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THE KINETIC ANOMERIC EFFECT. ADDITIONS OF NUCLEOPHILES AND OF DIPOLAROPHILES TO N-GLYCOSYLNITRONES AND TO N-PSEUDOGLYCOSYLNITRONES.

Rolf Huber and Andrea Vasella*

Organisch-Chemisches Institut der Universität Zürich
Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

Dedicated to Duilio Arigoni

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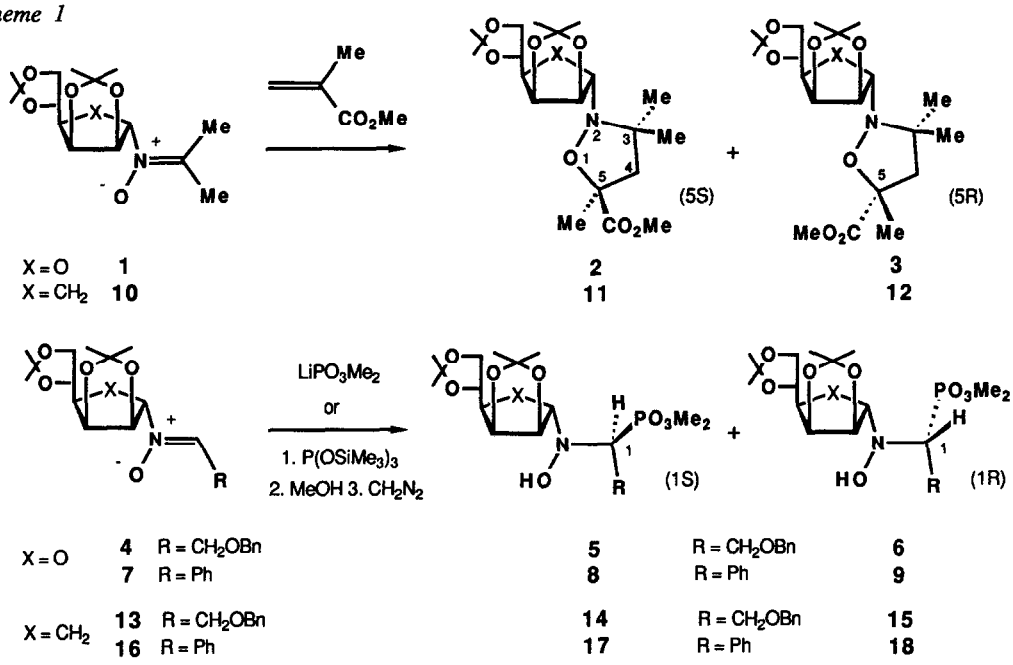
Summary. - To prove the hypothesis of the role of a kinetic anomeric effect in the highly diastereoselective additions of nucleophiles and of dipolarophiles to N-glycosylnitrones, we compared these additions to those to analogous N-pseudoglycosylnitrones, having a methylene group in place of the furan ring oxygen. An almost complete loss of the diastereoselectivity was found for the addition of lithium dimethyl phosphite, tris(trimethylsilyl)phosphite and methyl methacrylate to the N-pseudoglycosylnitrones which moreover reacted more slowly, as predicted by the hypothesis of the kinetic anomeric effect. Pseudo first order kinetics for the $ZnCl_2$ promoted addition of $P(OSiMe_3)_3$ to nitrones were measured; activation energies, diastereoselectivities and the influence of Lewis acids are discussed.

1. Introduction. - The 1,3-dipolar cycloaddition of N-glycosylnitrones to methyl methacrylate leads to N-glycosylisoxazolidines with a high degree of diastereoselectivity. Thus, the D-mannofuranosylnitrone **1** gave the (5S)-configurated isoxazolidine **2** with a diastereomeric excess (d.e.) of over 90%.[1] The addition of lithium dialkyl phosphites to C-alkyl-N-mannofuranosylnitrones, such as **4** (*Scheme 1*), and the addition of tris(trimethylsilyl)phosphites to C-aryl-N-mannofuranosylnitrones, such as **7**, gave the corresponding (1S)-configurated N-hydroxy-N-glycosylaminophosphonates (**5**, **6**, **8** and **9**, respectively). These additions also proceed highly diastereoselectively.[2]

The diastereoselectivity observed in these reactions has been rationalized[1,2] on the basis of a stereoelectronic effect in combination with steric effects. The former is responsible for the enhanced reactivity and the latter determines both the relative population of the relevant conformers and the direction of attack of the 1,3-dipolarophile and of the nucleophile.

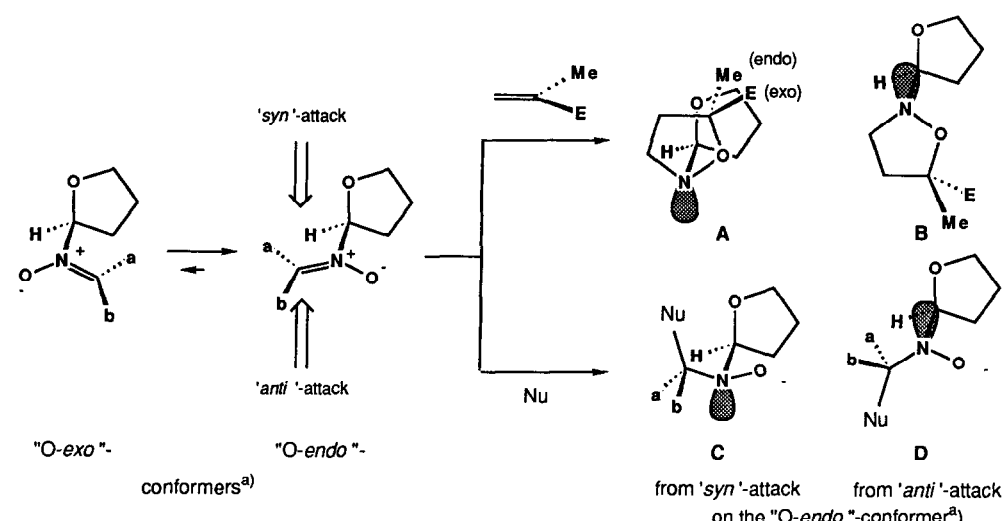
(i) *Conformation of the reacting nitrone.* In the course of both the nucleophilic addition and the LUMO-controlled[3] 1,3-dipolar cycloaddition, a doubly occupied, nonbonding sp^3-orbital at the N-atom (n_N) is formed (*Fig. 1*). The stabilizing (exo)-anomeric effect present in those conformers of the product possessing a coplanar arrangement of the n_N-orbital and the σ^*-orbital of the C(1),O bond (**A** - **D**, *Fig. 1*) is postulated to be effective already in the corresponding transition states and to lower their energy (= *kinetic anomeric effect*). To this $n_N/\sigma^*_{C(1),O}$-interaction in the appropriate conformers of the products and of the transition states leading to them

Scheme 1



corresponds in the starting material (nitrones) an orbital interaction between the LUMO of the nitrone function and the σ*-orbital of the C(1),O-bond. This interaction is possible in two (the 'O-*endo*' and the 'O-*exo*'-) conformers.[4] The influence of the nitrone C-substituents upon the degree of the diastereoselectivity was rationalized by a (destabilizing) steric interaction between the nitrone C-substituents and the glycosyl moiety in the 'O-*exo*'-conformation. Thus, we postulated the 'O-*endo*'-conformer to be the one preferred in the ground state and the one

Fig. 1: Attack of Dipolarophile and Nucleophile to N-Glycosylnitrones.

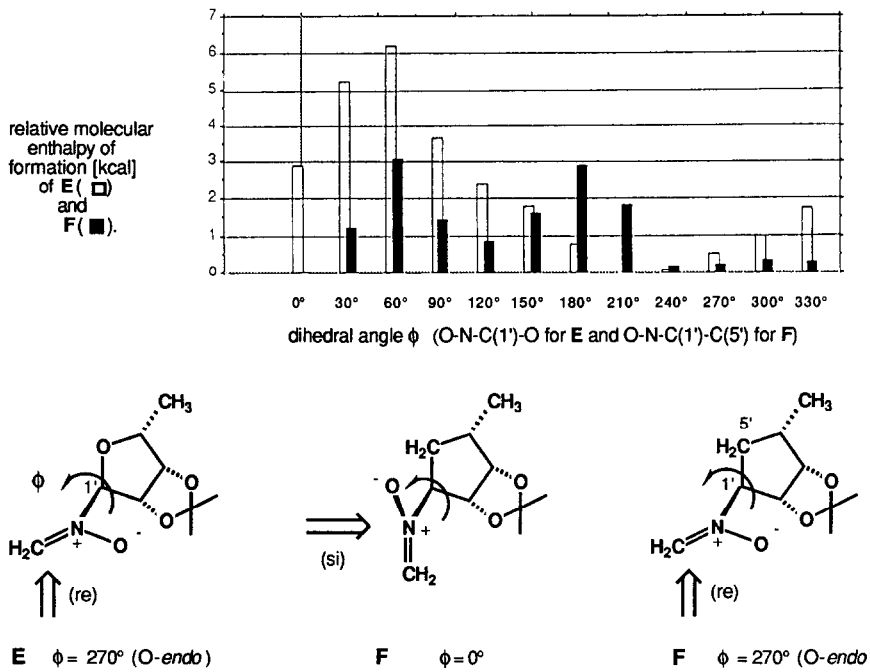


[a]) substituents on C ≠ C(2) of the tetrahydrofuran ring are omitted

leading to the major products. N.*O*.e. experiments[2c,d] indicate that such a conformer is indeed preferred in the ground state and this finding is corroborated by the X-ray analysis of the nitrone **4** (dihedral angle $\phi = 291°$, compare *Fig. 2*) and by AM1-calculations (see below).

(ii) *Direction of attack.* The conjugative stabilization expected by the interaction of the $n_N/\sigma^*C(1),O$-orbitals may be higher in an antiperiplanar than in a synperiplanar arrangement (**A** and **C** vs. **B** and **D**, *Fig. 1*). This energy difference should favour a '*syn*'-attack both of a dipolarophile and of a nucleophile, while steric interactions of the dipolarophile and the nucleophile with the glycosyl moiety should lead mainly to an '*anti*'-attack (*Fig. 1*). The known (Z)-configuration of the nitrone **4**, the hypothesis that it reacts mainly *via* its 'O-*endo*'-conformer and the (1S)-configuration of the major product **5** mean that an 'anti'-attack is preferred. The direction of attack was determined by examining the products of the 1,3-dipolar cycloaddition of methyl methacrylate, on the one hand, and those of the nucleophilic addition of lithium dibenzyl phosphite, on the other hand, to a conformationally and configurationally defined spiro nitrone. A preferred 'anti'-attack was found for the cycloaddition[5] (ratio of cycloadducts resulting from an anti-attack to those resulting from a syn-attack = 85:15). The nucleophilic addition of the phosphite gave exclusively the phosphonate resulting from an anti attack.[5] Thus, steric effects appear to be more important than the difference of the stereoelectronic effects in the antiperiplanar vs. synperiplanar orbital arrangement.

Fig. 2: Molecular Enthalpy of Formation of the Model Compounds **E** *and* **F** *vs. the Dihedral Angle* ϕ.[a])



E $\phi = 270°$ (O-*endo*) **F** $\phi = 0°$ **F** $\phi = 270°$ (O-*endo*)

a) Relative to the enthalpy of formation of the most stable conformer of **E** and **F** (=0).

Of central importance for the rationalization of the observed diastereoselectivities is the hypothesis of a kinetic anomeric effect linked to the presence of a N-alkoxyalkyl substituent; i.e. to the ring oxygen in the tetrahydrofuran moiety. To test this hypothesis, we intended to compare the N-glycosylnitrones (N-alkoxy

alkylnitrones) and the analogous N-pseudoglycosylnitrones (N-alkylnitrones) with regard to both the diastereoselectivity and the rates of their reaction with phosphites, on the one hand, and of their 1,3-dipolar cycloaddition to methyl methacrylate, on the other hand.

The effect of the substitution of the ring oxygen by a methylene group upon the ground state conformations of the corresponding nitrones was evaluated by calculating the energy of twelve conformers of the model nitrones **E** and **F** as represented in *Fig. 2*. The relevance of these calculations for the transition state conformation derives from the assumption of an early and thus educt-like transition state for the addition of nucleophiles and for the 1,3-dipolar cycloaddition.[6] AM1-calculations[7] indicated an energy-minimum for an 'O-*endo*'-like conformation of both model nitrones (**E**: $\phi_{min} = 221°$, ΔE_{exo}-$\Delta E_{endo} = 3.1$ kcal; **F**: $\phi_{min} = 0$ and 240°, ΔE_{exo}-$\Delta E_{endo} = 1.2$ kcal). The curve depicting the energy dependence on the torsion angle ϕ for **F** is much shallower than the one for **E**. Competing transition states may thus result from the two conformers of **F** characterized by dihedral angles $\phi = 0°$ and $\phi = 270°$, respectively and one expects a low selectivity of the attack upon N-pseudoglycosylnitrones of the type **F** by 1,3-dipolarophiles and by nucleophiles.

2. Synthesis of N-Pseudoglycosylnitrones.- To obtain these carbaanalogues, we required the cyclopentylhydroxylamine **46** (*Scheme 6*). As a key step in its preparation we used an intramolecular olefination, as described by *Lim* and *Marquez*[8a] and by *Altenbach* et al.[8b] for the analogous *ribo*-series. The addition of $LiCH_2PO_3Et_2$[9] to the mannonolactone **19**[10] gave the phosphonate **20** (74%, *Scheme 2*) as a single product of unknown configuration at the anomeric centre. The base-catalyzed isomerization of **20** yielded the hydroxy-ketophosphonate **21** (67%) and (unreacted or reformed) starting material **20** (30%).

The hydroxyketone **21** was oxidized[11] to the unstable diketone **22** (80-90%). The IR spectrum of **22** shows a single, strong absorption for the carbonyl groups at 1734 cm^{-1}. In the ^{13}C-NMR spectrum, the signals of the carbonyl groups appear as singlets at 204.4 and 200.0 ppm, respectively.

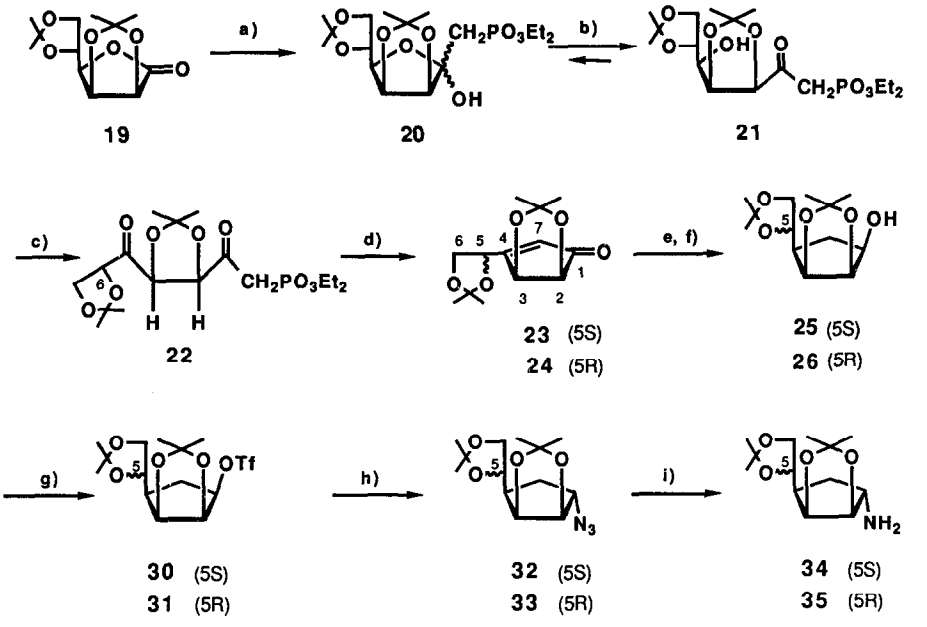
The cyclization of the diastereomerically pure diketone **22** in the presence of $KHCO_3$ and 18-crown-6[12] led to a mixture of the epimeric cyclopentenones **23** and **24** (33% from **21**) in a ratio of 1:2 as determined by the integration of the H-C(2)-signals in the ^{1}H-NMR spectrum. Base catalyzed epimerizations leading to a partial racemization of the product obtained by an analogous olefination of a *ribo*-configurated precursor (lacking the centre of chirality corresponding to C(6) of **22**) has been described by *Lim* et al.[13]

Strong absorptions at 1727 and 1626 cm^{-1} in the IR spectrum of the mixture of **23** and **24** are consistent with the α,β-unsaturated carbonyl group. In the ^{13}C-NMR spectrum, the signals at 201.4, at 173.7 and 173.4, and at 115.6 and 115.5 ppm, respectively, characterize C(1), C(4) and C(7). The (S)-configuration at C(5) of **23**, was determined at a later stage by an X-ray analysis of the phosphonate **47** (*Fig. 3*).

Hydrogenation of a mixture of **23** and **24**, followed by reduction[14] gave a mixture of the protected α-L-pseudogulose[15] **25** and β-D-pseudomannose **26** (82%), from which **25** was obtained by crystallization (hexane, ~30%).

The H-C(1)-signal in the ^{1}H-NMR spectrum of **25** with a coupling constant $J_{H\text{-}C(1),H\text{-}C(2)}$ of 5.4 Hz, confirms the α-L-configuration.[8a,b]

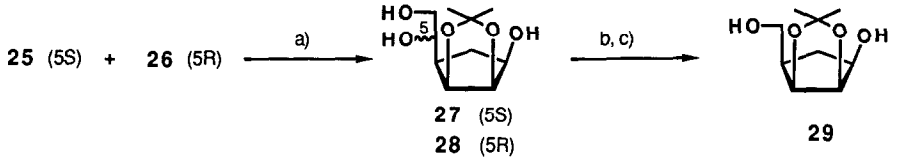
Scheme 2



a) BuLi, $CH_3PO_3Et_2$, THF, -50°, 20 min, 74-90%. b) t-BuOK, EtOH, 52-55°, 5 h, 67% of **21** and 30% of **20**. c) $(CF_3CO)_2O$-DMSO, CH_2Cl_2, -60°C / 1h, then Et_3N. d) 18-crown-6, $KHCO_3$, C_6H_6, 60-80°, 4 h, 33% from **21**. e) H_2, 10% Pd/C, MeOH, r.t., 30 min. f) $NaBH_4$, $CeCl_3$, MeOH, r.t., 30 min, 82% (steps e and f). g) $(CF_3SO_2)_2O$, Py, CH_2Cl_2, -30°, 15 min. h) NaN_3, DMF, r.t., 93% (steps g and h). i) H_2, 10% Pd/C, MeOH, r.t., 30 min, quant.

The assumption that **25** and **26** are epimeric at C(5) was checked by hydrolysing a (1:2)-mixture of **25** and **26** with $AcOH/H_2O$ to the triols **27** and **28** (*Scheme 3*), which upon treatment with periodate and then with $NaBH_4$[16] gave **29** (85%) as a single compound.

Scheme 3



a) $AcOH/H_2O$ (1:1.5)r.t., 5.5 h. b) Phosphate buffer (pH 6.8), $NaIO_4$, r.t., 75 min. c) $NaBH_4$, r.t., 15 min (85%).

Following a procedure of *Kini* and *Hennen*[17], the mixture of **25** and **26** was transformed *via* the triflates **30** and **31** (*Scheme 2*) into the azides **32** and **33** (93%), which were separated by chromatography.

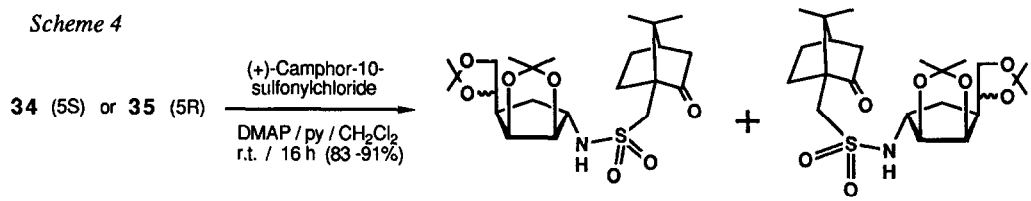
The IR spectra of **32** and **33** show a strong peak at 2100 cm^{-1} attributed to the azide function. In the ^1H-NMR spectra of **32** and **33**, the coupling constants $J_{H\text{-}C(1)/H\text{-}C(2)}$ of 1.3 and 1.4 Hz confirm the α-D- and β-L-configuration of **32** and **33**, respectively.

Hydrogenation (MeOH, 10% Pd/C) of the azides **32** and **33** yielded quantitatively the 'L-*gulo*'- and the 'D-*manno*'-amines **34** and **35**. A sample of chromatographed, but not crystallized 'L-*gulo*'-amine **34**, obtained from crystallized **25**, showed an $[\alpha]_D$ of +50°, whereas a similiarly purified sample of **34**, obtained from

chromatographed, but not crystallized **25** showed an $[\alpha]_D$ +35°; the ^{1}H- and ^{13}C-NMR spectra of the two samples of **34** could not be distinguished from each other and are consistent with the presence of a single, pure compound. Thus, one or both samples were partially racemized. The sample of **34**, characterized by an $[\alpha]_D$ = +35°, led to a mixture of the diastereoisomeric camphor-10-sulfonamides (*Scheme 4*) **36** and **37** in a ratio of 5.5:1(as determined by the integration of several peaks in the ^{1}H-NMR); the sample of **34** ($[\alpha]_D$ = + 50°) gave only **36**. ^{1}H-NMR-shift experiments with the two samples of the amine **34** in the presence of Eu(tfc)$_3$[18] confirmed these results.

The 'D-*manno*'-amine **35** prepared from amorphous **33** and showing an $[\alpha]_D$ = -36° was over 90% enantiomerically pure, as judged from the diastereomeric purity of the crude sulfonamide **38** and from ^{1}H-NMR-shift experiments with **35** in the presence of Eu(tfc)$_3$. No evidence for a partial racemization during the synthesis of the 'D-*manno*'-amine **35** was detected.

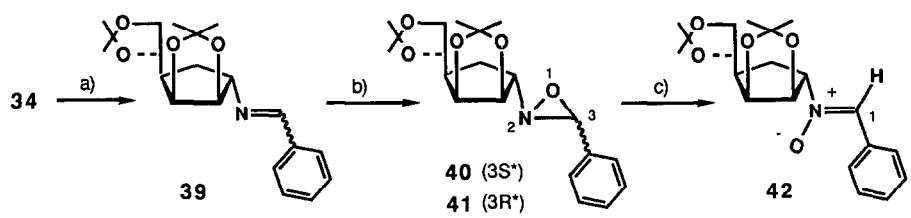
Scheme 4



The synthesis of the N-pseudoglycosylnitrones was first continued with the 'L-*gulo*'-amine **34**, obtained as the major diastereoisomer. The crude imine **39** (*Scheme 5*), obtained from **34** and benzaldehyde according to *Grundke et al.*[19], was oxidized with MCPBA[20] to a 3:1 mixture of the oxaziridines **40** and **41** (73%), which were separated by chromatography. For the synthesis of the C-phenylnitrone **42**, a transformation of the oxaziridines **40** and **41** into the corresponding hydroxylamine was not required, since thermolysis of either **40** and **41** at 200° gave **42** directly (55%).

The UV spectra (λ_{max}- and ε-values) of **42** and of other N-alkylnitrones differ hardly from those of the corresponding N-alkoxyalkyl analogues, indicating a small influence of the tetrahydrofuran ring oxygen on the π-π* transition.

Scheme 5

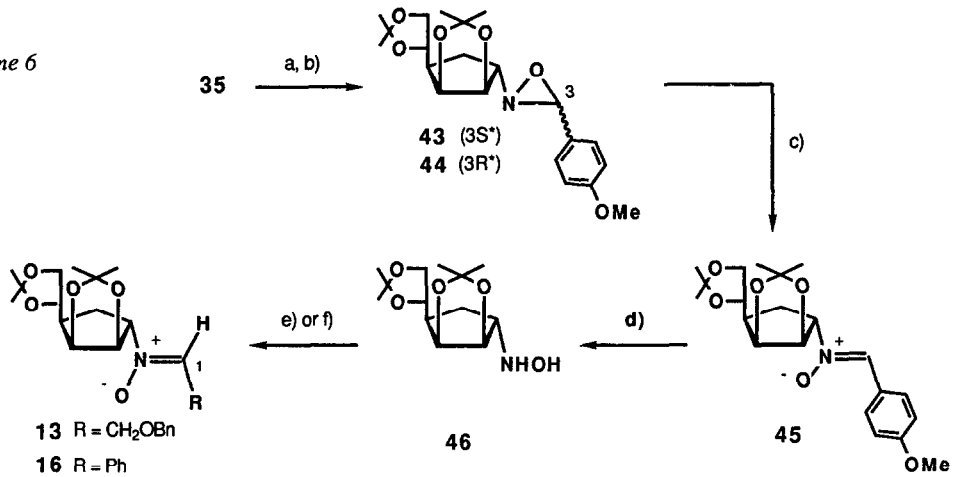


a) Benzaldehyde, Na_2CO_3, MeOH, r.t., 20 h. b) MCPBA, THF, 0°, 4 h, 73%. c) 200°, 3 min, 20 torr, 55%.

For the synthesis of the 'D-*manno*' configurated benzylnitrone **13**, a modified route *via* the N-cyclopentylhydroxylamine **46** (*Scheme 6*) had to be chosen, since 3-alkyl substituted oxaziridines isomerize under thermal conditions to the corresponding N-alkyl amides.[21] The transformation of the 'D-*manno*' amine

into the oxaziridines **43** and **44** was analogous to the one of the 'L-*gulo*'-amine into the oxaziridines **40** and **41**. The thermal isomerization of the methoxyphenyl substituted oxaziridines **43** and **44**, however, proceeds at a lower temperature (130°, ca. 60%) than the one of the phenyl substituted oxaziridines **40** and **41**. For preparative purposes, we preferred an isomerization in AcOH soln. at 100°, yielding the nitrone **45** in 78%. Treatment of **45** with hydroxylamine in AcOH gave the cyclopentylhydroxylamine **46**, which in the presence of excess benzyloxyacetaldehyde and benzaldehyde gave the nitrones **13** (68%) and **16** (72% from **45**), respectively. Both nitrones are diastereomerically pure. An indication for the (Z)-configuration of **13** and **16** is given by the similar chemical shift values of the $H_2C(2)$-signals of the pseudoglycosylnitrone **13** and of the N-glycosylnitrone **4** and by similar chemical shifts of the ortho phenyl hydrogen signals of **16** and **7**. The (Z)-configuration of **4** has been established by X-ray analysis[2b] and the one of the 'L-*gulo*'-nitrone **42** was evidenced by a strong n.*O*.e. between H-C(1) and H-C(1').

Scheme 6



a) Anisaldehyde, MeOH, Na_2CO_3, r.t., 18 h. b) MCPBA, THF, 0°, 90 min, 71% (**43**:**44** = 1.7:1.). c) AcOH, 100°, 5 min, 78%. d) $NH_2OH{\cdot}HCl$, $NaHCO_3$, AcOH, r.t., 4 h. e) 2-Benzyloxyacetaldehyde, $CHCl_3$, r.t., 10 min, 68%. f) Benzaldehyde, $CHCl_3$, r.t., 6 h, 72%.

3. Comparison of the reactivity of N-glycosyl- and N-pseudoglycosylnitrones.

3.1. Addition of phosphites.- a) *$LiPO_3Me_2$*. As described[2b], addition of $LiPO_3Me_2$ at -25° to a soln. of the N-glycosylnitrone **4** (*Scheme 4*) in CH_2Cl_2 or THF gave the diastereomeric phosphonates **5** and **6** in 85-90% yield and with a diastereoselectivity of 80 and 88% (*Table 2*), respectively. Under analogous conditions, the N-pseudoglycosylnitrone **13** (*Scheme 1*) gave the phosphonates **14** and **15** (87-90%) with a d.e. of 28 (CH_2Cl_2) and 42% (THF). The diastereoselectivity was determined by the integration of the well separated ^{31}P-signals of the diastereoisomers **14** and **15**. It is thus distinctly lower for the addition to the N-pseudoglycosylnitrone **13**.

The spectra of **14** and **15** are consistent with the proposed structure.[22] In particular, comparison of the data presented in *Table 1* shows that the C(1)-signals of the (1S)-configurated phosphonates **5**, **8**[2c] and **47** (see below) appear at a lower field and show a smaller (C,P)-coupling than those of their (1R)-diastereomers **6**, **9** and **48**. Also, the ^{31}P-signals of **5**, **8** and **47** consistently appear at a higher field than those of **6**, **9** and **48**. By extrapolation, **14** and **15** were assigned the (1S) and (1R) configuration, respectively.

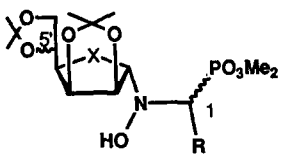


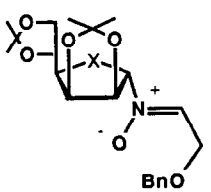
Table 1: Selected NMR-Data of N-Hydroxyaminophosphonates.

	R	X	^{31}P-NMR δ[a]	^{1}H-NMR C(1): δ, J(C,P)[a]	^{13}C-NMR of C(1) H-C(1): δ, J(H,P)[a]
5 (1S, 5'R)	CH_2OBn	O	26.9	60.4; J = 151.4	[b]
6 (1R, 5'R)	CH_2OBn	O	27.0	59.1; J = 167.5	[b]
14 (1S, 5'R)	CH_2OBn	CH_2	27.6	61.57; J = 154.1	3.65; J = 19.0
15 (1R, 5'R)	CH_2OBn	CH_2	27.7	61.56; J = 161.0	3.63; J = 21.2
8 (1S, 5'R)	Ph	O	23.8	67.4; J = 163.7	4.39; J = 20.5
9 (1R; 5'R)	Ph	O	25.8	65.5; J = 167.8	4.73; J = 13.6
17 (1S, 5'R)	Ph	CH_2	24.8	68.9; J = 164.2	4.48; J = 18.5
18 (1R, 5'R)	Ph	CH_2	25.4	67.9; J = 167.2	4.36; J = 20.2
47 (1S, 5'S)	Ph	CH_2	25.0	68.9; J = 163.8	4.43; J = 20.0
48 (1R, 5'S)	Ph	CH_2	25.6	67.9; J = 168.1	4.36; J = 17.6

[a]) Chemical shifts (δ) in ppm; coupling constants J(H,P) in Hz. [b]) Signal not resolved.

The glycosylnitrone **4** (soln. in THF) reacts at -25° practically instantaneously (as evaluated by TLC-methods) whilst the pseudoglycosylanalogue **13** reacts more slowly. A similar relation of reactivities (approx. 1:8, corresponding to $\Delta\Delta G^{\neq}$ of about 1 kcal/mol) is observed when the reactions are run in CH_2Cl_2, but reaction times are notably longer (*Table 2*). Although the diastereoselectivity of the addition to the pseudoglycosylnitrone **13** is somewhat higher when the reaction is performed in CH_2Cl_2, the difference of diastereoselectivities of these additions to the glycosyl- and to the pseudoglycosylnitrone **4** and **13**, respectively, is clearly higher when THF is used as a solvent. The difference in diastereoselectivities ($\Delta\Delta\Delta G^{\neq}$) corresponds to a value of 0.6 kcal/mol for solutions in CH_2Cl_2 and of 1.1 kcal/mol for solutions in THF.

Table 2: Addition of $LiPO_3Me_2$ *to the N-Glycosylnitrone* **4** *and to the N-Pseudoglycosylnitrone* **13** *at -25° (cf. Scheme 1).*

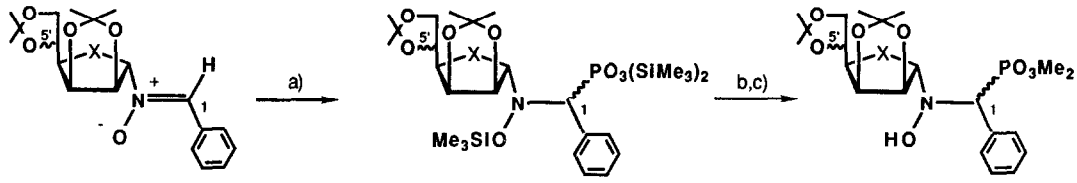


nitrone	solvent	time required for complete reaction	diastereoselectivity
4 (X=O)	THF	< 5 sec	**5** (94) : **6** (6)
13 (X=CH_2)	THF	30-40sec	**14** (64) : **15** (36)
4 (X=O)	CH_2Cl_2	25 sec	**5** (90) : **6** (10)
13 (X=CH_2)	CH_2Cl_2	200 sec	**14** (71) : **15** (29)

b) *$P(OSiMe_3)_3$*. The C-phenyl-N-glycosylnitrone **7** did not react with lithium dialkyl phosphites.[2c] As described[2c], the reaction of **7** with $P(OSiMe_3)_3$ in the presence of catalytic amounts of $HClO_4$ or of $ZnCl_2$ (≥ 1 equiv.) gave the *bona fide* silyl esters **A**, which were hydrolysed (MeOH, 0°C) and esterified (CH_2N_2) to yield the diastereomeric phosphonates **8** and **9** (88-93%, *Scheme 7* and *Table 3*) with a d.e. of 90% ($HClO_4$) and 88% ($ZnCl_2$), respectively. Under analogous conditions, the 'D-*manno*' C-phenyl-N-pseudoglycosylnitrone **16**

led to the phosphonates **17** and **18** (83%) with a d.e. of 26% ($HClO_4$) and 14% ($ZnCl_2$); the 'L-*gulo*' nitrone **42** gave the phosphonates **47** and **48** (72-77%) with a complete loss of diastereoselectivity by catalysis with $HClO_4$ and a d.e. of 4% in the presence of $ZnCl_2$. The diastereoisomers were chromatographically separated.

Scheme 7



7	X = O		X = O	**8** (1S) and	**9** (1R)
16	X = CH_2 (5'R)	**A**	X = CH_2 (5'R)	**17** (1S) and	**18** (1R)
42	X = CH_2 (5'S)		X = CH_2 (5'S)	**47** (1S) and	**48** (1R)

a) Cf. *Table 3*. b) MeOH, 0°, 2 min. c) CH_2N_2/Et_2O, 0°.

The absolute configuration at C(1) of the N-glycosylhydroxyaminophoshonate **8** is known.[2b] The (S)-configuration at C(1) and C(5') of the L-*gulo*-N-pseudoglycosylphosphophosphonate **47** was established by the X-ray-analysis of a racemate (*Fig. 3*), obtained by crystallization from a soln. of optically active, but evidently partially racemized **47**. The same regularities in the NMR spectra as mentioned above (*Table 1*) allow the assignment of the (1S)- and (1R)-configuration to **17** and **18**, respectively. No similar regularities are detected in the ^{1}H-NMR-data for H-C(1) of the phosphonates **8**, **9**, **14**, **15**, **17**, **18**, **47** and **48** (*Table 1*).

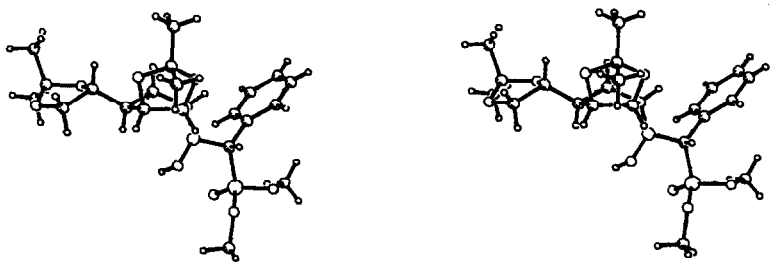
The difference of reactivity of the glycosyl- and pseudoglycosylnitrones **7**, **16** and **42** in this $HClO_4$-catalyzed addition of $P(OSiMe_3)_3$ to **4** and **13** is much larger then the one observed for the addition of $LiPO_3Me_2$ and corresponds to a $\Delta\Delta G^{\neq}$ of at the least 2.3 kcal/mol (comparison of the nitrones **7** and **16**), Although the difference of the diastereoselectivities corresponds to a $\Delta\Delta\Delta G^{\neq}$ value of only 1 kcal/mol, one notices that the diastereoselectivity of the $HClO_4$-catalyzed addition of $P(OSiMe_3)_3$ to the pseudoglycosylnitrones **16** and **42** are very low.

The addition of $P(OSiMe_3)_3$ to C-phenyl-N-glycosylnitrones is also promoted by $ZnCl_2$.[2c] The results of these additions (1 equiv. $ZnCl_2$) to the N-glycosylnitrone **7** are given in *Table 3*. Again, the analogous additions to the C-phenyl-N-pseudoglycosylnitrones **16** and **42** are much slower. From TLC-experiments (*Table 3*) one evaluates an approximate difference of reactivity for these additions to **7** and **16** corresponding to a value of $\Delta\Delta G^{\neq}$ of ca. 2.7 kcal/mol.

Table 3: Addition of $P(OSiMe_3)_3$ *to C(1)-Phenyl-N-glycosyl- and C(1)-Phenyl-N-glycosylnitrones.*

nitrone	solvent	temp.	catalyst	time required for complete reaction	^{31}P-NMR (ratio) (1S)	(1R)
7 (X=O, 5'R)	CH_2Cl_2/C_6H_6	-45°	$HClO_4$	<5sec	**8** (5)	: **9** (95)
16 (X=CH_2, 5'R)	CH_2Cl_2/C_6H_6	-45°	$HClO_4$	15-20 min	**17** (37)	: **18** (63)
42 (X=CH_2, 5'S)	CH_2Cl_2/C_6H_6	-45°	$HClO_4$	5-10 min	**47** (50)	: **48** (50)
7 (X=O, 5'R)	C_6H_6	r.t.	$ZnCl_2$	0.5 h	**8** (6)	: **9** (94)
16 (X=CH_2, 5'R)	C_6H_6	r.t.	$ZnCl_2$	> 48 h	**17** (43)	: **18** (57)
42 (X=CH_2, 5'S)	C_6H_6	r.t.	$ZnCl_2$	24 h	**47** (48)	: **48** (52)

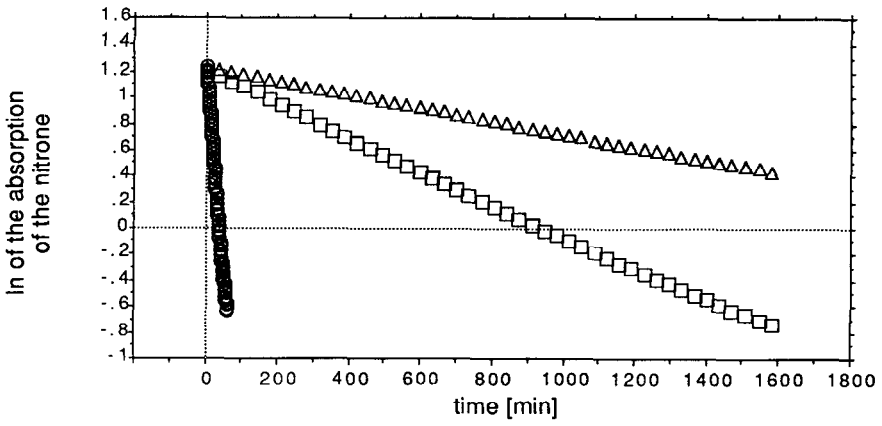
Fig. 3: ORTEP Representation of the N-Hydroxyaminophosphonate **47** (1S).



Crystallographic data have been submitted to the Cambridge Data Centre. The compound crystallized from Et_2O/hexane in colourless crystals of the space group $P\bar{1}$ with one molecule in the asymmetric unit: a = 6.716(1), b = 13.200(3), c = 14.252(3) Å, α = 76.17(2), β = 83.46(2), γ = 78.28(2) ° at ca. -140°C. Intensity measurements (until $\sin\Theta/\lambda = 0.70$ Å^{-1}) at ca. -140°C were made with a *Nicolet-R3* diffractometer (graphite monochromator, MoK_α). The structure has been solved by the heavy-atom method; SHELXTL.[23] The compound is a racemate as evident from the space group.[24]

To obtain precise values for this difference of reactivity, we studied the kinetics of the addition of $P(OSiMe_3)_3$ to the nitrones **7**, **16** and **42** (*Scheme 7*) in the presence of a large excess of the phosphite (*Fig. 4* and *Table 4*). The decrease of the concentration of a benzene soln. of the nitrones **7**, **16** and **42** (c_0=0.2 10^{-5} M) containing $ZnCl_2$ (c_0=0.1 10^{-1} M) and $P(OSiMe_3)_3$ (c_0=0.5 M) was determined by measuring the UV-absorption of the nitrones at 305 nm. The linear dependency of the natural logarithm of absorption on the reaction time shown in *Fig. 4* demonstrates the expected first order kinetics. A divergence from linearity is observed towards the end of the reaction when the rate of the addition is slowed down. This might be due to an 'aging' of the catalyst, an assumption based on the observation that a soln. of P(OSiMe3)3 and $ZnCl_2$ in benzene, which was stored for 30 h under N_2 before use, reacted with the N-glycosylnitrone **5** with a rate of 6.2 10^{-3} (first order), i.e. 5 times more slowly than a freshly prepared soln. A difference of reactivity for the addition to **7** and **16** of $\Delta\Delta G^{\neq}$ of 2.5 kcal/mol results from the k-values given in *Fig. 4*.

Fig. 4: Addition of $P(OSiMe_3)_3$ to the Nitrones **5**, **16** *and* **42**. *Plot of the Natural Logarithm of the Extinction Coefficient of* **5**, **16** *and* **42** *at 305 nm vs. Reaction Time.*



o **7** (k = 31 10^{-3} min^{-1}) □ **16** (k = 0.5 10^{-3} min^{-1}) Δ **42** (k = 1.3 10^{-3} min^{-1})

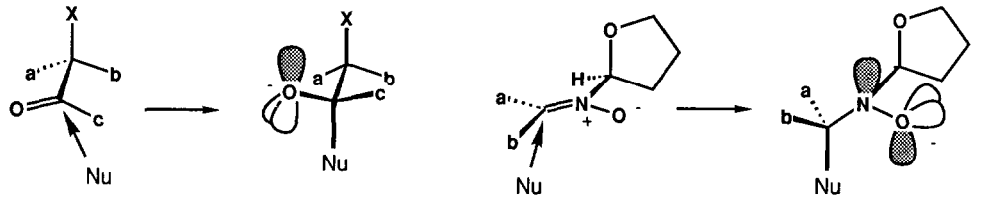
3.2. 1,3-Dipolar cycloaddition. The 1,3-dipolar cycloaddition to methyl methacrylate of the N-glycosylnitrone **1** (*Scheme 1*), formed *in situ* from the 2,3:5,6-di-O-isopropylidene-D-mannose oxime and acetone under reflux, gave predominantly the (5S)-configurated isoxazolidine **2** (5S, d.e. ≥ 90%).[1] Similarly, the N-pseudoglycosylnitrone **10**, formed *in situ* from the hydroxylamine **46** (*Scheme 6*) and acetone under reflux, reacted with methyl methacrylate to give the diastereomeric (5R) and (5S)-isoxazolidines **11** and **12** (83%, d.e. 28.6%, as determined by integration of the H-C(2)-signal in the ^{1}H-NMR spectrum and by HPLC).

In the ^{1}H-NMR spectra of **11** and **12**, H-C(2') is characterized by signals at 4.94 (J = 5.3) and 4.67 ppm (J = 5.2 Hz). The absolute configuration at C(5) was deduced from the molecular rotation of **11** and **12**.[25]

For this 1,3-dipolar cycloaddition, we observed the same reaction time of 2 days for both nitrones **1** and **10**. The rate determining step may well be the formation of the nitrones, at least for **1**, by analogy to the formation of the nitrone **4** (*Scheme 3*) from 2,3:5,6-di-O-isopropylidene-D-mannose oxime and benzyloxyacetaldehyde, which requires 15 h at r.t. in $CHCl_3$, while the formation of the analogous N-pseudoglycosylnitrone **13** requires only 10 minutes under similar conditions. In keeping with this, by ^{1}H-NMR-spectroscopy, one only observes the formation of two diastereomeric (N-glycosyl)(N-hydroxyethyl)hydroxylamines from 2,3-O-isopropylidene-5-O-tritylribose oxime and acetaldehyde (r.t., $CDCl_3$).

4. Discussion.- A comparison of the diastereoselectivities and (where available) reaction times of the N-glycosyl- vs. N-pseudoglycosylnitrones shows the profound influence of the ring oxygen. This influence is similar for the addition of phosphorus nucleophiles and for the 1,3-dipolar cycloaddition of N-glycosylnitrones. These nitrones are more reactive and more selective. This is in keeping with the postulate of the kinetic anomeric effect. In contrast to steric effects, which lead to an increase of the energy of selected transition states, this stereoelectronic effect lowers the energy of selected transition states and leads to an useful combination of enhanced reactivity and (in combination with steric effects) selectivity, hence its relevance.

Fig. 5: Comparison of Orbital Interactions.



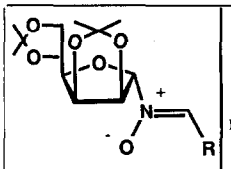
A similar combination of selectivity and reactivity is found in the 1,2 addition of nucleophiles to carbonyl compounds possessing an electronegative α-substituent. In this case, a combination of $\sigma^*_{C,X}/\pi^*_{C=O}$ orbital interaction and steric effects determines the course of the reaction. It may be instructive to compare the Anh-Eisenstein-Felkin[26] rationalization of this 1,2-induction with our rationalization of the asymmetric induction in the addition of nucleophiles to N-alkoxyalkylnitrones. The $\sigma^*_{C,X}/\pi^*_{C=O}$ orbital interaction is analogous to the $\sigma^*_{C,O}$/LUMO(nitrone) orbital interactions, both lead to a lowering of the acceptor orbital energy. These interactions disappear in the course of the addition to be replaced by one or two anomeric effects, one for the addition

of sufficiently electronegative nucleophiles to such ketones ($n_O/\sigma^*_{C,Nu}$, see **B** in *Fig. 5*) and two for the addition to N-(alkoxyalkyl)nitrones of which one ($n_N/\sigma^*_{C,O}$) is independent of the nature of the nucleophile. The favourable effect of the interaction of the lone pairs on N and O (see **D** in *Fig. 5*) has been discussed.[2c]

The differences of activation energies which are responsible for the difference of reactivity ($\Delta\Delta G^{\neq}$) and for the difference of diastereoselectivities ($\Delta\Delta\Delta G^{\neq}$) are of the order of 1-2.7 kcal/mol for the former and of 0.6 - 1.1 kcal/mol for the latter. The difference of these values is not surprising, since the kinetic anomeric effect will influence the activation energy for both the syn- and anti-addition to both the 'O-*endo*'- and the 'O-*exo*'-conformers of glycosylnitrones, and thus become effective for the rates of all these additions, which, however, do not all lead to the same diastereoisomer. Thus the $\Delta\Delta G^{\neq}$-values derived from the reactivity differences are an (approximate) measure for the kinetic anomeric effect and they correspond qualitatively to the values expected on the basis of the anomeric effect in the ground state. As expected, they are particularly high for Lewis acid promoted reactions.

5. Coda: The Lewis acid promoted addition of $P(OSiMe_3)_3$ to N-glycosylnitrones. As shown in the previous paragraph, Lewis acid catalysis has a strong influence upon both the reactivity and the diastereoselectivity of nucleophilic additions to N-glycosylnitrones.[27] This is useful, since either enantiomer of the aglycons may be obtained from a single N-glycosylnitrone. In the following, we propose a rationalization of the results of the promotion of nucleophilic additions to N-glycosylnitrones by different Lewis acids. They depend both on the nature of the Lewis acid and - in the case of $ZnCl_2$ - on the stoichiometry[28] (cf. *Table 4*).

Table 4: Addition of $P(OSiMe_3)_3$ *to Various Nitrones. Influence of Lewis Acids upon the Configuration* [d.e.] *of the Predominantly Formed Phosphonates.*[2a,c]

	nitrones R =	**7** Ph	**50** 4-^{t}Bu-Ph	**4** CH_2OBn	**51** $CHMe_2$	**52** $(CH_2)_2SMe$
Lewis acid	solvent	abs. configuration [d.e.] of the predominant formed phosphonate				
$HClO_4$ [a]	CH_2Cl_2/C_6H_6	R [84-80%]	R [90%]	S [30%]	R [95%]	R [45%]
$Zn(TfO)_2$ [a]	THF	R [90-92%]	--	R [17%]	--	R [79%]
$ZnCl_2$ (1 eq.)	C_6H_6	R [83%]	--	S [2%]	--	R [39%]
$ZnCl_2$ (0.01 eq.)	C_6H_6	S [79%]	S [75%]	S [88%]	S [44%]	S [61%]
none	CH_2Cl_2	--[b]	--[b]	S [66%]	--[c]	--

[a]) Configuration and d.e. were not markedly influenced by the amount (ca 0.03-1 eq.) of catalyst. [b]) Addition of $P(OSiMe_3)_3$ did not occur. [c]) Decomposition of the nitrone.

Three factors were considered relevant for the diastereoselectivity of the reactions: a) the configurations of the nitrones (Z/E interconversion), b) the conformational equilibrium ('O-*endo*' vs. 'O-*exo*' conformers), c) the direction of attack of $P(OSiMe_3)_3$.

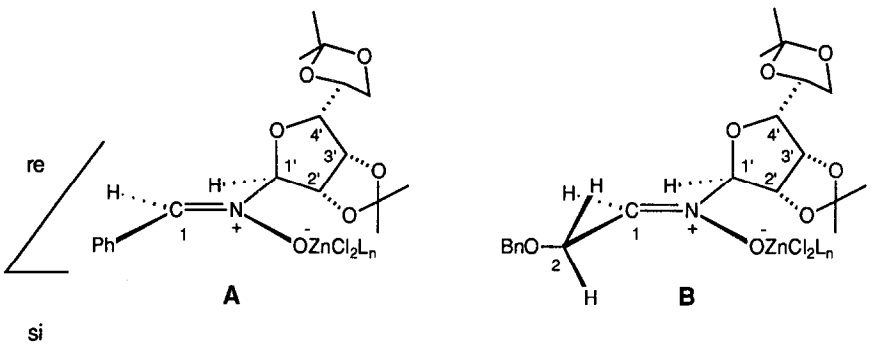
No evidence was found by ^{1}H-NMR and TLC for a (Z/E)-isomerization of the nitrones in the presence of Lewis acids. To evaluate the influence of $ZnCl_2$ upon the 'O-*endo*' vs. 'O-*exo*' equilibrium of the C-phenyl- and C-benzyloxymethylnitrone **7** and **4** we examined their ^{1}H-NMR spectra (400 MHz) in the presence of 0.4 equiv. $ZnCl_2$. The chemical shift differences induced by the Lewis acid are listed in *Table 5*.

Table 5: Differences of the Chemical Shifts ($\Delta\delta$, ppm) *in the ^{1}H-NMR Spectra* (C_6D_6) *of the Nitrones* **4** *and* **7** *upon the Addition of 0.4 Equiv. of* $ZnCl_2$

$\Delta\delta$ for	H-C(1)	H-C(2)	H'-C(2)	H-C(1')	H-C(2')	H-C(3')	H-C(4')	H-C(5')	H-C(6')	H'-C(6')	CH_2Ph
7	0.35	---	---	0.18	0.53	0.23	0.09	0.03	0.08	0.01	---
4	0.43	0.54	0.36	0.08	0.55	0.15	0.13	0.05	0.01	0.03	0.12/0.08

The $\Delta\delta$-values observed for H-C(1) and H-C(1') of the C-phenylnitrone **7** indicate a coordination of $ZnCl_2$ with the oxygen of the nitrone function (see formula **A** in *Fig. 6*). The particularly high $\Delta\delta$-value for H-C(2') is only compatible with an 'endo'-conformation. Both O-C(2') and O-C(3') are sterically not accessible for a bidentate coordination and the low $\Delta\delta$-value of H-C(4') is not in keeping with a complexation of O-C(4').

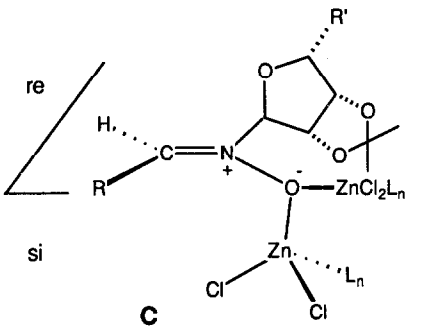
Fig. 6: Complexes of N-Glycosylnitrones with Zinc Chloride.



Similarly, the $\Delta\delta$-value for H-C(1), H-C(2') and H-C(4') of the C-benzyloxymethylnitrone indicate a coordination of $ZnCl_2$ by the oxygen of the nitrone function in an 'O-*endo*' conformation (**B** in *Fig. 6*). It is tempting to postulate an involvement of the benzyloxy group in the formation of the complex with $ZnCl_2$, but the following findings are difficult to reconcile with this hypothesis: i) H- and H'-C(2), but not $H_2C(Ph)$ are strongly deshielded upon addition of $ZnCl_2$. ii) $J_{gem.}$ for the $C(2)H_2$ group is large (16 Hz) and unaffected by the addition of $ZnCl_2$. iii) H-C(1) couples with the same constant with both H- and H'-C(2) (4.5 Hz in the absence; 3.2 and 3.4 Hz in the presence of $ZnCl_2$). These findings are more easily rationalized (disregarding the orientation of the benzyl group) by a conformation as indicated in formula **B** (*Fig. 6*). Inspection of Dreiding models indicates that in this conformation a shielding of the H-C(1') by the phenyl group is possible.

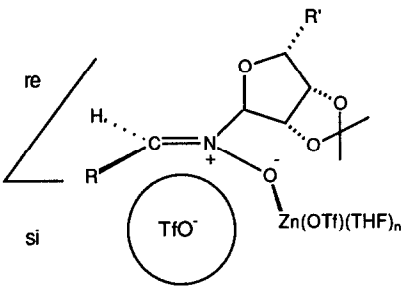
These findings lead to the conclusion that the Lewis acids influence the diastereoselectivity of the addition of $P(OSiMe_3)_3$ to N-glycosylnitrones by determing the direction of attack of the nucleophile.In the absence of a Lewis acid, additions of $P(OSiMe_3)_3$ to nitrone **4** leads mainly to induction of the (S) configuration, similarly to the addition of $LiPO_3R_2$ to C-alkyl-N-glycosylnitrones. This result has been explained[2c] by the preferred attack

of the si-face (= 'anti'-attack, see *Fig. 1*). The same direction of attack is observed upon addition of catalytic amounts of $ZnCl_2$, which mainly complexes in the plane of the nitrone function. Increasing amounts of $ZnCl_2$ lead to a coordination of the oxygen of the nitrone function with two molecules of $ZnCl_2$ (formula C); the second one occupying the sterically accessible si-face forcing the nucleophile to attack the re-side. The low diastereoselectivities observed for the addition to **4** in the presence of 1 equiv. of $ZnCl_2$ may be interpreted as the result of two opposite factors: obstruction of the approach of $P(OSiMe_3)_3$ to the si-side of the nitrone by a second equiv. of coordinating $ZnCl_2$ and obstruction of the approach to the re-side by the benzyloxy group.

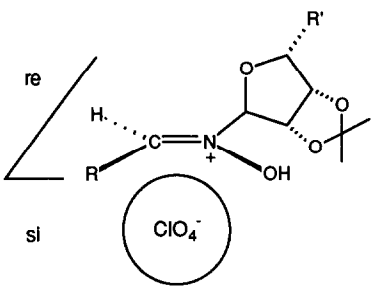


C

Fig. 7: Complexes of N-Glycosylnitrones with Zinc Triflate and Perchloric Acid.



D



E

The highly selective re-attack in the presence of $Zn(OTf)_2$ is almost independent of the amount of catalyst. This can be rationalized by postulating the formation of a complex **D**. Here, the si-side of the nitrone function is blocked by the triflate counterion, which is liberated through coordination of the Zn(II)-ion to better ligands, such as the nitrone and (one or more) THF molecules. The assumption that triflate functions as a bridging ligand implying a concentration independent coordination of the nitrone with a $Zn(OTf)_2$ dimer or oligomer also rationalizes our observations.

Finally, the concentration independent effect of $HClO_4$ (pK_a = -10) is explained by protonation of the nitrone (**E** in *Fig. 7*, pK_a[29] of **E** >> -10) and by blocking of the si-side by the perchlorate counterion.

Experimental part.

General.[2b,c] DMF was freshly distilled i.v. (20 torr). 3-Chloro-perbenzoic acid (MCPBA, *Fluka* pract., containing 15% of 3-chlorobenzoic acid) was dried before use. Molecular sieves were dried in a salt bath at ca 250° under h.v. Kieselgel 60 (Merck, 15-40 μm) was used for medium pressure liquid chromatography (MPLC).[30] The integrals of the peaks of diastereomeric pairs determined by ^{31}P-NMR are written in brackets after the chemical shifts.

Diethyl (3,4:5,6-Di-O-isopropylidene-β-D-manno-2-heptulofuranosyl)phosphonate (**20**). A soln. of n-butyl lithium in hexane (61 ml, ca. 0.1 mmol) was added at -70° to a soln. of $CH_3PO_3Et_2$ (17.8 g, 117 mmol) in THF (420 ml). After stirring at -50° for 30 min, a soln. of **19** (21.35 g, 87.7 mmol) in THF (120 ml) was added. After 15 min at -50°, the mixture was brought to pH 7-8 with sat. NH_4Cl (ca. 60 ml). Most of the solvent was evaporated and the residue obtained was extracted with CH_2Cl_2 (6x 100 ml). Usual work up and FC (Et_2O/hexane 4:1) gave **20** (25.1 g, 74%).
R_f (CH_2Cl_2/MeOH 9:1): 0.71. $[\alpha]_D(25)$ = +7.6° (c=1.2, $CHCl_3$). IR: 3370w, 2990s, 2940m, 2910m, 2460w, 1475w, 1440m, 1382s, 1373s, 1339w, 1322w, 1160s, 1099m, 1070-1020s, 1002s, 1118s, 930w, 890s, 868s. ^{1}H-NMR: 5.62 (s, OH); 4.84 (ddd, J = 5.8, 3.8, J(C,P) = 1.3, H-C(4)); 4.47 (d, J = 5.8, H-C(3)); 4.37 (ddd, J = 7.6, 6.2, 4.9 H-C(6)); 4.22-4.08 (m, H-C(5), 2x $POCH_2$); 4.04 (dd, J = 8.4, 6.3, H-C(7)); 3.99 (dd, J = 8.4, 4.9, H'-C(7)); 2.39 (dd, J = 15.4, J(C,P) = 17.6, H-C(1)); 2.20 (dd, J = 15.5, J(C,P) = 18.2, H'-C(1)); 1.46 (s, CH_3); 1.43 (s, CH_3); 1.37 (s, CH_3); 1.33 (dt, J = 7.1 J(C,P) = 3.7, 2x $POCH_2C\underline{H}_3$); 1.32 (s, CH_3). ^{13}C-NMR: 112.8 (s); 109.1 (s); 103.6 (d, J(C,P) = 7.6); 85.9 (dd, J(C,P) = 10.8); 80.2 (d); 79.5 (d); 77.6 (d); 73.0 (d); 66.7 (t); 62.8 (dt, J(C,P) = 5.9); 61.6 (dt, J(C,P) = 6.7); 30.9 (dt, J(C,P) = 136.6); 26.8 (q); 25.9 (q); 25.1 (q); 24.5 (q); 16.37 (dq, J(C,P) = 6.5); 16.24 (dq, J(C,P) = 7.1). ^{31}P-NMR: 29.2. Anal. calc. for $C_{17}H_{31}O_9P$ (410.40): C 49.75, H 7.61, P 7.55; found: C 49.48, H 7.68, P 7.36.

Diethyl (3,4:5,6-Di-O-isopropylidene-D-manno-2-heptulosyl)phosphonate (**21**). A soln. of **20** (26.97 g, 61.1 mmol) in EtOH (135 ml) was added to a soln. of $C(CH_3)_3OK$ (35.1 g, 313 mmol) in EtOH (1.2 l). The mixture was stirred for 2 h at 52-55°, then cooled to 12° and brought to pH ~ 6 with glacial AcOH. The concentrated mixture was taken up in H_2O (300 ml) and extracted with CH_2Cl_2 (5x 300 ml). Usual work up and FC (silica, AcOEt/hexane/MeOH 100:100:2.3) gave **21** (18.18 g, 67.4%) and unreacted **20** (8.69 g, 32.2%).
R_f (CH_2Cl_2/MeOH 9:1) 0.55. $[\alpha]_D(25)$ = +27.9° (c=1.2, $CHCl_3$). IR: 3560w, 3400w v. br., 2990s, 2935m, 2908m, 2460w, 1717s, 1475w, 1453w, 1443w, 1383s, 1372s, 1155s, 1070-1020s, 972s, 880m. ^{1}H-NMR: 4.54 (d, J = 7.6, H-C(3); 4.38 (dd, J = 7.5, J(C,P) = 2.0, H-C(4); 4.22-4.01 (m, 1 H-C(6), 2 H-C(7), 2x $POCH_2$); 4.74-4.62 (m, H-C(5)); 3.55 (dd, J = 14.0, J(C,P) = 23.0, H-C(1)); 3.22 (dd, J = 14.0, J(C,P) = 22.2, H'-C(1)); 2.27 (d, OH); 1.48 (s, CH_3); 1.42 (s, 2 CH_3); 1.34 (dt, J = 7.1, J(C,P) = 0.5, 2x $POCH_2C\underline{H}_3$ and CH_3). ^{13}C-NMR: 202.1 (d, J(C,P) = 6.9); 110.0 (s); 109.3 (s); 80.7 (dd, J(C,P) = 1.5); 77.0 (d); 76.2 (d); 70.5 (d); 66.7 (t); 62.7 (dt, J(C,P) = 6.3); 62.5 (dt, J(C,P) = 6.4); 37.7 (dd, J(C,P) = 130.3), 26.7 (q); 26.6 (q); 26.2 (q); 25.2 (q); 16.2 (q); 16.1 (q). ^{31}P-NMR: 32.2. Anal. calc. for $C_{17}H_{31}PO_9$ (410.40): C 49.76, H 7.61, P 7.55; found C 49.48, H 7.84, N 7.39.

Diethyl (3,4:5,6-Di-O-isopropylidene-D-glycero-L-erythro-2,5-heptodiulosyl)phosphonate (**22**). A soln. of $(CF_3CO)_2O$ (12.6 ml, 90.3 mmol) in CH_2Cl_2 (35 ml) was added dropwise at -60°C to DMSO (11.1 ml) and CH_2Cl_2 (75 ml). The mixture was stirred for 10 min. A soln. of **21** (15.1 g, 36.8 mmol) in CH_2Cl_2 (35 ml) was added dropwise over 15 min, the mixture was stirred at -60° for 90 min and then Et_3N (21.6 ml) was added. After 1 h at -60°, the mixture was diluted with H_2O (150 ml) and extracted with CH_2Cl_2 (3x 150 ml). The organic extracts were washed with satd. $CuSO_4$ (150 ml) and H_2O (150 ml). Usual work up gave crude **22** (15.95 g), which was used as such in the next step. An anal. sample was obtained by FC (silica, AcOEt/hexane 2:1).
R_f (AcOEt) 0.37. IR: 3600-3200w, 2942m, 2917m, 1734s, 1562m (br.), 1447w (br.), 1385s, 1377s, 1152s, 1060s, 1030s, 970s, 858s. ^{1}H-NMR: 5.04 (d, J = 5.5, H-C(3)); 4.88 (t, J = 6, H-C(6)); 4.86 (d, J = 5.6, H-C(4)); 4.3-4.1 (m, 2 H-C(7) and 2x $POCH_2$); 3.59 (dd, J = 13.8, J(H,P) = 22.6, H-C(1)); 3.21 (dd, J = 13.8, J(H,P) = 22.8, H'-C(1)); 1.47 (s, CH_3); 1.45 (s, CH_3); 1.42 (s, CH_3); 1.41 (s, CH_3); 1.35 (dt, J = 7, J(H,P) = 0.5, $POCH_2C\underline{H}_3$); 1.34 (dt, J = 7, J(H,P) = 0.5, $POCH_2C\underline{H}_3$). ^{13}C-NMR: 204.4 (s); 200.0 (s); 112.6 (s); 110.9 (s); 81.1 (d); 78.5 (d); 78.1 (d); 65.5 (t); 62.6 (dt, J(C,P) = 6); 62.5 (dt, J(C,P) =6); 37.8 (dt, J(C,P) = 128.6); 25.9 (q); 25.8 (q); 25.6 (q); 25.0 (q); 16.1 (q); 16.0 (q). ^{31}P-NMR: 31.7. Anal. calc. for $C_{17}H_{29}O_9P$ (408.38): C 50.00, H 7.16, P 7.58; found: C 49.70, H 7.42, P 7.35.

(3aS, 4'S, 6aS)- and (3aS, 4'R, 6aS)-3a,6a-Dihydro-2,2-dimethyl-6-(2,2-dimethyldioxolan-4-yl)-4H-cyclopenta-1,3-dioxol-4-one (**23** and **24**). A suspension of crude **22** (15.95 g), $KHCO_3$ (3.77 g) and 18-crown-6 (10.2 g) in benzene (1.4 l) was stirred at 70-80° for 4 h. The mixture was washed with H_2O (700 ml) and the aqueous phase was extracted with Et_2O (2x 700 ml). Usual work up and FC (silica, hexane/Et_2O 1:1) gave a ca. 2:1 mixture (^{1}H-NMR) of **23** and **24** (3.04 g, 32.5% from **21**).
Data of the mixture of **23** and **24**: R_f (AcOEt/toluene 2:1) 0.60. $[\alpha]_D(25)$ = +44.1° (c=1.8, $CHCl_3$). IR: 2995m, 2940m, 1727s, 1626m, 1455w, 1377s, 1140s (br.), 1075s (br.), 995w, 964w, 939w, 870m. ^{1}H-NMR: **23**: 6.20 (dd, J = 1.2, 0.4, H-C(7)); 5.15 (d, J = 5.6, H-C(2)); 4.82 (ca. dt, J = 7, 1.1, H-C(5)); 4.55 (dd, J = 6.4, 0.4, H-C(3)); 4.35 (dd, J = 8.6, 6.8, H-C(6)); 3.84 (dd, J = 8.5, 7.2, H'-C(6)); 1.49 (s, CH_3); 1.46 (s, CH_3); 1.41 (s, 2x CH_3). **24**: 6.19 (d, J = 1.5, H-C(7)); 5.14 (d, J = 5.8, H-C(2)); 5.05 (dt, J = 7, 1.5, H-C(5)); 4.53 (d, J = 5.8, H-C(3)); 4.33(dd, J = 7, 8.5, H-C(6)); 3.86 (dd, J = 7, 8.5, H'-C(6)); 1.49 (s, CH_3); 1.46 (s, CH_3); 1.41 (s, 2x CH_3). ^{13}C-NMR: **23**: 201.4 (s); 173.7 (s); 128.1 (d); 115.6 (s); 109.9 (s); 78.1 (d); 77.7 (d); 74.7 (d); 68.3 (t); 27.2(q); 25.9 (2x q); 25.6 (q). Anal. calc. for $C_{13}H_{18}O_5$ (254.28): C 61.41, H 7.14; found: C 61.36, H 7.23. **24**: 201.4 (s); 173.4 (s); 129.2 (d); 115.5 (s); 110.5 (s); 77.9 (d); 77.5 (d); 73.6 (d); 67.5 (t); 27.3 (q); 26.0 (2x q); 25.5 (q).

Pseudo-2,3:5,6-di-O-isopropylidene-α-L-gulose ((3aS, 4R, 4'R, 6R, 6aS)-*3a,4,5,6a-Tetrahydro-2,2-dimethyl-4-hydroxy-6-(2,2-dimethyldioxolan-4-yl)-6H-cyclopenta-1,3-dioxole*) (**25**) and *Pseudo-2,3:5,6-di-O-isopropylidene-β-D-mannose* ((3aS, 4R, 4'S, 6R, 6aS)-*3a,4,5,6a-Tetrahydro-2,2-dimethyl-4-hydroxy-6-(2,2-dimethyldioxolan-4-yl)-6H-cyclopenta-1,3-dioxole*) (**26**). A methanolic soln. (70 ml) of **23** and **24** (1.76 g, 6.93 mmol) was hydrogenated with H_2/10% Pd/C (180 mg) at r.t. for 30 min. The catalyst was removed by filtration (*Celite*) and the hydrogenation was repeated in the presence of fresh 10% Pd/C (180 mg). The concentrated, crude mixture (2.14 g) was diluted with MeOH (57 ml). After addition of $CeCl_3 \cdot 6H_2O$ (8.3 g) $NaBH_4$ (270 mg) was added to the clear solution in small portions over 1-2 min. After 30 min, H_2O (50 ml) was added to the mixture. Extraction with Et_2O (5x 50 ml), usual work up and FC (silica, AcOEt/hexane 1:2) gave a mixture of **25** and **26** (1.46 g, 81.6%). Crystallization from hexane afforded diastereomerically pure **25** (~30%).

25: M.p. 72°C. R_f (AcOEt/toluene 2:1): 0.32. $[\alpha]_D(25) = +21.2°$ (c=1.1, $CHCl_3$). IR (KBr): 3485s, 2990s, 2980s, 2955m, 2935m, 2920m, 2905m, 2885m, 2860w, 1455m, 1404m, 1383s, 1370s, 1280m, 1246s, 1231m, 1210s, 1157m, 1152m, 1138m, 1100s, 1067s, 1056s, 1038m, 1004m, 987m, 978m, 964w, 949w, 930w, 918w, 881m, 852m, 841s, 817m. ^{1}H-NMR: 4.46 (t, J = 5.4, H-C(2)); 4.44 (t, J = 5.4, H-C(3)); 4.19-4.13 (m, H-C(6) and H-C(5)); 3.88 (Sept., J(H-1,H-3) =J(H-1,H'-7) = 5.4, J(H-1,H-7) =J(OH) = 10.8, H-C(1)); 3.74-3.67 (m, 'H-C(6)); 2.31 (d, J = 10.8, H-O, exch. with D_2O); 2.16 (ca. quint., J(H'-7,H-7) = 11.5, J(H'-7,H-1) =J(H'-7,H-4) = 5.5, H'-C(7)); 1.66 (m, H-C(4)); 1.57 (ddd, J(H-7,H'-7) = 12, J(H-7,H-1) =11, J(H-7,H-4) = 10, H-C(7)); 1.47 (s,CH_3); 1.41 (s, CH_3); 1.36 (s, CH_3); 1.31 (s, CH_3). ^{13}C-NMR: 110.8 (s), 108.8 (s); 79.3 (d); 79.0 (d); 76.4 (d); 72.3 (d); 68.3 (t); 42.7 (d); 34.4 (t); 27.0 (q); 25.6 (q, 2xCH_3); 24.0 (q). Anal. calc. for $C_{13}H_{22}O_5$ (258.31): C 60.45, H 8.58; found: C 60.54, H 8.67.

26: ^{13}C-NMR (from a mixture of **25** and **26**): 110.6 (s); 108.8 (s); 79.1 (d); 78.5 (d); 74.6 (d); 72.26 (d); 68.0 (t); 42.63 (d); 31.9 (t); 27.0 (q); 25.6 (2x q); 24.1 (q).

Pseudo-2,3-O-isopropylidene-α-D-lyxose ((3aS, 4R, 6R, 6aS)-*3a,4,5,6a-Tetrahydro-2,2-dimethyl-4-hydroxy-6-hydroxymethyl-6H-cyclopenta-1,3-dioxole*) (**29**). A soln. of **25** and **26** (ca. 2:1, 150 mg, 0.58 mmol) in AcOH (1 ml) and H_2O (1.5 ml) was stirred at r.t. for 5.5 h. After evaporation of the solvents, the residue was taken up in 0.025 M Na_2HPO_4/KH_2PO_4 buffer-soln. (7 ml, pH 6.8) and treated with $NaIO_4$ (200 mg, 0.94 mmol) at r.t. for 75 min. $BaCO_3$ (200 mg, 1 mmol) was added. The resultant suspension was vigorously stirred for 10 min and then filtered. $NaBH_4$ (150 mg, 4 mmol) was added to the filtrate. After 15 min at r.t., the reaction mixture was brought to pH 7-7.5 with 100% AcOH. Solvents were evaporated. The crude was dried under h.v., taken up in H_2O and continuously extracted with CH_2Cl_2 for 20 h. FC (silica, AcOEt/MeOH 19:1) gave **29** (93 mg, 85.2%).

M.p. 80°. R_f (AcOEt/MeOH 10:1) 0.32. $[\alpha]_D(25) = +0.5°$ (c=2.3, MeOH). IR (KBr): 3600-3100s, 2985s, 2960m, 2930s, 2900s, 2882s, 2835m, 1478m, 1453s, 1430m, 1384s, 1372s, 1341m, 1318m, 1279s, 1259m, 1239s, 1218s, 1172s, 1160s, 1133s, 1090s, 1030s, 1010s, 991s, 969s, 940s, 909w, 880s, 858m, 829m, 810m, 801m. ^{1}H-NMR: 4.66 (ca. t, J = 5.5, H-C(3)); 4.49 (t, J = 5.5, H-C(2); 3.96-3.88 (m, H-C(1)); 3.85 (dd, J = 11.1, 4.1, H-C(5); 3.75 (dd, J = 11.0, 6.8, H'-C(5)); 2.35 (br. s, OH); 2.15 (br. s, OH); 1.9-1.8 (m, H-C(6) and H-C(4)); 1.65-1.55 (m, H'-C(6)); 1.50 (s, CH_3); 1.35 (s, CH_3). ^{13}C-NMR: 110.7 (d); 80.3 (s); 79.1 (d); 72.3 (d); 61.6 (t); 40.3 (d); 32.2 (t); 25.6 (q); 24.0 (q). Anal. calc. for $C_9H_{16}O_4$ (188.22): C 57.43, H 8.57; found: C 57.69, H 8.61.

Pseudo-2,3:5,6-di-O-isopropylidene-β-L-gulofuranosylazide ((3aS, 4R, 4'R, 6R, 6aS)-*3a,4,5,6a-Tetrahydro-4-azido-2,2-dimethyl-6-(2,2-dimethyldioxolan-4-yl)-6H-cyclopenta-1,3-dioxole*) (**32**). $(CF_3SO_2)_2O$ (1.2 ml, 7.3 mmol) was added dropwise to a mixture of CH_2Cl_2 (15 ml) and pyridine (5 ml) at -30°. After 20 min, a soln. of **25** (1.00 g, 3.87 mmol) in CH_2Cl_2 (5 ml) was added dropwise over 5 min at -30° to the resulting white suspension. The mixture was kept at -30° for 15 min and poured into ice-water (50 ml). Extraction with CH_2Cl_2 (4x 50 ml), usual work up and drying under h.v. (2 h) gave crude **30** (1.64 g), which was taken up in DMF (5.5 ml) and added to a vigorously stirred suspension of NaN_3 (2 g, 33 mmol), tetramethylurea (0.2 ml) and DMF (7.5 ml). After 15 min, H_2O (50 ml) was added to the mixture. Extraction with CH_2Cl_2 (6x 50 ml), usual work up and FC (silica, hexane/AcOEt 1:1) gave **32** (1.02 g, 93%).

R_f (hexane/AcOEt 2:1) 0.48. $[\alpha]_D(25) = -0.9°$ (c=1.2, $CHCl_3$). IR: 2985s, 2935s, 2970w, 2100s, 1451w, 1440w, 1380s, 1372s, 1160s, 1110m, 1060s, 993m, 910w, 895m, 885m, 860m, 841m. ^{1}H-NMR: 4.53 (t, J = 5.2, H-C(3)); 4.44 (dd, J = 5.5, 1.4, H-C(2)); 4.17 (ca. dd, J = 7.0, 5.4, H-C(6)); 4.13 (dt, J = 9.2, 6.0, H-C(5)); 3.99 (d, J = 4.5, H-C(1)); 3.75 (ca. dt, 6.3, 1.5, H'-C(6)); 2.18-2.08 (m, H-C(4)); 2.03 (br. dd, J = 13, 6, H-C(7)); 1.94 (dt, J = 13.0, 4.6, H'-C(7)); 1.43 (s, CH_3); 1.41 (s, CH_3); 1.36 (s, CH_3); 1.26 (s, CH_3). ^{13}C-NMR: 110.7 (s); 108.9 (s); 84.7 (d); 79.9 (d); 76.5 (d); 68.5 (t); 65.6 (d); 45.7 (d); 32.1 (t); 27.0 (q); 25.8 (q); 25.7 (q); 23.7 (q). Anal. calc. for $C_{13}H_{21}N_3O_4$ (283.33): C 55.11, H 7.47, N 14.83; found: C 55.29, H 7.45, N 14.87.

Treatment of a mixture of the alcohols **25** and **26** in a similar manner gave a mixture of the azides **32** and **33**, which were separated by MPLC (hexane/AcOEt 10:1).

*Pseudo-2,3:5,6-di-*O*-isopropylidene-*α*-D-mannofuranosylazide* (*(*3aS, 4R, 4'S, 6R, 6aS*)-3a,4,5,6a-Tetrahydro-4-azido-2,2-dimethyl-6-(2,2-dimethyldioxolan-4-yl)-*6H*-cyclopenta-1,3-dioxole*) (**33**). From a mixture of **30** and **31**. For procedure see preparation of **32**.
R_f (hexane/AcOEt 2:1) 0.4. $[\alpha]_D(25)$ = -4.9° (c=1.3, $CHCl_3$). IR: 2990s, 2940m, 2875w, 2100s, 1452w, 1438m, 1381s, 1373s, 1155s, 1113w, 1066s, 1056s, 993m, 962w, 888m, 844m. ^{1}H-NMR: 4.73 (t, J = 5.1, H-C(3)); 4.41 (dd, J = 5.4, 1.3, H-C(2)); 4.26 (dt, J = 8.8, 6.2, H-C(5)); 4.02 (dd, J = 8.3, 6.1, H-C(6)); 3.96 (ca. d, J = 4.4, H-C(1)); 3.67 (dd, J = 8.3, 6.2, H'-C(6)); 2.28-2.15 (m, H-C(4)); 1.77 (dt, J = 13.0, 4.8, H-C(7)); 1.54 (ca. dd, J = 13, 6, H-C(7)); 1.44 (s, CH_3); 1.43 (s, CH_3); 1.38 (s, CH_3); 1.31 (s, CH_3). ^{13}C-NMR: 110.5 (s); 108.8 (s); 84.2 (d); 79.7 (d); 74.6 (d); 67.8 (t); 65.6 (d); 45.5 (d); 29.4 (t); 26.9 (q); 25.8 (q); 25.6 (q); 23.8 (q). Anal. calc. for $C_{13}H_{21}N_3O_4$ (283.33): C 55.11, H 7.47, N 14.83; found: C 55.29, H 7.45, N 14.87.

*Pseudo-2,3:5,6-di-*O*-isopropylidene-β-L-gulofuranosylamine* (*(*3aS, 4R, 4'R, 6R, 6aS*)-3a,4,5,6a-Tetrahydro-4-amino-2,2-dimethyl-6-(2,2-dimethyldioxolan-4-yl)-*6H*-cyclopenta-1,3-dioxole*) (**34**). A methanolic suspension (26 ml) of **32** (1.155 g, 4.08 mmol) and 10% Pd/C (165 mg) was hydrogenated at r.t. for 30 min. Filtration (*Celite*) and concentration gave spectroscopically pure amine **34** (1.06 g, quant.), which was used as such in the next step. An anal. sample was obtained by crystallization (hexane).
M.p. 82-84°C. R_f (AcOEt/hexane 1:2) 0.03, (AcOEt/MeOH 2:1) 0.47; $[\alpha]_D(25)$ = +50.8° (c=1.1, $CHCl_3$). IR: 3650-3100m, 2990s, 2940m, 2900m, 1625w (v.br.), 1456w, 1443w, 1381s, 1372s, 1249s, 1210s, 1160s, 1093m, 1060s, 1035m, 993m, 958w, 798m. ^{1}H-NMR: 4.58 (t, J = 5.4, H-C(3)); 4.26 (br. dd, J = 5.6, 1.2, H-C(2)); 4.23-4.08 (m, H-C(6) and H-C(5)); 3.78-3.67 (m, H'-C(6)); 3.47 (d, J = 4.7, H-C(1)); 2.43-2.26 (m, H-C(4)); 1.92 (dt, J = 12.7, 5.0, H-C(7)); 1.72 (dd, J = 12.9, 5.9, H'-C(7)); 1.42 (s, CH_3); 1.40 (s, CH_3); 1.37 (s, CH_3); 1.25 (s, CH_3);1.19 (s, NH_2, exch. with D_2O). ^{13}C-NMR: 109.9 (s); 108.5 (s); 87.5 (d); 80.5 (d); 77.1 (d); 68.7 (t); 56.1 (d); 45.2 (d); 35.5 (t); 27.0 (q); 25.9 (q); 25.7 (q); 23.7 (q). Anal. calc. for $C_{13}H_{23}NO_4$ (257.33): C 60.68, H 9.01, N 5.44; found: C 60.42, H 9.25, N 5.70.

*(*3S*)- and (*3R*)-Pseudo-*N*-(2,3:5,6-di-*O*-isopropylidene-β-L-gulofuranosyl)-3-phenyl-oxaziridine* (*(*3R*,3'aS, 4'S, 4"R, 6'R, 6'aS*)- and (*3S*, 3'aS, 4'S, 4"R, 6'R, 6'aS*)-3a,4,5,6a-Tetrahydro-*N*-[2',2'-dimethyl-6'-(2",2"-dimethyldioxolan-4"-yl)-*6H*-cyclopenta-1,3-dioxole-4-yl]-3-phenyloxaziridine*) ((3S*)-**40** and (3R*)-**41**). A methanolic suspension (19 ml) of **34** (1.015 g, 3.94 mmol), benzaldehyde (0.45 ml, 4.04 mmol) and anh. Na_2CO_3 (940 mg) in MeOH (19 ml) was stirred at r.t. for 20 h. Filtration under N_2, evaporation of solvents and drying of the residue under h.v. (2 h) gave a residue, which was taken up in THF (30 ml) and treated with MCPBA (1.37 g, 8 mmol) at 0°. After 4 h at 0°, the mixture was brought to pH 8-9 with ca. 0.2M NaOH. Extraction with CH_2Cl_2 (4x 40 ml), usual work up and FC (silica, Et_2O/hexane 5:1) gave a ca. 3:1 mixture (^{1}H-NMR) of (3S*)-**40** and (3R*)-**41** (1.033g, 72.5%).
Data of the mixture of **40** and **41**: R_f (Et_2O/hexane 1:3) 0.21. $[\alpha]_D(25)$ = +36.0° (c=1.4, $CHCl_3$). IR: 3090w, 3070w, 2985s, 2935m, 2870w, 1456m, 1440w, 1399m, 1311m, 1296w, 1160s, 1110m, 1085w, 1058s, 1027m, 1011m, 970m, 904m, 851s, 840m. ^{1}H-NMR: **40**: 7.45-7.36 (m, 5 H); 4.83 (dd, J = 5.5, 1.1, H-C(2')); 4.69 (t, J = 5.3, H-C(3')); 4.56 (s, H-C(3)); 4.19 (dd, J = 7.9, 5.8, H-C(6')); 4.12 (ddd, J = 9.3, 6.9, 5.9, H-C(5')); 3.72 (dd, J = 7.6, 7.1, H'-C(6')); 2.74 (d, J = 5.7, H-C(1')); 2.45-2.37 (m, H-C(4')); 2.03 (dt, J = 12.9, 5.9, H-C(7')); 1.93 (dd, J = 13.3, 6.6, H'-C(7')); 1.43 (CH_3); 1.34 (2x CH_3); 1.30 (CH_3). **41**: 7.45-7.36 (m, 5 H); 4.65 (s, H-C(3)); 4.55 (t, J = 5.5, H-C(3')); 4.46 (d, J = 5.5, 1.1, H-C(2')); 4.23-4.17 (m, H-C(6') and H-C(5')); 3.78-3.73 (m, H'-C(6')); 2.58-2.48 (m, H-C(4')); 2.30 (dd, 13.4, 6.0, H'-C(7')); 2.79 (d, J = 5.1, H-C(1')); 1.99 (dt, J = 12.4, 5.0, H-C(7')); 1.46 (CH_3); 1.43 (CH_3); 1.39 (CH_3); 1.24 (CH_3). ^{13}C-NMR: **40**: 134.4 (s); 130.1 (d); 128.4 (d); 127.5 (d); 110.3 (s); 108.7 (s); 84.4 (d); 81.1 (d); 80.5(d); 77.1 (d); 76.0 (d); 68.6 (d); 46.1 (d); 31.7 (t); 26.9 (q); 26.0 (q); 25.7 (q); 23.8 (q). **41**: 134.4 (s); 130.1 (d); 128.4 (d); 127.6 (d); 110.7 (s); 108.8 (s); 83.1 (d); 80.8 (d); 80.3 (d); 76.8 (d); 76.1 (t); 68.6 (d); 45.5 (d); 32.4 (t); 27.0 (q); 26.0 (q); 25.7 (q); 23.8 (q). Anal. calc. for $C_{20}H_{27}NO_5$ (361.44): C 66.45, H 7.53, N 3.88; found: C 66.53, H 7.70, N 3.68.

*Pseudo-*N*-(2,3:5,6-di-*O*-isopropylidene-β-L-gulofuranosyl)phenylmethanimine N-oxide* (*(*3'aS, 4'S, 4"R, 6'R, 6'aS*)-3a,4,5,6a-Tetrahydro-*N*-[2',2'-dimethyl-6'-(2",2"-dimethyldioxolan-4"-yl)-*6H*-cyclopenta-1,3-dioxole-4'-yl]phenylmethanimine N-oxide*) (**42**). A mixture of **40** and **41** (400 mg, 1.106 mmol) was heated in a *Kugelrohr*-oven at 200° for 3 min at 20 torr and then immediately cooled to r.t. FC (Et_2O/hexane 1:1) of the resulting yellow-brown oil gave nitrone **42** (220 mg, 55%) and a mixture of unreacted **40** and **41** (90 mg, 22 %). **42** was crystallized from Et_2O/hexane.
M.p. 123-124°C; R_f (hexane/i-PrOH 10:1) 0.29; $[\alpha]_D(25)$ = -23.5° (c=1.1, $CHCl_3$); UV (MeOH): 294 (20941). IR (KBr): 3080w, 3060w, 3020w, 2985m, 2940m, 2905w, 1581m, 1566w, 1488w, 1460w, 1452m, 1430w, 1380s, 1370m, 1346w, 1323w, 1309w, 1287m, 1260m, 1252m, 1210s, 1162s, 1151s, 1140w, 1118m, 1075s, 1050s, 990m, 970w, 925w, 905w, 876s, 862w, 852w, 815w, 795w, 752w, 694m. ^{1}H-NMR: 8.21-8.17 (m, 2 H); 7.48 (s, H-C(1)); 7.43-7.40 (m, 3 H); 5.06 (d, J = 5.4, H-C(2')); 4.74 (t, J = 5.5, H-C(3')); 4.44(d, J = 7.0, H-C(1')); 4.20 (dd, J = 7.9, 5.8, H-C(6')); 3.92 (ddd, J = 9.5, 7.0, 6.0, H-C(5')); 3.76 (dd, J = 7.6, 7.2, H'-C(6')); 2.95 (dddd, J = 12.0, 9.6, 7.0, 5.6, H-C(4')); 2.41 (dd, J = 14.1, 7.0, H-C(7')); 2.28 (ddd, J = 14.1, 11.7, 7.2, H'-C(7'); 1.46 (s, CH_3); 1.40 (s, CH_3); 1.36 (s, CH_3); 1.29 (s, CH_3).

^{13}C-NMR: 133.7 (d); 130.4 (d); 130.2 (s); 128.39 (d); 128.35 (d); 110.8 (s); 108.6 (s); 85.0 (d); 81.8 (d); 79.8 (d); 77.2 (d); 68.6 (t); 47.1 (d); 34.7 (t); 26.8 (q); 26.2 (q); 25.7 (q); 23.9 (q). Anal. calc. for $C_{20}H_{27}NO_5$ (361.44): C 66.46, H 7.53, N 3.88; found: C 66.26, H 7.71, N 3.99.

*Pseudo-2,3:5,6-di-*O*-isopropylidene-*α*-*D*-mannofuranosylamine* ((3aS, 4R, 4'S, 6R, 6aS)*-3a,4,5,6a-Tetrahydro-4-amino-2,2-dimethyl-6-(2,2-dimethyldioxolan-4-yl)-*6H*-cyclopenta-1,3-dioxole*) (**35**). From azide **33**. For procedure see preparation of **34**.

R_f (AcOEt/MeOH 2:1) 0.47. $[\alpha]_D(25)$ = -36.1° (c = 1.4, $CHCl_3$). IR: 3500-3200w, 3380w, 2985s, 2030s, 1600w (br.), 1450w, 1441w, 1379s, 1370s, 1155s, 1065s, 993m, 978m, 951m, 896m, 864s, 842s. ^{1}H-NMR: 4.77 (t, J = 5.1, H-C(3)); 4.34-4.23 (m, H-C(2) and H-C(5)); 4.03 (dd, J = 8.2, 6.1, H-C(6)); 3.68 (dd, J = 6.5, 8.1, H'-C(6)); 3.44 (d, J = 5.1, H-C(1)); 2.50-2.37 (m, H-C(4)); 1.75 (dt, J = 12.9, 4.9, H-C(7)); 1.62 (s, NH_2); 1.5-1.3 (m, H'-C(7)); 1.44 (s, CH_3); 1.43 (s, CH_3); 1.39 (s, CH_3); 1.31 (s, CH_3). ^{13}C-NMR: 109.8 (s); 108.7 (s); 87.3 (d); 80.2 (d); 75.1 (d); 68.0 (t); 56.1 (d); 45.1 (d); 32.5 (t); 27.0 (q); 25.9 (q); 25.7 (q); 23.8 (q).

(3S)- and (3R*)-Pseudo-*N*-[(2,3:5:6-di-*O*-isopropylidene-*α*-*D*-mannofuranosyl]-3-[(4'-methoxy)-phenyl]oxaziridine* ((3S*,3'aS, 4'S, 4"S, 6'R, 6'aS)*- and (*3R*, 3'aS, 4'S, 4"S, 6'R, 6'aS)*-3a,4,5,6a-Tetrahydro-*N*-[2',2'-dimethyl-6'-(2",2"-dimethyldioxolan-4"-yl)-*6H*-cyclopenta-1,3-dioxole-4'-yl](3-phenyl)oxaziridine*)((3S*)-**43** and (3R*)-**44**). Anisaldehyde (190 ml, 1.6 mmol) and anh. Na_2CO_3 (300 mg) were added to a soln. of the amine **35** (400 mg, 1.55 mmol) in MeOH (6 ml). The suspension was stirred at r.t. overnight. Filtration under N_2 and concentration gave an oil, which was dried under h.v. for 2 h. The solid residue was taken up in abs. THF (10 ml) and treated at O°C with MCPBA (400 mg). After 90 min, the mixture was brought to pH ~ 9 with ca. 0.2 M NaOH. Extraction with CH_2Cl_2 (5x), usual work up and FC (Et_2O/hexane 37:63) gave a mixture of (3S*)-**43** and (3R*)-**44** (433 mg, 71%).

(3S*)-**43**: R_f (Et_2O/hexane 37:63) 0.19. $[\alpha]_D(25)$ = -69.6° (c = 1.6, $CHCl_3$). IR: 3080w, 3040w, 2990s, 2960m, 2940s, 2880w, 2840w, 1725w (br.), 1614s, 1590w, 1515m, 1455m, 1440m, 1382s, 1372s, 1306m, 1168s, 1109m, 1060s, 1015m, 996m, 972m, 948w, 912m, 865m. ^{1}H-NMR: 7.32 (d, J = 8.9, 2H); 6.90 (d, J = 8.8, 2H); 4.88 (t, J = 5.1, H-C(3')); 4.81 (dd, J = 5.3, 0.8, H-C(2')); 4.49 (s, H-C(3)); 4.26 (dt, J = 8.5, 6.3, H-C(5')); 3.97 (dd, J = 8.3, 6.1, H-C(6'); 3.82 (s, OCH_3); 3.62 (dd, J = 8.2, 6.4, H'-C(6')); 2.69 (d, J = 5.86, H-C(1')); 2.61-2.51 (m, H-C(4'); 1.84 (dt, J = 13.2, 6.0, H-C(7')); 1.52-1.4 (m, H'-C(7'); 1.43 (s, CH_3); 1.40 (s, CH_3); 1.36 (s, CH_3); 1.35 (s, CH_3). ^{13}C-NMR: 161.2 (s); 129.0 (d); 126.4 (s); 113.9 (d); 110.1 (s); 108.6 (s); 83.9 (d); 81.1 (d); 80.3 (d); 75.8 (d); 75.0 (d); 67.6 (t); 55.3 (d); 46.0 (d); 28.7 (t); 26.9 (q); 25.9 (q); 25.6 (q); 23.9 (q). Anal. calc. for $C_{21}H_{29}NO_6$ (391.46): C 64.43, H 7.47, N 3.58; found: C 64.50, H 7.47, N 3.40.

(3R*)-**44**: M.p. 124°. R_f (Et_2O/hexane 37:63) 0.28. $[\alpha]_D(25)$ = +48.9° (c = 1.6, $CHCl_3$). IR: 3080w, 3035w, 2990s, 2965w, 2940s, 2880w, 2842w, 1725w (br.), 1680w (br.), 1614s, 1590w, 1580w, 1512m, 1456m, 1440m, 1382s, 1372s, 1306m, 1275m, 1168s, 1160s, 1110m, 1068s, 1055s, 1034s, 1018m, 990w, 971w, 925w, 901w, 870m. ^{1}H-NMR: 7.34 (d, 2H); 6.91 (d, 2H); 4.79 (t, J = 5.1, H-C(3')); 4.62 (s, H-C(3)); 4.44 (dd, J = 5.4, 0.5, H-C(2')); 4.30 (dt, J = 9.1, 6.2, H-C(5')); 4.07 (dd, J = 8.2, 6.0, H-C(6')); 3.82 (s, OCH_3); 3.78 (dd, J = 8.1, 6.4, H'-C(6'); 2.71 (d, J = 4.0, H-C(1'); 2.7-2.55 (m, H-C(4')); 1.9-1.7 (m, 2H-C(7')); 1.46 (s, CH_3); 1.45 (s, CH_3); 1.41 (s, CH_3); 1.30 (s, CH_3). ^{13}C-NMR: 161.1(s); 128.9 (d); 126.3 (s); 113.8 (d); 110.4 (s); 108.8 (s); 82.5 (d); 80.5 (d); 80.3 (d); 76.2 (d); 75.0 (d); 68.0 (t); 55.2 (d); 45.4 (d); 29.8 (t); 26.9 (q); 25.9 (q); 25.7 (q); 23.8 (q). Anal. calc. for $C_{21}H_{29}NO_6$ (391.46): C 64.43, H 7.47, N 3.58; found: C 64.15, C 7.23, H 3.75.

*Pseudo-*N*-(2,3:5,6-di-*O*-isopropylidene-*α*-*D*-mannofuranosyl)-(4-methoxyphenyl)methanimine* N*-Oxide* ((3'aS, 4'S, 4"S, 6'R, 6'aS)*-3a,4,5,6a-Tetrahydro-*N*-[2',2'-dimethyl-6'-(2",2"-dimethyldioxolan-4"-yl)-*6H*-cyclopenta-1,3-dioxol-4'-yl](4-methoxyphenyl)methanimine* N*-oxide*) (**45**). A soln. of the mixture of the oxaziridines **43** and **44** (130 mg, 0.332 mmol) in AcOH (5 ml) was heated at 100°C for 5 min. Evaporation of the solvents, finally under h.v., followed by FC (hexane/Et_2O 45:155) gave the nitrone **45** (101 mg, 78%).

M.p. 165-166°. R_f (Et_2O) 0.43. $[\alpha]_D(25)$ = +55.1° (c = 1.1, $CHCl_3$). IR (KBr): 3060w, 3030w, 2990m, 2980m, 2950m, 2940m, 2890m, 2835w, 1607s, 1582m, 1567m, 1508s, 1488w, 1469w, 1462w, 1447m, 1420m, 1385m, 1377m, 1370m, 1346w, 1324w, 1309m, 1289m, 1254s, 1210s, 1205s, 1180s, 1163s, 1146s, 1133m, 1112m, 1070s, 1050s, 1030s, 1010m, 990m, 971w, 955w, 948w, 904w, 889w, 872m, 845s, 813m. ^{1}H-NMR: 8.18 (d, J = 8.8, 2H); 7.40 (s, H-C(1)); 6.93 (d, J = 9.0, 2H); 5.03 (d, J = 5.1, H-C(2')); 4.94 (t, J = 5.1, H-C(3')); 4.33 (m, H-C(1')); 4.23 (dt, J = 9.2, 6.4, H-C(4')); 4.01 (dd, J = 8.0, 6.0, H-C(6')); 3.85 (s, OCH_3); 3.72 (dd, J = 8.2, 6.7, H'-C(6'); 3.14-3.07 (m, H-C(4')); 2.05-1.98 (m, 2H-C(7')); 1.47 (s, CH_3); 1.44 (s, CH_3); 1.39 (s, CH_3); 1.34 (s, CH_3). ^{13}C-NMR: 161.1 (s); 133.4 (d); 130.4 (d); 123.1 (s); 113.8 (d); 110.7 (s); 108.8 (s); 85.2 (d); 81.9 (d); 79.7 (d); 75.3 (d); 67.8 (t); 55.2 (d); 47.3 (d); 31.4 (t); 26.9 (q); 26.4 (q); 25.8 (q); 24.1 (q). Anal. calc. for $C_{21}H_{29}NO_6$ (391.46): C 64.43, H 7.47, N 3.58; found: C 64.21, H 7.70, N 3.49.

*Pseudo-*N*-(2,3:5,6-di-*O*-isopropylidene-*α*-*D*-mannofuranosyl)hydroxylamine* ((3aS, 4R, 4'S, 6R, 6aS)*-3a,4,5,6a-Tetrahydro-2,2-dimethyl-6-(2,2-dimetyldioxolan-4-yl)-4-hydroxyamino-*6H*-cyclopenta-1,3-dioxole*)

(**46**). NH_2OH·HCl (48.7 mg, 0.70 mmol) and $NaHCO_3$ (53.2 mg, 0.70 mmol) were dissolved in MeOH (7 ml) by use of an ultra sonic bath (30 min) and then nitrone **45** (163 mg, 0.42 mmol) and AcOH (40 µl, 0.7 mmol) were added. The mixture was concentrated after 4 h. FC (Et_2O/MeOH 99.5:0.5) and drying under h.v. gave hydroxylamine **46** (110.5 mg, quant.).
R_f (Et_2O) 0.25. $[\alpha]_D(25)$ = -30.6° (c = 2.1, $CHCl_3$). IR: 3590m, 3580-3100w, 3280w, 2990s, 2940s, 2880m, 1720w (br.), 1602w, 1453w, 1381s, 1372s, 1160s, 1100m, 1062s, 1035s, 1005m, 972m, 940w, 920w, 895m. ^{1}H-NMR: 5.5 (s, 2H, NHOH); 4.71 (t, J = 5.2, H-C(3)); 4.49 (dd, J = 5.5, 1.1, H-C(2)); 4.27 (dt, J = 8.7, 6.2, H-C(5)); 4.01 (dd, J = 8.0, 6.1, H-C(6)); 3.66 (dd, J = 8.2, 6.3, H'-C(6)); 3.47 (d, J = 6.0, H-C(1)); 2.3-2.1 (m, H-C(4)); 1.75 (dt, J = 13.2, 6.1, H-C(7)); 1.44-1.36 (m, H'-C(7)); 1.44 (s,CH_3); 1.42 (s,CH_3); 1.38 (s,CH_3); 1.32 (s,CH_3). ^{13}C-NMR: 110.2 (s); 108.7 (s); 82.9 (d); 80.3 (d); 75.1 (d); 67.7 (t); 67.1 (d); 45.4 (d); 28.0 (t); 27.0 (q); 26.1 (q); 25.6 (q); 23.9 (q). Anal. calc. for $C_{13}H_{23}NO_5$ (273.31): C 57.13, H 8.47, N 5.13; found: C 57.19, H 8.46, N 5.21.

Pseudo-N-*(2,3:5,6-Di*-O-*isopropylidene*-α-D-*mannofuranosyl)(2-benzyloxyethan)imine* N-*oxide* (*(*3'aS, 4'S, 4"S, 6'R, 6'aS*)-3a,4,5,6a-Tetrahydro*-N-*[2',2'-dimethyl-6'-(2",2"-dimethyldioxolan-4"-yl)*-6H-*cyclopenta-1,3-dioxol-4'-yl](2-benzyloxyethan)imine* N-*oxide*) (**13**). Freshly distilled 2-benzyloxyacetaldehyde (86 µl) was added to a soln. of hydroxylamine **46** (171 mg, 0.63 mmol) in $CHCl_3$ (2 ml). After 10 min., solvents were evaporated and the residue was dried under h.v. Crystallization from Et_2O/hexane gave the nitrone **13** (173 mg, 68%). The mother liquor was treated with a methanolic NH_2OH·AcOH solution as described for **46**. Usual work up and FC yielded 53 mg (31%) of the educt **46**.
M.p. 111.5-112.5. R_f (Et_2O) 0.31. $[\alpha]_D(25)$ = +19.4 (c = 0.9, $CHCl_3$). UV(cyclohexane): 244 (10130). IR (KBr): 3080m, 3055w, 2990m, 2945m, 2890m, 2860m, 2845m, 2815w, 2770w, 1606m, 1500w, 1472m, 1460m, 1456m, 1447m, 1433w, 1380s, 1371s, 1331w, 1320m, 1311m, 1290m, 1262s, 1210s, 1190m, 1169s, 1140m, 1122s, 1093m, 1071s, 1065s, 1034m, 1020m, 1004m, 990m, 969m, 955w, 930w, 920w, 897m, 883w, 863s, 819w, 801w, 754s, 702s. ^{1}H-NMR: 7.38-7,31 (m, 5H); 6.96 (t, J = 4.5, H-C(1)); 4.89 (br. d, J = 5.3, H-C(2')); 4.85 (t, J = 5.0, H-C(3')); 4.57 (s, OCH_2Ph); 4.42 (d, J = 4.5, 2H-C(2)); 4.22-4.17 (m, H-C(5')); 4.20 (d, J = 8.3, H-C(1')); 3.99 (dd, J = 8.1, 6.1, H-C(6')); 3.68 (dd, J = 8.1, 6.6, H'-C(6')); 3.02-2.92 (m, H-C(4')); 1.96 (dt, J = 13.2, 7.4, H-C(7')); 1.85 (br. dd, J = 13.3, 7.1, H'-C(7')); 1.44 (s, CH_3); 1.42 (s, CH_3); 1.38 (s, CH_3); 1.32 (s, CH_3). ^{13}C-NMR: 137.0 (s); 136.5 (d); 128.3 (d); 127.8 (d); 127.7 (d); 110.6 (s); 108.7 (s); 84.4 (d); 81.5 (d); 78.1 (d); 74.9 (d); 73.5 (t); 67.6 (t); 65.2 (t); 46.9 (d); 31.0 (t); 27.7 (q); 26.2 (q); 26.0 (q); 23.9 (q). Anal. calc. for $C_{22}H_{31}NO_6$ (405.49): C 65.17, H 7.71, N 3.45; found: C 65.38, H 7.79, N 3.32.

Pseudo-N-*(2,3:5,6-di*-O-*isopropylidene*-α-D-*mannofuranosyl)phenylmethanimine* N-*oxide* (*(*3'aS, 4'S, 4"S, 6'R, 6'aS*)-3a,4,5,6a-Tetrahydro*-N-*[2',2'-dimethyl-6'-(2",2"-dimethyldioxolan-4"-yl)*-6H-*cyclopenta-1,3-dioxol-4'-yl](phenyl)methanimine* N-*oxide*) (**16**). A soln. of freshly distilled benzaldehyde (81 µl, 1.5 equiv.) and of hydroxylamine **46** (145 mg, 0.54 mmol) in $CHCl_3$ (3 ml) was kept at r.t. for 6 h. Evaporation of the solvents, drying of the residue under h.v. and crystallization from CH_2Cl_2/Et_2O/hexane gave 112 mg (59 %) of the nitrone **16**. FC (CH_2Cl_2/Et_2O/hexane 3.5:3.5:3) of the mother liquor gave further **16** (25 mg, 13 %).
M.p. 166 -167°. R_f (Et_2O) 0.53. $[\alpha]_D(25)$ = +43.2° (c = 1.1, $CHCl_3$). UV(cyclohexane): 298 (20815). IR: 3085w, 3055w, 2910m, 2955w, 2940m, 2890m, 2885m, 1885m, 2860m, 1579m, 1566m, 1560w, 1487w (br.), 1452s, 1440w, 1435w, 1378s, 1370s, 1350w (br); 1323w, 1304 (br.), 1287w, 1260s, 1252s, 1209s (br.), 1183m, 1179m, 1162s, 1148s, 1133m, 1122w, 1071s, 1065s, 1051s, 1029m, 1002m, 990m, 970w, 951w, 928m, 905w, 892w, 871m, 852m, 928m, 810m, 753m, 694s. ^{1}H-NMR: 8.20-8.17 (m, 2H Ph); 7.48 (s, H-C(1)); 7.43-7.41 (m, 3H Ph); 5.04 (d, J = 5.3, H-C(2')); 4.94 (t, J = 5.0, H-C(3')); 4.39 (dd, J = 7.8, 1.5, H-C(1')); 4.24 (dt, J = 9.0, 6.4, H-C(5')); 4.01 (dd, J = 8.2, 6.1, H-C(6')); 3.72 (dd, J = 8.2, 6.7, H-C(6')); 3.14-3.05 (m, H-C(4')); 2.1-1.95 (m, 2H-C(7')); 1.48 (s, CH_3); 1.44 (s, CH_3); 1.39 (s, CH_3); 1.35 (s, CH_3). ^{13}C-NMR: 133.7 (d); 130.4 (d); 130.2 (s); 128.43 (d); 128.38 (d); 110.8 (s); 108 (s); 85.1 (d); 81.9 (d); 80.2 (d); 75.2 (d); 67.8 (t); 47.2 (d); 31.5 (t); 26.8 (q); 26.4 (q); 25.7 (q); 24.1 (q). Anal. calc. for $C_{20}H_{27}NO_5$ (361.44): C 66.46, H 7.53, N 3.38 ; found: C 66.52, H 7.52, N 3.99.

General procedure (I) for the addition of lithium dialkylphosphites to the nitrones **4** *and* **13**. A soln. (10 ml, THF or CH_2Cl_2) of HPO_3Me_2 (1.3 ml) was treated at -25° with $C(CH_3)_3OLi$ (177 mg) and stirred for 10 min. The indicated amount of the cold soln. of the phosphite (-25°) was added (by a syringe) to a soln. of the nitrone (THF or CH_2Cl_2, -25°). After completion of the reaction, the mixture was quenched with aq. NH_4Cl (2 g/100 ml) and extracted with CH_2Cl_2 (5x). Usual work up gave crude mixtures of diastereomeric N-hydroxy-aminophosphonates, which were analyzed by ^{31}P-NMR-spectroscopy.

*(*1S*)-* and *(*1R*)-Dimethyl (2-benzyloxy)*[1*-(2,3:5,6-Di*-O-*isopropylidene*-α-D-*mannofuranosyl)hydroxy-amino]ethylphosphonate* (*(1S)*-**5** *and (1R)*-**6**). See general procedure I and *Table 6* entry 1 and 2. Usual work up and drying under h.v. gave 80 mg of crude (1S)-**5** and (1R)-**6**.[2c]

(1S)- and (1R)-Pseudo-dimethyl (2-Benzyloxy)[1-(2,3:5,6-di-O-isopropylidene-α-D-mannofuranosyl)-hydroxyamino]ethylphosphonate (*(1S, 3'aS, 4'S, 4"S, 6'R, 6'aS)- and (1R, 3'aS, 4'S, 4"S, 6'R, 6'aS)-Dimethyl (2-Benzyloxy){1-[2',2'-dimethyl-6'-(2",2"-dimethyldioxolan-4"-yl)-3',4',5',6a'-tetrahydro-cyclopenta-1,3-dioxol-4'-yl]hydroxyamino}ethylphosphonate*) ((1S)-**14** and (1R)-**15**). See general procedure I and *Table 6*, entry 3 and 4. The crude mixture of (1S)-**14** and (1R)-**15**) (entry 3) was crystallized at 4° from Et_2O/hexane to give 24 mg (63%) of (1S)-**14** (diastereomerically pure, ^1H- and ^{31}P-NMR). Crystallization of the remaining mother liquor from cyclohexane/hexane at 4°C gave 9 mg (24%) of (1R)-**15** (d.e. > 86%, ^{31}P-NMR).

(1S)-**14**: M.p. 146° (dec. above 140°). R_f (AcOEt) 0.30. HPLC (*Zorbax-Sil*; hexane/tert-butylmethylether/-MeOH 150:150:6; flow 1.5 ml/min): k' = 8.8. $[\alpha]_D(25)$ = +5.2 (c = 0.6, EtOH). IR: 3600-3100w, 3560w, 3090w, 3070w, 3030w, 2990m, 2955m, 2940m, 2870w, 2860w, 1600w (br.), 1490w, 1460w, 1455m, 1381m, 1372m, 1158m, 1115m, 1100m, 995m, 972m, 890m, 897m. ^1H-NMR: 7.35-7.34 (m, 4H); 7.33-7.27 (m, 1H); 5.90 (s, NOH); 4.69 (t, J = 5.1, H-C(3')); 4.60 (d, J = 5.5, H-C(2')); 4.56 (s, 2H, CH_2Ph)); 4.24 (dt, J = 8.8, 6.3, H-C(5')); 4.05 (dd, J = 10.4, 6.8, H-C(2)); 4.00 (dd, J = 8.2, 6.2, H-C(6')); 3.83 (dt, J = 10.6, 4.3, H'-C(2)); 3.78 (d, J(C,P) = 10.8, $POCH_3$); 3.74 (d, J(C,P) = 10.8, $POCH_3$); 3.67 (d, J = 4.7, H-C(1')); 3.65 (ddd, J = 6.8, 4.1, J(C,P) = 19, H-C(1)); 2.40-2.32 (m, H-C(4')); 1.76 (dd, J = 14.1, 6.9, H-C(7')); 1.69 (dt, J = 14, 5.6, H'-C(7')); 1.43 (s); CH_3); 1.40 (s, CH_3); 1.38 (s, CH_3); 1.31 (s, CH_3). ^{13}C-NMR: 137.7 (s); 128.2 (d); 127.6 (d); 109.9 (s); 108.6 (s); 83.1 (d); 80.2 (d); 75.1 (d); 73.2 (t); 70.6 (dd, J(C,P) = 10.3); 67.9 (t): 66.3 (dt, J(C,P) = 9.0); 61.6 (dd, J(C,P) = 154.1); 53.1 (dq, J(C,P) = 6.8); 52.6 (dq, J(C,P) = 7.0); 45.2 (d); 28.1 (t); 26.9 (q); 26.1 (q); 25.6 (q); 24.0 (q). ^{31}P-NMR: 27.61. MS (CI): 516.3 (M+1, 100%). Anal. calc. for $C_{24}H_{38}NO_9P$ (515.43): C 55.91, H 7.43, N 2.72; found: C 55.62, H 7.57, N 2.63.

(1R)-**15**: M.p. 106-107°. R_f (AcOEt) 0.30. HPLC (conditions see (1S)-**14**): k' = 9.4. $[\alpha]_D(25)$ = -22.8° (c = 0.6, $CHCl_3$). IR: 3600-3100w, 3560w, 3090w, 3060w, 3030w, 2990s, 2955m, 2935m, 2870w, 2860w, 1600w (br.), 1490w, 1475w, 1452m, 1381m, 1371s, 1158m, 1110m, 1095s, 1055s, 1040s (br.), 995m, 973w, 940w, 885w, 878m. ^1H-NMR: 7.37-7.28 (m, 5H); 5.83 (s, NOH); 4.73 (d, J = 5.1, H-C(2')); 4.69 (t, J = 5.1, H-C(3')); 4.53 (d, J(C,P) = 4.8, 2H, OCH_2Ph); 4.23 (dt, J = 8.9, 6.2, H-C(5')); 4.08 (dt, J = 10.6, 7.7, H-C(2)); 4.00 (dd, J = 8.2, 6.1, H-C(6')); 3.8-3.74 (m, 1H-C(2)); 3.79 (d, J(C,P) = 10.7, $POCH_3$); 3.74 (d, J(C,P) = 10.7, $POCH_3$); 3.63 (ddd, J = 7.3, 3.7, J(C,P) = 21.2, H-C(1)); 3.62 (dd, J = 8.2, 6.4, H'-C(6'); 3.58 (d, J = 5.6, H-C(1')); 2.34-2.25 (m, H-C(4')); 1.67 (dt, J = 13.8, 5.8, H-C(7')); 1.59 (br. dd, J = 13.8, 6.2, H'-C(7')); 1.44 (s, CH_3); 1.42 (s, CH_3); 1.38 (s, CH_3); 1.31 (s, CH_3). ^{13}C-NMR: 137.7 (s); 128.4 (d); 127.7 (d); 127.6 (d); 109.9 (s); 108.7 (s); 83.7 (d); 80.0 (d); 75.1 (d); 73.4 (t); 70.5 (dd, J(C,P) = 13.1); 68.0 (t); 65.3 (t, J(C,P) = 9.9); 61.6 (dd, J(C,P) = 161.0); 53.2 (dq, J = 6.9); 52.8 (dq, J(C,P) = 6.7); 45.4 (d); 27.8 (t); 27.0 (q); 26.1 (q); 25.6 (q); 24.1 (q). ^{31}P-NMR: 27.7. MS (CI): 516.3 (M+1, 100).

General procedure (II) for the addition of $P(OSiMe_3)_3$ *to the nitrones* **7**, **16** *and* **42**.

A) Catalysis by $HClO_4$: The indicated amount of 70% $HClO_4$ was added at -40° to a soln. of the nitrone and$P(OSiMe_3)_3$ in CH_2Cl_2/benzene (1:1). After completion of the reaction, MeOH was added at -40° and the mixture was kept for 2 min at that temp. It was then treated with CH_2N_2 (excess CH_2N_2 was destroyed with AcOH), concentrated and dried under h.v. (See *Table 7*)

B) Catalysis by $ZnCl_2$: The indicated amount of $ZnCl_2$ was melted under h.v. (0.1 torr). A soln. of the nitrone in benzene was added to the $ZnCl_2$ and the mixture was boiled under reflux for 15 min. $P(OSiMe_3)_3$ was added at the indicated temperature. After completion of the reaction, the mixture was cooled to 0°. MeOH was added and after 2 min the mixture was treated with CH_2N_2, concentrated and dried under h.v. (See *Table 7*)

(1S)- and (1R)-Pseudo-dimethyl [(2,3:5,6-di-O-isopropylidene-α-D-mannofuranosyl)hydroxyamino]-(phenyl)methylphosphonate (*(1S, 3'aS, 4'S, 4"S, 6'R, 6'aS)- and (1R,3'aS, 4'S, 4"S, 6'R, 6'aS)-dimethyl {[2',2'-dimethyl-6'-(2",2"-dimethyldioxolan-4"-yl)-3',4',5',6a'-tetrahydro-cyclopenta-1,3-dioxol-4'-yl]hydroxyamino}(phenyl)methylphosphonate*) ((*1S*)-**17** and (*1R*)-**18**). See general procedure IIA. Nitrone **16** (50 mg, 138 mmol), $P(OSiMe_3)_3$ (0.4 ml), CH_2Cl_2/benzene (1:1, 2 ml), 70% $HClO_4$ (5 μl). The reaction was complete after 20 min. MeOH (4 ml). FC (silica, CH_2Cl_2/MeOH 100:3) gave a mixture of (1S)-**17** and (1R)-**18** (54 mg, 83%), which were separated by semi-preparative HPLC (conditions see below).

(1S)-**17** (minor isomer): R_f (CH_2Cl_2/MeOH 100:3) 0.33. HPLC (see (1R)-**18**): k' = 4.33. $[\alpha]_D(25)$ = -2° (c = 0.9, $CHCl_3$). IR: 3660w, 3540w, 3260m (v. br.), 3090w, 3060w, 3030w, 2985s, 2950m, 2935m, 2870w, 2850w, 1600w, 1490w, 1452m, 1380s, 1371s, 1155m, 1115m, 1055s (br.), 1035s (br.), 970w, 935w, 915w, 900w, 878m, 835m. ^1H-NMR: 7.57-7.54 (m, 2H); 7.38-7.32 (m, 3H); 7.09 (s, NOH); 4.78 (d, J = 5.5, H-C(2')); 4.71 (t, J = 5.1, H-C(3')); 4.48 (d, J(C,P) = 18.5, H-C(1)); 4.13 (dt, J = 9.0, 6.4, H-C(5')); 3.86 (dd, J = 8.9, 6.1, H-C(6')); 3.80 (d, J(C,P) = 11.0, POMe); 3.38 (dd, J = 8.0, 6.9, H'-C(6')); 3.31 (J(C,P) = 10.5, POMe); 3.15 (d, J = 6.7, H-C(1')); 2.46-2.35 (m, H-C(4')); 1.69 (br. dd, J ~ 13, 6.5, H-C(7')); 1.60 (dt, J = 12.9, 7.0, H'-C(7')); 1.37 (s, CH_3), 1.34 (s, 2xCH_3), 1.31 (s, CH_3). ^{13}C-NMR: 133.3 (s); 130.5 (dd, J(C,P) = 6.9); 128.4 (d); 110.2 (s); 108.7 (s); 82.3 (d); 81.0 (d); 75.3 (d); 70.1 (dd, J(C,P) = 14.0); 68.9 (dd, J(C,P) = 164.2); 67.9 (t); 53.28 (2q); 45.9 (d); 29.2 (t); 26.9 (q); 26.3 (q); 25.7 (q); 24.3 (q). ^{31}P-NMR: 24.8.

(1R)-**18** (major isomer): R_f (CH_2Cl_2/MeOH 100:3) 0.33. HPLC (Lichrosorb Si60 (7μ), CH_2Cl_2/MeOH 100:3,

flow 4 ml / min, 254 nm): k' = 3.42. $[\alpha]_D(25)$ = +23° (c = 0.9, $CHCl_3$). IR: 3670w, 3540w, 3600-3100w, 3090w, 3070w, 3030w, 2990m, 2955m, 2940m, 2875w, 2855w, 1602w, 1492w, 1453m, 1440w, 1382m, 1372m, 1160m, 1115m, 1070-1030s, 970w, 945w, 935w, 925w, 905w, 880m (br.). ^{1}H-NMR: 7.49-7.46 (m, 2H Ph); 7.38-7.33 (m, 3H Ph); 6.26 (s, NOH); 4.80 (d, J = 5.5, H-C(2')); 4.67 (t, J = 5.4, H-C(3'); 4.36 (d, J = 20.2, H-C(1)); 4.21 (dt, J = 8.6, 6.3, H-C(5')); 4.01 (dd, J = 8.1, H-C(6')); 3.78 (d, J (C,P) = 10.8, $POCH_3$); 3.12 (d, J = 6.30, H-C(1')); 2.55-2.45 (m, H-C(4)); 1.63 (dd, J = 13.6, 6.3, H-C(7')); 1.51 (dt, J = 13.3, 6.5, H'-C(7')); 1.44 (s, CH_3); 1.38 (s, CH_3); 1.34 (s, CH_3); 1.26 (s, CH_3). ^{13}C-NMR: 132.7 (d, J(C,P) = 3.8); 130.3 (dd, J(C,P) = 6.9); 128.45 (dd, J(C,P) = 1.5); 128.34 (dd, J(C,P) = 2.7); 109.5 (s); 108.5 (s); 84.7 (d); 80.3 (d); 75.4 (t); 68.95 (dd, J(C,P) = 15.0); 67.88 (t); 67.86 (dd, J(C,P) = 167.2); 53.3 (dq, J(C,P) = 6.9); 53.1 (dq, J(C,P) = 7.1); 46.2 (d); 26.9 (q); 26.0 (q); 25.9 (t); 25.6 (q); 23.8 (q). ^{31}P-NMR: 25.4. MS (CI): 472.2 (M+1, 100). Anal. calc. for $C_{22}H_{34}NO_8P$ (471.49): C 56.04, H 7.27, N 2.97; found: C 55.83, H 7.48, N 2.79.

(1S)- and (1R)-Pseudo-dimethyl [(2,3:5,6-Di-O-isopropylidene-β-L-gulofuranosyl)hydroxyamino](phenyl)methylphosphonate ((1S, 3'aS, 4'S, 4"R, 6'R, 6'aS)- *and* (1R,3'aS, 4'S, 4"S, 6'R, 6'aS)*-dimethyl {[2',2'-dimethyl-6'-(2",2"-dimethyldioxolan-4"-yl)-3',4',5',6a'-tetrahydro-cyclopenta-1,3-dioxol-4'-yl]hydroxyamino}(phenyl)methylphosphonate*) ((1S)-**47** and (1R)-**48**).

i) *Catalysis by $HClO_4$:* See general procedure IIA. Nitrone **42** (41 mg, 113 µmol) $P(OSiMe_3)_3$ (150 µl), CH_2Cl_2/benzene (1:1, 1.5 ml), 70% $HClO_4$ (1 µl). The reaction was complete after 10 min. MeOH (0.5 ml). FC (silica, hexane/i-PrOH 5:1) gave a mixture of (1S)-**47** and (1R)-**48** (41 mg, 77 %).

ii) *Catalysis by $ZnCl_2$:* $ZnCl_2$ (12 mg, 81 µmol), nitrone **42** (30 mg, 83 µmol), benzene (0.5 ml), $P(OSiMe_3)_3$ (50 µl). The reaction was complete after 24 h. MeOH (0.4 ml). FC (silica, hexane/i-PrOH 5:1) gave (1S)-**47** and (1R)-**48** (28 mg, 72 %).

(1S)-**47**: M.p. 149° (Et_2O/hexane). R_f (hexane/i-PrOH 5:1) 0.26. IR (KBr): 3700-3100m, 3280s, 3065w, 3030w, 2980m, 2970m, 2935m, 2915m, 2870w, 2850w, 2827w, 1493w, 1457m, 1410w, 1385m, 1380m, 1370m, 1290w, 1273m, 1250m, 1233s, 1204s, 1180m, 1175m, 1170m, 1162m, 1155m, 1085m, 1063s, 1045s, 1030s, 1025s, 972w, 943w, 916w, 908w, 885m, 864w, 843w, 832m, 809w, 794w, 768w, 742m, 704m. ^{1}H-NMR: 7.56-7.49 (m, 2 H); 7.44-7.31 (m, 3 H); 6.29 (br. s, OH exch. with D_2O); 4.77 (d, J = 5.4, H-C(2')); 4.53 (t, J = 5.8, H-C(3')); 4.50 (d, J(H,P) =17.6, H-C(1)); 4.12 (dd, J = 7.6, 5.8, H-C(6')); 4.04 (dt, J = 9.0, 5.9, H-C(5')); 3.79 (d, J(H,P) = 11.0, OMe); 3.68 (dd, J = 7.3, 6.1, H'-C(6')); 3.25 (br. d, J = 7, H-C(1')); 2.43-2.21 (m, H-C(4')); 2.19-1.84 (m, H-C(7') and H'-C(7')); 1.36 (s, CH_3); 1.324 (s, CH_3); 1.319 (s, CH_3); 1.27 (s, CH_3). ^{13}C-NMR: 133.6 (d, J(C,P) = 4.4); 130.4 (dd, J(C,P) = 7.0); 128.4 (dd, J(C,P) =1.8); 128.3 (d); 110.5 (s); 108.4 (s); 82.2 (d); 81.2 (d); 69.4 (dd, J(C,P) = 13.6); 68.9 (dd, J(C,P) = 163.8); 68.7 (t); 53.26 (dq, J(C,P) = 4.9); 53.14(dq, J(C,P) = 7.1); 45.7 (d); 32.7 (t); 26.9 (q); 26.3 (q); 25.6 (q); 24.3 (q). ^{31}P-NMR: 25.0. Anal. calc. for $C_{22}H_{34}NO_8P$ (471.49): C 56.04, H 7.27, N 2.97, P 6.57; found: C 55.83, H 7.48, N 2.95, P 6.30.

(1R)-**48**: R_f (hexane/i-PrOH 5:1) 0.21. IR (KBr): 3700-3100m, 3275s, 3060w, 3030w, 2983s, 2957m, 2935m, 2905m, 2855m, 1640w (br), 1497w, 1463m, 1454m, 1380m, 1327s, 1265m, 1245s, 1214s, 1207s, 1181m, 1167m, 1120w, 1100m, 1070s, 1497w, 1463m, 1454m, 1380m, 1327s, 1265m, 1245s, 1214s, 1207s, 1181m, 1167m, 1120w, 1100m, 1070s, 1050s, 1036s, 1020s, 973w, 948w, 932w, 923w, 903w, 883w, 857w, 843w, 828m, 788m, 758m, 724m, 705m. ^{1}H-NMR: 7.53-7.48 (m, 2H); 7.40-7.30 (m, 3H); 6.62 (s, OH, exch. with D_2O); 4.83 (d, J = 5.6, H-C(2')); 4.52 (t, J = 5.7, H-C(3')); 4.43 (d, J(H,P) = 20.0, H-C(1)); 4.17 (dd, J = 7.7, 5.8, H-C(6')); 4.05 (dt, J = 9.4, 6.2, H-C(5')); 3.78 (d, J(H,P) = 10.8, OMe); 3.72 (dd, J = 7.7, 6.3, H'-C(6'); 3.46 (d, J(H,P) = 10.5, OMe); 3.10 (d, J = 6.0, H-C(1')); 2.46-2.26 (m, H-C(4')); 2.08 (br. dd, J = 12.5, 6.4, H-C(7')); 1.70 (dt, J = 12.0, 6.4, H'-C(7')); 1.45 (s, CH_3); 1.37 (s, CH_3); 1.32 (s, CH_3); 1.20 (s, CH_3). ^{13}C-NMR: 132.2 (d, J(C,P) = 2.8); 130.6 (dd, J(C,P) = 7.1); 128.4 (d); 109.7 (s); 108.5 (s); 85.1 (d); 80.5 (d); 77.8 (d); 68.62 (t); 68.60 (dd, J(C,P) = 15.8); 67.3 (dd, J(C,P) = 168.1); 53.34 (dq, J(C,P) = 6.6); 53.21 (dq, J(C,P) = 7.1); 46.5 (d); 29.1 (t); 27.0 (q); 26.0 (q); 25.7 (q); 23.8 (q). ^{31}P-NMR: 25.6. Anal. calc. for $C_{22}H_{34}NO_8P$ (471.49): C 56.04, H 7.27, N 2.97, P 6.57; found: C 56.18, H 7.48, N 2.79, P 6.43.

(1S)- and (1R)-Dimethyl [(2,3:5,6-Di-O-isopropylidene-α-D-mannofuranosyl)hydroxyamino](phenyl)-methylphosphonate ((1S)-**8** and (1R)-**9**).

i) *Catalysis by $HClO_4$:* See general procedure IIA. Nitrone **7** (163 mg, 0.45 mmol), CH_2Cl_2/benzene (1:1, 10 ml), $P(OSiMe_3)_3$ (0.25 ml), -45°C, $HClO_4$ (2 µl, 14 µmol). The reaction was complete within 5 min. MeOH (2 ml). FC (silica, AcOEt) gave (1S)-**8** and (1R)-**9** (207 mg, 93%). ^{31}P-NMR of the crude mixture: (1S)-**8**: 23.9 ppm [1.0], (1R)-**9**: 25.8 ppm [16.1].

ii) *Catalysis by $ZnCl_2$:* See general procedure IIB. $ZnCl_2$ (0.2 mg, 1.47 mmol), nitrone **7** (280 mg, 0.77 mmol), benzene (4.5 ml), $P(OSiMe_3)_3$ (0.5 ml), reflux for 24 h. MeOH (1 ml). FC (AcOEt) gave of (1S)-**8** (290 mg, 79.5%) and (1R)-**9** (29.4 mg, 8.1%). ^{31}P-NMR of the crude mixture: (1S)-**8**: 23.8 ppm [11.0], (1R)-**9**: 26.2 ppm [1.0].

(1S)-**8**: R_f (AcOEt) 0.30. $[\alpha]_D(25)$ = +27.7° (c= 1.3, $CHCl_3$). IR (KBr): 3700-3100s, 3240s, 3060m, 3030m, 2990s, 2955s, 2935m, 2855m, 2830w, 1630m (br), 1496m, 1462m, 1454m, 1445m, 1381s, 1372s, 1237s, 1220w, 2990s, 2955s, 2935m, 2855m, 2830w, 1630m (br), 1496m, 1462m, 1454m, 1445m, 1381s,

1372s, 1237s, 1220s, 1196m, 1162m, 1128m, 1115s, 1100s, 1055s, 1030s, 977w, 955w, 946m, 938w, 926w, 914w, 892w, 854s, 840m, 822m, 788s, 776m, 647m, 637m, 600s. ^{1}H-NMR: 7.63-7.58 (m, 2H, Ph); 7.38 (m, 3H, Ph); 7.21 (s, OH); 5.08 (d, J = 6.0, H-C(2')); 4.85 (s, H-C(1')); 4.78 (dd, J = 6.0, 4.0, H-C(3')); 4.39 (d, J(H,P) = 20.5, H-C(1)); 4.15-4.05 (m, H-C(5')); 3.91 (dd, J = 8.6, 4.0, H-C(6')); 3.83 (d, J(H,P) = 10.8, OCH_3); 3.8-3.7 (m, H-C(4')); 3.33 (d, J(H,P) = 10.5, OCH_3); 3.13 (dd, J(H,P) = 8.6, 4.9, H'-C(6')); 1.45 (s, CH_3); 1.32 (s, 2 CH_3); 1.30 (s, CH_3). ^{13}C-NMR: 134.5 (d, J(C,P) = 2.9); 130.1 (dd, J(C,P) = 7.3); 128.1 (d); 112.0 (s); 108.9 (s); 100.6 (dd, J(C,P) = 16.2); 84.0 (d); 83.7 (d); 80.6 (d); 73.0 (d); 67.4 (dd, J(C,P) =163.7); 66.8 (t); 53.5 (dq, J(C,P) = 7.6); 53.3 (dq, J(C,P) = 7.4); 26.6 (CH_3); 25.9 (CH_3); 25.1 (CH_3), 24.3 (CH_3). ^{31}P-NMR: 23.8. Anal. calc. for $C_{21}H_{32}NO_9P$ (473.46): C 53.27, H 6.81, N 2.96, P 6.54; found: C 53.46, H 7.04, N 3.12, P 6.35.

(1R)-**9**: R_f (AcOEt) 0.26. $[\alpha]_D(25)$ = +58.6° (c= 1.4, $CHCl_3$). IR ($CHCl_3$): 3530w, 3250m, 3090w, 3060w, 3030w, 2990s, 2955m, 2880w, 2855w, 1491w, 1453m, 1381s, 1372s, 1160s, 1112s, 1065s (br), 1040s (br), 973m, 954m, 923w, 887m. ^{1}H-NMR: 8.26 (s, OH); 7.6-7.5 (m, 2 H); 7.4-7.3 (m, 3 H); 5.15 (d, J = 6.1, H-C(2')); 4.86 (dd, J = 6.1, 4.3, H-C(3')); 4.73 (d, J(H,P) = 13.6, H-C(1)); 4.51-4.45 (m, H-C(4')); 4.46 (s, H-C(1')); 4.12 (d, J = 5.6, H-C(6')); 3.80 (d, J(H,P) = 11.0, OCH_3); 3.27 (d, J(P,H) = 10.3, OCH_3); 1.48 (CH_3); 1.40 (2x CH_3); 1.21 (CH_3). ^{13}C-NMR: 132.9 (d, J(C,P) = 6.9); 130.1 (dd, J(C,P) = 6.8)); 128.7 (dd, J(C,P) = 1.9); 128.5 (d, J(C,P) = 2.6); 111.8 (s); 109.0 (s); 95.6 (dd, J(C,P) = 15.9); 84.6 (d); 84.1 (d); 80.7 (d); 73.9 (d); 66.9 (t); 65.5 (d, J(C,P) = 167.8); 53.2 (dq, J(C,P) = 7); 26.8 (q); 25.7 (q); 25.3 (q); 23.9 (q). ^{31}P-NMR: 25.8. Anal. calc. for $C_{21}H_{32}NO_9P$ (473.46): C 53.27, H 6.81, N 2.96, P 6.54; found: C 53.53, H 7.05, N 3.05, P 6.41.

(1S)-N-Pseudo-(2',3':5'6'-di-O-isopropylidene-β-L-gulofuranosyl)-10-((2-oxo-1,7,7-trimethyl-bicyclo-[2.2.1])*heptane)-sulfonamide* ((1S,3'aS, 4'S, R"S, 6'R, 6'aS)-N-*[2',2'-dimethyl-6'-(2",2"-dimethyldioxolan-4"-yl)-3',4',5',6a'-tetrahydro-cyclopenta-1,3-dioxol-4'-yl]-10-((2-Oxo-1,7,7-trimethyl-bicyclo*[2.2.1])-*heptane)sulfonamide* (**36**) *and (1S)-Pseudo-N-(2',3':5':6'-di-O-isopropylidene-α-D-gulofuranosyl)-10-((2-Oxo-1,7,7-trimethyl-bicyclo*[2.2.1])*heptan)sulfonamide* ((1S, 3'aR, 4'R, 4"R, 6'S, 6'aR)-N-*[2',2'-dimethyl-6'-(2",2"-dimethyldioxolan-4"-yl)-3',4',5',6a'-tetrahydro-cyclopenta-1,3-dioxol-4'-yl]-10-((2-Oxo-1,7,7-trimethyl-bicyclo*[2.2.1])*heptan)sulfonamide* (**37**). A soln. of the amine **34** (105 mg, 0.384 mmol, $[\alpha]$ = +36°), (+)-camphersulfonylchloride (180 mg, 0.72 mmol), DMAP (20 mg, 0.16 mmol) and pyridine ((0.5 ml) in CH_2Cl_2 (3 ml) was stirred at r.t. overnight. The mixture was washed with sat. $NaHCO_3$, sat. $CuSO_4$ and H_2O, followed by usual work up to give 200 mg of crude product (**36**:**37** = 5.5:1, ^{1}H-NMR). FC (AcOEt/hexane 1.2:2) gave 165 mg (91%) of **36** and **37**. Repeated FC gave diastereomerically pure **36** and **37**.

36: R_f (AcOEt/hexane 1:1) 0.67. $[\alpha]_D(25)$ = +41.7° (c = 1.1, $CHCl_3$). IR: 3380w (br.), 3270w, 3030w, 2990s, 2965s, 2940s, 2900m, 1738s, 1480w, 1453m, 1415m, 1393m, 1383s, 1374s, 1340s, 1285m, 1160s, 1138s, 1104m, 1090s, 1065s, 1055s, 1032s, 981m, 967m, 954w, 922m, 899m, 870m. ^{1}H-NMR: 5.58 (d, J = 3.4, NH); 4.81 (dd, J = 5.5, 1.3, H-C(2')); 4.57 (t, J = 5.4, H-C(3')); 4.20 (dd, J = 7.8, 5.9, H-C(6')); 4.14 (dt, J = 8.8, 6.2, H-C(5')); 3.76 (dd, J = 7.8, 6.5, H'-C(6'); 3.77-3.74 (m, H-C(1'); 3.44 (d, J = 15.3, 1H, CH_2SO_2); 2.93 (d, J = 15.2, 1H, CH_2SO_2); 2.40 (ddd, J = 18.7, 4.8, 2.6, 1H); 2.2-1.9 (m, 9H); 1.425 (s, CH_3); 1.420 (s, CH_3); 1.36 (s, CH_3); 1.26 (s, CH_3); 1.00 (s, CH_3); 0.94 (s, CH_3). ^{13}C-NMR: 217.4 (s); 110.4 (s); 108.8 (s); 86.5 (d); 79.8 (d); 76.7 (d); 68.5 (t); 59.5 (s); 59.3 (d); 49.4 (t); 49.0 (s); 46.0 (d); 43.0 (t); 42.8 (d); 33.4 (t); 27.2 (t); 27.02 (t); 26.97 (q); 25.8 (q); 25.7 (q); 23.8 (q); 19.9 (q); 19.3 (q). MS (CI): 472.4 (M+1, 100). Anal. calc. for $C_{23}H_{37}NO_7$ (471.61): C 58.58, H 7.91, N 2.97; found: C 58.64, H 8.13, N 2.82.

37: R_f (AcOEt/hexane 1:1) 0.60. $[\alpha]_D(25)$ = +1.5 (c = 1.8, $CHCl_3$). IR: 3385w, 3275w (br.), 3030w, 2990s, 2965m, 2940m, 2900m, 1738s, 1480w, 1450w (br.), 1415m, 1394m, 1383s, 1375s, 1337s, 1285m, 1162s, 1149s, 1105m, 1090m, 1060s (br.), 1037s, 981m, 968m, 954w, 921m, 894m, 860m (br.). ^{1}H-NMR (C_6D_6): 5.25 (d, J = 5.1, NH); 4.57 (d, J = 5.6, H-C(2')); 4.29 (ddd, J = 7.6, 7.0, 6.0, H-C(5')); 4.18 (dd, J = 7.9, 5.9, H-C(6')); 4.10 (t, J = 5.2, H-C(3')); 4.01 (t (br.), J ~ 5, H-C(1')); 3.69 (dd, J = 7.8, 7.1, H'-C(6')); 3.41 (d, J = 15.1, 1H, CH_2SO_2); 2.79 (d, J = 15.1, 1H, CH_2SO_2); 2.27-2.23 (m, 1H); 2.18-2.04 (m, 3H); 1.91 (dt, J = 18.4, 3.9, 1H); 1.79 (m, 1H); 1.5 -1.25 (m, 3H); 1.48 (s, CH_3); 1.33 (s, CH_3); 1.30 (s, CH_3); 1.03 (s, CH_3); 0.60 (s, CH_3); 0.48 (s, CH_3). ^{13}C-NMR: 217.3 (s); 110.9 (s); 108.8 (s); 86.0 (d); 79.9 (d); 76.4 (d); 68.6 (t); 59.2 (s); 59.0 (d); 50.6 (t); 48.8 (s); 45.3 (d); 43.0 (t); 42.8 (d); 34.1 (t); 26.99 (t and q); 26.89 (t); 25.9 (q); 25.6 (q); 23.9 (q); 19.9 (q); 19.5 (q). MS (CI): 472.1 (M+1, 24), 414.3 (M-57, 100).

(1S)-Pseudo-N-(2',3':5':6'-Di-O-isopropylidene-α-D-mannofuranosyl)-10-((2-Oxo-1,7,7-trimethyl-bicyclo[2.2.1])*heptan)-sulfonamide* ((1S, 3'aS, 4'S, 4"R, 6'R, 6'aS)-N-*{[2',2'-dimethyl-6'-(2",2"-dimethyl-dioxolan-4"-yl)-3',4',5',6a'-tetrahydro-cyclopenta-1,3-dioxol-4'-yl]-10-((2-Oxo-1,7,7-trimethyl-bicyclo-*[2.2.1])*heptan)sulfonamide* (**38**). For the procedure see **36**: Amine **35** (52 mg, 0.20 mmol); (+)-camphersulfonylchloride (100 mg, 0.4 mmol); pyridine (0.3 ml); DMAP (60 mg, 0.2 mmol); 4 h, r.t. Usual work up gave 118 mg of crude product (d.e. > 90%, ^{1}H-NMR). FC (hexane/AcOEt 2:1) gave **38** (78 mg, 82.6%).

R_f (AcOEt/hexane) 0.57. $[\alpha]_D(25)$ = +13.2° (c = 1.4, $CHCl_3$). IR: 3385w, 3270w, 3030w, 2990s, 2965m, 2965m, 2940m, 2900m,1737s, 1480w, 1450m (br.), 1417m, 1393m, 1382s, 1373s, 1336s, 1285m, 1148s, 1115m, 1103m, 1068s, 1054s, 1033s, 978m, 967m, 951w, 930m, 920m, 900m. ^{1}H-NMR: 5.51 (d, J = 4.9,

NH); 4.75 (t, J = 5.1, H-C(3')); 4.52 (dd, J = 5.4, 1.0, H-C(2')); 4.25 (dt, J = 8.9, 6.2, H-C(5')); 4.01 (dd, J = 8.3, 6.1, H-C(6')); 3.80 (t, J = 5.0, H-C(1')); 3.67 (dd, J = 8.2, 6.5, H'-C(6')); 3.44 (d, J = 15.2, 1H, CH_2SO_2); 2.95 (d, J = 15.1, 1H, CH_2SO_2); 2.41 (ddd, J = 18.7, 4.8, 2.9, 1H); 2.32-2.23 (m, H-C(4')); 2.23-2.10 (m, 2H); 2.08-1,91 (m, 3H); 1.82 (dt, J = 13.0, 5.2, H-C(7')); 1.72 (dd, J = 13.0, 5.5, H-C(7')); ca. 1.5-1.4 (m, 1H); 1.433 (s, CH_3); 1.428 (s, CH_3); 1.374 (s, CH_3); 1.298 (s, CH_3); 1.01 (s, CH_3); 0.93 (s, CH_3).^{13}C-NMR: 217.7 (s); 110.7 (s); 108.9 (s); 85.7 (d); 79.9 (d); 74.8 (d); 68.0 (t); 59.5 (s); 59.3 (d); 50.4 (t); 49.0 (s); 45.4 (d); 43.0 (t); 42.8 (d); 31.5 (t); 27.14 (t); 27.0 (t and q); 25.9 (q); 25.7 (q); 23.9 (q); 20.0 (q); 19.4 (q). MS (CI): 472.2 (M+1, 100). Anal. calc. for $C_{23}H_{37}NO_7$ (471.61): C 58.58, H 7.91, N 2.97; found: C 58.74, H 8.04, N 2.80.

(5S)- and (5R) Pseudo-methyl 2-(2,3:5,6-Di-O-isopropylidene-α-D-mannofuranosyl)-3,3,5-trimethylisoxazolidine-5-carboxylate (*(3'aS, 4'S, 4"R, 5S, 6'R, 6'aS)- and (3'aS, 4'S, 4"R, 5R, 6'R, 6'aS)-N-{[2',2'-dimethyl-6'-(2",2"-dimethyldioxolan-4"-yl)-3',4',5',6a'-tetrahydro-cyclopenta-1,3-dioxol-4'-yl]-3,3,5-trimethylisoxazolidine-5-carboxylate)* ((5S)-**2** and (5R)-**3**). A suspension of the hydroxylamine **46** (49 mg,178 mmol), acetone (2.2 ml), methyl methacrylate (0.9 ml) and molecular sieves (4 Å) was boiled under reflux for 48 h. Filtration, concentration and FC (silica, Et_2O/hexane 1:4) gave a mixture of (5S)- and (5R)-**2** (61 mg, 83%, ratio 1:1.7, determined by HPLC and by integration of the signals of H-C(2') in the ^{1}H-NMR spectra (400 MHz)). Semi-preparative HPLC (conditions see below) gave (5S)-**2** (36 mg) and (5R)-**3** (22 mg).
(5S)-**2**: R_f (Et_2O/hexane 1:4) 0.27. HPLC (Lichrosorb Si60 (7μ), Et_2O/hexane 1:4, 4 ml/min, 230 nm): k' = 8.22. $[\alpha]_D(25)$ = -63.7° ($CHCl_3$, c = 0.9). IR: 3030w, 2990s, 2950s, 2940s, 2875m, 1732s, 1455m, 1438m, 1383s, 1372s, 1308m, 1300m, 1163s, 1120m, 1095m, 1060s (br.), 1110m, 992m, 978m, 955m, 948m, 920w, 880m, 855m, 850m. ^{1}H-NMR: 4.94 (d, J = 5.3, H-C(2')); 4.67 (t, J = 5.2, H-C(3')); 4.22 (dt, J = 8.9, 6.4, H-C(5')); 3.99 (dd, J = 8.0, 6.1, H-C(6'); 3.73 (s, OCH_3), 3.60 (dd, J = 8.0, 6.7, H'-C(6')); 3.21 (d, J = 5.8, H-C(1')); 2.76 (d, J = 12.6, H-C(4)); 2.51-2.41 (m, H-C(4')); 1.85 (d, J = 12.7, H'-C(4)); 1.68 (dt, J = 13.3, 6.0, H-C(7')); 1.54 (dt, J = 12.6, 5.3, H'-C(7')); 1.43 (s, 2xCH_3); 1.41 (s, CH_3); 1.38 (s, CH_3); 1.33 (s, CH_3); 1.20 (s, CH_3), 1.14 (s,CH_3). ^{13}C-NMR: 175.9 (s); 109.4 (s); 108.6 (s); 83.5 (d); 80.1 (d); 79.9 (s); 75.2 (d); 68.0 (t); 64.7 (d); 63.3 (s); 54.9 (t); 52.0 (d); 45.4 (d); 29.1 (t); 26.9 (q); 26.8 (q); 26.0 (q); 25.7 (q); 24.0 (q); 23.0 (q); 22.1 (q). MS (CI): 414.4 (M+1, 100%). Anal. calc. for $C_{21}H_{35}O_7N$ (413.51): C 61.00, H 8.53 N 3.39; found: C 61.25, H 8.74, N 3.30.
(5R)-**3**: R_f (Et_2O/hexane 1:4) 0.24. HPLC (conditions see (5S)-**2**): k' = 9.33. $[\alpha]_D(25)$ = + 17.9° ($CHCl_3$, c = 1.8). IR: 3030w, 2990s, 2950s, 2935s, 2878m, 1731s, 1455m, 1439m, 1383s, 1372s, 1350w, 1300m (br.), 1163s, 1123s, 1097m, 1060s (br.), 1009m, 991m, 976m, 949m, 918m, 895m, 880m, 850m, 830m. ^{1}H-NMR: 4.67 (t, J = 5.2, H-C(3')); 4.59 (d, J = 5.5, H-C(2')); 4.23 (dt, J = 9.4, 6.3, H-C(5')); 4.03 (dd, J = 8.0, 6.1, H-C(6')); 3.74 (s, OCH_3); 3.69 (dd, J = 8.0, 6.6, H'-C(6')); 3.27 (d, J = 5.8, H-C(1'); 2.75 (d, J = 12.6, H-C(4)); 2.47-2.37 (m, H-C(4')); 1.91 (dd (br.), J ~ 13, 7, H-C(7')); 1.90 (d, 12.7); 1.65 (dt, J = 12.8, 5.9, H'-C(7')); 1.444 (s, CH_3); 1.436 (s, CH_3); 1.42 (s, CH_3); 1.39 (s, CH_3); 1.30 (s, CH_3); 1.24 (s, CH_3), 1.22 (s, CH_3). ^{13}C-NMR: 175.7 (s); 109.8 (s); 108.7 (s); 83.7 (d); 80.3 (d); 79.6 (s); 75.3 (d); 68.2 (t); 65.1 (d); 63.3 (s); 55.0 (t); 52.2 (d); 45.6 (d); 29.0 (t); 27.0 (q); 26.1 (q); 25.6 (q); 24.1 (q); 23.5 (q); 23.2 (q).MS (CI): 414.3 (M+1, 100).

Kinetic measurements. All solutions were freshly prepared under a N_2-atmosphere. $ZnCl_2$ (150 mg, 0.11 mmol) was slowly melted (*Bunsen* burner) at ca. 0.1 torr, then benzene (8ml) and $P(OSiMe_3)_3$ (2 ml) were added. The $ZnCl_2$ was dissolved by use of an ultrasonic bath (25°, 15 min). Portions of 3ml of the clear solutior were transferred by a dry syringe into the UV cells, and immediately afterwards 0.3-0.35 ml of a soln. of the corresponding nitrone (700 μg) in benzene (1 ml) was added. The cells were closed and vigorously shaken. The kinetic measurements were started within 2 min. Measurements were made at 25.3°. The k-values are the average of 4 measurements.

nitrone	k [min-1]	$\tau_{1/2}$ [min]
7	31±2.8 10^{-3}	22
16	0.478±0 067 10^{-3}	1450
42	1.29±0 22 10^{-3}	537

The nitrone **16** (20 mg, 55 μmol) was added to the $ZnCl_2$/$P(OSiMe_3)_3$/benzene-soln. (4 ml). After 48 h at r.t., the mixture was taken to dryness (avoiding contact with moisture, h.v.). The crude product was taken up in MeOH (2 ml) at 0°. After 2 min CH_2N_2 in EtO_2 was added. ^{31}P-NMR of the crude product: (1S)-**17**: 25.9 [1.3]; (1R)-**18**: 25.2 [1.0].

Table 6: Addition of $LiPO_3Me_2$ *to the Nitrones* **4** *and* **13**. *(See General Procedure I)*

entry	nitrone	solvent	temp.	$LiPO_3Me_2$-soln.	reaction time	^{31}P-NMR-data of the resulting phosphonates [Integral, chem. shift (ppm)]
1	**4** (60 mg, 150 µmol)	CH_2Cl_2 (4 ml)	-25°C	0.5 ml	25 sec	(1S)-**5** [9, 26.92] : (1R)-**6** [1.0, 27.01]
2	**4** (60 mg, 150 µmol)	THF (4 ml)	-25°C	0.5 ml	< 3 sec	(1S)-**5**[16, 26.70] : (1R)-**6** [1.0, 27.01]
3	**13** (30 mg, 74 µmol)	CH_2Cl_2 (2 ml)	-25°C	0.25 ml (R = Me)	~ 200 sec	(1S)-**14** [2.5, 26.61] : (1R)-**15** [1.0, 26.70]
4	**13** (30 mg, 74 µmol)	THF (2 ml)	-25°C	0.25 ml (R = Me)	30-40 sec	(1S)-**14** [1.8, 26.60] : (1R)-**15** [1.0, 26.69]

Table 7: Addition of $P(OSiMe_3)_3$ *to the Nitrones* **7**, **16** *and* **42**. *(See General Procedure II)*

entry	nitrone(s)	solvent	$P(OSiMe_3)_3$	temp.	catalyst	reaction time	^{31}P-NMR of the corresp. phosphonates [Integral, chem. shift (ppm)]
1	**16** (35 mg, 97 µmol)	0.5 ml	100 µl	-45°C	$HClO_4$ (10 µl, 58 µmol)	20 min	(1S)-**17** (1, 24.82) : (1R)-**18** (1.7,25.40)
2	**42** (60 mg, 166 µmol)	1 ml	100 µl	-45°C	$HClO_4$ (1.0 µl, 7 µmol)	10 min	(1S)-**47** (1, 25.25) : (1R)-**48** (1, 25.79)
3	**7** (15 mg, 41 µmol) **42** (15 mg, 41 µmol)	0.5 ml	50 µl	-45°C	$HClO_4$ (0.5 µl, 4 µmol)	10 min	(1S)-**8** (1, 23.79) : (1R)-**9** (17, 26.08) (1S)-**47** (1, 25.10) : (1R)-**48** (1, 25.74)
4	**7** (60 mg, 165 µmol) **42** (300 mg ,83 µmol)	1.5 ml	150 µl	r.t.	$ZnCl_2$ (34 mg, 250 µmol)	24 h	(1S)-**8** (1, 23.95) : (1R)-**9** (15, 26.07) (1S)-**47** (1, 25.23) : (1R)-**48** (1, 25.91)
5	**42** (30 mg, 83 µmol)	0.5 ml	50 µl	r.t.	$ZnCl_2$ (12 mg, 81 µmol)	24 h	(1S)-**47** (1, 25.33) : (1R)-**48** (1, 25.88)

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   Independently, by a MNDO calculation *Mzengeza* and *Whitney* found a difference of 3.32 kcal for the heats of formation of the 'O-endo'- and 'O-exo'-conformers (ΔE_{exo}-ΔE_{endo}) of E. See S. Mzengeza, R. A. Whitney, *J. Org. Chem.* **1988**, *53*, 4074.
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15. The tetrahydrocyclopenta-1,3-dioxole derivatives are named as pseudo sugar derivatives having a methylene group (=C(7)) at the place of the tetrahydrofuran ring oxygen (= O-C(5)). See G.E. Mc Cashland, S. Furata, L.J. Durham, *J. Org. Chem.* **1966**, *31*, 1516; H. Paulsen, W. von Deym, W. Röben, *Liebigs Ann. Chem.* **1984**, 433.
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18. Eu(tfc)3 = Tris[3-((trifluormethyl)hydroxymethylene)-d-camphorato]europium (III); 5% soln. of **34** or **35** in $CDCl_3$; stepwise addition of ca. 0.1, 0.2, 0.3, 0.6 and 1.2 equiv. Eu(tfc)3. See L. Goering, J.N. Eibenberry, G.S. Koermer, *J. Am. Chem. Soc.* **1971**, *93*, 5913.
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22. In the chemically induced mass spectra of **5** and **14**, both pure compounds according to ^1H-, ^{13}C- and ^{31}P-NMR spectra and elemental analysis, peaks for M+1 and M+1-16 were observed.The relative intensity of these peaks depends upon the temperature of the inlet system: the higher the temperature, the more intensive the M+1-16 peak. Presumably, a thermal loss of an oxygen atom precedes the CI-MS fragmentation. An analogy is found in the disproportionation of N-hydroxy-α-aminocarboxylic acids to aminocarboxylic acids and oximinocarboxylic acids (oximes; see E. Bühler, G.B. Brown, *J. Org. Chem.* **1967**, *32*, 265.).
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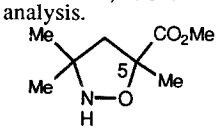
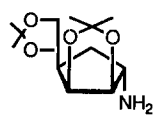
25. The evidence derives from the molecular rotations of the enantiomeric isoxazolidines (5S)- and (5R)-**54** and of the amine **34**. Calc. $[M]_D$ for **11** (5S) = -346° and for **12** (5R) = +160°. Exp. values for **11** = -263° and for **12** = +74.



(5R)-**49**: $[M]_D$= +253°
(5S)-**49**: $[M]_D$= -253°



32 : $[M]_D$= -93°

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28. *Helmchen* et al. observed a diastereofacial selectivity of the dienophiles in an asymmetric Diels-Alder reaction of a chiral acrylate and cyclopentadiene (or isoprene) depending on both the nature of the Lewis-acid ($TiCl_4$ or $EtAlCl_2$) and on the ratio of the acrylate to the catalyst. *Bloch* and *Gilbert* found a dependence of the diastereofacial selectivity on the solvent (addition of alkylmagnesium bromide to a chiral aldehyde). See T. Poll, G. Helmchen, B. Bauer, *Tetrahedron Lett.* **1984**, *25*, 2191; T. Poll, A. Sobczak, H. Hartmann, G. Helmchen, *ibid* **1987**, 3965; R. Bloch, L. Gilbert, *ibid* **1987**, *28*, 423.
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