Amino Sugars. XXXII. Ammonolysis and Azidolysis of Benzyl 2,3-Anhydro-4-azido-4-deoxypentopyranosides

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Ammonolysis and azidolysis of four benzyl 2,3-anhydro-4-azido-4-deoxypentopyranosides of α-D-*lyxo*, α-D-*ribo*, β-L-*lyxo*, and β-L-*ribo* configurations, were studied. Ratios of two ring-opening isomers and relative reaction rates were determined, factors controlling the direction of ring opening being discussed.

The ring-opening reaction of anhydro sugars with nucleophiles has been widely used not only for amino sugar synthesis by the reaction with ammonia or azide ion[1] but also for various kinds of carbohydrate derivatives.[2] In these reactions the formation of two kinds of *trans* α-hydroxy products is possible, depending on which carbon atom is attacked by the nucleophiles. Anhydropyranosides are well known to exist mainly in half-chair conformation.[3,4] When the conformation is fixed by a fused-ring such as in 4,6-*O*-benzylidene-2,3-anhydrohexopyranosides and 1,6 : 2,3-dianhydrohexopyranoses,[2] the predominant product is a *trans*-diaxial ring-opening product as postulated by the Fürst-Plattner rule.[5] On the other hand, the conformationally flexible anhydropyranoside like anhydropentopyranoside gives two ring-opening products in various ratios according to substituents on the pyranoside and to the character of nucleophiles. There is little systematic study on such ring-opening reaction, and the finding of the reversed ring-opening mode between ammonolysis and azidolysis of benzyl 2,3-anhydro-4-azido-4-deoxy-β-L-ribopyranoside (**4**)[6] prompted us to study the same reactions of all four stereochemical counterparts of benzyl 2,3-anhydro-4-azido-4-deoxypentopyranoside.

Results

All four stereochemical counterparts, namely, α-*lyxo* (**1**),[7] α-*ribo* (**2**),[7] β-*lyxo* (**3**),[8] and β-*ribo* (**4**)[6] isomers of benzyl 2,3-anhydro-4-azido-4-deoxypentopyranoside were prepared as reported previously. D-Enantiomer and L-enantiomer were used, for the α-anomers and β-anomers, respectively, because of availability of their starting materials.

Ammonolysis reactions of **1**,[6] **3**,[7] and **4**[8] in methanol at 90—95 °C gave 2-amino derivatives predominantly (40—70% yields of isolation). The ratios of two ring-opening isomers, 2-amino and 3-amino derivatives, were determined by means of densitometer (Method A) and optical rotational values (Method B). In method A the reaction mixture was developed on a silica gel TLC plate using benzene–pyridine as a solvent, the spots being detected by ninhydrin or sulfuric acid. In method B the ratio was calculated from the optical rotational value of the product mixture using that of each component. When the two isomers were well separated on TLC, the weights of products isolated by preparative TLC were also used for the estimation of the ratios of products (Method C). The results are summarized in Table 1. In each case the yield of the product mixture was over 90%. The ratios obtained by the different methods agreed with each other. In the case of **2**, closer mobility on TLC of two products may cause a slightly larger deviation of the ratios by method A. Thus, predominant formation of 2-amino derivatives could be ascertained for all four isomers.

Structures of newly obtained ammonolysis products of **2** were elucidated easily by NMR data, *viz.*, the

Table 1. Ratios of ammonolysis and azidolysis products

2,3-Anhydro sugars	Products[a]	Ratios of 2- and 3-substituted products/%							
		Ammonolysis				Azidolysis			
		NH_3/MeOH			NH_3/H_2O				
		A[b]	B[b]	C[b]	A	A	B	C	D[b]
1 (α-lyxo)	2-	64		60*	61	22[c]		15[c]*	16
	3-	36		40*	39	78[c]		85[c]*	84
2 (α-ribo)	2-	64	72*		55	44	52	51*	
	3-	36	28*		45	56	48	49*	
3 (β-lyxo)	2-	75	71*		73	57[c]		55[c]*	57
	3-	25	29*		27	43[c]		45[c]*	43
4 (β-ribo)	2-	60	66*		65	30	23	18*	
	3-	40	34*		35	70	77	82*	

a) 2- =2-Substituted product, 3-=3-substituted product. b) The following methods were used for estimation; A: densitometer, B: optical rotation, C: weight, D: NMR (see Experimental). c) Isolated as 3-acetates. *These values were used for the estimation of relative rates described in Discussion.

TABLE 2. NMR DATA OF AMMONOLYSIS AND AZIDOLYSIS PRODUCTS (100 MHz, $CDCl_3$)

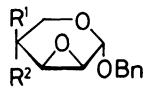
Compound	Chemical shifts δ							Coupling constants/Hz						Other signals
	H-1	H-2	H-3	H-4	H-5a	H-5e	$PhCH_2O$	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5a}$	$J_{4,5e}$	$J_{5a,5e}$	
7a	4.17	2.99	3.75		3.56	4.04	4.55, 4.91	7.5	9.1	2.3	1.5	2.3	12.5	2.79(NH_2+OH)
8a	4.89	3.38	2.93	3.28	3.59	3.74	4.50, 4.78	3.5	10.1	9.0	9.0	6.2	10.5	2 25(NH_2+OH)
5c	5.01	3.15	5.48	3.60—3.82			4.58, 4.80	3.5	10.5	~9.5	—	—	—	2.20(OAc)
6c	4.43	5.15	3.74	3.82	3.57	4.02	4.53, 4.83	6.0	8.3	3.9	1.8	4.0	12.2	2.05(OAc)
7b	4.32	3.65		3.77	3.50	4.02	4.61, 4.90	6.8	—	3.0	2.0	3.0	12.9	2.82(OH)
8b	4.93		3.20—3.80				4.52, 4.78	2.0	—	—	—	—	—	2.36(OH)
8b[a]	4.70	2.52	3.06	3.60	3.82	4.19	4.72, 5.12	3.5	9.5	9.5	10.5	4.7	10.5	2.56(OH)
9c	4.36	3.44	4.89	3.62	3.20	4.06	4.66, 4.91	8.9	10.2	10.2	10.8	5.3	11.5	2.14(OAc)
10c	5.15	5.09		3.6—4.3			4.51, 4.74	3.9	9.3	—	—	—	—	2.11(OAc)
10c[b]	5.10	5.25	3.65	2.86	3.16	3.32	4.10, 4.38	3.6	10.5	3.9	1.7	1.5	12.3	1.67(OAc)
11b	5.03	3.52	4.26	3.93	3.76	3.95	4.58, 4.76	3.4	10.2	3.5	2.5	1.5	10.9	2.52(OH)

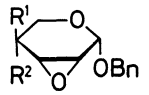
a) **8b**: $Pr(FOD)_3$ ≒6:1. b) In C_6D_6.

TABLE 3. REACTION RATES OF AMMONOLYSIS AND AZIDOLYSIS

	2,3-Anhydro sugars	Conversion ratios/%			Relative reaction rates[a]
		1h	3h	6h	
Ammonolysis[b]	1	63.6	100	100	3.5
	2	18.8	26.7	38.3	1.0
	3	19.3	28.2	35.3	1.0
	4	41.1	69.5	84.9	2.2
		30 min	70 min	130 min	
Azidolysis[c]	1	39.3	55.6	73.4	1.0
	2	76.1	94.0	95.8	1.9
	3	44.8	70.5	85.7	1.1
	4	58.3	80.3	95.1	1.5

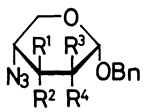
a) Calculated from the conversion rates at 1 h for ammonolysis and 30 min for azidolysis. b) In methanol at 95°C (sealed tube). c) In 2-methoxyethanol at 110 °C.

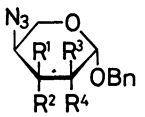




	R^1	R^2
1 (α-*lyxo*)	H	N_3
4 (β-*ribo*)	N_3	H

	R^1	R^2
2 (α-*ribo*)	H	N_3
3 (β-*lyxo*)	N_3	H





	R^1	R^2	R^3	R^4
5a	OH	H	H	NH_2
5b	OH	H	H	N_3
5c	OAc	H	H	N_3
6a	H	NH_2	OH	H
6b	H	N_3	OH	H
6c	H	N_3	OAc	H
7a	H	OH	NH_2	H
7b	H	OH	N_3	H
8a	NH_2	H	H	OH
8b	N_3	H	H	OH

	R^1	R^2	R^3	R^4
9a	H	OH	NH_2	H
9b	H	OH	N_3	H
9c	H	OAc	N_3	H
10a	NH_2	H	H	OH
10b	N_3	H	H	OH
10c	N_3	H	H	OAc
11a	OH	H	H	NH_2
11b	OH	H	H	N_3
12a	H	NH_2	OH	H
12b	H	N_3	OH	H

chemical shift of H_1 and the coupling constants of ring protons. H_1 signals of 2-amino (**7a**) and 3-amino (**8a**) derivatives appear at δ 4.17 ($J_{1,2}$=7.5 Hz) and δ 4.89 ($J_{1,2}$=3.5 Hz), indicating axial-axial and equatorial-axial orientations of H_1 and H_2, respectively. This and the coupling constants of other ring protons confirmed α-D-*arabino* (**7a**) and α-D-*xylo* (**8a**) configurations (Table 2).

Ammonolysis reaction in aqueous ammonia was also examined. In this reaction, the anhydro sugar did not dissolve at first, but went into solution with the progress of the reaction. Little difference was observed between the two solvents, methanol and water (third column, Table 1). The reason for the slightly different ratio for the products of **2** is not clear.

The 2,3-anhydro sugars was then treated with sodium azide in 2-methoxyethanol containing 5% water at 110 °C in the presence of ammonium chloride. The ratios of two ring-opening products, 2-azido and 3-azido derivatives, were determined by the same method as described above.

Estimation from NMR spectra was used as the fourth method (Method D) in the cases of azidolysis products of **2** and **3** because of poor separation on TLC. The reaction mixture could be separated on TLC after *O*-acetylation, the ratios being determined also by Methods A and C. As shown in Table 1 the results obtained from the various methods agree with each other. The error of these values was estimated to be about 5%, but the densitometric method may give a larger error since the difference of color development for each compound has

Table 4. Conformational equilibria of benzyl 2,3-anhydro-4-azido-4-deoxypentopyranosides

2,3-Anhydro sugars	Solvents	Coupling constants/Hz				Ratios of conformers $^0H_5$: $^5H_0$
		$J_{1,2}$	$J_{3,4}$	$J_{4,5a}$ [a]	$J_{4,5e}$ [a]	
1	$CDCl_3$ [7]	<0.5	<0.5	8.0 [b]	8.0 [b]	77 : 23 ($J_{4,5a}$)
	CD_3OD	<0.5	— [c]	7.7 [b]	7.7 [b]	74 : 26 ($J_{4,5a}$)
2	$CDCl_3$ [7]	2.7	—	—	—	82 : 18* ($J_{1,2}$)
	$CDCl_3$+Eu(FOD)$_3$	3.0	<0.5	9.3	4.2	95 : 5 ($J_{1,2}$) 93 : 7 ($J_{4,5a}$)
	$CDCl_3$+Pr(FOD)$_3$	3.0	<0.5	12.0	5.5	95 : 5 ($J_{1,2}$) 100 : 0 ($J_{4,5a}$)
	CD_3OD	2.9	—	—	—	91 : 9* ($J_{1,2}$)
3	$CDCl_3$	2.0	—	2.4	1.3	— [d]
	CD_3OD	1.3	—	2.8	2.0	— [e]
4	$CDCl_3$	<0.5	—	3.8	—	73 : 27 ($J_{4,5a}$)
	$CDCl_3$+Pr(FOD)$_3$	<0.5	3.8	4.5	3.0	57 : 43 ($J_{3,4}$) 64 : 36 ($J_{4,5a}$)
	CD_3OD	<0.5	—	4.5	—	64 : 36* ($J_{4,5a}$)

a) The suffixes 5a and 5e designate the axially and equatorially oriented protons on C-5, respectively, in the $^0H_5$ conformation. b) Analyzed as AB_2 and confirmed by simulation. c) Could not be obtained from the spectrum. d) The ratios estimated by $J_{1,2}$ and $J_{4,5a}$ are 50 : 50 and 89 : 11, respectively. e) The ratios estimated by $J_{1,2}$ and $J_{4,5a}$ are 18: 82 and 85 : 15, respectively. *These values were used for the estimation of relative rates (see Discussion).

not been considered.

Structures of these azidolysis products could be ascertained by their NMR data (Table 2). The products from **1** and **3** were characterized again as *O*-acetyl derivatives.

In order to elucidate the above result, *i.e.* the different regioselectivity in the ammonolysis and azidolysis reactions, the relative reaction rates and the conformations of these 2,3-anhydropentopyranosides were examined. The reactions were carried out in sealed tubes and followed by TLC. The conversion ratios determined densitometrically and the relative reaction rates estimated from the conversion ratios after the shortest reaction time examined are summarized in Table 3. The relative reaction rates are qualitative, but show a clear difference in the relative reactivities of the 2,3-anhydro sugars.

The pyranoside ring in 2,3-anhydropyranosides takes two half-chair forms, $^0H_5$ and $^5H_0$. The conformational equilibrium between these two forms was estimated by the coupling constants of vicinal ring protons, $J_{4,5}$ together with $J_{1,2}$ and $J_{3,4}$. The following standard values[4] were used for estimation: $J_{4a,5a}$ 9.9, $J_{4e,5e}$ 1.5; *cis*-$J_{1peq,2}$ 3.1, *cis*-$J_{1pax,2}$ 0.9; *cis*-$J_{3,4peq}$ 5.4, *cis*-$J_{3,4pax}$ 1.7 Hz.[9] Although the ratios estimated by $J_{4,5}$ should be more reliable considering the magnitude of difference in two conformers, those by $J_{1,2}$ and $J_{3,4}$ also indicate predominant conformers in the cases of the isomers having *cis*-relationship between H_1 and H_2, or H_3 and H_4. While the first-order analysis of H_4, H_5, and H_5, in **3**[8] and **4**[6] were possible, the NMR signals of the corresponding protons in **1** and **2** were not well separated. Coupling constants concerning these protons could be obtained in the aid of lanthanoid shift reagents or simulation (Table 4).

Predominance of $^0H_5$ conformation was confirmed in the cases of **1** and **2**, while **4** adopts $^0H_5$ conformation slightly preferentially than $^5H_0$ conformation (last column, Table 4). The use of lanthonoid shift reagents seems to cause no remarkable change of conformation[10] as supposed in the cases of **2** and **4**. In the case of **3** the ratios estimated by $J_{1,2}$ and $J_{4,5}$ are totally different, indicating a deviation from the half-chair conformation. The values of $J_{1,2}$, $J_{4,5a}$ and $J_{4,5e}$ are in line with the flattened half-chair conformation. The dihedral angles H-1–C-1/C-2–H-2, H-4–C-4/C-5–H-5a, and H-4–C-4/C-5–H-5e are 40°, 55°, and 65°, respectively. They were determined by assuming the Karplus-type dependence of coupling constants.[11,12] Thus, the predominant existence of $^0H_5$ conformation in **1**, **2**, and **4**, and also the flattened half-chair conformation of **3** confirm the importance of the anomeric effects on the conformational stability, observed in some 2,3-anhydropyranosides taking half-chair conformation.[13]

Discussion

In order to examine the factors affecting the regiospecificity of ring-opening reactions the results were analysed with the following assumptions.

1) The epoxides **1**, **2**, and **4** react with the nucleophiles in one of two half-chair conformations according to the Fürst-Plattner rule (Fig. 1).

2) The mutual conformational inversion is much faster than the reaction.

3) Epoxide **3** reacts in the flattened half-chair conformation, where the attack of nucleophiles can take place both at C-2 and C-3.

Although the deviation from the Fürst-Plattner rule, *i.e.*, *trans* diequatorial ring opening, was observed even in the conformationally rigid system especially when the favorable reaction site due to this rule is C-2, which is contrariwise the electronically unfavorable one[14] in the case of 2,3-anhydropyranosides such as 2,3-anhydro-4,6-*O*-benzylideneallopyranosides,[15] the contribution of such ring opening may be negligible as the first approximation. The expected relative small value of the free energy of conformational inversion in these epoxides also supports the assumption. The second assumption may be admitted for a reaction, whose activation energy is much higher than the free energy of conformational conversion. The reactions discussed here seem to

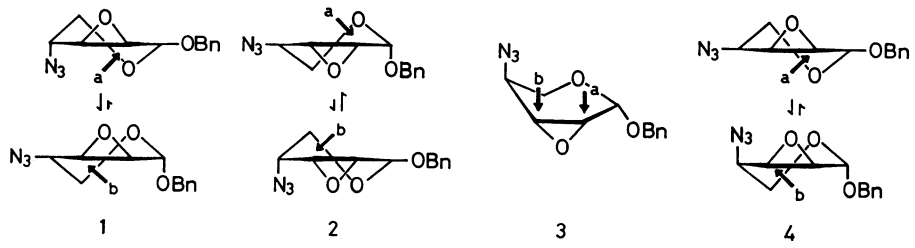


Fig. 1. Conformations and stereoelectronically preferred reaction sites of 2,3-anhydro-4-azido-4-deoxypentopyranosides.

correspond to this case, judging from those of substituted cyclohexene derivatives (25—30 kJ/mol),[16] which adopt a similar half-chair conformation to 2,3-anhydropentopyranoside.

The relative reaction rate of each conformer or site, K_a and K_b, were estimated by means of the equations,

$$K = N_aK_a + N_bK_b,$$

$$\frac{P_a}{P_b} = \frac{N_aK_a}{N_bK_b},$$

where N and P represent the mole fractions of two conformers (Table 4) and products (Table 1), respectively, and K is the relative reaction rate of each epoxide (Table 3). Suffixes a and b indicate the conformers or positions which give the 2- and 3-substituted products, respectively. The following relative reaction rates were obtained, where the standards are the same as in Table 3 and the comparison is significant only in the same reaction. In general the azidolysis reaction is faster than the ammonolysis. These results give useful informations for synthetic purpose.

	1a	**1b**	**2a**	**2b**	**3a**	**3b**	**4a**	**4b**
Ammonolysis	12	1.7	0.8	3.1	0.7	0.3	4.0	1.2
Azidolysis	0.8	1.0	1.1	10	0.6	0.5	0.75	1.9

(a) Among several possible interactions between the nucleophile and the reactant epoxide the dipole-dipole interaction between C_2---nucleophile and two C_1–O dipoles in the transition state may be the most effective factor as indicated in the cases of **1a** and **4a**. These conformers show higher reactivities than the other in ammonolysis, and lower reactivities in azidolysis. The differene ccould be explained by reverse direction of C_2---nucleophile diople as shown in Fig. 2.[17] A comparison of the reactivity between **2a** and **4a** shows the effect, which affects only **4a**. Thus the electronic character of the nucleophile controls the direction of ring opening.

(b) If the reactivity is not markedly increased or decreased by the dipole-dipole interaction, the attack of the nucleophile at the electronically favorable C-3 position predominates, as is well known in the reaction of 2,3-anhydro sugars.[1] In ammonolysis, **2b**, **1b**, and **4b**

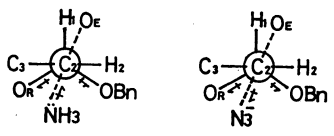


Fig. 2. Dipole-dipole interactions at the transition state of substitution on C-2 (O_E and O_R represent the oxygens in the epoxide and pyranoside rings, respectively.)

have higher reactivities except **1a** and **4a**, while in azidolysis **2b** and **4b** show the same tendency.

(c) The electronic or steric interactions between the nucleophile and the quasi-axial substituent (azido or benzyloxy group on the carbon adjacent to the epoxide) were also suggested by comparing **1a** with **4a** and **2b** with **4b**. There seems to be a little difference in the nature of the interactions between these groups and the nucleophiles. The axial azido group accerelates ammonolysis and retards azidolysis, while the axial benzyloxy group retards both reactions.

The evaluation of these interactions would be helpful for prediction of the ammonolysis and azidolysis products of 2,3-anhydropentopyranosides.

Experimental

General. Melting points were determined with a Beckmann Mel-temp melting point apparatus and are not corrected. Optical rotations were measured in methanol (M), unless otherwise stated, using a 0.5-dm tube with a Carl Zeiss LEP-Al or a JASCO DIP-4 polarimeter. IR spectra were recorded with a Hitachi EPI-G2 grating spectrometer, and NMR spectra with a JEOL JNM PS-100 spectrometer in chloroform-*d* containing tetramethylsilane as an internal reference. Chemical shifts and coupling constants are recorded in δ and Hz units, IR frequencies in cm^{-1}. All NMR data are summerized in Table 2. Evaporation was carried out in a rotary evaporator under reduced pressure. The products were recrystallized from ethanol unless otherwise stated. TLC was performed on silica gel (Merck Kieselgel H type 60) using the following developing solvent: A, benzene–pyridine (3 : 2); B, benzene–pyridine (7 : 3); C, benzene–methanol (200 : 1).

Benzyl 2,3-anhydro-4-azido-4-deoxypentopyranosides having α-D-*lyxo* (**1**), α-D-*ribo* (**2**), β-L-*lyxo* (**3**), and β-L-*ribo* (**4**) configurations were prepared according to published procedure.[6-8]

Ammonolysis of 2,3-Anhydropentopyranosides. A solution of 2,3-anhydro sugar (250 mg, 1 mmol) in methanol (20 ml) saturated with ammonia was heated in a sealed tube at 95 °C. After complete disappearance of the starting material the reaction solution was evaporated to give a crystalline mixture of products, which was separated on preparative TLC with the developing solvent A or B. Ammonolysis products of **1** (**5a** and **6a**),[6] **3** (**9a** and **10a**),[7] and **4** (**11a** and **12a**)[8] have been reported.

*Benzyl 2-Amino-4-azido-2,4-dideoxy-α-D-arabinopyranoside (**7a**) and Benzyl 3-Amino-4-azido-3,4-dideoxy-α-D-xylopyranoside (**8a**).* Ammonolysis of **2** was performed for 48 h, two isomeric products being separated as described above. **7a**: mp 119—121 °C, $[\alpha]_D$ +42.7° (*c* 1.1, M); IR (KBr): 3260 and 3330 (NH_2 and OH), 2100 (N_3), 700, and 730 (Phenyl). Found: C, 54.25; H, 5.97; N, 20.80%. Calcd for $C_{12}H_{16}N_4O_3$: C,

54.55; H, 6.10; N, 21.20%. **8a**: mp 122—124 °C, $[\alpha]_D$ +118° (*c* 0.75, M); IR(KBr): 3320 (NH_2 and OH), 2100 (N_3), 700 and 735 (Phenyl). Found: C, 54.41; H, 6.13; N, 20.95%. Calcd for $C_{12}H_{16}N_4O_3$: C, 54.55; H, 6.10; N, 21.20%. NMR data: see Table 2.

Azidolysis of 2,3-Anhydropentopyranosides. A suspension of 2,3-anhydro sugar (250 mg, 1 mmol), sodium azide (250 mg, 3.8 mmol), and ammonium chloride (100 mg, 1.9 mmol) in 2-methoxyethanol–water (14 : 1, 20 ml) was heated in a sealed tube at 110 °C. After the reaction had been completed, the insoluble material was filtered off, and the filtrate evaporated. The residue was extracted with methanol, the mixture of two isomeric products obtained by evaporation of the extract being separated by preparative TLC with multiple development using solvent C.

Benzyl 3-O-Acetyl-2,4-diazido-2,4-dideoxy-α-D-xylopyranoside (5c) and Benzyl 2-O-Acetyl-3,4-diazido-3,4-dideoxy-α-D-arabinopyranoside (6c). Azidolysis of **1** was performed for 4 h as described above. Since a mixture of two isomeric products (**5b** and **6b**) obtained could not be separated on TLC, it was acetylated with acetic anhydride in pyridine in the usual way to give **5c** and **6c**, which were separated by prepaprative TLC with developing solvent C. **5c**: sirup $[\alpha]_D$ +229° (*c* 0.6, M); IR(NaCl): 2100 (N_3), 1755 (OAc), 695, and 738 (Phenyl). Found: C, 50.66; H, 4.92; N, 24.89%. Calcd for $C_{14}H_{16}N_6O_4$: C, 50.60; H, 4.85; N, 25.29%. **6c**: sirup, $[\alpha]_D$ +49.9° (*c* 1.7, M); IR(NaCl): 2100 (N_3), 1745 (OAc), 695, and 740 (Phenyl). Found: C, 51.04; H. 4.86; N, 24.93%. Calcd for $C_{14}H_{16}N_6O_4$: C, 50.60; H, 4.85; N, 25.29%. NMR data: see Table 2.

Benzyl 2,4-Diazido-2,4-dideoxy-α-D-arabinopyranoside (7b) and Benzyl 3,4-Diazido-3,4-dideoxy-α-D-xylopyranoside (8b). Azidolysis of **2** as described for **1** gave **7b** and **8b**, which could be separated without acetylation. **7b**: sirup, $[\alpha]_D$ +26.5° (*c* 0.6, M); IR(NaCl): 3320 (OH), 2110 (N_3), 700, and 745 (Phenyl). Found: 49.30; H, 4.48; N, 28.68%. Calcd for $C_{12}H_{14}N_6O_3$: C, 49.65; H, 4.86; N, 28.95%. **8b**: sirup, $[\alpha]_D$ +259° (*c* 0.7, M); IR(NaCl): 3400 (OH), 2110 (N_3), 700, and 745 (Phenyl). Found: C, 49.27; H, 4.52; N, 28.67%. Calcd for $C_{12}H_{14}N_6O_3$: C, 49.65; H, 4.86; N, 28.95%. NMR data: see Table 2.

Benzyl 3-O-Acetyl-2,4-diazido-2,4-dideoxy-β-L-xylopyranoside (9c) and Benzyl 2-O-Acetyl-3,4-diazido-3,4-dideoxy-β-L-arabinopyranoside (10c). Azidolysis of **3** and separation of the isomeric products were carried out in the same way as described for **5c** and **6c**. **9c**: mp 107—110 °C, $[\alpha]_D$ +18.0° (*c* 0.6, M); IR(KBr): 2100 (N_3), 1755 (OAc), 715, and 750 (Phenyl). Found: C, 50.60; H, 4.64; N, 24.96%. Calcd for $C_{14}H_{16}N_6O_4$: C, 50.60; H, 4.85; N, 25.29%. **10c**: sirup, $[\alpha]_D$ +168° (*c* 0.9, M); IR(NaCl): 2105 (N_3), 1748 (OAc), 700, and 740 (Phenyl). Found: C, 50.24; H, 4.59; N, 24.91%. Calcd for $C_{14}H_{16}N_6O_4$: C, 50.60; H, 4.85; N, 25.29%. NMR data: see Table 2.

Benzyl 2,4-Diazido-2,4-dideoxy-β-L-arabinopyranoside (11b) and Benzyl 3,4-Diazido-3,4-dideoxy-β-L-xylopyranoside (12b). Azidolysis of **4** and separation of the isomeric products were carried out in the same way as described for **7a** and **8b**. **11b**: sirup, $[\alpha]_D$ +173° (*c* 0.7, M); IR(NaCl): 3380 (OH), 2100 (N_3), 700 and 740 (Phenyl). Found: C, 49.76; H, 4.60; N, 28.91%. Calcd for $C_{12}H_{14}N_6O_3$: C, 49.65; H, 4.86; N, 38.95. **12b**: reported.[8] NMR data: see Table 2.

Ratios of Ammonolysis and Azidolysis Products. Method A. In order to estimate the ratio with a densitometer, TLC was performed using Merck silica gel plate and self-made one, whose uniformity of thickness was checked densitometrically before use, with solvent A or B for the ammonolysis products and C for azidolysis ones. Each spot was detected by sulfuric acid and also by ninhydrin in the case of the ammonolysis products, and measured at 560 nm with an Atago Kemic densitometer. Each sample was developed, detected, and determined densitometrically three times separately, and the values were averaged. Method B. An analytically pure mixture of the products was obtained by preparative TLC with the same solvent system as described for Method A. Its rotational value compared with that of each component gave the desired ratio. Method C. In some cases, where the products could be well separated on TLC, the ratios were also obtained from the amount of isolated isomers by preparative TLC using the same solvents as described above. Method D. The ratio was estimated from the intensity of H_1 and H_{5a} signals in the NMR spectra of the analytically pure mixture of azidolysis products obtained by Method B.

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