119. Glycosylidene Carbenes

Part 12[1])

A New Synthesis and Some Reactions of Spirooxiranes

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The diazirine **1**, upon thermolysis or photolysis in either acetone or cyclohexanone, at different concentrations, yielded the spiro epoxides **2** and **3**, and **4** and **5**, respectively (*Scheme 1*). Yields of **2** and **3** depended both on the temperature and the concentration, and correlated inversely with the yield of the major by-product, the enol-derived glycoside **6**. Other by-products were the benzyloxyglycal **7** and the lactone azines **8**. $ZnCl_2$-Promoted methanolysis of **2** under mild conditions yielded a mixture of the ulosides **9** and **10** (1.2:1); similarly, **4** yielded **11** and **12** (1.8:1; *Scheme 2*). More strongly acidic conditions converted **11** into **12**, evidencing that $ZnCl_2$-promoted methanolysis proceeds under kinetic control, which is rationalized. The diazirine **13**, upon thermolysis or photolysis in either acetone or cyclohexanone, yielded the α-D-configurated spiro epoxides **14** and **16**, and the α-D-configurated dihydrooxazoles **15** and **17**, respectively (*Scheme 3*), which are either formed by ring-opening of β-D-epoxides, or by competitive interception of the initially formed, hypothetical addition products of the intermediate carbene to the ketones. The glycosylidene carbenes, derived from **1** or **13** are not very reactive towards ketones, yields are good only when sterically unhindered ketones are used in large excess.

1. Introduction. – The basic and nucleophilic character of alkoxy alkyl carbenes, and particularly of glycosylidene carbenes, is shown by the deprotonation of hydroxy compounds (*cf.* [2] and ref. cit. therein) [3–7] and by their addition to acceptor-substituted alkenes [8–15]. The addition of such alkoxy alkyl carbenes to carbonyl compounds, however, was not reported, although it is known for closely related siloxy and for chloro carbenes [16–24]. Glycosylidene carbenes should react with ketones and aldehydes to form reactive, chain-elongated, and preparatively useful spirooxiranes. Simple representatives of such spirooxiranes have been obtained by epoxidation of methylidene derivatives [25] or by intramolecular substitution of heptuloses [26]. They have been used for the synthesis of glycosides [25], of phosphonates [27], and of higher-carbon sugars [28].

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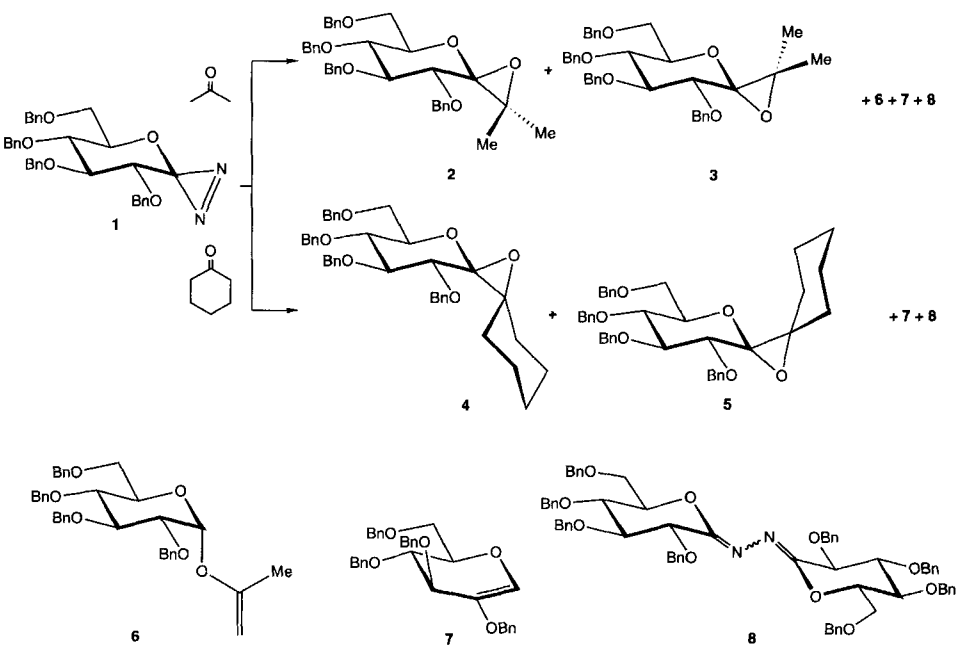
2. Results and Discussion. – *2.1. Addition of* **1** *to Acetone and to Cyclohexanone (Scheme 1).* Thermolysis of a dilute solution (0.025M) of the diazirine **1** in acetone at 23° gave the anomeric epoxides **2** and **3** (63%; 2.4:1). Photolysis at –84°, at the same concentration, afforded **2** and **3** in lower yields and with a lower diastereoselectivity (38%; 2:1). Thermolysis at a higher concentration (0.14M) gave a still lower yield of **2** and **3** (33%; 2.1:1), which fell to 10% (**2**/**3** 1.4:1), when the carbene was generated photolytically at –84°. Thus, yields depend both upon concentration and temperature; they are also inversely correlated to the yield of the major by-product, the enol-derived glycoside **6**, which was obtained in 19% upon irradiation of 0.14M **1** in acetone, while the additional by-products, the benzyloxy glycal **7** [29] and the lactone azines **8** [29], amounted to 5–10%. The glycoside **6** may be formed either by glycosidation of the enol or by deprotonation of acetone by the carbene; it appears that the reaction conditions affect the basic and nucleophilic properties of the glycosylidene carbene[3]) to a different extent. The yields of the crude spiro epoxide **2** and particularly of **3** are sensibly higher than those indicated for the pure compounds, as they decompose rapidly on silica gel, even in the presence of Et_3N.

Scheme 1



[3]) We found no indication for the intermediate formation of diazo compounds (*cf.* [14]).

Thermolysis of 0.107M **1** in cyclohexanone gave 78% of the spiro epoxides **4** and **5** in a ratio of 1.9:1. Only small amounts of the by-products **7** and **8**, and no glycosides were observed. Chromatographic separation of **4** and **5** posed no problem.

Incorporation of acetone into **2** and **3** is evident from elemental analysis and from the NMR spectra (*Tables 1* and *2*), particularly from the appearance of 2*s* (6 H) at 1.58 and 1.44 ppm for **2** and at 1.47 and 1.43 ppm for **3**. The configuration is assigned on the basis of NOE experiments [14] [30]. The anomer **2** gives a strong NOE for H–C(5)[4]) and for the Me group at 1.58 ppm upon irradiation of the *s* of the Me group at 1.44 ppm. Irradiation of H–C(5) results in a strong NOE for H–C(3), H–C(6), and the Me group at 1.44 ppm. These experiments evidence the β-D-configuration and a pseudoaxial orientation of the Me_2C group. Irradiation of the Me group of **3** resonating at 1.43 ppm causes an NOE for H–C(2), the benzyl group at 4.40 ppm, and the Me group at 1.47 ppm, in keeping with the pseudoequatorial orientation of the Me_2C group. Only one of the Me signals of **2** and **3** appears at a relatively low field, presumably due to the deshielding effect of the BnO–C(2) group. In agreement with this, $\Delta\delta$(Me) is larger (0.14 ppm) for **2** than for **3** (0.04 ppm).

The structure of the enol-derived glycoside **6** is evidenced by its mild hydrolysis to tetra-*O*-benzyl-glucose, the elemental analysis, and IR bands at 1260 and 1065 cm^{-1}, characteristic for vinyl ethers. The ^{1}H-NMR spectrum shows three *s*'s. A sharp *s* (3 H) at 1.79 ppm is assigned to the vinylic Me group, two broad *s*'s at 4.57 and 4.08 ppm (each 1 H) are assigned to the olefinic H. The ^{13}C-NMR spectrum shows the *q* of Me at 20.55 ppm, and a *t* of CH_2C at 86.92 ppm. The ESI-MS is characterized by the peak at 603 ([*M* + Na]$^+$).

The incorporation of cyclohexanone in **4** and **5** is evidenced by the elemental analysis and by the NMR spectra. Moreover, the CI-MS (NH_3) gives rise to peaks at *m/z* 638 ([*M* + 18]$^+$), 621 ([*M* + 1]$^+$), and 513 ([M – 107]$^+$) for both compounds. The determination of the anomeric configuration is based on the similarity of the ^{1}H- and ^{13}C-NMR data of **2** and **3** with those of compounds **4** and **5** (*Tables 1* and *2*). The epoxides **2–5**, however, do not appear to follow *Hudson*'s rule of isorotation, the β-D-anomers being more strongly dextrorotatory than the α-D-anomers.

Table 1. *Selected ^{1}H-NMR Chemical Shifts* [ppm] *of the Spirooxiranes* **2–5**, **14**, *and* **16**[4])

	H–C(2)	H–C(3)	H–C(4)	H–C(5)	H_A–C(6)	H_B–C(6)	Me	Me'
2	4.02	3.81	3.81	3.56	3.70	3.70	1.58	1.44
3	3.89	4.17	4.02	4.12	3.70	3.57	1.47	1.43
4	4.04	3.83	3.83	3.64	3.71	3.71	–	–
5	3.96	4.20	4.05	4.16	3.70	3.57	–	–
14	4.77	4.09	3.79	4.40	4.33	3.71	1.36	1.31
16	4.81	4.08	3.80	4.42	4.33	3.71	–	–

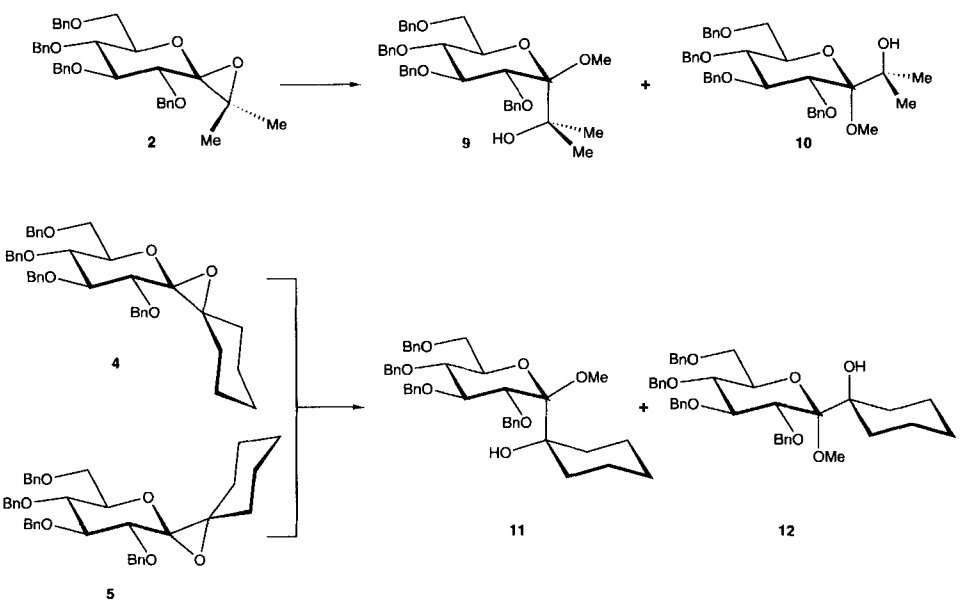
Table 2. *Selected ^{13}C-NMR Chemical Shifts* [ppm] *of the Spirooxiranes* **2–5**, **14**, *and* **16**[4])

	2	**3**	**4**	**5**	**14**	**16**
C(1)	88.70	87.76	89.40	88.19	86.25	86.71
C(1')	64.45	65.55	68.88	69.88	62.43	67.53
Me	20.24	21.24	–	–	21.61	–
Me'	19.41	19.70	–	–	18.77	–

[4]) In the *General Part* and in the *Tables*, the same numbering as for **1** is used for the addition products to acetone. The C-atoms stemming from the C=O group is C(1').

2.2. *Methanolysis of the Epoxides* **2**, **4**, *and* **5** (*Scheme 2*). The epoxide **2** reacted with MeOH in the presence of a catalytic amount of anh. $ZnCl_2$ to give the anomers **9** and **10** (86%; 1.2:1). Similarly, treatment of the epoxide **4** with MeOH and cat. $ZnCl_2$ gave the anomers **11** and **12** (87%; 1.8:1), which were obtained in 79% yield (1.7:1), when the crude epoxides **4** and **5** were treated with MeOH only. Treatment of **5** with MeOH/$ZnCl_2$ yielded over 98% of **11** and **12** in almost equal amounts.

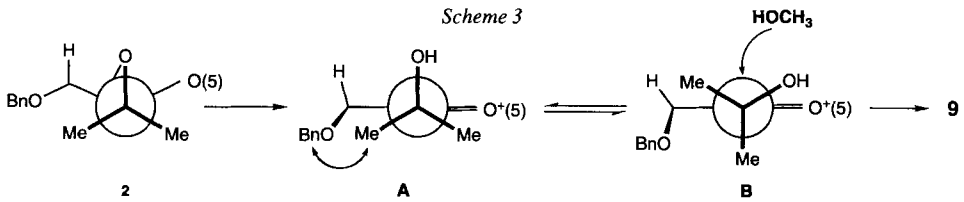
Scheme 2



The glycoside **9** was inert to the action of $NaBH_4$/MeOH, unlike a hemiacetal; it was also stable under the conditions of its formation, as was **11**. However, treatment with HCl in MeOH at room temperature converted **11** quantitatively into **12**. These results show that the glycosides are formed under conditions of kinetic control. The lack of stereospecificity in the ring opening of **2** excludes an S_N2 mechanism. A participation of the BnO–C(2) group under these conditions is not likely; the most convincing explanation postulates an S_N1-type process, in which breaking of the C(1)–O bond (→ **A** in *Scheme 3*) is quickly followed by rotation around the C(1)–C(1')[4]) bond (→ **B**), to alleviate the destabilizing 1,5 interaction between the BnO–C(2) and the *cis*-Me (or, for **11**, *cis*-CH_2) group. This leads to a conformer where the axial approach of MeOH is hindered by one of the Me (or CH_2) groups, so that the stereoelectronic/conformational bias for the axial attack is (partially) neutralized (*Scheme 3*).

Incorporation of MeOH in **9** and **10** is evidenced by the elemental analysis and the appearance of 4 *s*'s in the ^{1}H-NMR spectra. A broad *s*, exchangable with D_2O (**9**: 2.49 ppm; **10**: 2.05 ppm), is assigned to the OH group. A

Scheme 3



sharp *s*, integrating for 3 H (**9**: 3.36 ppm, **10**: 3.47 ppm) is assigned to the MeO groups. It corresponds to a *q* in the ^{13}C-NMR spectra (**9**: 48.79 ppm; **10**: 51.59 ppm). C(1) of the β-D-anomer **9** (102.36 ppm) resonates at lower field than C(1) of the α-D-anomer **10** (101.31 ppm), similarly to what is found for the anomeric epoxides. CI-MS of **9** and **10** (NH_3) shows a peak at *m/z* 630, which is assigned to $[M + 18]^+$. The IR spectra of **9** and **10** show a broad OH absorption at 3580–3460 (**9**) and 3560–3460 cm^{-1} (**10**).

Incorporation of MeOH in **11** and **12** is evidenced by elemental analysis and the appearance of two *s*'s in the ^{1}H-NMR spectra. A broad *s*, exchangable with D_2O (**11**: 2.22 ppm; **12**: 2.4 ppm), is assigned to the OH group. A sharp *s* (3 H; **11**: 3.33 ppm; **12**: 3.47 ppm) and a *q* (**11**: 48.68 ppm; **12**: 51.79 ppm) in the ^{13}C-NMR spectra is assigned to the MeO group. The CI-MS shows a similar fragmentation pattern for **11** and **12**; peaks at *m/z* 638, 621, 603, 513, and a base peak at 91. The peak at *m/z* 638 arises from loss of MeOH from $[M + 18]^+$. The configuration of **9–12** is evidenced by NOE's, H,C-correlation studies, and chemical transformations. The β-D-glycoside **9** shows a strong NOE for H–C(2) upon irradiation of the MeO signal; a weak NOE is observed for H–C(4) and the 2 Me groups. Irradiation at the OH resonance leads to a strong NOE for H–C(3) and H–C(5), and a weak NOE for the 2 Me groups. The configuration of the β-D-glycoside **11** is assigned on the basis of a strong NOE for H–C(2), upon irradiation of the MeO signal, and by comparison of its ^{1}H- and ^{13}C-NMR data with those of the analog **9** (*Table 3* and *4*).

Table 3. *Selected ^{1}H-NMR Chemical Shifts* [ppm] *of the Glycosides* **9–12**, *and the Dihydro-1,3-oxazoles* **15** *and* **17**[4])

	H–C(2)	H–C(3)	H–C(4)	H–(5)	H_A–C(6)	H_B–C(6)	MeO
9	3.94	4.23	3.75	4.21	3.75	3.75	3.36
10	3.71	4.17	3.71	3.71	3.71	3.71	3.47
11	3.92	4.29	3.73	4.23	3.73	3.73	3.33
12	3.80	4.12	3.83	3.83	3.83	3.83	3.47
15	4.23	4.12	3.57	4.50	4.41	3.65	–
17	4.21	4.10	3.56	4.50	4.41	3.66	–

Table 4. *Selected ^{13}C-NMR Chemical Shifts* [ppm] *of the Spirooxiranes* **9–12**, *and the Dihydro-1,3-oxazoles* **15** *and* **17**[4])

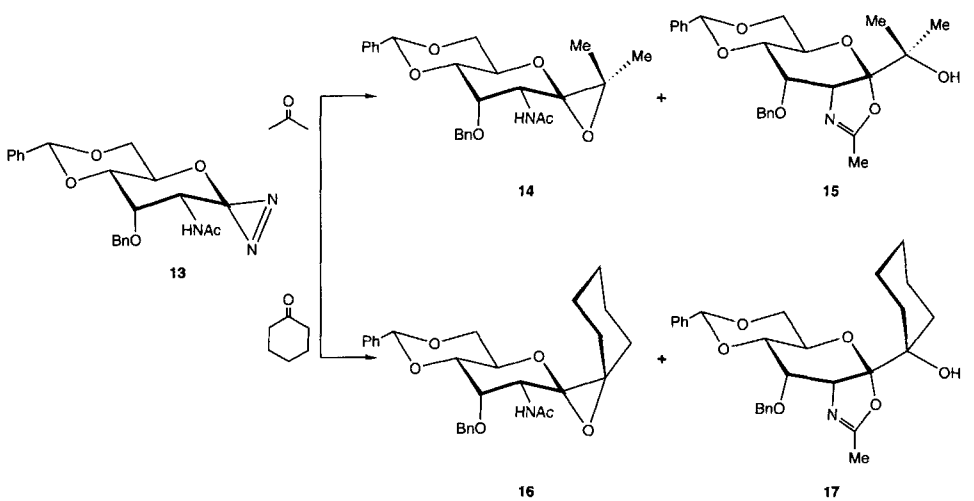
	9	**10**	**11**	**12**	**15**	**17**
C(1)	102.36	101.31	102.40	101.57	111.90	111.78
C(1')	78.48	77.20	79.37	76.33	74.61[a])	75.20
Me	28.42	27.91	–	–	23.26	–
Me'	25.54	24.90	–	–	14.47	–
MeO	48.79	51.59	48.68	51.79	–	–

[a]) From the ^{13}C-NMR spectrum it is not evident, whether this signal is a *s* or a *t*. It could be interchanged with the signal at 74.57 ppm.

2.3. *Reaction of the Diazirine* **13** *with Acetone and Cyclohexanone* (*Scheme 4*). Thermolysis of **13** in acetone under reflux gave mainly two products of very different polarity (68%; 1.8:1), which proved to be the spiro epoxide **14** and the dihydrooxazole **15**. Similarly, thermolysis of **13** in cyclohexanone at 60° gave 83% of the spiro epoxide **16** and the dihydrooxazole **17** (1.5:1), which were readily separated by FC. The anomeric configuration of **14** and **16** is in keeping with the dihydrooxazole structure of **15** and **17**. These latter products result most probably from nucleophilic opening by the acetamido group of the β-D-configurated epoxides, which were expected, but not found, or from the attack by the acetamido instead of the oxy group onto the oxycarbenium center of the zwitterions resulting from nucleophilic addition of the presumed intermediate carbene to either acetone or cyclohexanone.

Thus, in spite of their relatively low reactivity towards ketones[5]), as evidenced by the large excess of acetone and cyclohexanone which is required to obtain good yields, glycosylidene carbenes are sufficiently nucleophilic to allow the preparation, in good yields, and under mild conditions, of higher-carbon, branched-chain saccharides.

Scheme 4



The incorporation of acetone in **14** and **15** is evidenced by 2 new *s*'s in the ^{1}H-NMR spectra (**14**: 1.36 and 1.31 ppm; **15**: 1.27 and 1.17 ppm) and by 2 new *q*'s in the ^{13}C-NMR spectra (**14**: 21.61 and 18.77 ppm; **15**: 23.26 and 22.94 ppm), which are assigned to the geminal Me groups. Both compounds give rise to a peak at *m/z* 440 in the CI-MS, corresponding to $[M + 1]^+$, in agreement with their elemental analysis. The incorporation of

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[5]) Sterically hindered ketones such as camphor and 4-(*tert*-butyl)cyclohexanone did not react with **1**. The reaction of **13** with benzaldehyde proceeded similarly to the one with acetone, but in less satisfactory yields, and afforded, besides two α-D-epoxides (27%), and a mixture of diastereoisomeric, chain-elongated dihydrooxazoles (12%), a number of by-products, among which lactone azines, a 2-acetamidoglycal, and a dihydrooxazole, all derived from **13**.

cyclohexanone in **16** and **17** is evidenced by the cyclohexylidene signals in the ^{1}H-NMR (**16**: 1.69–1.31 ppm (*m*, 5 CH_2); **17**: 1.84–1.60 (*m*, 4 CH_2, 1 OH), 1.55–1.38 ppm (*m*, 1 CH_2)) and the ^{13}C-NMR spectra (**16**: 31.05–24.64 ppm (5 *t*); **17**: 29.65–20.95 ppm (5 *t*)). Both compounds give rise to a $[M + 1]^+$ peak at 480 *m/z* (CI-MS), in agreement with their elemental analysis.

The presence of an acetamido group in **14** and **16** is clearly seen from the NH *d* at 5.93 ppm (**14**) and 5.97 ppm (**16**), the NH*Ac s* at 1.70 ppm (**14** and **16**) in the ^{1}H-NMR spectra, and the IR bands at 3430, 1665, and 1490 cm^{-1} (**14**) and 3440, 1670, and 1500 cm^{-1} (**16**). The anomeric configuration of **14** and **16** is based on NOE's, ^{13}C-NMR spectra, and chemical evidence. According to $^3J(2,3)$, $^3J(3,4)$, and $^3J(4,5)$, the pyranose ring of **14** and **16** assumes a $^4C_1$ conformation. Irradiation of either one of the 2 Me groups of **14** gives an NOE at H–C(2) (0.4 and 0.8% resp.). The irradiation of the Me group resonating at 1.36 ppm leads to a smaller NOE at H–C(2), but also causes an NOE at H–C(5) (0.6%) and H_{eq}–C(6) (0.3%), indicative of its *cis*-orientation relative to O-C(5) and a pseudoaxial orientation of the oxirane O-atom. The weak NOE's are in keeping with the relatively large distances between the C-atom of this Me group and H–C(2), H–C(5), and H_{eq}–C(6), amounting to 3.99, 4.84, and 4.95Å, respectively, as calculated with the ALCHEMY program. Unfortunately, the *m* of the cyclohexyl substituent of **16** can not be used for NOE experiments. Comparison of the chemical shifts of C(1) of **14** and **16** (86.25 and 86.75 ppm, resp.) suggests that the oxirane O-atom in **16** also assumes a pseudoaxial orientation. The typical *d* of the Me group resonating at 1.97 (**15**) and 1.98 ppm (**17**), characterized by a ^5J(Me,2) of 1.0 Hz, the absence of the NH signal in the ^{1}H-NMR spectra of **15** and **17**, and the signal of the sp^2-hybridized C-atom at 166.24 (**15**) and 165.52 ppm (**17**) further evidence the formation of a dihydrooxazole. The IR spectra of **15** and **17** show OH bands at 3590 cm^{-1} and the absorption of the C=N bond at 1670 cm^{-1} [30].

We thank the Swiss National *Science Foundation* and *F. Hoffmann–La Roche AG*, Basle, for their generous support and Mr. *R. Husi* for his skillful technical assistance.

Experimental Part

1. *General.* See [30]. A *Philips HPK-125* high-pressure Hg lamp, equipped with a *Solidex* filter, was used for photochemical reactions. High performance liquid chromatography (HPLC): *Spherisorb* silica gel (5 mm) 250 × 4.6 mm column. Calculations were effected with the program ALCHEMY II for PC (*Tripos Associates*).

2. *Reaction of* **1** *with Acetone.* 2.1. A soln. of **1** (94 mg, 0.171 mmol) in acetone (1.2 ml) was stirred for 6 h under N_2 and then evaporated. FC (hexane/AcOEt 8:2) gave **2/3**. The products were separated by prep. HPLC (hexane/AcOEt 9:1): **2** (22 mg, 23%), **3** (10.6 mg, 11%), and **6** (4.2 mg, 4%).

2.2. The reaction was carried out as described in *2.1*, but using 6.8 instead of 1.2 ml of acetone. Prep. HPLC gave **2** (43.9 mg, 44%), **3** (18 mg, 19%), and **6** (2.4 mg, 2%).

2.3. A soln. of **1** (94 mg, 0.171 mmol) in acetone (1.2 ml) was irradiated for 4 h at –84° (AcOEt/N_2) under N_2, and then evaporated and chromatographed: **2** (5.9 mg, 6%), **3** (4.1 mg, 4%), and **6** (18.6 mg, 19%).

2.4. A soln. of **1** (94 mg, 0.171 mmol) in acetone (6.8 ml) was irradiated for 4 h at –84° (AcOEt/N_2) under N_2, and then evaporated. Chromatography gave **2** (24.9 mg, 25%), **3** (12.2 mg, 12%), and **6** (12.8 mg, 13%).

*2,3-Anhydro-4,5,6,8-tetra-*O*-benzyl-1-deoxy-2-*C*-methyl-β-*D*-gluco-oct-3-ulopyranose* (= *(1R)-2,3,4,6-Tetra-*O*-benzyl-3',3'-dimethylspiro[[1,5]anhydro-*D*-glucitol-1,2'-oxirane]*; **2**). R_f (hexane/AcOEt 7:3) 0.35. $[\alpha]_D^{22}$ = +52.4 (*c* = 0.89, $CHCl_3$). IR: 3090*w* (sh), 3060*w*, 3030*w* (sh), 3000*m*, 2960*w* (sh), 2920*w*, 2860*w*, 1950*w*, 1870*w*, 1810*w*, 1495*w*, 1455*m*, 1375*w*, 1360*w*, 1235*w*, 1150*m* (sh), 1090*s*, 1030*m*, 1010*w* (sh), 910*w*, 700*s*, 675*w* (sh). ^{1}H-NMR (400 MHz): 7.35–7.15 (*m*, 20 arom. H); 4.96 (*d*, *J* = 11.0, PhC*H*); 4.89 (*d*, *J* = 11.3, PhC*H*); 4.85 (*d*, *J* = 10.8, PhC*H*); 4.77 (*d*, *J* = 11.0, PhC*H*); 4.62 (*d*, *J* = 11.8, PhC*H*); 4.56–4.50 (*m*, 2 PhC*H*); 4.04–3.99 (*m*, *X* of *ABX*, H–C(4)); 3.83–3.79 (*m*, *AB* of *ABX*; H–C(5), H–C(6)); 3.70 (*d*, *J* = 3.3, 2 H–C(8)); 3.58–3.54 (*m*, H–C(7)); 1.58 (*s*, Me); 1.44 (*s*, Me). ^{13}C-NMR: 138.39 (*s*); 138.03 (*s*); 137.85 (*s*); 128.32–127.67 (*m*); 88.70 (*s*, C(3)); 84.33 (*d*); 79.04 (*d*); 77.79 (*d*); 76.16 (*d*); 75.23 (*t*); 75.02 (*t*); 74.12 (*t*); 73.43 (*t*); 68.81 (*t*, C(8)); 64.45 (*s*, C(2)); 20.24 (*q*, Me); 19.41 (*q*, Me). CI-MS: 582 (13), 581 (38, $[M+1]^+$), 564 (28), 563 (73) 473 (100), 455 (59), 365 (30), 338 (19), 337 (81), 181 (40), 91 (28). Anal. calc. for $C_{37}H_{40}O_6$ (580.72): C 76.53, H 6.94; found: C 76.34, H 6.84.

2,3-Anhydro-4,5,6,8-tetra-O-*benzyl-1-deoxy-2*-C-*methyl*-α-D-gluco-*oct-3-ulopyranose* (= *(1S)-2,3,4,6-Tetra*-O-*benzyl-3',3'-dimethylspiro[[1,5]anhydro*-D-*glucitol-1,2'-oxirane]*; **3**). R_f(hexane/AcOEt 7:3) 0.30. $[\alpha]_D^{22}$ = +25.4 (*c* = 0.39, $CHCl_3$). M.p. 76–77°. IR: 3070*w*, 3030*w* (sh), 3000*m*, 2960*m* (sh), 2930*m*, 2870*m*, 1950*w*, 1870*w*, 1810*w*, 1585*w*, 1495*m*, 1460*w* (sh), 1455*m*, 1405*w* (sh), 1375*w* (sh), 1360*m*, 1315*w* (br.), 1265*w*, 1235*w*, 1145*m* (sh), 1115*s* (sh), 1090*s* (br.), 1055*m* (sh), 1030*m*, 955*w*, 930*w*, 910*w*, 710*w* (sh), 700*s*, 670*w*, 665*w*. ^{1}H-NMR (400 MHz, C_6D_6): 7.30–7.04 (*m*, 20 arom. H); 4.88 (*d*, *J* = 11.4, PhC*H*); 4.77 (*d*, *J* = 11.5, PhC*H*); 4.73–4.70 (*m*, 2 PhC*H*); 4.65 (*d*, *J* = 11.4, PhC*H*); 4.44 (*d*, *J* = 11.5, PhC*H*); 4.40 (*d*, *J* = 12.2, PhC*H*); 4.30 (*d*, *J* = 12.1, PhC*H*); 4.17 (*t*, *J* = 8.2, H–C(5)); 4.12 (*ddd*, *J* = 1.9, 3.6, 10.0, H–C(7)); 4.02 (*dd*, *J* = 8.2, 10.0, H–C(6)); 3.89 (*d*, *J* = 8.4, H–C(4)); 3.70 (*dd*, *J* = 3.6, 10.9, H_A-C(8)); 3.57 (*dd*, *J* = 1.9, 10.9, H_B–C(8)); 1.47 (*s*, Me); 1.43 (*s*, Me). ^{13}C-NMR: 138.27 (*s*); 138.15 (*s*); 137.92 (*s*); 137.46 (*s*); 128.34–127.31 (*m*); 87.76 (*s*, C(3)); 84.78 (*d*); 77.74 (*d*); 77.25 (*d*); 74.32 (*t*); 74.14 (*t*); 73.77 (*t*); 73.39 (*d*); 73.26 (*t*); 68.07 (*t*, C(8)); 65.55 (*s*, C(2)); 21.24 (*q*, Me); 19.70 (*q*, Me). CI-MS: 599 (41), 598 (100, $[M + NH_4]^+$).

1-Methylethenyl 2,3,4,6-Tetra-O-*benzyl*-α-D-*glucopyranoside* (**6**). R_f (hexane/AcOEt 7:3) 0.43. IR: 3090*w* (sh), 3060*w*, 3000*w*, 2910*m* (br.), 2860*m*, 1670*w* (sh), 1630*w* (br.), 1495*w*, 1450*m*, 1380*w* (sh), 1360*m*, 1305*w* (sh), 1260*m*, 1195*m* (sh), 1140*m* (sh), 1090*s* (sh), 1065*s*, 1045*s* (sh), 1030*s*, 980*m*, 910*m*, 880*w*, 820*w* (br.), 690*w* (br.), 660*w* (sh). ^{1}H-NMR (400 MHz, C_6D_6): 7.34–7.07 (*m*, 20 arom. H); 5.48 (*d*, *J* = 3.5, H–C(1)); 5.01 (*d*, *J* = 11.4, PhC*H*); 4.97 (*d*, *J* = 11.3, PhC*H*); 4.82 (*d*, *J* = 11.3, PhC*H*); 4.66 (*d*, *J* = 11.4, PhC*H*); 4.57 (br. *s*, 1 olef. H); 4.47 (*d*, *J* = 11.8, PhC*H*); 4.43 (*d*, *J* = 10.3, PhC*H*); 4.40 (*d*, *J* = 11.8, PhC*H*); 4.33–4.29 (*m*, H–C(3), PhC*H*); 4.08 (br. *s*, 1 olef. H); 4.01–3.99 (*m*, H–C(5)); 3.91 (*t*, *J* ≈ 9.4, H–C(4)); 3.75 (*dd*, *J* = 3.6, 10.9, H_A–C(6)); 3.62 (*dd*, *J* = 1.7, 10.9, H_B–C(6)); 3.60 (*dd*, *J* = 3.4, 9.6, H–C(2)); 1.79 (*s*, Me).^{13}C-NMR: 157.05 (*s*); 138.80 (*s*); 138.28 (*s*); 138.17 (*s*); 138.0 (*s*); 128.41–127.28 (*m*); 93.80 (*d*, C(1)); 86.92(*t*, CH_2=C); 81.99 (*d*); 79.57 (*d*); 76.37 (*d*); 75.65 (*t*); 75.11(*t*); 73.43 (*t*); 72.98 (*t*); 70.53 (*d*); 68.21 (*t*, C(6); 20.55 (*q*). ESI-MS 603.5 ($[M + Na]^+$). Anal. calc. for $C_{37}H_{40}O_6$ (580.72): C 76.53, H 6.9; found: C 76.39, H 7.01.

3. *Hydrolysis of* **6** *to 2,3,4,6-Tetra-O-benzyl*-D-*glucose*. SiO_2 was added to a soln. of **6** (10 mg, 0.017 mmol) in CH_2Cl_2 (2 ml; freshly passed through a column of basic alumina). The mixture was allowed to stand for 24 h. Filtration and evaporation yielded 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (8.7 mg, 96%), identified by ^{1}H-NMR, IR, and CI-MS.

4. *Reaction of* **1** *with Cyclohexanone*. 4.1. A soln. of **1** (113 mg, 0.205 mmol) in cyclohexanone (1.7 ml) was stirred for 4 h at r.t. and then evaporated. FC (hexane/AcOEt 8:2) gave **4/5**. Prep. HPLC (hexane/AcOEt 9:1) yielded **4** (65 mg, 51%) and **5** (34 mg, 27%).

4.2. A soln. of **1** (113 mg, 0.205 mmol) in cyclohexanone (1.7 ml) was irradiated for 1 h at –30°. Prep. HPLC (hexane/AeOEt 9:1) gave **4** (47.6 mg, 38%) and **5** (25.7 mg, 20%).

1,1'-Anhydro-2,3,4,6-tetra-O-*benzyl-1*-C-*(1-hydroxycyclohexyl)*-β-D-*glucopyranose* (=*(1R)-2,3,4,6-Tetra*-O-*benzyldispiro[[1,5]anhydro*-D-*glucitol-1,2'-oxirane-3',1''-cyclohexane]*; **4**). R_f (CH_2Cl_2/hexane 17:3) 0.56. $[\alpha]_D^{22}$ = +52.3 (*c* = 1.2, $CHCl_3$). IR: 3060*m*, 3025*m* (sh), 3010*s*, 2930*s*, 2900*s* (sh), 2860*s*, 1950*s*, 1875*w*, 1810*w*, 1605*w*, 1585*w*, 1495*m*, 1460*m* (sh), 1455*s*, 1400*w*, 1360*w*, 1330*m* (br.), 1260*m*, 1240*m*, 1210*w*, 1145*s*, 1080*s* (br.), 1030*s*, 1010*s* (sh), 950*m*, 905*m*, 860*w*, 830*w*, 700*s*, 660*w*, 645*w*. ^{1}H-NMR (400 MHz): 7.35–7.18 (*m*, 20 arom. H); 4.96 (*d*, *J* = 11.1, PhC*H*); 4.90 (*d*, *J* = 11.2, PhC*H*); 4.87 (*d*, *J* = 10.8, PhC*H*); 4.78 (*d*, *J* = 11.1, PhC*H*); 4.65–4.52 (*m*, 4 H, PhC*H*); 4.05–4.03 (*m*, H–C(2)); 3.84–3.82 (*m*, 2 H–C(3), H–C(4)); 3.71 (*d*, *J* = 3.4, 2 H–C(6)); 3.65–3.62 (*m*, H–C(5)); 2.13–2.05 (*m*, 1 H); 1.98–1.90 (*m*, 1 H); 1.84–1.55 (*m*, 7 H); 1.53–1.43 (*m*, 1 H). ^{13}C-NMR: 138.30 (*s*); 137.96 (*s*); 137.84 (*s*); 137.70 (*s*); 128.23–127.39 (*m*); 89.40 (*s*, C(1)); 84.02 (*d*); 79.15 (*d*); 77.64 (*d*); 76.03 (*d*); 74.88 (*t*); 74.83 (*t*); 73.82 (*t*); 73.24 (*t*); 68.88 (*s*); 68.77 (*t*, C(6)); 29.44 (*t*); 28.83 (*t*); 25.72 (*t*); 24.74 (*t*); 24.40 (*t*). CI-MS: 638 (10, $[M + NH_4]^+$), 621 (11, $[M + 1]^+$), 603 (16), 513 (31), 276 (100), 108 (35), 91 (16). Anal. calc. for $C_{10}H_{44}O_6$ (620.78): C 77.39, H 7.14; found: C 77.59, H 7.36.

1,1'-Anhydro-2,3,4,6-tetra-O-*benzyl-1*-C-*(1-hydroxycyclohexyl)*-α-D-*glucopyranose* (=*(1S)-2,3,4,6-Tetra*-O-*benzyldispiro[[1,5]anhydro*-D-*glucitol-1,2'-oxirane-3',1''-cyclohexane]*; **5**). R_f(CH_2Cl_2/hexane 17:3) 0.41. $[\alpha]_D^{22}$ = +18.2 (*c* = 0.62, $CHCl_3$). IR: 3060*w*, 3015*w* (sh), 3000*m*, 2930*s*, 2860*m*, 1950*w*, 1870*w*, 1810*w*, 1605*w*, 1585*w*, 1495*m*, 1460*m* (sh), 1455*s*, 1400*w* (br.), 1360*m*, 1330*w* (sh), 1315*w*, 1260*w* (sh), 1235*w* (br.), 1160*m* (br.), 1150*m*, 1090*s* (br.), 1030*s*, 1010*m* (sh), 950*w* (br.), 905*w*, 860*w*, 845*w*, 820*w* (br.), 700*s*, 670*w* (sh), 665*w*, 650*w*. ^{1}H-NMR (400 MHz, C_6D_6): 7.41–7.02 (*m*, 20 arom. H); 4.88 (*d*, *J* = 11.4, PhC*H*); 4.80 (*d*, *J* = 11.3, PhC*H*); 4.75 (*d*, *J* = 11.3, PhC*H*); 4.72–4.63 (*m*, 2 PhC*H*); 4.51 (*d*, *J* = 11.3, PhC*H*); 4.39 (*d*, *J* = 12.1, PhC*H*); 4.29 (*d*, *J* = 12.2, PhC*H*); 4.20 (*t*, *J* = 8.0, H–C(3)); 4.17–4.15 (*m*, H–C(5)); 4.05 (*dd*, *J* = 8.0, 9.9, H–C(4)); 3.96 (*d*, *J* = 8.1, H–C(2)); 3.70 (*dd*, *J* = 3.6, 10.9, H_A-C(6)); 3.57 (*dd*, *J* = 1.7, 10.9, H_B–C(6)); 2.01–1.26 (*m*, 10 H). ^{13}C-NMR: 138.32 (*s*); 138.23 (*s*); 138.09 (*s*); 137.48 (*s*); 128.35–127.69 (*m*); 88.19 (*s*, C(1)); 84.66 (*d*); 77.73 (*d*);

77.70 (*d*); 76.42 (*t*); 75.25 (*t*); 74.56 (*t*); 73.79 (*t*); 73.33 (*d*); 69.88 (*s*); 68.15 (*t*, C(6)); 30.70 (*t*); 29.28 (*t*); 25.77 (*t*); 24.77 (*t*); 24.66 (*t*). CI-MS: 639 (36), 638 (78, $[M + NH_4]^+$), 622 (17), 621 (42), 603 (64), 513 (100), 495 (31), 423 (39), 406 (13), 405 (50), 108 (59), 91 (47). Anal. calc. for $C_{40}H_{44}O_6$ (620.78): C 77.39, H 7.14; found: C 77.14, H 6.90.

5. *Methanolysis of* **2**. Dry MeOH (1 ml), a minimum amount of CH_2Cl_2 to obtain a homogenous soln., and anh. $ZnCl_2$ (2 mg) were added to **2** (38 mg, 0.065 mmol). The mixture was stirred at 23° for 6 h and then evaporated. FC (hexane/AcOEt 9:1) gave **9** (18.6 mg, 47%) and **10** (15.4 mg, 39%).

*Methyl 4,5,6,8-Tetra-*O*-benzyl-1-deoxy-2-*C*-methyl-β-*D*-gluco-oct-3-ulopyranoside* (**9**). R_f (hexane/Et_2O 7:3) 0.35. $[\alpha]_D^{22} = +40.7$ (*c* = 0.85, $CHCl_3$). IR: 3650*w*, 3580*w* (br.), 3460*w* (br.), 3090*w* (sh), 3060*w*, 3025*w* (sh), 3000*m*, 2930*m* (br.), 2860*m*, 1950*w* (br.), 1870*w* (br.), 1810*w* (br.), 1750*w* (br.), 1730*w* (br.), 1585*w* (br.), 1495*w*, 1470*w* (sh), 1465*w* (sh), 1455*m*, 1395*w*, 1385*w*, 1360*m*, 1325*w* (sh), 1305*w* (sh), 1260*w*, 1235*w* (sh), 1210*w*, 1180*m* (sh), 1135*m* (sh), 1090*s* (br.), 1065*s* (br.), 1030*s*, 995*m* (sh), 955*w*, 910*w*, 835*w* (br.), 700*s*, 670*w* (sh), 660*w*. ^{1}H-NMR (400 MHz): 7.34–7.22 (*m*, 20 arom. H); 4.91 (*d*, *J* = 11.1, PhC*H*); 4.84 (*d*, *J* = 11.6, PhC*H*); 4.81 (*d*, *J* = 12.2, 2 PhC*H*); 4.67 (*d*, *J* = 10.3, PhC*H*); 4.64 (*d*, *J* = 10.4, PhC*H*); 4.60 (*d*, *J* = 12.2, PhC*H*); 4.55 (*d*, *J* = 12.2, PhC*H*); 4.33 (*t*, *J* = 8.0, H–C(5)); 4.22–4.19 (*m*, H–C(7)); 3.94 (*d*, *J* = 7.7, H–C(4)); 3.78–3.72 (*m*, H–C(6), H–C(8)); 3.36 (*s*, MeO); 2.49 (br. *s*, OH, exchanged with D_2O); 1.46 (*s*, Me); 1.29 (*s*, Me). ^{13}C-NMR: 138.68 (*s*); 138.55 (*s*); 138.41 (*s*); 137.62 (*s*); 128.60–126.87 (*m*); 102.36 (*s*, C(3)); 84.21 (*d*); 81.28 (*d*); 78.48(*s*, C(2)); 78.37 (*d*); 74.84 (*t*); 74.49 (*t*); 74.35 (*t*); 73.47 (*d*); 73.23 (*t*); (69.32 (*t*, C(8)); 48.79 (*q*, MeO); 28.42 (*q*, Me); 25.54 (*q*, Me). CI-MS: 630 (5, $[M + NH_4]^+$), 598 (15), 581 (21), 554 (53), 473 (46), 337 (43), 181 (27), 108 (19), 91 (100). Anal. calc. for $C_{38}H_{44}O_7$ (612.76): C 74.49, H 7.24; found: C 74.53, H 7.50.

*Methyl 4,5,6,8-Tetra-*O*-benzyl-1-deoxy-2-*C*-methyl-α-*D*-gluco-oct-3-ulopyranoside* (**10**). R_f (hexane/Et_2O 7:3) 0.14. $[\alpha]_D^{22} = +52.8$ (*c* = 0.64, $CHCl_3$). IR: 3660*w* (sh), 3610*w* (sh), 3560*w* (br.), 3460*w*, 3085*w* (sh), 3060*w*, 3025*w* (sh), 3000*m*, 2960*m* (sh), 2930*m*, 2860*w* (br.), 1950*w* (br.), 1875*w* (br.), 1810*w* (sh), 1790*w* (br.), 1730*w* (br.), 1710*w* (br.), 1605*w* (br.), 1585*w* (br.), 1495*w*, 1465*w* (sh), 1455*m*, 1390*w*, 1365*m* (br.), 1345*w* (sh), 1260*m*, 1165*s*, 1130*m* (br.), 1090*s* (br.), 1080*s* (sh), 1070*s* (br.), 1045*s* (br.), 1030*s*, 985*m* (sh), 910*w*, 860*w*, 805*w* (sh), 795*w* (sh), 715*m*, 700*s*, 670*w* (br.). ^{1}H-NMR (400 MHz): 7.38–7.21 (*m*, 20 arom. H); 5.02 (*d*, *J* = 10.9, PhC*H*); 4.95 (*d*, *J* = 11.1, PhC*H*); 4.89 (*d*, *J* = 11.1, PhC*H*); 4.87 (*d*, *J* = 10.8, PhC*H*); 4.71 (*d*, *J* = 10.9, PhC*H*); 4.62 (*d*, *J* = 10.8, PhC*H*); 4.58–4.54 (*m*, 2 PhC*H*); 4.19–4.14 (*m*, H–C(5)); 3.78–3.64 (*m*, H–C(4), H–C(6), H–C(7), 2 H–C(8)); 3.47 (*s*, MeO); 2.05 (br. *s*, OH, exchanged with D_2O); 1.40 (*s*, Me); 1.27 (*s*, Me). ^{13}C-NMR: 138.55 (*s*); 138.24 (*s*); 138.06 (*s*); 137.66 (*s*); 128.60–127.47 (*m*); 101.31 (*s*, C(3)); 84.38 (*d*); 81.03 (*d*); 78.83 (*d*); 77.20 (*s*, C(2)); 75.53 (*t*); 75.12 (*t*); 74.72 (*t*); 73.20 (*t*); 72.41 (*d*); 68.72 (*t*, C(8)); 51.59 (*q*, MeO); 27.91 (*q*); 24.90 (*q*). CI-MS: 630 (6, $[M + NH_4]^+$), 598 (22), 581 (27), 553 (59), 473 (53), 337 (49), 240 (20), 181 (25), 108 (23), 91(100).

6. *Attempted Equilibration of* **9**. $ZnCl_2$ (1 mg) was added to a soln. of **9** (20.0 mg, 0.03 mmol) in dry MeOH (2 ml) and a minimum amount of CH_2Cl_2. After 2 days, TLC showed only a spot for **9**.

7. *Attempted Reduction of* **9**. $NaBH_4$ (7.0 mg, 0.19 mmol) was added to a soln. of **9** (40.0 mg, 0.06 mmol) in MeOH (1 ml) at –20°, and the mixture was stirred for 2 h. No reaction was observed. The temp. was gradually raised to reflux. Only starting material was present after 2 days, according to TLC.

8. *Methanolysis of* **4** *and* **5**. 8.1. *Methanolysis of* **4**. Dry MeOH (0.6 ml), a minimum amount of CH_2Cl_2 to obtain a homogeneous soln., and anh. $ZnCl_2$ (1 mg) were added to **4** (24 mg, 0.038 mmol). The mixture was stirred at 23° for 6 h and then evaporated. FC (hexane/AcOEt 8:2) afforded **11** (13.8 mg, 56%) and **12** (7.6 mg, 31%).

8.2. *Methanolysis of* **5**. As described in 8.1, with MeOH (2 ml), CH_2Cl_2, $ZnCl_2$ (2 mg) and **5** (14 mg, 0.023 mmol): **11** (7.5 mg, 50%) and **12** (7.2 mg, 48%).

8.3. *Methanolysis of* **4**/**5**. A soln. of **1** (113 mg, 0.205 mmol) in cyclohexanone (1.7 ml) was stirred at 23° for 4 h, evaporated, and treated with MeOH (2 ml). A minimum amount of CH_2Cl_2 was added to obtain a homogeneous soln., which was evaporated after 30 min. FC (hexane/AcOEt 8:2) afforded **11** (67 mg, 50%) and **12** (39 mg, 29%).

*Methyl 2,3,4,6-Tetra-*O*-benzyl-1-*C*-(1-hydroxycyclohexyl)-β-*D*-glucopyranoside* (**11**). R_f (hexane/Et_2O 7:3) 0.33. $[\alpha]_D^{22} = +44.8$ (*c* = 0.66, $CHCl_3$). IR: 3670*w* (sh), 3610*w* (sh), 3580*w* (sh), 3520*w* (br.), 3480*w* (br.), 3060*w*, 3030*w* (sh), 3010*m*, 2930*s*, 2860*m*, 1950*w* (br.), 1870*w* (br.), 1810*w* (br.), 1755*w* (sh), 1745*w* (sh), 1730*w* (br.), 1605*w*, 1585*w*, 1495*m*, 1455*s*, 1395*w* (sh), 1360*m*, 1330*w*, 1310*w*, 1275*w* (sh), 1260*m* (br.), 1150*s* (sh), 1130*s*

(sh), 1090*s* (br.), 1070*s*, 1065*s* (sh), 1030*s*, 1000*m* (sh), 980*m*, 960*m*, 910*w*, 880*w* (sh), 835*w* (br.), 820*w*, 700*s*, 670*w* (sh), 660*w*. ^{1}H-NMR (400 MHz): 7.35–7.21 (*m*, 20 arom. H); 4.90 (*d*, *J* = 11.0, PhC*H*); 4.83 (*d*, *J* = 11.1, PhC*H*); 4.82 (*d*, *J* = 10.8, PhC*H*); 4.81 (*d*, *J* = 11.0, PhC*H*); 4.64 (*d*, *J* = 10.9, PhC*H*); 4.63 (*d*, *J* = 11.1, PhC*H*); 4.62 (*d*, *J* = 12.1, PhC*H*); 4.53 (*d*, *J* = 12.1, PhC*H*); 4.29 (*t*, *J* = 8.4, H–C(3)); 4.23 (br. *dt*, *J* = 2.9, 10.2, H–C(5)); 3.92 (*d*, *J* = 8.3, H–C(2)); 3.76–3.69 (*m*, H–C(4), 2 H–C(6)); 3.33 (*s*, MeO); 2.22 (br. *s*, OH, exchanged with D_2O); 2.32–1.15 (*m*, 10 H). ^{13}C-NMR: 138.72 (*s*); 138.58 (*s*); 138.46 (*s*); 137.74 (*s*); 128.34–127.30 (*m*); 102.40 (*s*, C(1)); 84.24 (*d*); 81.27 (*d*); 79.37 (*s*); 78.38 (*d*); 74.97 (*t*); 74.45 (*t*); 74.38 (*t*); 73.32 (*d*); 73.20 (*t*); 69.34 (*t*, C(6)); 48.68 (*q*, MeO); 33.70 (*t*); 30.80 (*t*); 25.71 (*t*); 21.58 (*t*); 21.31 (*t*). CI-MS: 638 (10), 621 (42), 603 (43), 553 (25), 513 (37), 181 (24), 108 (35), 91 (100). Anal. calc. for $C_{41}H_{48}O_7$ (652.83): C 75.43, H 7.41; found: C 75.20, H 7.26.

*Methyl 2,3,4,6-Tetra-*O*-benzyl-1-*C*-(1-hydroxycyclohexyl)-α-*D*-glucopyranoside* (**12**). R_f (hexane/Et_2O 7:3) 0.15. IR: 3680*w* (sh), 3620*w* (sh), 3560*w* (br.), 3440*w* (sh), 3090*w* (sh), 3060*w* (sh), 3025*w* (sh), 3000*m*, 2940*m*, 2860*m*, 1970*w* (sh), 1950*w* (sh), 1940*w* (sh), 1870*w*, 1805*w* (br.), 1730*w* (br.), 1610*w*, 1585*w*, 1495*w*, 1465*w* (sh), 1455*m*, 1405*w* (sh), 1385*w*, 1365*m*, 1330*w*, 1310*w*, 1275*w*, 1260*w*, 1240*w*, 1225*w*, 1195*w*, 1165*m*, 1155*m* (br.), 1135*m*, 1080*s* (br.), 1050*s* (br.), 1030*s*, 1005*m*, 985*m*, 965*w*, 940*w* (sh), 905*w*, 875*w*, 860*w*, 840*w* (sh), 820*w* (br.), 810*w*, 795*w*, 700*s*, 675*w* (sh), 660*w* (br.), 635*w* (br.). ^{1}H-NMR (400 MHz): 7.37–7.19 (*m*, 20 arom. H); 5.01 (*d*, *J* = 10.9, PhC*H*); 4.95 (*d*, *J* = 11.1, PhC*H*); 4.89 (*d*, *J* = 11.1, PhC*H*); 4.77 (*d*, *J* = 10.8, PhC*H*); 4.76 (*d*, *J* = 10.9, PhC*H*); 4.61 (*d*, *J* = 10.7, PhC*H*); 4.57–4.53 (*m*, 2 PhC*H*); 4.12 (*t*, *J* = 8.8, H–C(3)); 4.06-3.60 (*m*, H–C(2), H–C(4), H–C(5), 2 H–C(6)); 3.47 (*s*, MeO); 2.4 (br. *s*, OH, exchanged with D_2O); 1.78–1.38 (*m*, 10 H). ^{13}C-NMR: 138.53 (*s*); 138.18 (*s*); 138.01 (*s*); 137.68 (*s*); 128.54–127.44 (*m*); 101.57 (*s*, C(2)); 84.45 (*d*); 80.66 (*d*), 78.77 (*d*), 76.33 (*s*, C(1)); 75.44 (*t*), 75.05 (*t*); 74.75 (*t*); 73.11 (*t*); 72.24 (*d*); 68.67 (*t*, C(6)); 51.79 (*q*, MeO); 34.22 (*t*); 31.57 (*t*), 25.70 (*t*); 21.48 (*t*); 21.25 (*t*). CI-MS: 638 (12), 622 (27), 621 (61), 603 (59), 553 (55), 513 (48), 181 (25), 108 (26), 91 (100).

9. *Equilibration of* **11**. 9.1. A soln. of **11** (7.8 mg, 0.01 mmol) in MeOH (1 ml) was added to a soln. of $SOCl_2$ (0.1 ml) in MeOH (1 ml). After 5 h, TLC showed only a spot for **12**. The mixture was evaporated: 7.8 mg of **12**, which was identified by ^{1}H-NMR.

9.2. $ZnCl_2$ (1 mg) was added to a soln. of **11** (7.8 mg, 0.01 mmol) in dry MeOH (1 ml) and a minimum amount of CH_2Cl_2. After 4 days, TLC showed only a spot for the starting material.

10. *4-Acetamido-2,3-anhydro-5-*O*-benzyl-6,8-*O*-benzylidene-1,4-dideoxy-2-*C*-methyl-α-*D*-allo-oct-3-ulopyranose (= (1S) -2-Acetamido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-3,3'-dimethylspiro[1,5]anhydro-*D*-allitol-1,2'-oxirane];* **14**) *and 4-Amino-5-*O*-benzyl-6,8-*O*-benzylidene-1,4-dideoxy-3-*O*,4-N-(ethan-1-yl-1-ylidene)-α-*D*-allo-oct-3-ulopyranose* (**15**). Acetone (20 ml) was stirred under N_2 in the presence of ground 3Å-molecular sieves (500 mg). After 30 min, **13** (205.2 mg, 0.50 mmol) was added at once. The mixture was heated to 60° (bath temp.) for 5.5 h, cooled to 23°, and filtered through *Celite*. The residue was washed with acetone (3 × 2 ml) and MeOH (2 × 2 ml). The filtrate was evaporated and the remaining slightly brown oil was dried for 18 h at 0° under high vacuum to give 238.6 mg of crude material. FC (13.5 g of SiO_2, 150 ml of AcOEt/hexane 1:2, 150 ml of AcOEt/hexane 1:1, and 350 ml of AcOEt) gave 97.6 mg (44%) of **14**. The remaining pooled fractions were separated by prep. HPLC (CH_2Cl_2/MeOH 98:2): 53.2 mg (24%) of **15**.

Data of **14**: R_f (Et_2O/AcOEt/hexane 3:3:4) 0.22. $[\alpha]_D^{25} = -107.9$ (*c* = 1.12, $CHCl_3$). IR: 3430*m*, 2990*w*, 2920*m*, 2860*m*, 1665*s*, 1490*m*, 1450*m*, 1370*m*, 1310*w*, 1120*s*, 1090*s*, 1070*s*, 1015*s*, 910*w*. ^{1}H-NMR: 7.51–7.46 (*m*, 2 arom. H); 7.40–7.28 (*m*, 8 arom. H); 5.93 (*d*, *J* = 9.8, NH); 5.56 (*s*, PhC*H*); 5.04 (*d*, *J* = 12.0, PhC*H*); 4.77 (*dd*, *J* = 3.5, 9.8, H–C(4)); 4.58(*d*, *J* = 12.1, PhC*H*); 4.40 (*dt*, *J* = 5.3, 9.7, H–C(7)); 4.33 (*dd*, *J* = 5.4, 10.0, H_{eq}–C(8)); 4.09 (*t*, *J* ≈ 2.8, H–C(5)); 3.79 (*dd*, *J* = 2.2, 9.4, H–C(6)); 3.71 (*t*, *J* = 10.1, H_{ax}–C(8)); 1.70 (*s*, AcN); 1.36 (*s*, Me); 1.31 (*s*, Me). ^{13}C-NMR: 168.64 (*s*); 138.05 (*s*); 137.25 (*s*); 129.02–126.07 (*m*); 101.89 (*d*); 86.25 (*s*); 79.37 (*d*); 75.71 (*d*); 74.35 (*t*); 68.92 (*t*); 62.43 (*s*); 62.00 (*d*); 46.48 (*d*); 22.92 (*q*); 21.61 (*q*); 18.77 (*q*). CI-MS: 441 (21), 440 (74, $[M + 1]^+$), 383 (25), 382 (100), 333 (15), 332 (44), 314 (23), 275 (24), 274 (99), 168 (23), 149 (17), 107 (13), 91 (44). Anal. calc. for $C_{25}H_{29}NO_6$ (439.52): C 68.32, H 6.65, N 3.19; found: C 68.26, H 6.83, N 3.05.

Data of **15**: R_f (Et_2O/AcOEt/hexane 3:3:4) 0.02. $[\alpha]_D^{25} = +187.9$ (*c* = 1.09, $CHCl_3$). IR: 3590*w*, 2990*m*, 2950*m*, 2860*m*, 1670*s*, 1450*m*, 1380*m*, 1135*s*, 1100*s*, 1060*s*, 1020*s*, 980*s*, 905*m*. ^{1}H-NMR: 7.52–7.27 (*m*, 10 arom. H); 5.56 (*s*, PhC*H*); 4.75 (*s*, 2 PhC*H*); 4.50 (*dt*, *J* = 5.4, 9.7, H–C(7)); 4.41 (*dd*, *J* = 5.4, 10.2, H_{eq}–C(8)); 4.23 (*qd*, *J* ≈ 1.1, 5.6, H–C(4)); 4.12 (*dd*, *J* = 2.1, 5.6, H–C(5)); 3.65 (*t*, *J* = 10.1, H_{ax}–C(8)); 3.57 (*dd*, *J* = 2.2, 9.3, H–C(6)); 1.97 (*d*, *J* = 0.8, Me); 1.27 (*s*, Me); 1.17(*s*, Me). ^{13}C-NMR: 166.24 (*s*); 138.82 (*s*); 137.26 (*s*); 129.13–126.22 (*m*); 111.90 (*s*); 101.88 (*d*); 77.42 (*d*); 74.61 (*s* or *t*); 74.57 (*s* or *t*); 72.26 (*d*); 69.42 (*t*); 63.48 (*d*); 60.15

(*d*); 23.26 (*q*); 22.94 (*q*); 14.47 (*q*). CI-MS: 441 (28), 440 (100, $[M + 1]^+$), 151 (16), 107 (31), 103 (11). Anal. calc. for $C_{25}H_{29}NO_6$ (439.52): C 68.32, H 6.65, N 3.19; found: C 68.09, H 6.71, N 3.14.

2-Acetamido-1,1'-anhydro-3-O-benzyl-4,6-O-benzylidene-2-deoxy-1-C-(1-hydroxycyclohexyl)-α-D-allopyranose (= *(1S)-2-Acetamido-3-O-benzyl-4,6-O-benzylidene-2-deoxydispiro[[1,5]anhydro-D-allitol-1,2'-oxirane-3',1''-cyclohexane];* **16**) *and 2-Amino-3-O-benzyl-4,6-O-benzylidene-2-deoxy-1-O,2-N-(ethan-1-yl-1-ylidene)-1-C-(1-hydroxycyclohexyl)-α-D-allopyranose* (**17**). A soln. of **13** (123 mg, 0.30 mmol) in cyclohexanone (2.5 ml) was heated to 60° (bath temp.) under N_2 for 3 h and then evaporated. The residue was dried under high vacuum and crystallized from MeCN to yield 65.7 mg (45%) of **16**. FC (5 g of SiO_2, 10 ml of CH_2Cl_2/MeOH 99:1 and 90 ml of CH_2Cl_2/MeOH 98:2) of the mother liquor yielded 6.8 mg (5%) of **16** and 48.0 mg (33%) of **17**.

Data of **16**: R_f (AcOEt/hexane 1:1) 0.48. $[\alpha]_D^{25} = -101.4$ ($c = 1.08$, $CHCl_3$). IR: 3440*m*, 3000*m*, 2940*s*, 2860*m*, 1670*s*, 1500*s*, 1455*m*, 1370*m*, 1325*w*, 1315*w*, 1125*s*, 1100*s*, 1065*s*, 1025*s*, 965*w*, 910*w*. ^{1}H-NMR: 7.54–7.48 (*m*, 2 arom. H); 7.44–7.29 (*m*, 8 arom. H); 5.97 (*d*, $J = 9.8$, NH); 5.57 (*s*, PhC*H*); 5.04 (*d*, $J = 12.0$, PhC*H*); 4.81 (*dd*, $J = 3.5, 9.8$, H–C(2)); 4.60 (*d*, $J = 12.0$, PhC*H*); 4.42 (*dt*, $J = 5.3, 10.0$, H–C(5)); 4.33 (*dd*, $J = 5.2, 9.9$, H_{eq}–C(6)); 4.08 (*t*, $J \approx 2.8$, H–C(3)); 3.80 (*dd*, $J = 2.2, 9.4$, H–C(4)); 3.71 (*t*, $J = 10.1$, H_{ax}–C(6)); 1.70 (*s*, Me); 1.69-1.31 (*m*, 10 H). ^{13}C-NMR: 168.58 (*s*); 138.08 (*s*); 137.33 (*s*); 129.10–126.14 (*m*); 101.99 (*d*); 86.71 (*s*); 79.47 (*d*) 75.68 (*d*); 74.43 (*t*); 69.05 (*t*); 67.53 (*s*); 61.91 (*d*); 46.89 (*d*); 31.05 (*t*); 28.58 (*t*); 25.56 (*t*); 24.81 (*t*); 24.64 (*t*); 23.02 (*q*). CI-MS: 481 (32), 480 (100, $[M + 1]^+$), 382 (20), 373 (16), 372 (56), 354 (27), 107 (75). Anal. calc. for $C_{28}H_{33}NO_6$ (479.59): C 70.13, H 6.94, N 2.92; found: C 69.85, H 6.86, N 2.90.

Data of **17**: R_f (AcOEt/hexane 1:1) 0.06. $[\alpha]_D^{25} = +184.5$ ($c = 1.29$, $CHCl_3$). IR: 3590*w*, 2940*s*, 2860m 1670*s*, 1450*m*, 1380*m*, 1350*m*, 1260*m*, 1150*s*, 1100*s*, 1090*s*, 1065*s*, 1025*s*, 985*s*, 910*s*. ^{1}H-NMR: 7.52-7.46 (*m*, 2 arom. H); 7.43–7.32 (*m*, 5 arom. H); 7.31–7.23 (*m*, 3 arom. H); 5.56 (*s*, PhC*H*); 4.79–4.71 (*m*, 2 H, PhC*H*); 4.50 (*dt*, $J = 5.4, 9.7$, H–C(5)); 4.41 (*dd*, $J = 5.4, 10.2$, H_{eq}-C(6)); 4.21 (*qd*, $J \approx 1.1, 5.6$, H–C(2)); 4.10 (*dd*, $J = 2.1, 5.6$, H–C(3)); 3.66 (*t*, $J = 10.1$, H_{ax}-C(6)); 3.56 (*dd*, $J = 2.2, 9.4$, H–C(4)); 1.98 (*d*, $J = 1.0$, Me); 1.84–1.60 (*m*, 9 H, 1 H exchanged with D_2O); 1.55–1.38 (*m*, 2 H). ^{13}C-NMR: 165.2 (*s*); 138.77 (*s*); 137.19 (*s*); 128.92–126.09 (*m*); 111.78 (*s*); 101.65 (*d*); 77.30 (*d*); 75.20 (*s*); 74.37 (*t*); 72.24 (*d*); 69.28 (*t*); 63.47 (*d*); 59.88 (*t*); 29.65 (*t*); 29.28 (*t*); 25.49 (*t*); 21.00 (*t*); 20.95 (*t*); 14.39 (*q*). CI-MS: 481 (28), 480 (100, $[M + 1]^+$). Anal. calc. for $C_{28}H_{33}NO_6$ (479.59): C 70.13, H 6.94, N 2.92; found: C 70.21, H 6.97, N 2.86.

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