex)$ # 0.3 Hz. [h] $J(4,6ex) = 1.3$ Hz. [i] Boat $B_{O,3}$(D) conformation of 6,8-dioxabicyclo[3.2.1]octane skeleton. [j] $J(1,4) = 0.6$ Hz. [k] $J(1,4) = 0.6$ Hz. [l] $J(1,2\alpha) = 2.0$ Hz, $J(1,2\beta) = 2.3$ Hz, $J(2\alpha,2\beta) = 14.5$ Hz, $J(2\alpha,3) = 2.0$ Hz, $J(2\beta,3) = 7.0$ Hz.

oil. $[\alpha]_D = +117.1$ ($c = 0.64$, $CHCl_3$). HR MS (FAB) analysis found $m/z = 452.0722$ [$M^+ + H$], $C_{20}H_{23}INO_3$ requires 452.0723.

1,6-Anhydro-2-*O*-benzyl-4-bromo-3,4-dideoxy-3-tosylamino-β-D-glucopyranose (24): This compound was prepared from **5** (100 mg, 0.26 mmol), Bu_4NBr (150 mg, 0.47 mmol) and NH_4Br (800 mg, 8.16 mmol), after 20.5 h of reflux. Yield 61 mg (51%, after recrystallization 21.4 mg, 18%), m.p. 55−58 °C (dec.). $[\alpha]_D = -44.3$ ($c = 0.036$, $CHCl_3$). $C_{20}H_{22}BrNO_5S$ (468.4): calcd. C 51.29, H 4.73, Br 17.06, N 2.99, S 6.85; found C 51.22, H 4.97, Br 17.06, N 2.99. In addition, 25 mg (25%) of unchanged starting epimine **5** was isolated.

1,6-Anhydro-2-*O*-benzyl-4-iodo-3,4-dideoxy-3-tosylamino-β-D-glucopyranose (25): This compound was prepared from **5** (100 mg, 0.26 mmol), Bu_4NI (150 mg, 0.4 mmol) and NH_4I (800 mg, 5.5 mmol), after 17 h of reflux. Yield 102 mg (77%, after recrystallization 48 mg, 36%), m.p. 65−68 °C (dec.). $[\alpha]_D = -55.1$ ($c = 0.33$, $CHCl_3$). $C_{20}H_{22}INO_5S$ (515.4): calcd. C 46.61, H 4.30, I 24.62, N 2.72, S 6.22; found C 46.68, H 4.40, I 24.83, N 2.75, S 6.20.

1,6-Anhydro-4-benzylamino-3-bromo-3,4-dideoxy-β-D-glucopyranose (27): This compound was prepared from **6** (50 mg, 0.21 mmol), Bu_4NBr (200 mg, 0.6 mmol) and NH_4Br (600 mg, 6.1 mmol), after 19 h of reflux. Yield 38 mg (56%) of colourless oil. $[\alpha]_D = +56.9$ ($c = 0.32$, $CHCl_3$). HR MS (FAB) analysis found $m/z = 314.0336$ [$M^+ + H$], $C_{13}H_{17}BrNO_3$ requires 314.0392.

1,6-Anhydro-4-*O*-benzyl-2-bromo-2,3-dideoxy-3-tosylamino-β-D-glucopyranose (30): This compound was prepared from **7** (100 mg, 0.26 mmol), Bu_4NBr (90 mg, 0.28 mmol) and NH_4Br (250 mg, 2.55 mmol), after 18 h of reflux. Yield 64 mg (53%, after recrystallization 36 mg, 30%), m.p. 136−139 °C. $[\alpha]_D = +114.8$ ($c = 0.22$, $CHCl_3$). $C_{20}H_{22}BrNO_5S$ (468.4): calcd. C 51.29, H 4.73, Br 17.06, N 2.99; found C 51.21, H 4.83, Br 17.04, N 3.00.

1,6-Anhydro-4-*O*-benzyl-2-iodo-2,3-dideoxy-3-tosylamino-β-D-glucopyranose (31): This compound was prepared from **7** (100 mg, 0.26 mmol), Bu_4NI (100 mg, 0.27 mmol) and NH_4I (400 mg, 2.75 mmol), after 18 h reflux. Yield 126 mg (95%, after recrystallization 89 mg, 67%), m.p. 70−73 °C. $[\alpha]_D = +174.3$ ($c = 0.23$. $CHCl_3$). $C_{20}H_{22}INO_5S$ (515.4): calcd. C 46.61, H 4.30, I 24.62, N 2.72; found C 46.90, H 4.49, I 24.81, N 2.59.

1,6-Anhydro-4-*O*-benzyl-3-benzylamino-2-bromo-2,3-dideoxy-β-D-glucopyranose (33) and 1,6-Anhydro-4-*O*-benzyl-3-benzylamino-2-bromo-2,3-dideoxy-β-D-mannopyranose (35): These compounds were prepared from **8** (50 mg, 0.15 mmol), Bu_4NBr (200 mg, 0.6 mmol)

Table 7. Carbon-13 chemical shifts (100 MHz) of *N*-benzylamino derivatives **12**, **14**−**15**, **19**−**22**, **26**−**28** and **33**−**36** in $CDCl_3$

Compound	C-1	C-2	C-3	C-4	C-5	C-6	O*CH*$_2$C$_6$H$_5$	N*CH*$_2$C$_6$H$_5$	C$_6$H$_5$
12	101.87	57.32	58.25	76.83	73.96	65.50	71.63	51.30	139.54, 137.13, 128.63(2), 128.52(2), 128.16(2), 127.85(2), 127.22(2)
14	103.78	23.85	58.72	77.32	75.14	65.92	71.36	51.34	137.92, 137.32. 128.66(2), 128.38(2), 128.31(2), 128.21, 128.07(2), 127.17
15	101.37	60.44	40.50	78.42	74.75	65.84	71.92	50.86	136.88(2), 128.73(2), 128.68(2), 128.57(2), 128.02(2), 127.82, 127.65
19[a]	100.20	76.34	58.95	57.32	74.86	66.48	72.41	50.73	139.49, 137.04, 128.62(2), 128.53(2), 128.21, 128.11(2), 128.02(2), 127.22
20	99.90	75.99	57.97	52.92	76.11	64.54	72.86	51.28	140.07, 137.42, 128.65(2), 128.38(2), 128.24, 128.21(2), 128.17(2),127.14
21[a]	99.99	75.08	58.51	34.92	77.61	65.13	72.71	51.31	140.01, 137.45, 128.64(2), 128.29(2), 128.28(2), 128.21, 128.12(2), 127.07
22	100.58	77.32	40.25	59.29	74.35	66.34	72.57	50.09	128.87, 128.85, 128.71(2), 128.39, 128.26(2), 128.17(2), 127.72(2), 127.33
26[a]	102.37	69.84	60.12	61.38	74.60	66.10	-	52.74	132.02, 128.62(2), 128.32(2), 127.54
27	100.90	71.12	59.79	55.73	75.04	63.45	-	52.18	139.55, 128.59(2), 127.98(2), 127.39
28	103.58	71.26	62.44	45.42	78.83	68.22	-	51.87	130.49, 129.63, 129.16, 128.39, 128.07, 127.29
33	102.27	66.74	59.18	77.55	75.34	65.95	70.80	52.26	139.48, 137.22, 128.54(2), 128.45(2), 128.27(2), 127.89(2), 127.83, 127.35
34	103.62	24.59	59.75	77.93	75.34	66.06	70.67	52.23	139.49, 137.21, 128.55(2), 128.43(2), 128.30(2), 127.92(2), 127.79, 127.32
35	102.44	54.40	58.71	78.60	74.83	65.34	71.25	53.81	139.93, 137.69, 128.52(2), 128.48(2), 128.41(2), 127.90(2), 127.69, 127.15
36[a]	100.26	29.62	52.41	77.62	74.68	65.29	71.09	52.06	129.45, 128.43(2), 127.78(2), 127.32

[a] At 125.7 MHz

and NH_4Br (600 mg, 6.1 mmol), after 23 h of reflux. A mixture of isomeric bromo derivatives **33** and **35** was formed, and the individual compounds were separated by column chromatography on silica gel (50 g, solvent mixture S_3). **33:** Yield 14.4 mg (29%) of colourless oil. $[\alpha]_D = +37.1$ ($c = 0.28$, $CHCl_3$). HR MS (FAB) analysis found $m/z = 404.0783$ [$M^+ + H$], $C_{20}H_{23}BrNO_3$ requires 404.0861. **35:** Yield 12.2 mg (28%) of colourless oil. $[\alpha]_D = -27.5$ ($c = 0.24$, $CHCl_3$). HR MS (FAB) analysis found $m/z = 404.0745$ [$M^+ + H$], $C_{20}H_{23}BrNO_3$ requires 404.0861. In addition, 15 mg (30%) of epimine **8** was isolated.

1,6-Anhydro-4-*O*-benzyl-3-benzylamino-2-iodo-2,3-dideoxy-β-D-glucopyranose (34): This compound was prepared from **8** (50 mg, 0.15 mmol), Bu_4NI (300 mg, 0.8 mmol) and NH_4I (300 mg, 2.1 mmol), after 19 h of reflux. Yield 52 mg (68%) of colourless oil. $[\alpha]_D = +23.1$ ($c = 1.19$, $CHCl_3$). HR MS (FAB) analysis found $m/z = 452.0736$ [$M^+ + H$], $C_{20}H_{23}INO_3$ requires 452.0723.

General Procedure for Treatment of Epimines 2, 4 and 6 with Azide: A solution of benzylepimine **2**, **4** or **6**, sodium azide and ammonium chloride in 2-methoxyethanol (10 mL) and water (2 mL) was heated under reflux for given time. After the mixture had cooled to room temp., the reaction solvents were evaporated to dryness (at 70−80 °C) and the solid residue was extracted with chloroform (70 mL). The extract was dried with Na_2SO_4, and the solvents were evaporated to leave a brown oil. This oil was dissolved in toluene (10 mL, for **12** and **19**) or in dichloromethane (30 mL, for **26**), stirred with charcoal and filtered through a short (3 cm) column of silica gel to remove coloured impurities. After concentration, the filtrate gave a colourless, uncrystallizable oil, which was dried in a vacuum dessicator over P_2O_5. The ^1H and ^{13}C NMR spectra are summarized in Tables 4 to 7.

1,6-Anhydro-3-azido-4-*O*-benzyl-2-benzylamino-2,3-dideoxy-β-D-glucopyranose (12): This compound was prepared from **2** (500 mg, 1.67 mmol), NaN_3 (440 mg, 6.77 mmol) and NH_4Cl (2.5 g, 46.7 mmol), after 7 h of reflux. Yield 538 mg (94%), $[\alpha]_D = -19$ ($c = 0.8$ $CHCl_3$). HR MS (FAB) analysis found $m/z = 367.1785$ [$M^+ + H$], $C_{20}H_{23}N_4O_3$ requires 367.1770.

1,6-Anhydro-3-azido-2-*O*-benzyl-4-benzylamino-3,4-dideoxy-β-D-glucopyranose (19): This compound was prepared from **4** (200 mg, 0.62 mmol), NaN_3 (180 mg, 2.77 mmol) and NH_4Cl (1 g, 18.7 mmol), after 8.5 h of reflux. Yield 203 mg (88%). $[\alpha]_D = -62.4$ ($c = 0.48$, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu} = 2100$ [$\nu(N_3)$], 3332 [ν(NH)] cm^{-1}. HR MS (FAB) analysis found $m/z = 367.1842$ [$M^+ + H$], $C_{20}H_{23}N_4O_3$ requires 367.1770.

1,6-Anhydro-4-azido-3-benzylamino-3,4-dideoxy-β-D-glucopyranose (26): This compound was prepared from **6** (160 mg, 0.67 mmol), NaN_3 (180 mg, 2.77 mmol) and NH_4Cl (1 g, 18.7 mmol), after 7.5 h of reflux. Yield 166 mg (87.8%). $[\alpha]_D = -24$ ($c = 0.46$, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu} = 2102$ [$\nu(N_3)$], 3342 [ν(NH)], 3560 [ν(OH)] cm^{-1}. HR MS (FAB) analysis found $m/z = 277.1300$ [$M^+ + H$], $C_{13}H_{17}N_4O_3$ requires 277.1301.

1,6-Anhydro-2-azido-4-*O*-benzyl-2,3-dideoxy-3-tosylamino-β-D-glucopyranose (32): Epimine **7** (50 mg, 0.13 mmol), lithium azide (60 mg, 1.23 mmol) and ammonium trifluoroacetate (35 mg, 0.27 mmol) were dissolved in DMSO (4 mL) and heated with stirring at 110 °C for 19 h. After consumption of epimine **7**, the reaction mixture was cooled to room temp. and poured onto crushed ice (30 mL). The separated solid was filtered off and air-dried. Crude product **32** (48 mg, 87%) was recrystallised from a methanol/diethyl ether/petroleum ether mixture to afford pure **32** (38.5 mg, 70%), m.p. 146−147 °C. $[\alpha]_D = +129.4$ ($c = 0.17$, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu} = 2101$ [$\nu(N_3)$], 3375 [ν(NH)], 1343 [$\nu(SO_2)$], 1164 [$\nu(SO_2)$] cm^{-1}. $C_{20}H_{22}N_4O_5S$ (430.5): calcd. C 55.80, H 5.15, N 13.02, S 7.45; found C 55.76, H 5.20, N 12.68, S 7.23.

General Procedure for Treatment of Epimines 2, 4, 6 and 8 with Hydrobromic Acid: Epimine **2**, **4**, **6** or **8** was dissolved in ethanol

(5−10 mL), and 48% aqueous HBr was added with cooling. The solution was heated under reflux for given time. After cooling to room temp., the reaction mixture was poured into 5% aqueous $NaHCO_3$ (15 mL), ethanol was evaporated in a rotary vacuum evaporator, and the residual solution was extracted with dichloromethane (total 60−80 mL). The extract was washed with water and dried with Na_2SO_4, and the solvents were evaporated to afford a colourless oil, which was dried in a vacuum dessicator over phosphorus pentoxide. TLC analysis (S_2) showed continuous transformation of the pure bromo derivative into a mixture of the bromo derivative hydrobromide and the corresponding benzylepimine (a composition of ca. 1:1 was estimated from the ^1H NMR spectrum of the mixture by integration of 1-H proton signals). This mixture was impossible to separate by chromatography (LC, HPLC). Thus, all data for bromo derivatives were obtained by analyses of these mixtures; yields and optical rotation values were recalculated for bromo derivatives as for individual compounds. The ^1H and ^{13}C NMR spectra are summarized in Tables 6 and 7.

1,6-Anhydro-4-*O*-benzyl-2-benzylamino-3-bromo-2,3-dideoxy-β-D-glucopyranose Hydrobromide (15): This compound was prepared from **2** (100 mg, 0.31 mmol) and HBr (1.6 mL, 14.2 mmol), after 5 h of reflux. Yield 86.5 mg of colourless oil. Composition of the oil: bromide **15** (72%) and epimine **2** (28%). Calculated yields: epimine **2** (24 mg, 24%) and bromide **15** (62.5 mg, 50%). $[\alpha]_D = -25$ ($c = 0.14$, $CHCl_3$). HR MS (FAB) analysis of the mixture found for **15** $m/z = 404.0864$ $[M^+ + H]$, $C_{20}H_{23}BrNO_3$ requires 404.0861.

1,6-Anhydro-2-*O*-benzyl-4-benzylamino-3-bromo-3,4-dideoxy-β-D-glucopyranose Hydrobromide (22): This compound was prepared from **4** (100 mg, 0.31 mmol) and HBr (1.6 mL, 14.2 mmol), after 18 h of reflux. Yield 102 mg of colourless oil. Composition of the oil: bromide **22** (41%) and epimine **4** (59%). Calculated yields: epimine **4** (60 mg, 60%) and bromide **22** (42 mg, 33%). $[\alpha]_D = -29.9$ ($c = 0.28$, $CHCl_3$). HR MS (FAB) analysis of the mixture found for **22** $m/z = 404.0875$ $[M^+ + H]$, $C_{20}H_{23}BrNO_3$ requires 404.0861.

1,6-Anhydro-3-benzylamino-4-bromo-3,4-dideoxy-β-D-glucpyraonose Hydrobromide (28): This compound was prepared from **6** (50 mg, 0.21 mmol) and HBr (1 mL, 8.9 mmol), after 48 h of reflux. Yield 62 mg of colourless oil. Composition of the oil: bromide **28** (48%) and epimine **6** (52%). Calculated yields: epimine **6** (32.4 mg, 64%) and bromide **28** (29.5 mg, 44%). $[\alpha]_D = -169.9$ ($c = 0.48$, $CHCl_3$). HR MS (FAB) analysis of the mixture found for **28** $m/z = 314.0311$ $[M^+ + H]$, $C_{13}H_{17}BrNO_3$ requires . 314.0392.

1,6-Anhydro-4-*O*-benzyl-3-benzylamino-2-bromo-2,3-dideoxy-β-D-glucopyranose (33): This compound was prepared from **8** (50 mg, 0.15 mmol) and HBr (0.8 mL, 7.1 mmol), after 19 h reflux. Yield 33 mg (53%) of a colourless oil after chromatography (S_3). The compound was identical (NMR, TLC) to the bromo derivative prepared by treatment of epimine **8** with the $Bu_4NBr + NH_4Br$ mixture. In addition, unchanged starting epimine **8** (12 mg, 24%) was isolated.

Treatment of Bromo Derivatives 15, 22, 28 and 33 with Bu_4NBr and NH_4Br in Toluene: A mixture of the bromo derivative **15**, **22** or **28** and the corresponding epimine **2**, **4** or **6** (prepared by the reactions with HBr described above) was added to a suspension of pulverized Bu_4NBr (200 mg, 0.62 mmol) and NH_4Br (600 mg, 6.1 mmol) in dry toluene (10 mL) and heated under reflux for given time. The transformation of bromo derivatives was monitored by TLC (S_3) and stopped after their consumption. The brown suspension was concentrated to dryness, and the solid residue was partitioned between water (5 mL) and dichloromethane (40 mL). The aqueous layer was extracted twice with dichloromethane (total 40 mL) and the combined organic fractions were washed with water and dried with sodium sulfate. The dichloromethane solution was concentrated, and the residue was chromatographed on silica gel (40−50 g, mixture S_2) to purify the bromo derivative **13**, **20** or **27**. The uncrystallizable oils were dried in a vacuum dessicator over phosphorus pentoxide. The NMR spectra of bromo derivatives **13**, **20** and **27** are identical with those summarized in Tables 6 and 7. **13**: Prepared from the mixture of **15** and **2** (86.5 mg), after 16 h of reflux. Yield 50 mg (40%). In addition, epimine **2** (40 mg, 40%) was isolated. **20**: Prepared from the mixture of **22** and **4** (87 mg), after 20 h of reflux. Yield 70 mg (80%). **27**: Prepared from the mixture of **28** and **6** (55 mg), after 19 h of reflux. Yield 31 mg (56%). Bromo derivative **33** (10 mg, 0.025 mmol), Bu_4NBr (50 mg, 0.15 mmol) and NH_4Br (150 mg, 1.5 mmol) in dry toluene (2 mL) were mixed and heated under reflux for 23 h. After workup (as described above), the resulting oil was analysed by NMR spectroscopy, which showed the following composition: **33** (58.5%), **35** (28.8%), **8** (12.7%). The calculated yields of compounds **8**, **33** and **35** were 10, 58 and 29%, respectively.

Reduction of Bromo Derivatives 33 and 35 To Afford the Dideoxy Derivative 36: A solution of bromo derivative **33** (32 mg, 0.08 mmol) or **35** (12 mg, 0.03 mmol) and triethylamine (50 μL) in ethyl acetate (30 mL) was hydrogenated for 1 h after addition of Raney nickel catalyst (freshly prepared from 3 g of alloy according to ref.[22]). TLC (S_1) showed complete transformation of **33** or **35** into **36**. The catalyst was filtered off through Celite and washed several times with dichloromethane (total 50 mL). The combined filtrates were concentrated to dryness, and the residue was dissolved in a small amount (1 mL) of ethanol. Ether was added to the solution, and precipitated $Et_3N{\cdot}HBr$ was removed by filtration. After evaporation of the solvent, dideoxy derivative **36** was obtained as a colourless oil, contaminated with traces of triethylamine hydrobromide. The yield of **36** was 30 mg from **33** and 8.5 mg from **35**, respectively. $[\alpha]_D = -17.8$ ($c = 0.09$, $CHCl_3$). The ^1H and ^{13}C NMR spectra are summarized in Tables 6 and 7. GC-MS: m/z (%) = 91 (100), 234 (68), 324 (0.3) $[M^+ - H]$, 325 (0.3) $[M^+]$, 326 (0.1), $[M^+ + H]$.

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