158. From 1-(Silyloxy)butadiene to 4-Amino-4-deoxy-DL-erythrose and to 1-Amino-1-deoxy-DL-erythritol Derivatives *via* hetero-*Diels-Alder* Reactions with Acylnitroso Dienophiles

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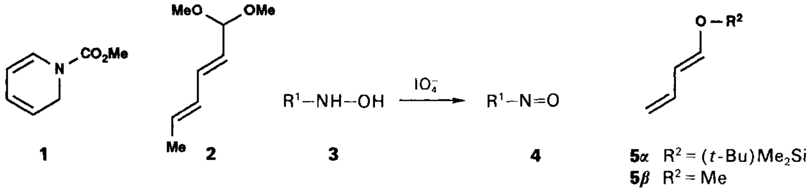
Acylnitroso dienophiles **4** reacted instantly with 1-(silyloxy)butadiene **5α** and led in good yield to the regioisomeric cycloadducts **6** (major) and **7** (minor; *Scheme 2, Table 1*). *cis*-Hydroxylation of these primary cycloadducts with OsO_4 (catalyst) occurred stereospecifically and in high yield (→**8** and **9**, resp.; *Scheme 2*). It was followed by reductive ring cleavage to give either 1-amino-1-deoxy-DL-erythritol or 4-amino-4-deoxy-DL-erythrose derivatives **10** and **14**, respectively, depending on the nature of the reducing agent (*Schemes 3* and *4*).

Introduction. – In two preceding publications, we described the stereospecific syntheses of some racemic amino-deoxysugar derivatives which belong to the lyxose [1], and to the ribose and allose series [2]. In all cases, the first step was a hetero-*Diels-Alder* cycloaddition of the dienes **1** and **2** with acylnitroso dienophiles **4** (R′ = RCO), the latter being prepared by *in situ* oxidation of the corresponding hydroxamic acids **3** with $(Pr_4N)IO_4$ [3]. *cis*-Hydroxylation of the primary cycloadducts with OsO_4, followed by reductive cleavage of the N–O bond led to the target molecules, *i.e.* the aminosugars.

In the lyxose series, both regioisomeric *Diels-Alder* cycloadducts were formed, in a ratio which depended upon the acylnitroso R group. The formation of these pairs of regioisomers was best explained by frontier MO interaction (FMO theory) between the diene and the dienophile partners [1]. In the ribose and allose series, the cycloadditions were regiospecific; in our opinion, this is best explained by a steric effect which overrides the orbital interaction [2].

We describe herein the synthesis of some racemic 4-amino-4-deoxy-erythrose and 1-amino-1-deoxy-erythritol derivatives by a similar approach to the one cited above, the starting material being the 1-(silyloxy)butadiene **5α**. This diene had already been described [4] and was easily obtained using either one of the following procedures: *i*) crotonaldehyde and silyl chloride in benzene solution in the presence of Et_3N and $ZnCl_2$

Scheme 1



[5] or *ii*) crotonaldehyde and silyl chloride in MeCN solution in the presence of NaI [6]. The second procedure was preferable since it led easily and in good yield (84%) to the *trans*-diene **5α** as the only isolated product.

***Diels-Alder* Cycloadditions.** – *Diels-Alder* cycloadditions were performed at 0° with (silyloxy)diene **5α**, the hydroxamic-acid precursors **3a–h** being oxidized *in situ* with $(Pr_4N)IO_4$ to the corresponding acylnitroso dienophiles **4a–h** which reacted at once with the diene (*Scheme 2*). In most cases, both regioisomers **6aα–hα** and **7bα–hα** were formed, their ratio depending on the nature of R of the dienophile RCONO (= R′NO; **4**) (*Table 1*). The ratio **6**/**7** (crude mixtures) was determined in all cases by ^{13}C-NMR. Type-**6** cycloadducts, which by convention are called direct adducts, turned out to be the major

Scheme 2

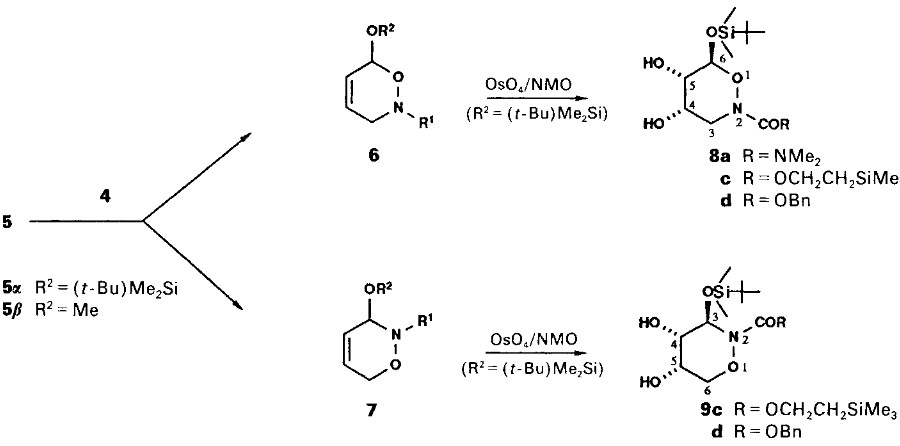


Table 1. *Cycloadducts* **6** *and* **7** *Obtained by* Diels-Alder *Reactions of Dienes* **5α** *and* **5β** *with Dienophiles* $R^1{-}N{=}O$ (**4**) (with the exception of nitrosobenzene **4i**). The latter ones are generated *in situ* from hydroxamic acid precursors $R^1{-}NH{-}OH$ (**3**).

Dienophile series	R^1 in **3**, **4**, **6**, **7**	Diene	Overall yields [%]	Relative amount [%] of adducts[a]	
				6	**7**
a	$CONMe_2$	**5α**	85	100	–
		5β	85[b]	100	–
b	COPh	**5α**	66	89	11
		5β	83[b]	70	30
c	$CO_2(CH_2)_2SiMe_3$	**5α**	97[b]	74	26
d	CO_2Bn	**5α**	93[b]	67	33
e	CO_2Me	**5α**	68	72	28
f	$COCH_2Ph$	**5α**	56	55	45
g	COMe	**5α**	79	55	45
h	SO_2Ph	**5α**	50	100	–
i	Ph	**5α**	100[b]	80	20

[a] As determined by ^{13}C-NMR of the crude mixture of cycloadducts.

[b] As determined for the crude reaction products.

products in all experiments. In two instances, cycloadditions were regiospecific since **6aα** (R = $CONMe_2$) and **6hα** (R = SO_2Ph) were the only reaction products.

Since nitrosobenzene (**4i**) was known to undergo regiospecific cycloaddition with 1,2-dihydropyridines [7], it was of interest to check its reaction with (silyloxy)diene **5α**. The direct adduct **6iα** was the major product, the inverse adduct **7iα** being formed in 20% yield only. The latter is rather unstable and could not be isolated. *McClure* and *Danishevsky*, who investigated the *Diels-Alder* cycloaddition of nitrosobenzene with 1-(trimethylsilyloxy)butadiene, did not mention the formation of any minor regioisomer [8].

The (*E*)-1-methoxybutadiene **5β**, which was prepared according to [9], led to very similar results when allowed to react with the acylnitroso dienophiles **4a** and **4b**: in the former case, the direct adduct **6aβ** was obtained as the only product, whereas in the second one, both regioisomers **6bβ** and **7bβ** were formed.

In most cases, the cycloadducts could be separated and analysed. The N,O-acetal functionality of the inverse adducts **7** proved to be relatively unstable though, so that only in a few instances could these adducts be isolated (**7bβ**, **7cβ–gβ**).

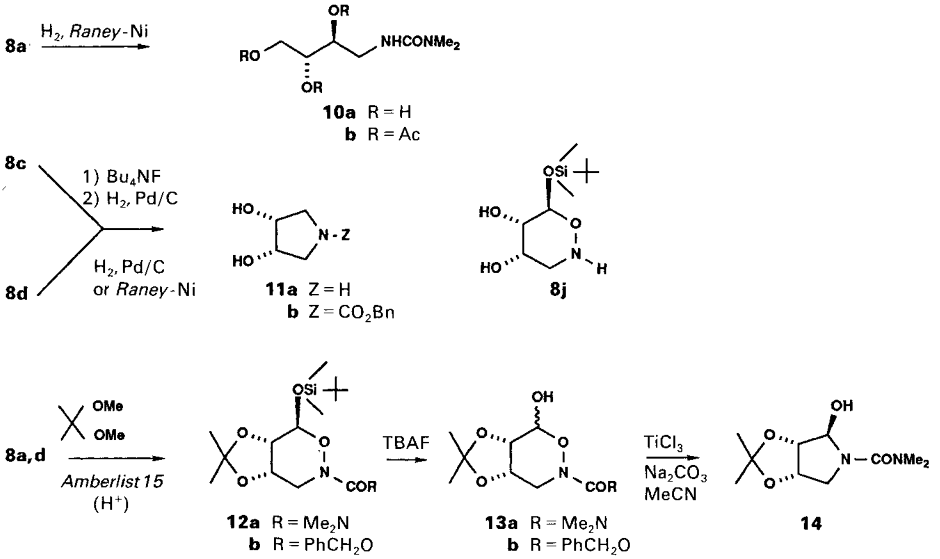
When the regioselectivities observed with the acyclic dienes above are compared with those of 1,2-dihydropyridines [1], two conclusions are apparent: *i*) If R in RCONO (**4**) is an alkoxy or an amino group (**4a, c, d**), the regioselectivities are very similar in both series and are best explained by orbital factors. *ii*) If R is an alkyl or an aryl group, the regioselectivities are markedly different in the two series. Whereas only the inverse adducts are formed from dihydropyridines, the acyclic dienes give direct and inverse adducts. These results point to a pronounced steric interaction between the R and the silyloxy (or MeO) groups, so that the inverse adducts **7** are disfavoured, this steric factor counterbalancing the orbital factor. This is particularly pronounced for R = Ph (see **4b**) where the steric interaction is most pronounced since the conjugation of benzoyl with the N lone-pair is strongest. As a consequence, the inverse adducts **7bα** and **7bβ** are formed as very minor reaction products (*Table 1*).

Bis-hydroxylation to *cis*-Diols 8 and 9. – The crude mixture **6**/**7** of the primary *Diels-Alder* cycloadducts was submitted to bis-hydroxylation with catalytic amounts of OsO_4 in the presence of *N*-methylmorpholine *N*-oxide (NMO) as co-oxidant according to [10]. In all instances, the reaction was stereospecific, each cycloadduct leading to a single *cis*-diol (*Scheme 2*): the direct adducts **6aα, cα, dα** gave diols **8a, c, d**, and the inverse adducts **7cα, dα** led to diols **9c, d**, respectively. The oxidation with OsO_4 is sensitive to steric effects and always takes place *anti* with respect to the silyloxy group, as anticipated from previous results [1] [2] [7]. These diols could easily be separated and purified, either by crystallisation or by chromatography.

Reductive N–O Bond Cleavage of Diols 8a, c, d and 9c, d. – The choice of the best method for reductive cleavage of the N–O bond depends on the nature of the Z groups and on whether the adducts belong to the direct- or to the inverse-adduct series. It appears that the reduction of *O,N*-disubstituted hydroxylamines is usually difficult to achieve [11], the reagents being activated *Raney*-Ni [2] [11], $TiCl_3$ [11], or sodium amalgam [12].

Direct-Adduct Series. Activated *Raney*-Ni in MeOH or EtOH is a powerful reagent which cleaves reductively the N–O bond and reduces the ensuing aldehyde to a primary alcohol. Thus, diol **8a** led directly to the crystalline acyclic 1-amino-1-deoxy-DL-erythritol

Scheme 3

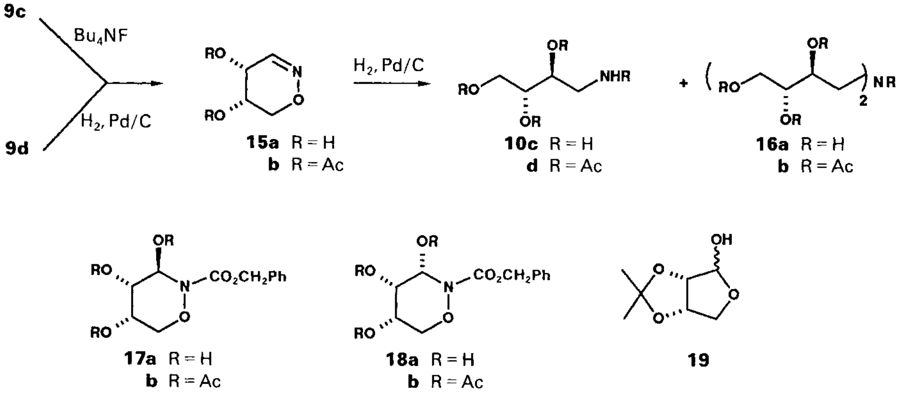


10a which was characterised as such and as its triacetate **10b** (*Scheme 3*). Using a similar methodology, the benzyloxycarbonyl derivative **8d** gave the cyclic 1-amino-1,4-anhydro-1-deoxyerythritol **11a**, a pyrrolidinediol, as the result of hydrogenolysis of the N–O and of the CO_2–CH_2Ph bonds, followed by decarboxylation and intramolecular reductive amination of the aldehyde. The same reaction took place on hydrogenation of **8d** with Pd/C at 40–50°; at room temperature, intermediate **8j** could even be isolated, hydrogenolysis of the benzyl moiety being obviously a fast process. The doubly silylated diol **8c** led to the cyclic diol **11a**, after deprotection with Bu_4NF (the (t-Bu)Me_2SiO group was removed at room temperature after 15 min, the Me_3Si group at 50° only after 5 h) followed by hydrogenolysis/hydrogenation over Pd/C. In all instances, the formation of pyrrolidinediol **11a** was quantitative, this compound being characterized as its *N*-[(benzyloxy)carbonyl] derivative **11b** (*Scheme 3*).

$TiCl_3$ reduction was carried out with diols **8a**, **d** after protection of the OH functions to avoid complexation of the products with the Ti-salts and after removal of the (t-Bu)-Me_2Si group. Thus, acetonides **12a**, **b** were prepared according to [13] and desilylated with Bu_4NF to the hemiacetals **13a** (isomer mixture) and **13b** (single isomer), respectively (*Scheme 3*). N–O bond cleavage of **13a** to give the racemic 4-amino-4-deoxyerythrose **14** was achieved with $TiCl_3$ according to the method of *Mattingly* and *Miller* [11], but using MeCN to which Na_2CO_3 was added instead of H_2O (see *Exper. Part*). When intermediates **12a** and **13a** were not isolated, **14** was formed in 65% overall yield. Single isomer **13b** was not reduced by $TiCl_3$.

Inverse-Adduct Series. Hydrogenolysis (Pd/C) at room temperature of the benzyloxy derivative **9d** was a fast process which was followed immediately by elimination of the silyloxy group to give oxazinediol **15a** as the only product (characterised as diacetate **15b**; *Scheme 4*). Treatment of **9c** with Bu_4NF at 80° in MeCN led to the same oxazinediol **15a**. Catalytic (Pd/C) hydrogenation at 40° of **15a** gave either the acyclic aminotriol **10c**

Scheme 4



(characterized as **10d**) or the iminobis[triol] **16a** (characterized as **16b**), depending on the reaction conditions. Under neutral conditions, **16a** was obtained as a result of reductive condensation of amine **10c** with the short-lived imine intermediate which is first formed on reductive cleavage of the N–O bond of **15a**. This is but another illustration of the well known reductive N-alkylation during catalytic hydrogenolysis of nitriles and oximes [14].

Exhaustive hydrogenolysis (Pd/C) of diol **9d** in EtOH gave directly iminobis[triol] **16a**. The trihydroxy compounds **17a** and **18a**, obtained from **9b** by treatment with Bu$_4$NF and characterized as the acetates **17b** and **18b**, respectively, led analogously to **16a**. In the presence of conc. HCl (4 equiv.), catalytic hydrogenolysis of **9d** (Pd/C) gave the aminotriol **10c** as the only product, whereas in the presence of ammonia (10 equiv.), a mixture **10c**/**16a** was formed.

Structural and Conformational Analyses. – ^{1}H- and ^{13}C-NMR spectroscopy permitted the determination of configurations and conformations of the new products.

Direct Adducts **6aα–6hα, 6aβ, 6bβ** *and Inverse Adducts* **7bα–7hα, 7bβ**. The NMR spectra of **6** and **7** agree with their 3,6-dihydro-2*H*-oxazine structures and are analogous to those reported earlier for similar compounds [2]. ^{1}H-NMR spectroscopy does not allow easy distinction between H–C(3) and H–C(6), the chemical shift of these two H-atoms being very similar (see *Tables 2* and *4*). On the contrary, ^{13}C-NMR spectra permit a clearcut distinction between the two regioisomers: in the direct adducts **6**, the secondary atom C(3) appears at *ca.* 45 ppm and the tertiary atom C(6) at *ca.* 93 ppm; in regioisomers **7**, both C(3) and C(6) appear at *ca.* 70 ppm (see *Tables 3* and *5*).

The conformation of these primary cycloadducts follows from the magnitude of the coupling constants ^3J(H,H) and ^4J(H,H) and is in line with some well documented examples taken from the literature [2] [15]. Coupling constants are very characteristic in the inverse adducts **7** (*Table 4*): ^3J(3,4) and ^3J(5,6′) are *ca.* 4.0–4.5 Hz, ^4J(3,5) and ^4J(4,6′) *ca.* 1.5 Hz; these values clearly indicate that H–C(3) and H′–C(6) are pseudoequatorial. The pseudoaxial H–C(6) appears with $^3J(5,6) = 1.5$–2.0 and $^4J(4,6) = 2.0$–2.5 Hz. This is corroborated by the homoallylic ^5J(3,6): the value is small (*ca.* 0.5 Hz) between two pseudoequatorial H-atoms, but larger (*ca.* 2 Hz) between the pseudoequatorial H–C(3) and the pseudoaxial H–C(6). These cycloadducts have a pseudochair conformation **7A** in which the silyloxy (or methoxy) group is pseudoaxial (see *Scheme 5*).

In the direct adducts **6**, the coupling constants are intermediate in magnitude when compared to those of the inverse adducts **7** (*Tables 2* and *4*). This is due to an equilibrium between the two pseudochair conformations **6A** and **6B**, **6A** being predominant (silyoxy group pseudoaxial; *Scheme 5*). The rather modest ^3J(5,6) values (*ca.* 2 Hz) of the pseudoequatorial acetalic H–C(6) is due to the pronounced electronegativity of the two O-atoms of the acetal functionality which lowers the magnitude of the coupling constant [16]. Such an example has also been described by *Lemieux* and coworkers in the unsaturated pyranose series [17].

Table 2. *^{1}H-NMR Data* ($CDCl_3$) *of the Direct Adducts* **6aα–6iα**, **6aβ**, *and* **6bβ**. 80 MHz, 300 K; δ in ppm, J in Hz; internal standard TMS.

	H−C(3)	H′−C(3)[a])	H−C(4)	H−C(5)	H−C(6)	(*t*-Bu)Si	Me_2Si		Other data	J(3,3′)	J(3,4)	J(3′,4)	J(3,5)	J(3′,5)	J(3,6)	J(3′,6)	J(4,5)	J(4,6)	J(5,6)
6aα	3.82		6.01	5.75	5.54	0.92	0.14	0.16	3.01 (Me_2N)	–	3.3[b])		1.9[b])		1.5[b])		10.0	0.9	2.1
6bα[c])	4.28	4.51	6.02	5.76	5.41	0.79	−0.20	−0.17	7.40, 7.74 (Ph)	18.0	2.7	3.6	2.2	2.2	2.2	1.4	10.3	1.0	2.3
6cα	4.07		5.91	5.77	5.51	0.92	0.19	0.21	1.02, 4.25 ($(CH_2)_2$); 0.04 (Me_3Si)	17.3	3.2[b])		2.4[b])		1.7[b])		10.1	0.9	2.1
6dα	4.10		5.90	5.77	5.50	0.88	0.10	0.13	7.34 (Ph); 5.19 (CH_2)	–	3.2[b])		2.4[b])		1.7[b])		10.1	0.9	2.1
6eα[d])	4.00	4.18	5.93	5.77	5.49	0.92	0.18	0.20	3.76 (MeO)	17.3	2.5	3.9	2.5	2.2	1.8	1.5	10.1	0.9	2.1
6fα	4.06	4.44	5.97	5.76	5.56	0.95	0.20		3.86 (CH_2); 7.29 (Ph)	18.2	2.3	3.5	2.0	1.6	1.6	1.0	10.1	0.7	2.1
6gα	3.95	4.41	5.95	5.74	5.50	0.91	0.16		2.15 (Ac)	17.9	2.4	4.1	2.6	2.1	1.8	1.0	10.3	0.8	2.2
6hα[d])	3.59	3.72	5.91	5.71	5.55	0.90	0.14		7.58, 7.92 (Ph)	15.5	3.1	3.8	2.2	2.1	1.7	1.7	10.0	1.0	2.1
6iα[e])	3.68	3.88	6.09	5.90	5.63	0.93	0.16	0.22	7.30 (H_m); 7.13 (H_o); 6.99 (H_p)	16.1	2.5	4.5	2.5	1.8	1.8	1.1	9.8	1.2	2.5
6aβ	3.85		6.13	5.80	5.08	–	–		3.55 (MeO); 3.03 (MeN)	–	3.3[b])		1.8[b])		1.5[b])		10.2	1.2	2.6
6bβ	4.02	4.93	6.09	5.78	4.89	–	–		2.77 (MeO); 7.70, 7.42 (Ph)	18.4	1.8	4.4	2.3	1.7	2.2	0.7	10.3	0.9	2.9

[a]) H′−C(3) is equatorial and on the same side as the (*t*-Bu)Me_2SiO or MeO group.

[b]) Mean values of coupling constants with H−C(3) and H′−C(3).

[c]) At 400 MHz.

[d]) δ and J values calculated with iteration program Laocoon III (Panic).

[e]) At 250 MHz.

Table 3. *^{13}C-NMR Data* (C_6D_6) *of Direct Adducts* **6aα–6iα**, **6aβ**, *and* **6bβ**. 62.9 MHz, 300 K; δ in ppm, ^1J(C,H) in Hz, internal standard C_6D_6 (128.0 ppm).

	C(3)	C(4),C(5)	C(6)	Me_2Si	Me_3*C*Si	*Me*$_3$CSi	C=O	Other data
6aα	46.3	126.5, 126.7	93.7	–4.6, –4.1	18.3	25.8	161.9	37.7 (Me_2N)
6aα[a])	45.7 (J = 139)	126.2 (J = 163), 126.5 (J = 164)	93.3 (J = 161)	–5.0, –4.5 (J = 118)	17.9	25.9 (J = 124)	161.8	37.7 (Me_2N, J = 136)
6bα	42.1	125.4, 126.5	93.9	–5.8, –4.7	18.2	25.7	169.6	134.7 (C_{ipso}); 130.7 (C_p); 129.7, 128.0 (C_o, C_m)
6bα[a])	42.0 (J = 140)	125.1 (J = 164), 126.7 (J = 165)	93.8 (J = 163)	–6.0, –5.0 (J = 119)	17.9	25.4 (J = 125)	169.8	134.0 (C_{ipso}); 130.6 (C_p); 129.1, 127.8 (C_o, C_m)
6cα	44.6	125.2, 127.6	93.5	–5.1, –4.0	18.3	25.9	155.8	18.0 (OCH_2*C*H_2Si); 64.1 (O*C*H_2CH_2Si)
6dα	44.5	125.0, 127.4	93.5	–5.3, –4.1	18.2	25.8	155.5	67.7 (Ph*C*H_2); 136.6 (C_{ipso}); 128.7, 128.6 (C_o, C_m, C_p)
6eα	44.4	125.1, 127.3	93.4	–5.3, –4.2	18.3	25.8	156.0	52.5 (MeO)
6fα	41.5	125.5, 125.6	93.9	–4.8, –4.1	18.2	25.7	170.0	40.5 (Ph*C*H_2); 135.7 (C_{ipso}); 129.8, 128.6 (C_o, C_m, C_p)
6gα	41.2	125.6, 125.8	93.8	–5.0, –4.2	18.2	25.7	169.7	20.4 (*Me*CO)
6hα	47.2	124.3, 127.8	94.8	–5.2, –4.1	18.2	25.8	–	133.7 (C_{ipso}); 129.8, 128.9 (C_o, C_m, C_p)
6iα	52.0	122.3, 126.0	93.7	–4.6, –3.6	18.3	26.0	–	151.2 (C_{ipso}); 128.4 (C_p); 129.0 (C_m); 116.1 (C_o)
6aβ[a])	44.7 (J = 140)	123.0 (J = 167), 126.9 (J = 165)	99.2 (J = 164)	–	–	–	161.4	56.3 (MeO, J = 143); 36.7 (Me_2N, J = 138)
6bβ[a])	41.1 (J = 142)	122.9 (J = 170), 126.3 (J = 168)	99.9 (J = 166)	–	–	–	169.5	56.3 (MeO); 133.9 (C_{ipso}); 129.9 (C_p); 128.4 (C_o); 127.4 (C_m)

[a]) In $CDCl_3$, 20.1 MHz, internal standard $CDCl_3$ (77.0 ppm).

Table 4. *^1H-NMR Data* (C_6D_6) *of the Inverse Adducts* **7bα**, **7eα**–**7gα**, *and* **7bβ**. 80 MHz, 300 K; δ in ppm, *J* in Hz, internal standard TMS.

	H–C(6)	H'–C(6)[a])	H–C(5)	H–C(4)	H–C(3)	(*t*-Bu)Si	Me$_2$Si	Other data	*J*(6,6')	*J*(5,6)	*J*(5,6')	*J*(4,6)	*J*(4,6')	*J*(3,6)	*J*(3,6')	*J*(4,5)	*J*(3,5)	*J*(3,4)
7bα	3.81	3.55	5.26	5.60	6.32	1.01	0.29	7.15, 7.87 (Ph)	15.6	1.6	4.0	2.2	1.6	2.0	0.6	10.1	0.8	4.0
7eα[b])	3.71	4.15	5.33	5.58	5.83	0.97	0.21	3.46 (MeO)	15.9	1.6	4.3	2.6	1.7	2.1	0.4	10.1	1.0	4.2
7fα	3.62		5.24	5.52	6.05	0.93	0.15 0.18	3.65 (CH_2); 7.15 (Ph)	–	3.1[c])		2.0[c])		1.9	0.6	10.1	0.8	4.1
7gα	3.77	3.62	5.27	5.56	6.09	0.97	0.23	1.92 (Ac)	15.5	1.4	4.4	2.4	1.7	2.1	0.4	10.2	1.1	4.2
7bβ	3.70	3.49	5.23	5.56	5.98	–	–	7.16, 7.84 (Ph); 3.40 (MeO)	16.1	1.7	3.9	2.2	1.6	2.1	0.8	10.3	1.1	4.1

[a]) H'–C(6) is equatorial and *cis* to the (*t*-Bu)Me$_2$SiO or MeO group.

[b]) δ and *J* values are calculated with iteration program Laocoon III (Panic).

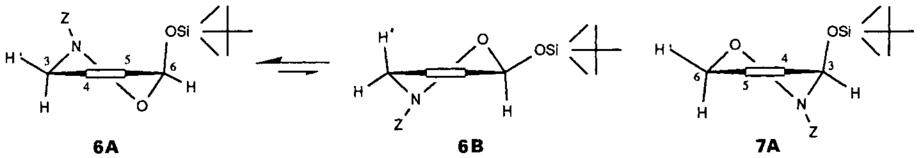
[c]) Mean values of coupling constants with H–C(6) and H'–C(6).

Table 5. *^{13}C-NMR Data* (C_6D_6) *of Inverse Adducts* **7bα**–**7gα**, **7iα**, *and* **7bβ**. 62.9 MHz, 300 K; internal standard C_6D_6 (128.0 ppm).

	C(3)	C(4),C(5)	C(6)	Me$_2$Si	Me$_3$*C*Si	*Me*$_3$CSi	C=O	Other data
7bα[a])	71.6	125.8, 125.5	68.6	–4.9, –4.2	18.2	25.8	168.8	134.6 (C_{ipso}); 131.0 (C_o); 129.2, 128.0 (C_m, C_p)
7cα	74.3	125.6, 125.7	67.9	–4.7, –4.1	18.3	26.0	154.6	17.8 (OCH_2CH_2Si); 64.3 (OCH_2CH_2Si); –1.5 (Me_3Si)
7dα	74.4	125.3, 126.6	68.0	–4.8, –4.2	18.2	25.9	154.5	67.7 ($PhCH_2$); 36.5 (C_{ipso}); 128.6 (C_o, C_m, C_p)
7eα	74.3	125.4, 125.6	67.9	–4.8 [b])	18.3	25.9	154.9	52.6 (MeO)
7fα	70.4	125.8, 126.2	69.0	–4.9, –4.2	18.2	26.0	170.3	39.6 ($PhCH_2$); 135.3 (C_{ipso}); 130.0, 128.6 (C_o, C_m, C_p)
7gα	70.0	125.7, 126.3	68.7	–4.9, –4.2	18.2	26.0	169.2	20.6 (*Me*CO)
7iα	79.6	122.6, 126.3	68.3	–4.1, –3.9	18.4	26.0	–	147.9 (C_{ipso}); 129.0 (C_m); 128.4 (C_p); 118.0 (C_o)
7bβ[a])[c])	77.2	122.7, 127.5	68.8	–	–	–	169.7	55.7 (MeO); 133.2 (C_{ipso}); 131.1 (C_p); 128.5 (C_o); 127.9 (C_m)

[a]) At 20.1 MHz. [b]) Undetermined. [c]) In $CDCl_3$.

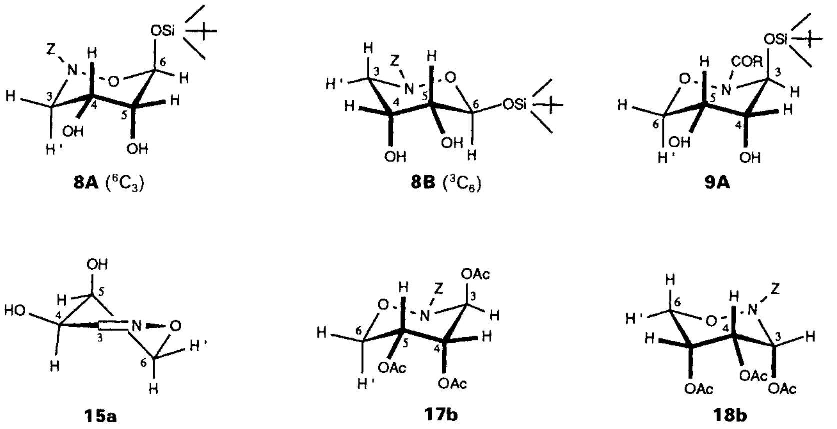
Scheme 5



6A **6B** **7A**

Diols **9c**, **d** *from Inverse Adducts, Triacetates* **17b** *and* **18b**, *and Oxazine* **15a**. Diols **9c**, **d** occur in a well defined chair conformation, the silyloxy group being axial. This clearly follows from an inspection of their ^{1}H-NMR spectra (*Table 6*): *i*) the large coupling (J = 10–11 Hz) between H–C(5) and one of the 2 H–C(6) points to their *trans*-diaxial topology; *ii*) a small $^4J(4,6)$ of 0.5–1.0 Hz (W-long-range coupling) is observed for the other H–C(6) (equatorial); *iii*) a less classical $^5J(3,6)$ (so-called zig-zag coupling) is also observed between 2 equatorial H-atoms for which there is precedence in the literature [18]. The conformation of compounds **9c**, **d** is as indicated in **9A**, the two OH groups being *trans* with respect to the axial silyloxy substituent (*Scheme 6*).

Scheme 6



The isomeric triacetates **17b** and **18b** of triols **17a** and **18a**, respectively, are derivatives of diol **9d**. The ^{1}H-NMR spectrum of **17b** shows coupling constants similar to those of **9c** and **9d** (*Table 6*); it follows that their relative configurations and their conformations are identical (*Scheme 6*). In isomer **18b**, all 3 AcO groups are on the same side, and its conformation (*Scheme 6*) is deduced from its ^{1}H-NMR spectrum (*Table 6*; no large ^3J, *i.e.* no *trans*-diaxial H-atoms; ^4J between H–C(3) and H–C(5) (W long-range coupling), *i.e.* axial orientation of AcO–C(3)).

The structure of oxazine **15a** follows from its method of formation. Its conformation (*Scheme 6*) is ascertained by the J(H,H) values of its diacetate **15b** (*Table 6*; no large ^3J, *i.e.* no *trans*-diaxial H-atoms; small ^3J between olefinic H–C(3) and pseudoaxial H–C(4) and small ^4J between H–C(3) and equatorial H–C(5) (W long-range coupling)).

Diols **8a**, **c**, **d**, **j** *from Direct Adducts*. The diols from the direct adducts are in an equilibrium between the two $^6C_3$ and $^3C_6$ chair conformations **8A** and **8B**, respectively (*Scheme 6*), this equilibrium being dependent upon the nature of the substituent at the N-atom. The coupling constants of the *N*-unsubstituted product **8j** are analogous to those observed for diols **9** (which have a different numbering though). Nevertheless, the largest $J(3,4)$ of **8j** is smaller than $J(5,6_{ax})$ of **9** (*trans*-diaxial). This clearly indicates that in the case of **8j** the $^6C_3$ conformation **8A** is merely predominant in its equilibrium with the $^3C_6$ conformation **8B**, its relative amount being *ca.* 65%[1]). Thus the silyloxy group is predominantly axially oriented, the two OH substituents being *trans* with respect to it. The

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[1]) The borderline values for $J(3,4)$ are taken as follows: $J(H_{ax},H_{ax}) = 11.5$ and $J(H_{eq},H_{eq}) = 1.5$ Hz [19] [20].

Table 6. *^{1}H-NMR Data of Diols* **8** *and* **9** *and of Derivatives* **12a**, **13a,b**, **15b**, **17b**, *and* **18b**. 300 K; δ in ppm, *J* in Hz, internal standard TMS.

	Solvent frequency (MHz)	H–C(3)	H'–C(3)[a]	H–C(4)	H–C(5)	H–C(6)	Me_2Si	*t*-Bu	Other data	*J*(3,3')	*J*(3,4)	*J*(3',4)	*J*(4,5)	*J*(5,6)	Other data
8a	C_6D_6 (250)	2.98	3.80	3.71	3.34	4.82	0.08, 0.09	0.99	2.60 (Me_2N); 4.93 (OH–C(4)); 2.79 (OH–C(5))	14.9	2.4	2.8	3.8	7.4	*J*(4,OH-4) = 6.1, *J*(5,OH-5) = 9.4
8c	C_6D_6 (250)	3.24	4.00	3.64	3.32	5.30	0.28, 0.35	0.99	0.98, 4.27 ($(CH_2)_2$); –0.08 (Me_3Si)	13.8	2.3	4.1	3.4	6.4	*J*(4,OH-4) ~ 2.0, *J*(5,OH-5) ~ 5.0
8d	C_6D_6 (250)	3.18	3.91	3.55	3.30	5.24	0.18, 0.28	0.94	5.09 (CH_2); 7.16 (C_6H_5); 1.92 (OH)	13.8	2.3	4.0	3.4	6.5	
8j	$CDCl_3$/10% CD_3OD (80)	3.16	3.02	3.93	3.63	5.08	0.15	0.93	2.65 (NH,OH_2)	13.8	4.5	8.8	3.4	3.6	*J*(3',5) = 0.6, *J*(3',6) = 1.0
12a	$CDCl_3$ (80)	3.51	3.80	4.40	3.87	5.05	0.14, 0.17	0.92	2.94 (Me_2N); 1.38, 1.51 (Me_2C)	14.3	3.6	2.8	5.5	5.6	
13a (maj.)	$CDCl_3$ (80)	3.59	3.70	4.46	3.95	5.13	–	–	2.95 (Me_2N); 1.39, 1.53 (Me_2C)	14.0	4.0	3.5	5.6	5.4	
13a (min.)	$CDCl_3$ (80)	3.16	3.77	4.52	4.23	5.12	–	–	2.95 (Me_2N); 1.39, 1.53 (Me_2C)	13.3	7.7	6.5	5.5	2.8	
13b	$CDCl_3$ (80)	3.88	3.97	4.36	4.03	5.21	–	–	5.19 ($PhCH_2$); 7.37 (Ph) 1.36, 1.45 (Me_2C)	14.4	4.5	4.5	5.4	4.6	

	Solvent frequency (MHz)	H–C(6)	H'–C(6)[a]	H–C(5)	H–C(4)	H–C(3)	Me_2Si	*t*-Bu	Other data	*J*(6,6')	*J*(5,6)	*J*(5,6')	*J*(4,5)	*J*(3,4)	Other data
9c	C_6D_6 (400)	3.60	3.89	4.01	3.68	5.84	0.19, 0.23	0.96	0.97, 4.30 ($(CH_2)_2$); –0.07 ($SiMe_3$)	10.6	5.4	10.7	2.5	2.6	*J*(5,OH-5) = 7.5, *J*(4,OH-4) = 2.8, *J*(4,6) = *J*(3,6) = 0.5
9d	C_6D_6 (400)	3.53	3.83	3.89	3.82	5.78	0.19, 0.23	0.93	5.11 ($PhCH_2$); 7.03–7.26 (Ph)	10.7	5.4	10.8	2.9	2.2	*J*(5,OH-5) = 7.9, *J*(4,OH-4) = 3.0, *J*(4,6) = *J*(3,6) = 0.8, *J*(3,5) = 0.5
17b	C_6D_6/$CDCl_3$ 1:1 (400)	3.88	4.06	5.40	5.36	6.84	–	–	5.11 ($PhCH_2$); 7.1–7.3 (Ph); 1.72, 1.75, 1.78 (3 Ac)	10.8	5.5	10.0	3.2	3.0	*J*(3,6) = *J*(4,6) = 0.8
18b	C_6D_6/$CDCl_3$ 1:1 (400)	3.68	3.89	5.00	5.05	6.98	–	–	5.04, 5.15 ($PhCH_2$); 7.25 (Ph); 1.83, 1.86, 1.92 (3 Ac)	13.0	1.5	1.8	4.0	4.2	*J*(3,6') = *J*(3,5) = 0.8
15b	C_6D_6 (250)	3.47	3.74	5.01	4.95	6.82	–	–	1.62 (2 Ac)	12.3	1.8	5.0	4.6	1.8	*J*(3,5) = 1.8, *J*(4,6) = 1.8

[a] H' is *cis* to the diol or diacetate moiety.

Table 7. *^{1}H-NMR Data* ($CDCl_3$) *of Amino Sugars and Derivatives* **10b**, **d**, **14**, *and* **19**. 80 MHz, 300 K; δ in ppm, J in Hz, internal standard TMS.

	H–C(1)	H′–C(1)	H–C(2)	H–C(3)	H–C(4)	H′–C(4)	NH	Other data	J(1,1′)	J(1,2)	J(1′,2)	J(2,3)	J(3,4)	J(3,4′)	J(4,4′)	Other data
10b[a])	3.30	3.71	5.08	5.23	4.22	4.32	4.82	2.07, 2.09, 2.11 (3 AcO); 2.90 (Me_2N)	14.6	3.7	5.9	6.7	6.0	3.0	12.2	J(NH,1) = 6.2, J(NH,1′) = 5.2
10d[b])	3.39	3.67	5.08	5.18	4.21	4.31	5.71	2.06, 2.08, 2.10 (3 AcO); 1.97 (AcN)	14.8	3.6	5.8	6.5	5.7	3.3	12.2	J(NH,1) = 6.1, J(NH,1′) = 6.2
14a	5.31	–	4.49	4.80	3.57	3.47		1.31, 1.44 (Me_2C); 2.91 (Me_2N); 4.30 (OH)	–	0	–	6.0	3.8	0.9	11.1	
19 (min., α-L-anomer)	4.98	–	4.47	4.74	3.54	3.96		1.38, 1.54 (Me_2C)	–	3.7	–	6.4	4.0	1.2	11.0	
19 (maj., β-L-anomer)	5.41	–	4.57	4.82	4.07	4.00		1.32, 1.40 (Me_2C)	–	0	–	6.0	3.4	0	10.2	

[a]) At 400 MHz.

[b]) At 250 MHz. Same numbering as for **10b**.

N-substituted diols **8a, c, d** show very similar *J* values which differ markedly from those of the *N*-unsubstituted diol **8j**. Since **8j** is formed by catalytic hydrogenolysis of *N*-[(benzyloxy)carbonyl]-diol **8d**, it follows that the relative configuration of all diols is the same; not so as far as their conformation is concerned! The fact that long-distance *J* values are no longer observed for diols **8a, c, d** is best explained by assuming that the conformational equilibrium is now in favour of the $^3C_6$ chair **8B** (*ca.* 75%)[1]) in which H–C(5) and H–C(6) are axial.

Acyclic Products **10b**, **10d**, *and* **16b**. ^{1}H-NMR spectroscopy permitted the unambiguous determination of the relative configuration of the acyclic products **10b** and **10d** (*Table 7*). Two terminal CH_2 groups can easily be distinguished in **10b, d**, one showing a coupling constant with the amidic *NH* atom. This CH_2NH moiety also shows that the initially present functionality had been drastically reduced. Since the acyclic compounds were formed from the *cis*-diols **8a** and **9c, d**, they are obviously 1-amino-1-deoxy-DL-erythritol derivatives.

The (acetylimino)bis[triacetate] **16b** shows a complex NMR spectrum. Firstly, it is an equimolar (statistical) mixture of the *meso*- and the *rac*-compound. Secondly, each stereoisomer appears as a mixture of two rotamers (AcN) which are no longer symmetrical species. As a consequence, four sets of ^{1}H-NMR peaks appear for each CH_2 H-atom, and in the ^{13}C-NMR spectrum, the signal of each C-atom is a set of four peaks [21].

Pyrrolidines **11a, b** *and* **14**. The structure of pyrrolidinediols **11a, b** is straightforward, since only three peaks appear in the ^{1}H-NMR due to the presence of a plane of symmetry (see *Exper. Part*).

The structure of 4-amino-4-deoxy-erythrose **14** was ascertained by comparing its ^{1}H-NMR spectrum with those of the α- and β-L-anomers of 2,3-*O*-isopropylideneerythrofuranose (**19**) which was prepared according to [22] (see *Table 7*) and whose β-DL-anomer showed the closest NMR relationship with **14**. In particular the absence of any coupling between the anomeric proton and H–C(2) clearly points to a *trans*-relationship [23] and, therefore, to a β-DL-configuration for **14**.

Anomeric Effect and Conformational Analysis. – We demonstrated above the existence of a conformational equilibrium ($^6C_3 \rightleftarrows {}^3C_6$) of the primary adducts **6** and the corresponding diols **8** of the direct-adduct series (*Schemes 5* and *6*). In contrast, adducts **7** and the corresponding diols **9** of the inverse-adduct series occur in a unique conformation in which the silyloxy or the MeO–C(3) group are either pseudoaxial (**7**) or axial (**9**). This latter observation is to be related to the very pronounced anomeric effect of *N*-acylated piperidine aminosugars in which the anomeric substituent is *always* axial [1] [20c]. Clearly the anomer effect is much more pronounced in piperidine than in pyranose sugars, an observation we had already described previously [2].

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Experimental Part

General. Raney-Ni (slurry in H_2O), $(Pr_4N)IO_4$, Pd/C catalysts (5 and 10%), acetohydroxamic acid (**3g**; *purum*), benzenesulfonohydroxamic acid (**3h**), Bu_4NF, 2,2-dimethoxypropane, and benzyl chloroformate were purchased from *Fluka*, (*t*-Bu)Me_2SiCl from *Aldrich*, crotonaldehyde from *Merck*, and NaI from *Prolabo*; NaI was made anhydrous by melting and then kept over P_2O_5 in a dessicator. Anh. MeCN was kept over CaH_2 under Ar. Et_3N was distilled and then kept under Ar in the presence of 4-Å molecular sieves. The usual solvents were freshly distilled. The chlorinated ones were kept over Na_2CO_3.

Flash chromatography (FC): silica gel (*Merck 60*, 230–400 mesh). TLC: Al roll silica gel (*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: *Bruker WP-80-DS*, *AC-F-250*, and *VM-400* using double-irradiation techniques; tetramethylsilane TMS (^{1}H-NMR) and $CDCl_3$ or C_6D_6 ($\delta(CDCl_3) = 77.0$ or $\delta(C_6D_6) = 128.0$ with respect to TMS; ^{13}C-NMR) as internal references; δ in ppm and *J* in Hz. High resolution (HR) MS were measured on a *MAT-311* spectrometer at the University of Rennes. Microanalyses were carried out by the Service Central de Microanalyses of the CNRS, Vernaison.

Hydroxamic Acids. – *Phenylacetohydroxamic Acid* (**3f**), *Methyl* N-*Hydroxycarbamate* (**3e**), *and* N,N-*Dimethylcarbamohydroxamic Acid* (**3a**) were prepared according to [1].

Benzohydroxamic Acid (**3b**) *and Benzyl* N-*Hydroxycarbamate* (**3d**) were prepared according to [24] with some modifications as follows. **3b**: To a stirred mixture of $NH_2OH \cdot HCl$ (69.2 g, 1 mol, 1.4 equiv.) and K_2CO_3 (119 g, 0.86 mol, 1.2 equiv.) in Et_2O (0.5 l) and H_2O (10 ml) at 0° was added dropwise benzoyl chloride (82.5 ml, 100 g, 0.71 mol). This soln. was left at r.t. overnight. The Et_2O soln. was separated and the solid phase extracted several times with boiling AcOEt. After evaporation of the combined org. solvents, the crude residue was recrystallised in AcOEt: **3b** (79 g, 87%). M.p. 128–130° ([25]: 125–128°).

3d: To a stirred mixture of $NH_2OH \cdot HCl$ (22.6 g, 0.33 mol, 1.1 equiv.) and K_2CO_3 (43.5 g, 0.31 mol, 1.05 equiv.) in Et_2O (0.3 l) and H_2O (5 ml) at 0° was added dropwise benzyl chloroformate (43 ml, 51.5 g, 0.30 mol). This soln. was stirred at r.t. overnight and then filtered, the solid residues being washed with Et_2O. The Et_2O soln. was evaporated and the crude residue recrystallized in toluene/cyclohexane 3:2: **3d** (36.8 g, 73%). M.p. 67–68° ([26]: 67–68°).

2-(Trimethylsilyl)ethyl N-*Hydroxycarbamate* (**3c**) was prepared according to the method describe for **3d** [27].

Dienes. – *1-Methoxybuta-1,3-diene* (**5β**) was prepared according to [22].

*1-{[(*tert*-Butyl)dimethylsilyl]oxy}buta-1,3-diene* (**5α**). To a stirred soln. of crotonaldehyde (5.5 ml, 66 mmol), Et_3N (10 ml, 65 mmol) and (*t*-Bu)$SiMe_2Cl$ (10 g, 65 mmol) in anh. MeCN (10 ml) was added dropwise a soln. of NaI (10.5 g, 70 mmol) in anh. MeCN (50 ml). After 7 h at 50°, the mixture was poured onto ground ice (150 g) and extracted with pentane (4 × 80 ml). The org. soln. was washed with aq. sat. NH_4Cl soln. until neutrality, dried ($MgSO_4$), and evaporated. The crude liquid was distilled under vacuum: **5α** (10.2 g, 84%). B.p. 66–68°/13 Torr. IR (CCl_4): 2940, 2930, 2890, 2860, 1645, 1465, 1255, 995, 915, 885, 820, 730. ^1H-NMR (80 MHz, $CDCl_3$): 6.53 (*m*, H–C(1)); 6.19 (*m*, H–C(3)); 5.70 (*m*, H–C(2)); 4.95 (*m*, H–C(4)); 4.78 (*m*, H'–C(4)); *J*(1,2) = 12.0, *J*(1,3) = 0.7, *J*(1,4) = 0.7, *J*(1,4') = 0.6, *J*(2,3) = 10.9, *J*(2,4) = 0.6, *J*(2,4') = 0.3, *J*(3,4) = 17.0, *J*(3,4') = 10.3, *J*(4,4') = 1.9. ^{13}C-NMR (62.9 MHz, $CDCl_3$): −5.2 (Me_2Si); 18.3 (Me_3CSi); 25.6 (Me_3CSi); 111.7 (C(4)); 114.4 (C(3)); 133.4) (C(2)); 145.3 (C(1)). MS: 184 (16), 147 (22), 127 (71), 103 (2), 75 (100). HR-MS: 184.1276 ($C_{10}H_{20}OSi$, calc. 184.1283).

***Diels-Alder* Cycloadducts.** – *General Procedure for Acylnitroso Dienophiles.* To a stirred soln. of a diene **5** (1 g) in CH_2Cl_2 (10 ml) at 0° and containing some 4 Å molecular sieves and $(Pr_4N)IO_4$ (0.3 equiv.) was added portionwise a hydroxamic acid **3** (1 equiv.; for quantities larger than 1 g a soln. of the hydroxamic acid in CH_2Cl_2 was added dropwise to the preceding soln.). After 1 h, some Et_2O was added and the soln. treated with 1M Na_2CO_3, then with Na_2SO_3 (reduction of I_2), and then washed with H_2O. The aq. solns. were extracted with Et_2O, and the combined org. soln. was dried ($MgSO_4$) and evaporated. The oily residue was submitted to ^1H- and ^{13}C-NMR to determine the relative amounts of cycloadducts.

*6-{[(*tert*-Butyl)dimethylsilyl]oxy}-3,6-dihydro-*N,N*-dimethyl-2*H*-1,2-oxazine-2-carboxamide* (**6aα**). To **5α** (0.50 g, 2.74 mmol) in CH_2Cl_2 (5 ml) were added $(Pr_4N)IO_4$ (0.35 g, 0.92 mmol) and **3a** (0.29 g, 2.76 mmol). Adduct **6aα** (0.75 g, 91%) was purified by FC (AcOEt/cyclohexane 3:7): colourless oil (0.63 g, 80%). IR (CCl_4): 2940, 2925, 1675, 1660, 1395, 1255, 1195, 1065, 1035, 835. ^1H-NMR: *Table 2*. ^{13}C-NMR: *Table 3*. MS: 286 (2), 269 (4), 229 (4), 214 (4), 155 (2), 127 (29), 72 (100), 57 (9). HR-MS: 286.1755 ($C_{13}H_{26}N_2O_3Si$, calc. 286.1712).

*2-Benzoyl-6-{[(*tert*-butyl)dimethylsilyl]oxy}-3,6-dihydro-2*H*-1,2-oxazine* (**6bα**) *and 2-Benzoyl-3-{[(*tert*-butyl)dimethylsilyl]oxy}-3,6-dihydro-2*H*-1,2-oxazine* (**7bα**). To **5α** (0.11 g, 0.58 mmol) in CH_2Cl_2 (1 ml) were added $(Pr_4N)IO_4$ (80 mg, 0.25 mmol) and **3b** (80 mg, 0.58 mmol). The adducts (0.14 g, 76%) were separated and purified by FC (AcOEt/hexane 3:7): **6bα** (0.11 g, 60%) as yellow oil and **7bα** (10 mg, 6%) as yellow oil which was unstable on silica gel.

6bα: IR (CCl_4): 2950, 2920, 1660, 1645, 1390, 1255, 1240, 1190, 1180, 1105, 1025, 835, 700. ^1H-NMR: *Table 2*. ^{13}C-NMR: *Table 3*. MS: 319 (1), 262 (4), 214 (2), 127 (16), 105 (100), 77 (55), 57 (6). HR-MS: 319.1596 ($C_{17}H_{25}NO_3Si$, calc. 319.1603).

7bα: IR (CCl_4): 2940, 2920, 1670, 1650, 1400, 1370, 1340, 1250, 1130, 1075, 880, 840, 690. ^1H-NMR: *Table 4*. ^{13}C-NMR: *Table 5*. MS: 319 (1), 304 (2), 262 (36), 127 (18), 105 (100), 77 (36), 57 (9). HR-MS: 319.1577 ($C_{17}H_{25}NO_3Si$, calc. 319.1603).

*2-(Trimethylsilyl)ethyl 6-{[(*tert*-Butyl)dimethylsilyl]oxy}-3,6-dihydro-2*H*-1,2-oxazine-2-carboxylate* (**6cα**) *and 2-(Trimethylsilyl)ethyl 3-{[(*tert*-Butyl)dimethylsilyl]oxy}-3,6-dihydro-2*H*-1,2-oxazine-2-carboxylate* (**7cα**). To **5α** (2.02 g, 10.95 mmol) in CH_2Cl_2 (8 ml) were added $(Pr_4N)IO_4$ (1.93 g, 5.12 mmol) and **3c** (1.94 g, 10.96 mmol): **6cα**/**7cα** as yellow oil (3.82 g, 97%) which was not separated and used as such for *cis*-hydroxylation (see below). IR (CCl_4): 2980, 2970, 2950, 2930, 1740, 1705, 1475, 1465, 1415, 1400, 1365, 1330, 1255, 1220, 1185, 1150, 1115, 1040, 945, 860, 845, 790. ^1H-NMR: *Table 2*. ^{13}C-NMR: *Tables 3* and *5*.

*Benzyl 6-{[(*tert*-Butyl)dimethylsilyl]oxy}-3,6-dihydro-2*H*-1,2-oxazine-2-carboxylate* (**6dα**) *and Benzyl 3-{[(*tert*-Butyl)dimethylsilyl]oxy}-3,6-dihydro-2*H*-1,2-oxazine-2-carboxylate* (**7dα**). To **5α** (1.5 g, 8.13 mmol) in CH_2Cl_2 (30 ml) were added $(Pr_4N)IO_4$ (1.03 g, 2.73 mmol) and **3d** (1.36 g, 8.16 mmol): **6dα**/**7dα** as a yellow oil (2.64 g, 93%) which was purified by FC (AcOEt/cyclohexane 1:9) leading to **6dα** (68%). Crude **6dα**/**7dα** was used for *cis*-hydroxylation (see below). IR (**6dα**/**7dα**): 2940, 2920, 2840, 1740, 1710, 1390 1350, 1250, 1215, 1120, 1035, 840,

700. ^{1}H-NMR: *Table 2.* ^{13}C-NMR: *Tables 3* and *5.* MS: 292 (1), 248 (15), 184 (4), 174 (5), 143 (5), 127 (15), 91 (100), 75 (36), 73 (10), 65 (5). HR-MS: 349.1701 ($C_{18}H_{27}NO_4Si$, calc. 349.1709).

*Methyl 6-{[(*tert*-Butyl)dimethylsilyl]oxy}-3,6-dihydro-2*H*-1,2-oxazine-2-carboxylate* (**6eα**) *and Methyl 3-{[(*tert*-Butyl)dimethylsilyl]oxy}-3,6-dihydro-2*H*-1,2-oxazine-2-carboxylate* (**7eα**). To **5α** (0.16 g, 0.86 mmol) in CH_2Cl_2 (1 ml) were added $(Pr_4N)IO_4$ (0.12 g, 0.31 mmol) and **3e** (0.13 g, 1.39 mmol). Adducts **6eα**/**7eα** (0.22 g, 91%) were purified by FC (CH_2Cl_2) and separated by prep. TLC (AcOEt/hexane 3:7).

6eα: Colourless oil. IR (CCl_4): 2950, 1750, 1710, 1450, 1385, 1255, 1220, 1195, 1180, 1115, 1035, 840. ^{1}H-NMR: *Table 2.* ^{13}C-NMR: *Table 3.* HR-MS: 273.1390 ($C_{12}H_{23}NO_4Si$, calc. 273.1396).

7eα: Colourless oil. IR (CCl_4): 2910, 2860, 1745, 1715, 1450, 1375, 1340, 1310, 1255, 1110, 1080, 1050, 840. ^{1}H-NMR: *Table 4.* ^{13}C-NMR: *Table 5.* MS: 289 (5), 258 (13), 216 (100), 148 (13), 142 (30), 127 (9). HR-MS: 258.1019 ($C_{11}H_{20}NO_4Si$, $[M - CH_3]^+$, calc. 258.1161).

*6-{[(*tert*-Butyl)dimethylsilyl]oxy}-3,6-dihydro-2-(phenylacetyl)-2*H*-1,2-oxazine* (**6fα**) *and 3-{[(*tert*-Butyl)dimethylsilyl]oxy}-3,6-dihydro-2-(phenylacetyl)-2*H*-1,2-oxazine* (**7fα**). To **5α** (0.12 g, 0.62 mmol) in CH_2Cl_2 (1 ml) were added $(Pr_4N)IO_4$ (83 mg, 0.22 mmol) and **3f** (95 mg, 0.63 mmol). Adducts **6fα**/**7fα** (0.15 g, 72%) were purified and separated by FC (CH_2Cl_2).

6fα: Colourless crystals. M.p. 62° (pentane). IR (CCl_4): 2930, 1670, 1650, 1430, 1390, 1260, 1220, 1200, 1110, 1025, 835, 780, 730. ^{1}H-NMR: *Table 2.* ^{13}C-NMR: *Table 3.* MS: 333 (7), 276 (18), 208 (13), 184 (19), 158 (22), 127 (42), 91 (100), 75 (31), 57 (5). HR-MS: 333.1912 ($C_{18}H_{27}NO_3Si$, calc. 333.1760). Anal. calc. for $C_{18}H_{27}NO_3Si$ (333.50): C 64.83, H 8.16, N 4.20, Si 8.42; found: C 65.1, H 8.1, N 4.1, Si 7.9.

7fα: Yellow oil. IR (CCl_4): 2960, 2940, 2900, 2860, 1675, 1665, 1405, 1380, 1250, 1190, 1070, 1050, 860, 840, 780. ^{1}H-NMR: *Table 4.* ^{13}C-NMR: *Table 5.* MS: 318 (2), 276 (100), 208 (16), 193 (8), 143 (5), 127 (13), 91 (82), 75 (96), 65 (9). HR-MS: 318.1579 ($C_{17}H_{24}NO_3Si$, $[M - CH_3]^+$, calc. 318.1525).

*2-Acetyl-6-{[(*tert*-butyldimethyl)silyl]oxy}-3,6-dihydro-2*H*-1,2-oxazine* (**6gα**) *and 2-Acetyl-3-{[(*tert*-butyl)dimethylsilyl]oxy}-3,6-dihydro-2*H*-1,2-oxazine* (**7gα**). To **5α** (0.10 g, 0.55 mmol) in CH_2Cl_2 (1 ml) were added $(Pr_4N)IO_4$ (68 mg, 0.16 mmol) and **3g** (45 mg, 0.6 mmol). Adducts **6gα**/**7gα** were purified by FC (AcOEt/CH_2Cl_2 5:95).

6gα (44 mg, 31%): Yellow oil. IR (CCl_4): 2950, 2930, 1680, 1660, 1395, 1260, 1225, 1110, 1030, 840. ^{1}H-NMR: *Table 2.* ^{13}C-NMR: *Table 3.* MS: 257 (3), 200 (19), 184 (11), 158 (16), 140 (7), 132 (32), 127 (74), 113 (5), 103 (29), 99 (11), 83 (11), 75 (100). HR-MS: 257.1466 ($C_{12}H_{23}NO_3Si$, calc. 257.1447).

7gα (28 mg, 20%): Yellow oil. IR (CCl_4): 2940, 2910, 1685, 1400, 1380, 1255, 1080, 860, 840. ^{1}H-NMR: *Table 4.* ^{13}C-NMR: *Table 5.* MS: 200 (62), 142 (5), 132 (49), 127 (19), 117 (12), 99 (5), 84 (11), 75 (100), 69 (12). HR-MS: 242.1217 ($C_{11}H_{20}NO_3Si$, $[M - CH_3]^+$, calc. 242.1212).

*6-{[(*tert*-Butyl)dimethylsilyl]oxy}-3,6-dihydro-2-(phenylsulfonyl)-2*H*-1,2-oxazine* (**6hα**). To **5α** (0.14 g, 0.78 mmol) in CH_2Cl_2 (1 ml) were added $(Pr_4N)IO_4$ (99 mg, 0.26 mmol) and **3h** (0.13 g, 0.78 mmol). Adduct **6hα** was purified by FC (AcOEt/hexane 1:1): yellow oil (0.14 g, 50%). IR (CCl_4): 2910, 2875, 2850, 1450, 1390, 1375, 1175, 835. ^{1}H-NMR: *Table 2.* ^{13}C-NMR: *Table 3.* MS: 355 (17), 325 (19), 215 (17), 141 (27), 77 (100), 57 (15). HR-MS: 354.9792 ($C_{16}H_{25}NO_4SSi$, calc. 355.1273).

*6-{[(*tert*-Butyl)dimethylsilyl]oxy}-3,6-dihydro-2-phenyl-2*H*-1,2-oxazine* (**6iα**) *and 3-{[(*tert*-Butyl)dimethylsilyl]oxy}-3,6-dihydro-2-phenyl-2*H*-1,2-oxazine* (**7iα**). To **5α** (0.19 g, 1.01 mmol) in CH_2Cl_2 (1.5 ml) was added PhNO (99 mg, 0.92 mmol). After 6 h at r.t. and evaporation, the crude mixture was separated by prep. TLC (AcOEt/cyclohexane 3:7).

7iα: Unstable, decomposition during isolation. It was characterised by its ^{13}C-NMR in the crude residue of the adducts. ^{13}C-NMR: *Table 5.*

6iα: Yellow oil (146 mg, 81%). IR ($CHCl_3$): 2960, 2930, 2860, 1600, 1490, 1290, 1110, 1090, 1065, 1040, 1000, 835, 780, 755. ^{1}H-NMR: *Table 2.* ^{13}C-NMR: *Table 3.* MS: 291 (10), 223 (1), 234 (10), 184 (59), 159 (7), 148 (6), 127 (100), 113 (8), 101 (8), 99 (10), 77 (18), 75 (80), 73 (32), 59 (7), 51 (7). HR-MS: 291.1666 ($C_{16}H_{25}NO_2Si$, calc. 291.1654).

*3,6-Dihydro-6-methoxy-*N,N*-dimethyl-2*H*-1,2-oxazine-2-carboxamide* (**6aβ**). To **5β** (0.19 g, 2.26 mmol) in CH_2Cl_2 (2.5 ml) were added $(Pr_4N)IO_4$ (0.286 g, 0.76 mmol) and **3a** (0.236 g, 2.36 mmol). Crude **6aβ** (0.36 g, 85%) was purified by FC (CH_2Cl_2): yellow oil. IR (CCl_4): 1675, 1660, 1488, 1390, 1195, 1108, 1062, 1030. ^{1}H-NMR: *Table 2.* ^{13}C-NMR: *Table 3.* HR-MS: 186.1012 ($C_8H_{14}N_2O_3$, calc. 186.1004).

*2-Benzoyl-3,6-dihydro-6-methoxy-2*H*-1,2-oxazine* (**6bβ**) *and 2-Benzoyl-3,6-dihydro-3-methoxy-2*H*-1,2-oxazine* (**7bβ**). To **5β** (1.22 g, 14.5 mmol) in CH_2Cl_2 (10 ml) were added $(Pr_4N)IO_4$ (1.65 g, 4.4 mmol) and **3b** (1.83 g, 13.3 mmol). The crude **6bβ**/**7bβ** (2.5 g, 83%) were purified and separated by FC (CH_2Cl_2).

6bβ (1.06 g, 35%): Colourless crystals. M.p. 98–99° ((i-Pr)$_2$O). IR (KBr): 2940, 2820, 1628, 1600, 1450, 1430, 1235, 1110, 1020, 827, 782, 610, 598. ^{1}H-NMR: *Table 2.* ^{13}C-NMR: *Table 3.* Anal. calc. for $C_{12}H_{13}NO_3$ (219.23): C 65.74, H 5.98, N 6.39; found: C 65.5, H 6.0, N 6.4.

7bβ (0.6 g, 18%): Yellow oil. IR (CCl_4): 1665, 1650, 1368, 1190, 1080, 1045, 865, 695. ^1H-NMR: *Table 4.* ^{13}C-NMR: *Table 5.* HR-MS: 219.0891 ($C_{12}H_{13}NO_3$, calc. 219.0895).

Bicyclic Diols and Their Acetates. – *General Procedure for* cis-*Hydroxylation.* The catalyst was prepared according to [28] from OsO_4 (1 g) and 1 ml of 70% *t*-BuOOH in 200 ml of *t*-BuOH. The *cis*-hydroxylation was performed according to [10]: To a stirred soln. of oxazine **6** or **6/7** (10 mmol) in 16 ml of acetone/H_2O 5:3 at 0° were added *N*-methylmorpholine *N*-oxide hydrate (NMO; 2.0 g, 1.5 mmol) and the catalyst soln. (2–10 ml). The mixture was kept at r.t. or at 40° overnight, treated with a few ml of an aq. sulfite soln., neutralised with 5N H_2SO_4 (*ca.* 2 ml), and extracted with AcOEt and with AcOEt/acetone 1:1. The combined org. soln. was washed with brine, dried ($MgSO_4$), and evaporated.

General Procedure for Acetylation. The diol was acetylated overnight in pyridine (8 ml, 0.1 mol) with Ac_2O (4.08 g, 0.04 mol, 4 equiv.). Excess Ac_2O was distroyed with MeOH and after evaporation and addition of toluene, the soln. was evaporated again.

t-*6-{[(*tert-*Butyl)dimethylsilyl]oxy}-*r-*4,*c-*5-dihydroxy-*N,N-*dimethyl-1,2-oxazinane-2-carboxamide* (**8a**). To **6aα** (1.29 g, 4.5 mmol) in acetone (5 ml) and H_2O (3 ml) were added NMO (0.93 g, 6.8 mmol) and the catalyst soln. (1 ml). Standard workup gave **8a** (1.28 g, 88%). Colourless crystals. M.p. 109–110° (AcOEt/i-Pr_2O). IR (KBr): 3250, 2910, 2840, 1645, 1455, 1395, 1250, 1160, 1120, 1050, 1025, 860, 830, 770. ^1H-NMR: *Table 6.* Anal. calc. for $C_{13}H_{28}N_2O_5Si$ (320.46): C 48.72, H 8.81, N 8.74, Si 8.76; found: C 48.8, H 8.8, N 8.6, Si 8.5.

Diacetate of **8a**: Colourless crystals. M.p. 79° (AcOEt/cyclohexane 3:7). IR (KBr): 2920, 1740, 1650, 1370, 1235, 1220, 1150, 1120, 1060, 835, 780. ^1H-NMR ($CDCl_3$, 80 MHz): 3.65 (*m*, 2 H–C(3)); 5.43 (*m*, H–C(4)); 4.92 (*dd*, H–C(5)); 5.22 (*d*, H–C(6)); 2.94 (*s*, Me_2N); 2.05 (*s*, Ac); 2.09 (*s*, Ac); 0.92 (*s*, *t*-Bu); 0.18, 0.17 (2*s*, Me_2Si); $J(3,4) = 5.9$, $J(4,5) = 3.5$, $J(5,6) = 4.4$. MS: 347 (5), 344 (3), 200 (6), 143 (12), 117 (9), 101 (8), 72 (100), 59 (3). HR-MS: 404.2224 ($C_{17}H_{32}N_2O_7Si$, calc. 404.1978). Anal. calc. for $C_{17}H_{32}N_2O_7Si$: C 50.47, H 7.97, N 6.92, Si 6.94; found: C 50.5, H 8.1, N 6.8, Si 6.9.

2-(Trimethylsilyl)ethyl t-*6-{[(*tert-*Butyl)dimethylsilyl]oxy}-*r-*4,*c-*5-dihydroxy-1,2-oxazinane-2-carboxylate* (**8c**) *and 2-(Trimethylsilyl)ethyl* r-*3-{[(*tert-*Butyl)trimethylsilyl]oxy}-*t-*4,*t-*5-dihydroxy-1,2-oxazinane-2-carboxylate* (**9c**). To crude **6cα/7cα** (3.8 g, 10.6 mmol) in acetone (12 ml) and H_2O (6 ml) were added NMO (2.24 g, 16.6 mmol) and the catalyst soln. (10.5 ml, 0.2 mmol). After 6 h at 40°, the crude **8c/9c** (4.1 g, 99%) were separated and purified by fractional crystallisation and medium-pressure column chromatography ($CHCl_3$/AcOEt 6:4).

8c: Colourless crystals (2.2 g, 55%). M.p. 99° (hexane). IR (KBr): 3540, 3460–3100, 2950, 2925, 1700, 1460, 1250, 1225, 1120, 1050, 940, 885, 845, 780. ^1H-NMR: *Table 6.* Anal. calc. for $C_{16}H_{35}NO_6Si_2$ (393.62): C 48.82, H 8.96, N 3.56, Si 14.27; found: C 49.0, H 9.1, N 3.6, Si 13.1.

9c: Colourless crystals (0.95 g, 23%). M.p. 68° (hexane). IR (KBr): 3500, 3460, 2960, 2940, 1690, 1395, 1350, 1255, 1115, 1080, 870, 840. ^1H-NMR: *Table 6.* Anal. calc. for $C_{16}H_{35}NO_6Si_2$ (393.62): C 48.82, H 8.96, N 3.56, Si 14.27; found: C 49.1, H 9.2, N 3.5, Si 12.7.

Benzyl t-*6-{[(*tert-*Butyl)dimethylsilyl]oxy}-*r-*4,*c-*5-dihydroxy-1,2-oxazinane-2-carboxylate* (**8d**) *and Benzyl* r-*3-{[(*tert-*Butyl)dimethylsilyl]oxy}-*t-*4,*t-*5-dihydroxy-1,2-oxazinane-2-carboxylate* (**9d**). To the crude **6dα/7dα** (2.64 g, 7.6 mmol) in acetone (6 ml) and H_2O (5 ml) were added NMO (1.49 g, 11.0 mmol) and the catalyst soln. (4 ml, 0.08 mmol). After 4d at r.t., the crude **8d/9d** (2.56 g, 90%) were separated and purified by fractional crystallisation (petroleum ether/C_6H_6). Separation was also achieved by prep. TLC (Et_2O).

8d: Colourless crystals. M.p. 88° (cyclohexane). IR (KBr): 3480, 3430, 2940, 1680, 1430, 1370, 1250, 1205, 1150, 1110, 1010, 970, 780. ^1H-NMR: *Table 6.* Anal. calc. for $C_{18}H_{29}NO_6Si$ (383.51): C 56.37, H 7.62, N 3.65, Si 7.32; found: C 56.4, H 7.4, N 3.6, Si 7.1.

9d: Colourless crystals. M.p. 109° (benzene/petroleum ether). IR (KBr): 3420, 3320, 2950, 1690, 1455, 1410, 1110, 1080, 1025, 1010, 870, 845, 780. ^1H-NMR: *Table 6.* Anal. calc. for $C_{18}H_{29}NO_6Si$ (383.51): C 56.37, H 7.62, N 3.65, Si 7.32; found: C 56.6, H 7.7, N 4.0, Si 7.6.

t-*6-{[(*tert-*Butyl)dimethylsilyl]oxy}-1,2-oxazinane-*r-*4,*c-*5-diol* (**8j**). A stirred soln. of **8d** (140 mg; 0.36 mmol) in abs. EtOH (10 ml), to which 5% Pd/C (53 mg) had been added, was put under H_2 (1 atm) for 30 min at r.t. After filtration over *Celite* and evaporation, **8j** (70 mg, 70%) was obtained as colourless crystals (AcOEt). M.p. 127°. IR (KBr): 3410, 3100, 2920, 1440, 1350, 1250, 1120, 1080, 1050, 835, 775. ^1H-NMR: *Table 6.* Anal. calc. for $C_{10}H_{23}NO_4$ (249.38): C 48.16, H 9.30, N 5.62, Si 11.26; found: C 48.2, H 9.4, N 5.6, Si 10.9.

1-Amino-1-desoxy-DL-erythritol Derivatives. – *Activated* Raney-*Ni.* Moist *Raney*-Ni was weighted and immediately put in 96% EtOH. This suspension was stirred under H_2 after 3 degassing procedures. The whole process was repeated 3 times with abs. EtOH.

N,N-*Dimethyl-*N′-*[(2*RS*,3*SR*)-2,3,4-trihydroxybutyl]urea* (**10a**). A stirred soln. of **8a** (0.30 g, 0.93 mmol) in abs. EtOH (6 ml), to which activated *Raney*-Ni (1.2 g weighted humid) had been added, was kept under H_2 (1 atm) overnight at r.t. After filtration over *Celite* and evaporation **10a** (0.17 g, 95%) was crystallised and washed with Et_2O. Colourless crystals. M.p. 110° ($EtOH/Et_2O$). IR (KBr): 3600–3000, 2930–2880, 1600, 1540, 1440, 1370, 1350, 1320, 1230, 1060, 1025. Anal. calc. for $C_7H_{16}N_2O_4$ (192.21): C 43.74, H 8.39, N 14.58; found: C 43.8, H 8.6, N 14.3.

Triacetate **10b** *of* **10a**: Yellow oil. IR (CCl_4): 3400, 2940, 1740, 1640, 1535, 1370, 1220, 1050, 770. ^1H-NMR: *Table 7*. MS: 319 (2), 318 (1), 198 (8), 156 (5), 143 (9), 115 (2), 101 (33), 72 (84), 43 (100). HR-MS: 318.1527 ($C_{13}H_{22}N_2O_7$, calc. 318.1427).

*(2*RS,*3*SR*)-4-(Acetylamino)butane-1,2,3-triyl Triacetate* (**10d**). Diol **9d** (62 mg, 0.16 mmol) in abs. EtOH (1 ml) and conc. HCl (0.1 ml, 1.2 mmol) was hydrogenolysed over 10% Pd/C (96 mg) for 3 d at r.t. under H_2. The mixture was filtered over *Celite*, the soln. evaporated, and the oily residue (34 mg) treated with Ac_2O (0.21 ml, 2.2 mmol) in pyridine (0.45 ml, 5.6 mmol). After evaporation of the reagents, the residue was purified by prep. TLC (AcOEt/EtOH 8:2): **10d** (27 mg, 60%). Colourless crystals. M.p. 108° (Et_2O). IR (neat): 3300, 3080, 2960, 1740, 1655, 1545, 1430, 1370, 1220, 1050. ^1H-NMR: *Table 7*. HR-MS: 290.1274 ($C_{12}H_{20}NO_7$, $[M + H]^+$, calc. 290.1240).

cis-*Pyrrolidine-3,4-diol* (**11a**) *and Benzyl* cis-*3,4-Dihydroxypyrrolidine-1-carboxylate* (**11b**). a) *From* **8c**. A soln. of Bu_4NF (1.66 g, 4.6 mmol) and **8c** (0.6 g, 1.5 mmol) in MeCN (2 ml) was heated for 5 h at 50° under Ar. After evaporation, a brown sirup (2.31 g) was obtained. Catalytic hydrogenation (1 atm) of this sirup (1.34 g) in abs. EtOH (2 ml) over 10% Pd/C (109 mg) at 40° overnight, followed by centrifugation and evaporation of the solvents, gave a brown sirup (1.07 g) to which 10% aq. $NaHCO_3$ soln. (1.5 ml) was added. To the resulting mixture, kept at 0°, was added dropwise benzyl chloroformate (0.21 ml, 1.5 mmol). After 1.5 h, the mixture was diluted with AcOEt (20 ml), the org. phase dried ($MgSO_4$) and evaporated, and the residue purified by FC (AcOEt): **11b** as yellow oil (61 mg, 34% overall from **8c**).

b) *From* **8d**. Catalytic hydrogenolysis (1 atm) of **8d** (0.380 g, 1.0 mmol) in abs. EtOH (20 ml) over 10% Pd/C (202 mg) at 50° overnight, followed by filtration over *Celite* and evaporation, gave crude **11a** (114 mg, quant.) as an orange oil, to which 10% aq. $NaHCO_3$ soln. (2 ml) was added. To the resulting mixture, kept at 5°, was added dropwise benzyl chloroformate (0.32 ml, 2.2 mmol). After 1.5 h, the mixture was diluted with acetone (10 ml) and AcOEt (10 ml), dried ($MgSO_4$), and evaporated and the resulting orange oil (445 mg) purified by FC (AcOEt): **11b** (62 mg, 37%) as yellow oil which crystallised in the cold. M.p. 67° ($AcOEt/Et_2O$). Colourless crystals. IR (KBr): 3430, 3300, 2950, 1700, 1660, 1460, 1440, 1420, 1360, 1210, 1100, 1085, 690. ^1H-NMR (80 MHz, $CDCl_3$): 7.34 (*s*, 5 H); 5.12 (*s*, 2 H); 4.25 (*m*, 2 H); 3.60 (*m*, 4 H); 2.30 (*m*, 2 OH). Anal. calc. for $C_{12}H_{15}NO_4$ (237.25): C 60.75, H 6.37, N 5.90; found: C 60.8, H 6.1, N 5.9.

^1H-NMR of crude **11a** (80 MHz, D_2O): 3.08 (*dd*, $J = 4.5$, 12.5, 2 H); 3.37 (*dd*, $J = 5.5$, 12.5, 2 H); 4.43 (*m*, 2 H).

4-Amino-4-deoxy-DL-erythrose Derivatives. – t-*6-{[(*tert*-Butyl)dimethylsilyl]oxy}-*r-*4,*c-*5-(isopropylidenedioxy)-*N,N-*dimethyl-1,2-oxazinane-2-carboxamide* (**12a**). To a stirred suspension of **8a** (0.70 g, 2.2 mmol) in 2,2-dimethoxypropane (2.1 ml, 17.3 mmol) was added some *Amberlyst-15* (H^+ form; 20 mg) at r.t. under Ar. After 2 h, the mixture was diluted with acetone, filtered, and evaporated: **12a** (770 mg, 96%). Yellowish oil. IR (CCl_4): 2910, 1675, 1400, 1380, 1250, 1225, 1215, 1200, 1175, 1100, 1070, 940, 850. ^1H-NMR: *Table 6*. MS: 360 (2), 345 (2), 303 (21), 285 (4), 103 (21), 72 (100). HR-MS: 360.2082 ($C_{16}H_{32}N_2O_5Si$, calc. 360.2080).

*6-Hydroxy-*r-*4,*c-*5-(isopropylidenedioxy)-*N,N-*dimethyl-1,2-oxazinane-2-carboxamide* (**13a**). Addition of Bu_4NF (0.26 g, 0.83 mmol) to a soln. of **12a** (0.20 g, 0.55 mmol) in MeCN (2 ml) under Ar led instantly to reaction. After evaporation, the crude residue was purified by FC (AcOEt/cyclohexane 6:4): colourless crystals (0.11 g, 80%). M.p. 130° ($AcOEt/Et_2O$ 4:6). IR (KBr): 3240, 2490, 1645, 1490, 1405, 1385, 1240, 1210, 1160, 1090, 1060, 1020, 1000, 925. ^1H-NMR: *Table 6*. Anal. calc. for $C_{10}H_{18}N_2O_5$ (246.26): C 48.77, H 7.37, N 11.38; found: C 48.5, H 7.3, N 11.2.

r-*2-Hydroxy-*t-*3,*t-*4-(isopropylidenedioxy)-*N,N-*dimethylpyrrolidine-1-carboxamide* (**14**). A soln. of **12a** (0.77 g, 2.17 mmol) in MeCN (15 ml) was treated with Bu_4NF (1.06 g, 2.9 mmol) whereby the colour changed from brown to yellow. After dilution of the soln. with MeCN (20 ml) and addition of Na_2CO_3 (18 g), $TiCl_3$ (1.67 g, 10.8 mmol) was added portionwise over 1 h, the pH being kept above 5. The suspension, initially violet, gradually turned colourless and was filtered. After evaporation, the residue was purified by FC (AcOEt/cyclohexane 9:1): **14** (325 mg, 65%). Colourless crystals. M.p. 82° (i-Pr_2O/AcOEt 9:1). IR (KBr): 3280, 2940, 1606, 1500, 1450, 1390, 1280, 1260, 1240, 1205, 1160, 1070, 1020, 865. ^1H-NMR: *Table 7*. Anal. calc. for $C_{10}H_{18}N_2O_4$ (230.26): C 52.16, H 7.88, N 12.17; found: C 52.3, H 7.6, N 12.1.

Benzyl t-*6-Hydroxy-*r-*4,*c-*5-(isopropylidenedioxy)-1,2-oxazinane-2-carboxylate* (**13b**). To a stirred suspension of **8d** (0.402 g, 1.05 mmol) in 2,2-dimethoxypropane (1.2 ml, 10 mmol) was added some *Amberlist-15* (20 mg) at r.t. under Ar. After 1.5 d, the mixture was filtered and the filtrate evaporated: crude **12b** (0.511 g). To a soln. of this latter in anh. MeCN (6 ml) was added Bu_4NF (0.452 g, 1.2 mmol). After 15 min, the mixture was filtered and the filtrate evaporated: **13b** (0.273 g, 89%). Colourless crystals. M.p. 112° ($AcOEt/Et_2O$ 2:1). IR (KBr): 3370, 1695, 1450, 1400, 1300, 1240, 1215, 1150, 1040, 945, 920. ^{1}H-NMR: *Table 6*. Anal. calc. for $C_{15}H_{19}NO_2$ (309.32): C 58.24, H 6.19, N 4.53; found: C 58.0, H 6.3, N 4.5.

cis-5,6-Dihydro-4H-1,2-oxazine-4,5-diol (**15a**) *and Its Diacetate* **15b**. A stirred soln. of **9c** (57 mg, 0.14 mmol) and Bu_4NF (0.16 g, 0.45 mmol) in anh. MeCN (0.2 ml) was left to react 1 h at r.t. and 5 h at 50°. After evaporation and FC (AcOEt/EtOH 8:2), **15a** (15 mg, quant.) was obtained as colourless oil. This was treated with Ac_2O (66 µl, 0.7 mmol) in pyridine (0.14 ml, 1.7 mmol) and the mixture separated by prep. TLC (AcOEt): **15b** (32 mg, quant.) as yellow oil.

15a: ^{1}H-NMR (250 MHz, CD_3OD): 7.16 (*t*, H–C(3)); 4.62 (br. *s*, OH); 4.14 (*m*, H–C(4)); 4.03 (*m*, 2 H–C(6)); 3.95 (*m*, H–C(5)).

15b: IR (film): 2940, 1750, 1375, 1240, 1085, 1050, 1030, 960. ^{1}H-NMR: *Table 6*. MS: 149 (1), 117 (1), 99 (6), 71 (2), 60 (1), 58 (2), 43 (100). HR-MS: 201.0640 ($C_8H_{11}NO_5$, calc. 201.0637).

4,4'-(Acetylimino)bis[(2RS,3SR)-butane-1,2,3-triyl Triacetate] (**16b**). *a*) Catalytic hydrogenolysis (1 atm) of **9d** (102 mg, 0.26 mmol) was performed in abs. EtOH (8 ml) over 10% Pd/C (42 mg) at 40° overnight. After filtration over *Celite* and evaporation, crude **16a** (32 mg, quant.) was isolated and at once acetylated overnight in pyridine (0.35 ml) with Ac_2O (0.28 mmol). The mixture was separated and purified by prep. TLC (AcOEt): **16b** (26 mg, 39%). Colourless oil.

b) As described in *a*) with hydrogenolysis of **17a/18a** (see below; 100 mg, 0.37 mmol), abs. EtOH (1 ml), 10% Pd/C (34 mg; **16a** (40 mg, quant.)), pyridine (0.55 ml), and Ac_2O (0.25 ml, 2.6 mmol): **16b** (40 mg, 42%). Colourless oil. IR (film): 3475, 2975, 1745, 1655, 1430, 1370, 1220, 1050. ^{1}H-NMR (400 MHz, $CDCl_3$): 2.035, 2.040, 2.045, 2.052, 2.055, 2.057, 2.074, 2.080, 2.090, 2.102, 2.110, 2.112 (AcO); 3.12–3.92 ($C(H_2N)$); 4.13–4.35 (CH_2O); 5.12–5.33 (CH–O). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 20.59, 20.63, 20.68, 20.70, 20.74, 20.83, 20.85, 20.88, 21.33, 21.40 ($\mathit{C}H_3CO$); 44.67, 44.77, 48.04, 48.45 (CH_2N); 61.48, 61.54, 61.67, 61.73 (CH_2O); 169.47, 167.51, 169.88, 169.99, 170.08, 170.13, 170.20, 170.43, 170.45, 170.60, 171.25, 171.34 ($CH_3\mathit{C}O$). MS: 400 (4), 399 (12), 357 (10), 344 (5), 314 (20), 302 (19), 260 (88), 218 (20), 200 (20), 98 (7), 80 (11), 43 (100). HR-MS: 400.1596 ($C_{18}H_{26}NO_9$, $[M - AcO - AcOH]^+$, calc. 318.1427), 399.1517 ($C_{18}H_{25}NO_9$, $[M - AcOH]^+$, calc. 399.1529).

Benzyl r-3,t-4,t-5-Triacetoxy-1,2-oxazinane-2-carboxylate (**17b**) *and Its (r-3,c-4,c-5)-Isomer* **18b**. To a stirred soln. of **9d** (235 mg, 0.61 mmol) in MeCN (3 ml), was added Bu_4NF (326 mg, 0.90 mmol) at r.t. under Ar. After 30 min, the solvent was evaporated and the residue purified by FC (AcOEt/EtOH 8:2): **17a/18a** as a greenish resin (0.17 g, 96%). Compounds **17a** and **18a** could be distinguished by 2D TLC (AcOEt/EtOH 8:2). The mixture **17a/18a** (60 mg, 0.22 mmol) was acetylated overnight in pyridine (0.3 ml, 3.7 mmol) with Ac_2O (0.15 ml, 1.6 mmol). The resulting **17b/18b** (71 mg, 81%) were purified and separated by prep. TLC (Et_2O).

17b: Yellow oil (34 mg, 38%). IR (film): 2950, 1750, 1370, 1240, 1215, 1100, 1050, 1025. ^{1}H-NMR: *Table 6*. ^{13}C-NMR (100.6 MHz, $CDCl_3$): 169.53, 169.35 ($\mathit{C}OOCH_3$); 156.38 (C=O); 128.62, 128.55, 128.39 (arom. C); 77.45 (C(3)); 68.51 ($Ph\mathit{C}H_2$); 67.68 (C(6)); 65.53 (C(4)); 63.94 (C(5)); 20.69, 20.58, 20.38 ($COO\mathit{C}H_3$). MS: 252 (2), 293 (4), 149 (3), 108 (4), 99 (7), 91 (100), 71 (4), 65 (8), 57 (11), 43 (46). HR-MS: 395.1217 ($C_{18}H_{21}NO_9$, calc. 395.1216).

18b: Yellow oil (38 mg, 43%). IR (film) 2950, 1750, 1375, 1245, 1220, 1115, 1075, 1020, 950. ^{1}H-NMR: *Table 6*. ^{13}C-NMR (100.6 MHz, $CDCl_3$): 170.3, 169.4, 169.3 ($\mathit{C}OOCH_3$); 134.95 (C_{ipso}); 128.63, 128.60, 128.53 (arom. C); 75.44 (C(3)); 72.69 (C(6)); 68.80 ($Ph\mathit{C}H_2$); 65.51, 65.46 (C(4), C(5)); 20.84, 20.59, 20.41 ($COO\mathit{C}H_3$). MS: 292 (2), 176 (2), 145 (3), 91 (100), 85 (3), 65 (5), 43 (31). HR-MS: 395.1217 ($C_{18}H_{21}NO_9$, calc. 395.1216).

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