179. Syntheses of Amino-dideoxyallose and Amino-deoxyribose Derivatives Using Acylnitroso Dienophiles

by **Albert Defoin**[a]), **Hans Fritz**[b]), **Guillaume Geffroy**[a]), and **Jacques Streith**[a])*

[a]) Ecole Nationale Supérieure de Chimie, Université de Haute-Alsace, 3, rue Alfred Werner, F-68093 Mulhouse Cedex

[b]) Physikalische Abteilung, *Ciba-Geigy AG*, CH-4002 Basel

Dedicated to Professor *Elias J. Corey* on the occasion of his 60th birthday

(26.VII.88)

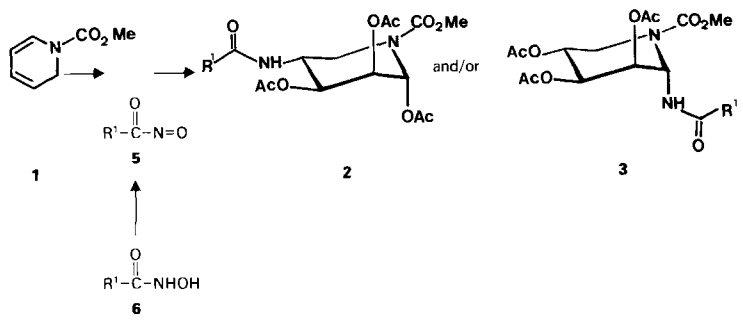
The dimethyl acetals **4** of (*E*)-2,4-pentadienal and of (*E,E*)- and (*E,Z*)-2,4-hexadienals undergo regio- and stereospecific cycloaddition reactions with *in-situ*-generated acylnitroso dienophiles **5a** and **5b**, leading thereby to the corresponding dihydrooxazines **7a–d** and **8c–d**. *cis*-Glycolization of these latter adducts stereospecifically gave the dihydro derivatives **9a–d** and **10d** which, after sequential hydrogenolysis, deacetalization, and instant cyclization, led to the aminodeoxyribose derivatives **17a**, **17f**, and **18**, and to the amino-dideoxyallose compounds **17c** and **17h**. These piperidino-deoxysugar derivatives exhibit a strong anomeric effect, *i.e.* OH–C(1) is always axial, which is explained in terms of a $n_N(\pi)$-σ^*(C–OH) orbital compression, as compared to the less pronounced one in the more classical pyranose series.

Introduction. – In a previous publication, we described the three-step synthesis of the aminolyxose derivatives **2** and **3**, starting from the readily accessible 1,2-dihydropyridine derivative **1** [1] *(Scheme 1)*. The first step was a *Diels-Alder* reaction between **1** and a series of acylnitroso dienophiles **5** which were prepared *in situ* by oxidation of the corresponding hydroxamic acids **6** using tetraalkylammonium periodates [2]. Some of these dienophiles reacted in a regiospecific manner; some others proved to be slightly or not at all regioselective. These results could be accounted for by making use of the FMO theory, and in particular by considering the relative magnitude of the AO coefficients of the HOMO of **1** and the LUMO's of the acylnitroso dienophiles [1]. The ensuing reaction steps were straightforward: *cis*-glycolization with OsO_4 turned out to be *anti* with respect to the N–O bridge, *in all cases*. It was followed by hydrogenolysis of this latter N–O bond, leading to the racemic lyxose derivatives **2** and **3**. This three-step synthesis afforded *in a stereospecific manner four asymmetric centres*, the final lyxose derivatives **2** and **3** being racemic[1]). Configuration as well as conformations are as indicated in *Scheme 1*. They were ascertained unambiguously by high-field ^{1}H-NMR techniques [1].

We describe herein the synthesis of some (±)-aminodeoxyribose and (±)-amino-dideoxyallose derivatives, according to a methodology similar to the one described above, the diene components being the dimethyl acetals **4a**, **4b**, and **4c** of (*E*)-2,4-penta-

[1]) In *Schemes 1–4* and in certain names, only the D-enantiomers are given. However, all compounds are racemic.

Scheme 1

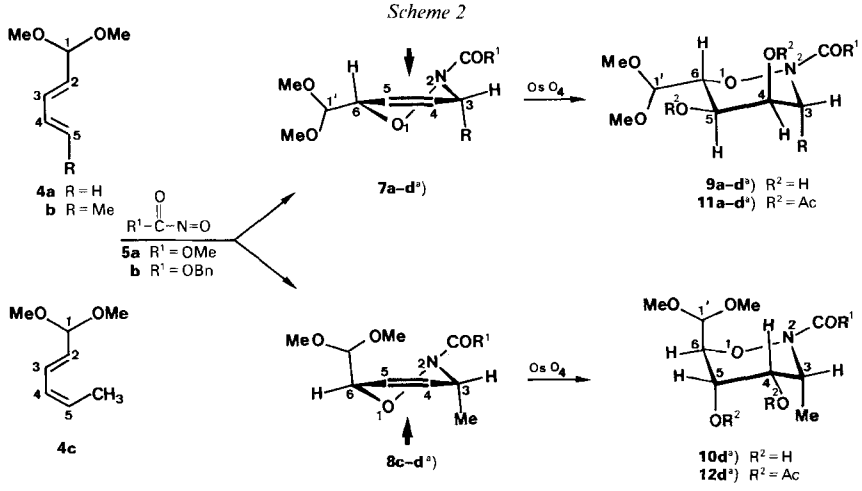


dienal, (*E,E*)-, and (*E,Z*)-2,4-hexadienal, respectively[2]). It is worthy of note that similar reaction sequences have been used by *Belleau et al.*, starting from methyl sorbate and from an α-chloronitroso dienophile [4], and by *Schmidt et al.* who used (*E*)-2,4-pentadienal and dimethyl azodicarboxylate [5].

The acetals **4** were prepared according to some known methodologies using methyl orthoformate in the presence of catalytic amounts of ammonium nitrate [6] or of *Amberlyst-15* [7]. The commercially available 2,4-hexadienal (= sorbaldehyde) is a 8:2 mixture of the (*E,E*)- and of the (*E,Z*)-isomers, respectively.

Reactivity of Some Acylnitroso Dienophiles with 4a and 4b/4c: Adducts 7 and 8. – The acylnitroso dienophiles **5** are short-lived and highly reactive species. On the contrary, the dienes **4** *(Scheme 2)* react rather sluggishly, if at all, in *Diels-Alder* cycloadditions. Therefore, it was expected that these dienes would react in an incomplete manner with dienophiles **5**. To check the propensity to act as diene partners, the mixture **4b**/**4c** was

Scheme 2



[a]) **a** R = H, R^1 = OMe; **b** R = H, R^1 = OBn; **c** R = Me, R^1 = OMe; **d** R = Me, R^1 = OBn.

[2]) For a preliminary communication, see [3].

Table 1. *Acylnitroso Dienophiles* $R^1CON{=}O$ **5**, *Formed* in situ *from the Corresponding Hydroxamic Acids* $R^1CONHOH$ **6**, *and Overall Yields of* cis *and* trans *Cycloadducts* **7** *and* **8**[a]), *Respectively, when Equimolar Amounts of* **4b,c** *and of* **5a–e** *Are Used*

5 and **6**	R^1	Overall yield [%] of **7**/**8**
a	MeO	73 (**7c**/**8c**)
b	BnO	85 (**7d**/**8d**)
c	$PhCH_2$	40
d	Ph	23
e	Me_2N	< 5

[a]) The **7**/**8** ratio is 8:2 in all cases; see *Exper. Part.*

reacted with equimolar amounts of the acylnitroso species **5a–e** (see *Table 1*), the reaction being monitored by ^{1}H-NMR by measuring the relative intensities of Me–C(5) of **4b**/**4c** (1.8 ppm) and of Me–C(3) of **7**/**8** (1.4 ppm).

The results which are collected in *Table 1* clearly show *i)* that the (methoxycarbonyl)-nitroso dienophile **5a** and the (benzyloxycarbonyl)nitroso dienophile **5b** lead to the best overall yields of adducts **7**/**8** (**7c**/**8c** and **7d**/**8d**, resp.) and *ii)* that the **7**/**8** ratio is 8:2 *in all cases*, which is also the ratio of the dienes **4b**/**4c**. The configuration of the adducts having been demonstrated (see below), it follows that the major *cis* adducts **7c** and **7d** stem from the major (*E*,*E*)-diene **4b**, and the minor *trans* adducts **8c** and **8d** from the minor (*E*,*Z*)-diene **4c**. These results demonstrate the concertedness of the various *Diels-Alder* cycloadditions.

Consideration of *Table 1* led us to choose **5a** and **5b** as the ideal partners for the hetero-*Diels-Alder* cycloadditions with the dienes **4a–c** (see below).

The most striking feature of all the cycloadditions described herein (see *Exper. Part*) is their being *regiospecific*, the O-atom of the N–O bond appearing *always* on the side of the dimethyl-acetal group, *i.e. only* adducts **7** and **8** are formed. The dimethyl-acetal group exerts a profound steric hindrance which, in our opinion, is the *determinant factor* for the observed regioselectivity. *Kresze* had already described the impact of steric interactions upon the degree of regioselectivity during *Diels-Alder* cycloadditions of 1,4-disubstituted 1,3-dienes with chloroalkyl- and arylnitroso dienophiles [9]. In most of these cases though cycloadditions proved to be non-regiospecific.

We believe that the relative magnitudes of the MO coefficients of the HOMO's (dienes **4**) and of the LUMO's (acylnitroso dienophiles **5**) do not play any role: the MO coefficients of the butadiene termini of the dienes **4** should be of similar magnitude since neither R (H or CH_3) nor the acetal function exert any significant influence upon them[3]). Therefore, and whatever the LUMO dissymmetry of the acylnitroso dienophiles [1], in terms of HOMO/LUMO interaction, there should not be any regioselectivity.

Synthesis of Aminodideoxyallose and Aminodeoxyribose Derivatives 17–19. – a) *Stereospecific* cis-*Glycolization* anti *with Respect to the Dimethyl-Acetal Group.* The adducts **7a–d** and **8c,d** were oxidized with catalytic amounts of OsO_4 in the presence of *N*-methylmorpholine *N*-oxide (NMO) in H_2O/acetone solutions [10]. In all instances, only one *cis*-glycol was formed, albeit with different reaction rates. Glycolization was performed at 40° to completion, within 2 days with the (*E*)-2,4-pentadienal adducts **7a** and **7b**, within 1 day with the (*E*,*E*)-2,4-hexadienal adducts **7c** and **7d**, and led to **9a–d** in

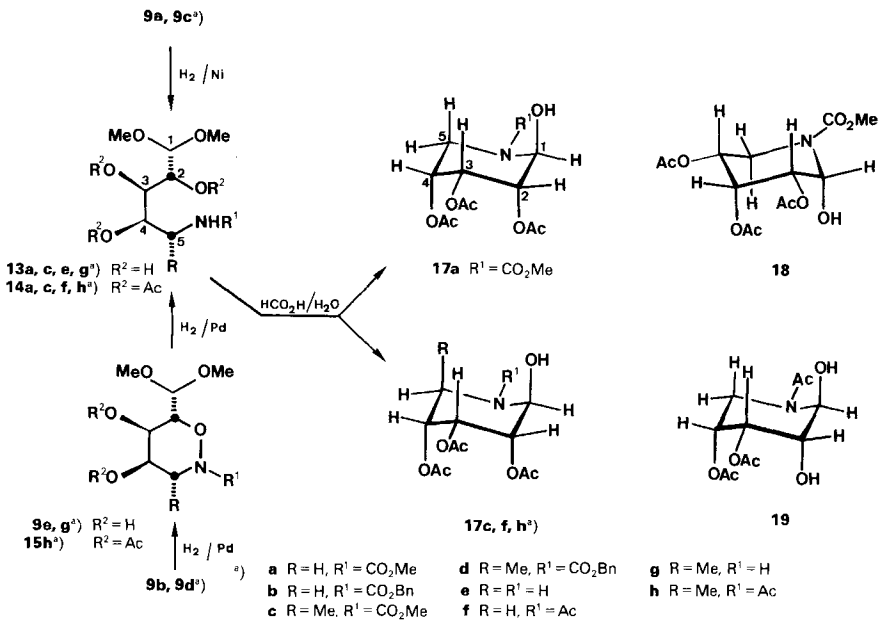
[3]) This means that any $\pi \rightarrow \sigma^*$ delocalization of the acetal function is neglected.

which the glycol moiety is *trans* with respect to the acetal group (as well as to the Me group in **9c** and **9d**). Of the two minor adducts **8c** and **8d**, only **8d** was oxidized with OsO_4/NMO: at 60°, the reaction was not complete after 7 days, leading thereby in poor yield to **10d** whose glycol functionality is *anti* with respect to the acetal group. The pseudoaxial acetal and methyl groups obviously lead to steric hindrance and, therefore, to a pronounced reduction of the reaction rate. It should be noticed, furthermore, that the acetal group of **7** and **8** is far more bulky than Me, so that the OsO_4 attack occurs only from the side (arrows in *Scheme 2*) which is *anti* with respect to that group.

Adducts **7c,d** and **8c,d** proved difficult to separate, but as the former reacted much faster with OsO_4/NMO than the latter, the mixtures **7**/**8** were reacted with OsO_4 and the polar glycols **9c,d** separated from the unreacted and much less polar adducts **8c,d**. Most of the glycols **9a–d** and **10d** could be isolated as crystalline compounds. The structural analyses were performed with their diacetyl derivatives **11a–d** and **12d** (see below).

b) *Hydrogenolysis of the N–O Bond.* Hydrogenolysis of the N–O bridge proved to be more difficult with the (methoxycarbonyl)oxazines **9a** and **9c** than with the [(benzyloxy)carbonyl]oxazines **9b** and **9d**, since neither Pd/C under H_2 pressure, nor Hg/Al or Hg/Na [11], nor Zn in AcOH [12a] permitted cleavage of the O–NCO_2Me bond. Only activated *Raney*-Ni at 40° in EtOH solution hydrogenolyzed **9a** and **9b** to the triols **13a** and **13c**, respectively, which were characterized as their triacetate derivatives **14a** and **14c**. Similar results have been described with *N*-hydroxyazetidinones [12b]. Compounds **13a** and **13c** are 5-amino-5-deoxyribose and 5-amino-5,6-dideoxyallose derivatives, respectively, both being in the acetal and, therefore, in the open-chain form *(Scheme 3)*.

Scheme 3



Hydrogenolysis of the N–O bridge was performed easily with the [(benzyloxy)-carbonyl]oxazines **9b** and **9d** using Pd/C under atmospheric H_2 pressure at 40° in EtOH. It could be shown that hydrogenolysis of the *N*-[(benzyloxy)carbonyl] functionality occurred with the fastest reaction rate (within 20 min) leading, after spontaneous decarboxylation of the intermediate carbamic acid, to the dihydroxytetrahydrooxazines **9e** and **9g**, respectively, this latter one having been characterized as its triacetate derivative **15h**. Hydrogenolysis of the N–O bond proved to proceed at a much slower rate (20–30 h) and gave, from **9e** and **9g**, the expected open-chain ribose **13e** and allose **13g** (acetal form), both of which bear a free NH_2 group. They were characterized as their triacetates **14f** and **14h**, respectively. It is worth mentioning that EtOH is the solvent of choice for these hydrogenolyses, since some by-products appeared in MeOH which resulted from a condensation with formaldehyde. For example, hydrogenolysis of **9d** in MeOH, followed by peracetylation gave, in addition to the expected tetraacetylated aminoallose **14h**, the triacetylated derivative **16** of 1,3-oxazine (see below *Scheme 4*).

c) *Aldehyde-Deprotection Followed by Ring Closure.* Removal of the aldehyde-protecting acetal moiety from **14** was performed in 90% HCOOH at 50°, leading thereby to the corresponding cyclic aminodeoxysugars. The intermediate free acyclic aldehyde reacted instantly in a intramolecular fashion with the acetamido group. In the allose series (**14c** and **14h**), only the β-D-anomer[1]) was formed, *i.e.* **17c** and **17h**, respectively (for the configurational and conformational analyses of all piperidinoses, see below).

In the ribose series (**14a** and **14f**), deprotection conditions which are identical to the ones described above gave different results depending on the nature of the R^1NH group. The *N*-acetyl compound **14f** led to a mixture of the β-D-anomeric[1]) piperidinose **17f** (major product) and of the partly deacetylated (at O–C(2)) β-D-anomeric[1]) piperidinose **19** (16%). The *N*-(methoxycarbonyl) compound **14a** gave both the β-D-anomer[1]) **17a** and the α-D-anomer[1]) **18** as a 4:1 mixture.

We believe that under the above described experimental conditions, the thermodynamically most favoured products are formed. These can only be piperidinose derivatives. As a consequence, the β-D-anomers[1]) **17c** and **17h** of the allose series, and the β-D-anomers[1]) **17f** and **19** of the ribose series should be the most stable ones. As a matter of fact, *Hanessian* observed the formation of one anomer only for 5-(acetamido)-5-deoxy-D-ribopyranose, but without demonstrating which one he obtained [13]. On the other hand, *Paulsen* observed that both α- and β-D-anomers were formed (in a 2:1 ratio) with 5-[(benzyloxycarbonyl)amino]-5-deoxy-D-ribopyranose [14], a result which is analogous to the one described above (β-D/α-D[1]) mixture **17a**/**18**).

Compound **10d** being but a minor product, we did not transform it to the aminosugar which would have been an aminotalose.

Structural Analyses by NMR Techniques. – *3,6-Dihydro-2*H*-oxazines* **7a–d** *and* **8a–d**. The sequence of the atoms for the planar structures was demonstrated by ^{13}C-NMR, whereas conformations and relative configurations were ascertained by ^{1}H-NMR, these spectral data being all collected in *Table 2* and *Tables 3* and *4*, respectively.

The NMR data are consistent with the presence of one olefinic double bond in each adduct (sp^2 C-atoms at δ 120–130 ppm; olefinic protons at 5.8–6.0 ppm). The magnitude of $J(4,5)$ (*ca.* 10 Hz) is as expected for a (*Z*) double bond in a six-membered ring. *Table 2* shows, furthermore, that the C-atom sequences of the adducts are as indicated in *Scheme 2*.

Table 2. *^{13}C-NMR Spectra* ($CDCl_3$) *of Dihydro-2*H-*oxazines* **7a–d** *and* **8c,d**. 20.1 MHz, 300 K; δ in ppm and J in Hz, internal standard TMS[a]).

	C(1′)	C(3)	C(4)	C(5)	C(6)	C=O	*Me*–C(3)	2 MeO	CO_2Me	CH_2	C(2″), C(6″)	C(3″), C(5″)	C(4″)	C(1″)
7a[b])	103.4	44.8	123.7[c])	124.2[d])	77.1	156.1	–	54.0; 55.4	53.0	–	–	–	–	–
7b	103.1 (J = 163)	44.6 (J = 141)	123.5[c]) (J = 166)	124.1[d]) (J = 167.5)	76.8 (J = 148)	155.2	–	53.3; 55.0 (J = 142)	–	67.3 (J = 148.5)	127.8[e]) (*J ca.* 161)	128.2 (*J ca.* 161)	127.9[f]) (*J ca.* 161)	135.2
7c	102.3 (J = 164)	49.9 (J = 142)	129.2 (J = 164)	123.0 (J = 166)	75.9 (J = 148)	154.9	17.4 (J = 129)	52.1; 54.9 (J = 143)	52.3 (J = 148)	–	–	–	–	–
7d	102.3 (J = 164.5)	50.0 (J = 141)	129.3 (J = 164.5)	123.2 (J = 165)	75.9 (J = 149)	154.4	17.7 (J = 128.5)	51.8; 55.0 (J = 143)	–	67.1 (J = 148.5)	127.6[e]) (*J ca.* 160)	128.1 (*J ca.* 160)	127.8[f]) (*J ca.* 160)	135.8
8c	104.3 (J = 164.5)	50.1 (J = 142.5)	128.7 (J = 166)	123.0 (J = 167)	77.9 (J = 147.5)	155.2	16.0 (J = 128.5)	55.0; 55.2 (J = 143)	52.5 (J = 148)	–	–	–	–	–
8d	104.3 (J = 165)	50.4 (J = 143)	128.9 (J = 164)	123.2 (J = 167)	78.1 (J = 148)	154.8	16.2 (J = 130)	55.0; 55.2 (J = 143)	–	67.4 (J = 148)	128.1 (*J ca.* 160)	128.4 (*J ca.* 162)	128.1 (*J ca.* 160)	136.1

[a]) With respect to $CDCl_3$ which appears at 77.00 ppm.
[b]) Measured at 75.4 MHz; ^1J omitted.
[c]) Or C(5).
[d]) Or C(4).
[e]) Or C(4″).
[f]) Or C(2″), C(6″).

Table 3. *^{1}H-NMR Spectral Data* (C_6D_6) *of Dihydro-2*H-*oxazines* **7a–d** *and* **8c,d**. 80 MHz, 300 K; J in Hz, internal standard TMS.

	J(1′,6)	J(R_{ax},3eq)	J(3ax,4)	J(3ax,5)	J(3ax,6)	J(3eq,4)	J(3eq,5)	J(3eq,6)	J(4,5)	J(4,6)	J(5,6)	J_{gem} (CH_2)
7a[a])	6.2	17.4	2.6	2.3	2.8	3.8	2.1	2.9	10.4	2.2	2.2	–
7b[b])	6.2	17.6	*ca.* 2.6	*ca.* 2.0	*ca.* 2.6	*ca.* 3.2	*ca.* 1.8	*ca.* 2.7	10.5	2.0	2.0	–
7c	5.8	6.7	–	–	–	4.1	1.2	2.6	10.4	2.0	1.2	–
7d	6.0	6.6	–	–	–	4.2	1.5	2.5	10.2	2.0	1.3	12.3
8c	6.5	6.5	–	–	–	4.4	1.3	0.8	10.4	1.4	3.5	–
8d	6.4	6.6	–	–	–	4.6	1.4	0.8	10.1	1.8	3.7	12.3

[a]) Measured at 300 MHz.
[b]) First-order spectrum.

Table 4. *^{1}H-NMR Spectral Data* ($CDCl_3$) *of Dihydro-2*H*-oxazines* **7a–d** *and* **8c,d**. 80 MHz, 300 K; δ in ppm, internal standard TMS.

	H–C(1′)	R_{ax}–C(3)	H_{eq}–C(3)	H–C(4)	H–C(5)	H–C(6)	2 MeO	CO_2Me	OCH_2	Ph
7a	4.37	4.08	4.14	5.94	5.92	4.50	3.43, 3.49	3.80	–	–
7b	4.34	4.10	4.15	5.91	5.91	4.50	3.39, 3.39	–	5.21	7.34
7c	4.31	1.33	4.52	5.90	5.86	4.63	3.45, 3.46	3.78	–	–
7d	4.30	1.33	4.48	5.86	5.84	4.60	3.36, 3.41	–	5.17, 5.21	7.33
8c	4.44	1.29	4.43	5.90[a])	5.86[b])	4.25	3.39, 3.51	3.80	–	–
8d	4.40	1.29	*ca.* 4.45	5.89[a])	5.85[b])	4.27	3.35, 3.36	–	5.16, 5.30	7.36

[a]) Or H–C(5).
[b]) Or H–C(4).

Table 5. *^{1}H-NMR Spectral Data* ($CDCl_3$) *of Diacetates* **11a–d**, **12d**, *and* **15h**. 80 MHz, 300 K; δ in ppm and J in Hz, internal standard TMS.

	H–C(1′)	R_{ax}–C(3)	H_{eq}–C(3)	H–C(4)	H–C(5)	H–C(6)	2 MeO	Ac	CO_2Me	OCH_2	Ph	J(1′,6)	J(R_{ax},3eq)	J(3eq,4)	J(3ax,4)	J(4,5)	J(5,6)
11a[a])	4.48	3.64	4.19	5.23	5.21	4.27	3.45, 3.45	2.05, 2.08	3.80	–	–	4.1	14.5	4.1	2.3	3.4	8.3
11b[b])	4.45	3.65	4.21	5.23	5.20	4.28	3.39, 3.39	1.92, 2.03	–	5.20	7.36	4.0	14.5	3.8	2.0	3.2	8.7
11c	4.45	1.43	4.45	5.07	5.42	4.27	3.47, 3.47	2.05, 2.10	3.82	–	–	4.2	7.1	2.8	–	3.3	9.3
11d	4.46	1.45	4.50	5.07	5.42	4.30	3.40, 3.41	1.93, 2.00	–	5.23	7.37	4.2	7.2	2.7	–	3.2	9.3
12d[a])[c])	4.62	1.37	4.38	5.31	5.31	4.05	3.34, 3.36	2.04, 2.07	–	5.21	7.36	5.9	6.8	5.4	–	3.8	3.2
15h	4.39	1.36	4.77	5.14	5.41	4.12	3.45, 3.49	2.02, 2.08	2.18[d])	–	–	4.1	7.3	3.0	–	3.2	9.5

[a]) J values (C_6D_6) calculated using a ITRCAL program.
[b]) J values measured in C_6D_6 and $CDCl_3$.
[c]) J(3eq, 5) = 0.5 Hz.
[d]) MeCON.

The question arises as to the assignment of the allylic C-atoms C(3) and C(6) which are connected to the N and to the ring O-atoms. As a rule, the chemical shift of a secondary C-atom connected to an O-atom is *ca.* 70–80 ppm, whereas for a C-atom connected to an N-atom the chemical shift is *ca.* 50–60 ppm (the acetal C-atoms at *ca.* 100 ppm are easily identified). In the pentadienal adducts **7a,b**, the 'primary' C(3) and the 'secondary' C(6) atoms can be distinguished by their multiplicities; furthermore, the 'primary' C-atoms appear as the most shielded ones, therefore, they are connected to N(2) and identified as C(3). In the hexadienal adducts **7c,d** and **8c,d**, both series of allylic C-atoms are 'secondary'; they can be distinguished by their long-range coupling constants with the olefinic protons: the most deshielded C-atoms appear as simple *t*'s ($J \approx 8$ Hz), whereas the most shielded C-atoms appear as complex *m*'s since they undergo additional coupling with the Me group. This was demonstrated for **7c** and **8c** as follows: irradiation of Me at 16–17 ppm leads to a simple *t* which is analogous to the ones described above. Thus, the C-atom bearing the Me group is connected to N(2) and identified as C(3). Clearly, in all adducts **7** and **8** the ring O-atoms appear on the side of the acetal moiety, demonstrating thereby the same regiospecificity of all cycloaddition reactions.

Conformations and relative configurations of adducts **7** and **8** could be ascertained unambiguously by the detailed ^{1}H-NMR analyses (values of the coupling constants between allylic and olefinic H-atoms) which had been made by *Firl* with 1,2,3,6-tetrahydropyridazine derivatives [15]. From these latter studies, it appears that pseudo-equatorial allylic protons show vicinal coupling constants ^3J of 4–5 Hz and long-range coupling constants ^4J of 1.5 Hz. Pseudoaxial allylic protons have similar values for ^3J (1.5 Hz) and for ^4J (2.0 Hz)[4]. The H,H coupling constants of **7** and **8** *(Table 3)* show the adducts to be in pseudochair conformations. In the hexadienal-adduct series, H–C(3) is always pseudoequatorial. The major adducts **7c,d** can easily be distinguished from the minor ones **8c,d** by consideration of ^3J and ^4J of H–C(6): thus, $^3J(5,6)$ and $^4J(4,6)$ *(Table 3)* permit assignment of H–C(6) to a pseudoaxial orientation in **7c,d** and to a pseudoequatorial one in **8c,d**. Clearly **7c,d** are the *cis* and **8c,d** the *trans* adducts, as would be expected for *supra/supra Diels-Alder* cycloadditions. It is worth noticing that in both series **7c,d** and **8c,d**, the Me group has a pseudoaxial orientation and forces the adducts into the pseudochair conformation (see *Scheme 2*).

In the pentadienal adducts **7a,b**, H–C(6) is pseudoaxial (see *Scheme 2*). Nevertheless, $^3J(5,6)$ and $^4J(4,6)$ are less characteristic when compared to the ones of **7c,d** and **8c,d** so that an equilibrium may be postulated between the pseudochair conformation – by far the major conformation – shown in *Scheme 2* and the other pseudochair conformation.

*Tetrahydro-2*H*-oxazines* **9a–d**, **10d**, **11a–d**, **12d**, *and* **15h**. ^{1}H-NMR data of some of these compounds are collected in *Table 5*. They permit assignment of the conformation and the relative configuration of some diacetyl and triacetyl derivatives.

Diacetates **11a–d** and the triacetyl derivative **15h** all appear with a large coupling constant ($^3J(5,6) = 8$–10 Hz), indicating that H–C(5) and H–C(6) are *trans* diaxial. Clearly, they occur in chair conformations (see *Scheme 2*) for the D-enantiomer series. The other ^3J(H,H) values of **11a–d** and **15h** are much smaller, *e.g.* the medium to small magnitudes of $^3J(4,5)$ demonstrate that H–C(4) is equatorial. From these various data, one deduces that the 2 AcO groups are oriented *cis* to one another, as expected, and *trans* with respect to the equatorial acetal group. As to Me–C(3) of **11c,d** and of **15h**, it is axial out of necessity, *i.e. cis* with respect to the acetal group, since these products are derivatives of the major adducts **7c,d**.

Diacetate **12d**, a derivative of the minor adduct **8d**, appears with some peculiar ^{1}H-NMR features since all ^3J values are rather small. Furthermore, a long-range $^4J(3,5)$ of 0.5 Hz (W effect) could be measured, indicating that H–C(3) and H–C(5) are both equatorial. Therefore, AcO–C(5) and Me–C(3) are axial, and AcO–C(4) is equatorial since **10d** results from a *cis*-glycolization of **8d**. Lastly, the acetal group of **12d** must be axial, being oriented *trans* with respect to Me–C(3). The structure of **10d** (**12d**; see *Scheme 2*) is reminiscent of the hexahydropyridazine **20** *(Scheme 4)* having the same substituents, the same relative configuration, and similar ^{1}H-NMR data [5].

Cyclic Aminosugars **17a**, **17c**, **17f**, **17h**, *and* **18**. The ^{1}H- and ^{13}C-NMR data of these triacetates are collected in *Tables 6* and *7*.

The *N*-acetyl compounds **17f** and **17h** appear as two rotamers each at r.t.; the chemical shifts of their H-atoms have been determined between –20 and –30°. Restricted rotation being less severe in the carbamate derivatives **17a**, **17c**, and **18**, these compounds appear as homogeneous entities at temperatures between +25 and +50° in

[4]) For the value of some allylic coupling constants, see also [16] [17].

Table 6. *^{1}H-NMR Spectra* ($CDCl_3$) *of the Acetylated Aminosugars* **17a,c,g,h** *and* **18**. δ in ppm and J in Hz, internal standard TMS.

	H–C(1)	H–C(2)	H–C(3)	H–C(4)	H_{eq}–C(5)	H_{ax}–C(5)	Me–C(5)	OH	MeO	Ac	Frequency, Temp.
17a	5.84	5.22	5.35	5.23	4.18	3.52	–	[a])	3.75	2.01, 2.07, 2.09	400 MHz, 323 K
17c	5.81	5.28	5.57	5.18	4.42	–	1.44	3.67	3.77	2.02, 2.09, 2.10	80 MHz, 323 K
17f (A)	6.05	5.18	5.34	5.25	3.78	3.86	–	5.50	–	2.02, 2.08, 2.11, 2.12	400 MHz, 243 K
17f (B)	5.50	5.25	5.35	5.25	4.56	3.25	–	5.83	–	2.01, 2.07, 2.14, 2.15	
17h (A)	6.12	5.33[b])	5.60	5.23	4.13	–	1.58	5.52	–	2.05, 2.05, 2.10, 2.11	400 MHz, 253 K
17h (B)	5.57	5.32[c])	5.60	5.23	4.79	–	1.41	5.15	–	2.14, 2.15, 2.18, 2.25	
18	5.84	4.90	5.67	4.93	4.09	3.33	–	3.27	3.70	2.01, 2.10, 2.18	400 MHz, 323 K

	J(1,2)	J(1,5eq)	J(2,3)	J(2,4)	J(3,4)	J(4,5eq)	J(4,5ax)	J(5eq,5ax)	J(5,Me)	J(1,OH)	Frequency, Temp.
17a	2.5	1.2	3.5	*ca.* 1	3.5	2.6	2.0	14.8	–	–	400 MHz, 323 K
17c	2.6	1.0	3.6	1.0	3.4	2.0	–	–	7.3	3.8	80 MHz, 323 K
17f	3.0	0.8	3.5	[a])	3.5	2.5	2.0	15.0	–	–	400 MHz, 243 K
17h	2.6	$\neq 0$	3.6	1.2	3.5	2.2	–	–	7.5	–	400 MHz, 330 K
18	4.0	$\neq 0$	3.1	–	2.8	5.4	11.6	12.6	–	–	400 MHz, 323 K

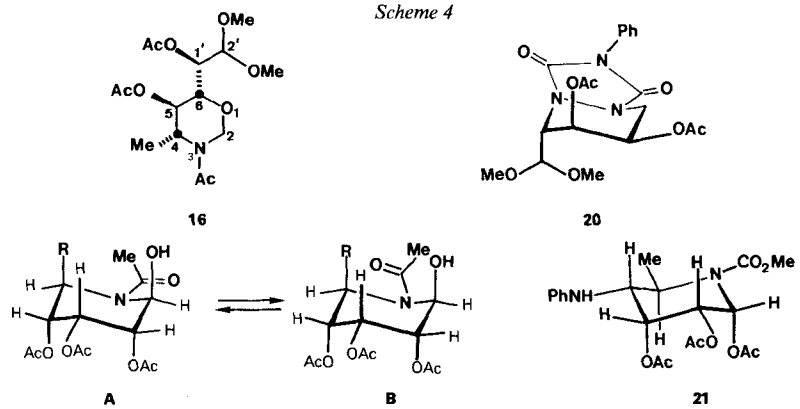
[a]) Not observed.
[b]) Or **17h (B)**.
[c]) Or **17h (A)**.

Table 7. *^{13}C-NMR Spectra* ($CDCl_3$) *of Rotamers* **A** *and* **B** *of Aminosugar* **17h**. 100.6 MHz, 300 K; δ in ppm, internal standard TMS; J values omitted[a]).

17h	C(1)	C(2)	C(3)	C(4)	C(5)	*Me*–C(5)[b])	Me*C*ON	Me*C*OO	*Me*CON	*Me*COO
A	74.5	68.5	63.2	69.6	54.2	20.2	173.1	170.3, 170.5, 170.6	22.2	21.0, 21.2, 21.3
B	79.8	68.2	63.5	69.8	49.9	19.0	172.8	170.4, 170.5, 170.7	22.3	21.0, 21.2, 21.3

[a]) Precise assignments could be determined for rotamers **A** and **B** only with C(1), C(5), and *Me*–C(5).
[b]) As determined by a double-irradiation technique.

Scheme 4



16 **20** **A** **B** **21**

^{1}H-NMR. The relative configuration of these compounds and of their immediate acyclic precursors **13** and **14** are identical, at least at C(2), C(3), and C(4) (and for C(5) in the hexose series). Nevertheless, aldehyde deprotection followed by cyclization generated an additional asymmetric centre, *i.e.* the anomeric C-atom, whose configuration had to be ascertained. In ideal cases, the existence of a long-range $^4J(1,5)$ (W effect) demonstrates unambiguously the equatorial orientation of H–C(1) and, therefore, the axial one of OH–C(1). This is nicely demonstrated for the carbamate derivatives **17a** and **17c** ($^4J(1,5) = 1.0$–1.2 Hz; see *Table 6*). By the same token, the axial orientation of Me–C(5) of **17c** is ascertained. In other aminosugar derivatives, the W effect can be deduced only by irradiation of the anomeric H–C(1) (→sharpening of the H_{eq}–C(5) *m*, due to the vanishing of the W coupling).

Chemical-shift anisotropy induced by the AcN carbonyl group of **17f** and **17h** confirms the favoured equatorial position of the anomeric H–C(1). *Paulsen* and coworkers had already observed the chemical-shift anisotropy of *N*-acetylpiperidinoses, which depends strongly on the rotamer under consideration *(Scheme 4)* [18]: thus, a strong deshielding of the equatorial H–C(1) of rotamer **A** with respect to H–C(1) of rotamer **B** ($\Delta\delta = +0.7$ ppm) and a shielding of axial R–C(5) (H–C(5)) of **B** with respect to **A** ($\Delta\delta = -0.5$ ppm) should be observed. As a consequence, in the pentanose series, the two H–C(5) appear in rotamer **B** with well differentiated chemical shifts and with similar ones in rotamer **A** [18]. For the *N*-acetyl compounds **17f** and **17h**, these shielding/deshielding effects are indeed observed *(Table 6)*.

Allose compounds **17c** and **17h** show a distinct $^4J(1,5)$ (W effect; see *Table 6* and decoupling); clearly these aminosugars appear in their axial β-D-anomer forms[1]), with the chair conformation and the overall configuration as indicated in *Scheme 3*.

In the ribose series, the minor aminosugar anomer **18** represents a peculiar case since a large coupling constant appears ($^3J(4,5ax) = 11.6$ Hz) which clearly points to the chair conformation and configuration shown in *Scheme 3*. Hence, H–C(2) is axial too, and since $^3J(1,2)$ is small, H–C(1) is equatorial: compound **18** is the α-D-anomer[1]) whose anomeric OH group is axial. The major aminoriboses **17a** and **17f** show only small $^3J(4,5ax)$, thus, H–C(4) is equatorial. Furthermore, OH–C(1) being axial (see above and *Table 6*), it follows that **17a** and **17f** are β-D-anomers[1]) (see *Scheme 3*). Comparison with *Paulsen*'s ^{1}H-NMR data for the α- and the β-D-anomers of the peracetylated *N*-[(benzyloxy)carbonyl]piperidines of the ribose series [14] confirmed our attributions for the ribose derivatives **17a** and **18**.

The ^{13}C-NMR data of the *N*-acetylallose **17h** (rotamers **A** and **B**; *Table 7*) corroborate the attributed structure. Noticeable in particular is the stronger shielding of C(5) being bound to an N-atom as compared to the other four ring C-atoms. Comparison with the chemical shifts of Me_2N of *N,N*-dimethylacetamide allows the identification of C(1) and C(5) for the two rotamers of **17h**. The Me group *cis* with respect to the carbonyl function of *N,N*-dimethylacetamide is more shielded by 3 ppm than the *trans* one [19]. The difference of shielding of C(1) and C(5) for the two rotamers of **17h** amounts to 4–5 ppm *(Table 7)*.

The Anomeric Effect. – The present-day interpretation of the anomeric effect, *i.e.* the preferential axial orientation of the X–C(1) substituent (X being an electronegative group) of the hemiacetal-like function of the pyranose in a chair conformation, is based upon the interaction between the occupied $n_O(\pi)$ orbital of the ring O-atom and the antibonding σ^*(C–X) orbital. When these two orbitals are antiperiplanar (C–X axial),

they lead to a stabilizing effect with respect to the anomer in which C–X is equatorial [20–23]. When the O-atom ring is replaced by an N-atom (which is less electronegative than O), the energy of the $n_N(\pi)$ orbital is increased with respect to the one of $n_O(\pi)$. This leads to a stronger interaction with the σ^*(C–X) orbital (*i.e.* to orbital compression), and, therefore, to an anomeric effect which is stronger than in the pyranose series [1] [21–23].

When X is an alkyl group, the orbital interactions with the ring heteroatom become more complex, as was shown by *Wolfe* with a quantummechanical treatment [20]. The C–C bond presents two antibonding MO's of similar energy: the σ^*(C–C) MO and a π^*(C–C) MO whose symmetry is quite different. As a consequence, the interaction between this latter π^*(C–C) MO and the $n_N(\pi)$ (or the $n_O(\pi)$) orbitals is optimal when the anomeric substituent is equatorial (see [23]). The net result of these two opposing interactions is a weakening of the above defined anomeric effect.

Ribose Series. In this series, there is only one substituent in α position to the ring N-atom, *i.e.* the anomeric OH group which is *always and only axial* in both the α-D-anomer[1]) **18** and the β-D-anomers **17a** and **17f**. These geometric parameters point to a pronounced anomeric effect, which we had already observed in the piperidinolyxose series [1]. Actually, *Paulsen* had shown that such a strong anomeric effect is found in all *N*-acylated piperidinopentoses, whose magnitude is estimated at *ca.* 3 kcal/mol [14].

Allose Series. The aminoalloses **17c** and **17h** show two substituents in the immediate vicinity of the ring N-atom, *i.e.* OH–C(1) and Me–C(5). Since these aminosugars have been obtained under equilibrating conditions, they are thermodynamically favoured. Both are the axial β-D-anomers[1]) having the $^1C_4$(D) chair conformation (see *Scheme 3*). It is worth noticing that in this chair conformation, four out of the five C-substituents are axial, leading thereby to two severe 1,3-diaxial interactions. In terms of conformational analysis, **17c** and **17h** would, therefore, appear as three-dimensional oddities; at least at first sight. After all, α-D- as well as β-D-hexopyranoses which have the same configuration as **17c** and **17h** (*i.e.* allopyranose derivatives) both occur preferentially in the inverse $^4C_1$(D) chair conformations in which the $HOCH_2$–C(5) substituent is equatorial [24] [25].

In the piperidinose context though, we must keep in mind that the ring N-atom is sp^2-hybridized, since it is part of a urethane (as in **17c**) or of an amide function (as in **17f**). This hybridization produces *i)* a strong anomeric effect which forces the OH–C(1) substituent to be axial *(vide supra)* and *ii)* a strong steric effect which would be manifest in the alternative $^4C_1$(D) chair conformation because of the severe steric repulsion between the equatorial Me–C(5) substituent and the *N*-acyl group. Therefore, we believe that both the anomeric effect and the steric effect act together in favour of the $^1C_4$(D) conformation of **17c** and **17f** (see *Scheme 3*). Similar steric features have been observed with β-D-xylopyranoses [26] [27] as well as with α-D-idopyranoses [24] [25] [28].

We can even estimate the relative magnitude of the two effects *i)* and *ii)* by considering the stereostructure of the α-D-allopiperidinose derivative **21** whose synthesis has been described in a previous paper [29]. In (D_6)acetone solution, the $^4C_1$(D) conformation with equatorial Me–C(5) turned out to be the dominant conformation, demonstrating thereby that the anomeric effect is somewhat stronger than the steric one[5]).

Clearly, in the *N*-acylhexopiperidinose series, the steric situation is quite different from the one observed in the hexopyranose series. In these latter ones, the $HOCH_2$–C(5)

[5]) In $CDCl_3$ solution though, this $^4C_1$(D) 'chair' was shown to be a skewed conformation [29], a result which indicates that the steric effect is not negligible.

substituent has a very strong propensity to adopt an equatorial orientation. This steric effect, which has been termed the 'proximity correction' by *David,* is stronger than the OH–C(1) anomeric effect.

This very proximity correction is also observed in nojirimicine which is nothing but glucopiperidinose (*i.e.* 5-amino-5-deoxyglucose) and whose ring N-atom is not acylated, preventing, therefore, the equatorial $HOCH_2$–C(5) substituent from any steric interaction (with NH) [23] [30]. Furthermore, the N-atom of nojirimicine being sp^3-hybridized, the $n_N(\pi)$-σ^*(O–H) orbital interaction becomes weaker, allowing thereby the occurrence of both the equatorial β-D-anomer and the axial α-D-anomer [23].

*The Steric Effect in the Conformational Analysis of the Methylated Dihydro- and Tetrahydro-2*H*-oxazines.* The steric effect ((Me–C(5) axial) we have just described in the *N*-acylpiperidinose series also occurs in the major cycloadducts **7c,d**, where Me–C(3) is pseudoaxial, and in their dihydroxy (**9c,d**) and diacetoxy derivatives **11c,d** in which Me–C(3) is axial. Similarly, in the minor cycloadducts **8c,d**, the Me–C(3) is pseudoaxial and in the dihydroxy (**10d**) and diacetoxy derivatives **12d**, Me–C(3) is axial, forcing thereby the rather bulky dimethyl-acetal group to occupy a pseudoaxial and axial position, respectively *(Scheme 2).*

The support of the *Centre National de la Recherche Scientifique (URA-135)* is gratefully acknowledged.

Experimental Part

General. (*E*)-2,4-Pentadienal: prepared according to [32]. 2,4-Hexadienal: (*E,E*)/(*E,Z*) mixture (8:2) from *Aldrich* and from *Lancaster Synthesis. Raney* Ni (slurry in H_2O), Pr_4NIO_4, Pd/C, and methyl orthoformate: from *Fluka. Amberlyst-15:* from *Rohm & Haas. C*-(Benzyloxy)carbohydroxamic acid (**6b**) and benzohydroxamic acid (**6d**): prepared according to [33]. *C*-(Methoxy)carbohydroxamic acid (**6a**) and phenylacetohydroxamic acid (**6c**): prepared according to [1]. Flash chromatography (FC) [31]: silica gel (*Merck 60;* 230–400 mesh). TLC: alumina roll (*Merck 60* F_{254}). M.p.: *Kofler* hot bench or *Büchi SMP 20* apparatus; corrected. IR spectra (cm^{-1}): *Perkin-Elmer 157-G.* ^{1}H- and ^{13}C-NMR spectra: *Varian T-60, SC-300, Bruker WP-80-DS,* and *WM-400* using double-irradiation techniques; tetramethylsilane (= TMS; ^{1}H-NMR) and $CDCl_3$ ($\delta(CDCl_3) = 77.00$ with respect to TMS; ^{13}C-NMR) as internal references; δ in ppm and J in Hz. High-resolution (HR)MS: *MAT-311* spectrometer, measured at the University of Rennes. Microanalyses were carried out by the Service Central de Microanalyses of the *CNRS.*

1. Acetals. – 1.1. *1,1-Dimethoxypenta-2,4-diene* (**4a**). A soln. of 2,4-pentadienal (3 g, 37 mmol) in methyl orthoformate (20.2 ml, 0.18 mol) was stirred at –20° under Ar in the presence of *Amberlyst-15* (2.25 g) for 1 h according to [7]. The filtered soln. was stirred at r.t. in the presence of Na_2CO_3 (1 g) for 15 min, concentrated to ⅓, and distilled *i.v.* to give **4a** as a colourless liquid (1.8 g, 38%). B.p. 54–55°/20 Torr (40°/10 Torr). IR (CCl_4): 2930, 2830, 1605, 1445, 1355, 1195, 1105, 1055, 1005, 905. ^{1}H-NMR ($CDCl_3$, 60 MHz): 3.35 (*s*, 2 MeO); 4.76 (*d*, $J = 4.5$, H–C(1)); 4.90–6.70 (*m*, 5 olef. H).

1.2. *1,1-Dimethoxyhexa-2,4-dienes* (**4b** and **4c**). To a stirred soln. of distilled 2,4-hexadienal (20 ml, 0.186 mol) in MeOH (25 ml) under Ar at r.t. were successively added methyl orthoformate (25.1 ml, 0.23 mol) and NH_4NO_3 (1 g, 12 mmol). The mixture was left to react for 1.5 d at r.t. according to [6]. Na_2CO_3 (1 g) was then added; after 15 min, MeOH was evaporated and the residue filtered and distilled *i.v.* over a few grains of Na_2CO_3: **4b**/**4c** (8:2) as a colourless liquid (16.4 g, 62%). B.p. 78°/25 Torr. IR (CCl_4): 2995, 2940, 2830, 1665, 1450, 1355, 1195, 1130, 1055, 995. ^{1}H-NMR ($CDCl_3$, 80 MHz): 1.76 (*d*, $J = 6.4$, Me–C(5)); 3.31 (*s*, 2 MeO); 4.79 (*d*, $J = 5.0$, H–C(1) of **4b**); 4.86 (*d*, $J \approx 5$, H–C(1) of **4c**); 5.20–6.90 (*m*, 4 olef. H).

2. Cycloadducts. – 2.1. *General Procedure.* To a stirred soln. of an acetal in $CHCl_3$ (0.5 mmol/ml) which was kept at 0° over a few beads of 4-Å molecular sieves were added Pr_4NIO_4 (0.3 equiv. with respect to the amount of hydroxamic acid) and then portionwise the hydroxamic acid. After evaporation of the soln. to near dryness, the products were separated by FC.

2.2. *Methyl 6-(Dimethoxymethyl)-3,6-dihydro-2*H*-1,2-oxazine-2-carboxylate* (**7a**). As in *2.1* with **4a** (1.27 g, 9.92 mmol), $CHCl_3$ (19 ml), Pr_4NIO_4 (3.74 g, 9.92 mmol), and *C*-(methoxy)carbohydroxamic acid (**6a**; 2.71 g, 29.8 mmol). After FC (AcOEt/cyclohexane 3:7), **7a** was isolated (1.44 g, 67%) as a colourless oil. IR (CCl_4): 2960, 2840,

1710, 1450, 1370, 1215, 1100, 1075. ^{1}H-NMR: *Tables 3* and *4*. ^{13}C-NMR: *Table 2*. HR-MS: 217.0969 ($C_9H_{15}NO_5$, M^+, calc. 217.0950).

2.3. *Benzyl 6-(Dimethoxymethyl)-3,6-dihydro-2*H*-1,2-oxazine-2-carboxylate* (**7b**). As in *2.1* with **4a** (0.67 g, 5.23 mmol), $CHCl_3$ (10 ml), Pr_4NIO_4 (0.988 g, 2.62 mmol), and benzohydroxamic acid (**6d**; 1.29 g, 7.7 mmol). After FC (AcOEt/cyclohexane 2:8), **7b** was isolated (0.93 g, 61%) as a colourless liquid. IR (CCl_4): 2960, 2930, 2900, 2830, 1710, 1655, 1410, 1350, 1210, 1130, 1095, 1075. ^{1}H-NMR: *Tables 3* and *4*. ^{13}C-NMR: *Table 2*. HR-MS: 155.0584 ($C_7H_9NO_3$, $M^+ - MeO - OCH_2Ph$, calc. 155.0582).

2.4. *Methyl* cis- *and* trans-*6-(Dimethoxymethyl)-3,6-dihydro-3-methyl-2*H*-1,2-oxazine-2-carboxylate* (**7c** and **8c**, resp.). As in *2.1* with **4b**/**4c** (0.974 g, 6.86 mmol), $CHCl_3$ (12 ml), Pr_4NIO_4 (1.72 g, 4.57 mmol), and *C*-(methoxy)carbohydroxamic acid (**6a**; 1.25 g, 13.7 mmol). After FC (AcOEt/cyclohexane 2:8), **7c** (0.78 g, 49%) and **7c**/**8c** (6:4; 0.642 g, 40%) were isolated. A second FC led to pure **8c**.

Adduct **7c**: colourless oil. IR ($CHCl_3$): 2960, 2940, 2840, 1700, 1650, 1450, 1400, 1380, 1375, 1325, 1190, 1120, 1070. ^{1}H-NMR: *Tables 3* and *4*. ^{13}C-NMR: *Table 2*. HR-MS: 156.0665 ($C_7H_{10}NO_3$, $M^+ - HC(OMe)_2$, calc. 156.0660).

Adduct **8c**: colourless oil. IR (CCl_4): 2960, 2935, 2840, 1710, 1655, 1445, 1360, 1300, 1195, 1115, 1080. ^{1}H-NMR: see *Tables 3* and *4*. ^{13}C-NMR: *Table 2*.

2.5. *Benzyl* cis- *and* trans-*6-(Dimethoxymethyl)-3,6-dihydro-3-methyl-2*H*-1,2-oxazine-2-carboxylate* (**7d** and **8d**, resp.). As in *2.1* with **4b**/**4c** (2.87 g, 20 mmol), $CHCl_3$ (50 ml), Pr_4NIO_4 (5.01 g, 13 mmol), and (benzyloxy)-hydroxamic acid (**6d**; 6.70 g, 40 mmol). FC (toluene/AcOEt 9:1) gave **7d** and **8d** (8:2; 5.65 g, 91%). They were separated by means of several FC (toluene/AcOEt 20:1).

Adduct **7d**: colourless oil. IR (CCl_4): 2940, 2840, 1710, 1420, 1360, 1320, 1300, 1287, 1070. ^{1}H-NMR: *Tables 3* and *4*. ^{13}C-NMR: *Table 2*. HR-MS: 232.0944 ($C_{12}H_{14}NO_3$, $M^+ - HC(OMe)_2$, calc. 232.0973).

Adduct **8d**: colourless oil. IR (film): 2940, 2840, 1740, 1710, 1460, 1410, 1360, 1305, 1200, 1115, 1080. ^{1}H-NMR: *Tables 3* and *4*. ^{13}C-NMR: *Table 2*.

2.6. *Small-Scale General Procedure for the Synthesis of the Other Adducts of* Table 1. To a stirred soln. of **4b**/**4c** in $CDCl_3$ (0.7 mmol/ml) kept at 0° were added successively Pr_4NIO_4 (0.33 equiv.) and a hydroxamic acid (1 equiv.). The mixture was left to warm up to r.t. and then washed successively with sat. aq. Na_2SO_3 soln. (0.5 ml), 2N Na_2CO_3 (1 ml), and twice with H_2O (1 ml). The resulting $CDCl_3$ soln. was directly used for the NMR determination of the relative amounts of the adduct(s) and the unreacted acetal(s), or separated by prep. TLC.

2.7. cis- *and* trans-*6-(Dimethoxymethyl)-3,6-dihydro-3-methyl-2-(phenylacetyl)-2*H*-1,2-oxazines* (**7** and **8**, resp.; $R^1 = PhCH_2$). As in *2.6* with **4b**/**4c** (54 mg, 0.38 mmol), $CDCl_3$ (0.5 ml), Pr_4NIO_4 (47 mg, 0.12 mmol), and phenylacetohydroxamic acid (**6c**; 57 mg, 0.38 mmol). Prep. TLC (AcOEt/cyclohexane 3:7) led to the isolation of **7** (major) and **8** (minor; see *Table 1*). **7** ($R^1 = PhCH_2$): IR (film): 2940, 2840, 1670, 1655, 1605, 1420, 1200, 1135, 1080. ^{1}H-NMR ($CDCl_3$, *J* values in C_6D_6, 80 MHz): 1.26 (*d*, Me–C(3)); 3.42 (*s*, MeO); 3.44 (*s*, MeO); 3.79 (*s*, CH_2); 4.21 (*d*, H–C(1′)); 4.34 (*m*, H–C(6)); 4.76 (*m*, H–C(3)); 5.84 (*m*, H–C(4), H–C(5)); 7.29 (*m*, arom. H); $J(1',6) = 6.4$, $J(3,Me) = 6.4$, $J(3,4) = 4.2$, $J(3,5) = 1.4$, $J(3,6) = 2.8$, $J(4,5) = 10.6$, $J(4,6) = 2.2$, $J(5,6) = 1.4$. HR-MS: 260.1277 ($C_{15}H_{18}NO_3$, $M^+ - OCH_3$, calc. 260.1286).

2.8. cis- *and* trans-*2-Benzoyl-6-(dimethoxymethyl)-3,6-dihydro-3-methyl-2*H*-1,2-oxazines* (**7** and **8**, resp.; $R^1 = Ph$). As in *2.6* with **4b**/**4c** (85 mg, 0.60 mmol), $CDCl_3$ (0.9 ml), Pr_4NIO_4 (75 mg, 0.2 mmol), and benzohydroxamic acid (**6d**; 82 mg, 0.6 mmol). Prep. TLC (AcOEt/cyclohexane 3:7) led to the isolation of **7** (major) and **8** (minor; see *Table 1*). **7** ($R^1 = Ph$): IR ($CHCl_3$): 3000, 2940, 2840, 1630, 1450, 1130, 1075. ^{1}H-NMR ($CDCl_3$, 80 MHz): 1.43 (*d*, Me–C(3)); 3.08 (*s*, MeO); 3.37 (*s*, MeO); 4.18 (*d*, H–C(1)); 4.46 (*m*, H–C(6)); 4.91 (*m*, H–C(3)); 5.82 (*m*, H–C(5)); 6.02 (*m*, H–C(4)); 7.57 (*m*, arom. H); $J(1',6) = 6.4$, $J(3,Me) = 6.9$, $J(4,5) = 10.2$.

3. Cyclic Diols and Acetates. – 3.1. *General Procedure A*. The catalytic oxidizing agent was a soln. of OsO_4 (1 g) to which 70% *t*-BuOOH (1 ml) in *t*-BuOH (200 ml) was added [34]. To a soln. of an adduct (10–15 mmol) in acetone (10 ml) and H_2O (6 ml), 1-methylmorpholine 1-oxide (NMO, 1.5 equiv.) and the cat. OsO_4 soln. (2 ml) were added. Workup as in *3.2*.

3.2. *General Procedure B*. To a soln. of an adduct (10 mmol) in acetone (50 ml) and H_2O (100 ml), NMO (1.1 equiv.) and the cat. OsO_4 soln. (10 ml) prepared as above were added. Workup: after addition of Na_2SO_3 (1 g) and neutralisation with 5N H_2SO_4, the mixture was saturated with NaCl and extracted several times with AcOEt. The combined org. solns. were dried ($MgSO_4$), filtered over *Celite*, and evaporated: crude diols.

3.3. *Acetylations*. A diol (1 mmol) was dissolved in pyridine (0.8 ml, 10 mmol) and reacted overnight at r.t. with Ac_2O (0.35 ml, 4 mmol). MeOH (1–2 ml) was added. After 15 min, some toluene was added and the soln. evaporated: crude diacetate. Alternative workup: the crude reaction mixture was diluted with AcOEt (20 ml), washed with 1N HCl (10 ml), H_2O (10 ml), 2N Na_2CO_3 (10 ml), and brine. The org. soln. was dried ($MgSO_4$) and evaporated: crude diacetate.

3.4. *Methyl* t-*6-(Dimethoxymethyl)-3,4,5,6-tetrahydro-*r-*4,*c-*5-dihydroxy-2*H-*1,2-oxazine-2-carboxylate* (**9a**). As in *3.1* with **7a** (1.44 g, 6.65 mmol) in acetone (4.6 ml) and H_2O (2.8 ml), NMO (1.35 g, 10 mmol), and the cat. OsO_4 soln. (1.4 ml). Reaction at 40° for 4 d. The crude product was purified by FC (AcOEt): **9a** (1.11 g, 66%) as colourless crystals. M.p. 70–72° (Et_2O/MeOH 10:1). IR ($CHCl_3$): 3500, 3030, 2940, 2840, 1710, 1450, 1375, 1225, 1130, 1080, 1055. ^{1}H-NMR ($CDCl_3$, 60 MHz): 3.52 (*s*, 2 MeO); 3.78 (*s*, CO_2Me); 3.16–4.46 (*m*, 7 H); 4.58 (*d*, $J = 4$, H–C(1′)).

Diacetate **11a**. From **9a** (91 mg, 0.36 mmol) according to *3.3*. The crude product was purified by prep. TLC (AcOEt): **11a** (96 mg, 79%) as colourless crystals. M.p. 72–73° (toluene/cyclohexane). IR (KBr): 2940, 2840, 1740, 1725, 1450, 1365, 1245, 1215, 1135, 1045, 1030. ^{1}H-NMR: *Table 5*. Anal. calc. for $C_{13}H_{21}NO_9$ (335.31): C 46.57, H 6.31, N 4.18; found: C 46.6, H 6.3, N 4.1.

3.5. *Benzyl* t-*6-(Dimethoxymethyl)-3,4,5,6-tetrahydro-*r-*4,*c-*5-dihydroxy-2*H-*1,2-oxazine-2-carboxylate* (**9b**). As in *3.2* with **7b** (0.955 g, 3.26 mmol) in acetone (17 ml) and H_2O (34 ml), NMO (0.484 g, 3.58 mmol), and the cat. OsO_4 soln. (3.3 ml). Reaction at 40° for 2 d. The crude product was purified by FC (AcOEt): **9b** (0.745 g, 70%) as a colourless oil.

Diacetate **11b**. From **9b** (80 mg, 0.24 mmol) according to *3.3*. The crude product was purified by prep. TLC (AcOEt): **11b** (60 mg, 60%) as a colourless oil. IR ($CHCl_3$): 3020, 3000, 2960, 2940, 2840, 1740, 1375, 1245, 1230, 1210, 1070. ^{1}H-NMR: *Table 5*. MS: no $M^{+\cdot}$, 192 (0.6), 157 (0.3), 130 (0.7), 107 (1), 91 (36), 76 (3), 75 (100).

3.6. *Methyl* c-*6-(Dimethoxymethyl)-3,4,5,6-tetrahydro-*t-*4,*t-*5-dihydroxy-*r-*3-methyl-2*H-*1,2-oxazine-2-carboxylate* (**9c**). As in *3.2* with **7c** (1.80 g, 7.76 mmol) in acetone (33 ml) and H_2O (56 ml), NMO (1.155 g, 8.54 mmol), and the cat. OsO_4 soln. (8 ml). Reaction at 40° for 20 h gave **9c** (2.06 g, *ca.* 100%) as colourless crystals. M.p. 68–69° (AcOEt/(i-Pr)$_2$O). IR ($CHCl_3$): 3520, 3000, 2940, 2840, 1710, 1450, 1380, 1325, 1135, 1080, 1060. ^{1}H-NMR ($CDCl_3$, 80 MHz): 1.31 (*d*, $J = 7.4$, Me–C(3)); 3.54 (*s*, 2 MeO); 3.77 (*s*, CO_2Me); 3.20–4.75 (*m*, 7 H). Anal. calc. for $C_{10}H_{19}NO_7$ (265.26): C 45.28, H 7.22, N 5.28; found: C 45.5, H 7.4, N 5.3.

Diacetate **11c**. From **9c** (0.158 g, 0.59 mmol) according to *3.3*: **11c** (0.183 g, 88%) as colourless crystals. M.p. 85.5–86.5° (C_6H_6/hexane). IR (CCl_4): 2960, 2840, 1750, 1715, 1445, 1370, 1320, 1240, 1220, 1130, 1070. ^{1}H-NMR: *Table 5*. Anal. calc. for $C_{14}H_{23}NO_9$ (349.33): C 48.13, H 6.64, N 4.01; found: C 48.3, H 6.7, N 3.9.

3.7. *Benzyl* c-*6-(Dimethoxymethyl)-3,4,5,6-tetrahydro-*t-*4,*t-*5-dihydroxy-*r-*3-methyl-2*H-*1,2-oxazine-2-carboxylate* (**9d**). As in *3.2* with **7d** (0.915 g, 2.98 mmol) in acetone (15 ml) and H_2O (32 ml), NMO (0.443 g, 3.28 mmol), and the cat. OsO_4 soln. (3 ml). Reaction at 40° overnight gave **9d** (0.854 g, 84%) as colourless crystals which were washed with Et_2O. M.p. 92–93° (C_6H_6/cyclohexane). IR (KBr): 3510, 2960, 2870, 1690, 1400, 1350, 1305, 1290, 1160, 1130, 1095, 1085, 1070, 1045, 945, 755, 700. ^{1}H-NMR ($CDCl_3$, 80 MHz): 1.30 (*d*, $J = 7.3$, Me–C(3)); 3.40 (*s*, MeO); 3.48 (*s*, MeO); 5.2 (*m*, CH_2); 7.34 (*s*, 5 arom. H); 3.50–4.60 (*m*, 7 H). ^{13}C-NMR ($CDCl_3$, 20.1 MHz): 13.8 (*qd*, $J = 128$, Me–C(3)); 53.3 (*qd*, $J = 143$, MeO); 55.4 (*d*, $J = 143$, C(3)); 55.5 (*qd*, $J = 143$, MeO); 64.2 (*d*, $J = 147$, C(6)); 67.3 (*t*, $J = 149$, CH_2); 68.5 (*d*, $J = 148$, C(4) or C(5)); 76.0 (*d*, $J = 147$, C(5) or C(4)); 103.5 (*dm*, $J = 163$, C(1′)); 127.6 (*d*, $J = 160$, arom. C_o); 127.8 (*d*, arom. C_p); 128.1 (*d*, $J = 160$, arom. C_m); 135.8 (*sm*, arom. C (subst.)); 156.0 (*st*, CO). Anal. calc. for $C_{16}H_{23}NO_7$ (341.35): C 56.29, H 6.79, N 4.10; found: C 56.4, H 6.8, N 4.1.

Diacetate **11d**. From **9d** (0.112 g, 0.33 mmol) according to *3.3*. The crude product was purified by prep. TLC (AcOEt/cyclohexane 5:5): **11d** (77 mg, 55%) as a colourless oil. IR (CCl_4): 2950, 2840, 1750, 1715, 1375, 1310, 1240, 1220, 1130, 1070. ^{1}H-NMR: *Table 5*. HR-MS: 425.1693 ($C_{20}H_{27}NO_9$, $M^{+\cdot}$, calc. 425.1685).

3.8. *Benzyl* t-*6-(Dimethoxymethyl)-3,4,5,6-tetrahydro-*c-*4,*c-*5-dihydroxy-*r-*3-methyl-2*H-*1,2-oxazine-2-carboxylate* (**10d**). As in *3.1* with **8d** (0.500 g, 1.62 mmol) in acetone (2 ml) and H_2O (1.2 ml), NMO (0.264 g, 1.95 mmol), and the cat. OsO_4 soln. (0.4 ml). Reaction at 60° for 6 d gave a mixture (410 mg) which was separated by FC (AcOEt): **8d** (352 mg, 70%) and **10d** (38 mg, 7%) as a colourless oil. IR ($CHCl_3$): 3520, 3010, 2940, 2840, 1710, 1450, 1410, 1290, 1075, 695. ^{1}H-NMR ($CDCl_3$, 60 MHz): 1.53 (*d*, $J = 7$, Me–C(3)); 3.35 (*s*, MeO); 3.42 (*s*, MeO); 4.48 (*d*, $J = 5$, H–C(1′)); 5.18 (*s*, CH_2); 7.35 (*s*, 5 arom. H); 3.70–4.40 (*m*, 6 H).

Diacetate **12d**. From **10d** (38 mg, 0.11 mmol) according to *3.3*. The crude product was purified by prep. TLC (AcOEt/cyclohexane 3:7): **12d** (33 mg, 69%) as a colourless oil. IR ($CHCl_3$): 3030, 3010, 2940, 2840, 1745, 1370, 1240, 1050, 920, 695. ^{1}H-NMR: *Table 5*.

4. Hydrogenolyses. – 4.1. *General Procedure A.* Activated *Raney*-Ni was prepared by weighing *Raney*-Ni (in H_2O) approximatively while wet and washing it under H_2 several times with 96% EtOH and finally with abs. EtOH. To the stirred soln. of a diol (1 mmol) in abs. EtOH (7 ml) activated *Raney*-Ni (*ca.* 1 g) was added under H_2 (1 atm.) at 40°. After consumption of the starting material, the catalyst was removed by centrifugation. After the usual workup, the product was acetylated with Ac_2O (0.57 ml, 6 mmol) in pyridine (1.2 ml, 15 mmol) as described in *3.3*.

4.2. *General Procedure B.* A stirred soln. of a diol (1 mmol) in abs. MeOH or EtOH (20 ml) containing 5% Pd/C (40 mg) was put under H_2 (1 atm) and kept at 40° until complete consumption of the starting material. After

filtration of the mixture over *Celite* and evaporation of the solvent, the crude residue was acetylated according to *3.3* (2 equiv. of Ac_2O and 4 equiv. of pyridine per HO–C group).

4.3. *5-Deoxy-5-[(methoxycarbonyl)amino]-*DL*-ribose Dimethyl Acetal* (**13a**). From **9a** (0.674 g, 2.68 mmol) and *Raney*-Ni according to *4.1*: **13a** (0.653 g, 96%) as a colourless oil. IR ($CHCl_3$): 3450, 2940, 1710, 1545, 1265, 1080, 980. ^{1}H-NMR ($CDCl_3$, 60 MHz): 5.80 (*m*, NH); 4.80 (*s*, OH); 4.52 (*d*, J = 4, H–C(1)); 3.68 (*s*, CO_2Me); 3.50 (*s*, 2 MeO); 4.20–3.40 (*m*, H–C(2) to H–C(5)).

Acetylation and purification by FC (AcOEt/cyclohexane 5:5) gave *triacetate* **14a** (0.809 g, 79%) as a colourless oil. IR ($CHCl_3$): 3450, 2940, 2840, 1740, 1520, 1370, 1230, 1210, 1060. ^{1}H-NMR ($CDCl_3$, 80 MHz): *Table 8*. HR-MS: 320.1347 ($C_{13}H_{22}NO_8$, $M^+ - CO_2CH_3$, calc. 320.1345).

4.4. *5,6-Dideoxy-5-[(methoxycarbonyl)amino]-*DL*-allose Dimethyl Acetal* (**13c**). From **9c** (0.195 g, 0.74 mmol) and *Raney*-Ni according to *4.1*: **13c** (0.178 g, 91%) as a colourless resin. IR ($CHCl_3$): 3460, 3000, 2960, 2840, 1708, 1510, 1452, 1235, 1072. ^{1}H-NMR ($CDCl_3$, 60 MHz): 1.16 (*d*, J = 6.5, Me–C(5)); 3.5–4.2 (*m*, H–C(2) to H–C(5), 2 OH); 3.52 (*s*, 2 MeO); 3.68 (*s*, CO_2Me); 4.53 (*d*, J = 4.5, H–C(1)); 5.62 (*d*, J = 9, NH).

Acetylation of **13c** gave the *triacetate* **14c** (0.197 g, 68%) as colourless crystals. M.p. 70–71° ((i-Pr)$_2$O). IR (KBr): 3370, 2980, 2940, 2840, 1760, 1745, 1720, 1520, 1380, 1370, 1255, 1230, 1215, 1130, 1085, 1075, 1050, 1035. ^{1}H-NMR: *Table 8*. Anal. calc. for $C_{16}H_{27}NO_{10}$ (393.38): C 48.85, H 6.92, N 3.56; found: C 48.7, H 7.1, N 3.6.

4.5. *c-6-(Dimethoxymethyl)-3,4,5,6-tetrahydro-*t*-4,*t*-5-dihydroxy-*r*-3-methyl-2*H*-1,2-oxazine* (**9g**). From **9d** (107 mg, 0.31 mmol) in MeOH (5 ml) according to *4.2*. After 20 min, **9g** was obtained in quantitative yield as a colourless oil. ^{1}H-NMR ($CDCl_3$, 60 MHz): 4.48 (*d*, J = 4.5, H–C(1′)); 4.30 (*s*, 2 OH, 1 NH); 4.20–3.00 (H–C(2), H–C(3), H–C(4)); 3.53 (*s*, MeO); 3.50 (*s*, MeO); 1.27 (*d*, J = 7.5, Me–C(3)).

Acetylation of **9g** and prep. TLC (AcOEt) led to *triacetate* **15h** (98 mg, 98%) as a colourless oil. IR (CCl_4): 2940, 2840, 1750, 1675, 1370, 1235, 1220, 1075. ^{1}H-NMR: *Table 5*. HR-MS: 333.1383 ($C_{14}H_{23}NO_8$, M^+, calc. 333.1423).

4.6. *5-(Acetamido)-2,3,4-tri-*O*-acetyl-5-deoxy-*DL*-ribose Dimethyl Acetal* (**14f**). From **9b** (322 mg, 0.98 mmol) in EtOH according to *4.2* for 30 h. Acetylation gave colourless crystalline **14f** (281 mg, 78%). M.p. 101–102° (AcOEt/cyclohexane). IR (KBr): 3260, 3080, 2960, 2840, 1750, 1735, 1635, 1570, 1430, 1370, 1215, 1130, 1105, 1055. ^{1}H-NMR: *Table 8*. Anal. calc. for $C_{15}H_{25}NO_9$ (363.36): C 49.58, H 6.94, N 3.86; found: C 49.8, H 7.2, N 3.9.

4.7. *5-(Acetamido)-2,3,4-tri-*O*-acetyl-5,6-dideoxy-*DL*-allose Dimethyl Acetal* (**14h**). From **9d** (68 mg, 0.20 mmol) in EtOH according to *4.2* for 20 h. Acetylation gave **14h** (52 mg, 60%) as colourless crystals. M.p. 110.5–111.5° (benzene/Et_2O). IR (KBr): 3270, 3080, 2980, 2840, 1740, 1650, 1560, 1370, 1210, 1145, 1080, 1035. ^{1}H-NMR: *Table 8*. Anal. calc. for $C_{16}H_{27}NO_9$ (377.38): C 50.92, H 7.21, N 3.71; found: C 51.2, H 7.4, N 3.6.

4.8. *5-Acetoxy-6-(1′-acetoxy-2′,2′-dimethoxyethyl)-3-acetyl-3,4,5,6-tetrahydro-4-methyl-2*H*-1,3-oxazine* (**16**). When *Exper. 4.7* was repeated in MeOH, **16** (5–15%) was obtained in addition to **14h**. Separation by FC (AcOEt/cyclohexane 5:5) led to **16** as a colourless oil. IR (CCl_4): 2940, 2840, 1750, 1650, 1415, 1370, 1225, 1080, 670. ^{1}H-NMR (C_6D_6, 80 MHz, 343 K): 1.25 (*d*, Me–C(4)); 1.65 (*s*, AcO); 1.67 (*s*, AcO); 1.77 (*s*, AcN); 3.12 (*s*, MeO); 3.20 (*s*, MeO); 3.90 (*dd*, H–C(6)); 4.22 (*qd*, H–C(4)); 4.49 (*d*, H–C(2′)); 4.80 (*s*, 2 H–C(2)); 5.37 (*dd*, H–C(5)); 5.51 (*dd*, H–C(1′)); J(1′,2′) = 5.5, J(1′,6) = 4.2, J(4,5) = 1.8, J(4, Me) = 7.0, J(5,6) = 5.5. HR-MS: 347.1578 ($C_{15}H_{25}NO_8$, M^+, calc. 347.1580).

5. Deacetalisation. – 5.1. *2,3,4-Tri-*O*-acetyl-5-deoxy-5-[(methoxycarbonyl)amino]-β-*D*-ribopyranose*[1]) (**17a**) *and the Corresponding α-*D*-Ribopyranose*[1]) **18**. A soln. of **14a** (509 mg, 1.34 mmol) in 90% HCOOH (6.6 ml) was heated at 55° under Ar for 4 h. After removal of the solvents, the crude mixture was separated by FC (AcOEt/cyclohexane 3:7): **17a** (215 mg, 48%) followed by **18** (59 mg, 13%).

*β-*D*-Isomer*[1]) **17a**. M.p. 124–125° (AcOEt/cyclohexane). IR (KBr): 3360, 2970, 1750, 1730, 1670, 1450, 1375, 1245, 1230, 1145, 1070, 1045. ^{1}H-NMR: *Table 6*. Anal. calc. for $C_{13}H_{19}NO_9$ (333.29): C 46.85, H 5.74, N 4.20; found: C 46.9, H 5.6, N 4.1.

*α-*D*-Isomer*[1]) **18**. Colourless resin which was further purified by prep. TLC (AcOEt/cyclohexane 5:5). IR ($CHCl_3$): 3560, 3020, 2950, 1750, 1710, 1445, 1370, 1230, 1210, 1070, 1045, 1010, 950, 910. ^{1}H-NMR: *Table 6*. HR-MS: 318.0810 ($C_{12}H_{16}NO_9$, $M^+ - CH_3$, calc. 318.0825).

5.2. *2,3,4-Tri-*O*-acetyl-5,6-dideoxy-5-[(methoxycarbonyl)amino]-β-*D*-allopyranose*[1]) (**17c**). A soln. of **14c** (175 mg, 0.44 mmol) in 90% HCOOH (4 ml) was heated at 50° under Ar for 3 h. After evaporation of the solvents, the solid residue was recrystallized (AcOEt/(i-Pr)$_2$O): colourless **17c** (95 mg, 61%). M.p. 135°. IR (KBr): 3410, 2990, 2960, 1740, 1690, 1450, 1375, 1250, 1225, 1095, 1075, 1060. ^{1}H-NMR: *Table 6*. Anal. calc. for $C_{14}H_{21}NO_9$ (347.32): C 48.41, H 6.09, N 4.03; found: C 48.3, H 6.1, N 4.0.

5.3. *5-(Acetamido)-2,3,4-tri-*O*-acetyl-5-deoxy-β-*D*-ribopyranose*[1]) (**17f**) *and 5-(Acetamido)-3,4-di-*O*-acetyl-5-deoxy-β-*D*-ribopyranose*[1]) (**19**). A soln. of **14f** (414 mg, 1.14 mmol) in 90% HCOOH (5.5 ml) was heated at 55°

Table 8. *^{1}H-NMR Spectra* ($CDCl_3$) *of the Open-Chain Aminosugar Acetates* **14a,c,f,h**. 80 MHz, 300 K; δ in ppm and J in Hz, internal standard TMS.

	H–C(1)	H–C(2)	H–C(3)	H–C(4)	H–C(5)	H′–C(5)	Me–C(5)	NH	MeO	R^1	AcO
14a	4.48	5.22	5.36	5.16	3.66	3.26	–	4.93	3.34, 3.42	3.67	2.07, 2.09, 2.12
14c	4.52	5.21	5.34	5.15	4.00	–	1.12	5.02	3.32, 3.41	3.66	2.09, 2.09, 2.09
14f	4.47	5.20	5.35	5.17	3.74	3.31	–	5.78	3.33, 3.40	1.96	2.07, 2.09, 2.11
14h	4.53	5.20	5.33	5.08	4.27	–	1.09	6.04	3.33, 3.41	1.96	2.10, 2.10, 2.12

	J(1,2)	J(2,3)	J(3,4)	J(4,5)	J(4,5′)	J(5,5′)	J(5,NH)	J(5′,NH)	J(5,Me)
14a	6.4	3.9	5.6	3.2	6.4	14.8	8.0	6.0	–
14c[a])	6.8	3.7	6.9	2.9	–	–	8.4	–	6.9
14f	6.4	3.5	6.4	2.9	6.8	15.0	5.8	6.0	–
14h[a])	6.8	3.6	7.0	2.8	–	–	8.2	–	6.9

[a]) Calculated spectrum using the ITRCAL program.

under Ar for 4 h. After evaporation of the solvents, the crude mixture was separated by FC (AcOEt): crystalline **17c** (208 mg, 57%) followed by crystalline **19** (50 mg, 16%).

Triacetate **17f**. M.p. 147–148° (AcOEt). IR (KBr): 3240, 2960, 1745, 1735, 1630, 1440, 1370, 1255, 1235, 1070. ^{1}H-NMR: *Table 6*. Anal. calc. for $C_{13}H_{19}NO_8$ (317.29): C 49.21, H 6.04, N 4.41; found: C 49.3, H 5.9, N 4.4

Diacetate **19**. M.p. 139–140° (AcOEt). IR (KBr): 3280, 2940, 1745, 1620, 1440, 1370, 1240, 1220, 1055. ^{1}H-NMR ($CDCl_3$, 400 MHz, 243 K; 2 rotamers **A** and **B**): 6.08, 5.56 (2*d*, H–C(1) of **A** and **B**); 4.06 (*m*, H–C(2)); 5.29, 5.22 (2*m*, H–C(3) of **A** and **B**); 5.36, 5.29 (2*m*, H–C(4) of **A** and **B**); 3.81 (br., 2 H–C(5) of **A**); 4.56, 3.25 (2 br. *d*, J = 14, 2 H–C(5) of **B**). Anal. calc. for $C_{11}H_{17}NO_7$ (275.25): C 48.00, H 6.22, N 5.09; found: C 48.1, H 6.1, N 5.0.

5.4. *5-(Acetamido)-2,3,4-tri-*O*-acetyl-5,6-dideoxy-β-*D*-allopyranose*[1]) (**17h**). A soln. of **14h** (160 mg, 0.42 mmol) in 90% HCOOH (3.3 ml) was heated at 55° under Ar for 3 h. After evaporation of the solvents, the solid residue was recrystallized leading to colourless **17h** (115 mg, 81%). M.p. 165–166° (AcOEt/cyclohexane). IR (KBr): 3230, 2980, 2940, 1750, 1630, 1435, 1370, 1250, 1225, 1070, 1040. ^{1}H-NMR: *Table 6*. ^{13}C-NMR: *Table 7*. Anal. calc. for $C_{14}H_{21}NO_8$ (331.32): C 50.75, H 6.39, N 4.23; found: C 50.8, H 6.4, N 4.2.

REFERENCES

[1] A. Defoin, H. Fritz, C. Schmidlin, J. Streith, *Helv. Chim. Acta* **1987,** *70,* 554.
[2] G.W. Kirby, J.G. Sweeny, *J. Chem. Soc., Chem. Commun.* **1973,** 704; G.E. Keck, R.R. Webb, J.B. Yates, *Tetrahedron* **1981,** *37,* 4007; G.E. Keck, St.A. Fleming, *Tetrahedron Lett.* **1978,** 4763.
[3] A. Defoin, H. Fritz, G. Geffroy, J. Streith, *Tetrahedron Lett.* **1986,** *27,* 4727.
[4] B. Belleau, Yum-Kin Au-Young, *J. Am. Chem. Soc.* **1963,** *85,* 64.
[5] R.R. Schmidt, R. Scheibe, *Liebigs Ann. Chem.* **1980,** 1307.
[6] J.A. Van-Allan, *Org. Synth.* **1963,** Coll. Vol. 4, 21; see also [1].
[7] S.A. Patwardhan, Sukh Dev, *Synthesis* **1974,** 348; E.C. Taylor, Chih Shu Chiang, *ibid.* **1977,** 467.
[8] I. Fleming, in 'Frontier Orbitals and Organic Chemical Reactions', J. Wiley & Sons, London, 1976.
[9] G. Kresze, J. Firl, *Fortsch. Chem. Forsch.* **1969,** *11,* 245.
[10] V. van Rheenen, R. Kelly, D. Cha, *Tetrahedron Lett.* **1976,** 1973.
[11] G.E. Keck, S. Fleming, D. Nickell, P. Weider, *Synth. Commun.* **1979,** *9,* 281.
[12] a) S. Zeeh, H. Metzger, in 'Houben-Weyl, Methoden der Organischen Chemie', Georg Thieme Verlag, Stuttgart, 1971, Vol. 10/1, p. 1257; b) Ph.G. Mattingly, M.J. Miller. *J. Org. Chem.* **1980,** *45,* 410.
[13] S. Hanessian, *J. Org. Chem.* **1967,** *32,* 163; S. Hanessian, *Chem. Ind. (London)* **1965,** 1296.
[14] H. Paulsen, F. Leupold, *Chem. Ber.* **1969,** *102,* 2804.
[15] J. Firl, *Chem. Ber.* **1969,** *102,* 2169.
[16] V.F. Bystrov, *Russ. Chem. Rev.* **1972,** *41,* 281.
[17] M. Barfield, R.S. Spear, S. Sternhell, *Chem. Rev.* **1976,** *76,* 593.
[18] H. Paulsen, K. Todt, *Chem. Ber.* **1967,** *100,* 3385; H. Paulsen, K. Todt, *Adv. Carbohydr. Chem.* **1968,** *23,* 115; H. Paulsen, K. Todt, H. Ripperger, *Chem. Ber.* **1968,** *101,* 3365.
[19] W. Mc Farlane, *J. Chem. Soc., Chem. Commun.* **1970,** 418.
[20] S. Wolfe, Myung-Hwang Whangbo, D.J. Mitchell, *Carbohydr. Res.* **1979,** *69,* 1.
[21] O. Eisenstein, Nguyen Trong Anh, Y. Jean, A. Devaquet, J. Cantacuzène, L. Salem, *Tetrahedron* **1974,** *30,* 1717.
[22] S. David, O. Eisenstein, W.J. Hehre, L. Salem, R. Hoffmann, *J. Am. Chem. Soc.* **1973,** *95,* 3806.
[23] B.M. Pinto, S. Wolfe, *Tetrahedron Lett.* **1982,** *23,* 3687.
[24] S.J. Angyal, *Angew. Chem.* **1969,** *81,* 172; *ibid. Int. Ed.* **1969,** *8,* 157.
[25] J. Augé, S. David, *Tetrahedron* **1984,** *40,* 2101.
[26] C.V. Holland, D. Horton, J.S. Jewell, *J. Org. Chem.* **1967,** *32,* 1818.
[27] H. Paulsen, F. Garrido Espinosa, W.P. Trautwein, K. Heyns, *Chem. Ber.* **1968,** *101,* 179.
[28] H. Paulsen, Z. Györgydeák, M. Friedmann, *Chem. Ber.* **1974,** *107,* 1590.
[29] G. Augelmann, J. Streith, H. Fritz, *Helv. Chim. Acta* **1985,** *68,* 95.
[30] S. Inouye, T. Tsuruoka, T. Ito, T. Niida, *Tetrahedron* **1968,** *23,* 2125.
[31] W.C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978,** *43,* 2923.
[32] M.P. Schneider, M. Goldbach, *J. Am. Chem. Soc.* **1980,** *102,* 6114.
[33] C.R. Hauser, W.B. Renfrow, Jr., *Org. Synth.* **1963,** Coll. Vol. II, 67; E. Boyland, R. Nery, *J. Chem. Soc. (C)* **1966,** 354.
[34] K. Akashi, R.E. Palermo, K.B. Sharpless, *J. Org. Chem.* **1978,** *43,* 2063.