41.2, 41.9, 44.0, 50.9, 55.9, 62.2, 136.8, 213.8.

Reaction of the Dibromoquinone 4 with Cyclopentadiene. To a solution of **4** (800 mg, 2.42 mmol) in benzene (25 mL) was added cyclopentadiene (319 mg, 4.8 mmol), and the mixture was refluxed for 4 h. Removal of the solvent under vacuum gave a residual solid, which on washing with hexane to remove the excess of cyclopentadiene gave a 78% yield of a mixture (62:38, estimated by ^{1}H NMR spectrum) of the endo,syn adduct **12** and endo,anti adduct **10**. The mixture was chromatographed on silica gel (25 g), and elution with a mixture (1:20) of ethyl acetate and hexane gave the endo,syn adduct, 10aβ,8aβ-dibromo-1α,4α,5α,8α-tetrahydro-1,4:5,8-dimethanoanthracene-9,10-dione (**12**), mp 171 °C, on recrystallization from a mixture of dichloromethane and hexane: IR ν_{max} (KBr) 1645, 1600, 740 cm^{-1}; UV λ_{max} (methanol) 258 nm (ϵ 9000), 320 (1060); ^{1}H NMR ($CDCl_3$) δ 2.28 (2 H, s), 2.32 (2 H, AB q, $J_1 = J_2 = 12$ Hz), 3.67 (2 H, dd, $J_1 = J_2 = 2$ Hz), 4.0 (2 H, br s), 5.92 (2 H, dd, $J_1 = J_2 = 2$ Hz), 6.76 (2 H, dd, $J_1 = J_2 = 2$ Hz); ^{13}C NMR ($CDCl_3$) δ 45.9, 49.8, 55.6, 69.5, 72.8, 137.2, 142.1, 166.6, 186.1. Anal. Calcd for $C_{16}H_{12}Br_2O_2$: C, 48.52; H, 3.05. Found: C, 48.30; H, 3.04.

Further elution of the column with the same solvent mixture gave the endo,anti adduct, 10aα,8aβ-dibromo-1α,4α,5β,8β-tetrahydro-1,4:5,8-dimethanoanthracene-9,10-dione (**10**), mp 199 °C, on recrystallization from a mixture of dichloromethane and hexane: IR ν_{max} (KBr) 1675, 1600, 800, 720 cm^{-1}; UV λ_{max} (methanol) 270 nm (ϵ 6770), 320 (990); ^{1}H NMR ($CDCl_3$) δ 2.28 (2 H, s), 2.36 (2 H, AB q, $J_1 = J_2 = 12$ Hz), 3.70 (2 H, dd, $J_1 = J_2 = 2$ Hz), 4.14 (2 H, dd, $J_1 = J_2 = 2$ Hz), 6.12 (2 H, dd, $J_1 = J_2 = 2$ Hz), 6.94 (2 H, dd, $J_1 = J_2 = 2$ Hz); ^{13}C NMR ($CDCl_3$) δ 46.2, 49.6, 55.7, 73.2, 76.7, 137.3, 142.7, 166.7, 185.4. Anal. Calcd for $C_{16}H_{12}O_2Br_2$: C, 48.12; H, 3.05. Found: C, 48.32; H, 3.02.

1α,4α,5α,8α-Tetrahydro-1,4:5,8-dimethanoanthracene-9,10-dione (7). To a solution of the *endo,syn*-dibromo adduct **12** (100 mg, 0.25 mmol) in 5 mL of acetone was added 30% $TiCl_3$ (3 mL), under nitrogen atmosphere, and the reaction mixture was stirred for 30 min at room temperature. The mixture was poured into brine (20 mL), and the aqueous phase was extracted with ethyl acetate (3 × 20 mL). The combined organic extracts were washed with sodium bicarbonate solution and brine and later dried over anhydrous sodium sulfate. Removal of the solvent under vacuum gave the crude diol **17** (60 mg; IR ν_{max} (KBr) 3300, 1560, 1300 cm^{-1}).

The diol **17** (50 mg) was dissolved in 3 mL of ethyl acetate and stirred vigorously with silver(I) oxide (50 mg) and anhydrous sodium sulfate (75 mg) for 30 min. Removal of the solvent under vacuum gave a residual solid, which was recrystallized from a mixture of dichloromethane and hexane to give the *syn*-bisnorbornenoquinone adduct **7** (48 mg, 95%), mp 205 °C: IR ν_{max} (KBr) 1640, 1550, 1180, 750 cm^{-1}; UV λ_{max} (methanol) 278 nm (ϵ 14 300), 330 (1000), 430 (150); ^{1}H NMR ($CDCl_3$) δ 2.28 (4 H, br s), 4.04 (4 H, br s), 6.8 (4 H, dd, $J_1 = J_2 = 1.5$ Hz); ^{13}C NMR ($CDCl_3$) δ 48.1, 73.9, 142.7, 160.3, 181.1. Mol wt calcd for $C_{16}H_{12}O_2$ 236.0837, found (high-resolution mass spectrometry) 236.0833.

1α,4α,5β,8β-Tetrahydro-1,4:5,8-dimethanoanthracene-9,10-dione (8).[3c] Compound **8** was prepared from the endo,anti adduct **9** as per a reported procedure,[3c] mp 250 °C dec (lit.[3c] mp 250 °C dec): IR ν_{max} (KBr) 1640, 1550, 1180, 750 cm^{-1}; UV λ_{max} (methanol) 283 nm (ϵ 16 380), 348 (600), 430 (150); ^{1}H NMR ($CDCl_3$) δ 2.24 (4 H, m), 4.0 (4 H, m), 6.84 (4 H, dd, $J_1 = J_2 = 1.5$ Hz); ^{13}C NMR ($CDCl_3$) δ 48.1, 74.0, 142.7, 160.3, 181.1.

Reaction of the Quinone 2 with 5,5-Dimethoxy-1,2,3,4-tetrachlorocyclopentadiene. A mixture of **2** (5.0 g, 0.03 mmol) and 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene (8.0 g, 0.03 mmol) in dry toluene (30 mL) was refluxed for 12 h. Removal of the solvent under vacuum and washing of the residual solid with hexane gave a 90% yield of a mixture of the endo,anti adduct **13** and endo,syn adduct **14** (77:23, estimated by ^{1}H NMR spectrum). The mixture was chromatographed on silica gel (400 g), and slow elution with a mixture (1:20) of ethyl acetate and hexane gave the endo,anti adduct, 5β,6,7,8β-tetrachloro-1α,4α,8aα,10aα-tetrahydro-1,4-methano-5,8-dimethoxymethanoanthracene-9,10-dione (**13**), mp 208–209 °C, on recrystallization from a mixture of dichloromethane and hexane: IR ν_{max} (KBr) 1660, 1600 cm^{-1}; UV λ_{max} (methanol) 268 nm (ϵ 6560), 320 (910), 400 (90); ^{1}H NMR ($CDCl_3$) δ 2.24 (2 H, AB q, $J_1 = J_2 = 7$ Hz), 3.6 (5 H, s), 3.68 (3 H, s), 3.92 (2 H, dd, $J_1 = J_2 = 2$ Hz), 6.8 (2 H, dd, $J_1 = J_2 = 2$ Hz); ^{13}C NMR ($CDCl_3$) δ 48.6, 52.0, 53.1, 57.1, 71.1, 77.7, 111.2, 129.1, 141.8, 167.9, 188.1. Anal. Calcd for $C_{18}H_{14}O_4Cl_4$: C, 49.57; H, 3.23. Found: C, 49.52; H, 3.17.

Further elution of the column with the same solvent mixture gave the endo,syn adduct, 5α,6,7,8α-tetrachloro-1α,4α,8aβ,10aβ-tetrahydro-1,4-methano-5,8-dimethoxymethanoanthracene-9,10-dione (**14**), mp 199–201 °C, after recrystallization from a mixture of dichloromethane and hexane: IR ν_{max} (KBr) 1660, 720 cm^{-1}; UV λ_{max} (methanol) 270 nm (ϵ 6250), 316 (1050), 400 (90); ^{1}H NMR ($CDCl_3$) δ 2.22 (2 H, br s), 3.44–3.46 (2 H, m), 3.53 (3 H, s), 3.64 (3 H, s), 4.04 (2 H, dd, $J_1 = J_2 = 2$ Hz), 6.8 (2 H, dd, $J_1 = J_2 = 2$ Hz); ^{13}C NMR ($CDCl_3$) δ 48.6, 52.1, 53.1, 56.6, 74.6, 77.5, 111.2, 128.8, 142.5, 167.3, 187.7. Anal. Calcd for $C_{18}H_{14}O_4Cl_4$: C, 49.57; H, 3.24. Found: C, 49.66; H, 3.25.

Irradiation of 13. *syn*-5,6,7,8-Tetrachloro-16,16-dimethoxyheptacyclo[10.2.1.1^{5,8}.0^{2,11}.0^{4,9}.0^{2,6}.0^{7,11}]octadec-13-ene-3,10-dione (21). The adduct **13** (50 mg, 0.11 mmol) was dissolved in 5 mL of dry benzene and diluted to 125 mL with hexane, and the solution was irradiated for 2 h, with use of Pyrex filter. Removal of the solvent under vacuum gave a residual solid, which was chromatographed on silica gel (5 g). Elution with a mixture (1:10) of ethyl acetate and hexane gave **21** (35 mg, 70%), mp 180 °C, after recrystallization from a mixture of dichloromethane and hexane: IR ν_{max} (KBr) 1760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.98 (2 H, AB q, $J_1 = J_2 = 10$ Hz), 3.01 (2 H, br s), 3.14 (2 H, s), 3.66 (3 H, s), 3.68 (3 H, s), 6.32 (2 H, br s); ^{13}C NMR ($CDCl_3$) δ 41.5, 44.8, 51.5, 51.9, 58.0, 69.8, 74.2, 75.4, 105.4, 136.5, 201.1. Anal. Calcd for $C_{18}H_{14}O_4Cl_4$: C, 49.57; H, 3.23. Found: C, 49.50; H, 3.19.

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Regioselective De-O-benzylation with Lewis Acids

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Simple and highly regioselective de-O-benzylations of poly-O-benzylated monosaccharides and polyols with Lewis acids ($SnCl_4$ and $TiCl_4$) were developed. Spectral studies on intermediate complexes showed that three appropriately situated metal chelating functional groups were necessary for the selective de-O-benzylation.

Benzyl protecting groups are widely used in organic chemistry, and various methods for benzylation and debenzylation have been reported.[1] In particular, the recent development of organotin-mediated regioselective O-

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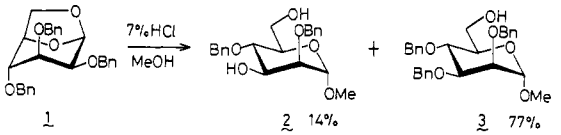
benzylation of polyol compounds[2] has made a significant contribution to the advance of carbohydrate chemistry. The few known examples of regioselective de-O-benzylation include that of perbenzylated methyl lyxoside by Grignard reagent,[3] perbenzylated methyl ribofuranoside with tin tetrachloride,[4] and perbenzylated 1,6-anhydrohexoses catalyzed by palladium–carbon.[5] We describe here simple and highly regioselective de-O-benzylations of 1,6-anhydrohexose derivatives, of tri-*O*-benzylglycerol, and of related compounds with two Lewis acids, $SnCl_4$ and $TiCl_4$, and propose a possible reaction mechanism.

Results and Discussion

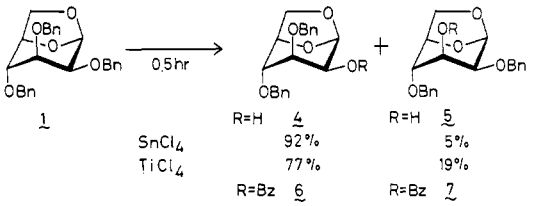
Reaction of 1,6-Anhydrohexopyranose Derivatives with Lewis Acids. Acid-catalyzed methanolysis of 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-mannopyranose (**1**) gave the expected methyl 2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (**3**) together with 14% of methyl 2,4-di-*O*-benzyl-α-D-mannopyranoside (**2**), a very useful synthetic intermediate for 3,6-branched mannooligosaccharides. This finding



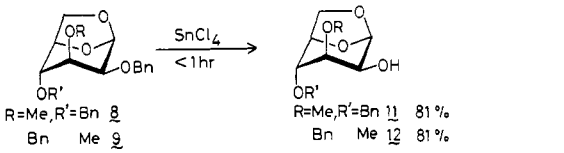
1 **2** 14% **3** 77%

prompted us to investigate the regioselective de-O-benzylation of **1** with Lewis acids ($SnCl_4$, $TiCl_4$, $BF_3{\cdot}Et_2O$, $AlCl_3$, $TiBr_4$, $ZnCl_2$, and $ZrCl_4$) in dichloromethane at room temperature. De-O-benzylation with Lewis acids had been reported before.[6,7] TLC analyses of the reaction mixtures showed that $SnCl_4$ and $TiCl_4$ converted **1** (R_f 0.72) completely into **4** (R_f 0.33) and **5** (R_f 0.51) within half an hour. Other Lewis acids reacted sluggishly with **1** to give complex mixtures. After chromatographic purification, the reactions of **1** with $SnCl_4$ or $TiCl_4$ gave crystalline **4** (92%) and syrupy **5** (5%) (or 77% and 19%), respectively.[8]

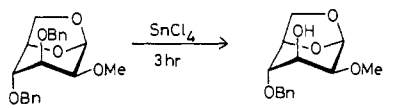
The structures of **4** and **5** were confirmed on the basis of ^1H NMR spectroscopy. Although it was reported that PF_5 could cleave the 1,6-anhydro ring of **1** even at −78 °C without de-O-benzylation[9] and that $TiCl_4$ and $TiBr_4$ react with 1,6-anhydro-2,3,4-tri-*O*-acetyl-β-D-gluco- and -D-galactopyranose to give the corresponding glycosyl halides,[10] the ^1H NMR spectra of **4** and **5** showed the characteristic signals of 1,6-anhydromannose,[11,12] a broad singlet and two double-doublets, assigned to H-1 and two H-6 protons. The ^1H NMR spectra of **4** and **5** further indicated the presence of two benzyloxy groups and one hydroxy group in their structures. The positions of the hydroxy group in **4** and **5** were determined from the downfield shift of H-2 and H-3 in the ^1H NMR spectra of their *O*-benzoyl derivatives **6** and **7**, respectively. Thus compounds **4** and **5** are 1,6-anhydro-3,4-di-*O*-benzy-β-D-mannopyranose and 1,6-anhydro-2,4-di-*O*-benzyl-β-D-mannopyranose, respectively.



1 R=H **4** 92% R=H **5** 5%
$SnCl_4$ / $TiCl_4$ 77% 19%
R=Bz **6** R=Bz **7**

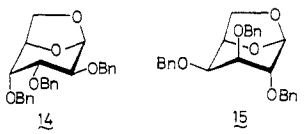


R=Me,R'=Bn **8** R=Me,R'=Bn **11** 81%
Bn Me **9** Bn Me **12** 81%



10 **13** 81%

In order to investigate the scope, limitation, and mechanism of the regioselective de-O-benzylation, the reactions of several other 1,6-anhydrohexose derivatives with $SnCl_4$ or $TiCl_4$ were examined. The reactions of 1,6-anhydro-2,4-di-*O*-benzyl-3-*O*-methyl-β-D-mannopyranose (**8**) and 1,6-anhydro-2,3-di-*O*-benzyl-4-*O*-methyl-β-D-mannopyranose (**9**) with $SnCl_4$ proceeded rapidly to give in high yield, 2-O-debenzylated compounds **11** and **12**, respectively, whereas the reaction of 1,6-anhydro-3,4-di-*O*-benzyl-2-*O*-methyl-β-D-mannopyranose (**10**) with $SnCl_4$ proceeded slowly to give 3-O-debenzylated compound **13** in 81% yield. The reactions of 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-altropyranose (**14**) (a C-3 epimer of **1**) and 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-galactopyranose (**15**) (a C-2



14 **15**

and C-4 epimer of **1**) very slowly gave complex mixtures with $SnCl_4$ or $TiCl_4$ (see the Experimental Section). These results suggested that three continuous cis-oriented alkoxy groups at C-1, C-2, and C-3 were necessary for the successful regioselective de-O-benzylation of 1,6-anhydrohexoses.

However, the reaction of 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose (**16**), which is a C-2 epimer of **1**, with $SnCl_4$ (or $TiCl_4$) gave a 40:60 (or 45:55) mixture of 1,6-anhydro-3,4-di-*O*-benzyl-β-D-glucopyranose (**17**) and 1,6-anhydro-2,3-di-*O*-benzyl-β-D-glucopyranose (**18**) in good yield.

The structurally similar pairs **17** and **18**, and their *O*-benzoyl derivatives **19** and **20**, could not be separated by chromatographic methods and were determined on the basis of the ^1H NMR spectra of the mixtures. Although the chemical shifts of H-1 of **17** and **18** were almost identical, those of **19** and **20** were different from each other. The H-1 signal at lower field (5.586 ppm) was assigned to that of **19** and the one at higher field (5.539 ppm) to that of **20**, so that the ratios of **19** and **20** (**17** and **18**) could be determined. The successful selective de-O-benzylation of gluco derivative **16** indicated that the three oxygen atoms

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(10) (a) Zemplen, G.; Gerecs, A. *Ber.* **1931**, *64*, 1545. (b) Zemplen, G.; Gerecs, A.; Flesch, H. *Ibid.* **1938**, *71*, 774. (c) Zemplen, G.; Gerecs, A.; Valatin, T. *Ibid.* **1940**, *73*, 575.
(11) Budešínský, M.; Trnka, T.; Černeý, M. *Collect. Czech. Chem. Commun.* **1979**, *44*, 1949.
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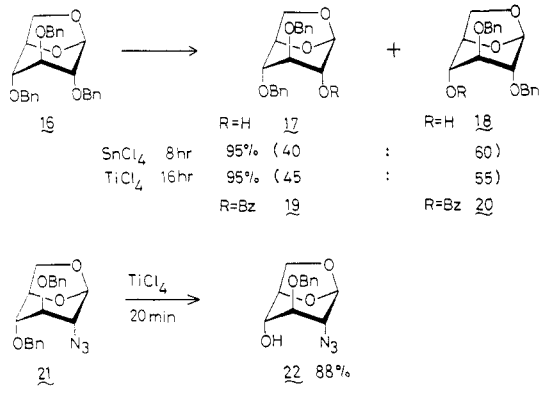
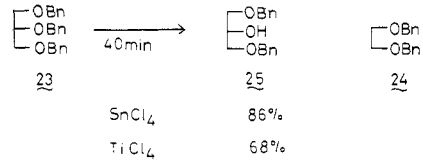
O-5(1), O-2, and O-4 played an important role in de-O-benzylation as did the three oxygens, O-1(6), O-2, and O-3, of manno derivative **1**.



In the reaction of 1,6-anhydro-2-azido-3,4-di-*O*-benzyl-2-deoxy-β-D-glucopyranose (**21**)[13] with $TiCl_4$, the azido group plays a role similar to oxygen, because it has lone pair electrons to coordinate with Lewis acid. Expectedly, **21** gave 1,6-anhydro-2-azido-3-*O*-benzyl-2-deoxy-β-D-glucopyranose (**22**) in 88% yield.

The above results indicated that three suitably situated alkoxy or azido groups were necessary for the selective de-O-benzylation.

Reactions of Perbenzyl Ether of Glycerol and Ethylene Glycol with Lewis Acids. In order to confirm the rule described above, the reaction of 1,2,3-tris(benzyloxy)propane (**23**) and 1,2-bis(benzyloxy)ethane (**24**) with Lewis acids were carried out as simple models.



The reaction of **23** (three continuous oxygen functions) with $SnCl_4$ or $TiCl_4$ gave 1,3-bis(benzyloxy)-2-hydroxypropane (**25**) in 86% or 68% yield. On the other hand, no de-O-benzylation took place with 1,2-bis(benzyloxy)ethane (**24**). These results strongly suggested that three properly arranged alkoxy groups in a molecule were necessary for the selective de-O-benzylation.

Structural Analyses of the Tin or Titanium Complexes. It can be assumed that the primary products of these reactions were tin or titanium alkoxides, which were hydrolyzed to the corresponding alcohols during the workup process. The structures of these metal alkoxides could be elucidated by examining the ^1H and ^{13}C NMR spectra (Figures 1 and 2) of the reaction mixture of **1** and $SnCl_4$ in $CDCl_3$, which were different from those of either starting material **1** or the product **4** and changed into a spectrum of mixture of **4** and benzyl chloride by addition of D_2O to the reaction mixture. The ^1H NMR spectrum (Figure 1b) of the reaction mixture showed the downfield shifts for H-1,2,3,6 and 3-*O*-CH_2Ph and the high field shifts for H-4 and 4-*O*-CH_2Ph compared with those of **1** or **4**.

These chemical shift changes could be explained by the formation of complex **1′**. The electron densities of H-1,2,3,6 and 3-*O*-CH_2Ph were decreased by the coordination of O-1(6),2,3 to the tin atom bearing three chlorine atoms.

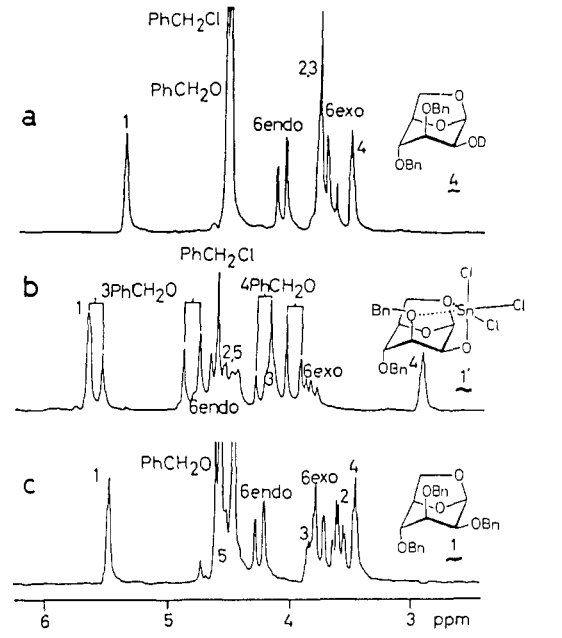


Figure 1. ^1H NMR (100 MHz) spectra of the tin complexes **1′** (a) b + D_2O, (b) **1** + $SnCl_4$, (c) **1** (see the Experimental Section).

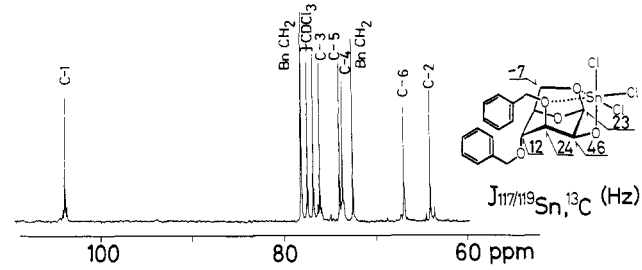
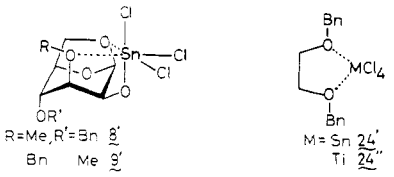


Figure 2. ^{13}C NMR (50 MHz) spectrum of the tin complex **1′**. The satellite peaks can be observed at C-1,2,3,4 due to coupling with $^{117/119}Sn$ (see the Experimental Section).

Due to coordination of O-3 with the tin atom the aromatic ring of the 3-*O*-benzyl group hung over the H-4 and methylene group of 4-*O*-CH_2Ph, resulting in the higher field shifts of these protons. The methylene signals of 3- and 4-*O*-benzyl groups of **1′** were assigned by comparison with those of **8** and **9** under similar ^1H NMR conditions. Thus, the ^1H NMR spectrum of **8′** (reaction mixture of **8** and $SnCl_4$, see the Experimental Section) showed the signals of benzyl chloride, H-4, and methylene protons of a benzyloxy group at normal regions and a 3-*O*-methyl group shifted downfield. The ^1H NMR spectrum of **9′** (reaction mixture of **9** and $SnCl_4$, see the Experimental Section) showed the signals of benzyl chloride and downfield shifts of 3-*O*-benzyl protons at 4.77 and 5.61 ppm and upfield shift of H-4 (4.55 ppm) and 4-*O*-methyl protons (3.00 ppm). These results supported not only the complex formation between O-1(6),2,3 and tin atom but also the conformation of the complex and the assignments of protons in their ^1H NMR spectra.



More direct evidence of the formation of the tin complex of **1** and $SnCl_4$ was obtained by ^{13}C NMR spectroscopy in $CDCl_3$. All signals were assigned by selective proton-decoupling and INEPT experiments. The formation of

(13) Although compound **21** had been prepared from 1,6-anhydroglucose (see ref 21), we prepared it from **4** (Experimental Section). The synthesis of 1,6-anhydro-2-azido-2-deoxy-β-D-glucopyranose derivatives from 1,6-anhydro-2-*O*-triflyl-β-D-mannopyranose derivatives and lithium azide has been reported. Kloosterman, M.; de Nijs, M. P.; van Boom, J. H. *J. Carbohydr. Chem.* **1986**, *5*, 215.

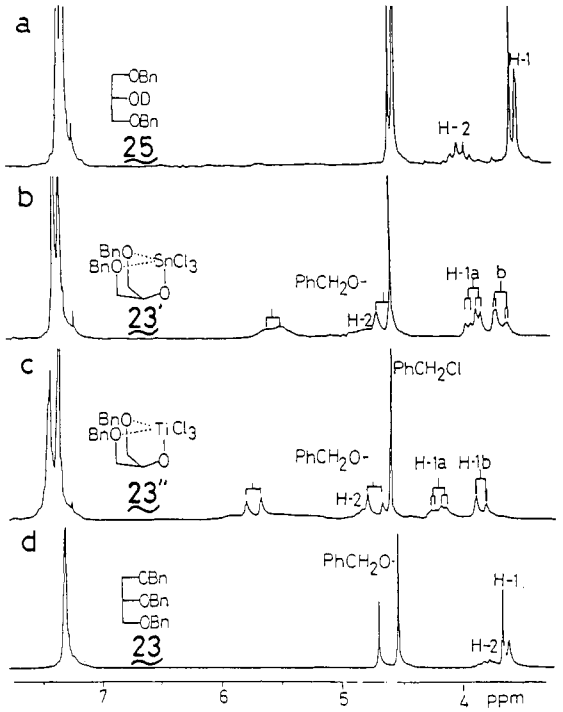


Figure 3. ^1H NMR (100 MHz) spectra of the complexes **23′** and **23″** and the related compounds. (a) b + D_2O, (b) **23** + $SnCl_4$, (c) **23** + $TiCl_4$, (d) **23** (see the Experimental Section).

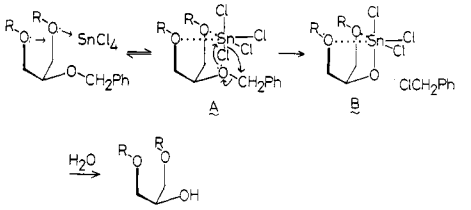
benzyl chloride was confirmed by the presence of a methylene signal at 46.3 ppm. Characteristics of the ^{13}C NMR spectrum were the C-2 signal, which appeared at the highest field among sugar carbons, and the observations of the satellite peaks for C-1, 103.9 ppm (J 23 Hz); C-2, 63.8 ppm (J = 46 Hz); C-3, 75.6 ppm (J = 24 Hz); C-4, 73.3 ppm (J = 12 Hz); and C-6, 66.7 ppm (J = 7 Hz ?) due to coupling between ^{13}C and $^{117/119}Sn$. The satellite peaks due to coupling with ^{117}Sn and ^{119}Sn would superimpose with each other because the gyromagnetic ratio of ^{117}Sn is close to that of ^{119}Sn.[14] The ratio of the intensity of the satellite peaks to that of main peak was ca. 16:84, consistent with the ratio of the natural abundance of ^{117}Sn + ^{119}Sn to that of NMR inactive Sn nuclei (the natural abundance of another NMR active nucleus ^{115}Sn (0.35%) was negligible).[14] Thus the structure of the tin complex was elucidated as shown in Figures 1 and 2.

The ^1H NMR spectra of the reaction mixtures of 1,2,3-tris(benzyloxy)propane (**23**) with $SnCl_4$ or $TiCl_4$ are shown in Figure 3. The spectra of the mixtures showed the remarkably downfield shifted (ca. 1 ppm) H-2 and moderately downfield shifted (ca. 0.05–0.6 ppm) methylene protons of glycerol compared with those of starting material **23**. The singlet methylene at 4.591 ppm of benzyl chloride and the characteristic nonequivalent methylene signals of the benzyl groups were observed in both cases ($SnCl_4$ and $TiCl_4$). By addition of D_2O to the reaction mixtures, the ^1H NMR spectra changed to that of a mixture of alcohol **25** and benzyl chloride. These NMR spectra also suggested the formation of complex **23′** and **23″** between three oxygen atoms and the Lewis acids.

Although no reaction occurred between **24** and Lewis acids as described above, the NMR spectra of the mixtures of **24** and $SnCl_4$ or $TiCl_4$ were different from that of **24**; in comparison with the spectrum of **24**, these spectra showed the downfield shifts (ca. 0.3–0.9 ppm) of methylene

(14) Smith, P. J.; Tupciauskas, A. P. *Ann. Rep. NMR Spectrosc.* **1978**, *8*, 291.

Scheme I. Reaction Mechanism of the Regioselective De-O-benzylation

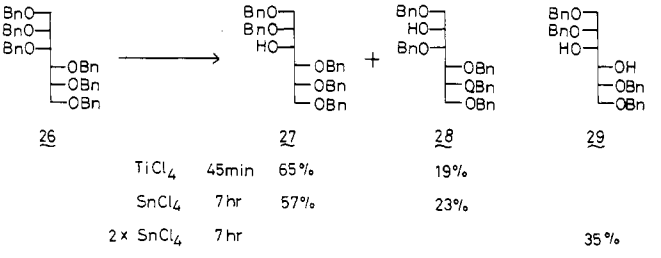


groups of both ethylene glycol and benzyl group (see the Experimental Section). By addition of D_2O to these mixtures, the spectra expectedly returned to that of **24**. The formation of the complex **24′** and **24″** was estimated on the basis of the NMR spectra.

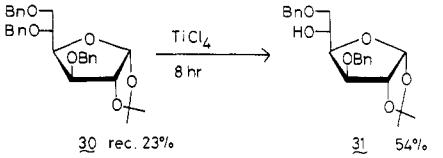
The Reaction Mechanism. On the basis of the results described above, a possible reaction mechanism was proposed as follows. (1) The tin or titanium atoms first form a six-coordinated bipyramidal complex **A** with two suitable located alkoxy oxygen atoms. The order of the reactivity for complexation will be primary > secondary > tertiary alkoxy group. (2) One of the four chlorine atoms on the complexed metal is then replaced by a third benzyloxy oxygen atom suitably situated to attack the metal atom in the same molecule resulting in formation a new oxygen–metal bond and a benzyl chloride because of high oxygenophilicity of the metal atom and high stability of the benzyl carbonium ion. (3) The metal alkoxide B can be hydrolyzed with water to give the selectively de-O-benzylated alcohol. (Scheme I).

Therefore, it is necessary for de-O-benzylation that a molecule contains three properly arranged metal chelating functional groups. At least one of them should be a benzyloxy group.

Application of the Reaction to Other Polybenzyl Ethers. The reaction of 1,2,3,4,5,6-hexa-*O*-benzyl-D-mannitol (**26**) with 1 equiv of $SnCl_4$ or $TiCl_4$ gave 1,2,3,5,6-penta-*O*-benzyl-D-mannitol (**27**) (57%) and 1,2,3,4,6-penta-*O*-benzyl-D-mannitol (**28**) (23%) (or 65% and 19%), respectively. Two equivalents of $SnCl_4$ converted **26** in low yield mainly to 1,2,5,6-tetra-*O*-benzyl-D-mannitol (**29**), which is a starting material for the 2,3-di-*O*-benzylglyceraldehyde derivative.



The reaction of 3,5,6-tri-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose (**30**) with $TiCl_4$ and DMF[15] gave 5-de-O-benzylated compound **31** (54%). The oxygen atoms O-5,6 and O-3 or -4 might be involved in the complexation in this molecule.



The products of this simple regioselective de-O-benzylation with Lewis acids will serve as glycosyl accep-

(15) The reaction without DMF gave **31** in 29% yield.

tors leading to oligosaccharides and other regiospecifically substituted derivatives.

Experimental Section

General Procedure. Melting points were taken with a Yanako Model P hot-plate apparatus and are uncorrected. The ^1H NMR spectra were recorded at 100 MHz on a JEOL JNM FX-100 instrument with TMS as an internal standard in $CDCl_3$. The ^{13}C NMR spectra were recorded at 25 MHz on the same instrument for ^1H NMR and at 50 MHz on a Varian XL-200 instrument in $CDCl_3$, which was used as an internal standard (77.05 ppm). All NMR data were of first-order analysis. IR spectra were recorded on a JASCO A-202 infrared spectrometer. Specific rotations were measured on a JASCO J-20 instrument at 589 nm. Merck silica gel 60 (Art. 7734) was used for column chromatography and Merck silica gel 60 F_{254} (Art. 5548) was used for both preparative and analytical thin-layer chromatographies (TLC).

Reactions of 1,6-Anhydro-2,3,4-tri-*O*-benzyl-β-D-mannopyranose (1) with Some Lewis Acids. To a solution of **1**[16] (100 mg) in dry CH_2Cl_2 (10 mL) was added (1) $SnCl_4$ (26 μL), (2) $TiCl_4$ (25 μL), (3) $ZrCl_4$ (25 mg), (4) $TiBr_4$ (25 mg), (5) $ZnCl_2$ (25 mg), (6) $AlCl_3$ (25 mg), and (7) $BF_3{\cdot}Et_2O$ (25 μL). The reactions were monitored by TLC ($CHCl_3$–EtOAc, 9:1).

In the case of (1) $SnCl_4$ and (2) $TiCl_4$, the starting material (R_f 0.72) was completely converted to two products **4** and **5** (R_f 0.33 and 0.5, respectively) within 20 min. In the case of (3) $ZrCl_4$ and (6) $AlCl_3$, the starting material remained and a spot of **4** and more polar compounds ($R_f < 0.1$) could be detected after 16 h. In the case of (7) $BF_3{\cdot}Et_2O$ and (4) $TiBr_4$, the starting material was completely consumed within 10 min, and many spots including **4** could be detected by TLC. No reaction was observed in the case of (5) $ZnCl_2$ even after 24 h.

Reactions of 1,6-Anhydro-2,3,4-tri-*O*-benzyl-β-D-mannopyranose (1) with $SnCl_4$ or $TiCl_4$. To a solution of **1** (95 mg, 2.0 g) in dry CH_2Cl_2 (10 mL, 150 mL), $SnCl_4$, or $TiCl_4$ (26 μL, 0.5 mL) was added at room temperature. After 30 min, the products were isolated by the **common procedure** as follows: The reaction mixture was poured into cold saturated $NaHCO_3$, and the reaction flask was washed with CH_2Cl_2. The washing was also poured into the aqueous solution, and the organic layer was separated. The water layer was once extracted with CH_2Cl_2. These organic layers were combined and washed with saturated NaCl. The solution was passed through a Celite pad, and the filtrate was dried over $MgSO_4$. After removal of $MgSO_4$, the solution was concentrated to a syrup, which was applied to a silica gel column chromatography (i.d. 20 × 140 mm, C_6H_6–EtOAc = 17:3). In the case of $SnCl_4$, two fractions were obtained and were concentrated to give **4** (69 mg 92%), which was crystallized from Et_2O [mp 54–56 °C, $[\alpha]^{23}_D$ −58.5° (*c* 0.76, $CHCl_3$); IR (KBr) 3400, 740, 695 cm^{-1}; ^1H NMR δ ppm 7.32 (10 H, b s, 2 C_6H_5), 5.336 (1 H, b s, H-1), 4.40–4.55 (5 H, (4.505, s, 4.480, s, 2 $PhCH_2O$), H-5), 4.050 (1 H, dd, $J_{5,6_{endo}}$ = 1.0, $J_{6_{endo},6_{exo}}$ = 7.1 Hz, H-6_{endo}), 3.747 (2 H, m, H-2,3), 3.663 (1 H, dd, $J_{5,6_{exo}}$ = 6.1, $J_{6_{endo},6_{exo}}$ = 7.1 Hz, H-6_{exo}), 3.475 (1 H, m, H-4), 3.0 (1 H, b s, 2-OH). Anal. C, 70.32; H, 6.44. Calcd: C, 70.15; H, 6.47.] and **5** (4 mg, 5%): $[\alpha]^{23}_D$ −28.2° (*c* 0.56, $CHCl_3$) [lit.[8] $[\alpha]^{20}_D$ −26.4° (*c* 1.02, $CHCl_3$)]; ^1H NMR δ ppm 7.321 (10 H, b s, 2 C_6H_5), 5.409 (1 H, b s, H-1), 4.45–4.75 (5 H, (4.620, s, 4.691, 4.530, AB q, J_{HCH} = 11.7 Hz, 2 $PhCH_2O$), H-5), 4.05–4.20 (2 H, (4.158, dd, $J_{5,6_{endo}}$ = 1.0, $J_{6_{endo},6_{exo}}$ = 7.1 Hz, H-6_{endo}, 4.12, m, H-3)), 3.55–3.72 (3 H, (3.652, dd, $J_{5,6_{endo}}$ = 5.9, $J_{6_{endo},6_{exo}}$ = 7.3 Hz, H-6_{exo}), H-2,4), 3.15 (1 H, b s, 3-OH). Anal. C, 70.25; H, 6.50. Calcd: C, 70.1; H, 6.47.

In the case of $TiCl_4$, chromatographic purification (i.d. 38 × 440 mm, $CHCl_3$–EtOAc, 9:1) of the reaction mixture gave **4** (1.22 g, 77%) and **5** (0.31 g, 19%).

Compounds **4** and **5** were benzoylated (BzCl/Pyr) to give **6** [IR (film) 1720 cm^{-1}; ^1H NMR δ ppm 8.1 (2 H, m, *o*-2H of C_6H_5CO), 7.2–7.7 (13 H, m, *m*-, *p*-3H of C_6H_5CO, 2 C_6H_5), 5.581 (1 H, b s, H-1), 5.103 (1 H, dd, $J_{1,2}$ = 1.7, $J_{2,3}$ = 5.6 Hz, H-2), 4.35–4.70 (5 H, m, 2 $PhCH_2O$, H-5), 4.345 (1H, dd, $J_{5,6_{endo}}$ = 1.0, $J_{6_{endo},6_{exo}}$ = 7.1 Hz, H-6_{endo}), 4.164 (1 H, sep, $J_{1,3} = J_{3,4} = J_{3,5}$ = 1.7 Hz, $J_{2,3}$ = 5.6 Hz, H-3), 3.793 (1 H, dd, $J_{5,6_{exo}}$ = 5.9, $J_{6_{endo},6_{exo}}$ = 7.1 Hz, H-6_{exo}), 3.512 (1 H, b t, $J_{3,4} = J_{4,5}$ = 1.8 Hz, H-4)] and **7**: IR (film) 1720 cm^{-1}; ^1H NMR δ ppm 8.1 (2 H, m, *o*-2H of C_6H_5CO), 7.2–7.7 (13 H, m, *m*-, *p*-3H of C_6H_5CO, 2 C_6H_5), 5.674 (1 H, sep, $J_{1,3} = J_{3,4} = J_{3,5}$ = 1.7, $J_{2,3}$ = 5.3 Hz, H-3), 5.500 (1 H, b s, H-1), 4.41–4.93 (5 H, (4.868, 4.702, AB q, J_{HCH} = 12.2 Hz, $PhCH_2O$, 4.643, 4.476, AB q, J_{HCH} = 12.2 Hz, $PhCH_2O$, 4.55, H-5)), 4.410 (1 H, dd, $J_{5,6_{endo}}$ = 0.7, $J_{6_{endo},6_{exo}}$ = 7.5 Hz, H-6_{endo}), 3.75–3.90 (2 H, (3.827, dd, $J_{5,6_{exo}}$ = 5.6, $J_{6_{endo},6_{exo}}$ = 7.3 Hz, H-6_{exo}, 3.781, dd, $J_{1,2}$ = 1.2, $J_{2,3}$ = 5.1 Hz, H-2)), 3.568 (1 H, b s, H-4).

1,6-Anhydro-2,4-di-*O*-benzyl-3-*O*-methyl-β-D-mannopyranose (8). To a solution of **5** (530 mg) in DMF (10 mL) was added NaH (90 mg) at room temperature. After 30 min the suspension was cooled with ice–water, and MeI (0.4 mL) was added to this suspension. After 12 h MeOH (1 mL) was added, and the suspension was concentrated to a syrup, which was dissolved in CH_2Cl_2 (20 mL), and was washed with water. The solution was dried over $MgSO_4$ and concentrated to a syrup, which was purified by silica gel column chromatography (i.d. 25 × 190 mm, C_6H_6–EtOAc, 5:1) to give syrupy **8** (560 mg, 100%): R_f 0.72 ($CHCl_3$–EtOAc, 4:1); $[\alpha]^{23}_D$ −208° (*c* 0.8, $CHCl_3$); IR (film) 740, 700 cm^{-1}; ^1H NMR δ ppm 7.35 (10 H, m, 2 C_6H_5), 5.422 (1 H, b s, H-1), 4.4–4.8 (5 H, (4.68, 4.54, AB q, $PhCH_2O$, 4.637, s, $PhCH_2O$, 4.525, m, H-5)), 4.132 (1 H, dd, $J_{5,6_{endo}}$ = 0.7, $J_{6_{endo},6_{exo}}$ = 7.1 Hz, H-6_{endo}), 3.5–3.8 (4 H, (3.710, dd, $J_{5,6_{exo}}$ = 5.9, $J_{6_{endo},6_{exo}}$ = 7.1 Hz, H-6_{exo}), H-2,3,4), 3.348 (3 H, s, 3-OCH_3). Anal. C, 70.81; H, 6.71. Calcd C, 70.76; H, 6.78.

1,6-Anhydro-2,3-di-*O*-benzyl-4-*O*-methyl-β-D-mannopyranose (9). 1,6-Anhydro-2,3-*O*-isopropylidene-β-D-mannopyranose[17] (800 mg) was methylated with NaH (350 mg) and MeI (0.9 mL) in DMF (20 mL) by the same method as that described for **8**. Purification of the product by silica gel column chromatography (i.d. 12 × 300 mm, C_6H_6–EtOAc, 9:1) gave a syrupy 1,6-anhydro-2,3-*O*-isopropylidene-4-*O*-methyl-β-D-mannopyranose (700 mg, 81%): R_f 0.36 (C_6H_6–EtOAc, 9:1); IR (film) 1380, 1370 cm^{-1}.

The solution of the methylated compound (580 mg) and pyridinium *p*-toluenesulfonate (790 mg) in MeOH (4 mL) and water (1 mL) was heated at 60 °C for 1 h. After cooling, *p*-toluenesulfonate ion was removed by the treatment with Dowex 1×2 (OH^- form), and the solution was concentrated and coevaporated with toluene to give syrupy 1,6-anhydro-4-*O*-methyl-β-D-mannopyranose (410 mg, 87%): R_f 0.06 (C_6H_6–EtOAc, 4:5).

The de-O-isopropylidenated compound (410 mg) was benzylated (NaH, BnCl/DMF). Purification of the product by silica gel column chromatography (i.d. 30 × 300 mm, C_6H_6) gave 1,6-anhydro-2,3-di-*O*-benzyl-4-*O*-methyl-β-D-mannopyranose (**9**) (620 mg, 75%): $[\alpha]^{23}_D$ −49.5° (*c* 0.3, $CHCl_3$); R_f 0.91 ($CHCl_3$–MeOH, 9:1); IR (film) 740, 700 cm^{-1}; ^1H NMR δ ppm 7.3 (10 H, m, 2 C_6H_5), 5.441 (1 H, b s, H-1), 4.4–4.9 (5 H, (4.781, 4.586, AB q, J_{HCH} = 12.5 Hz, $PhCH_2O$, 4.566, s, $PhCH_2O$, 4.53, H-5)), 4.296 (1 H, dd, $J_{5,6_{endo}} < 1.0$, $J_{6_{endo},6_{exo}}$ = 7.1 Hz, H-6_{endo}), 3.6–3.9 (2 H, (3.763, dd, $J_{5,6_{exo}}$ = 5.6, $J_{6_{endo},6_{exo}}$ = 7.1 Hz, H-6_{endo}, 3.800, H-3)), 3.514 (1 H, dd, $J_{1,2}$ = 1.7, $J_{2,3}$ = 5.1 Hz, H-2), 3.2-3.3 (4 H, (3.279, s, 4-OCH_3, 3.27, H-4)). Anal. C, 70.59; H, 6.84. Calcd: C, 70.76; H, 6.78.

1,6-Anhydro-3,4-di-*O*-benzyl-2-*O*-methyl-β-D-mannopyranose (10). Compound **4** (500 mg) was methylated (NaH, MeI/DMF). The product was purified by silica gel column chromatography to give syrupy 1,6-anhydro-3,4-di-*O*-benzyl-2-*O*-methyl-β-D-mannopyranose (**10**) (460 mg, 88%): R_f 0.21 (C_6H_6–EtOAc, 5:1); $[\alpha]^{23}_D$ −63.8° (*c* 0.02, $CHCl_3$); IR (film) 740, 700 cm^{-1}; ^1H NMR δ ppm 7.33 (10 H, m, 2 C_6H_5), 5.505 (1 H, s, H-1), 4.3–4.9 (5 H, (4.492, 4.679, AB q, $PhCH_2O$, 4.480, s, $PhCH_2O$, 4.43, H-5)), 4.205 (1 H, dd, $J_{5,6_{endo}}$ = 1.0, $J_{6_{endo},6_{exo}}$ = 7.1 Hz, H-6_{endo}), 3.880 (1 H, sep, $J_{2,3}$ = 5.1, $J_{1,3} = J_{3,5} = J_{3,4}$ = 1.8 Hz, H-3), 3.720 (1 H, dd, $J_{5,6_{exo}}$ = 5.9, $J_{6_{endo},6_{exo}}$ = 7.1 Hz, H-6_{exo}), 3.3–3.5 (5 H, (3.468, H-4, 3.397, dd, $J_{1,2}$ = 1.9, $J_{2,3}$ = 5.1 Hz, H-2, 3.387, s, 2-OCH_3)). Anal. C, 70.64; H, 6.88. Calcd: C, 70.76; H, 6.78.

Reaction of 1,6-Anhydro-2,4-di-*O*-benzyl-3-*O*-methyl-β-D-mannopyranose (8) with $SnCl_4$. To a solution of **8** (100 mg) in dry CH_2Cl_2 (5 mL) was added $SnCl_4$ (32 μL) at room temperature. After 1 h the reaction was stopped, and the mixture was worked up by the common procedure. Silica gel column chromatography (i.d. 20 × 150 mm, C_6H_6–EtOAc, 3:1) of the crude

(16) Sondheimer, S. J.; Eby, R.; Schuerch, C. *Carbohydr. Res.* **1987**, *60*, 187.

(17) Horton, D.; Jewell, J. S. *Carbohydr. Res.* **1966**, *2*, 251.

product gave 1,6-anhydro-4-*O*-benzyl-3-*O*-methyl-β-D-mannopyranose (**11**) (60 mg, 81%): R_f 0.28 (C_6H_6–EtOAc, 3:1); $[\alpha]^{23}_D$ −77.2° (*c* 0.07, $CHCl_3$); ^1H NMR δ ppm 7.370 (5 H, m, C_6H_5), 5.338 (1 H, b s, H-1), 4.681 (2 H, s, $PhCH_2O$), 4.547 (1 H, m, $J_{5,6_{exo}}$ = 5.9 Hz, H-5), 3.977 (1 H, dd, $J_{5,6_{endo}}$ = 1.0, $J_{6_{endo},6_{exo}}$ = 7.1 Hz, H-6_{endo}), 2.60–2.90 (2 H, (3.692, dd, $J_{5,6_{exo}}$ = 5.9, $J_{6_{endo},6_{exo}}$ = 7.1 Hz, H-6_{exo}), H-2) 2.40–2.60 (2 H, m, H-3,4), 3.336 (3 H, s, OCH_3), 3.02 (1 H, d, $J_{2,OH}$ = 11.2 Hz, 2-OH). Anal. C, 63.25; H, 7.00. Calcd: C, 63.14; H, 6.81.

Compound **11** was benzoylated (BzCl/Pyr) to give 1,6-anhydro-2-*O*-benzoyl-4-*O*-benzyl-3-*O*-methyl-β-D-mannopyranose: $[\alpha]^{23}_D$ −257° (*c* 0.1, $CHCl_3$); ^1H NMR δ ppm 8.13 (2 H, m, *o*-2H of C_6H_5CO), 7.3–7.7 (8 H, m, *m*-, *p*-3H of C_6H_5CO, C_6H_5), 5.578 (1 H, b s, H-1), 5.060 (1 H, dd, $J_{1,2}$ = 1.9, $J_{2,3}$ = 5.6 Hz, H-2), 4.725 (2 H, s, $PhCH_2O$), 4.635 (1 H, m, $J_{5,6_{exo}}$ = 5.9 Hz, H-5), 4.206 (1 H, dd, $J_{5,6_{endo}}$ = 1.0, $J_{6_{endo},6_{exo}}$ = 7.3 Hz, H-6_{endo}), 3.980 (1 H, sep, $J_{1,3} = J_{3,4} = J_{3,5}$ = 1.7, $J_{2,3}$ = 5.6 Hz, H-3), 3.793 (1 H, dd, $J_{5,6_{exo}}$ = 5.9, $J_{6_{endo},6_{exo}}$ = 7.3 Hz, H-6_{exo}), 3.578 (1 H, b t, $J_{3,4} = J_{4,5}$ = 1.7 Hz, H-4), 3.314 (3 H, s, H-4).

Reaction of 1,6-Anhydro-2,3-di-*O*-benzyl-4-*O*-methyl-β-D-mannopyranose (9) with $SnCl_4$. To a solution of **9** (100 mg) in dry CH_2Cl_2 (5 mL) was added $SnCl_4$ (32 μL) at room temperature. After 1 h, the reaction was stopped and was worked up by the common procedure. The crude products were purified by a silica gel column chromatography (i.d. 20 × 300 mm, C_6H_6–EtOAc, 4:1) to give 1,6-anhydro-3-*O*-benzyl-4-*O*-methyl-β-D-mannopyranose (**12**) (60 mg, 81%): R_f 0.27 (C_6H_6–EtOAc, 4:1); $[\alpha]^{23}_D$ −70.7° (*c* 0.18, $CHCl_3$); ^1H NMR δ ppm 7.356 (5 H, m, C_6H_5), 5.336 (1 H, b s, H-1), 4.652 (2 H, s, $PhCH_2O$), 4.564 (1 H, m, $J_{5,6_{exo}}$ = 5.6 Hz, H-5), 4.130 (1 H, dd, $J_{5,6_{endo}}$ = 1.0, $J_{6_{endo},6_{exo}}$ = 7.1 Hz, H-6_{endo}), 3.5–3.85 (3 H, (3.763, dd, $J_{5,6_{exo}}$ = 5.6, $J_{6_{endo},6_{exo}}$ = 7.1 Hz, H-6_{exo}), H-2,3), 3.353 (3 H, s, OCH_3), 3.304 (1 H, b s, H-4). Anal. C, 63.19; H, 6.79. Calcd: C, 63.41; H, 6.81.

The product **12** was benzoylated (BzCl/Pyr) to give 1,6-anhydro-2-*O*-benzoyl-3-*O*-benzyl-4-*O*-methyl-β-D-mannopyranose: ^1H NMR δ ppm 8.1 (2 H, m, *o*-2H of C_6H_5CO), 7.3–7.7 (8 H, m, *m*-, *p*-3H of C_6H_5CO, C_6H_5), 5.564 (1 H, b s, H-1), 5.034 (1 H, dd, $J_{1,2}$ = 2.0, $J_{2,3}$ = 5.4 Hz, H-2), 4.45–4.74 (3 H, (4.506, 4.677, AB q, J_{HCH} = 12.3 Hz, $PhCH_2O$), H-5), 4.352 (1 H, dd, $J_{5,6_{endo}}$ = 1.0, $J_{6_{endo},6_{exo}}$ = 7.1 Hz, H-6_{endo}), 4.147 (1 H, sep, $J_{1,3} = J_{3,4} = J_{3,5}$ = 1.7, $J_{2,3}$ = 5.4 Hz, H-3), 3.839 (1 H, dd, $J_{5,6_{exo}}$ = 5.9, $J_{6_{endo},6_{exo}}$ = 7.1 Hz, H-6_{exo}), 3.3–3.4 (4 H, (3.348, s, OCH_3, 3.328, m, H-4)).

Reaction of 1,6-Anhydro-3,4-di-*O*-benzyl-2-*O*-methyl-β-D-mannopyranose (10) with $SnCl_4$. To a solution of **10** (82 mg) in dry CH_2Cl_2 (5 mL) was added $SnCl_4$ (30 μL) at room temperature. After 3 h, the reaction was stopped and was worked up by the common procedure. Purification of the crude product by silica gel column chromatography gave pure 1,6-anhydro-4-*O*-benzyl-2-*O*-methyl-β-D-mannopyranose (**13**) (50 mg, 81%): R_f 0.21 ($CHCl_3$–EtOAc, 9:1); $[\alpha]^{23}_D$ −43.6° (*c* 0.19, $CHCl_3$); IR (film) 3500, 740, 700 cm^{-1}; ^1H NMR δ ppm 7.356 (5 H, m, C_6H_5), 5.471 (1 H, b s, H-1), 4.676 (2 H, s, $PhCH_2O$), 4.575 (1 H, m, $J_{5,6_{exo}}$ = 5.6 Hz, H-5), 4.1–4.3 (2 H, (4.179, dd, $J_{5,6_{endo}}$ = 1.0, $J_{6_{endo},6_{exo}}$ = 7.3 Hz, H-6_{endo}), H-3), 3.6–3.8 (2 H, (3.700, dd, $J_{5,6_{exo}}$ = 5.9, $J_{6_{endo},6_{endo}}$ = 7.3 Hz, H-6_{exo}, 3.635, b s, H-4)), 3.35–3.48 (4 H, (3.475, s, OCH_3, 3.423, dd, $J_{1,2}$ = 2.0, $J_{2,3}$ = 5.1 Hz, H-2)), 3.008 (1 H, d, $J_{3,OH}$ = 2.7 Hz, 3-OH).

Compound **13** was benzoylated (BzCl/Pyr) to give 1,6-anhydro-3-*O*-benzoyl-4-*O*-benzyl-2-*O*-methyl-β-D-mannopyranose: $[\alpha]^{23}_D$ −8.5° (*c* 0.01, $CHCl_3$); ^1H NMR δ ppm 8.1 (2 H, m, *o*-2H of C_6H_5CO), 7.2–7.7 (8 H, m, *m*-, *p*-3H of C_6H_5CO, C_6H_5), 5.716 (1 H, sep, $J_{1,3} = J_{3,4} = J_{3,5}$ = 1.7, $J_{2,3}$ = 5.1 Hz, H-3), 5.569 (1 H, b s, H-1), 4.905, 4.739 (2 H, AB q, J_{HCH} = 12.5 Hz, $PhCH_2O$), 4.603 (1 H, b d, $J_{5,6_{exo}}$ = 5.6 Hz, H-5), 4.119 (1 H, dd, $J_{5,6_{endo}}$ = 1.0, $J_{6_{endo},6_{exo}}$ = 7.3 Hz, H-6_{endo}), 3.830 (1 H, dd, $J_{5,6_{exo}}$ = 5.6, $J_{6_{endo},6_{exo}}$ = 7.3 Hz, H-6_{exo}), 3.5–3.7 (2 H, (3.610, dd, $J_{1,2}$ = 1.7 Hz, H-2, 3.566, b s, H-4)), 3.377 (3 H, s, OCH_3).

1,6-Anhydro-2,3,4-tri-*O*-benzyl-β-D-altropyranose (14). 1,6-Anhydro-β-D-altropyranose[18] (230 mg) was benzylated (NaH, BnCl/DMF) to give **14** (600 mg, 98%): R_f 0.57 (C_6H_6–EtOAc, 9:1); ^1H NMR δ ppm 7.329 (15 H, b s, 3 C_6H_5), 5.356 (1 H, d, $J_{1,2}$ = 1.2 Hz, H-1), 4.4–4.9 (7 H, (4.839, 4.678, AB q, $PhCH_2O$, 4.817, 4.687, AB q, $PhCH_2O$, 4.736, 4.609, AB q, $PhCH_2O$, 4.55, m, H-5)), 3.5–3.9 (5 H, m, H-2,3,4,6_{endo},6_{exo}). Anal. C, 75.12; H, 6.42. Calcd: C, 74.97; H, 6.52.

Reaction of 1,6-Anhydro-2,3,4-tri-*O*-benzyl-β-D-altropyranose (14) with $SnCl_4$ and $TiCl_4$. To a solution of **14** (50 mg, 60 mg) in dry CH_2Cl_2 (5 mL, 6 mL) was added $SnCl_4$ or $TiCl_4$ (25 μL, 26 μL) at room temperature. In the case of $SnCl_4$, after 3 days, the reaction was stopped and was worked up by the common procedure. Silica gel column chromatography of the products (i.d. 10 × 150 mm, C_6H_6–EtOAc, 4:1) gave syrupy 1,6-anhydro-2,3-di-*O*-benzyl-β-D-altropyranose (13 mg, 33%) [R_f 0.20 ($CHCl_3$–EtOAc, 5:1); $[\alpha]^{23}_D$ −78.9° (*c* 0.13, $CHCl_3$); IR (film) 3400, 740, 700 cm^{-1}; ^1H NMR δ ppm 7.35 (10 H, m, 2 C_6H_5), 5.370 (1 H, d, $J_{1,2}$ = 1.5 Hz, H-1), 4.723 (2 H, s, $PhCH_2O$), 4.711 (2 H, s, $PhCH_2O$), 4.635 (1 H, m, H-5), 3.50–3.95 (5 H, m, H-2,3,4,6_{endo},6_{exo}), 2.3 (1 H, b s, OH)] and the starting material (7 mg, 14%).

The product was benzoylated (BzCl/Pyr) for structural analysis. After preparative TLC ($CHCl_3$), 1,6-anhydro-4-*O*-benzoyl-2,3-di-*O*-benzyl-β-D-altropyranose was obtained: ^1H NMR δ ppm 8.1 (2 H, m, *o*-2H of C_6H_5CO), 7.2–7.7 (13 H, m, *m*-, *p*-3H of C_6H_5CO, 2 C_6H_5), 5.456 (2 H, m, H-1,4), 4.50–4.92 (5 H, (4.859, 4.690, AB q, J_{HCH} = 12.0 Hz, $PhCH_2O$, 4.732, 4.559, AB q, J_{HCH} = 12.0 Hz, $PhCH_2O$, 4.7, H-5)), 3.70–4.05 (4 H, (3.935, dd, $J_{3,4}$ = 4.4, $J_{2,3}$ = 8.8 Hz, H-3), H-2,6_{endo},6_{exo}).

In the case of $TiCl_4$, after 3 days, the reaction was stopped and was worked up by the common procedure. Silica gel column chromatography (i.d. 10 × 150 mm, EtOAc) gave 1,6-anhydro-2-*O*-benzyl-β-D-altropyranose (24 mg, 40%): R_f 0.20 (EtOAc); $[\alpha]^{23}_D$ −130° (*c* 0.03, $CHCl_3$); ^1H NMR δ ppm 7.4 (5 H, m, C_6H_5), 5.394 (1 H, d, $J_{1,2}$ = 1.7 Hz, H-1), 4.738 (2 H, s, $PhCH_2O$), 4.62 (1 H, m, H-5), 3.65–3.95 (4 H, m, H-3,4,6_{endo},6_{exo}), 3.428 (1 H, dd, $J_{1,2}$ = 1.7, $J_{2,3}$ = 8.3 Hz, H-2), 2.32 (2 H, b s, 2 OH).

Reaction of 1,6-Anhydro-2,3,4-tri-*O*-benzyl-β-D-galactopyranose (15) with $SnCl_4$ or $TiCl_4$. To a solution of **15**[19] (160 mg, 200 mg) in dry CH_2Cl_2 (15 mL, 20 mL) was added $SnCl_4$ or $TiCl_4$ (40 μL, 50 μL) at room temperature. In the case of $SnCl_4$, after 10 min, no reaction was observed and after 24 h many spots including starting material were detected by TLC ($CHCl_3$–EtOAc, 5:1). After 24 h, the reaction was worked up by the common procedure. Chromatographic purification of the products (i.d. 22 × 200 mm, C_6H_6–EtOAc, 9:1) gave syrupy 1,6-anhydro-2,4-di-*O*-benzyl-β-D-galactopyranose (15 mg, 10%); R_f 0.34 ($CHCl_3$–EtOAc, 5:1); $[\alpha]^{23}_D$ −37.0° (*c* 0.27, $CHCl_3$); IR (film) 3400, 740, 700 cm^{-1}; ^1H NMR δ ppm 7.3–7.4 (10 H, m, 2 C_6H_5), 5.377 (1 H, b t, $J_{1,2}$ = 1.5, $J_{1,3}$ = 1.5 Hz, H-1), 4.5–4.8 (4 H, (4.612, 4.717, AB q, J_{HCH} = 10.5 Hz, $PhCH_2O$, 4.538, 4.691, AB q, J_{HCH} = 12.2 Hz, $PhCH_2O$), 4.414 (1 H, b t, $J_{4,5}$ = 4.4, $J_{5,6_{exo}}$ = 5.6 Hz, H-5), 4.268 (1 H, dd, $J_{5,6_{endo}}$ < 1.0, $J_{6_{endo},6_{exo}}$ = 7.6 Hz, H-6_{endo}), 4.100 (1 H, m, H-3), 3.870 (1 H, b t, $J_{3,4}$ = 4.6, $J_{4,5}$ = 4.4 Hz, H-4), 3.55–3.70 (2 H, (3.605, m, $J_{4,6_{exo}}$ = 0.7, $J_{5,6_{exo}}$ = 5.6 Hz, H-6_{exo}, 3.571, t, $J_{1,2}$ = 1.5, $J_{2,3}$ = 1.5 Hz, H-2)). The stating material **15** (51 mg 31%) was recovered.

The product was benzoylated (BzCl/Pyr) to give 1,6-anhydro-3-*O*-benzoyl-2,4-di-*O*-benzyl-β-D-galactopyranose: ^1H NMR δ ppm 8.07 (2 H, m, *o*-2H of C_6H_5CO), 7.2–7.7 (13 H, m, *m*-, *p*-3H of C_6H_5CO, 2 C_6H_5), 5.648 (1 H, m, H-3), 5.363 (1 H, t, $J_{1,2}$ = 1.5, $J_{1,3}$ = 1.5 Hz, H-1), 4.40–4.95 (6 H, (4.853, 4.653, AB q, J_{HCH} = 11.2 Hz, $PhCH_2O$, 4.466, 4.653, AB q, J_{HCH} = 11.2 Hz, $PhCH_2O$, 4.45, m, H-5,6_{endo})), 4.059 (1 H, b t, $J_{3,4}$ = 4.4, $J_{4,5}$ = 4.4, $J_{4,6_{exo}}$ < 1.0 Hz, H-4), 3.733 (1 H, ddd, $J_{4,6_{exo}}$ < 1.0, $J_{5,6_{exo}}$ = 4.4, $J_{6_{endo},6_{exo}}$ = 7.7 Hz, H-6_{exo}), 3.559 (1 H, b t, $J_{1,2}$ = 1.5, $J_{2,3}$ = 1.5 Hz, H-2).

In the case of $TiCl_4$, the reaction was stopped after 13.5 h. After chromatographic purification (i.d. 18 × 360 mm, $CHCl_3$), 1,6-anhydro-2,4-di-*O*-benzyl-β-D-galactopyranose (7 mg, 4%) (see the reaction **15** with $SnCl_4$) and the stating material (160 mg, 80%) were recovered. The structures of other minor products were not studied.

Reaction of 1,6-Anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose (16) with $SnCl_4$ or $TiCl_4$. To a solution of **16**[20] (106 mg, 102 mg) in dry CH_2Cl_2 (10 mL, 10 mL) was added $SnCl_4$ or

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$TiCl_4$ (30 μL, 28 μL) at room temperature. After 16 h (8 h), the reaction was stopped and was worked up by the common procedure. The resulting syrup was purified by silica gel column chromatography (i.d. 15 × 245 mm, $CHCl_3$–EtOAc, 9:1) to give a mixture of 1,6-anhydro-3,4-di-*O*-benzyl-β-D-glucopyranose (**17**) and 1,6-anhydro-2,3-di-*O*-benzyl-β-D-glucopyranose (**18**) (40:60) (80 mg, 95%): R_f 0.47 ($CHCl_3$–EtOAc, 9:1); $[\alpha]^{23}_D$ −43.0° (*c* 0.5, $CHCl_3$); IR (film) 3400, 735, 695 cm^{-1}; ^1H NMR δ ppm 7.33 (10 H, b s, 2 C_6H_5), 5.446 (1 H, b s, H-1), 4.4–4.7 (5 H, (4.529, s, $PhCH_2O$, 4.548, 4.401, AB q, J_{HCH} = 12.0 Hz, $PhCH_2O$, 4.468, 4.643, AB q, J_{HCH} = 12.2 Hz, $PhCH_2O$), H-5), 4.10–4.24 (1 H, (4.221, dd, $J_{5,6_{endo}}$ = 1.0, $J_{6_{endo},6_{exo}}$ = 6.8 Hz, H-6_{endo}, 4.152, dd, $J_{5,6_{endo}}$ = 1.0, $J_{6_{endo},6_{exo}}$ = 6.8 Hz, H-6_{endo})), 3.60–3.79 (3 H, (3.724, dd, $J_{5,6_{endo}}$ = 5.9, $J_{6_{endo},6_{exo}}$ = 7.1 Hz, H-6_{exo}, 3.712, dd, $J_{5,6_{exo}}$ = 5.9, $J_{6_{endo},6_{exo}}$ = 7.1 Hz, H-6_{exo}, 3.635, m, H-3, H-2 of **17**, H-4 of **18**)), 3.375 (1 H, m, H-2 of **18**, H-4 of **17**), 2.4 (1 H, b s, 2-OH of **17**, 4-OH of **18**). Anal. C, 70.20; H, 6.41. Calcd: C, 70.15; H, 6.47.

In the case of $TiCl_4$, a mixture of **17** and **18** (45:55) was obtained by the similar procedure of purification described above (77 mg, 95%): $[\alpha]^{23}_D$ −45.2° (*c* 0.6, $CHCl_3$); ^1H NMR was similar to that of the products in the case of $SnCl_4$.

These mixtures were benzoylated (BzCl/Pyr) to give a mixture of 1,6-anhydro-4-*O*-benzoyl-2,3-di-*O*-benzyl-β-D-glucopyranose (**20**) and 1,6-anhydro-2-*O*-benzoyl-3,4-di-*O*-benzyl-β-D-glucopyranose (**19**), which could not be separated from each other by silica gel column chromatography: ^1H NMR data of the mixture obtained from the products by treatment with $SnCl_4$ δ ppm 8.1 (2 H, m, *o*-2H of C_6H_5CO), 7.2–7.6 (13 H, m, *m*-, *p*-3H of C_6H_5CO, 2 C_6H_5), 5.583 (0.4 H, b s, H-1 of **19**), 5.539 (0.6 H, b s, H-1 of **20**), 5.010 (1 H, m, H-2 of **19**, H-4 of **20**), 4.40–4.91 (5 H, (4.589, 4.844, AB q, J_{HCH} = 12.0 Hz, $PhCH_2O$, 4.763, 4.602, AB q, J_{HCH} = 12.0 Hz, $PhCH_2O$, 4.478, s, $PhCH_2O$, 4.458, s, $PhCH_2O$), H-5), 4.05–4.25 (1 H, (4.202, dd, $J_{5,6_{endo}}$ = 1.0, $J_{6_{endo},6_{exo}}$ = 7.3 Hz, H-6_{endo}, 4.127, dd, $J_{5,6_{endo}}$ = 1.0, $J_{6_{endo},6_{exo}}$ = 7.3 Hz, H-6_{endo})), 3.65–3.85 (3 H, (3.778, dd, $J_{5,6_{exo}}$ = 5.6, $J_{6_{endo},6_{exo}}$ = 7.3 Hz, H-6_{exo}, 3.760, dd, $J_{5,6_{exo}}$ = 5.6, $J_{6_{endo},6_{exo}}$ = 7.3 Hz, H-6_{exo}, 3.698, m, H-4 of **19**, H-2 of **20**)). The ^1H NMR spectrum of the mixture obtained from the products by the treatment with $TiCl_4$ was similar to that of the products in the case of $TiCl_4$ except for the signals at 5.586 ppm (0.45 H, b s, H-1) of **19** and 5.539 ppm (0.55 H, b s, H-1 of **20**).

1,6-Anhydro-2-azido-3,4-di-*O*-benzyl-2-deoxy-β-D-glucopyranose (21). To a stirred solution of **4** (600 mg) in dry CH_2Cl_2 (3 mL) was added a solution of trifluoromethanesulfonic anhydride (0.6 mL) and pyridine (0.35 mL) in dry CH_2Cl_2 (13 mL) at −10 °C. After 2 h at 0 °C, the reaction was stopped by addition of cold, saturated $NaHCO_3$ (15 mL), and the organic layer was washed with water, dried with $MgSO_4$, and concentrated. Pyridine was coevaporated with toluene. The resulting syrup of 1,6-anhydro-3,4-di-*O*-benzyl-2-*O*-[(trifluoromethyl)sulfonyl]-β-D-mannopyranose, which showed a single spot on TLC (R_f 0.73, $CHCl_3$–EtOAc, 9:1), was dissolved with DMF (2 mL) and was added to a suspension of NaN_3 (900 mg) and molecular sieves (4A) in DMF (6 mL). The suspension was vigorously stirred overnight at room temperature. The insoluble materials were filtered off, and CH_2Cl_2 (50 mL) was added to the filtrate, which was washed with water (50 mL × 2). The organic layer was dried with $MgSO_4$ and concentrated to a syrup, which was purified by silica gel column chromatography (i.d. 25 × 100 mm, $CHCl_3$) to give **21** (510 mg, 79%): R_f 0.72 ($CHCl_3$–EtOAc, 9:1); $[\alpha]^{23}_D$ +37.8° (*c* 0.34, $CHCl_3$) [lit.[21] $[\alpha]^{20}_D$ +37° (*c* 1, $CHCl_3$)]; IR (film) 2100, 740, 700 cm^{-1}; ^1H NMR δ ppm 7.33 (10 H, b s, 2 C_6H_5), 5.485 (1 H, b s, H-1), 4.4–4.7 (5 H, m, 2 $PhCH_2O$, H-5), 4.006 (1 H, dd, $J_{5,6_{endo}}$ = 0.9 Hz, $J_{6_{endo},6_{exo}}$ = 7.4 Hz, H-6_{endo}), 3.708 (1 H, dd, $J_{5,6_{exo}}$ = 6.1 Hz, $J_{6_{exo},6_{endo}}$ = 7.4 Hz, H-6_{exo}), ~3.66 (1 H, b s, H-3), 3.375 (1 H, b s, H-4), 3.272 (1 H, b s, H-2). Anal. C, 65.35; H, 5.70; N, 11.51. Calcd: C, 65.38; H, 5.76; N, 10.43.

Reaction of 1,6-Anhydro-2-azido-3,4-di-*O*-benzyl-2-deoxy-β-D-glucopyranose (21) with $TiCl_4$ or $SnCl_4$. To a solution of **21** (600 mL) in dry CH_2Cl_2 (30 mL) was added $TiCl_4$ (0.2 mL) at room temperature. After 20 min, a spot of starting material (R_f 0.72) had completely disappeared, and a new single spot (R_f 0.27) was detected by TLC ($CHCl_3$–EtOAc, 9:1). The solution was poured into ice–water (50 mL), and the organic layer was successively washed with saturated $NaHCO_3$ and water. The solution was dried with $MgSO_4$ and was concentrated to a syrup, which was purified by silica gel column chromatography (i.d. 10 × 150 mm, $CHCl_3$–EtOAc, 9:1) to give 1,6-anhydro-2-azido-3-*O*-benzyl-2-deoxy-β-D-glucopyranose (**22**)[22] (400 mg, 88%): R_f 0.26 ($CHCl_3$–EtOAc, 9:1); mp 48–49.5 °C; $[\alpha]^{23}_D$ −6.3° (*c* 0.2, $CHCl_3$) [lit.[22] $[\alpha]^{22}_D$ −5° (*c* 1.0, $CHCl_3$)]; IR (film) 3450, 2100, 740, 700 cm^{-1}; ^1H NMR δ ppm 7.34 (5 H, b s, C_6H_5), 5.449 (1 H, b s, H-1), 4.622 (2 H, s, $PhCH_2O$), 4.535 (1 H, b d, $J_{5,6_{exo}}$ = 5.8 Hz, H-5), 4.232 (1 H, dd, $J_{5,6_{endo}}$ < 1, $J_{6_{endo},6_{exo}}$ = 7.1 Hz, H-6_{endo}), 3.45–3.85 (4 H, (3.770, dd, $J_{5,6_{exo}}$ = 5.8, $J_{6_{endo},6_{exo}}$ = 7.1 Hz, H-6_{exo}, 3.71, b d, $J_{4,OH}$ = 10 Hz, H-4, 3.598, m, H-3, 3.519, b s, H-2)), 2.679 (1 H, b d, $J_{4,OH}$ = 10.3 Hz, 4-OH). Anal. C, 56.45; H, 5.47; N, 15.06. Calcd: C, 56.31; H, 5.45; N, 15.15.

Similar reaction with $SnCl_4$ instead of $TiCl_4$ proceeded very slowly; no reaction was observed after 0.5 h. A spot of **22** was slightly detected by TLC after 7 h. The starting material was not consumed even half after 2 days judged by TLC.

Compound **22** (7 mg) was benzoylated (BzCl/Pyr) to give 1,6-anhydro-2-azido-4-*O*-benzoyl-3-*O*-benzyl-2-deoxy-β-D-glucopyranose (9 mg, 93%): R_f 0.23 ($CHCl_3$); mp 118–121 °C; $[\alpha]^{23}_D$ −37.6° (*c* 0.1, $CHCl_3$); IR (film) 2100, 1710, 735, 710, 695 cm^{-1}; ^1H NMR δ ppm 8.1 (2 H, m, *o*-2H of C_6H_5CO), 7.3–7.8 (8 H, m, *m*-, *p*-3H of C_6H_5CO, C_6H_5), 5.583 (1 H, b s, H-1), 5.054 (1 H, b s, H-4), 4.62–4.89 (3 H, (4.825, 4.687, AB q, J_{HCH} = 12.0 Hz, $PhCH_2O$, 4.73, H-5)), 4.272 (1 H, dd, $J_{5,6_{endo}}$ = 1.0, $J_{6_{endo},6_{exo}}$ = 7.6 Hz, H-6_{endo}), 3.73–3.91 (2 H, (3.835, dd, $J_{5,6_{exo}}$ = 5.9, $J_{6_{endo},6_{exo}}$ = 7.5 Hz, H-6_{exo}, 3.752, m, H-3)), 3.350 (1 H, b s, H-2).

Reaction of 1,2,3-Tris(benzyloxy)propane (23) with $SnCl_4$ or $TiCl_4$. Compound **23** was prepared by benzylation (NaH, BnCl/DMF) of glycerol in 81% yield: R_f 0.66 (C_6H_6–EtOAc, 4:1); IR (film) 700, 740 cm^{-1}; ^1H NMR δ ppm 7.3 (15 H, s, 3 C_6H_5), 4.698 (2 H, s, 2-OCH_2Ph), 4.537 (4 H, s, 1,3-OCH_2Ph), 3.7–3.95 (1 H, m, H-2), 3.55–3.7 (4 H, m, H-1a,1b,3a,3b).

To a solution of **23** (160 mg) in dry CH_2Cl_2 (10 mL) was added 56 μL (53 μL) of $SnCl_4$ ($TiCl_4$) at room temperature. After 40 min, the reactions were worked up by the common procedure followed by chromatographic purification (silica gel, i.d. 20 × 150 mm, C_6H_6–EtOAc, 4:1) to give oily 1,3-bis(benzyloxy)-2-hydroxypropane (**25**) (100 mg, 80 mg, 86%, 68%): R_f 0.45 (C_6H_6–EtOAc, 4:1); ^1H NMR δ ppm 7.3 (10 H, b s, 2 C_6H_5), 4.546 (4 H, s, 2 $PhCH_2O$), 4.005 (1 H, m, H-3), 3.55 (4 H, m, H-1a,1b,3a,3b). Anal. C, 75.02; H, 7.24. Calcd: C, 74.97; H, 7.40.

Reaction of 1,2-Bis(benzyloxy)ethane (24) with $SnCl_4$ or $TiCl_4$. Compound **24** was prepared by benzylation (NaH, BnCl/DMF) of ethylene glycol in 79% yield: R_f 0.95 (C_6H_6–EtOAc, 4:1); IR (film) 700, 740 cm^{-1}; ^1H NMR δ ppm 7.33 (10 H, m, 2 C_6H_5), 4.576 (4 H, s, 2 $PhCH_2O$), 3.657 (4 H, s, $O(CH_2)_2O$). To a solution of **24** (110 mg) in dry CH_2Cl_2 (10 mL) was added 58 μL (55 μL) of $SnCl_4$ ($TiCl_4$) at room temperature. After 1 h, no reaction were observed in both cases, as judged by TLC and ^1H NMR analyses.

Reaction of 1,2,3,4,5,6-Hexa-*O*-benzyl-D-mannitol (26) with $SnCl_4$ or $TiCl_4$. Compound **26** was prepared by benzylation (NaH, BnCl/DMF) of D-mannitol in 82% yield: R_f 0.90 (C_6H_6–EtOAc, 20:1); mp 43.0–44.5 °C; $[\alpha]^{23}_D$ +74.1° (*c* 2.0, $CHCl_3$); ^1H NMR δ ppm 7.2–7.3 (30 H, m, 6 C_6H_5), 4.4–4.8 (12 H, (4.705, 4.570, AB q, J_{HCH} = 11.5 Hz, 2 $PhCH_2O$, 4.475, s, 2 $PhCH_2O$, 4.656, 4.415 AB q, J_{HCH} = 12.0 Hz, 2 $PhCH_2O$)), 3.6–4.1 (8 H, m, H-1a,1b,2,3,4,5,6a,6b).

(1) To a solution of **26** (200 mg) in dry CH_2Cl_2 (10 mL) was added $SnCl_4$ or $TiCl_4$ (35 μL, 35 μL) at room temperature. After 7 h or 45 min, the reaction was stopped and was worked up by the common procedure. In the case of $SnCl_4$, the purification of the products by silica gel column chromatography (i.d. 20 × 200 mm, C_6H_6–EtOAc, 20:1) gave 1,2,3,5,6-penta-*O*-benzyl-D-mannitol (**27**) (100 mg, 57%) [R_f 0.48 (C_6H_6–EtOAc, 20:1); $[\alpha]^{23}_D$ −23.0° (*c* 0.41, $CHCl_3$); ^1H NMR δ ppm 7.2–7.4 (25 H, m, 5 C_6H_5), 4.2–4.9 (10 H, (4.733, 4.598, AB q, J_{HCH} = 11.5 Hz, $PhCH_2O$, 4.564, s, $PhCH_2O$, 4.520, s, $PhCH_2O$, 4.578, 4.352, AB q, J_{HCH} = 11.5 Hz, $PhCH_2O$, 4.733, 4.331, AB q, J_{HCH} = 11.7 Hz, $PhCH_2O$)), 3.6–4.1 (8 H, m, H-1a,1b,2,3,4,5,6a,6b), 3.148, (1 H, d, $J_{4,OH}$ = 5.6 Hz, 4-OH)] and 1,2,3,4,6-penta-*O*-benzyl-D-mannitol (**28**) (40 mg, 23%):

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R_f 0.59 (C_6H_6–EtOAc, 20:1); $[\alpha]^{23}_D$ −12.8° (*c* 0.3, $CHCl_3$), ^1H NMR δ ppm 7.0–7.5 (25 H, m, 5 C_6H_5), 4.1–4.8 (10 H, m, 5 $PhCH_2O$), 3.5–4.1 (8 H, H-1a,1b,2,3,4,5,6a,6b), 3.15 (1 H, b s, 5-OH). In the case of $TiCl_4$, **27** and **28** were obtained in 65% and 19% yield, respectively, and the starting material **26** was recovered in 12% yield.

Compounds **27** and **28** were benzoylated (BzCl/Pyr) to give 3-*O*-benzoyl-1,2,4,5,6-penta-*O*-benzyl-D-mannitol [$[\alpha]^{23}_D$ +11.5° (*c* 0.26, $CHCl_3$); ^1H NMR δ ppm 8.037 (2 H, m, *o*-2H of C_6H_5CO), 7.0–7.6 (28 H, m, *m*-, *p*-3H of C_6H_5CO, 5 C_6H_5), 5.778 (1 H, dd, $J_{2,3}$ = 6.1, $J_{3,4}$ = 3.9 Hz, H-3), 4.3–4.8 (10 H, m, 5 $PhCH_2O$), 4.189 (1 H, t, $J_{3,4} = J_{4,5} \sim 4$ Hz, H-4), 4.055 (1 H, m, H-2), 3.5–4.0 (5 H, m, H-1a,1b,5,6a,6b)] and 2-*O*-benzoyl-1,3,4,5,6-penta-*O*-benzyl-D-mannitol: $[\alpha]^{23}_D$ +25.2° (*c* 2.0, $CHCl_3$); ^1H NMR δ ppm 8.0 (2 H, m, *o*-2H of C_6H_5CO), 7.0–7.6 (23 H, m, *m*-, *p*-3H of C_6H_5CO, 5 C_6H_5), 5.76 (1 H, m, H-2), 3.5–4.8 (17 H, m, 5 $PhCH_2O$, H-1a,1b,3,4,5,6a,6b).

(2) To a solution of **26** (207 mg) in dry CH_2Cl_2 (10 mL) was added $SnCl_4$ (78 μL) at room temperature. After 7 h, the reaction was stopped and was worked up by common procedure. Purification of the products by a silica gel column chromatography (i.d. 15 × 200 mm, C_6H_6–EtOAc, 9:1) gave 1,2,5,6-tetra-*O*-benzyl-D-mannitol (**29**) (54 mg, 35%): R_f 0.22 (C_6H_6–EtOAc, 20:1); $[\alpha]^{23}_D$ −12.4° (*c* 0.83, $CHCl_3$); ^1H NMR δ ppm 7.3 (20 H, m, 4 C_6H_5), 4.5–4.85 (8 H, (4.744, 4.615, AB q, J_{HCH} = 11.5 Hz, $PhCH_2O$, 4.544, s, $PhCH_2O$)), 3.968 (2 H, m, H-3,4), 3.711 (6 H, m, H-1a,1b,2,5,6a,6b), 3.032 (2 H, d, $J_{3,OH} = J_{4,OH}$ = 5.9 Hz, 3-OH, 4-OH).

Compound **29** was benzoylated (BzCl/Pyr) to give 3,4-di-*O*-benzoyl-1,2,5,6-tetra-*O*-benzyl-D-mannitol: $[\alpha]^{23}_D$ +46.1° (*c* 0.28, $CHCl_3$); ^1H NMR δ ppm 8.0 (4 H, m, *o*-2H of 2 C_6H_5CO), 7.2–7.6 (13 H, m, *m*-, *p*-3H of 2 C_6H_5CO, 4 C_6H_5), 5.994 (2 H, m, H-3,4), 4.539 (4 H, s, $PhCH_2O$), 4.466 (4 H, s, $PhCH_2O$), 3.5–4.1 (6 H, (3.96, m, H-2,5, 3.77, m, H-1a,6a, 3.66, m, H-1b,6b)).

Reaction 3,5,6-Tri-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose (30) with $TiCl_4$. Compound **30** was prepared by benzylation (NaH, BnCl/DMF) of 1,2-*O*-isopropyliene-α-D-glucofuranose[23] in 94% yield: R_f 0.79 (C_6H_6–EtOAc, 9:1); $[\alpha]^{23}_D$ −61.8° (*c* 0.3, $CHCl_3$); IR (film) 1380, 1370, 740, 700 cm^{-1}; ^1H NMR δ ppm 7.2–7.4 (15 H, m, 3 C_6H_5), 5.906 (1 H, d, $J_{1,2}$ = 3.7 Hz, H-1), 4.2–4.95 (8 H, (4.830, 4.482, AB q, J_{HCH} = 11.5 Hz, $PhCH_2O$, 4.583, s, $PhCH_2O$, 4.58, H-2, 4.656, 4.472 AB q, J_{HCH} = 11.5 Hz, $PhCH_2O$, 4.308, dd, $J_{3,4}$ = 2.9, $J_{4,5}$ = 9.0 Hz, H-4)), 3.8–4.2 (3 H, (4.118, d, $J_{3,4}$ = 2.9 Hz, H-3, 4.056, m, H-5, 3.91, dd, $J_{5,6a}$ = 1.7, $J_{6a,6b}$ = 10.5 Hz, H-6a)), 3.672 (1 H, dd, $J_{5,6b}$ = 5.61, $J_{6a,6b}$ = 10.5 Hz, H-6b), 1.480 (3 H, s, CH_3 of isopropylidene group), 1.308 (3 H, s, CH_3 of isopropylidene group).

To a solution of **30** (300 mg) and DMF (22 mg) in dry CH_2Cl_2 (15 mL) was added $TiCl_4$ (67 μL) at room temperature. After 8 h, the reaction was stopped and was worked up by the common procedure. The products purified by silica gel column chromatography (i.d. 20 × 220 mm) gave 3,6-di-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose (**31**) (131 mg, 54%): R_f 0.28 (C_6H_6–EtOAc, 9:1); $[\alpha]^{23}_D$ −14.5° (*c* 0.248 $CHCl_3$); IR (film) 3460, 1380, 1370, 740, 700 cm^{-1}; ^1H NMR δ ppm 7.3 (10 H, s, 2 C_6H_5), 5.920 (1 H, d, $J_{1,2}$ = 3.7 Hz, H-1), 4.4–4.8 (5 H, (4.694, 4.537, AB q, $PhCH_2O$, 4.59, H-2, 4.561, s, $PhCH_2O$)), 4.0–4.3 (3 H, m, H-3,4,5), 3.5–3.9 (2 H, m, H-6a, 6b), 3.48 (1 H, b s, 5-OH), 1.485 (3 H, s, CH_3 of isopropylidene group), 1.316 (3 H, s, CH_3 of isopropylidene group). The stating material **30** (70 mg 23%) was recovered.

Compounds **31** was acetylated (Ac_2O/Pyr) to give 5-*O*-acetyl-3,6-di-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose: R_f 0.47 (C_6H_6–EtOAc, 9:1); $[\alpha]^{23}_D$ +21.0 (*c* 0.2, $CHCl_3$); ^1H NMR δ ppm 7.3 (10 H, m, 2 C_6H_5), 5.906 (1 H, d, $J_{1,2}$ = 3.7 Hz, H-1), 5.329 (1 H, ddd, $J_{4,5}$ = 8.8, $J_{5,6a}$ = 2.5, $J_{5,6b}$ = 4.4 Hz, H-5), 4.3–4.7 (6 H, (4.608, d, $J_{1,2}$ = 3.7 Hz, H-2, 4.624, 4.427, AB q, J_{HCH} = 11.5 Hz, $PhCH_2O$, 4.56, 4.44, AB q, J_{HCH} = 12 Hz, $PhCH_2O$, 4.477, dd, $J_{3,4}$ = 3.2, $J_{4,5}$ = 8.8 Hz, H-4), 3.959 (1 H, d, $J_{3,4}$ = 3.2 Hz, H-3), 3.6–4.0 (2 H, 3.877, dd, $J_{6a,6b}$ = 11.2, $J_{5,6a}$ = 2.5 Hz, H-6a, 3.697, dd, $J_{6a,6b}$ = 11.2, $J_{5,6b}$ = 4.5 Hz, H-6b)), 1.931 (3 H, s, CH_3CO), 1.500 (3 H, s, CH_3 of isopropylidene group), 1.326 (3 H, s, CH_3 of isopropylidene group).

NMR of the Tin or Titanium Complexes. ^1H NMR. To a solutions of **1**, **8**, and **9** (20, 31, 31 mg) in $CDCl_3$ (1 mL) in NMR tube (i.d. 5 mm) was added $SnCl_4$ (6, 10, 10 μL) under a dry nitrogen atmosphere, and the tubes were sealed immediately. After 1 h, ^1H NMR spectra were measured at 100 MHz at 22 °C. The spectra of **1′** is illustrated in Figure 1. **8′**: δ ppm 7.4 (m, C_6H_5 of 4-*O*-benzyl group and benzylchloride), 5.581 6(b s, H-1), 4.794, 4.632 (AB q, J_{HCH} = 12.2 Hz, 4-OCH_2Ph), 4.5–4.78 (m, H-5,6_{endo}), 4.422 (d, $J_{1,2}$ = 1.7, $J_{2,3}$ = 5.9 Hz, H-2), 3.861 (dd, $J_{5,6_{exo}}$ = 5.1, $J_{6_{endo},6_{exo}}$ = 9 Hz, H-6_{exo}), 3.6–3.8 (m, H-3,4), 3.620 (s, OCH_3). **9**: δ ppm 7.5 (m, C_6H_5 of 3-*O*-benzyl group and benzylchloride), 5.574 (b s, $J_{1,2} = J_{1,3}$ = 1.7 Hz, H-1), 5.611, 4.770 (AB q, J_{HCH} = 12.2 Hz, 3-OCH_2Ph), 4.668 (d, $J_{6_{endo},6_{exo}}$ = 8.8 Hz, H-6_{endo}), 4.591 (s, $PhCH_2Cl$), ~4.55 (m, H-5), 4.385 (dd, $J_{1,2}$ = 1.7, $J_{2,3}$ = 6.3 Hz, H-2), 4.018 (m, $J_{1,3} = J_{3,4} = J_{3,5}$ = 1.8, $J_{2,3}$ = 6.3 Hz, H-3), 3.883 (dd, $J_{5,6_{exo}}$ = 5, $J_{6_{endo},6_{exo}}$ = 8.8 Hz, H-6_{exo}), 2.995 (s, OCH_3), 2.639 (b s, $J_{3,4} = J_{4,5}$ = 1.8 Hz, H-4).

To a solution of **24** (5 mg, 11 mg) in $CDCl_3$ (0.7 mL, 0.6 mL) was added $SnCl_4$ or $TiCl_4$ (5 μL, 5 μL) under a nitrogen atmosphere. After 0.5 h ^1H NMR spectra were measured. **24′**: δ ppm 7.3 (10 H, b s, 2 C_6H_5), 5.289 (4 H, s, 2 $PhCH_2O$), 3.985 (4 H, s, CH_2CH_2). **24″**: δ ppm 7.3 (10 H, b s, 2 C_6H_5), 5.428 (4 H, b s, 2 $PhCH_2O$), 4.046 (4 H, b s, CH_2CH_2). To a solution of **23** (8 mg, 9 mg) in $CDCl_3$ (5 mL) was added $SnCl_4$ or $TiCl_4$ (3 μL). After 0.5 h ^1H NMR were measured (see Figure 3).

^{13}C NMR. To a solution of **1** (60 mg, 340 mg) in $CDCl_3$ (0.4 mL, 2.6 mL) in NMR tube (i.d. 5 mm, i.d. 10 mm) was added $SnCl_4$ (16 μL, 95 μL) under a nitrogen atmosphere. After 1 h, ^{13}C NMR (complete proton decoupling, selective proton decoupling, INEPT) were measured at 25 and 50 MHz, respectively.

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