# 153. Glycosylidene Carbenes

## A New Approach to Glycoside Synthesis

Part 1

## Preparation of Glycosylidene-Derived Diaziridines and Diazirines[1])

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A new approach towards the synthesis of glycosides based upon a (formal) insertion of glycosylidene carbenes into O–H bonds is presented. The synthesis and characterization of the glycosylidene-derived diazirines **25**–**28**, precursors of glycosylidene carbenes, are described. The diazirines were prepared by the rapid, high-yielding oxidation of the diaziridines **20** and **22**–**24** with $I_2/Et_3N$. The diaziridines, the first examples of *C*- alkoxy-diaziridines, were formed in high yields by the reaction of the [(glycosylidene)-amino]methanesulfonates **14** and **17**–**19** with a saturated solution of $NH_3$ in MeOH. The diazirines are highly reactive compounds, losing $N_2$ at room temperature or below. The reaction of the *gluco*-configurated diazirine **25** with i-PrOH yielding a mixture of the $\alpha$- and $\beta$-D-glucosides **29** and **30** illustrates the potential of glycosylidene-derived diazirines as a new type of glycosyl donors.

**Introduction.** – The methods for the synthesis of glycosides have been substantially improved over the last years, due to advances in the understanding of the mechanism and to the introduction of new leaving groups and promoters [1]. As a rule, the fundamental features of the original *Koenigs-Knorr* synthesis, however, have been maintained[2]), *viz.* the substitution of an (activated) leaving group at the anomeric centre of the glycosyl donor by the glycosyl acceptor in a process located somewhere between the extreme cases of the $S_N1$ and $S_N2$ paradigm. The importance of glycosides and the high level of sophistication required for the successful preparation of the various types of glycosides make the search for fundamentally new methods both attractive and difficult. The assumption that the ion pair **2** (*Scheme 1*) is the ideal precursor for a glycoside **1** leads to the question, if **2** may be formed by deprotonation of the alcohol **4** by the ylide **3a**. This ylide is a resonance form of a glycosylidene carbene **3b**, which would be a new representative of the ambiphilic or nucleophilic alkoxycarbenes [3]. Glycosylidene carbenes may, thus, be glycosylating agents, independently of whether the mechanism of glycoside formation involves an initial deprotonation of the OH group of the glycosyl acceptor, as indicated in *Scheme 1*, or an insertion into the O–H bond [4]. Since carbenes can be generated by thermal or photochemical decomposition of diazirines under mild conditions (for leading references, see [5]), the availability of 1-azi-1-deoxy-glycoses **5**[3])

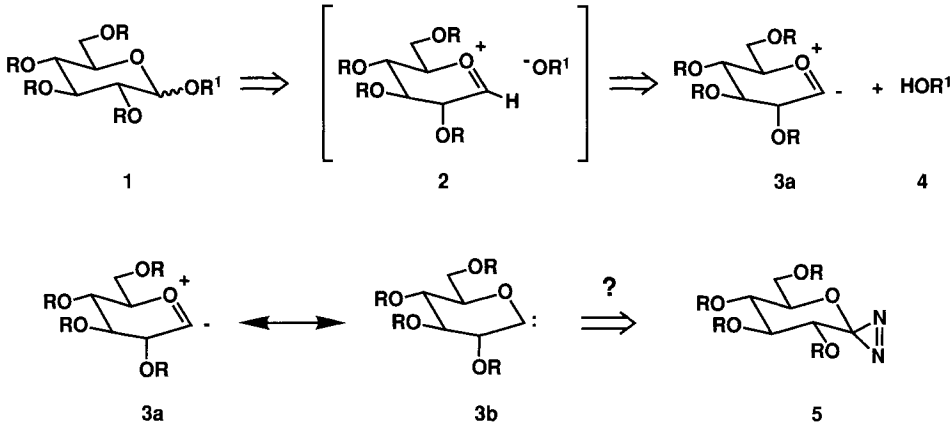
[1]) Presented at the '197th ACS National Meeting', Dallas, Texas, 9th –14th April 1989, Abstr. Carb 9.

[2]) For exceptions, see *e.g.* [2].

[3]) Glycosylidene-derived diazirines are referred to as 1-azi-1-deoxy-glycoses. Similarly, the corresponding diaziridines are referred to as 1-deoxy-1-hydrazi-glycoses.

might constitute the basis for a glycosidation method which would obviate the use of promoters, only generate $N_2$ as a by-product, and proceed – at the least upon photolytic activation – under very mild conditions. The first problem to be solved is the synthesis of 1-azi-1-deoxy-glycoses. We report on a method for their synthesis and on an exploratory experiment on their reaction with alcohols.

*Scheme 1*




1-Azi-1-deoxy-glycoses have not been described[4]). *Diazirines* are usually synthesized either by dehydrogenation of *N,N'*-unsubstituted diaziridines [7], which are synthesized in a separate step or formed as an intermediate, or then by the *Graham* reaction, *i.e.* by treatment of amidines with NaOCl [8]. This latter reaction yields 3-chloro-3*H*-diazirines, in which chloride may be substituted by other nucleophiles such as $RO^-$, $Br^-$, $F^-$, or $CN^-$. The well-documented diazirine exchange reactions [9] give access to diazirines which are otherwise difficult to obtain, particularly to 3-alkoxy-3*H*-diazirines.

The syntheses of *N,N'*-unsubstituted *diaziridines* are based on the reaction of a carbonyl compound, $NH_3$ and an electrophilic aminating agent such as chloramine or hydroxylamine-*O*-sulfonic acid. *O*-Tosylketoximes[5]) appear to react with $NH_3$ to give diaziridines in good yields only when the ketoximes possess electron acceptor substituents such as $CF_3$ or ROCO groups [11]. *O*-Tosyloximes of hexafluoroacetone and of dialkyl mesoxalates react with alkoxyamines to give the corresponding diazirines; *N*-alkoxy-diaziridines are assumed as intermediates [12]. *C*-Alkoxy-diaziridines[6]) have not been described.

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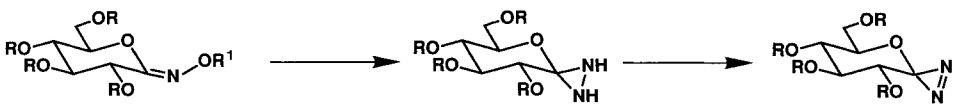
[4]) The known carbohydrate-derived diazirines have been prepared by *Lehmann* and coworkers [6] by the reaction of the corresponding ketones with $NH_3$ and $NH_2OSO_3H$ and oxidation of the intermediary diaziridines ($I_2$/$Et_3N$).

[5]) In one case, a trifluoromethyl substituted *O*-mesylketoxime served as starting material for the preparation of a diaziridine [10].

[6]) In contrast to the tetrahedral intermediates formed by attack of an alkoxide ion on an amidine or of an amine on an amide or iminoether, the alkoxydiaziridines, possessing only one lone pair antiperiplanar to a C–X bond, do not fulfil the conditions of the rule of *Deslongchamps* [13] for the cleavage of a C–X bond in a tetrahedral intermediate. They may, thus, be sufficiently stable to be isolated.

We planned to prepare 1-azi-1-deoxy-glycoses **5** from the corresponding 1-deoxy-1-hydrazi-glycoses **6**, which may be obtained from the reaction of $NH_3$ with (glycosylidene)amino sulfonates **7**. These sulfonates should be available from the corresponding aldonhydroximo-lactones **8** (see *Scheme 2*).

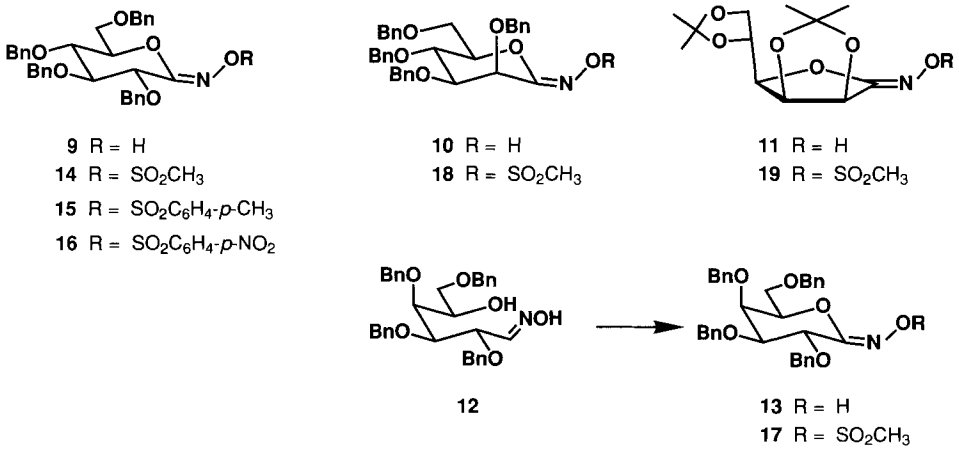
*Scheme 2*



**7** $R^1 = SO_2R_2$
**8** $R^1 = H$

**Results and Discussion.** – 1. *Preparation of (Glycosylidene)amino Sulfonates* (see *Scheme 3*). The preparation of the aldonhydroximo-lactones **9**, **10**, and **11** has already been described [14] [15]. Similarly, the galactonhydroximo-lactone **13** was prepared by oxidation of the crystalline aldoxime **12** with $MnO_2$ in MeOH [15] in a yield of 75%. The aldoxime **12** was obtained from 2,3,4,6-tetra-*O*-benzyl-D-galactopyranose [16] and $NH_2OH$ (99%).

*Scheme 3*



**9** R = H
**14** R = $SO_2CH_3$
**15** R = $SO_2C_6H_4$-*p*-$CH_3$
**16** R = $SO_2C_6H_4$-*p*-$NO_2$

**10** R = H
**18** R = $SO_2CH_3$

**11** R = H
**19** R = $SO_2CH_3$

**12**

**13** R = H
**17** R = $SO_2CH_3$

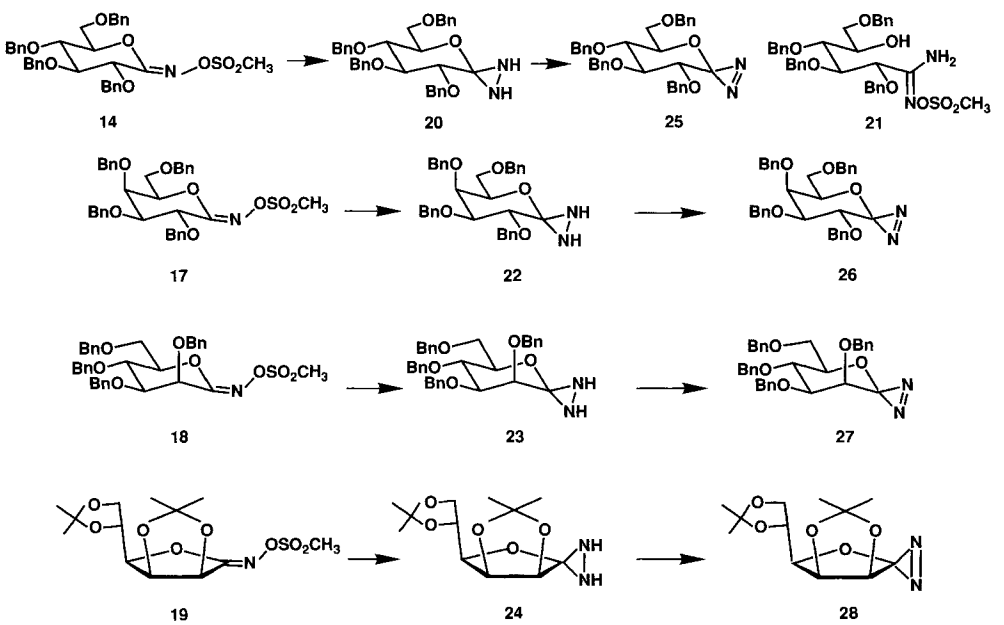
To evaluate the influence of the sulfonyl moiety upon the ease of formation of the diaziridines, we prepared the sulfonyl derivatives **14**[7]), **15**, and **16** from the gluconhydroximo-lactone **9** and the corresponding sulfonyl chlorides in the presence of $Et_3N$ in $CH_2Cl_2$ solution. The mesylates **17**–**19** were obtained in a similar way. These reactions proceeded in high yields. An excess of nosyl chloride is required for total conversion of **9** to **16**. The use of pyridine instead of $Et_3N$ required higher reaction temperatures and gave lower yields.

[7]) Previously obtained as an oil in 75% yield [14].

The IR spectra ($CHCl_3$) of the pyranoid mesylates **14**, **17**, and **18** show one C=N absorption at 1650, while the IR spectra ($CHCl_3$) of the pyranoid hydroximo-lactones **9**, **10**, and **13** show a double absorption between 1670 and 1630 $cm^{-1}$. The relative intensities of the two bands depend on the structure of the hydroximo-lactones and the solvent. The IR spectrum of **9** in KBr shows only one C=N band.The furanoid hydroximo lactone **11** has only one C=N absorption [14]. The sulfonyl bands of **14** and **17–19** are found at 1375–1365 and 1180–1175 $cm^{-1}$. In the $^1$H-NMR spectra of **14** and **17–19**, the $CH_3SO_2$-*singlets* appear between 3.16 and 3.00 ppm. Interestingly, the values of $J$(2,3) for the *gluco-* and *galacto*-configurated mesylates **14** and **17**, and for the corresponding hydroximo-lactones **9** and **13**, are much smaller than for the corresponding derivatives possessing an $sp^3$-configurated C(1)-atom ($J$(2,3) (**14**) = 2.0 Hz and $J$(2,3) (**17**) = 5.0 Hz). In conjunction with $J$(3,4) (**14**) = 4.1 Hz, these values show that the mesylates do not assume a chair-like conformation. In the $^{13}$C-NMR spectra, the C(1) signals appear at 157.36, 158.68, and 157.74 ppm for **14**, **17**, and **18**, respectively, and at 163.41 ppm for the five-membered derivative **19**, showing a downfield shift of the C(1) signals as compared to those of the corresponding hydroximo-lactones. The *gluco*-configurated tosylate **15** and nosylate **16** possess similar values for $J$(2,3) (= 2.0 Hz) and $J$(3,4) (= 4.5 and 4.0 Hz, respectively). The chemical shifts of C(1) of **15** and of **16** appear at 157.05 and 158.76 ppm, respectively.

2. *Preparation of 1-Deoxy-1-hydrazi-glycoses.* The mesylate **14** was unreactive towards $NH_3$ in THF solution. After 41 h at room temperature, 77% of **14** were recovered[8]). Treatment of **14** with a saturated $NH_3$ solution in MeOH at room temperature for 36 h, however, gave 82% of the crystalline diaziridine **20** and traces of the *O*-sulfonylamidoxime **21** (*Scheme 4*). The diaziridine **20** crystallized from the slightly concentrated reaction mixture at –25°. Conducting the reaction under a pressure of 6 bar of $NH_3$ at room temperature reduced the reaction time to 2.5 h. Not unexpectedly, the tosylate **15** reacted

*Scheme 4*




[8]) According to TLC, small amounts of a product had been formed, which decomposed during chromatography. It did, however, not oxidize $I^-$ to $I_2$ under acidic conditions, a reaction which is typical for diaziridines [7].

more slowly, only *ca.* 50% of **15** being converted to **20** after 48 h at room temperature. The nosylate **16** was almost completely converted to the diaziridine **20** within 40 h at room temperature. Workup was less efficient in this case, since crystallization of **20** from the reaction mixture was more difficult.

The alkoxy-diaziridine **20** oxidizes $I^-$ to $I_2$[8]). The mass spectrum (CI) shows a peak at *m/z* 553, corresponding to $[M + 1]^+$. In the IR spectrum ($CHCl_3$), the N–H band at 3270 $cm^{-1}$ is characteristic for diaziridines; 3,3-pentamethylenediaziridine [17] shows a band at 3260 $cm^{-1}$. The 400-MHz $^1$H-NMR spectrum of **20** shows two pairs (ratio 95:5) of *doublets*, one at 2.66 and 2.36 ppm, the other at 2.32 and 1.95 ppm; each characterized by a $J$ value of 9.4 Hz and exchanged by $D_2O$. These signals are attributed to the HN–NH groups of two diastereoisomeric diaziridines, both possessing the same relative configuration of the HN–NH moiety[9]). The signal of H–C(2) appears at 4.11 ppm as a *doublet*, indicating the absence of an H–C(1). The values of the coupling constants $J(2,3)$ and $J(3,4)$ of 9.4 and 9.1 Hz, respectively, are typical for the $^4C_1$-conformation of glucopyranoses and indicate $sp^3$-hybridization at C(1). In agreement with this, the $^{13}$C-NMR spectrum of **20** shows the C(1) signal as a *singlet* at 82.97 ppm. The $^{15}$N-NMR spectrum is characterized by two signals (*dd*) at –281.96 and –291.96 ppm in the region of $sp^3$-hybridized N-atoms and values for $^1J$(N,H) of 57.9 and 57.8 Hz and for $^2J$(N,NH) of 3.0 and 3.7 Hz, respectively [19].

Treatment of the *galacto*-configurated mesylate **17** with a saturated $NH_3$ solution in MeOH at room temperature for 8 h yielded the crystalline diaziridine **22** (83%, see *Scheme 4*). Reaction of the *manno*-configurated mesylate **18** required 44 h for completion. The diaziridine **23** was separated from $NH_4OSO_2CH_3$ by taking advantage of their different solubilities in $Et_2O$. Evaporation of the $Et_2O$ solution gave **23** as an oil which decomposed during attempted chromatography either on sillica gel, *Florisil* or aluminium oxide (neutral or basic) and was, thus, not purified any further. Diaziridine **24** was obtained as crystals in 70% yield after 18 h.

The characteristic data of these glycosylidene-derived diaziridines are listed in *Table 1*. Similarly as observed for **20**, the $^1$H-NMR spectra of **22** and **23** show two sets of HN–NH signals (**22**: ratio 95:5; **23**: ratio *ca.* 1:1) attributed in each case to two diastereoisomeric diaziridines. The similar $J$(HN,NH) values indicate the same *relative* configuration of the HN–NH moiety for all these isomers.

Table 1. *Characteristic Spectroscopic Data of the Glycosylidene-derived Diaziridines* **20** *and* **22–24**: *N–H Stretching Vibrations in the IR Spectra, NH Chemical Shifts and Values of* $J$(NH,NH) *in the* $^1$*H-NMR Spectra and C(1) Chemical Shifts in the* $^{13}$*C-NMR Spectra*

| Diaziridines | $\tilde{\nu}$(N–H) [$cm^{-1}$] | $\delta$(NH)[a]) [ppm] | $J$(NH,NH) [Hz] | $\delta$(C(1)) [ppm] |
|---|---|---|---|---|
| **20** | 3270 | 2.66, 2.36 | 9.4 | 82.97 |
| | | 2.32, 1.95 | 9.4 | |
| **22** | 3270 | 2.68, 2.25 | 9.4 | 83.28 |
| | | 2.41, 1.91 | 9.4 | |
| **23** | 3270 | 2.49, 1.90 | 8.6 | 81.61 |
| | | 2.04, 1.45 | 8.8 | |
| **24** | 3280 | 2.51, 2.21 | 9.5 | 90.83 |

[a]) For the two sets of NH signals, refer to *Results and Discussion, Chapt. 2.*

[9]) It is, at this stage, unclear, if the two N–H atoms are *cis*- or *trans*-oriented; the *trans*-orientation appears more probable [18].

3. *Preparation of 1-Azi-1-deoxy-glycoses.* Oxidation of the *gluco*-configurated diaziridine **20** with 1 equiv. of $I_2$ in the presence of an excess of $Et_3N$ in MeOH solution [6] at –25° yielded (91%) the diazirine **25** (*Scheme 4*),which crystallized during the reaction and was isolated by filtration. The crystals can be stored at –25° for 2–3 days, but decompose rapidly at room temperature. Other oxidation methods, using $Ag_2O$, HgO [7], $PbO_2$, or $MnO_2$, gave poor results. The 1-deoxy-1-hydrazi-glycoses **22** and **23** were oxidized with 1 equiv. of $I_2$ in the presence of $Et_3N$ in $Et_2O$ at –60° to the corresponding diazirines **26** and **27**, respectively (*Scheme 4*). In both cases, the precipitated $Et_3NHI$ was filtered off and the diazirines were obtained as oils in yields exceeding 90%. The diazirine **26** was homogeneous according to TLC and $^1$H-NMR. Its original solution is stable for 2 days at –25°; once isolated, **26** decomposes rapidly even at –25°. The diazirine **27** was obtained in only *ca.* 75% purity ($^1$H-NMR). The furanosylidene-derived diazirine **28** proved to be very unstable and could not be isolated even at low temperatures (–100°). It was shown to be formed by $^{13}$C-NMR monitoring of the reaction at –100° (*cf. Exper. Part*). Even at this temperature, the decomposition of **28** started before all starting material **24** had been consumed.

The characteristic data of the diazirines **25**–**28** are presented in *Table 2*. The UV spectrum of **25** in MeOH shows a maximum at 346 nm with a shoulder at 358 nm, the extinction coefficient $\varepsilon$ being small (~ 85) as expected for the n-$\pi^*$ transition of diazirines [6][8]. The N=N stretching vibrations appear between 1570 and 1560 $cm^{-1}$ [8] in the IR spectra of **25**–**27**. In the $^1$H-NMR spectrum of the mannopyranosylidene-derived diazirine **27**, the doublet of H–C(2) appears at a much higher field (2.91 ppm) than in the *gluco*- and *galacto*-diazirines **25** (4.12 ppm) and **26** (4.41 ppm), respectively. This is in agreement with the observed large chemical shift differences between axial and equatorial H-atoms adjacent to the diazirine ring in some 1,2-diazaspiro compounds, due to magnetic anisotropy effects [20]. The $^{13}$C-NMR spectra of **25**–**28** show a high-field shift for C(1) (as compared to the corresponding diaziridines), the *singlets* appearing at 57.00, 57.13, and 56.45 ppm for **25**–**27** and at 64.70 ppm for **28**.

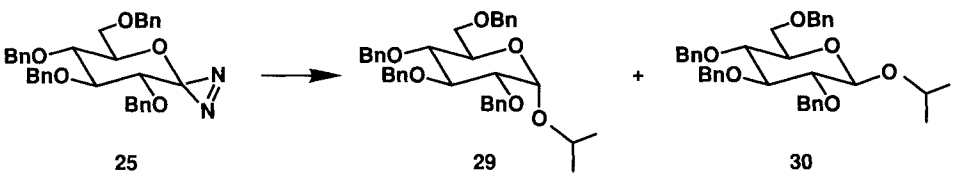
Table 2. *Characteristic Spectroscopic Data of the Glycosylidene-derived Diazirines* **25**–**28**: *N=N Absorptions in the IR Spectra, Chemical Shifts of H–C(2) in the $^1$H-NMR Spectra and of C(1) in the $^{13}$C-NMR Spectra*

| Diazirines | $\tilde{\nu}$ (N=N) [$cm^{-1}$] | $\delta$ (H–C(2)) [ppm] | $\delta$ (C(1)) [ppm] |
|---|---|---|---|
| **25** | 1560 | 4.12 | 57.00 |
| **26** | 1560 | 4.41 | 57.13 |
| **27** | 1570 | 2.91 | 56.45 |
| **28** | – | – | 64.70 |

4. *Exploratory Experiments on the Reaction of 1-Azi-1-deoxy-glycoses with Alcohols.* The complex reaction of carbenes and alkoxy carbenes obtained from diazirines with alcohols has been explored particularly from a mechanistic point of view (for some leading references see [21]), and has been shown to occur very rapidly [22]. Indeed, the methyl 2,3,4,6-tetra-*O*-benzyl-$\alpha$- and $\beta$-D-glucopyranosides [23] were found, in a 1:1 ratio, as by-products of the oxidation of the diaziridine **20** with $I_2$ in MeOH solution. To

see, if reasonable yields of glycosides may be obtained using only 1 equiv. of alcohol, we treated the diazirine **25** with 1 equiv. of i-PrOH in $CH_2Cl_2$ solution at room temperature. This afforded, after 5 h, a 2:1 mixture (anal. HPLC) of the glycosides **29** and **30** in a yield of 61% (*Scheme 5*).

*Scheme 5*




The anomeric isopropyl glucosides **29** and **30** have been mentioned by *Ito* and *Ogawa* [24]. They were separated by anal. HPLC; on a preparative scale, flash chromatography on silica gel gave pure samples of the crystalline $\beta$-D-glucoside **30** (higher $R_f$ value) and its anomer (see *Exper. Part*).

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## Experimental Part

*General.* See [14]. After workup, processing of the org. layer as usual implies drying ($MgSO_4$) and evaporation of the solvent at or below 40°. Qual. TLC: 0.25 mm precoated silica gel plates (*Merck*, Kieselgel *60* $F_{254}$) with the solvent systems indicated. Diazirines were specifically detected by spraying the plate with a 2% soln. of 4-(4-nitrobenzyl)pyridine in acetone and heating at 100° [25]. Flash chromatography (FC): silica gel *Merck 60* (0.040–0.063 mm). UV spectra ($\lambda_{max}$ in nm ($\varepsilon$)). $^1$H-, $^{13}$C-, and $^{15}$N-NMR spectra: chemical shifts in ppm relative to TMS as internal standard ($^1$H- and $^{13}$C-NMR) or relative to $CH_3NO_2$ as external standard [19] ($^{15}$N-NMR). Measuring temp. – if different from 25° – is indicated between brackets for each spectrum.

**1. Aldoximes and Hydroximo-lactones.** – *(E/Z)-2,3,4,6-Tetra-O-benzyl-D-galactose Oxime* (**12**). To a soln. of NaOEt (9.4 g, 0.409 mol of Na) in 1800 ml of 96% aq. EtOH, 56.9 g (0.818 mol) of $NH_2OH \cdot HCl$ were added, and the mixture was stirred at 60° for 1 h. Then, 55 g (0.102 mol) of 2,3,4,6-tetra-*O*-benzyl-D-galactopyranose [16] in 200 ml of EtOH were added. After 30 min at 60°, the mixture was filtered and the filtrate concentrated. The residue was taken up in $CH_2Cl_2$ and washed ($H_2O$). The org. layer was processed as usual to give 56.2 g (99%) of crude **12** as a ~3:1 mixture of the (*E*/*Z*)-isomers, which crystallized under high vacuum. IR: 3580*m*, 3340*w* (br.), 3090*w*, 3060*w*, 3030*w* (sh), 3000*m*, 2920*m* (sh), 2900*m* (sh), 2870*m*, 1970*w* (sh), 1950*w*, 1875*w*, 1810*w*, 1605*w*, 1590*w*, 1495*w*, 1455*m*, 1390*m*, 1360*m*, 1330*m*, 1305*m*, 1090*s*, 1065*s*, 1030*s*, 1015*s* (sh), 935*m*, 915*m* (sh), 875*m*, 690*m*, 660*m* (sh). $^1$H-NMR (200 MHz, $CDCl_3$): 8.98 (br. *s*, exchangeable with $D_2O$, 0.25 H, NOH ((*Z*)-**12**)); 8.56 (s, exchangeable with $D_2O$, 0.75 H, NOH ((*E*)-**12**)); 7.45 (*d*, *J* = 8.0, 0.75 H, H–C(1) ((*E*)-**12**)); 7.28–7.11 (*m*, 20 arom. H); 6.94 (*d*, *J* = 6.1, 0.25 H, H–C(1) ((*Z*)-**12**)); 5.05 (*dd*, *J* = 6.1, 2.8, 0.25 H, H–C(2) ((*Z*)-**12**)); 4.75–4.28 (*m*, 9 H); 4.18–3.85 (*m*, 3 H); 3.58–3.42 (*m*, 2 H); 2.93 (*d*, *J* = 7.1, exchangeable with $D_2O$, 0.75 H, OH); 2.03 (*s*, exchangeable with $D_2O$, 0.25 H, OH). $^{13}$C-NMR (50 MHz, $CDCl_3$): 152.3 (*d*, C(1) of (*Z*)-**12**); 150.31 (*d*, C(1) of (*E*)-**12**); 137.95 (*s*); 137.89 (*s*); 137.73 (*s*); 137.70 (*s*); 137.42 (*s*); 137.29 (*s*); 128.37–127.33 (*m*); 80.47 (*d*); 78.90 (*d*); 77.00 (*d*); 76.74 (*d*), 74.92 (*t*); 73.74 (*t*); 73.65 (*t*); 73.20 (*t*); 71.80 (*t*); 71.42 (*t*); 71.16 (*t*); 70.90 (*t*); 69.29 (*d*).

*2,3,4,6-Tetra-* O*-benzyl-*D*-galactonhydroximo-1,5-lactone* (**13**). A mixture of 55.2 g (0.10 mol) of crude **12** and of 25.4 g (0.31 mol) of $MnO_2$ [15] in 500 ml of dry MeOH was stirred at 60° for 19 h. The mixture was filtered through *Celite* and the filtrate evaporated. FC (hexane/AcOEt 9:1) of the residue gave 41.31 g (75%) of **13** as a colourless oil. $R_f$ (hexane/AcOEt 3:2) 0.38. $[\alpha]_D^{25}$ = +55.3 (*c* = 0.78, $CHCl_3$). IR: 3580*m*, 3400*w* (br.), 3090*w*, 3060*w*, 3030*w* (sh), 3000*m*, 2920*m*, 2870*m*, 1970*w* (sh), 1955*w*, 1880*w*, 1810*w*, 1660*w*, 1655*w* (sh), 1630*w*, 1605*w*, 1590*w*, 1495*w*, 1455*m*, 1390*m*, 1360*m*, 1320*w* (br.), 1260*m*, 1090*s*, 1070*s*, 1025*s*, 1010*s* (sh), 890*m*, 865*m*, 810*w*, 690*m*, 660*m*. $^1$H-NMR (200 MHz, $CDCl_3$): 7.66 (*s*, exchangeable with $D_2O$, OH); 7.36–7.18 (*m*, 20 arom. H); 4.76 (*d*, *J* = 11.5, PhC$H_2$); 4.74 (*d*, *J* = 11.7, PhC$H_2$); 4.64 (*d*, *J* = 12.0, PhC$H_2$); 4.57–4.41 (*m*, 5 PhC$H_2$, H–C(5)); 4.29 (*d*, *J* = 5.3, H–C(2)); 4.17 (*dd* ('*t*'), *J* = 3.3, H–C(4)); 3.87 (*dd*, *J* = 5.2, 3.0, H–C(3)); 3.82 (*dd*, *J* = 6.6, 10.4, $H_A$–C(6)); 3.75 (*dd*, *J* = 5.4, 10.4, $H_B$–C(6)). $^{13}$C-NMR (50 MHz, $CDCl_3$): 151.50 (*s*, C(1)); 137.80 (*s*); 137.67 (2*s*); 137.39 (*s*); 128.39–127.26 (*m*); 78.27 (2*d*); 74.18 (*d*); 73.46 (*t*); 73.30 (*t*); 72.45 (*d*); 72.45 (*t*); 71.73 (*t*); 68.50 (*t*). Anal. calc. for $C_{34}H_{35}NO_6$ (553.66): C 73.76, H 6.37, N 2.53; found: C 73.46, H 6.60, N 2.61.

**2. Sulfonates.** – 2.1. *Methanesulfonates. General Procedure.* To a soln. of the hydroximo-lactone and 2.4 equiv. of $Et_3N$ in $CH_2Cl_2$ at 0° were added dropwise 1.1 equiv. of MsCl. After the addition was completed, the mixture was diluted with $CH_2Cl_2$ and washed with aq. 1M $NaHCO_3$ and with $H_2O$. The org. layer was processed as usual.

*(2,3,4,6-Tetra-*O*-benzyl-*D*-glucopyranosylidene)amino Methanesulfonate* (**14**). Treatment of 20 g (0.036 mol) of **9** [14] and 12 ml (0.086 mol) of $Et_3N$ in 400 ml of $CH_2Cl_2$ with 3.2 ml (0.041 mol) of MsCl yielded, after crystallization from $Et_2O$/hexane 22.5 g (98.5%) of **14**. $R_f$ (hexane/AcOEt 1:1) 0.62. M.p. 64–65.5°. $[\alpha]_D^{25}$ = +39.5 (*c* = 1.1, $CHCl_3$). IR: 3090*w*, 3070*w*, 3030*w*, 3010*w*, 2920*w*, 2870*w*, 1955*w* (br.), 1875*w* (br.), 1810*w* (br.), 1750*w* (br.), 1650*m*, 1635*w* (sh), 1495*w*, 1455*m*, 1410*w*, 1370*s*, 1325*m*, 1290*w*, 1260*w*, 1180*s*, 1095*s* (sh), 1070*s*, 1030*m*, 1005*m* (sh), 970*s*, 910*w*, 840*s*, 690*m*. $^1$H-NMR (400 MHz, $CDCl_3$): 7.40–7.16 (*m*, 20 arom. H); 4.74 (*d*, *J* = 12.0, PhC$H_2$); 4.66–4.63 (*m*, H–C(5)); 4.65 (*d*, *J* = 12.3, PhC$H_2$); 4.59 (*d*, *J* = 12.3, PhC$H_2$); 4.55 (*d*, *J* = 11.0, PhC$H_2$); 4.53 (*d*, *J* = 11.8, PhC$H_2$); 4.49 (*d*, *J* = 11.7, PhC$H_2$); 4.48 (*d*, *J* = 11.3 PhC$H_2$); 4.35 (*d*, *J* = 11.8, PhC$H_2$); 4.16 (*d*, *J* = 2.0, H–C(2)); 3.94 (*dd*, *J* = 2.0, 4.1, H–C(3)); 3.86 (*dd*, *J* = 3.9, 10.0, H–C(4)); 3.83 (*dd*, *J* = 2.1, 11.5, $H_A$–C(6)); 3.76 (*dd*, *J* = 3.9, 11.6, $H_B$–C(6)); 3.12 (*s*, $CH_3$). $^{13}$C-NMR (50 MHz, $CDCl_3$): 157.36 (*s*, C(1)); 137.74 (*s*); 137.34 (*s*); 136.76 (*s*); 136.30 (*s*); 128.77–127.36 (*m*); 80.43 (*d*); 77.41 (*d*); 76.88 (*d*); 73.35 (*t*); 72.99 (*t*); 72.34 (*d*); 71.64 (*t*); 71.09 (*t*); 67.36 (*t*); 36.08 (*q*). Anal. calc. for $C_{35}H_{37}NO_8S$ (631.75): C 66.54, H 5.90, N 2.22, S 5.07; found: C 66.76, H 5.75, N 2.27, S 5.30.

*(2,3,4,6-Tetra-*O*-benzyl-*D*-galactopyranosylidene)amino Methanesulfonate* (**17**). Treatment of 2.8 g (5 mmol) of **13** and 1.7 ml (12 mmol) of $Et_3N$ in 60 ml of $CH_2Cl_2$ with 0.5 ml (6.4 mmol) of MsCl yielded after FC (hexane/AcOEt 4:1) and recrystallization from AcOEt/hexane 2.59 g (83%) of **17**. $R_f$ (hexane/AcOEt 3:2) 0.5. M.p. 83°. $[\alpha]_D^{25}$ = +14.7 (*c* = 1.0, $CHCl_3$). IR: 3090*w*, 3060*w*, 3030*w*, 3010*w*, 2930*w*, 2870*w*, 1955*w* (br.), 1875*w* (br.), 1810*w* (br.), 1655*w* (sh), 1640*m*, 1495*w*, 1450*m*, 1410*w* (sh), 1365*s*, 1325*m*, 1275*m*, 1175*s*, 1100*s*, 1080*s* (sh), 1065*s*, 1030*m*, 1015*m* (sh), 970*s*, 910*w*, 840*s*, 825*s*, 695*m*. $^1$H-NMR (400 MHz, $CDCl_3$): 7.39–7.21 (*m*, 20 arom. H); 4.85 (*d*, *J* = 11.3, PhC$H_2$); 4.84 (*d*, *J* = 11.4, PhC$H_2$); 4.64 (*d*, *J* = 12.0, PhC$H_2$); 4.59 (*d*, *J* = 11.4, PhC$H_2$); 4.57 (*d*, *J* = 12.2, PhC$H_2$); 4.54 (*d*, *J* = 11.3, PhC$H_2$); 4.53 (*d*, *J* = 12.4, PhC$H_2$); 4.48 (*d*, *J* = 11.9 PhC$H_2$); 4.45–4.41 (*m*, H–C(5)); 4.38 (*d*, *J* = 5.0, H–C(2)); 4.14 (*dd*, *J* = 1.9, 3.1, H–C(4)); 3.88 (*dd*, *J* = 4.9, 3.1, H–C(3)); 3.75 (*dd*, *J* = 6.0, 9.8, $H_A$–C(6)); 3.72 (*dd*, *J* = 7.0, 9.8, $H_B$–C(6)); 3.00 (*s*, $CH_3$). $^{13}$C-NMR (50 MHz, $CDCl_3$): 158.68 (*s*, C(1)); 137.61 (*s*); 137.40 (*s*); 137.30 (*s*); 136.81 (*s*); 128.64–127.53 (*m*); 80.08 (*d*); 78.66 (*d*); 74.60 (*d*); 74.34 (*t*); 73.51 (*t*); 72.30 (*t*); 72.12 (*t*); 71.90 (*d*); 67.47 (*t*); 35.93 (*q*). Anal. calc. for $C_{35}H_{37}NO_8S$ (631.75): C 66.54, H 5.90, N 2.22, S 5.07; found: C 66.58, H 6.04, N 2.28, S 5.28.

*(2,3,4,6-Tetra-*O*-benzyl-*D*-mannopyranosylidene)amino Methanesulfonate* (**18**). Treatment of 5.66 g (0.01 mol) of **10** and 3.4 ml (0.024 mol) of $Et_3N$ in 110 ml of $CH_2Cl_2$ with 0.9 ml (0.012 mol) of MsCl, yielded after FC (hexane/AcOEt 3:1), 5.23 g (81%) of **18** as a colourless oil. $R_f$ (hexane/AcOEt 2:1) 0.30. $[\alpha]_D^{25}$ = –16.5 (*c* = 1.04, $CHCl_3$). IR: 3090*w*, 3060*w*, 3030*w*, 3010*w*, 2920*w* (br.), 2870*m*, 1955*w* (br.), 1880*w* (br.), 1815*w* (br.), 1655*w* (sh), 1640*m*, 1490*w*, 1450*m*, 1370*s*, 1325*m*, 1295*m*, 1255*w*, 1175*s*, 1105*s* , 1080*s* (sh), 1070*s*, 1025*s*, 970*s*, 910*w*, 840*s*, 825*s*, 695*m*, 665*m*. $^1$H-NMR (400 MHz, $CDCl_3$): 7.41–7.38 (*m*, 2 arom. H); 7.38–7.26 (*m*, 16 arom. H); 7.22–7.18 (*m*, 2 arom. H) 4.81 (*d*, *J* = 11.0, PhC$H_2$); 4.80 (*d*, *J* = 12.3, PhC$H_2$); 4.63 (*d*, *J* = 12.0, PhC$H_2$); 4.59 (*d*, *J* = 11.9, PhC$H_2$); 4.56 (*d*, *J* = 12.3, PhC$H_2$); 4.54 (*d*, *J* = 11.8, PhC$H_2$); 4.53 (*d*, *J* = 11.0 PhC$H_2$); 4.52 (*d*, *J* = 12.0, PhC$H_2$); 4.34 (*dd* ('*t*'), *J* = 8.2, H–C(4)); 4.31 (*d*, *J* = 3.0, H–C(2)); 4.16 (*ddd* ('*dt*'), *J* = 8.2, 3.9, 3.3, H–C(5)); 3.81 (*dd*, *J* = 3.0, 8.2, H–C(3)); 3.80 (*dd*, *J* = 3.1, 11.3, $H_A$–C(6)); 3.76 (*dd*, *J* = 3.9, 11.3, $H_B$–C(6)); 3.12 (*s*, $CH_3$). $^{13}$C-NMR (50 MHz, $CDCl_3$): 157.74 (*s*, C(1)); 137.73 (*s*); 137.61 (*s*); 137.42 (*s*); 136.79 (*s*); 128.70–127.71 (*m*); 81.99 (*d*); 78.51 (*d*); 74.45 (*t*); 73.30 (*d*); 73.14 (*t*); 72.13 (*t*); 71.46 (*t*); 71.03 (*d*); 68.32 (*t*); 36.11 (*q*). Anal. calc. for $C_{35}H_{37}NO_8S$ (631.75): C 66.54, H 5.90, N 2.22, S 5.07; found: C 66.45, H 6.16, N 2.35, S 4.85.

*(2,3:5,6-Di-O-isopropylidene-D-mannofuranosylidene)amino Methanesulfonate* (**19**). Treatment of 30 g (0.11 mol) of **11** and 36 ml (0.26 mol) of $Et_3N$ in 600 ml of $CH_2Cl_2$ with 8.5 ml (0.11 mol) of MsCl gave, after crystallization from $Et_2O$/hexane and FC (hexane/AcOEt 2:1) of the mother liquor, 37.23 g (96.5%) of **19**. M.p. 101–102°. $R_f$ (hexane/AcOEt 1:1) 0.26. $[\alpha]_D^{25}$ = +92.4 (*c* = 1.08, $CHCl_3$). IR: 3030*w*, 2990*m*, 2940*w*, 2890*w*, 1680*m*, 1655*w* (sh), 1480*w*, 1455*w*, 1415*w*, 1375*s*, 1325*m*, 1250*m*, 1175*s*, 1155*m*, 1120*s*, 1090*s* (sh), 1070*s*, 1050*m* (sh), 1025*m*, 1005*w*, 975*s* (sh), 970*s*, 960*m*, 950*m*, 915*m*, 875*s*, 860*s*, 840*s*. $^1$H-NMR (200 MHz, $CDCl_3$): 5.31 (*d*, *J* = 5.4, H–C(2)); 4.93 (*dd*, *J* = 3.2, 5.5, H–C(3)); 4.50–4.44 (*m*, H–C(5)); 4.43 (*dd*, *J* = 3.3, 8.2, H–C(4)); 4.19 (*dd*, *J* = 5.0, 9.3, $H_A$–C(6)); 4.13 (*dd*, *J* = 3.9, 9.3, $H_B$–C(6)); 3.16 (*s*, $CH_3SO_2$); 1.52, 1.47, 1.44, 1.40 (4 *s*, $CH_3$). $^{13}$C-NMR (50 MHz, $CDCl_3$): 163.41 (*s*, C(1)); 115.06 (*s*); 110.02 (*s*); 84.25 (*d*); 78.15 (*d*); 77.37 (*d*); 72.23 (*d*); 66.37 (*t*); 35.96 (*q*); 26.93 (*q*); 26.78 (*q*); 25.77 (*q*); 25.04 (*q*). Anal. calc. for $C_{13}H_{21}NO_8S$ (351.43): C 44.43, H 6.02, N 4.00, S 9.12; found: C 44.62, H 6.09, N 4.17, S 9.03.

2.2. *(2,3,4,6-Tetra-O-benzyl-D-glucopyranosylidene)amino* p-*Toluenesulfonate* (**15**). A mixture of 1.0 g (1.80 mmol) of **9** and 0.25 ml (1.8 mmol) of $Et_3N$ in 20 ml of $CH_2Cl_2$ was stirred with 350 mg (1.83 mmol) of TsCl for 1 h at r.t. FC (hexane/AcOEt 3:1) afforded 1.25 g (98%) of **15**. $R_f$ (hexane/AcOEt 1:1) 0.55. IR: 3080*w*, 3060*w*, 3040*m*, 3000*m*, 2920*m*, 2860*m*, 1955*w* (br.), 1875*w* (br.), 1810*w* (br.), 1750*w* (br.), 1655*m* (sh), 1645*m*, 1600*w* , 1495*w*, 1455*m*, 1410*w*, 1370*s*, 1290*m*, 1255*m*, 1175*s*, 1090*s*, 1070*s*, 1030*s*, 910*w*, 840*s*, 690*s*. $^1$H-NMR (200 MHz, $CDCl_3$): 7.88 (*d*, *J* = 8.4, 2 arom. H); 7.39–7.11 (*m*, 22 arom. H); 4.63–4.37 (*m*, H–C(5), 6 PhC*H*$_2$); 4.23 (*d*, *J* = 11.7, PhC*H*$_2$); 4.21 (*d*, *J* = 11.9, PhC*H*$_2$); 4.01 (*d*, *J* = 1.7, H–C(2)); 3.83 (*dd*, *J* = 2.0, 4.5, H–C(3)); 3.79–3.67 (*m*, H–C(4), $H_A$–C(6), $H_B$–C(6)); 2.34 (*s*, $CH_3$). $^{13}$C-NMR (50 MHz, $CDCl_3$): 157.05 (*s*, C(1)); 144.67 (s); 137.80 (*s*); 137.37 (*s*); 136.79 (*s*); 136.27 (*s*); 132.63 (*s*); 129.40–127.35 (*m*); 80.71 (*d*); 77.25 (*d*); 76.87 (*d*); 73.36 (*t*); 73.02 (*t*); 72.18 (*d*); 71.43 (*t*); 70.50 (*t*); 67.44 (*t*); 21.54 (*q*).

2.3. *(2,3,4,6-Tetra-O-benzyl-D-glucopyranosylidene)amino* p-*Nitrophenylsulfonate* (**16**). A mixture of 1.0 g (1.8 mmol) of **9** and 0.6 ml (4.3 mmol) of $Et_3N$ in 20 ml of $CH_2Cl_2$ was stirred with 0.6 g (2.7 mmol) of *p*-nitrophenylsulfonylchloride for 30 min at 0°. FC (hexane/AcOEt 4:1) gave 1.32 g (99%) of **16**. $R_f$ (hexane/AcOEt 1:1) 0.66. IR: 3105*w*, 3095*w*, 3060*w*, 3005*m*, 2920*m*, 2870*m*, 1955*w* (br.), 1875*w* (br.), 1810*w* (br.), 1750*w* (br.), 1655*m* (sh), 1640*m*, 1610*m*, 1530*s*, 1495*m*, 1455*m*, 1405*m*, 1380*s*, 1365*s*, 1350*s*, 1310*m*, 1290*m*, 1185*s*, 1090*s*, 1070*s*, 1025*s*, 1015*s*, 910*m*, 855*s*, 835*s* (br.), 690*s*. $^1$H-NMR (200 MHz, $CDCl_3$): 8.08 (s, 4 arom. H); 7.40–7.05 (*m*, 20 arom. H); 4.63–4.37 (*m*, H–C(5), 5 PhC*H*$_2$); 4.35 (*d*, *J* = 12.1, PhC*H*$_2$); 4.30 (*d*, *J* = 11.5, PhC*H*$_2$); 4.21 (*d*, *J* = 11.5, PhC*H*$_2$); 3.98 (*d*, *J* = 2.0, H–C(2)); 3.86–3.78 (*m*, H–C(3), $H_A$–C(6)); 3.72 (*dd*, *J* = 3.6, 11.5, $H_B$–C(6)); 3.61 (*dd*, *J* = 4.0, 10.1, H–C(4)). $^{13}$C-NMR (50 MHz, $CDCl_3$): 158.76 (*s*, C(1)); 150.54 (s); 141.00 (*s*); 137.59 (*s*); 137.18 (*s*); 136.47 (*s*); 135.98 (*s*); 130.05 (*d*); 128.78–127.52 (*m*); 123.85 (*d*); 80.30 (*d*); 77.41 (*d*); 76.63 (*d*); 73.44 (*t*); 72.96 (*t*); 72.09 (*d*); 71.56 (*t*); 70.97 (*t*); 67.25 (*t*).

**3. Diaziridines.** – 3.1. *General Procedure for Reaction at Normal Pressure.* A sat. soln. of $NH_3$ in MeOH was added to the sulfonate, and the mixture was kept at r.t. until all starting material had disappeared, according to TLC. The diaziridines **20**, **22**, and **24** were crystallized from the mixture. The soln. of the oily diaziridine was evaporated, the residue taken up in $Et_2O$, and the precipitated $NH_4OSO_2CH_3$ filtered off to give the crude diaziridine.

3.2. *General Procedure for Reaction under Pressure.* $NH_3$ was condensed into a soln. of the sulfonate in MeOH at –50°. The autoclave was closed and the mixture stirred at r.t. under a pressure of *ca.* 6 bar, until all starting material had disappeared. Workup as described in *3.1*.

3.3. *General Remarks.* The diaziridines in their crystalline form can be kept at –25° for several weeks without remarkable decomposition. The oily diaziridine **23** decomposes quite rapidly. It is best conserved when being stored in the $NH_3$ soln. in the freezer.

*2,3,4,6-Tetra-O-benzyl-1-deoxy-1-hydrazi-D-glucopyranose* (**20**). After treatment of 10.0 g (0.016 mol) of **14** with 180 ml of a sat. $NH_3$ soln. in MeOH for 36 h according to *3.1*, half of the solvent was distilled off. Keeping the remaining soln. at –25° afforded 7.21 g (82%) of crystalline **20**. FC of the mother liquor (hexane/AcOEt 3:1, then 1:2) gave 700 mg (8%) of **20** as an oil, which decomposed in part on silica gel, and 520 mg (~5%) of a more polar side product **21**.

According to *3.2*, 10 ml of $NH_3$ were condensed to 100 mg (0.16 mmol) of **14** in 10 ml of MeOH. After 2.5 h, crystallization from the reaction mixture at –25° yielded 68 mg (78%) of **20**.

*Data of* **20**: $R_f$ (hexane/AcOEt 1:1) 0.48. M.p. 52–53°. IR: 3270*w*, 3090*w*, 3070*w*, 3040*w*, 3000*w*, 2910*m*, 2870*m*, 1950*w* (br.), 1875*w* (br.), 1810*w* (br.), 1720*w* (br.), 1490*w*, 1450*m*, 1390*w* (sh), 1360*m*, 1320*w*, 1280*m* (sh), 1270*m*, 1145*m*, 1120*s*, 1080*s*, 1040*s*, 1030*s*, 1000*m*, 950*m*, 910*w*, 880*w* (sh), 690–660*w* (br.). $^1$H-NMR (400 MHz, $CDCl_3$): 7.36–7.24 (*m*, 18 arom. H); 7.19–7.13 (*m*, 2 arom. H); 4.91 (*d*, *J* = 10.9, PhC*H*$_2$); 4.86 (*d*, *J* = 10.7, PhC*H*$_2$); 4.85 (*d*, *J* = 10.8, PhC*H*$_2$); 4.80 (*d*, *J* = 10.9, PhC*H*$_2$); 4.68 (*d*, *J* = 10.7, PhC*H*$_2$); 4.63 (*d*, *J* = 12.1, PhC*H*$_2$); 4.54 (*d*, *J* = 10.8, PhC*H*$_2$); 4.48 (*d*, *J* = 12.1, PhC*H*$_2$); 4.11 (*d*, *J* = 9.4, H–C(2)); 3.91 (*dd* ('*t*'), *J* =

9.9, 9.1, H–C(4)); 3.82–3.78 (*m*, H–C(5)); 3.78 (*dd*, *J* = 2.8, 10.7, $H_A$–C(6)); 3.70–3.65 (*m*, $H_B$–C(6)); 3.68 (*dd* ('*t*'), *J* = 9.1, 9.3, H–C(3)); 2.66 (*d*, *J* = 9.4, exchangeable with $D_2O$, NH); 2.36 (*d*, *J* = 9.4, exchangeable with $D_2O$, NH). $^{13}$C-NMR (50 MHz, $CDCl_3$): 138.35 (*s*); 137.97 (*s*); 137.62 (2*s*); 128.94–127.32 (*m*); 84.29 (*d*); 82.97 (*s*, C(1)); 77.00 (*d*); 76.53 (2*d*); 75.72 (*t*); 75.53 (*t*); 75.08 (*t*); 73.52 (*t*); 67.77 (*t*). $^{15}$N-NMR (40.6 MHz, $CDCl_3$): –281.96 (*dd*, *J* = 57.9, 3.0, N(1)); –291.96 (*dd*, *J* = 57.8, 3.7, N(2)). CI-MS: 553 (12), 445 (4), 147 (23), 108 (12), 107 (100), 92 (5), 91 (23), 87 (4), 73 (5), 71 (6), 69 (5). Anal. calc. for $C_{34}H_{36}N_2O_5$ (552.68): C 73.89, H 6.56, N 5.07; found: C 73.91, H 6.85, N 5.04.

*Data of 2,3,4,6-Tetra-*O*-benzyl -*N*$^1$-[(methylsulfonyl)oxy]-*D*-gluconamidine* (**21**): IR: 3520*m*, 3450*w* (br.), 3400*w*, 3350*w*, 3090*w*, 3060*w*, 3030*w*, 3000*w*, 2920*w*, 2870*m*, 1950*w* (br.), 1875*w* (br.), 1810*w* (br.), 1680*s*, 1560*w*, 1540*w*, 1495*w*, 1450*w*, 1345*s*, 1330*s* (sh), 1150*s*, 1145m, 1090*s*, 1070*s*, 1025*m*, 975*m*, 910*w*, 690*w*, 660*w*. $^1$H-NMR (200 MHz, $CDCl_3$): 7.41–7.20 (*m*, 20 arom. H); 6.66–6.63 (br. *s*, exchangeable with $D_2O$, NH); 5.63–5.61 (br. *s*, NH); 4.75–4.46 (*m*, 8 PhC*H*$_2$); 4.25 (*d*, *J* = 3.3, H–C(2)); 4.08 (*dd*, *J* = 3.3, 5.2, H–C(3)); 3.93–3.86 (*m*, H–C(4), H–C(5)); 3.66 (*dd*, *J* = 2.8, 9.8, $H_A$–C(6)); 3.58 (*dd*, *J* = 5.0, 9.9, $H_B$–C(6)); 3.09 (*s*, $CH_3$); 2.86 (br. *d*, exchangeable with $D_2O$, OH).

*2,3,4,6-Tetra-*O*-benzyl-1-deoxy-1-hydrazi-*D*-galactopyranose* (**22**). After treatment of 500 mg (0.79 mmol) of mesylate **17** with 60 ml of sat. $NH_3$ soln. in MeOH for 8 h at r.t., half of the solvent was evaporated. Keeping the remaining soln. at –25° yielded 363 mg (83%) of crystalline **22**. $R_f$ (hexane/AcOEt 3:2) 0.4. M.p. 89°. $[\alpha]_D^{25}$ = + 23.0 (*c* = 1.0, $CHCl_3$). IR: 3270*w*, 3095*w*, 3070*w*, 3040*w*, 3000*w*, 2920*w*, 2880*m*, 1950*w* (br.), 1875*w* (br.), 1810*w* (br.), 1605*w* , 1495*w*, 1455*m*, 1395*w*, 1360*m*, 1350*w* (sh), 1325*w*, 1275*m*, 1255*m*, 1100*s*, 1080*s*, 1065*s*, 1040*m*, 1030*m*, 985*w*, 945*m*, 910*w*, 900*w* (sh), 690*m*, 660*w* (sh). $^1$H-NMR (400 MHz, $CDCl_3$): 7.38–7.26 (*m*, 20 arom. H); 4.99 (*d*, *J* = 11.3, PhC*H*$_2$); 4.84 (*d*, *J* = 10.7, PhC*H*$_2$); 4.78 (*d*, *J* = 11.7, PhC*H*$_2$); 4.77–4.74 (*m*, 1 H, PhC*H*$_2$); 4.72 (*d*, *J* = 11.7, PhC*H*$_2$); 4.63 (*d*, *J* = 11.3, PhC*H*$_2$); 4.50 (*d*, *J* = 9.9, H–C(2)); 4.46 (*d*, *J* = 11.9, PhC*H*$_2$); 4.42 (*d*, *J* = 11.9, PhC*H*$_2$); 4.07 (*m*, H–C(4)); 3.96 (*m*, H–C(5)); 3.64 (*dd*, *J* = 2.2, 9.9, H–C(3)); 3.58 (*dd*, *J* = 7.6, 9.2, $H_A$–C(6)); 3.54 (*dd*, *J* = 5.9, 9.1, $H_B$–C(6)); 2.68 (*d*, *J* = 9.4, exchangeable with $D_2O$, NH); 2.25 (*d*, *J* = 9.4, exchangeable with $D_2O$, NH). $^{13}$C-NMR (50 MHz, $CDCl_3$): 138.29 (*s*); 138.17 (*s*); 137.92 (*s*); 137.64 (*s*); 128.72–127.44 (*m*); 83.28 (*s*, C(1)); 81.55 (*d*); 75.74 (*t*); 75.42 (*d*); 74.94 (*t*); 74.17 (*d*); 74.14 (*d*); 73.38 (*t*); 73.13 (*t*); 67.79 (*t*). Anal. calc. for $C_{34}H_{36}N_2O_5$ (552.68): C 73.89, H 6.56, N 5.07; found: C 73.67, H 6.56, N 5.28.

*2,3,4,6-Tetra-*O*-benzyl-1-deoxy-1-hydrazi-*D*-mannopyranose* (**23**). After treatment of 100 mg (0.158 mmol) of **18** in 2 ml of sat. $NH_3$ soln. in MeOH for 44 h at r.t., the solvent was evaporated. The residue was taken up in $Et_2O$ and the precipitated $NH_4OSO_2CH_3$ filtered off to afford 80.5 mg (91%) of crude **23** as *ca.* 1:1 mixture of two isomers according to $^1$H-NMR. IR: 3270*w*, 3090*w*, 3060*w*, 3030*w* (sh), 3000*m*, 2920*m*, 2870*m*, 1955*w* (br.), 1875*w* (br.), 1810*w* (br.), 1605*w*, 1495*w*, 1450*m*, 1365*m*, 1310*w*, 1280*w*, 1175*w*, 1120*s*, 1085*s*, 1025*s*, 1000*m* (sh), 970*m*, 950*w* (sh), 910*w*, 690*m*, 660*m*. $^1$H-NMR (300 MHz, $CDCl_3$): 7.36–7.10 (*m*, 20 arom. H); 4.85 (*d*, *J* = 11.2, PhC*H*$_2$); 4.73–4.38 (*m*, 7 PhC*H*$_2$); 3.99–3.90 (*m*, 1H); 3.91 (*dd*, *J* = 3.0, 7.4, 1H); 3.75–3.61 (*m*, 3H); 3.47 (*d*, *J* = 3.0, H–C(2)); 2.49 (*d*, *J* = 8.6, exchangeable with $D_2O$, NH); 2.04 (*d*, *J* = 8.8, exchangeable with $D_2O$, NH); 1.90 (*d*, *J* = 8.6, exchangeable with $D_2O$, NH); 1.45 (*d*, *J* = 8.8, exchangeable with $D_2O$, NH).

*1-Deoxy-1-hydrazi-2,3:5,6-di-*O*-isopropylidene-*D*-mannofuranose* (**24**). Reaction of 5.0 g (0.014 mol) of **19** with 100 ml of a $NH_3$ soln. in MeOH for 18 h yielded, after evaporation of half of the solvent and crystallization at –25°, 2.71 g (70%) of **24**. $R_f$ (hexane/AcOEt 3:2) 0.16. M.p. 86–87°. IR: 3280*w*, 2990*m*, 2940*m*, 2890*w*, 1450*w*, 1380*m*, 1370*m*, 1155*m*, 1145*m*, 1105*s*, 1070*s*, 1045*m*, 1015*w* (sh), 1005*w*, 995*w* (sh), 970*m*, 950*m*, 920*w*, 890*m*, 865*m*, 840*m*. $^1$H-NMR (200 MHz, $CDCl_3$): 4.96 (*dd*, *J* = 5.8, 3.3, H–C(3)); 4.76 (*d*, *J* = 5.8, H–C(2)); 4.45 (*ddd*, *J* = 8.0, 5.9, 4.3, H–C(5)); 4.16–3.98 (*m*, H–C(4), 2 H–C(6)); 2.51 (*d*, *J* = 9.3, exchangeable with $D_2O$, NH); 2.21 (*d*, *J* = 9.5, exchangeable with $D_2O$, NH). $^{13}$C-NMR (50 MHz, $CDCl_3$): 113.96 (*s*); 109.42 (*s*); 90.83 (*s*, C(1)); 80.95 (*d*); 80.25 (*d*); 79.36 (*d*); 72.97 (*d*); 66.67 (*t*); 26.95 (*q*); 26.20 (*q*); 25.63 (*q*); 25.13 (*q*). Anal. calc. for $C_{12}H_{20}N_2O_5$ (272.30): C 52.93, H 7.40, N 10.29; found: C 52.84, H 7.54, N 10.09.

**4. Diazirines.** – *1-Azi-2,3,4,6-tetra-*O*-benzyl-1-deoxy-*D*-glucopyranose* (**25**). Under $N_2$ at –25°, a soln. of 460 mg (1.81 mmol) of $I_2$ in 9 ml of dry MeOH was added dropwise over 15 min to a stirred mixture of 1.0 g (1.81 mmol) of **20** and 4 ml (28.7 mmol) of $Et_3N$ in 50 ml of dry MeOH. The precipitated crystalline **25** was filtered off. A second crop of crystals was obtained by concentration of the mother liquor and crystallization at –25°. Total yield of **25**: 911 mg (91%). $R_f$ (hexane/AcOEt 2:1) 0.60. M.p. 50°. UV (MeOH): 346 (85), 358 (sh). IR: 3090*w*, 3060*w*, 3030*w*, 3000*w*, 2910*m*, 2870*m*, 1955*w*, 1875*w*, 1810*w*, 1585*w*, 1560*w*, 1540*w* (sh), 1495*w*, 1450*m*, 1395*w*, 1360*m*, 1320*w*, 1310*w* (sh), 1255*w*, 1180*w*, 1145*m*, 1120*s*, 1085*s*, 1070*s*, 1025*s*, 1000*m* (sh), 910*w*, 690*w*, 660*w*. $^1$H-NMR (400 MHz, $CDCl_3$): 7.36–7.26 (*m*, 17 arom. H); 7.22–7.15 (*m*, 3 arom. H); 4.90 (*d*,

$J$ = 10.7, PhC$H_2$); 4.84 (*d*, $J$ = 11.0, PhC$H_2$); 4.82 (*d*, $J$ = 11.0, PhC$H_2$); 4.57 (*d*, $J$ = 10.8, PhC$H_2$); 4.55 (*d*, $J$ = 12.1, PhC$H_2$); 4.44 (*d*, $J$ = 12.1, PhC$H_2$); 4.22 (*d*, $J$ = 11.4, PhC$H_2$); 4.17 (*d*, $J$ = 11.4, PhC$H_2$); 4.12 (*d*, $J$ = 9.0, H–C(2)); 3.99 (*dd* ('*t*'), $J$ = 9.0, H–C(3)); 3.89 (*dd* ('*t*'), $J$ = 9.1, 9.6, H–C(4)); 3.75 (*ddd*, $J$ = 9.7, 3.4, 1.8, H–C(5)); 3.69 (*dd*, $J$ = 3.5, 11.0, $H_A$–C(6)); 3.54 (*dd*, $J$ = 1.8, 11.0, $H_B$–C(6)). $^{13}$C-NMR (100 MHz, $CD_2Cl_2$, –30°): 138.24 (*s*); 137.83 (*s*); 137.59 (*s*); 136.38 (*s*); 128.40–127.84 (*m*); 83.89 (*d*); 76.53 (*d*); 76.14 (*d*); 75.59 (*t*); 75.29 (*t*); 74.33 (*d*); 73.09 (*t*); 72.46 (*t*); 67.34 (*t*); 57.00 (*s*, C(1)).

*1-Azi-2,3,4,6-tetra-*O*-benzyl-1-deoxy-*D*-galactopyranose* (**26**). Under $N_2$ at –60°, a soln. of 92 mg (0.36 mmol) of $I_2$ in 0.5 ml of $Et_2O$ was added dropwise to a stirred soln. of 200 mg (0.36 mmol) of **22** and 0.8 ml (5.7 mmol) of $Et_3N$ in 10 ml of $Et_2O$. After the addition was completed, the precipitated $Et_3NHI$ was filtered off, the filtrate evaporated, and the residue dried at –40° and $10^{-6}$ Torr for 15 min to give 179 mg (90%) of **26**, which was clean according to TLC. $^1$H-NMR (400 MHz, $CD_2Cl_2$, –60°): 7.41–7.23 (*m*, 18 arom. H); 7.16–7.12 (*m*, 2 arom. H); 4.93 (*d*, $J$ = 10.6, PhC$H_2$); 4.78–4.72 (*m*, 2 PhC$H_2$); 4.52 (*d*, $J$ = 10.6, PhC$H_2$); 4.41 (*d*, $J$ = 9.6, H–C(2)); 4.40 (*d*, $J$ = 11.5, PhC$H_2$); 4.31 (*d*, $J$ = 11.5, PhC$H_2$); 4.23 (*d*, $J$ = 11.1, PhC$H_2$); 4.09 (*m*, H–C(4)); 4.00 (*d*, $J$ = 11.0, PhC$H_2$); 3.93–3.88 (*m*, H–C(5), H–C(3)); 3.35 (*d*, $J$ = 7.4, 2 H–C(6)). $^{13}$C-NMR (100 MHz, $CD_2Cl_2$, –40°): 137.92 (*s*); 137.80 (*s*); 137.30 (*s*); 136.59 (*s*); 128.25–127.43 (*m*); 81.09 (*d*); 75.27 (*d*); 74.92 (*t*); 73.73 (*d*); 73.02 (*t*); 72.62 (*t*); 72.49 (*t*); 72.04 (*d*); 67.47 (*t*); 57.13 (*s*, C(1)).

*1-Azi-2,3,4,6-tetra-*O*-benzyl-1-deoxy-*D*-mannopyranose* (**27**). Analogously to the synthesis of **26**, 100 mg (0.18 mmol) of crude **23** were oxidized with 46 mg (0.18 mmol) of $I_2$ in the presence of 0.4 ml (2.9 mmol) of $Et_3N$ in $Et_2O$ at –60° to give 93 mg (93%) of crude **27** in a puritiy of *ca.* 75% ($^1$H-NMR). $^1$H-NMR (400 MHz, $CD_2Cl_2$ –40°): 7.38–7.22 (*m*, 18 arom. H); 7.15–7.11 (*m*, 2 arom. H); 5.00 (*d*, $J$ = 11.9, PhC$H_2$); 4.87 (*d*, $J$ = 10.4, PhC$H_2$); 4.70–4.40 (*m*, 6 PhC$H_2$); 4.10 (*dd* ('*t*'), $J$ = 9.1, H–C(4)); 3.95 (*dd*, $J$ = 3.4, 9.1, H–C(3)); 3.75–3.70 (*m*, H–C(5)); 3.54 (*d*, $J$ = 9.5 2 H–C(6)); 2.91 (*d*, $J$ = 3.4, H–C(2)). $^{13}$C-NMR (100 MHz, $CD_2Cl_2$, –40°): 139.61 (*s*); 139.36 (*s*); 139.30 (*s*); 138.57 (*s*); 130.06–129.42 (*m*); 81.91 (*d*); 78.70 (*d*); 76.87 (*t*); 75.03 (*d*); 74.74 (*d*); 74.74 (*t*); 72.85 (2*t*); 69.51 (*t*); 56.45 (*s*, C(1)).

*1-Azi-1-deoxy-2,3:5,6-di-*O*-isopropylidene-*D*-mannofuranose* (**28**). The reaction was followed by $^{13}$C-NMR. At –100°, 23 mg (0.09 mmol) of $I_2$ were added to a soln. of 25 mg (0.09 mmol) of **24** in 0.5 ml of $CD_2Cl_2$ and 0.2 ml (1.4 mmol) of $Et_3N$. $^{13}$C-NMR (100 MHz, $CD_2Cl_2$, –100°): signals of the newly formed product: 113.52 (*s*); 108.58 (*s*); 79.30 (*d*); 78.44 (*d*); 77.71 (*d*); 72.09 (*d*); 65.59 (*t*); 64.70 (*s*, C(1)); 26.13 (*q*); 25.62 (*q*); 24.89 (*q*); 24.07 (*q*).

**5. Isopropyl 2,3,4,6-Tetra-*O*-benzyl-α- and -β-D-glucopyranoside** (**29** and **30**, resp.). Under $N_2$, 200 mg (0.36 mmol) of **25** were added to a soln. of 30 µl (0.39 mmol) of i-PrOH (dist. over Na) in 3 ml of dry $CH_2Cl_2$. After 5 h at r.t., **25** had completely disappeared. The mixture was evaporated. FC (hexane/AcOEt 8:1) of the residue yielded 129 mg (61%) of a 2:1 mixture **29**/**30**. The ratio of the anomers was determined by anal. HPLC (*LiChrosorb Si 60*, 1.5 ml/min, hexane/AcOEt 6:1): $t_R$ (**30**) 3.5, $t_R$ (**29**) 3.9 min.

*Data of* **29**: $R_f$ (hexane/AcOEt 6:1) 0.23. $^1$H-NMR (300 MHz, $CDCl_3$): 7.34–7.11 (*m*, 20 arom. H); 5.00 (*d*, $J$ = 10.8, PhC$H_2$); 4.88 (*d*, $J$ = 3.7, H–C(1)); 4.85–4.43 (*m*, 7 PhC$H_2$); 4.00 (*dd* ('*t*'), $J$ = 9.2, H–C(4)); 3.89 (*sept.*, $J$ = 6.2, H–C(1')); 3.87–3.82 (*m*, 1 H); 3.74 (*dd*, $J$ = 3.6, 10.6, $H_A$–C(6)); 3.68–3.60 (*m*, 2 H); 3.55 (*dd*, $J$ = 3.7, 9.8, H–C(2)); 1.23 (*d*, $J$ = 6.2, $CH_3$); 1.18 (*d*, $J$ = 6.1, $CH_3$). $^{13}$C-NMR (50 MHz, $CDCl_3$): 138.97 (*s*); 138.27 (2*s*); 137.98 (*s*); 128.37–127.53 (*m*); 94.78 (*d*, C(1)); 82.14 (*d*); 79.93 (*d*); 77.89 (*d*); 75.67 (*t*); 75.13 (*t*); 73.46 (*t*); 73.15 (*t*); 70.04 (*d*); 69.03 (*d*); 68.54 (*t*); 23.19 (*q*); 21.18 (*q*).

*Data of* **30**: $R_f$ (hexane/AcOEt 6:1) 0.25. M.p. 105–107°. $^1$H-NMR (300 MHz, $CDCl_3$): 7.98-7.15 (*m*, 20 arom. H); 4.97 (*d*, $J$ = 10.9, PhC$H_2$); 4.92 (*d*, $J$ = 10.9, PhC$H_2$); 4.81 (*d*, $J$ = 11.8, PhC$H_2$); 4.78 (*d*, $J$ = 11.1, PhC$H_2$); 4.74 (*d*, $J$ = 10.9, PhC$H_2$); 4.61 (*d*, $J$ = 12.3, PhC$H_2$); 4.56 (*d*, $J$ = 12.3, PhC$H_2$); 4.53 (*d*, $J$ = 10.9, PhC$H_2$); 4.46 (*d*, $J$ = 7.6, H–C(1)); 4.02 (*sept.*, $J$ = 6.2, H–C(1')); 3.73 (*dd*, $J$ = 1.9, 10.7, $H_A$–C(6)); 3.68–3.60 (*m*, $H_B$–C(6), H–C(4)); 3.54 (*dd* ('*t*'), $J$ = 8.7, 9.5, H–C(3)); 3.48–3.43 (*m*, H–C(5)); 3.43 (*dd* ('*t*'), $J$ = 7.9, 8.9, H–C(2)); 1.32 (*d*, $J$ = 6.2, $CH_3$); 1.24 (*d*, $J$ = 6.1, $CH_3$). $^{13}$C-NMR (50 MHz, $CDCl_3$): 138.70 (*s*); 138.56 (*s*); 138.31 (*s*); 138.16 (*s*); 128.37–127.57 (*m*); 102.21 (*d*, C(1)); 84.87 (*d*); 82.33 (*d*); 78.02 (*d*); 75.70 (*t*); 74.99 (*t*); 74.85 (*t*); 74.85 (*d*); 73.44 (*t*); 72.37 (*d*); 69.20 (*t*); 23.76 (*q*); 22.26 (*q*).

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