243. Diastereoselectivity in the Reaction of *N*-Glycosyl-nitrones: 1,3-Dipolar Cycloaddition and Addition of Phosphite Anion

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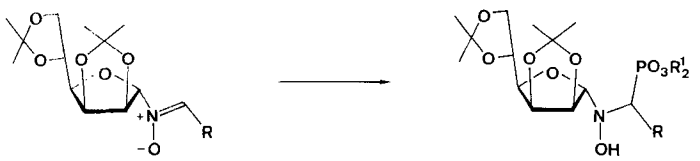
The direction of approach of dibenzyl phosphite on the one hand and of dipolarophiles on the other hand to the spironitrone **7** was examined. The nitrone **7** was prepared from the lactone **3**. The nucleophilic addition of dibenzyl phosphite gave **8** as a single adduct (86%). Its structure was established by X-ray analysis. From the cycloaddition of methyl methacrylate, the products **9a**, **9b**, **11a**, and **11b** (83:2:7.5:7.5, 81%) were isolated. The structure of the main adduct **9a** was established by an X-ray analysis of a derivative of it, and the structures of the other adducts were deduced from their NMR spectra. The cycloaddition of **7** and methyl acrylate gave the adducts **10a**, **10b**, **12a**, **13a**, **13b**, and **14a** (27:10:54:1:2:6, 87%). The structures of these compounds were deduced from their NMR spectra. The results are discussed in relation to prior hypothesis.

1. Introduction. – The nucleophilic addition of dialkyl phosphite anions to (*Z*)-*C*-alkyl-*N*-(2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranosyl)nitrones **1** gives the (1*S*)-*N*-glycosyl-*N*-hydroxyaminophosphonates **2** with a diastereoselectivity of about 90% [1] *(Scheme 1)*. A high diastereoselectivity had been predicted, based on the analogy between a LUMO-controlled 1,3-dipolar cycloaddition of *N*-glycosyl-nitrones and the addition of nucleophiles to it [1].

Scheme 1



1 **2**

a R = CH_2OBn, **b** R = $CHMe_2$, **c** R = CH_3

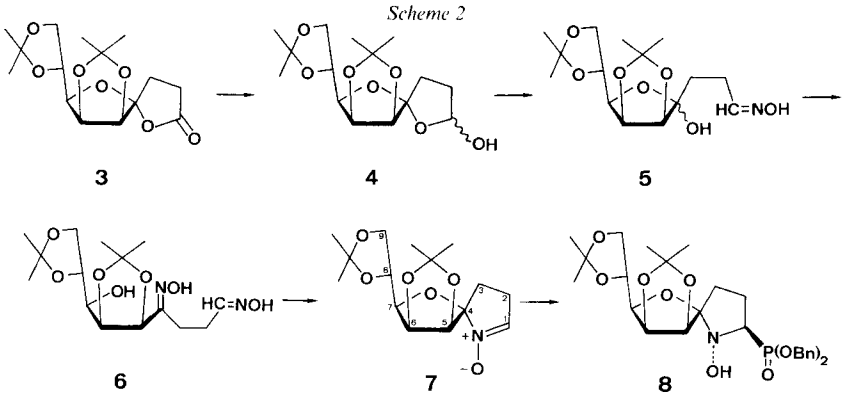
The rationalization of the stereochemistry postulates that the nitrone reacts in a conformation, where the planes of the nitrone function and the C(1)–O bond are perpendicular to each other, and where the alkylidene moiety of the nitrone function is sterically least congested. In the 1,3-dipolar cycloaddition of methacrylates, the dipolarophile approaches the nitrone either along the C(1)–O bond (*'endo'*-orientation of the CH_3 group) or from the side opposite to the C(1)–O bond (*'exo'*-orientation of the CH_3 group). The former mode of approach was given preference, since it leads to an antiperiplanar (*vs.* coplanar) arrangement of the developing lone pair at the N-atom and the C(1)–O bond, and also because the opposite sense of chirality is induced in the cycloaddi-

tion to acrylate [1] [2]. It was anticipated that dipolarophiles and nucleophiles should approach such nitrones from the same side.

According to these postulates, the nucleophilic addition of phosphite anions to **1** *(Scheme 1)* should have given the (1*R*)-configurated addition products **2**. Although a 1,3-dipolarophile and a charged nucleophile may not approach the nitrone from the same side – a charge-dipole interaction being involved in the latter case – the contrast between result and prediction requires a test of the validity of the above mentioned postulates for both the 1,3-dipolar cycloaddition of *N*-glycosyl-nitrones and the addition of nucleophiles to them.

2. Preparation of the Spironitrone 7. Addition of Lithium Dibenzyl Phosphite. – Examination of the stereochemistry of the nucleophilic addition of a dialkyl phosphite anion to a configurationally and conformationally defined nitrone on the one hand and of the 1,3-dipolar cycloaddition of the same nitrone on the other hand should reveal the direction of approach of both the anion and the 1,3-dipolarophile. The spironitrone **7** *(Scheme 2)* in which the nitrone function and the C(4)–O bond (corresponding to the C(1)–O bond in **1**) are about perpendicular to each other seemed to be appropriate.

Scheme 2



For its preparation, the spirolactone **3** [3] *(Scheme 2)* was first reduced with diisobutylaluminium hydride (DIBAH) to give a crystalline hemiacetal **4** (88%). Treatment of **4** with excess hydroxylamine in MeOH at reflux gave rapidly and quantitatively the oximes **5** (see below). Replacing the solvent by PrOH gave, after 20 h at reflux, a mixture consisting of **5**, the dioximes **6**, and some nitrone **7**. During chromatography on silica gel, **6** was transformed into **7**, which was obtained as a colourless oil in yields of up to 50% from **4**.

The hemiacetal **4** showed mutorotation ($[\alpha]_D^{25}$ = +46.5° → +39.9°, $CHCl_3$, 20 h). A 11:9 ratio of two main anomers was evident from ^{1}H-NMR spectroscopy. The configuration of the crystalline material is not known. The monooximes **5** are a 3:2 (*E*)/(*Z*)-mixture of mainly one (α-D?) hemiacetal. In the ^{1}H-NMR of **6**, two signals for H–C(1) showed the presence of at least two diastereoisomers ((*E*)/(*Z*) 3:2). The IR spectrum of **7** showed a characteristic nitrone band at 1580 cm^{-1} and no OH or C=O bands. The MS showed M^+ at *m/z* 313 and further peaks at *m/z* 298 and 282, indicating loss of a CH_3 group, and of a CH_3 group and monooxygen, respectively.

The ^{1}H- and ^{13}C-NMR spectra of **7** showed the presence of a single diastereoisomer. No other diastereoisomer was detectable among the reaction products. The configuration

at the anomeric centre is evident from the X-ray analysis of the addition product **8** and the transformed addition product **15** (see below). Similar values of the specific rotation of the spironitrone **7** ($[\alpha]_D^{25} = +42.4°$, $CHCl_3$) and of the spirolactone **3** ($[\alpha]_D^{25} = +47.7°$, $CHCl_3$) evidence the same configuration of the spiro centre.

The nucleophilic addition of lithium dibenzyl phosphite to **7** (CH_2Cl_2; −70° to −20°) gave **8** in a yield of 86% as a single diastereoisomer. Its ^{31}P-NMR spectrum showed a signal at 28.22 ppm, typical for *N*-hydroxyaminophosphonates [1] and its structure was established by an X-ray analysis[1]): the phosphoryl group at the pyrrolidine ring of **8** is arranged *trans* to the ring O-atom and also *trans* to the *N*-OH group.

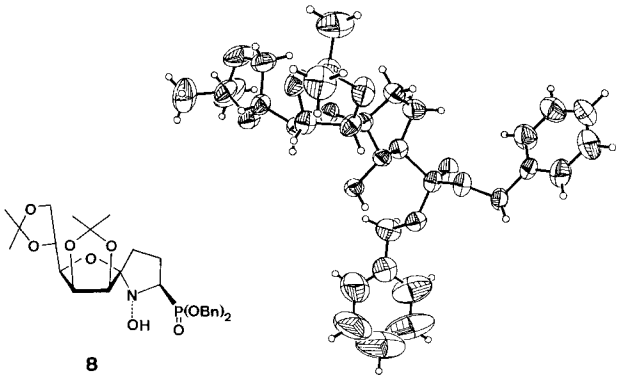
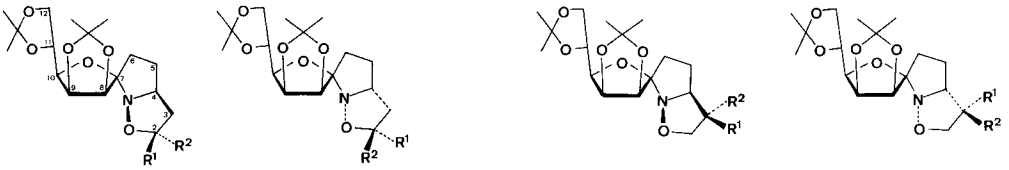


Fig. 1. *ORTEP Representation of the phosphonate* **8**



9a **11a** $R^1 = CO_2CH_3$, $R^2 = CH_3$
9b **11b** $R^1 = CH_3$, $R^2 = CO_2CH_3$

10a **12a** $R^1 = CO_2CH_3$, $R^2 = H$ **13a** **14a**
10b **12b** $R^1 = H$, $R^2 = CO_2CH_3$ **13b**

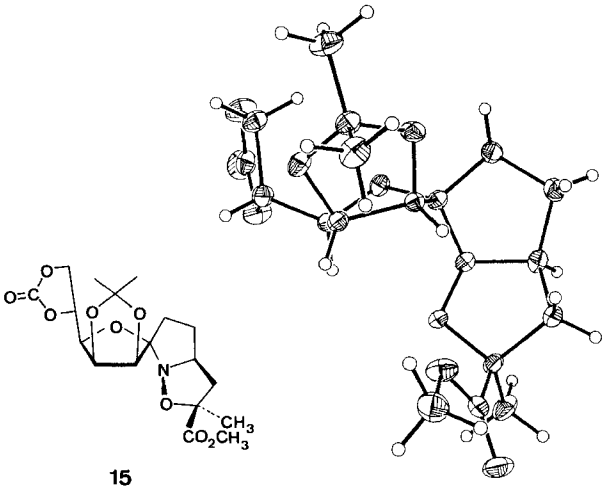
3. 1,3-Dipolar Cycloaddition of Methyl Methacrylate. – The addition of methyl methacrylate to **7** afforded 4 products (**9a**, **9b**, **11a**, and **11b**) in the ratio of 83:2:7.5:7.5 (see *Table 1*). Two fractions were obtained by column chromatography: a faster moving one, which upon crystallization gave the main adduct **9a** as colourless fine needles, and a slower moving one. Chromatography of the mother liquors of **9a** gave the adduct **9b**. ^{1}H-NMR spectroscopy showed the slower moving fraction to be a 1:1 mixture **11a**/**11b**. Both products were obtained as colourless fine needles after HPLC.

[1]) We thank Dr. *J. H. Bieri* and Mr. *R. Prewo* for the X-ray analysis of **8** and **15**. A more detailed report of these structures will be published later.

Table 1. *Ratios of Products of the 1,3-Dipolar Addition of Methyl Methacrylate and Acrylate to the Nitrone* **7**

	Addition of methyl methacrylate				Addition of methyl acrylate		
	Product	*Run*			Product	*Run*	
		1	*2*	*3*		*4*	*5*
Ratio of products [%]	**9a**	83	85.5	83	**10a**	27	25
	9b	2	1.5	1	**10b**	10	8.5
	11a	7.5	6.5	8	**12a**	54	56.5
	11b	7.5	6.5	8	**12b**	0	0
					13a	1	1
					13b	2	2
					14a	6	7
Total yield of products [%]		81	84	87		87	85

Selective hydrolysis of **9a** and treatment of the resulting diol with *N,N'*-carbonyldiimidazole yielded the cyclic carbonate **15** (57%). Crystallization from Et_2O/hexane gave crystals suitable for X-ray analysis (see *Footnote 1* and *Fig. 2*). At the pyrrolidine ring, C(3) and the O-atom of the isoxazolidine moiety are arranged *'trans'* to the ring O-atom of the furanose part. The $COOCH_3$ group is in *'endo'*-position of the bicyclic 2-oxapyrrolizidine ring system.



15

Fig. 2. *ORTEP Representation of the cyclocarbonate* **15**

The mass spectra of **9a**, **9b**, **11a**, and **11b** suggest that they are isomers. Their configurations were deduced from a comparison of their ^{1}H- and ^{13}C-NMR spectra with those of **15** (see *Table 2–4*).

In the ^{1}H-NMR spectra of **15**, **9a**, and **9b**, the doublets of H–C(8) appear at 5.08–5.13 ppm and those of **11a** and **11b** at 4.82–4.9 ppm. Thus, **9a** and **9b** must be *'anti'*-adducts and **11a** and **11b** *'syn'*-adducts[2]). In the ^{13}C-NMR spectrum, only C(8) of the *'anti'*-adducts should show a γ effect caused by the ring O-atom of the isoxazolidine

[2]) *'Syn'* and *'anti'* refer to the approach from the side of the C(4)–O bond of **7** *('syn')* or from the side opposite to it *('anti')*. *'endo'* or *'exo'* refer to the position of a substituent relative to the *cis*-annulated bicyclic 2-oxapyrrolizidine ring system.

Table 2. *^{1}H-NMR* (400 MHz, $CDCl_3$) *Chemical Shifts of the Addition Products to the Nitrone* **7**

Proton	Chemicals shifts [ppm]										
	15	**9a**	**9b**	**11a**	**11b**	**10a**	**10b**	**12a**	**14a/13a**[a][b]	**13b**[a]	**8**[c]
H–C(2)[d]	–	–	–	–	–	4.54	4.52	4.76	4.09 (4.19)	4.00	–
H′–C(2)[d]	–	–	–	–	–	–	–	–	4.26	4.10	–
H–C(3)[d]	2.42	2.43	1.80	2.21	2.01	2.40	2.26	2.43	3.27 (3.12)	3.74	–
H′–C(3)[d]	2.58	2.62	3.18	2.50	2.75	2.69	2.84	2.52	– (–)	–	–
H–C(4)[e]	3.95	3.96–3.88	3.89	4.07–3.96	3.96–3.84	4.03–3.97	4.00–3.83	3.89	3.95	4.15–4.08	3.63–3.59
H–C(5)[d]	1.54	1.55	1.56	1.83	1.81	1.50	1.61	1.83	1.91	1.50	
H′–C(5)[d]	2.10	2.06	2.14	2.06	2.03	2.23–2.10	2.12	2.11	2.12	1.98	2.14–1.66
H–C(6)[d]	1.86	1.82	1.87	1.90	1.98	1.88	1.86	1.92	1.90–1.83	1.86	
H′–C(6)[d]	2.33	2.32	2.33	2.23	2.25	2.23–2.10	2.48	2.25	2.24–2.16	2.18	
H–C(8)	5.10	5.08	5.13	4.82	4.90–4.82	5.05	5.12	4.92	4.80 (5.01)	5.00	4.83
H–C(9)	4.79	4.84	4.84	4.86		4.86	4.85	4.89	4.86 (4.81)	4.81	4.87
H–C(10)	4.45	4.08	4.05	4.30	4.50	4.07	4.02	4.33–4.29	4.24	4.03	4.43
H–C(11)	4.92	4.35	4.35	4.25	4.33	4.36	4.36		4.28 (4.32)	4.33	4.24
H–C(12)[d]	4.42	3.97	3.96	3.96	4.06	3.95	3.96	3.98	3.96	3.94	4.01
H′–C(12)[d]	4.56	4.07	4.06	4.02	4.10	4.06	4.07	4.08	4.04	4.04	4.05
CH_3–C(2)	1.48	1.51	1.50	1.48	1.63	–	–	–	– (–)	–	–
OCH_3	3.74	3.75	3.76	3.82	3.76	3.77	3.77	3.77	3.70 (3.73)	3.71	–
CH_3 of iso-propylidene	1.42 1.28	1.47, 1.44 1.37, 1.35	1.48, 1.44 1.37, 1.36	1.46, 1.44 1.36, 1.32	1.45, 1.43 1.37, 1.30	1.47, 1.43 1.37, 1.34	1.48, 1.43 1.37, 1.36	1.45, 1.44 1.38, 1.32	1.45, 1.44 1.38, 1.33	1.44, 1.41 1.35, 1.32	1.45, 1.42 1.36, 1.33

[a]) The same numbering as for **10** is used. The attribution to the *endo*- and *exo*-adducts **a** and **b**, resp., may be reversed.

[b]) Spectrum of a mixture **14a/13a** 9:1. Values of **13a** are in brackets.

[c]) An analogous numbering as for **10** is used. Additional signals: 7.38–7.26 (*m*, 10 H); 5.39 (*s*, OH, exchangeable with D_2O); 5.12–4.97 (*m*, 2 $PhCH_2$).

[d]) The geminal proton at lower field is marked with a prime.

[e]) Irradiation at H–C(4) allowed the unambiguous attribution of the signals of H–C(3), H′–C(3), H–C(5), and H′–C(5).

Table 3. *^{1}H-NMR Coupling Constants of the Addition Products to the Nitrone* **7**

Coupling	Coupling constant [Hz][a])										
	15	**9a**	**9b**	**11a**	**11b**	**10a**	**10b**	**12a**	**14a/13a**[b])	**13b**	**8**
$J(2,2')$	–	–	–	–	–	–	–	–	7.2 (6.0)	7.9	–
$J(2,3)$	–	–	–	–	–	7.2	6.4	8.9	7.0 (6.0)	7.4	–
$J(2,3')$	–	–	–	–	–	8.1	9.0	4.2	–	–	–
$J(2',3)$	–	–	–	–	–	–	–	–	9.0	7.9	–
$J(3,3')$	12.8	12.8	12.7	12.4	12.8	12.5	12.6	12.0	–	–	–
$J(3,4)$	7.4	7.4	4.3	6.7	8.7	1.8	2.8	8.9	7.0	7.4	–
$J(3',4)$	2.7	2.4	8.3	8.7	6.7	7.2	7.8	8.0	–	–	–
$J(4,5)$	5.0	8.0	4.5	5.0	5.0	9.0	8.0	4.5	3.5	5.7	n.d.[c])
$J(4,5')$	9.0	8.8	8.5	8.0	8.5	4.8	8.8	8.0	8.0	9.0	n.d.
$J(5,5')$	12.9	12.9	12.4	12.5	12.5	13.0	12.5	12.2	11.6	13.1	n.d.
$J((5,6)$	2.9	2.5	2.3	9.0	8.5	2.2	2.4	8.9	7.5	2.5	n.d.
$J(5,6')$	10.5	10.5	10.3	10.5	9.3	9.0	10.5	9.4	7.5	11.0	n.d.
$J(5',6)$	8.9	8.8	8.3	2.5	2.5	7.8	8.8	2.3	2.5	9.0	n.d.
$J(5',6')$	9.0	9.2	9.2	9.0	10.1	n.d.	9.1	8.5	10.5	8.7	n.d.
$J(6,6')$	13.6	13.5	13.4	12.5	13.4	12.8	13.4	13.4	n.d.	13.4	n.d.
$J(8,9)$	6.0	6.0	6.0	6.0	n.d.	6.0	6.0	6.1	6.0 (6.0)	6.0	6.1
$J(9,10)$	4.0	3.5	3.6	3.8	3.6	3.6	3.7	3.4	3.7 (3.6)	3.6	4.0
$J(10,11)$	3.0	8.1	8.0	7.7	6.5	8.1	8.1	n.d.	6.5 (8.3)	8.0	7.7
$J(11,12)$	8.5	4.3	4.6	4.3	6.3	4.4	4.3	4.6	4.6 (4.6)	4.3	5.0
$J(11,12')$	7.0	6.2	6.2	6.0	4.9	6.2	6.0	6.0	6.0 (6.3)	6.1	6.2
$J(12,12')$	8.4	8.6	8.6	8.7	8.7	8.7	8.6	8.6	8.7	8.6	8.5

[a]) All coupling constants were determined by first-order interpretation.

[b]) See *Table 2, Footnote b.*

[c]) Not distinguishable.

Table 4. *^{13}C-NMR* (400 MHz, $CDCl_3$) *Chemical Shifts of the Addition Products to the Nitrone* **7**

Carbon	Chemical shifts [ppm]											
	15	**9a**	**9b**	**11a**	**11b**	**10a**	**10b**	**12a**	**14a/13a**[a])[b])	**13b**[a])	**8**[c])	
C(1)	173.22	173.18	n.v.[d])	172.66	174.61	171.49	170.96	171.34	172.25 (171.65)	n.v.	–	
C(2)	82.96	82.63	82.58	87.55	87.77	74.91	75.65	80.37	72.96 (68.32)	67.02	–	
C(3)	46.26	46.36	45.98	45.45	46.83	40.37	40.17	41.16	55.29 (38.77)	51.51	–	
C(4)	64.55	64.47	64.47	62.76	63.41	64.03	63.92	62.35	66.68 (68.15)	65.29	60.68,	58.93[e])
C(5)	29.28	29.54	30.40	31.71	31.50	30.16	29.33[h])	30.77	30.46 (30.38)	30.03	30.60	
C(6)	28.74	28.85	29.39	25.89	26.02	29.29	29.26[h])	25.78	25.88 (29.66)	29.69	28.49,	28.42[f])
C(7)	110.25	109.89	109.04	106.03	105.78	110.21	109.91	106.15	106.54 (109.30)	110.05	105.64,	105.44[g])
C(8)	82.25	82.52	82.58	85.61	85.56	82.61	82.62	85.92	85.94 (82.41)	82.34	84.68	
C(9)	80.20	80.58	80.80	81.06	81.59	80.74	80.66	82.08	82.05 (80.84)	80.71	82.69	
C(10)	77.90	79.78	79.78	80.48	80.49	79.84	80.10	79.49	80.51 (79.84)	80.19	81.18	
C(11)	74.48	73.10	73.19	73.85	74.10	73.06	73.17	73.67	73.77 (73.16)	73.14	73.97	
C(12)	65.75	66.90	66.97	66.43	66.22	66.92	67.02	66.29	66.47 (67.04)	66.63	66.91	
CH_3O	52.39	52.31	52.47	52.63	52.69	52.27	52.30	52.21	52.21 (52.32)	52.08	–	
CH_3–C(2)	24.99	25.14[h])	22.94	25.44[h])	21.56	–	–	–	– (–)	–	–	
$(CH_3)_2C <$	25.43	26.83	26.87	26.82	26.84	26.78	26.90	26.65	26.78 (26.84)	26.91	26.76	
	23.89	25.94	26.02	25.97	25.85	25.92	25.98	25.80	25.88 (25.98)	26.00	25.90	
	–	25.25[h])	25.32	25.30[h])	25.47	25.26	25.31	25.33	25.36 (25.36)	25.34	25.35	
	–	24.65	24.77	24.49	24.36	24.58	24.63	24.30	24.42 (24.42)	24.60	24.25	
Other quart. C-atoms	154.61	111.96	112.08	112.44	112.43	112.21	112.30	112.21	112.51 (112.60)	112.41	112.09	
	112.37	108.93	108.95	108.93	108.87	109.12	109.22	108.64	108.94 (109.10)	109.26	108.97	

[a]) See *Table 2, Footnote a.*

[b]) See *Table 2, Footnote b.*

[c]) An analogous numbering as for **10** is used. Additional signals: 136.41 (*s*) and 136.22 (*s*, arom. C); 128.54–127.86 (several *d*, arom. C); 68.16, 68.09, 67.47, 67.40 (all *t*, 2 $PhCH_2$, ^2J(C,P) = 6.5 Hz).

[d]) Not visible in the spectrum.

[e]) ^1J(C,P) = 175.6 Hz.

[f]) ^3J(C,P) = 6.5 Hz.

[g]) ^3J(C,P) = 19.4 Hz.

[h]) Attribution may be reversed.

moiety. Indeed, C(8) of **15**, **9a**, and **9b** are shielded by 3 ppm in comparison with C(8) of **11a** and **11b**. The signal of C(7) shows characteristic chemical-shift values: 109–110.3 ppm for the *'anti'*- and 105.7–106.1 ppm for the *'syn'*-addition products indicating the structural relation between the N–O and the C(7)–O bond. A further characteristic property is the chemical-shift difference ($\Delta\delta$) between the signals of C(5) and C(6): large values ($\Delta\delta > 5$ ppm) being observed for *'syn'*- and small values ($\Delta\delta < 1$ ppm) for *'anti'*-adducts. Furthermore, a γ effect is expected between an *'endo'*-orientated CH_3–C(2) group and the bridgehead-atoms of the 2-oxapyrrolizidine moiety. One indeed finds a shielding of 3 ppm for the CH_3–C(2) signals of **9b** and **11b** (**9b** and **11b**: 22.9 and 21.6 ppm, resp.; **9a** and **11a**: 25.0 and 25.4 ppm, resp.). The *'endo'*-position of the CH_3–C(2) group is expected to cause a large chemical-shift difference for the H_2(C3) signals in the ^{1}H-NMR spectrum (*cf.* [2]). Indeed, **9b** ($\Delta\delta = 1.38$ ppm) and **11b** ($\Delta\delta = 0.74$ ppm) exhibit large differences and **15** ($\Delta\delta = 0.16$ ppm), **9a** ($\Delta\delta = 0.19$ ppm), and **11a** ($\Delta\delta = 0.29$ ppm) small differences. Thus, the adducts possessing an *'endo'*- (**9b**, **11b**) and *'exo'*-CH_3 group (**9a** and **11a**) are easily discerned.

4. 1,3-Dipolar Addition of Methyl Acrylate. – The addition of methyl acrylate to **7** yielded a more complex mixture (87%) than the addition of methyl methacrylate. Several fractions of the crude product were obtained by column chromatography and analyzed by ^{1}H-NMR spectroscopy (see *Exper. Part* and *Table 1*). Pure adducts (**10a**, **10b**, **12a**, and **13b**) were isolated by repeated column chromatography and by HPLC. Two minor adducts (**14a** and **13a**) could not be separated and were analyzed as a 9:1 mixture.

Since the MS show that all products are isomers, the addition is not completely regioselective. The 2-substituted adducts **10a**, **10b**, and **12a** (^{1}H-NMR: H–C(2) above 4.5 ppm and 2 H–C(3) below 3 ppm; ^{13}C-NMR: doublet of C(2) above 70 ppm and triplet of C(3) below 45 ppm) are easily recognized (see *Tables 2–4*). The 3-substituted 2-oxapyrrolizidines **13a**, **13b**, and **14a** exhibit the expected chemical shifts in their NMR spectra: the 2 H–C(2) and H–C(3) signals occur above 3 ppm, the triplet of C(2) above 65 ppm, and the doublet of C(3) below 56 ppm.

Analysis of the ^{1}H- and ^{13}C-NMR spectra (δ of H–C(8), C(7) and C(8), $\Delta\delta$ between C(5) and C(6)) allows the unambigous attribution of *'syn'*- (**12a**, **14a**) and *'anti'*-adducts (**10a**, **10b**, **13a**, **13b**). It remained to assign the configuration at C(2) (or C(3)). The absence of the CH_3 group at C(2) (no γ effect) makes the structure elucidation of **10a**, **10b**, and **12a** difficult. In these compounds, the $COOCH_3$ group should prefer a pseudoequatorial position. Therefore, $\Delta\delta$ of the 2 H–C(3) signals of the *'exo'*-adducts should be smaller than $\Delta\delta$ observed for the methacrylate adducts possessing an *'exo'*-$COOCH_3$ group, but still larger than the ones of the acrylate *'endo'*-adducts. Thus, **10b** ($\Delta\delta = 0.56$ ppm) is an *'exo'*-, and **10a** and **12a** ($\Delta\delta = 0.29$ and 0.09 ppm, resp.) are *'endo'*-adducts. Assuming a pseudoequatorial position of the $COOCH_3$ group, examination of models shows that the coupling constants $J(2,3)$, $J(2,3')$, $J(3,4)$, and $J(3',4)$ (see *Table 3*) are only compatible with the proposed configurational assignment. The same coupling constants of **12a** are only compatible with the *'endo'*-adduct. The *'exo'*-adduct **12b** having a pseudoequatorial $COOCH_3$ group must exhibit at least one small *trans*-coupling (≤ 4 Hz). However, this isomer was not detected in the mixture of cycloadducts. The configuration at C(3) of the 3-substituted 2-oxapyrrolizidines **13a**, **13b**, and **14a** cannot be deduced from spectroscopic data, because the vicinal coupling constants $J(3,4)$ are too similar to each other. The assignment is tentative and may be reversed.

In the NMR spectra of the phosphonate **8**, the chemical shifts of H–C(8) (4.83 ppm), C(7) (105.5 ppm), and C(8) (84.7 ppm) are in good agreement with those of the *'syn'* 1,3-dipolar cycloadducts suggesting a *trans*-configuration of the phosphoryl and the OH group in solution as it was found in the crystalline state.

5. Discussion. – The complete diastereoselectivity in the addition of the phosphite anion to **7** compares to one of about 90% for the addition to a conformationally undefined nitrone [1]. The diastereoselectivity observed for the induction at C(2) (C(5) of an isoxazolidine) is 81% for the cycloaddition of methyl methacrylate to **7** as compared to a d.e. of 75% for the addition to a similarly substituted, but conformationally undefined nitrone, both in favour of a (*S*)-configuration [2]. The corresponding diastereoselectivity for the cycloaddition of methyl acrylate to **7** is 42% and must be compared with the value of 28% (both in favour of a (*R*)-configuration) for the addition to a conformationally undefined nitrone having a lower degree of substitution (a factor expected to lead to lower diastereoselectivities) [2]. The qualitative and quantitative

agreement between the behaviour of **7** and its conformationally undefined analogs is therefore good.

In agreement with the proposed hypothesis [1] [2], the same mode of approach for the phosphite anion and for methyl methacrylate is observed and the *'anti'* approach of methyl methacrylate goes along with the *'exo'*-orientation of the CH_3 group, confirming the proposed, reactive conformation of the nitrone. Against the expectation, the approach from the side opposite to C(4)–O bond of **7** is preferred. Thus, either the stereoelectronic preference for an antiperiplanar as opposed to a synperiplanar arrangement of the developing lone pair and polar bond in the transition state is intrinsically weak and easily overridden by other factors, or these other factors are stronger than anticipated, or then there is a stereoelectronic preference for *'anti'* attack.

In the absence of pertinent calculations, a discussion of these possibilities is difficult. Certainly, one may advance charge-dipol repulsions favouring an *'anti'* attack of a charged nucleophile. One must, however, also explain that the ratio of *'anti' vs. 'syn'* attack in the addition to methyl methacrylate is 85:15 and for the addition of methyl acrylate 59:41, in favour of the *'syn'* attack. This may be due to a stronger interaction of the nitrone HOMO with the LUMO of the acrylate than with the LUMO of the methacrylate [4] [5]. The lower regioselectivity found in the cycloaddition of acrylate (see also [6] [7]) corresponds well with this explanation, which implies that HOMO-controlled cycloadditions would favour a *'syn'* attack. This may be compared to the opposite face selectivity in *Diels-Alder* additions (with normal electron demand) of alkoxyalkyl-substituted dienes and dienophiles: a preferred *'anti'* mode of addition of alkoxyalkyl-substituted dienophiles has been implied [8], a case analogous to a LUMO-controlled cycloaddition of a *N*-alkoxyalkyl-nitrone. This raises the question as to preferred *'syn'* or *'anti'* approach to *C*-alkoxyalkyl- [9] [10] and *C*-acyloxyalkyl-nitrones. A (weak) evidence may be deduced from the results of *Uskoković* and coworkers [11]. In the cycloaddition of (*Z*?)-*N*-benzyl-*C*-acetoxyalkyl-nitrones, 4 diastereoisomers were found, arising from a combination of *'syn' vs. 'anti'* approach of methyl methacrylate and the *'exo' vs. 'endo'* orientation of its CH_3 group. Whilst one type of face selectivity went along with an *'exo'/'endo'* ratio of about 92:8, the other type of face selectivity was accompagnied by an approximately 1:1 *'endo'/'exo'* ratio. This is in parallel with our results where the *'exo'/'endo'* ratio is 98:2 for the *'anti'*-addition product and 1:1 for the *'syn'*-addition product, indicating that the type of face selectivity favouring the 92:8 *'exo'/'endo'* ratio (major products) corresponds to an *'anti'* type of addition. If it should prove correct that also *C*-alkoxy- or *C*-acyloxyalkyl-substituted nitrones show the same face preference as *N*-alkoxyalkyl-nitrones do, one may question the importance of a lone-pair polar bond interaction in the transition state. This would be in keeping with an early transition state [12] [13] in 1,3-dipolar cycloadditions.

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Experimental Part

General. See [14] [15], except as noted below. Methyl acrylate and methacrylate, *N,N'*-carbonyldiimidazole (all *purum*) and PrOH *(puriss.)* were obtained from *Fluka*, DIBAH 20 H from *Schering*. Li(*t*-BuO) was sublimed immediately before use. NMR spectra were measured with a *Varian-XL-100* spectrometer (^{13}C-NMR (25 MHz)), *Varian-XL-200* spectrometer (^{1}H-NMR (200 MHz), ^{13}C-NMR (50 MHz), ^{31}P-NMR (80 MHz)), or *Bruker AM-400* spectrometer (^{1}H-NMR (400 MHz), ^{13}C-NMR (100 MHz)). ^{31}P-NMR spectra are reported to H_3PO_4 as external reference. For anal. HPLC a *Zorbax-Sil* column (4.6 × 250 mm) on a *Kontron* apparatus (*LC* pump *410*) was used and for prep. HPLC a *Zorbax-Sil* column (21.5 × 250 mm) on a *Du Pont 8800* apparatus with a *Du Pont* UV spectrophotometer or a *Knauer* differential refractometer. FC: Flash chromatography.

*2,3-Dideoxy-5,6:8,9-di-*O*-isopropylidene-α-*D*-manno-4-nonosulo-1,4:4,7-difuranose* (**4**). To a cooled soln. (−75°, CO_2/i-PrOH) of **3** (3.038 g, 9.67 mmol) [3] in dry Et_2O (40 ml), a soln. of DIBAH 20 H (10.5 ml, 12.6 mmol) was added through a syringe within 5 min. The clear soln. was stirred at −75° for 30 min. After addition of MeOH (1 ml), *Celite* (1 g), and decolourizing charcoal (1 g), the mixture was allowed to warm to r.t. After addition of 2N $NaHCO_3$ and further stirring at r.t. for 15 min, the mixture was filtered through a pad of *Celite*. The residue was washed twice with H_2O and CH_2Cl_2. The combined filtrates were diluted with AcOEt, washed with H_2O (3×), dried, and concentrated *i.v.* Crystallization of the residue from Et_2O/hexane 1:5 (60 ml) afforded 1.64 g of **4** (m.p. 71–72°). FC (100 g, hexane/AcOEt 2:1) [16] of the mother liquor gave 221 mg (7%) of **3**, 26 mg (1%) of 2,3:5,6-di-*O*-isopropylidene-D-mannose, and further 1.042 g of **4** (total yield of **4**: 2.682 g, 88%). For anal. a sample was dried for 2 h at 10^{-3} Torr. M.p. 72°, R_f 0.30 (hexane/AcOE 1:1), $[\alpha]_D^{25} = +46.5° \rightarrow +39.9°$ (c = 1,$CHCl_3$). IR ($CHCl_3$): 3600*m*, 3450*w* (br.), 3030*w*, 2990*s*, 2950*m*, 2940*m*, 2890*w*, 1725*w*, 1480*m*, 1455*m*, 1440*w*, 1405*w*, 1380*s*, 1370*s*, 1345*w*, 1160*s*, 1110*m*, 1070*s*, 1030*s*, 985*s*, 945*m*, 925*m*, 885*m*, 865*m*, 840*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 9.8 (*s*, 0.03 H, CHO); 5.6–5.46 (*m*, H–C(1)); 4.82 (*dd*, J = 6.0,3.8, H–C(6)); 4.62 (*d*, J = 6.0, 0.45 H) and 4.49 (*d*, J = 6.0, 0.55 H, H–C(1)); 4.43–4.25 (*m*, H–C(8)); 4.15–3.85 (*m*, H–C(7), 2 H–C(9)); 2.8–1.5 (*m*, 5 H); 1.46 (*s*, CH_3); 1.45 (*s*, CH_3); 1.38 (*s*, CH_3); 1.34 (*s*, CH_3). ^{13}C-NMR (25 MHz, $CDCl_3$)[3]: 115.18 (*s*), *114.92* (*s*); 112.26 (*s*), *112.11* (*s*); 108.69 (*s*); 99.91 (*d*), *98.93* (*d*); *85.68* (*d*), 84.68 (*d*); 79.66 (*d*), *79.59* (*d*); *79.21* (*d*), 78.92 (*d*); 72.91 (*d*); *66.52* (*t*), 66.42 (*t*); 32.28 (*t*), *31.39* (*t*); 30.60 (*t*), *29.67* (*t*); 28.86 (*q*), *26.61* (*q*); 25.73 (*q*); 25.04 (*q*); *24.67* (*q*), 24.50 (*q*). Cl-MS: 317 ($M^+ + 1$), 299 ($M^+ - CH_3$). Anal. calc. for $C_{15}H_{24}O_7$ (316.35): C 56.95, H 7.65; found: C 56.88, H 7.76.

Treatment of **4** *with* N*-Methylhydroxylamine.* To a freshly prepared soln. of NaOMe (920 mg (47.7 mmol) of Na in 40 ml of MeOH), *N*-methylhydroxylamine hydrochloride (3.34 g, 47.7 mmol) was added, and the resulting mixture was stirred at 70° for 15 min. After addition of a soln. of **4** (800 mg, 2.53 mmol) in MeOH (5 ml), the mixture was stirred at 70° for 15 min. After 5 min, TLC revealed that **4** was completely transformed into **5**. After addition of PrOH (80 ml), the temp. was raised to 110° and MeOH was distilled off. Molecular sieves 3Å (8 g) were added. After stirring for 20 h at 110°, the mixture was allowed to cool to r.t. Dilution with CH_2Cl_2 (100 ml), filtration through a pad of *Celite*, concentration of the filtrate *i.v.*, and FC (25 g of silica gel; 300 ml of hexane/AcOEt 2:1, 300 ml of hexane/AcOEt 1:1, and 300 ml of AcOEt) afforded a mixture **5**/**6**/**7** (539 mg, *ca.* 60%). With AcOEt/MeOH 9:1 (500 ml) as eluent 335 mg (43%) of **7** were obtained as a colourless syrup[4]).

*1,4-Anhydro-1-deoxo-2,3-dideoxy-1-imino-5,6:8,9-di-*O*-isopropylidene-α-*D*-manno-4-nonosulo-4,7-furanose* N*-oxide* (**7**). R_f 0.21 (AcOEt/CH_3OH 9:1); $[\alpha]_D^{25} = +42.2°$ (c = 1, $CHCl_3$). IR ($CHCl_3$): 2990*m*, 2940*m*, 2880*w*, 1580*m*, 1450*w*, 1380*s*, 1370*s*, 1350*w*, 1240*s*, 1175*m*, 1160*m*, 1100*s*, 1065*s*, 1035*m*, 1010*m*, 995*m*, 970*m*, 940*w*, 920*m*, 885*w*, 865*w*, 840*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 6.85 (br. *s*, $w_{1/2} \approx 6$, H–C(1)); 5.12–4.98 (*m*, H–C(5), H–C(6)); 4.80 (*dd*, J = 8.0, 3.5, H–C(7)); 4.28 (*dt*, J = 8.0, 5.5, H–C(8)); 4.02 (*dd*, J = 8.7, 5.5, H–C(9)); 3.99 (*dd*, J = 8.7, 5.5, H–C(9)); 2.85–2.50 (*m*, 2 H); 2.40–2.05 (*m*, 2 H); 1.48 (*s*, CH_3); 1.43 (*s*, CH_3); 1.38 (*s*, CH_3); 1.37 (*s*, CH_3). ^{13}C-NMR (25 MHz, $CDCl_3$): 134.49 (*d*); 112.61 (*s*); 109.56 (*s*); 108.85 (*s*); 83.06 (2*d*); 80.78 (*d*); 72.99 (*d*); 66.45 (*t*); 26.53 (*q*); 26.11 (*t*); 25.77 (*q*); 25.10 (*q*); 24.83 (*t*); 24.33 (*q*). MS: 313 (7, M^+), 298 (42), 282 (15), 255 (6), 238 (34), 197 (10), 186 (16), 172 (15), 155 (15), 154 (30), 141 (13), 139 (13), 138 (32), 127 (12), 126 (15), 125 (11), 114 (13), 113 (17), 110 (14), 109 (12), 108 (12), 101 (100), 100 (30), 99 (13), 98 (14), 97 (18), 96 (11), 94 (12), 85 (24), 84 (33), 83 (15), 82 (20), 81 (18), 80 (12), 73 (15), 72 (23), 71 (27), 69 (24), 68 (20), 67 (12), 59 (55), 57 (20), 55 (37), 54 (12), 49 (12), 43 (95), 42 (18), 41 (**45**), 39 (18).

A sample of the mixture **5**/**6**/**7** was purified by flash chromatography (hexane/AcOEt 1:1) yielding pure **5** (crystallized from Et_2O/hexane) and slightly impure **6** as an oil.

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[3]) In soln., **4** mainly consisted of 2 hemiacetals in the ratio of *ca.* 11:9. Signals of the predominant isomer are indicated in italics. Signals of other isomers (low intensities) are not listed.

[4]) The yield of **7** varied from 20 to 50%. The transformation of **6** into **7** occurred during the reaction and during chromatography. More **7** was obtained by repeating the reaction using the mixture **5**/**6**/**7** as starting material.

*2,3-Dideoxy-5,6:8,9-di-*O*-isopropylidene-*D*-manno-4-nonosulo-4,7-furanose 1-Oxime* (**5**). M.p. 109°; R_f 0.22 (hexane/AcOEt 1:1). IR ($CHCl_3$): 3590*m*, 3390*m* (br.), 2990*m*, 2940*m*, 2900*w*, 1450*w*, 1380*s*, 1370*s*, 1320*w*, 1160*s*, 1110*m*, 1065*s*, 970*m*, 890*m*, 860*m*, 840*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.51 (*t*, *J* = 5.6, 0.34 H) and 6.95–6.8 (br. *s*, 0.66 H, H–C(1)); 4.84 (*dd*, *J* = 5.9, 3,8, H–C(6)); 4.49 (*d*, *J* = 5.9, 0.66 H) and 4.46 (*d*, *J* = 5.9, 0.34 H, H–C(5)); 4.39 (*td*, *J* = 6.5, 5.5, H–C(8)); 4.20 (*dd*, *J* = 6.5, 3.8, 0.66 H) and 4.14 (*dd*, *J* = 6.5, 3.8, 0.34 H, H–C(7)); 4.07 (*dd*, *J* = 8.6, 6.5, H–C(9)); 3.99 (*dd*, *J* = 8.6, 5.5, H–C(9)); 2.75–1.8 (*m*, 5 H, 1 H exchangeable with D_2O); 1.47 (*s*, CH_3); 1.44 (*s*, CH_3); 1.38 (*s*, CH_3); 1.33 (*s*, CH_3). ^{13}C-NMR (25 MHz, $CDCl_3$)[5]: 151.27 (*d*); 112.33 (*s*); 108.66 (*s*); 106.08 (*s*), *105.96* (*s*); 84.59 (*d*); 79.93 (*d*); 78.69 (*d*), *78.55* (*d*); 73.16 (*d*); 66.20 (*t*); *31.66* (*t*), 31.31 (*t*); 31.62 (*t*), *26.76* (*t*); 26.55 (*q*); 25.70 (*q*); 25.12 (*q*); 24.27 (*q*). MS: 331 (0.5, M^+), 316 (13), 258 (4), 256 (4), 227 (7), 210 (7), 142 (18), 141 (12), 137 (14), 111 (12), 101 (62), 100 (40); 99 (18), 98 (14), 97 (14), 95 (11), 91 (26), 85 (14), 84 (16), 83 (14), 82 (12), 81 (19), 73 (17); 72 (22), 71 (15), 70 (11), 69 (20), 68 (14), 67 (12), 59 (42), 57 (35), 56 (15), 55 (33), 45 (11), 44 (13), 43 (100), 42 (15), 41 (54), 39 (11). Anal. calc. for $C_{15}H_{25}NO_7$ (331.36): C 54.37, H 7.60, N 4.22; found: C 54.27, H 7.42, N 4.15.

*2,3-Dideoxy-5,6:8,9-di-*O*-isopropylidene-*D*-manno-4-nonosulose 1,4-Dioxime* (**6**). R_f 0.09 (hexane/AcOEt 1:1). IR ($CHCl_3$): 3580*m*, 3340*m* (br.), 2990*s*, 2930*s*, 2900*m*, 1450*m*, 1380*s*, 1370*s*, 1160*m*, 1100*m*, 1065*s*, 970*m*, 885*m*, 840*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.58–7.34 (*m*, 0.6 H) and 6.9–6.76 (*m*, 0.4 H, H–C(1)); 4.76 (*d*, *J* = 8, 0.4 H); 4.25–3.8 (*m*, 3 H); 3.8–3.4 (*m*, 2.6 H); 2.9–1.8 (*m*, 5 H); 1.44 (*s*, CH_3); 1.43 (*s*, CH_3); 1.42 (*s*, CH_3); 1.38 (*s*, CH_3).

*Dibenzyl [(1*R*)-1,4-Anhydro-1,2,3-trideoxy-1-*C*-hydroxyamino-5,6:8,9-di-*O*-isopropylidene-α-*D*-manno-4-nonulo-4,7-furanos-1-yl]phosphonate* (**8**). Li(*t*-BuO) (40 mg, 5 mmol) was added to a cooled (−70°) soln. of dibenzyl phosphite (165 mg, 0.63 mmol) in CH_2Cl_2 (20 ml), and a few minutes later, a soln. of **7** (120 mg, 0.38 mmol) in CH_2Cl_2 (7 ml). After stirring at −70° for 2 h, the mixture was allowed to warm to −20° within 2 h. It was poured onto ice, washed twice with H_2O (50 ml), and dried ($MgSO_4$). Evaporation of the solvent, followed by FC (30 g of silica gel, hexane/AcOEt 1:1→hexane/AcOEt 1:3) yielded 190 mg (86%) of **8** (d.e. *ca.* 100%). Purification by prep. HPLC (hexane/CH_3OH 98:2; t_R 19.4 min) gave pure **8** as a colourless oil, which crystallized from pentane. For X-ray analysis, a sample was crystallized from pentane/CH_2Cl_2 according to the liquid-diffusion method [17]. M.p. 122–122.5°; R_f 0.40 (AcOEt); $[\alpha]_D^{25}$ = +8.3° (*c* = 1, $CHCl_3$). IR (KBr): 3290*m*, 3000*m*, 2960*m*, 2940*m*, 1460*m*, 1380*m*, 1370*m*, 1260*m*, 1205*s*, 1180*m*, 1125*w*, 1105*w*, 1070*s*, 1025*s*, 1000*s*, 970*s*, 920*w*, 910*w*, 875*m*, 840*m*. ^{1}H- and ^{13}C-NMR: *Tables 2–4*. ^{31}P-NMR (80 MHz, $CDCl_3$): 28.22. MS: 575 (1, M^+), 560 (3), 542 (1), 474 (3), 404 (8), 346 (11), 298 (7), 297 (7), 282 (9), 256 (11), 171 (30), 115 (10), 108 (23), 107 (29), 105 (29), 101 (47), 92 (22), 91 (100), 79 (35), 77 (26), 65 (20), 59 (26), 43 (99), 41 (33). Anal. calc. for $C_{29}H_{38}NO_9P$ (575.59): C 60.51, H 6.65, N 2.43, P 5.38; found: C 60.55, H 6.90, N 2.35, P 5.20.

Reaction of **7** *with Methyl Methacrylate*. A soln. of **7** (219 mg, 0.7 mmol) and methyl methacrylate (1 ml) in $CHCl_3$ (5 ml) was stirred at 70° for 30 min. Evaporation of the solvent and CC (30 g of silica gel, hexane/AcOEt 3:1) afforded 200 mg (69%) of a faster moving *Fraction A* (R_f 0.47 (hexane/AcOEt 1:1)) and 35 mg (12%) of a slower moving *Fraction B* (R_f 0.31). HPLC showed that the *Fraction A* was a mixture **9a**/**9b** 49:1. By crystallization and a second CC, **9a** and **9b** were obtained in pure form: **9a** as fine needles and **9b** as a colourless oil. ^{1}H-NMR spectroscopy of the *Fraction B* revealed a mixture **11a**/**11b** 1:1. Prep. HPLC (CH_2Cl_2/MeOH 98.5:1.5, t_R 18.1 min for **11a** and 16.3 min for **11b**) afforded **11a** and **11b**, each as a crystalline compound.

*Methyl 2,*N*:4,7-Dianhydro-3,4,5,6-tetradeoxy-4-*C*-hydroxyamino-8,9:11,12-di-*O*-isopropylidene-2-*C*-methyl* α-*D*-manno-*L*-erythro-7-dodeculo-7,10-furanosonate* (**9a**). M.p. 66°; R_f 0.47 (hexane/AcOEt 1:1); $[\alpha]_D^{25}$ = −48.8°(*c* = 0.7, $CHCl_3$); IR ($CHCl_3$): 3030*w*, 2990*s*, 2960*m*, 2940*m*, 2890*w*, 1740*s*, 1455*m*, 1435*w*, 1305*m*, 1165*m*, 1150*m*, (sh), 1115*s*, 1070*s*, 1045*s*, 990*w* (sh), 975*m*, 940*w*, 895*m*, 885*w* (sh), 860*m*, 845*m*, 820*w*. ^{1}H- and ^{13}C-NMR: *Tables 2–4*. MS: 413 (1.5, M^+), 398 (4), 354 (1), 340 (2), 312 (2), 200 (29), 199 (12), 144 (11), 141 (11), 140 (12), 119 (12), 101 (17), 100 (22), 99 (11), 98 (10), 84 (15), 83 (8), 81 (13), 71 (8), 69 (16), 68 (15), 67 (8), 59 (17), 57 (10), 55 (22), 53 (8), 43 (100), 42 (11), 41 (42), 39 (17). Anal. calc. for $C_{20}H_{31}NO_8$ (413.47): C 58.10, H 7.56, N 3.39; found: C 58.35, H 7.57, N 3.60.

*Methyl 2,*N*:4,7-Dianhydro-3,4,5,6-tetradeoxy-4-*C*-hydroxyamino-8,9:11,12-di-*O*-isopropylidene-2-*C*-methyl-* α-*D*-manno-*L*-threo-7-dodeculo-7,10-furanosonate* (**9b**). R_f 0.50 (hexane/AcOEt 1:1); $[\alpha]_D^{25}$ = −31.9° (*c* = 0.4, $CHCl_3$). IR ($CHCl_3$): 2990*s*, 2950*s*, 2930*s*, 2880*m*, 1735*s*, 1455*m*, 1435*m*, 1380*s*, 1370*s*, 1300*m*, 1260*m*, 1160*s*, 1150*s*, (sh), 1140*s*, 1125*m*, 1100*m*, 1070*s*, 1050*s*, 990*m*, 970*m*, 940*m*, 890*m*, 870*m*, 855*m*, 840*m*. ^{1}H- and ^{13}C-NMR: *Tables 2–4*. MS: 413 (1, M^+), 398 (8), 354 (2), 340 (1), 312 (6), 247 (4), 200 (26), 199 (9), 191 (7), 144 (7), 141 (11), 140 (12),

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[5]) Mainly 3:2 mixture of two isomers. Signals of the predominant isomer are indicated in italics. Signals of other isomers (low intensities) are not listed.

101 (21), 100 (18), 99 (11), 98 (14), 97 (9), 85 (8), 84 (13), 81 (11), 72 (7), 69 (16), 68 (11), 59 (17), 57 (11), 55 (12), 53 (7), 43 (100), 42 (9), 41 (48), 39 (21).

*Methyl 2,*N*:4,7-Dianhydro-3,4,5,6-tetradeoxy-4-*C*-hydroxyamino-8,9:11,12-di-*O*-isopropylidene-2-*C*-methyl-*α*-*D*-manno-*D*-erythro-7-dodeculo-7,10-furanosonate* (**11a**). M.p. 111°, R_f 0.31 (hexane/AcOEt 1:1); $[\alpha]_D^{25}$ = +71.9° (*c* = 0.6, $CHCl_3$). IR ($CHCl_3$): 2990*s*, 2955*s*, 2935*s*, 2890*m*, 2860*w*, 1735*s*, 1455*m*, 1440*m*, 1380*s*, 1370*s*, 1320*m*, 1305*m*, 1255*s*, 1165*s*, 1135*s*, 1090*s*, 1070*s*, 985*m*, 975*m*, 890*m*, 865*m*, 840*m*. ^{1}H- and ^{13}C-NMR: *Tables 2–4*. MS: 413 (3, M^+), 398 (4), 355 (2), 354 (2), 340 (4), 313 (2), 312 (2), 212 (3), 201 (5), 200 (51), 199 (23), 144 (16), 141 (13), 140 (21), 137 (6), 126 (7), 101 (22), 100 (33), 99 (14), 98 (14), 97 (7), 85 (9), 84 (14), 81 (13), 72 (10), 71 (8), 69 (16), 68 (12), 59 (19), 55 (14), 44 (9), 43 (100), 42 (8), 41 (33), 39 (14). Anal. calc. for $C_{20}H_{31}NO_8$ (413.47): C 58.10, H 7.56, N 3.39; found: C 58.08, H 7.55, N 3.51.

*Methyl 2,*N*:4,7-Dianhydro-3,4,5,6-tetradeoxy-4-*C*-hydroxyamino-8,9:11,12-di-*O*-isopropylidene-2-*C*-methyl-*α*-*D*-manno-*D*-threo-7-dodeculo-7,10-furanosonate* (**11b**). M.p. 114°; R_f 0.31 (hexane/AcOEt 1:1); $[\alpha]_D^{25}$ = +97.1° (*c* = 0.6, $CHCl_3$). IR ($CHCl_3$): 2990*s*, 2950*m*, 2940*m*, 2910*w*, (sh), 2880*w*, 1735*s*, 1480*w*, 1455*m*, 1435*m*, 1380*s*, 1370*s*, 1325*w*, 1290*m*, 1265*m*, 1190*s*, 1165*s*, 1080*s*, 1070*s*, 995*m*, 975*m*, 955*w*, 940*m* (sh), 935*m*, 905*m*, 890*m*, 865*m*, 840*m*. ^{1}H- and ^{13}C-NMR: *Tables 2–4*. MS: 413 (3, M^+), 398 (4), 355 (2), 354 (2), 340 (4), 312 (7), 296 (3), 212 (4), 201 (6), 200 (45), 199 (11), 141 (13), 140 (13), 137 (7), 119 (16), 101 (20), 100 (29), 99 (16), 98 (27), 97 (14), 85 (8), 84 (16), 83 (7), 81 (16), 71 (7), 69 (11), 68 (14), 59 (15), 55 (19), 43 (100), 42 (9), 41 (30), 39 (11). Anal. calc. for $C_{20}H_{31}NO_8$ (413.47): C 58.10, H 7.56, N 3.39; found: C 58.31, H 7.29, N 3.58.

Reaction of **7** *with Methyl Acrylate.* A soln. of **7** (53 mg, 0.17 mmol) and methyl acrylate (1 ml) in $CHCl_3$ (2 ml) was stirred at 70° for 30 min. Evaporation of the solvent and CC (30 g of silica gel, hexane/AcOEt 1:1) afforded 5.5 mg of a *Fraction A* (R_f 0.43 (hexane/AcOEt 1:1)), 12.5 mg of a *Fraction B* (R_f 0.36), 15 mg of a *Fraction C* (R_f 0.36 and 0.31), and 25.5 mg of a *Fraction D* (R_f 0.31). Total yield of adducts: 58.5 mg (87%). The ^{1}H-NMR showed that *A* was a mixture **13a**/**13b**/**14a** 13:9:65, *B* a mixture **10a**/**10b** 65:35, *C* a mixture **10a**/**10b**/**12a** 26:9:65, and *D* a mixture **10b**/**12a** (15:85 (see also *Table 1*). CC (35 g of silica gel, hexane/AcOEt 4:1) of the combined *Fractions C* and *D* afforded pure **12a** and **10a**/**10b**. Prep. HPLC (CH_2Cl_2/MeOH 98.5:1,5, t_R 13.5 min for **10a** and 15.3 min for **10b**) of this mixture, combined with *Fraction B*, gave pure **10a** and **10b**. Prep. HPLC of *Fraction A* (hexane/AcOEt 3:1, t_R 8.3 min for **13a**/**14a** and 11.1 min for **13b**) afforded pure **13b** and a mixture of **14a**/**13a** 9:1.

*Methyl 2,*N*:4,7-Dianhydro-3,4,5,6-tetradeoxy-4-*C*-hydroxyamino-8,9:11,12-di-*O*-isopropylidene-α-*D*-manno-*L*-erythro-7-dodeculo-7,10-furanosonate* (**10a**). R_f 0.36 (hexane/AcOEt 1:1); $[\alpha]_D^{25}$ = −23.6° (*c* = 0.8, $CHCl_3$). IR ($CHCl_3$): 3030*w*, 2990*s*, 2950*m*, 2900*w* (sh), 2880*w*, 1750*s*, 1730*s*, 1460*m* (sh), 1450*m*, 1380*s*, 1370*s*, 1265*m*, 1160*s*, 1135*m*, 1115*w*, 1065*s*, 1045*s*, 975*m*, 950*w*, 930*w*, 885*m*, 865*m*, 840*m*. ^{1}H- and ^{13}C-NMR: *Tables 2–4*. MS: 399 (2), 385 (8), 384 (34), 340 (18), 298 (22), 282 (10), 212 (10), 198 (10), 187 (12), 186 (100), 185 (27), 181 (8), 166 (8), 154 (10), 152 (9), 141 (39), 138 (9), 137 (12), 130 (32), 126 (42), 124 (9), 122 (8), 113 (10), 110 (9), 108 (13), 101 (42), 100 (24), 99 (23), 98 (27), 97 (18), 96 (8), 95 (10), 94 (9), 85 (19), 84 (18), 83 (13), 82 (13), 81 (26), 80 (12), 73 (11), 72 (18), 71 (12), 70 (22), 69 (17), 68 (25), 67 (9), 59 (34), 57 (12), 55 (30), 53 (13), 43 (96), 42 (18), 41 (33), 39 (17).

*Methyl 2,*N*:4,7-Dianhydro-3,4,5,6-tetradeoxy-4-*C*-hydroxyamino-8,9:11,12-di-*O*-isopropylidene-α-*D*-manno-*L*-threo-7-dodeculo-7,10-furanosonate* (**10b**). R_f 0.31 (hexane/AcOEt 1:1); $[\alpha]_D^{25}$ = −53.6° (*c* = 0.9, $CHCl_3$). IR ($CHCl_3$): 3020*w*, 2990*s*, 2950*m*, 2940*m*, 2890*w*, 1745*s*, 1480*w*, 1460*m*, 1455*m*, 1380*s*, 1370*s*, 1320*w*, 1160*s*, 1115*m*, 1070*s*, 1045*s*, 975*m*, 950*w*, 890*m*, 860*m*, 840*m*. ^{1}H- and ^{13}C-NMR: *Tables 2–4*. MS: 399 (4, M^+), 385 (5), 384 (27), 340 (10), 326 (5), 298 (13), 212 (8), 187 (12), 186 (100), 185 (46), 141 (26), 130 (43), 126 (18), 110 (8), 108 (8), 101 (33), 100 (13), 99 (18), 98 (24), 97 (10), 95 (8), 85 (15), 84 (12), 83 (9), 81 (21), 80 (8), 72 (12), 71 (8), 70 (16), 69 (12), 68 (19), 59 (23), 55 (21), 53 (9), 43 (72), 42 (12), 41 (25), 39 (12).

*Methyl 2,*N*:4,7-Dianhydro-3,4,5,6-tetradeoxy-4-*C*-hydroxyamino-8,9:11,12-di-*O*-isopropylidene-α-*D*-manno-*D*-erythro-7-dodeculo-7,10-furanosonate* (**12a**). M.p. 77°; R_f 0.31 (hexane/AcOEt 1:1); $[\alpha]_D^{25}$ = +75.7° (*c* = 1, $CHCl_3$). IR ($CHCl_3$): 3010*w*, 2990*s*, 2950*m*, 2940*m*, 2890*w*, 1740*s*, 1475*w*, 1455*m*, 1435*m*, 1380*s*, 1370*s*, 1325*w*, 1290*m*, 1160*s*, 1125*m*, 1070*s*, 1040*s*, 1015*m*, 990*m*, 975*m*, 920*w*, 905*m*, 885*m*, 865*m*, 840*m*. MS: 399 (4, M^+), 384 (18), 340 (9), 326 (9), 298 (20), 272 (10), 213 (15), 187 (10), 186 (79), 185 (25), 176 (24), 154 (19), 146 (12), 141 (28), 138 (10), 137 (10), 130 (25), 126 (30), 110 (14), 101 (31), 100 (18), 99 (23), 98 (27), 97 (19), 85 (15), 84 (16), 83 (10), 81 (22), 80 (10), 71 (12), 70 (18), 69 (18), 68 (23), 59 (29), 53 (13), 43 (100), 42 (24), 41 (39), 39 (20). Anal. calc. for $C_{19}H_{29}NO_8$ (399.44): C 57.13, H 7.32, N 3.51; found: C 57.12, H 7.43, N 3.72.

Data of **14a**/**13a** *9:1.* R_f 0.43 (hexane/AcOEt 1:1); $[\alpha]_D^{25}$ = +80.1 (*c* = 1, $CHCl_3$). IR ($CHCl_3$): 2990*s*, 2960*s*, 2940*s*, 2900*m* (sh), 1735*s*, 1455*m*, 1435*m*, 1380*s*, 1370*s*, 1350*m*, 1260*s*, 1160*s*, 1120*s*, 1065*s*, 1050*s*, 1020*m*, 970*m*, 960*m*, 910*m*, 890*m*, 865*m*, 840*m*. ^{1}H- and ^{13}C-NMR: *Tables 2–4*.

*Methyl 2-*C,N*:3,6-Dianhydro-2,3,4,5-tetradeoxy-3-*C*-hydroxyamino-2-*C*-hydroxymethyl-7,8:10,11-di-*O*-isopropylidene-α-*D*-manno-*L*-erythro-6-undeculo-6,9-furanosonate* (**13b**). R_f 0.43 (hexane/AcOEt 1:1); $[\alpha]_D^{25}$ = +1.6°

(c = 0.6, $CHCl_3$). IR ($CHCl_3$): 2990*s*, 2950*m*, 2940*m*, 2890*m*, 1740*s*, 1470*w*, 1465*m*, 1440*m*, 1380*s*, 1370*s*, 1325*m*, 1175*s*, 1160*s*, 1070*s*, 1050*s*, 1005*s*, 980*s*, 940*w*, 925*w*, 885*m*, 860*m* (sh), 840*m*. ^{1}H- and ^{13}C-NMR: *Tables 2–4*.

*Methyl 2,*N:*4,7-Dianhydro-11,12-*O*-carbonyl-3,4,5,6-tetradeoxy-4-*C*-hydroxyamino-8,9-*O*-isopropylidene-2-*C*-methyl-α-*D*-manno-*L*-erythro-7-dodeculo-7,10-furanosonate* (**15**). A soln. of **9a** (137 mg, 0.33 mmol) in AcOH/H_2O/CH_2Cl_2 8:2:5 (5 ml) was stirred at 50° for 20 h. After dilution with CH_2Cl_2 and neutralization with 2N K_2CO_3, the mixture was extracted with AcOEt. The org. layer was washed with 2N $NaHCO_3$ and brine, dried ($MgSO_4$) and concentrated *i.v.* The soln. of the oily residue (100 mg) and *N,N'*-carbonyldiimidazole (60 mg, 0.37 mmol) in dry benzene (5 ml) was stirred at 70° for 30 min. FC (25 g of silica gel, hexane/AcOEt 2:1 → AcOEt) afforded **15** (75 mg, 57%) and an impure, unknown product (78 mg). Crystallization (Et_2O/hexane) gave pure **15**. M.p. 134°; R_f 0.32 (hexane/AcOEt 1:1); $[\alpha]_D^{25} = -38.9°$ (c = 0.9, $CHCl_3$). IR ($CHCl_3$): 3020*w*, 2990*m*, 2955*m*, 2940*m*, 2880*w*, 2850*w*, 1800*s*, 1740*s*, 1475*w*, 1455*m*, 1445*m*, 1435*m*, 1385*s*, 1375*m*, 1315*m*, 1300*m*, 1270*m*, 1170*s*, 1070*s*, 1045*m*, 1000*m*, 975*m*, 935*m*, 900*m*, 885*m*, 860*w*, 820*w*. ^{1}H- and ^{13}C-NMR: *Tables 2–4*. MS: 399 (12, M^+), 384 (10), 340 (7), 324 (4), 312 (5), 200 (49), 199 (80), 198 (20), 144 (82), 140 (56), 138 (12), 112 (12), 109 (11), 101 (12), 100 (41), 99 (17), 98 (16), 97 (13), 85 (13), 84 (44), 82 (14), 81 (16), 80 (10), 71 (11), 69 (32), 68 (10), 67 (10), 59 (25), 57 (11), 56 (12), 55 (21), 53 (12), 43 (100), 42 (11), 41 (52), 39 (27). Anal. calc. for $C_{18}H_{25}NO_9$ (399.40): C 54.13, H 6.31, N 3.51; found: C 54.13, H 6.26, N 3.71.

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