Synthesis of Benzylated Cycloisomaltotri- and -hexaoside

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[11] Crystal structure analysis of **5b** ($[C_{28}H_{30}P][Li(C_4H_{10}O)_2]$): orange crystals, crystal dimensions: $0.35 \times 0.40 \times 0.50$ mm; $M_r = 552.7$; space group $P2_1/n$ (no. 14), $a = 20.966(5)$, $b = 15.888(5)$, $c = 21.845(3)$ Å, $\beta = 109.44(2)°$, $V = 6.862$ nm^3, $Z = 8$, $\rho_{calcd} = 1.07$ g cm^{-3}, $\mu = 0.91$ mm^{-1}, 10176 symmetry independent reflections ($2\theta_{max.} = 120°$, $T = 193$ K) of which 8472 reflections with $F > 4\sigma(F)$ were used for structure solution (direct method) and refinement (741 parameters), non-hydrogen atoms anisotropic; H atoms refined with a "riding" model: $R = 0.061$ ($Rw = 0.070$, $w^{-1} = \sigma^2(F) + 0.0003F^2$). An empirical absorption correction was carried out with the program DIFABS [12]. Two ether groups are disordered. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (FRG) on quoting the depository number CSD-57728 and the journal citation.

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[13] ^{13}C NMR (C_6D_6, 25 °C): $\delta[J_{CH}] = 140.86$(d) [5.4 Hz], 140.84(d) [46.6 Hz], 139.34(d) [15.2 Hz (CH)], 137.68(s), 135.46(d) [20.6 Hz (CH)], 135.11(d) [15.6 Hz], 129.95(d) [3.1 Hz (CH)], 129.92(d) [5.0 Hz (CH)], 129.08(d), [7.3 Hz (CH)], 128.70(s) [(CH)], 128.89(s) [(CH)], 128.58(s) [(CH)], 127.87(s) [(CH)], 127.61(d) [1.5 Hz (CH)], 124.12(s), 90.45(s). The C(H) resonances were determined by a dept-90 experiment.

Synthesis of Benzylated Cycloisomaltotri- and -hexaoside**

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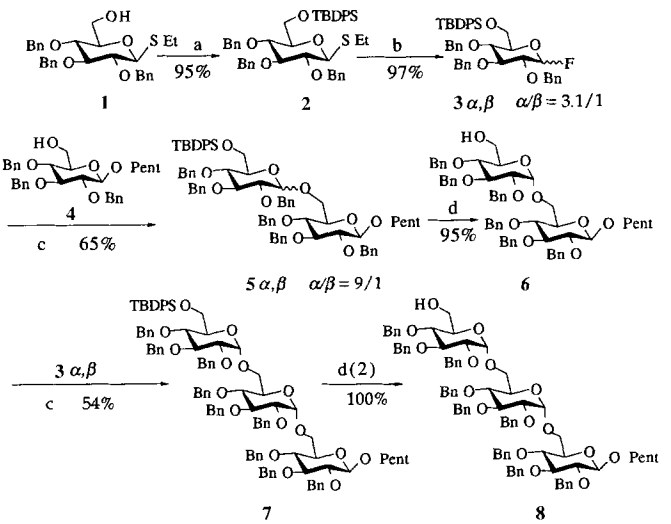
Cyclomaltooligosaccharides known as α-, β- and γ-cyclodextrins are obtained in large quantities by enzymic synthesis with cyclodextrin glycosyl transferase.[1] The well-known ability of cyclodextrins to include apolar molecules and their solubility in water can be improved by chemical modifications.[2] Very promising modifications are the per-3,6-anhydro-α- and -β-cyclodextrins,[3] and the per-2,3-anhydro-β-cyclodextrins[4] previously synthesized.

Besides these "derivatizations" of natural cyclodextrins, a parallel route based on chemical synthesis was developed by Ogawa et al.[5] and Vignon et al.[6] The strategy centers around the preparation of a linear precursor with the suitable number of sugar residues activated in such a way that the cyclization may be achieved. Beyond the inherent difficulties of glycosylation, chemical synthesis of cyclooligosaccharides as hosts for predefined guests is a challenge.[7]

It is in this context that we synthesized cyclooligosaccharides in the isomaltose series that may have new or optimized inclusion properties with respect to natural or modified cyclodextrins. The α-1,6-glucosidic linkage can be considered as a highly flexible bridge between two D-glucopyranosyl residues. Starting from this idea we designed the synthesis of oligocycloisomaltosides consisting of two, three, four, and six monomer units. We recently reported the first synthesis of benzylated cycloisomaltotetraoside[8] using a modification of the Mukaiyama method for the cycloglycosylation step.[9]

We report here on the synthesis of benzylated cycloisomaltotrioside **9** and benzylated cycloisomaltohexaoside **10**. The glycosylation method proposed by Fraser-Reid based on activation of pentenyl glycosides with I^+[10] was used for the cyclization of the linear precursor **8** (Scheme 1). Along with the



Scheme 1. Synthesis of the linear precursor **8** of the title compounds **9**, **10**, and **11**. Abbreviations: TBDPS = *tert*-butyldiphenylsilyl, Pent = pent-4-enyl. **a**: TBDPSCl, imidazole, DMF. **b**: diethylammonium sulfur trifluoride (1.5 equiv), *N*-bromosuccinimide, 1,2-dichloroethane, −15 °C. **c**: $AgClO_4$ (3 equiv)/$SnCl_2$ (3 equiv), Et_2O. **c'**: as in **c** but with 3 equiv reagents and 2.3 equiv **3**. **d**(1): HPLC; (2): tetrabutylammonium fluoride/THF (1 M), THF.

cyclic trimer **9** a small amount of the hexamer **10** and a nonsymmetric trimer **11** were also obtained (Scheme 2). These new compounds were characterized by NMR spectroscopy and mass spectrometry. Because of the symmetry of **9** and **10**, their NMR spectra, which exhibit the signals of a benzylated α-D-glucopyranoside, give no information about the number of monomers. The FAB$^+$ and DCI mass spectra clearly show molecular peaks consistent with the proposed structures of **9** and **10**. The NMR spectrum of **11** indicates three anomeric protons, two of which are α-configurated and one β-configurated according to the coupling constants. The molecular peak in the mass spectrum con-

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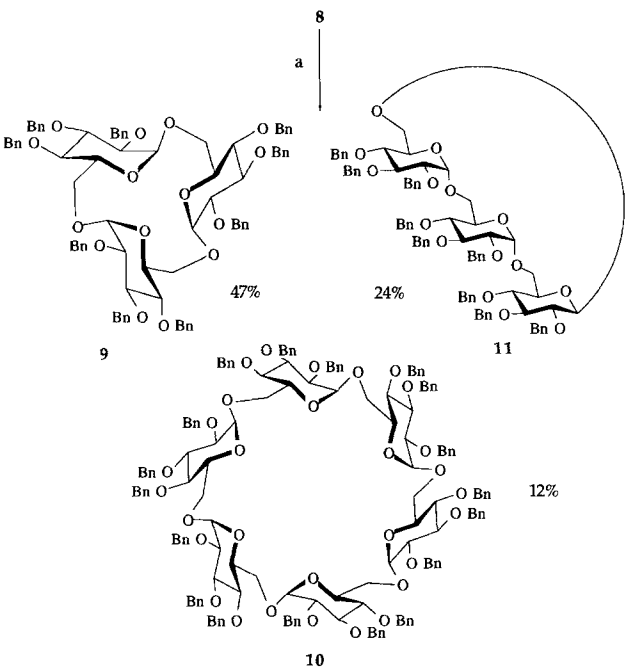
firmed the trimeric structure of **11**. Studies of conformational and inclusion properties of **9**–**11** are in progress.

Scheme 2 outlines the cycloglycosylation of the linear precursor **8**. The cyclization was carried out unter high-dilution conditions to favor the intramolecular glycosylation over intermolecular reaction; the yield is quite good (83%). A compromise was found



Scheme 2. Cycloglycosylation of the linear precursor **8** by the Fraser-Reid method giving the title compounds **9**, **10**, and **11**. **a**: iodonium dicollidine perchlorate (2 equiv), 1,2-dichloroethane/Et_2O (1:1).

between rate and stereoselectivity by using a 1:1 mixture of 1,2-dichloroethane and diethyl ether as solvent for the reaction. Our experience has shown that a higher proportion of the α-configurated product (1,2-*cis*-glycosylation) is obtained with this solvent system, but the rate is generally slowed dramatically.[10] In the typical experiment described here, all traces of the linear precursor **8** disappeared within approximately 30 minutes. As a result of the solvent system, but probably also because of the strained molecular structure of **9**, a significant amount (24%) of the nonsymmetric benzylated cycloisomaltotrioside **11** with one β-1,6- and two α-1,6-linkages was produced by 1,2-*trans*-glycosylation. It is very interesting to note that no trace of nonsymmetric cycloisomaltohexaoside (one β-1,6- and five α-1,6-glucosidic linkages) was detected. This is probably due to the fact that practically no strain develops during the cyclization step leading to **10**, in contrast to the formation of **9** which is stereoselective. A molecular mechanics simulation will be undertaken to confirm or reject this hypothesis. NMR data are given in Tables 1 and 2 for compounds **9**–**11**.

Table 1. ^1H and ^{13}C NMR data for **9** and **10** ($CDCl_3$, 400 MHz, 100 MHz, δ values, *J* [Hz]).

δ	H-1	H-2	H-3	H-4	H-5	H-6a	H-6b
9	4.82	3.40	3.84	3.11	4.15	3.51	4.06
10	4.94	3.30	3.93	3.65	3.77	3.65	3.71
J	1,2	2,3	3,4	4,5	5,6a	5,6b	6a, 6b
9	3.54	9.77	9–10	10.44	6.96	4.15	11.72
10	3.48	9.58	9–10	7.86	4.00	1.90	8.33
δ	C-1	C-2	C-3	C-4	C-5	C-6	
9	97.94	80.37	81.38	80.56	71.39	71.58	
10	97.46	80.51	81.56 [a]		71.26	66.57	

[a] Signal overlaps with that of the solvent.

Table 2. ^1H and ^{13}C NMR data for **11** ($CDCl_3$, 400 and 100 MHz, respectively, δ values, *J* [Hz]).

δ	H-1	H-1′	H-1″	C-1	C-1′	C-1″
11	4.25	4.59	4.77	104.55	97.88	97.24
J	1,2	1′,2′	1″,2″			
11	7.01	3.71	3.69			

Experimental Procedure

General: Thin-layer chromatograms (Riedel de Haen 37332) developed by charring. Column chromatography (SiO_2 Merck 7734). NMR spectroscopy (Bruker AM400 or Varian Unity-400). Mass spectrometry (ZAB-SEQ(VG) for FAB^- or DCI modes; NERMAG R10-10 for DCI).

Compound **1** was prepared from the 6-*O*-trityl compound [8] by detritylation [11] (BF_3, Et_2O). Subsequent treatment with *tert*-butyldiphenylsilyl chloride [12] afforded **2**, which was fluorinated following the method of Nicolaou et al. [13] to give **3**. Compound **4** was prepared from the 6-*O*-trityl compound previously described [11].

5: **4** and **3**α, β (1.46 equiv) were dissolved in diethyl ether, and molecular sieves 4 Å were added. A mixture of silver perchlorate (3 equiv) and molecular sieves 4 Å in diethyl ether/THF (2:1) was prepared separately. The two solutions were stirred for 24 h before mixing. Tin(II) chloride (3 equiv) was finally added. After 4 d at room temperature the reaction mixture was diluted with dichloromethane, filtered on celite, and washed (saturated NaCl solution). The crude product was directly purified by HPLC (Merck L-6200 pump; IOTA refractometer; commercial column: Si-60/5 μm, LiChroCART 250-4; toluene/ethyl acetate 98:2). **5**α 59%, R_f 0.51 (toluene/ethyl acetate 95:5); **5**β 6%, R_f 0.41 (same solvent). MS (FAB^-) *m/z* (%): 1321.8(43) [$(M+Cs)^+$]. **5**α ^1H NMR ($CDCl_3$, 400 MHz): δ = 4.40 (d, 1H, H-1, $J_{1,2}$ = 7.82 Hz), 5.08 (d, 1H, H-1′, $J_{1',2'}$ = 3.51 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 26.70 (*t*Bu), 28.88(2), 30.13(3), 62.82 (C-6′), 65.13 (C-6), 68.95(1), 96.62 (C-1′), 103.28 (C-1), 114.76(5), 137.91(4), 127.32–138.86 (C arom.). **5**β ^1H NMR ($CDCl_3$, 400 MHz): δ = 4.42 (d, 1H, H-1, $J_{1,2}$ = 7.98 Hz), 4.52 (d, 1H, H-1′, $J_{1',2'}$ = 7.77 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 26.96 (*t*Bu), 29.06(2), 30.32(3), 62.83 (C-6′), 66.50 (C-6), 69.61(1), 74.78, 75.30, 75.80, 76.06 (6 × CH_2Ph), 103.80 (C-1 or C-1′), 104.16 (C-1 or C-1′), 115.01(5), 127.9–136.06 (C arom.), 138.15(4).

6: To a solution of **5**α in THF was added a 1 M solution (2 equiv) of tetrabutylammonium fluoride in THF. After 2 d the reaction mixture was diluted with 1,2-dichloroethane, washed with saturated NaCl solution, concentrated, and purified by column chromatography (SiO_2, petroleum ether/ether 4:1) to give **6** in 95% yield. R_f 0.36 (hexane/ethyl acetate, 7:3). ^1H NMR ($CDCl_3$, 400 MHz): δ = 4.36 (d, 1H, H-1, $J_{1,2}$ = 7.83 Hz), 4.96 (d, 1H, H-1′, $J_{1',2'}$ = 3.39 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 28.91(2), 30.13(3), 61.79 (C-6′), 96.87 (C-1′), 103.39 (C-1), 114.81(5), 127.44–128.31 (C arom.).

7 was prepared in analogy to **5**, except 2.3 equiv 3α, β (3.1/1) were employed. Yield: 54%; R_f 0.75 (hexane/ethyl acetate 7:3). MS (FAB^+): *m/z* (%): 1754.7 (63) [$(M+Cs)^+$]. ^1H NMR ($CDCl_3$, 400 MHz): δ = 4.42 (d, 1H, H-1, $J_{1,2}$ = 7.84 Hz), 5.04 (d, 1H, H-1″, $J_{1'',2''}$ = 3.51 Hz), 5.10 (d, 1H, H-1′, $J_{1',2'}$ = 3.51 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 26.68 (*t*Bu), 28.87(2), 30.10(3), 62.62 (C-6″), 65.36, 65.49 (C-6 or C-6′), 68.98(1), 72.01, 72.20, 74.73, 74.85, 75.42, 75.59 (9 × CH_2Ph), 80.20 (C-2″), 81.68 (C-3′), 82.24 (C-2), 96.82 (C-1′, C-1″), 103.30 (C-1), 114.78(5), 127.3–135.7 (C arom.), 137.85(4).

8 was prepared in analogy to **6**. Yield: 100%; R_f 0.46 (hexane/ethyl acetate 6:4). MS (FAB^-): *m/z* (%): 1515.6 (65.5) [$(M+Cs)^+$].

9–**11**: **13**, **14**, **15**: After dissolution of **8** (26 mg, 1.85×10^{-2} mmol) in 1,2-dichloroethane/diethyl ether (3 mL, 1:1) iodonium dicollidine perchlorate (2 equiv) was added. Although **8** disappeared totally within 30 minutes, the reaction mixture was left under stirring for another 12 h. The reaction mixture was then diluted with dichloromethane, washed (saturated $Na_2S_2O_3$ solution), and dried (Na_2SO_4). The crude product mixture was separated in two steps by HPLC (Merck L-6200 pump; IOTA refractometer; commercial Si-60/5 mm, LiChroCART 250-4); first step:

(hexane/ethyl acetate 83:17; flow rate: 2 mL min^{-1}), **9**: 47%; t_r (retention time) 24.17 min; R_f 0.6 (hexane/ethyl acetate 7:3), MS (FAB$^+$): *m/z* (%): 865(62) [(2*M*/3+H)$^+$], 1297(42) [(*M*+H)$^+$], 1319(100) [(*M*+Na)$^+$], 2616(5) [(2*M*+Na)$^+$]; MS (DCI): *m/z* (%): 1313.6(100), [(*M*+NH$_3$)$^+$], and (**10**+**11**) t_r 42.42 min; second step: (toluene/ethyl acetate 75:25; flow rate: 2 mL min^{-1}), **10**: 12%; t_r 5.58 min; R_f 0.48 (toluene/ethyl acetate 9:1), MS (FAB$^+$): *m/z* (%): 431.2(100) [*M*/6+H)$^+$], 865.3(10) [(*M*/3+H)$^+$], 2727.5(80) [(*M*+Cs)$^+$], MS (DCI): *m/z* (%): 2610.4(100) [(*M*+NH$_3$)$^+$], **11**: 24%; t_r 8.49 min; R_f 0.26 (toluene/ethyl acetate 9:1), MS (FAB$^+$): *m/z* (%): 865(12) [(2*M*/3+H)$^+$], 1429.3(100) [(*M*+Cs)$^+$], MS (DCI): *m/z* (%): 1314.6(100) [(*M*+NH$_3$)$^+$].

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Synthesis and Structure of the Magnesium Imide [(thf)MgNPh]$_6$**

Tony Hascall, Karin Ruhlandt-Senge, and Philip P. Power*

Metal imides[1] may, most simply, be represented by the monomeric formula MNR (M = divalent metal, R = H, alkyl, or aryl group). In reality, however, monomeric structures are not observed in condensed phases owing to the tendency of the MNR units to associate strongly. In main group chemistry this behavior is exemplified by the polyiminoalanes (R'AlNR)$_n$[2] and compounds of the composition (MNR)$_n$ (where M is a main group 4 metal (Ge, Sn, or Pb) in a lower oxidation state).[3–5] Usually, association numbers of $n \geq 4$, are observed for these compounds, and the resulting structures are three-dimensional cages. At present, however, no well-characterized homometallic imido derivatives of the neighboring main group 2 elements have been reported.[6] In this paper, the first X-ray crystal structure of such a species is now described.

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The title compound **1** · THF was synthesized as a colorless

[(thf)MgNPh]$_6$ **1**

crystalline material by the straightforward reaction of Et_2Mg with H_2NPh in ether and crystallization from hexane/THF. The ^1H and ^{13}C NMR spectra are consistent with a 1:1 stoichiometry of THF and Ph ligands in **1**. The X-ray crystal structure analysis of **1**[7] reveals a slightly distorted hexagonal-prismatic framework of magnesium and nitrogen atoms arranged in an alternating manner at the apices (Fig. 1). Each nitrogen atom

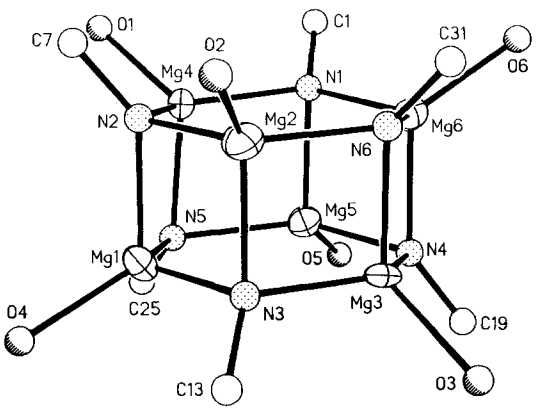

Fig. 1. Molecular structure of **1** (computer-generated). For clarity, only the oxygen atoms of the THF molecules, *ipso*-carbon atoms of the Ph substituents, and the Mg$_6$N$_6$ framework are shown.

bears a phenyl substituent, whereas the magnesium atoms are each solvated by a single THF donor molecule. The N and Mg atoms are thus tetracoordinated in a distorted-tetrahedral fashion. The average Mg–N distance between the six-membered rings (2.08 Å) is slightly longer than the average Mg–N bond length (2.05 Å) within the six-membered rings. In addition, the parallel, hexagonal Mg_3N_3 arrays are almost planar with a slight distortion toward chair configurations. The maximum deviation of Mg or N atoms from the best-fit plane is no greater than 0.08 Å. The average internal angle at the Mg atoms (122.7°) in the six-membered ring is greater than that at the N atoms (116.5°). The average Mg–O bond length is 2.04 Å and the average N–C distance is 1.37 Å.

The structure observed for **1** closely resembles those found for the related iminoalanes (R'AlNR')$_6$,[8, 9] which also possess hexagonal prismatic frameworks with slightly puckered Al_3N_3 ring planes. As in **1** the Al–N distances between the six-membered rings are longer (e.g. 1.956 vs. 1.898 Å in [HAlN(*i*Pr)]$_6$[8]) than those within the rings. The Mg–N bonds in **1** are, of course, longer than these distances owing to the larger radius of magnesium (1.45[10] vs. 1.3 Å[10] for Al). The Mg–N bond lengths in **1** are, in fact, very close to those observed (Mg–N = 2.09 Å) in the cubane species **2**[11] in which one of the Al–H corners is

[(HAl*t*Bu)$_3${MgN*t*Bu(thf)}] **2**

replaced by a Mg(thf) moiety. Compound **2** appears to be the only other instance of the involvement of a magnesium atom in a metal-imide cage structure.[6, 12] The Mg–N distances in cage species **1** and **2** can be regarded as being relatively short, since they involve λ^4-Mg-λ^4-N type bonds (cf. 2.055 for λ^4-Mg-λ^3-N connectivity in [(thf)$_2$Mg(N*t*Bu)$_2$(SiMeN*t*Bu)$_2$],[13] 2.118 Å for