all atoms except hydrogen. Hydrogen atoms were included with isotropic temperature factors at calculated positions.

Acknowledgment. The FORTICON8 and MOPAC computer programs were made available by R. Hoffmann and J. J. P. Stewart, respectively, through the Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN. GIVEIS was kindly furnished by S. Hagstrom, QCPE, Indiana University, Bloomington, IN.

Supplementary Material Available: Tables VI–IX, bond lengths, bond angles, anisotropic temperature factors, and hydrogen atom coordinates, respectively (3 pages). Ordering information is given on any current masthead page.

Disaccharide-Derived 2-Oxo- and 2-Oximinoglycosyl Bromides: Novel, Conveniently Accessible Building Blocks for the Expedient Construction of Oligosaccharides with α-D-Glucosamine, β-D-Mannose, and β-D-Mannosamine as Constituent Sugars[1]

Frieder W. Lichtenthaler,* Eisuke Kaji, and Sabine Weprek

Institut für Organische Chemie der Technischen Hochschule Darmstadt, D-6100 Darmstadt, West Germany

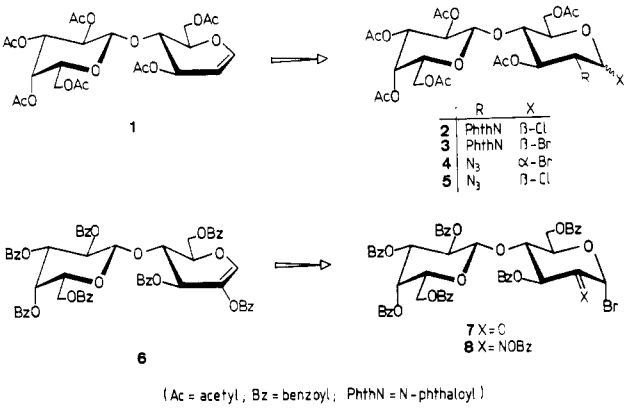
Received November 21, 1984

A concise, practical, large-scale adaptable approach has been developed for the transformation of bulk disaccharides such as lactose, maltose, and cellobiose into disaccharide building blocks suitably functionalized for direct glycobiosylation, i.e., benzoylated *glycosyl-(1→4)-glycosulosyl bromides* (**7**, **20**) and *glycosyl-(1→4)-2-benzooximinoglycosyl bromides* (**8**, **15**, **21**, and **22**). The methodology elaborated starts with the conversion of the basic disaccharides by benzoylation, HBr treatment, and dehydrobromination into their 2-hydroxyglycal esters **6**, **17a**, and **17b**; it is followed either by NBS-promoted methanolysis that effectively (85–90%) delivers the hexa-*O*-benzoyl-α-D-glycobiosulosyl bromides **7** and **20**, or, alternatively, by the high-yielding (70–75%) three-step sequence hydroxylaminolysis → benzoylation → photobromination, which provides the lactose-, maltose-, and cellobiose-derived heptabenzoyl-α-D-oximinoglycosyl bromides **8**, **21**, and **22**. The broad utility of these novel disaccharide building blocks with a nonparticipating group next to the anomeric center resides in the ease and uniformity with which stereocontrol over glycosidations can be effected: silver carbonate induced alcoholyses with simple primary and secondary hydroxyl components exclusively provide the β-glycosidulose **29** or its oximes (**24–26**), while the same reaction promoted with *s*-collidine in dioxane delivers the α-oximino glycosides **32–35** with high α-selectivity. In the disaccharides thus obtained reduction of the 2-oxo ($NaBH_4$) and 2-benzoyloximino functions (BH_3/THF) proceed with complete stereoanomeric control, hydride addition from the side opposite to the anomeric substituent converting α-anomers into α-D-glucosamine-containing disaccharides, e.g., α-D-lactosaminides **36–38**, while β-anomers as cleanly elaborate products with β-D-mannose (**30**) and β-D-mannosamine residues (**27**, **28**). Thus, the disaccharide building blocks newly introduced here not only provide an effective means for the attachment of α-linked lactosamine, maltosamine, and cellobiosamine units onto a given sugar hydroxyl but, moreover, are particularly serviceable for the methodologically more unique annelation of glycosyl-(1→4)-β-D-mannose and glycosyl-(1→4)-β-D-mannosamine blocks.

Oligosaccharides composed of more than one type of sugar unit such as the human blood group determinantes and the bacterial antigens are major carriers of biological information[2] which necessitates their regio- and stereocontrolled synthesis on a preparative scale. The impressive advances made toward this end within the past decade[3] usually comprised the stepwise construction of oligosaccharides from suitably blocked, anomerically activated monosaccharide components resulting in elongation of the saccharide chain by one sugar unit; alternately, if a disaccharide derivative was used for extension, it was synthesized a priori from the respective monosaccharide components.[3]

Considerably less attention has been given to approaches that explicitly utilize the synthetic potential inherent in the common, readily accessible disaccharides, when suitably protected and anomerically activated lactose, maltose, and cellobiose, for example, represent disaccharide building blocks with useful glycobiosylation capacity. First examples of monosaccharide glycobiosylations with simple peracylated disaccharide halogenoses date back to the thirties[4–6]—with moderate yields and questionable anom-

Scheme I



(1) This paper is dedicated to Professor R. U. Lemieux in appreciation of his pioneering contributions to carbohydrate chemistry in general and to the synthesis of oligosaccharides in particular, on the occasion of his 65th birthday.

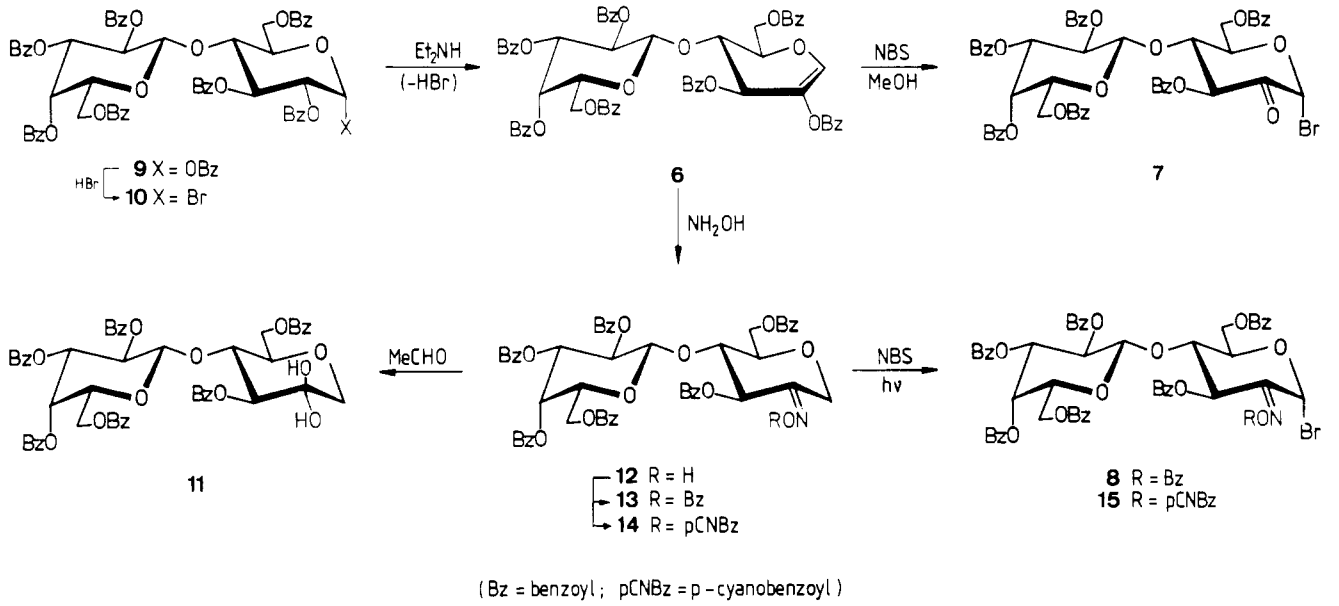
(2) Montreuil, J. *Adv. Carbohydr. Chem. Biochem.* **1980**, *37*, 157. Jennings, H. J. *Ibid.* **1983**, *41*, 155.

(3) For pertinent accounts of this development, see: Lemieux, R. U. *Chem. Soc. Rev.* **1978**, *7*, 423. Bochkov, A. F.; Zaikov, G. E. "Chemistry of the *O*-Glycosidic Bond: Formation and Cleavage"; Pergamon: Oxford, 1979; pp 80–153. Paulsen, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 155. Nashed, M. A.; Anderson, L. A. *J. Am. Chem. Soc.* **1982**, *104*, 7282.

(4) Helferich, B.; Schäfer, W. *Liebigs Ann. Chem.* **1926**, *450*, 229. Helferich, B.; Bredereck, H. *Ibid.* **1928**, *465*, 166.

0022-3263/85/1950-3505$01.50/0

Scheme II



eric purity of the products—and even today hepta-acetylcellobiosyl bromide is occasionally used for this purpose.[7] Nonetheless, these disaccharide building blocks have not acquired major importance due to the fact that they do not provide an entry in biologically relevant oligosaccharides with, e.g., amino sugar units or β-D-mannose residues.

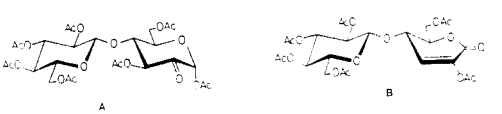
The very few disaccharide building blocks significant in this context appear to be the lactose-derived glycosyl halides **2**–**5**[8-11] with which lactosamine units may be introduced (Scheme I). Their access from the parent lactose, though, is not without preparative problems, since the conversion of the long-known[12] hexaacetyllactal **1** into **2**,[8] **3**,[9] **4**,[10] and **5**[11] via the nitroso halogenide procedure or the azidonitrate method requires up to eight steps and the costly separation of side products by fractional crystallization and/or tedious chromatography such that—aside a fortuitous case (26% for **1** → **5**)—overall yields at best average 15%.[13]

Obviously, new synthetic methodologies need to be developed for the transformation of any of the common, commercially available disaccharides into *disaccharide building blocks* suitably functionalized for direct *glycobiosylation* in such a way that heterooligosaccharides of biological importance may efficiently be constructed. We here describe a practical, previously unavailable approach to such disaccharide building blocks from lactose, cellobiose, and maltose via their hydroxyglycal esters (e.g., **6**) as principal intermediates; these are subsequently converted into *glycosyl-(1→4)-glycosulosyl bromides* of type **7** by *N*-bromosuccinimide-induced methanolysis,[14] or, alternatively, into *glycosyl-(1-4)-2-oximinoglycosyl bromides* of type **8** by enol ester hydroxylaminolysis,[15] O-benzoylation of the resulting oxime, and photobromination.[16] This paper also gives an assessment of their capabilities for α- and β-selective glycosylation and for stereocontrolled reduction of the oxo and oximino functions.[17]

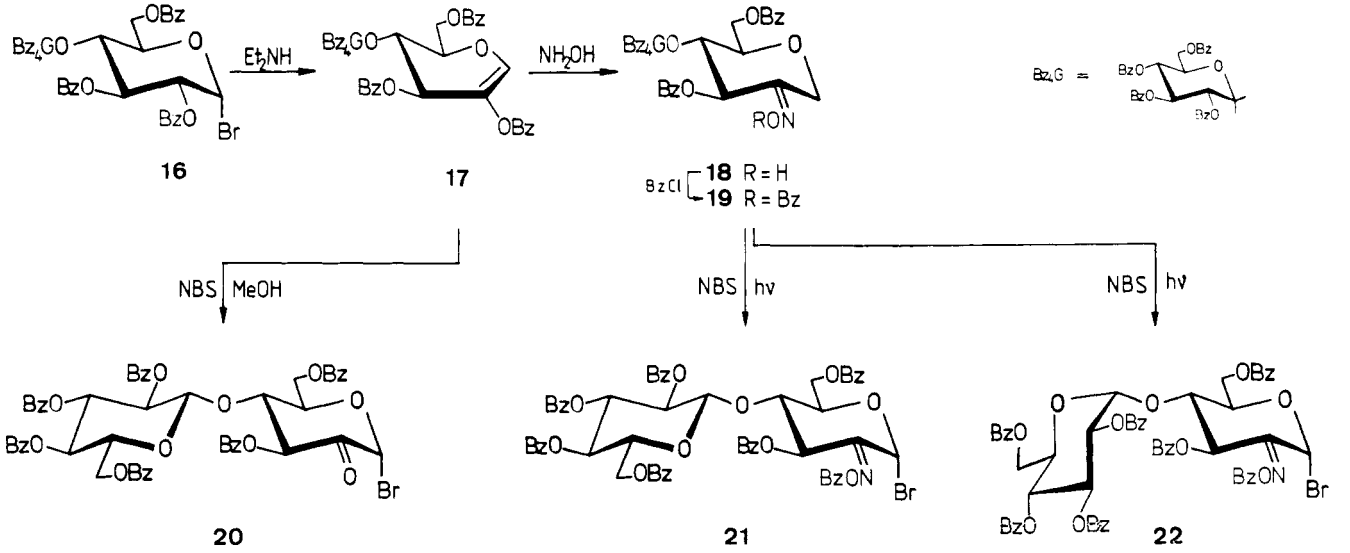
Results and Discussion

Lactose-Derived Building Blocks. Although the hepta-*O*-acetyl derivatives of hydroxylactal (**6**, Ac instead of Bz) and of hydroxycellobial are readily accessible from lactose and cellobiose[18] and, consequently, have been used for generation of a variety of other synthetically useful products,[19] they were considered less suited for the reactions to be performed, particularly for the photobromination step, in which acetoxy groups have been observed to give bromoacetyl and dibromoacetyl derivatives

(5) Freudenberg, K.; Wolf, A.; Knopf, E.; Zaheer, S. *Ber. Dtsch. Chem. Ges.* **1928**, *61*, 1743.
(6) Zemplén, G.; Gerecs, A. *Ber. Dtsch. Chem. Ges.* **1931**, *64*, 2458.
(7) Brundish, D. E.; Baddiley, J. E. *Carbohydr. Res.* **1968**, *8*, 308. Takeo, K.; Yasato, T.; Kuge, T. *Ibid.* **1981**, *93*, 148. Suguwara, F.; Nakayama, H.; Ogawa, T. *Ibid.* **1983**, *123*, C25.
(8) Ponpipom, M. M.; Bugianesi, R. L.; Shen, T. Y. *Tetrahedron Lett.* **1978**, 1717.
(9) Arnarp, J.; Lönngren, J. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2070.
(10) Lemieux, R. U.; Abbas, S. Z.; Burzynska, M. H.; Ratcliffe, R. M. *Can. J. Chem.* **1982**, *60*, 63.
(11) Paulsen, H.; Hölck, J.-P. *Liebigs Ann. Chem.* **1982**, 1121.
(12) Fischer, E.; Thierfelder, H. *Ber. Dtsch. Chem. Ges.* **1894**, *27*, 2031. Fischer, E.; Curme, G. O. *Ibid.* **1914**, *47*, 2047.
(13) Similar detrimental chromatographic separations are required for the conversion of hexaacetylcellobial, via azidonitration and anomeric chlorination, into 2-azido-2-deoxy-α-D-cellobiosyl chloride (21% of crystalline product: Shing, T. K. M.; Perlin, A. S. *Carbohydr. Res.* **1984**, *130*, 65) as well as for the generation of a syrupy, 90% pure 2-azido α-bromide from hexaacetylmaltal (Forsgren, M.; Norberg, T. *Carbohydr. Res.* **1983**, *116*, 39).
(14) Lichtenthaler, F. W.; Cuny, E.; Weprek, S. *Angew. Chem.* **1983**, *95*, 906; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 891.
(15) Lichtenthaler, F. W.; Jarglis, P. *Tetrahedron Lett.* **1980**, *21*, 1425; *Methods Carbohydr. Chem.* **1985**, *9*, in press.
(16) Lichtenthaler, F. W.; Jarglis, P. *Angew. Chem.* **1982**, *94*, 643; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 625. Lichtenthaler, F. W.; Jarglis, P.; Hempe, W. *Liebigs Ann. Chem.* **1983**, 1959.
(17) Essential portions of this work have been presented at the 2nd European Symposium on Carbohydrates, Budapest, August 1983, and the XII International Carbohydrate Symposium, Utrecht, July 1–7, 1984, Abstr. A 2.16.
(18) Maurer, K. *Ber. Dtsch. Chem. Ges.* **1930**, *63*, 25. Rao, D. R.; Lerner, L. M. *Carbohydr. Res.* **1972**, *22*, 345.
(19) See, for example, their ready transformation into glycosyl-glycosuloses of type A by chlorination and hydrolysis [Lichtenthaler, F. W.; Jarglis, P. *Chem. Ber.* **1980**, *113*, 495] or their efficient one-step conversion—by BF_3-catalyzed peroxidation [Jarglis, P.; Lichtenthaler, F. W. *Tetrahedron Lett.* **1982**, *23*, 3781]—into enol lactones of type B, which constitute useful chiral building blocks with suitable functional groups at one side of the pyranoid ring and differentiated *O*-blocking groups—one being the tetraacetylglucosyl moiety—at the other.



Scheme III



as side products.[20] Since benzoyl groups are more prone to yield stable, crystalline products, particularly at the glycosyl halide stage, and are not affected by photobromination conditions, they were used for blocking of sugar as well as of oxime hydroxyl groups.

For the hepta-*O*-benzoyl-2-hydroxy-D-lactal[21] **6** to be secured, the previously described[22] crude octabenzoate mixture of lactose (**9** + β-anomer) was subjected to treatment with hydrogen bromide-acetic acid, subsequent base-promoted dehydrobromination of the heptabenzoyl-α-D-lactosyl bromide (**10**) thus formed providing **6** in an overall yield of 70% for the three steps (Scheme II). Exposure of **6** to a slight excess of *N*-bromosuccinimide and methanol in dichloromethane solution (25 °C, 30 min) smoothly afforded the hexabenzoyl-α-D-lactosulosyl bromide **7** (90%). This remarkably efficient conversion which delivers methyl benzoate as the only other product obviously is initiated by formation of the 2-bromo adduct, is continued by attack of methanol at the 2-benzoyloxy group with liberation of the 2-carbonyl function as well as of bromide ion, and is terminated by α-selective capture of the halide by the oxocarboxonium intermediate thus formed.[14]

The three-step route to the respective *O*-benzoyloxime of lactosulosyl bromide, i.e., **6** → **8**, is as straightforward. In the first place, advantage is taken of the ready hydroxylaminolysis of enol ester functions yielding the respective ketoximes without affecting the primary or secondary ester functions.[15] Accordingly, exposure of **6** to hydroxylamine–pyridine at 70 °C for 20 h delivered the oxime **12** efficiently (89%), which can be deoximated to the parent ulose **11**, constituting, de facto, the hexabenzoate of a 4-O-galactosylated 1,5-anhydro-D-fructose. Isolable as its crystalline monohydrate in high yield (90%), **11**, in turn, may be subjected to photobromination to afford the ulosyl bromide **7** (76%). Hence, the three-step conversion **6** → **12** → **11** → **7** provides an alternative route to ulosyl bromides from hydroxyglycal esters.

For utilization of the oxime **12** in radical brominations, i.e., for making use of the oximino function as the captive ("pull") element of a captodative system,[23] blocking of the oxime hydroxyl group was essential since *N*-bromosuccinimide is known to oxidize ketoximes to bromo–nitroso compounds[24] while bromine in aqueous medium is a mild and efficient means for deoximation.[25] Although simple alkyl ethers of oximes survive NBS treatment[26] as do acetyl groups in the majority of cases,[16,27] the benzoyl ester function appeared to be the group of choice, or, alternatively, the *p*-nitrobenzoyl or *p*-cyanobenzoyl groups. Thus, **12** was converted under standard aroylation conditions into the respective *O*-aroyl oximes **13** and **14** as suitable substrates for the ensuing radical-induced refunctionalization at their proanomeric centers. Indeed, when allowed to react with *N*-bromosuccinimide in refluxing tetrachloromethane under irradiation **13** and **14** quickly elaborated the respective α-bromides **8** and **15**, isolable in crystalline form and in nearly quantitative yields. The emergence of the α-bromides as the exclusive products infers that the intermediate anomeric radical despite its delocalization over four bonds retains the α-selectivity usually shown by nondelocalized anomeric radicals.[28]

Noteworthy are the overall yields with which lactose now is convertible into two crystalline, stable, highly versatile disaccharide building blocks, i.e., 65% for ulosyl bromide **7** over four large-scale adaptable steps and 52% for the six-step sequence to the oximino analogue **8**. Since in either case preparation of the hydroxyglycal ester **6** makes up for the first three steps, which are easily combined into one continuous operation, the acquisition of these building

(20) Blattner, R.; Ferrier, R. J. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1528.

(21) This 2-hydroxyglycal-based term is retained here as a generic designation, in as much as official nomenclature for **6** requires 2,3,6-tri-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-1,5-anhydro-D-*arabino*-hex-1-enitol.

(22) Deferrari, J. O.; Thiel, I. M. E.; Cadenas, R. A. *Carbohydr. Res.* **1973**, *29*, 141.

(23) The ring oxygen provides the dative ("push") portion of the captodative situation at the proanomeric center in **12**. For terminology, see: Viehe, H. G.; Merényi, R.; Stella, L.; Janousek, Z. *Angew. Chem.* **1979**, *91*, 982; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 917.

(24) Iffland, D. C.; Criner, G. X. *J. Am. Chem. Soc.* **1953**, *75*, 4047.

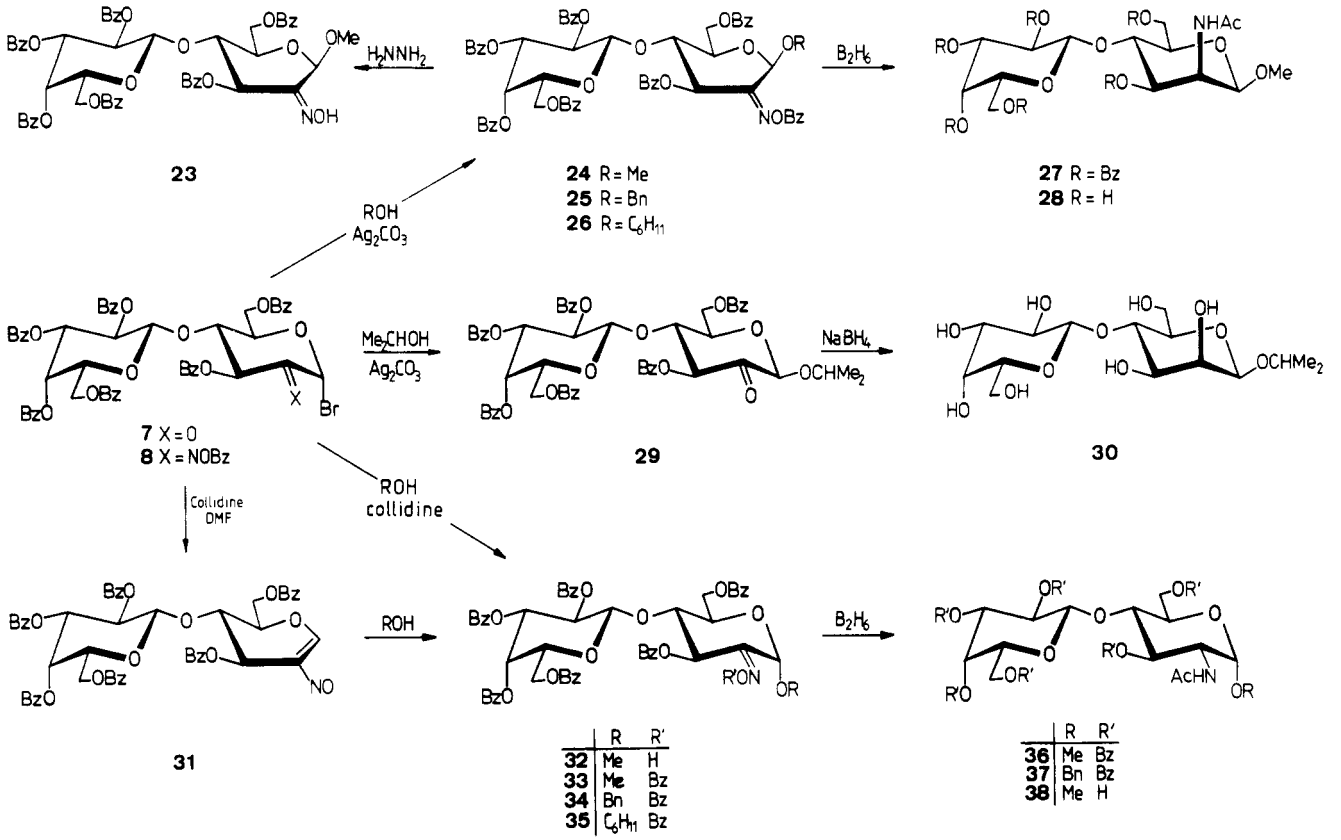
(25) Piloty, O. *Ber. Dtsch. Chem. Ges.* **1897**, *30*, 3164. For a recent rediscovery of the oxidative cleavage of ketoximes with aqueous bromine see: Olah, G. A.; Vankar, Y. D.; Prakasch, G. K. S. *Synthesis* **1979**, *113*.

(26) Chu, S.; Coviello, D. A. *J. Org. Chem.* **1971**, *36*, 3467.

(27) Ferrier, R. J.; Furneaux, R. H. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1996; *Austr. J. Chem.* **1980**, *33*, 1025. Ferrier, R. J.; Tyler, P. C. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1528, 2762, 2767. Somsák, L.; Batta, G.; Farkas, I. *Carbohydr. Res.* **1983**, *124*, 43.

(28) Praly, J. P. *Tetrahedron Lett.* **1983**, *24*, 3075. Adlington, R. M.; Baldwin, J. E.; Basak, A.; Kozyrod, R. P. *J. Chem. Soc., Chem. Commun.* **1983**, 944. Giese, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 753.

Scheme IV



blocks appears to be particularly convenient.

Building Blocks Derived from Maltose and Cellobiose. The methodology developed for the acquisition of **7** and **8** from lactose is applicable to other disaccharides without difficulties as is demonstrated in the sequel for maltose and cellobiose. Their conversion via the known[29,30] octabenzoates into the stable, crystalline α-bromides **16a** and **16b** was effected by the standard procedure, as was the subsequent dehydrobromination. The corresponding heptabenzoates of hydroxymaltal (**17a**) and hydroxycellobial (**17b**) were thus acquired in yields of over 70% for the three steps (Scheme III). The ensuing conversions proceeded favorably, e.g., the generation of cellobiosulosyl bromide **20** from glycal ester **17b** by treatment with NBS/methanol (77%) or the formation of the well-crystallizing oximes **18a** and **18b** in standard[15] hydroxylaminolyses. Their subsequent benzoylation and anomeric refunctionalization by photobromination proceeded as effectively, providing the stable, crystalline oximinoglycosyl bromides **21** and **22** in yields of over 70% for the three steps from **17**. Thus, cellobiose or the α-linked disaccharide maltose are as efficiently converted into ulosyl bromide-type disaccharide building blocks as lactose, sustaining the anticipation that the methodology elaborated is applicable to any other di- or oligosaccharide without alterations.

α- and β-Selective Glycosidations. With the viability of our approach to disaccharide-derived building blocks now on firm ground, attention was turned to an assessment of their penchant for stereocontrolled glycosidations.

An efficient control of the stereochemistry at the anomeric center implies that the conditions and the catalyst used for glycosidations are carefully matched with the reactivity of the glycosyl halide. In this respect, ulosyl bromides **7** and **20**, as well as their benzoyloximino analogues **8**, **21**, and **22** are stable, crystalline products storable for weeks without noticeable decomposition; hence, they must be considered as comparatively unreactive glycosyl donors. This conclusion conforms with the preparative finding that each of these disaccharide building blocks may be recovered from a methanolic solution at ambient temperature, methanolysis only occurring on heating under reflux (cf. below). Similarly relevant in this context is the fact—as was demonstrated with monosaccharide-derived examples[31]—that ulosyl bromides of type **7** instantaneously react with trimethylsilyl cyanide/boron trifluoride in acetonitrile, yet not with replacement of the anomeric bromine by cyanide but simply with formation of the respective cyanohydrin;[31] in line with this, oximinoglycosyl bromides of type **8** show no reaction under cyanation conditions.

In view of the low anomeric reactivity and the lack of a participating group next to the anomeric center, it was deemed that β-selective alcoholysis of these glycosyl bromides may be achievable under the conditions of the Koenigs–Knorr reaction,[32] such as, e.g., silver carbonate in a nonpolar solvent and in the presence of a desiccant to seize the water formed. Indeed, when lactosulosyl bromide **7**, in dichloromethane solution, was stirred with excess isopropyl alcohol in the presence of silver carbonate and molecular sieves for 5 h at room temperature, the isopropyl β-D-lactosuloside **29** had formed in an essentially stereospecific reaction, the respective α-anomer being not detectable (^{1}H NMR) in the reaction mixture. In similar fashion, the oximinoglycosyl bromide **8**, when subjected to treatment with methanol, benzyl alcohol, or cyclo-

(29) Thiel, I. M. E.; Deferrari, J. O.; Cadenas, R. A. *J. Org. Chem.* **1966**, *31*, 3704.
(30) Deferrari, J. O.; Thiel, I. M. E.; Cadenas, R. A. *J. Org. Chem.* **1965**, *30*, 3053.
(31) Lichtenthaler, F. W.; Weprek, S.; Nakamura, K., to be published.
(32) Igarashi, K. *Adv. Carbohydr. Chem. Biochem.* **1977**, *34*, 423.

hexanol, respectively, and silver carbonate/molecular sieves in dichloromethane,[33] was cleanly converted into the β-glycosides **24–26**, respectively, isolable in crystalline form in yields of 77–82% (Scheme IV). Here, too, the corresponding α-anomers, i.e., **33–35** (cf. below), could not be detected in the reaction mixture by either TLC, which is somewhat capricious due to similar mobilities, or ^{1}H NMR; since their conceivable presence is below 5%, the β-selectivity of these silver carbonate induced glycosidations[33] is estimated to be better than 20:1.

For α-selective alcoholysis of these glycobiosulosyl bromides, several procedures were evaluated with **8** as the model donor substrate and simple alcohols as the acceptors. Surprisingly, high α-selectivity is already achieved by refluxing **8** in methanol, yet not only α-glycosidation occurs but cleavage of the oxime ester function as well, to afford the α-D-lactosuloside oxime **32** (66%). Of the several reactions involved in this conversion, methanolysis is thought to be the first, since the resulting α-bromo oxime is expected[34] to dehydrobrominate to a nitrosoglycal intermediate of type **31** which is known[35] to add alcohols with high α-preference. This course is strongly substantiated by isolation of the anticipated intermediate and its conversion into the α-glycoside: treatment of **8** with base (*s*-collidine) in *N*,*N*-dimethylformamide readily delivered (67%) the 2-nitrosolactal ester **31** in di- or oligomeric form[36] and was cleanly converted into α-lactosuloside oxime **32** (69%) on refluxing with methanol.

Refluxing a glycosyl donor with the alcohol component being of rather limited general utility for the generation of α-glycosides, other methods had to be evaluated of which Lemieux's in situ anomerization procedure[37] or variations thereof appeared to be the most promising. When **8** is exposed to tetraethylammonium bromide in dichloromethane at room temperature, a gradual decrease in rotation is observable (+180° → 80° within 2 days), indicating that α → β-anomerization does take place yet obviously leads to the still rather stable β-bromide. Correspondingly, reaction of **8** with simple alcohols in dichloromethane and in the presence of tetraethylammonium bromine proceeds rather sluggishly, workup after 3 days providing glycosidic mixtures, e.g., of **33** and its β-anomer **24**, in ratios (^{1}H NMR) of 4:1 to 3:1 only. Use of the more reactive Helferich catalyst,[38] i.e., mercuric cyanide in dioxane or nitromethane, also favored α-glycosidation of **8**, yet to the extent of a 3:1 to 4:1 selectivity at best.

Preparatively useful α-selectivities of about 15:1 may be obtained by alcoholysis in dioxane solution in the presence of a sterically hindered pyridine base such as *s*-collidine. Accordingly, when exposing **8** to either methanol, benzyl alcohol, or cyclohexanol under such conditions for 2 days at room temperature, clean conversion into the respective α-D-lactosulosides **33–35** is effected, yields of isolated crystalline products being around 80%. The high α-selectivity which on the basis of ^{1}H NMR data of mother liquors is better than 15:1, and the solvent dependency (in nitromethane approximate 1:1 mixtures of anomers accumulate) give reason for the assumption that the base-induced removal of the anomeric bromine is assisted by the dioxane oxygen to generate an intermediate β-dioxonium ion[39] which is subsequently S_N2 displaced by the alcohol.

Stereoanomeric Control in Reductions of Oxo and Oximino Groups. The utility of disaccharide building blocks **7**, **8**, and **20–22** for the efficient construction of heterooligosaccharides will, at last, be determined by the stereoselectivity with which the 2-oxo and 2-benzoximino groups may be saturated. Thus, following the successful elaboration of α- and β-selective glycosidation procedures, the task of attaining high stereoselectivities in carbonyl and oxime reductions had to be addressed.

In the case of glycosid-2-uloses there is ample evidence for the stereoanomeric control of hydride reductions such that the hydride attacks the carbonyl function from the side opposite to the vicinal anomeric substituent. This high and in most cases essentially exclusive steric preference leads to α-D-glucosides from α-D-glycosiduloses[40] while β-ulosides, correspondingly, are converted into β-glycosides of *manno* configuration.[41] Accordingly, when isopropyl β-D-lactosuloside **29** is reduced with sodium borohydride an approximate 5:1 preference for the *manno* product is observed (TLC and ^{1}H NMR), allowing the isolation of galactosyl-(1→4)-β-D-mannoside **30**, after deblocking, in 72% yield. This preparatively quite satisfactory approach to oligosaccharides with β-D-*manno*-pyranosidic linkages (e.g., lactose → **30**, 44% for six steps) compares favorably with an alternate, more circuitous route,[42] which involves the intricate elaboration of a blocking group pattern in an oligosaccharide so that the 2-OH in a β-D-gluco unit can selectively be liberated, oxidized, and reduced.

For the stereoselective reduction of benzoyloximino functions in the β- (**24–26**) and α-glycosides (**33–35**), a series of reagents were evaluated, as, for example, sodium borohydride, sodium cyanoborohydride, triethylsilane, tributylstannane, zinc–copper/acetic acid, Pt/H_2, and Raney nickel/H_2, but neither was very promising with respect to stereoselectivity and completeness of saturation. The only effective, reliable method proved to be hydroboration with the borane–tetrahydrofuran complex, a methodology that has been successfully employed for the reduction of oximino and acetoyloximino functions in α-D-glycosidulose oximes providing the α-D-glucosaminide derivatives with high stereoselectivity.[43] Accordingly, when the α-D-lactosuloside oximes **33** and **34** were treated with borane in tetrahydrofuran (30 min at −10 °C → 25 °C) an essentially exclusive generation of the amino group in equatorial disposition was effected to give after N-acetylation the blocked α-methyl and α-benzyl *N*-acetyl-

(33) Use of silver silicate on alumina, a catalyst highly propagated recently as being superior to silver carbonate in β-selective glycosidations (Paulsen, H.; Lockhoff, O. *Chem. Ber.* **1981**, *114*, 3103), resulted in sluggish, usually incomplete reactions and inferior selectivity.

(34) Lemieux, R. U.; Nagabhushan, T. L.; James, K. *Can. J. Chem.* **1973**, *51*, 1.

(35) Lemieux, R. U.; Ito, Y.; James, K.; Nagabhushan, T. L. *Can. J. Chem.* **1973**, *51*, 7.

(36) The nonmonomeric nature of **31** was inferred from its colorlessness and the unresolved multiplet for H-1 and H-3 around δ 6.4. Whether the product is dimeric or forms higher oligomers, as observed for tri-*O*-acetyl-1,5-anhydro-2-deoxy-2-nitroso-D-*arabino*-hex-1-enitol,[34] remains to be established.

(37) Lemieux, R. U.; Hayami, J. *Can. J. Chem.* **1965**, *43*, 2162. Lemieux, R. U.; Morgan, A. R. *Ibid.* **1965**, *43*, 2205. Lemieux, R. U.; Hendriks, K. B.; Stick, R. V.; James, K. *J. Am. Chem. Soc.* **1975**, *97*, 4056.

(38) Helferich, B.; Weis, K. *Chem. Ber.* **1956**, *89*, 314.

(39) An analogous, tetrahydrofuran-derived oxonium ion intermediate has been proposed (Wulff, G.; Schmidt, W. *Carbohydr. Res.* **1977**, *53*, 37) to account for the formation of 4-bromobutyl tetra-*O*-acetyl-β-D-glucoside on exposure of acetobromoglucose to mercuric bromide in tetrahydrofuran (Helferich, B.; Zirner, J. *Chem. Ber.* **1971**, *104*, 1387).

(40) Lemieux, R. U.; James, K.; Nagabhushan, T. L. *Can. J. Chem.* **1973**, *51*, 27.

(41) Kondo, Y.; Onodera, K. *Agric. Biol. Chem.* **1974**, *38*, 2553. Miljković, M.; Gligorijevich, M.; Miljković, D. *J. Org. Chem.* **1974**, *39*, 2118. Lee, E. E.; Keaveney, G.; O'Colla, P. S. *Carbohydr. Res.* **1977**, *59*, 268.

(42) Shaban, M. A. E.; Jeanloz, R. W. *Carbohydr. Res.* **1976**, *52*, 115. Warren, C. D.; Augé, C.; Laver, M.; Suzuki, S.; Power, D.; Jeanloz, R. W. *Ibid.* **1980**, *82*, 71. Augé, C.; Warren, C. D.; Jeanloz, R. W.; Kiso, M.; Anderson, L. *Ibid.* **1980**, *82*, 85.

(43) Lemieux, R. U.; James, K.; Nagabhushan, T. L.; Ito, Y. *Can. J. Chem.* **1973**, *51*, 33. Lemieux, R. U.; James, K.; Nagabhushan, T. L. *Ibid.* **1973**, *51*, 48.

lactosaminides **36** and **37**, respectively, each isolated in crystalline form in yields of 76% and 80%. None of the 2-epimeric galactosyl-α-D-mannosaminide could be detected in the reaction mixture, the only minor products, isolable in yields of 4–5% following column separation (and conceivably formed thereby) being the 3-de-O-benzoylated derivatives of **36** and **37**, respectively. Thus the borane reduction of benzoyl-protected α-glycosidulose oximes proceeds with complete stereoanomeric control even with simple, sterically undemanding glycosidic residues.

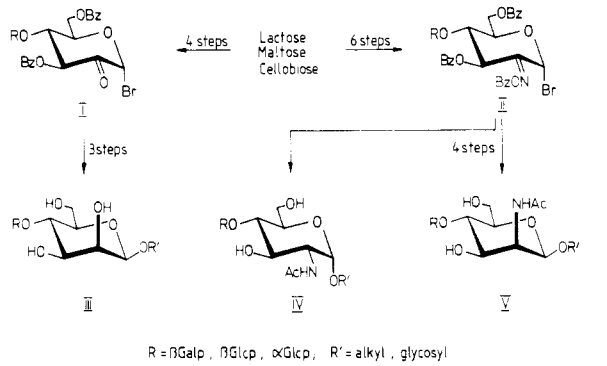
For the borane reduction of β-glucosidulose oximes there seem to be no precedents in the literature. It may be expected though from the clearcut conversion of **29** into the β-D-mannoside **30** that similar stereoanomeric control would be operative in the benzoxime analogues. Indeed, reduction of β-D-lactosuloside oxime **24** with borane in tetrahydrofuran proceeded smoothly (30 min, −10 °C) and uniformly (hydride addition from the α-side) to give the galactosyl-β-D-mannosaminide, isolated after N-acetylation in fully blocked form (**27**) in excellent yield (92%). Here, too, the only minor product detectable and isolable in 4% yield proved to be the 3-de-O-benzoylated derivative of **27**, rather than the 2-epimeric β-lactosaminide.

The final deblocking of the disaccharide glycosides obtained was readily accomplished, and the sodium methoxide/methanol induced transesterification proceeded effectively and uneventfully as exemplified by the high-yield conversions **27** → **28** and **36** → **38**. Thus, *N*-acetyl-α-D-lactosamine as well as galactosyl-β-D-mannosamine units may be glycosidically attached to a hydroxyl, conceivably to a sugar OH group, with comparable ease.

Configurational Assignments. Structural and configurational evidence for each of the 36 disaccharide derivatives newly described is provided by their 300-MHz ^{1}H NMR spectra which are usually first-order interpretable and warrant little comment beyond the information given in the experimental portion of this paper. The only peculiarities noticeable proved to be the unusually small coupling constants between H-3 and H-4 in the β-oximinoglycosides **23–26** ($J_{3,4}$ = 3.5–4.5 Hz), indicating that the usual $^4C_1$ conformation is substantially flattened around the anomeric center, conceivably toward the form depicted in the formulae. This distortion obviously results from the steric congestion engendered by 2-benzoyloximino and β-anomeric alkoxy groups, an effect that is not operative in the α-oximinoglycosyl derivatives which exhibit perfectly normal $J_{3,4}$ values of 8.5–9.5 Hz for the α-bromides as well as α-glycosides. In the case of the fully deprotected disaccharide–glycosides **28**, **30**, and **38**, more informative than ^{1}H NMR data were the ^{13}C NMR spectra, which were in full accord with expectations.[44]

Summary and Conclusions

The methodology detailed herein has resulted in the convenient conversion of bulk disaccharides such as lactose, cellobiose, and maltose into a diverse collection of *disaccharide building blocks* that, on one hand, are suitably functionalized for direct glycosylation and, on the other, embody structural features which allow the construction of heterooligosaccharides of biological importance. Key intermediates are the respective 2-hydroxyglycal esters of type **6**, which are either converted into glycosyl-(1→4)-oximinoglycosyl bromides **8**, **15**, **21**, or **22** in three steps—comprising hydroxylaminolysis, *O*-aroylation, and photobromination—or, alternately, into glycobiosulosyl bromides **7** or **20** in a one-step transformation, with overall yields based on the disaccharide educt averaging 50% and 65%, respectively. Despite of being comparatively stable and, consequently, storable glycosyl donors the lack of a participating group next to the anomeric center provides for their ready conversion into either α- or β-glycosides, stereoanomeric control simply being achievable by the proper choice of catalysts. Since the hydride reduction of oxo (sodium borohydride) and benzoximino functions (diborane/tetrahydrofuran) is also strongly stereocontrolled by the anomeric substituent—the hydride attacking exclusively or with high preference from the side opposite thereto—disaccharide glycosides are produced that have either α-D-*gluco* or β-D-*manno* configurated hexose or hexosamine units. By consequence, the overall methodology provides an efficient means for converting the reducing glucose portion of lactose, maltose, and cellobiose—or of any other reducing di- or oligosaccharide—via building blocks of the ulosyl bromide (I) and oximinoglycosyl bromide type (II) into either β-D-mannosidic units (I → III) or, alternately, into 2-aminohexoses of α-D-*gluco* (II → IV) and β-D-*manno* configuration (III → V):



Accordingly, these disaccharide building blocks are expected to lend themselves to the efficient attachment of α-linked lactosamine, maltosamine, and cellobiosamine units to any given sugar hydroxyl. The method's prime strength, though, would appear to lie in the annelation of glycosyl-(1→4)-β-D-mannose and glycosyl-(1→4)-β-D-mannosamine blocks onto a sugar chain inasmuch as difficulties still prevail with the direct incorporation of β-D-mannose and of 2-acetamido-2-deoxy-β-D-mannose residues, in particular. For the latter, for example, although important constituent sugars of pneumococcal vaccines[45] no preparatively satisfactory methods[46] are available as of now.

Various further ramifications in the use of these disaccharide building blocks for the construction of biologically relevant heterooligosaccharides are currently under investigation, their application to the synthesis of trisaccharides with central >-D-mannose, α-D-glucosamine, and β-D-mannosamine units having already been worked out successfully.[47]

Experimental Section

Melting points were recorded on a Büchi SMP-20 and Bock Monoscop apparatus and are uncorrected. Spectral measurements

(44) Bock, K.; Pedersen, C.; Pedersen, H. *Adv. Carbohydr. Chem. Biochem.* **1984**, *42*, 193.

(45) Shabarova, Z. A.; Buchanan, J. G.; Baddiley, J. *Biochim. Biophys. Acta* **1962**, *57*, 146. Jennings, H. J.; Rossel, K.-G.; Carlo, D. J. *Can. J. Chem.* **1980**, *58*, 1069. Ohno, H.; Yadomea, T.; Miyazaki, T. *Carbohydr. Res.* **1980**, *80*, 297.

(46) A recent preliminary report (Paulsen, H.; Lorentzen, J. P. *Carbohydr. Res.* **1984**, *133*, C1) indicated the possibility to prepare β-D-mannosamine-containing oligosaccharides via a difficulty accessible 2-azido-2-deoxy-α-D-mannosyl bromide.

(47) Lichtenthaler, F. W.; Kaji, E. *Liebigs Ann. Chem.*, in press.

were recorded on Perkin-Elmer 125 (IR), Perkin-Elmer 141 (rotations), and Varian XL-100/Bruker WM 300 (^{1}H NMR) instruments. TLC was carried out on Merck Silica Gel F_{254} and plastic sheets were used to monitor the reactions and to ascertain the purity of the products; solvent systems are given individually and were the same for TLC and column chromatography. The spots were visualized by UV light or by charring with 40% aqueous H_2SO_4. Column chromatography was done on Merck Kieselgel 60 (70–230 mesh).

Hepta-*O*-benzoyl-α-D-lactosyl Bromide (10). To a vigorously stirred suspension of lactose (25 g, 73 mmol) in dry pyridine (250 mL) was added benzoyl chloride (85 mL, 10 molar equiv) in small portions such that the temperature did not exceed 20 °C (cooling with a water bath). After completion of the addition (20 min) the mixture was heated for 4 h at 60 °C and 15 min at 100 °C,[22] followed by cooling and stirring into ice–water. The resulting syrup was washed by decantation until a powdery solid was obtained, which was then reprecipitated from 3:1 methanol–acetone to give 70 g of octabenzoyllactose as an approximate 2:1 mixture of **9** and its β-anomer (TLC with 19:1 benzene–ethyl acetate). Without further purification, the product was dissolved in 1,2-dichloroethane (250 mL), a 33% solution of HBr in acetic acid (90 mL) was added, and the mixture was kept at room temperature for 24 h. Evaporation in vacuo followed by repeated coevaporation with toluene and trituration of the residue with ether and excess pentane gave a solid which was collected and dried in vacuo: 56.5 g (84%) of **10** as a colorless amorphous powder; mp 101–104 °C; $[\alpha]^{20}_D$ +102.2° (*c* 1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.97 (d, 1 H, H-1′), 5.27 (dd, 1 H, H-2), 5.41 (dd, 1 H, H-3′), 5.6–5.9 (m, 2 H, H-2′, H-4′), 6.16 (dd, 1 H, H-3), 6.76 (d, 1 H, H-1[48]), 7.1–8.1 (7 C_6H_5), 3.7–4.6 (other protons); $J_{1',2'}$ = 7.5, $J_{2',3'}$ = 10.0, $J_{1,2}$ = 4.0, $J_{2,3}$ = 9.5, $J_{3,4}$ = 9.0 Hz. Anal. Calcd for $C_{61}H_{49}BrO_{17}$: C, 64.61; H, 4.36. Found: C, 64.56; H, 4.31.

2,3,6-Tri-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-1,5-anhydro-D-*arabino*-hex-1-enitol (6). A mixture of lactosyl bromide **10** (10.0 g, 8.8 mmol) and sodium iodide (5.0 g, 33.4 mmol) in 400 mL of dry acetone was stirred at room temperature for 15 min. Subsequently, diethylamine (10 mL, 96 mmol) was added dropwise, followed by stirring at ambient temperature for 16 h. The resulting orange suspension was filtered, and the filtrate was evaporated and partitioned between dichloromethane (200 mL) and water (100 mL). The organic phase was washed with 2 N HCl (50 mL) and water (4 × 50 mL), dried (Na_2SO_4), and evaporated to dryness to give orange-yellow syrup, which was eluted through a silica gel column with benzene/ethyl acetate (10:1). The resulting syrup was coevaporated twice with ethanol which resulted in crystallization. Recrystallization from ethanol gave 8.6 g (91%) of **6**: mp 94–96 °C; $[\alpha]^{20}_D$ +52° (*c* 1, $CHCl_3$); ^{1}H NMR (100 MHz, $CDCl_3$) δ 5.19 (d, 1 H, H-1′), 5.57 (dd, 1 H, H-3′), 5.86 (dd, 1 H, H-2′), 5.92 (br d, 1 H, H-4′), 6.33 (d, 1 H, H-3), 6.86 (s, 1 H, H-1), 7.1–8.1 (7 C_6H_5), 4.1–4.7 (m, 7 H, other protons); $J_{1',2'}$ = 8, $J_{2',3'}$ = 10, $J_{3',4'}$ = 3.5, $J_{4',5'}$ = 1, $J_{3,4}$ = 3.5 Hz. Anal. Calcd for $C_{61}H_{48}O_{17}$: C, 69.57; H, 4.59. Found: C, 69.49; H, 4.57.

3,6-Di-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-α-D-*arabino*-hexopyranos-2-ulosyl Bromide [Hexa-*O*-benzoyl-α-D-lactosulosyl Bromide] (7). A solution of hydroxylactal heptabenzoate **6** (4.2 g, 4 mmol) in dichloromethane (40 mL) containing molecular sieves (3 Å) and absolute methanol (0.19 mL, 4.7 mmol) was stirred at ambient temperature for 30 min, whereafter *N*-bromosuccinimide (0.90 g, 5 mmol) was added followed by stirring for another 30 min. Subsequently, the mixture is diluted with dichloromethane (60 mL), successively washed with 10% aqueous $Na_2S_2O_3$ solution (50 mL) and water (2 × 50 mL), dried (Na_2SO_4), and evaporated to a syrup, which for removal of methyl benzoate was precipitated from an ethereal solution by *n*-hexane: 3.7 g (90%) of **7** as an amorphous product, softening around 60 °C; $[\alpha]^{20}_D$ +123° (*c* 1, $CHCl_3$); MS (FD), *m/e* 1027 (M^+); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.00 (m, 3 H, H-5, 6-H_2), 4.53 and 4.72 (two dd, 1 H each, 6′-H_2), 4.61 (m, 1 H, H-5′), 4.67 (dd, 1 H, H-4), 5.01 (d, 1 H, H-1′), 5.46 (dd, 1 H, H-3′), 5.78 (dd, 1 H, H-2′), 5.82 (dd, 1 H, H-4′), 6.33 (d, 1 H, H-3), 6.42 (s, 1 H, H-1); $J_{3,4}$ = 9.3, $J_{4,5}$ = 9.6, $J_{1',2'}$ = 7.9, $J_{2',3'}$ = 10.4, $J_{3',4'}$ = 3.4, $J_{4',5'}$ = 1.8, $J_{5',6'a}$ = 1.3, $J_{5',6'b}$ = 3.3, $J_{6'a,6'b}$ = 12.4 Hz. Anal. Calcd for $C_{54}H_{43}O_{16}Br$: C, 63.10; H, 4.22. Found: C, 63.01; H, 4.16.

3,6-Di-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-1,5-anhydro-D-fructose Monohydrate (11). To a solution of oxime **12** (1.0 g, 0.96 mmol) in acetonitrile (5 mL) was added acetaldehyde (0.1 mL, 1.8 mmol) and HCl (1 mL). The mixture was stirred at room temperature for 3 h, followed by dilution with dichloromethane (15 mL), and washed with water (10 mL), saturated aqueous $NaHCO_3$ (10 mL), and water (3 × 10 mL). After drying (Na_2SO_4), the solution was evaporated to dryness and the residue was crystallized from ether–pentane: 0.84 g (90%) of **11**; mp 113–114 °C; $[\alpha]^{21}_D$ +40.2° (*c* 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.12 (d, 1 H, H-1a), 4.29 (d, 1 H, H-1e), 4.54 (t, 1 H, H-4), 4.73 (dd, 1 H, H-5′), 5.01 (d, 1 H, H-1′), 5.48 (dd, 1 H, H-3′), 5.77 (dd, 1 H, H-2′), 5.80 (d, 1 H, H-3), 5.82 (br d, 1 H, H-4′), 7.2–8.2 (6 C_6H_5), 3.9–4.5 (other protons); $J_{1a,1e}$ = 15.0, $J_{3,4}$ = $J_{4,5}$ = 9.5, $J_{1',2'}$ = 7.8, $J_{2',3'}$ = 10.3, $J_{3',4'}$ = 3.5, $J_{4',5'}$ ~ 1 Hz. Anal. Calcd for $C_{54}H_{44}O_{16}\cdot H_2O$: C, 67.08; H, 4.79. Found: C, 67.11; H, 4.73.

3,6-Di-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-1,5-anhydro-D-fructose Oxime (12). To a solution of **6** (7.4 g, 7.0 mmol) in pyridine (50 mL) was added hydroxylamine hydrochloride (1.85 g, 26.6 mmol), and the mixture was heated at 70 °C for 20 h. The resulting yellowish solution was diluted with ice–water (100 mL) and extracted with dichloromethane (2 × 100 mL). The organic phase was washed with water (100 mL), cold 1 N HCl (100 mL), and ice–water (4 × 100 mL). After drying (Na_2SO_4), the solution was evaporated and coevaporated with toluene to dryness. The residue was dissolved in chloroform and triturated with hexane to give a syrup, which was dried in vacuo to furnish 6.0 g (89%) of **12** as an amorphous powder: mp 103–105 °C; $[\alpha]^{20}_D$ +55° (*c* 1, $CHCl_3$); ^{1}H NMR (100 MHz, $CDCl_3$) δ 3.6 (m, 1 H, H-5), 4.96 (d, 1 H, H-1e), 5.14 (d, 1 H, H-1′), 5.57 (dd, 1 H, H-3′), 5.82 (dd, 1 H, H-2′), 5.93 (br d, 1 H, H-4′), 6.13 (d, 1 H, H-3), 7.1–8.1 (6 C_6H_5), 8.40 (s, 1 H, NOH, disappearing on deuteration), 4.1–4.5 (other protons); $J_{1a,1e}$ = 16.0, $J_{3,4}$ = 4.5, $J_{1',2'}$ = 8.0, $J_{2',3'}$ = 10.0, $J_{3',4'}$ = 3.5, $J_{4',5'}$ ≃ 1 Hz. Anal. Calcd for $C_{54}H_{45}NO_{16}$: C, 67.28; H, 4.70; N, 1.45. Found: C, 67.35; H, 4.73; N, 1.38.

3,6-Di-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-1,5-anhydro-D-fructose *O*-Benzoyloxime (13). A solution of oxime **12** (2.0 g, 2.1 mmol) and benzoyl chloride (2.4 mL, 21 mmol) in pyridine (12 mL) was stirred at room temperature for 4 h. The resulting mixture was diluted with dichloromethane and poured into ice–water. Successive washing of the organic phase with water, 1 N HCl, water, saturated aqueous $NaHCO_3$, and water was followed by drying (Na_2SO_4) and evaporation to dryness to yield a residue, which was crystallized from ethanol: 1.98 g (90%) of **13** as colorless prisms; mp 111–113 °C; $[\alpha]^{20}_D$ +53.5° (*c* 1, $CHCl_3$); ^{1}H NMR (100 MHz, $CDCl_3$) δ 3.75 (m, 1 H, H-5), 5.16 (d, 1 H, H-1′), 5.17 (d, 1 H, H-1e), 5.61 (dd, 1 H, H-3′), 5.85 (dd, 1 H, H-2′), 5.98 (br d, 1 H, H-4′), 6.35 (d, 1 H, H-3), 7.1–8.1 (7 C_6H_5), 4.2–4.6 (other protons); $J_{1a,1e}$ = 17, $J_{3,4}$ = $J_{1',2'}$ = 8, $J_{2',3'}$ = 9.5, $J_{3',4'}$ = 3, $J_{4',5'}$ ≃ 1 Hz. Anal. Calcd for $C_{61}H_{49}NO_{17}$: C, 68.60; H, 4.62; N, 1.31. Found: C, 68.56; H, 4.57; N, 1.24.

3,6-Di-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-1,5-anhydro-D-fructose *O*-(*p*-Cyanobenzoyl)oxime (14). A solution of oxime **12** (7.0 g, 7.3 mmol) and *p*-cyanobenzoyl chloride (2.4 g, 14.5 mmol) in pyridine (70 mL) was stirred at room temperature for 4 h. The reaction mixture was evaporated to remove pyridine and partitioned between dichloromethane and ice–water. The organic phase was washed with water, 1 N HCl, water, saturated aqueous $NaHCO_3$, and water. After drying (Na_2SO_4), the solution was evaporated to dryness to yield a residue which was purified by elution from a silica gel column with benzene–ethyl acetate (8:1) and recrystallized from ethanol: 6.75 g (85%) of **14**; mp 115 °C after sintering from 110 °C on; $[\alpha]^{18}_D$ +45.8° (*c* 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.77 (m, 1 H, H-5), 4.51 (d, 1 H, H-1a), 5.15 (d, 1 H, H-1e), 5.16 (d, 1 H, H-1′), 5.61 (dd, 1 H, H-3′), 5.82 (dd, 1 H, H-2′), 5.96 (br d, 1 H, H-4′), 6.33 (d, 1 H, H-3), 7.2–8.1 (Ar H), 4.3–4.5 (other protons); $J_{1a,1e}$ = 16.5, $J_{3,4}$ = 4.5, $J_{1',2'}$ = 8.0, $J_{2',3'}$ = 10.5, $J_{3',4'}$ =

(48) The anomeric proton (H-1) of **10** has been reported to give a 4.2 Hz doublet at δ 6.8 (Lundt, I.; Pedersen, C. *Acta Chem. Scand., Ser. B* **1976**, *B30*, 680), yet neither other NMR data nor any physical constants were advanced.

3.5, $J_{4',5'} \simeq 1$ Hz. Anal. Calcd for $C_{62}H_{48}N_2O_{17}$: C, 68.13; H, 4.43; N, 2.56. Found: C, 68.11; H, 4.39; N, 2.49.

3,6-Di-*O*-benzoyl-2-(benzoyloximino)-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-α-D-*arabino*-hexopyranosyl Bromide (8). A mixture of benzoyloxime **13** (3.2 g, 3 mmol) and freshly recrystallized *N*-bromosuccinimide (0.53 g, 3.3 mmol) in tetrachloromethane (60 mL) was irradiated with a 450-W heat lamp such that gentle reflux was effected (distance of the lamp, 10–15 cm). After 30 min the resulting yellowish solution was cooled (0 °C), the precipitate (succinimide) was filtered off, and the filtrate was evaporated to dryness. The residue was partitioned between dichloromethane (150 mL) and water (100 mL). The organic phase was washed with water (2 × 50 mL), dried (Na_2SO_4), and evaporated to a syrup, which crystallized by trituration with ether–pentane: 3.2 g (93%) of **8**; mp 120–122 °C; $[\alpha]^{20}_D$ +182° (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 4.60 (t, 1 H, H-4), 4.71 (m, 1 H, H-5′), 5.50 (d, 1 H, H-1′), 5.47 (dd, 1 H, H-3′), 5.79 (dd, 1 H, H-2′), 5.81 (br d, 1 H, H-4′), 6.61 (d with fine structure, 1 H, H-3), 7.2–8.2 (7 C_6H_5, H-1), 3.9–4.5 (other protons); $J_{1',2'} = 8.0$, $J_{2',3'} = 10.5$, $J_{3',4'} = 3.5$, $J_{4',5'} \simeq 1$, $J_{3,4} = J_{4,5} = 9.2$ Hz. Anal. Calcd for $C_{61}H_{48}BrNO_{17}$: C, 63.88; H, 4.22; N, 1.22. Found: C, 63.92; H, 4.20; N, 1.26.

3,6-Di-*O*-benzoyl-2-[(*p*-cyanobenzoyl)oximino]-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-α-D-*arabino*-hexopyranosyl Bromide (15). A mixture of (*p*-cyanobenzoyl)oxime **14** (2.0 g, 1.83 mmol) and *N*-bromosuccinimide (0.36 g, 2.01 mmol) in ethanol-free tetrachloromethane (40 mL) was irradiated with a 250-W visible lamp for 0.5 h, followed by workup of the mixture as described for **8**. Crystallization from ether–pentane gave 2.1 g (97%) of **15**: mp 120–123 °C; $[\alpha]^{19}_D$ +172.4° (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 4.61 (t, 1 H, H-4), 4.73 (m, 1 H, H-5′), 5.06 (d, 1 H, H-1′), 5.48 (dd, 1 H, H-3′), 5.79 (dd, 1 H, H-2′), 5.83 (br d, 1 H, H-4′), 6.61 (d, 1 H, H-3), 7.2–8.2 (Ar H, H-1), 3.9–4.8 (other protons); $J_{1',2'} = 8.0$, $J_{2',3'} = 10.5$, $J_{3',4'} = 3.5$, $J_{4',5'} \sim 1.5$, $J_{3,4} = J_{4,5} = 9.5$ Hz. Anal. Calcd for $C_{62}H_{47}BrN_2O_{17}$: C, 63.54; H, 4.04; N, 2.39. Found: C, 62.93; H, 3.95; N, 2.29.

Hepta-*O*-benzoyl-α-D-maltosyl Bromide (16a). Octa-*O*-benzoyl-β-D-maltose[29] (14.0 g, 12 mmol) was treated with a 33% solution of HBr in acetic acid (18 mL) as described for **10**. Crystallization from ether–pentane gave 11.2 g (83%) of **16a**: mp 161–163 °C dec; $[\alpha]^{20}_D$ +107.4° (*c* 1, $CHCl_3$); ^1H NMR (100 MHz, $CDCl_3$) δ 5.11 (dd, 1 H, H-2), 5.30 (dd, 1 H, H-2′), 5.69 (t, 1 H, H-4′), 5.80 (d, 1 H, H-1′), 6.0–6.3 (m, 2 H, H-3, H-3′), 6.78 (d, 1 H, H-1), 7.1–8.2 (7 C_6H_5), 4.2–4.9 (other protons); $J_{1,2} = 4$, $J_{2,3} = 10$, $J_{1',2'} = 4$, $J_{2',3'} = 10$, $J_{3',4'} = J_{4',5'} = 9.5$ Hz. Anal. Calcd for $C_{61}H_{49}BrO_{17}$: C, 64.61; H, 4.36. Found: C, 64.64; H, 4.32.

Hepta-*O*-benzoyl-α-D-cellobiosyl Bromide (16b). Octa-*O*-benzoyl-β-D-cellobiose[30] (12.0 g, 10.2 mmol) was treated with a 33% solution of HBr in acetic acid (15 mL) as described for **10**. Crystallization from ether provided 10.2 g (88%) of **16b**, mp 178–180 °C; $[\alpha]^{22}_D$ +85° (*c* 1, $CHCl_3$) [lit.[49] mp 200–202 °C; $[\alpha]^{25}_D$ +89° (*c* 1, $CHCl_3$)]; ^1H NMR (300 MHz, $CDCl_3$) δ 3.85 (m, 2 H, H-5′, H-6A); 4.09 (dd, 1 H, H-6B), 4.33 (dd, 1 H, H-4), 4.43 (ddd, 1 H, H-5), 4.54 (dd, 1 H, H-6′A), 4.64 (dd, 1 H, H-6′B), 5.03 (d, 1 H, H-1′), 5.19 (dd, 1 H, H-2), 5.43 (dd, 1 H, H-3), 5.54 (dd, 1 H, H-2′), 5.77 (dd, 1 H, H-3′), 6.14 (dd, 1 H, H-4′), 6.72 (d, 1 H, H-1); $J_{1,2} = 4.0$, $J_{2,3} = 9.7$, $J_{3,4} = 9.7$, $J_{4,5} = 10.0$, $J_{5,6A} = 5.2$, $J_{5,6B} = 2.6$, $J_{6A,6B} = 11.5$, $J_{1',2'} = 7.9$, $J_{2',3'} = J_{3',4'} = 9.7$, $J_{4',5'} = 9.5$, $J_{5',6'A} = 3.5$, $J_{5',6'B} = 1.7$, $J_{6'A,6'B} = 12.5$ Hz. Anal. Calcd for $C_{61}H_{49}BrO_{17}$: C, 64.61; H, 4.36; Br, 7.05. Found: C, 64.53; H, 4.28; Br, 6.97.

2,3,6-Tri-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl)-1,5-anhydro-D-*arabino*-hex-1-enitol (17a). A mixture of **16a** (10.0 g, 8.8 mmol), sodium iodide (5.0 g, 33 mmol), and diethylamine (10 mL, 96 mmol) in anhydrous acetone (300 mL) was stirred at room temperature for 16 h, followed by workup of the mixture as described for **6**. Crystallization from ethanol provided 9.05 g (97%) of **17a**: mp 97–99 °C; $[\alpha]^{20}_D$ +8.6° (*c* 1, $CHCl_3$); ^1H NMR (100 MHz, $CDCl_3$) δ 5.48 (dd, 1 H, H-2′), 5.6–5.8 (m, 2 H, H-1′, H-4′), 5.92 (d, 1 H, H-3), 6.24 (dd, 1 H, H-3′), 6.97 (s, 1 H, H-1), 7.2–8.1 (7 C_6H_5), 4.4–4.9 (other protons); $J_{1',2'} = 4.0$, $J_{2',3'} = 10$, $J_{3',4'} = 9.5$, $J_{3,4} = 4.0$ Hz. Anal. Calcd for $C_{61}H_{48}O_{17}$: C, 69.57; H, 4.59. Found: C, 69.49; H, 4.48.

2,3,6-Tri-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-1,5-anhydro-D-*arabino*-hex-1-enitol (17b). A mixture of cellobiosyl bromide **16b** (9.0 g, 8 mmol), sodium iodide (4.5 g, 30 mmol), and diethylamine (9 mL, 87 mmol) in anhydrous acetone (400 mL) was stirred at room temperature for 16 h, followed by workup of the mixture as described for **6**. Crystallization from ethanol provided 7.4 g (89%) of **17b**; mp 166–167 °C; $[\alpha]^{20}_D$ +15° (*c* 1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 4.16 (m, 1 H, H-5), 4.50 (dd, 1 H, H-4), 5.27 (d, 1 H, H-1′), 5.62 (t, 1 H, H-4′), 5.63 (dd, 1 H, H-2′), 5.92 (t, 1 H, H-3′), 6.30 (d, 1 H, H-3), 6.83 (s with fine structure, 1 H, H-1), 7.1–8.0 (7 C_6H_5), 4.3–4.7 (other protons); $J_{1,3} = 0.8$, $J_{3,4} = 4.0$, $J_{4,5} = 5.5$, $J_{1',2'} = 8.0$, $J_{2',3'} = J_{3',4'} = J_{4',5'} = 9.8$ Hz. Anal. Calcd for $C_{61}H_{48}O_{17}$: C, 69.57; H, 4.59. Found: C, 69.52; H, 4.56.

3,6-Di-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl)-1,5-anhydro-D-fructose Oxime (18a). A solution of maltal **17a** (5.5 g, 5.2 mmol) in pyridine (50 mL) and hydroxylamine hydrochloride (1.45 g, 21 mmol) was kept at 70 °C for 20 h. Workup of the mixture as described for **12** provided 4.32 g (86%) of **18a**: mp 107–109 °C; $[\alpha]^{20}_D$ +33.8° (*c* 1, $CHCl_3$); ^1H NMR (100 MHz, $CDCl_3$) δ 4.91 (d, 1 H, H-1e), 5.43 (dd, 1 H, H-2′), 5.61 (d, H-1′), 5.73 (t, 1 H, H-4′), 5.89 (d, 1 H, H-3), 6.15 (dd, 1 H, H-3′), 7.2–8.1 (6 C_6H_5), 7.40 (s, 1 H, NOH, disappearing on deuteration), 4.0–4.7 (other protons); $J_{1a,1e} = 17.0$, $J_{3,4} = 4.0$, $J_{1',2'} = 3.5$, $J_{2',3'} = 10.0$, $J_{3',4'} = J_{4',5'} = 9.0$ Hz. Anal. Calcd for $C_{54}H_{45}NO_{16}$: C, 67.28; H, 4.70; N, 1.45. Found: C, 67.34; H, 4.66; N, 1.55.

3,6-Di-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-1,5-anhydro-D-fructose Oxime (18b). A solution of hydroxycellobial **17b** (6.0 g, 5.7 mmol) in pyridine (50 mL) and hydroxylamine hydrochloride (1.6 g, 23 mmol) was kept at 70 °C overnight (13–15 h) and subsequently processed as described for the lactose-derived analogue **12** (cf. above) to afford 5.1 g (93%) of **18b** as an amorphous product, softening at 101–106 °C: $[\alpha]^{22}_D$ +14° (*c* 1, $CHCl_3$); ^1H NMR (100 MHz, $CDCl_3$) δ 3.6 (m, 1 H, H-5), 4.90 (d, 1 H, H-1e), 5.20 (d, 1 H, H-1′), 5.4–5.7 (m, 2 H, H-2′, H-4′), 5.92 (t, 1 H, H-3′), 6.12 (d, 1 H, H-3), 7.1–8.1 (6 C_6H_5), 8.54 (s, 1 H, NOH, disappearing on deuteration), 4.0–4.6 (other protons); $J_{1a,1e} = 16$, $J_{3,4} = 4$, $J_{1',2'} = 8$, $J_{2',3'} = J_{3',4'} = 9$ Hz. Anal. Calcd for $C_{54}H_{45}NO_{16}$: C, 67.28; H, 4.70; N, 1.45. Found: C, 67.20; H, 4.65; N, 1.43.

3,6-Di-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl)-1,5-anhydro-D-fructose *O*-Benzoyloxime (19a). Oxime **18a** (2.5 g, 2.6 mmol) was treated with benzoyl chloride (3 mL, 26 mmol) in pyridine (15 mL) as described for **13**. Aqueous workup and crystallization from ethanol gave 2.46 g (89%) of **19a**: mp 100–103 °C; $[\alpha]^{20}_D$ +44.7° (*c* 1, $CHCl_3$); ^1H NMR (100 MHz, $CDCl_3$) δ 4.1 (m, 1 H, H-5), 4.78 (d, 1 H, H-1a), 5.15 (d, 1 H, H-1e), 5.58 (dd, 1 H, H-2′), 5.74 (dd, 1 H, H-4′), 5.84 (d, 1 H, H-1′), 5.91 (d, 1 H, H-3), 6.16 (dd, 1 H, H-3′), 7.1–8.1 (7 C_6H_5), 4.3–4.9 (other protons); $J_{1e,1a} = 18.0$, $J_{3,4} = 4.0$, $J_{1',2'} = 4.0$, $J_{2',3'} = 10.0$, $J_{3',4'} = J_{4',5'} = 9.0$ Hz. Anal. Calcd for $C_{61}H_{49}NO_{17}$: C, 68.60; H, 4.62; N, 1.31. Found: C, 68.64; H, 4.59; N, 1.26.

3,6-Di-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-1,5-anhydro-D-fructose *O*-Benzoyloxime (19b). Oxime **18b** (2.0 g, 2.07 mmol) was treated with benzoyl chloride (2.4 mL, 21 mmol) in pyridine (12 mL) as described for **13**. Aqueous workup of the mixture and subsequent crystallization from ethanol afforded 2.03 g (92%) of **19b**: mp 187–189 °C; $[\alpha]^{18}_D$ +23.8° (*c* 0.5, $CHCl_3$); ^1H NMR (100 MHz, $CDCl_3$) δ 3.7 (m, 1 H, H-5), 5.14 (d, 1 H, H-1e), 5.22 (d, 1 H, H-1′), 5.5–5.7 (m, 2 H, H-2′, H-4′), 5.93 (t, 1 H, H-3′), 6.32 (d, 1 H, H-3), 7.1–8.1 (7 C_6H_5), 4.1–4.7 (other protons); $J_{1a,1e} = 16$, $J_{3,4} = 4$, $J_{1',2'} = 8$, $J_{2',3'} = J_{3',4'} = 9$ Hz. Anal. Calcd for $C_{61}H_{49}NO_{17}$: C, 68.60; H, 4.62; N, 1.31. Found: C, 68.49; H, 4.54; N, 1.38.

3,6-Di-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-α-D-*arabino*-hexopyranos-2-ulosyl Bromide (20). To a solution of 5.0 g (4.8 mmol) of hydroxycellobial heptabenzoate **17b** in 50 mL of dichloromethane were added methanol (0.3 mL, 6 mmol) and freshly glowed molecular sieves (3 Å), and the mixture was stirred 30 min at ambient room temperature. Subsequently, *N*-bromosuccinimide (1.1 g, 6 mmol) was added, and stirring was continued for another 15 min. The orange-colored solution was then diluted with dichloromethane (100 mL) followed by washing with 10% aqueous solution of $Na_2S_2O_3$ (2 × 50 mL)

(49) Kochetkov, N. K.; Khorlin, A. Y.; Bochkov, A. F.; Demushkina, L. B.; Zolutkhin, I. O. *Zh. Obsch. Khim.* **1967**, *37*, 1272.

and water (2 × 50 mL). Drying (Na_2SO_4) and removal of the solvent yielded a colorless syrup contaminated with some methyl benzoate. Trituration of an ether solution with *n*-hexane until beginning turbidity resulted in a flocculant precipitate, which was collected after standing overnight: 4.1 g (83%) of a uniform (R_f 0.56 in toluene/ethyl acetate, 10:1), amorphous product, softening at 104–112 °C; $[\alpha]^{20}_D$ +80° (*c* 0.3, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 3.83 (ddd, 1 H, H-5), 4.07 and 4.20 (two dd, 1 H each, 6-H_2), 4.5 (m, 3 H, H-5′, 6′-H_2), 4.64 (dd, 1 H, H-4), 5.05 (d, 1 H, H-1′), 5.53 (dd, 1 H, H-4′), 5.58 (dd, 1 H, H-2′), 5.79 (dd, 1 H, H-3′), 6.29 (d, 1 H, H-3), 6.38 (s, 1 H, H-1); $J_{3,4}$ = 9.0, $J_{4,5}$ = 9.0, $J_{5,6a}$ = 3.0, $J_{5,6b}$ = 4.5, $J_{6a,b}$ = 12.1, $J_{1',2'}$ = 7.9, $J_{2',3'} = J_{3',4'} = J_{4',5'}$ = 9.5 Hz. Anal. Calcd for $C_{54}H_{43}O_{16}Br$: C, 63.10; H, 4.22. Found: C, 62.99; H, 4.20.

3,6-Di-*O*-benzoyl-2-(benzoyloximino)-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-α-D-*arabino*-hexopyranosyl Bromide (21). A mixture of benzoyloxime **19b** (600 mg, 0.562 mmol) and *N*-bromosuccinimide (110 mg, 0.618 mmol) in ethanol-free tetrachloromethane (20 mL) was irradiated with a 450-W heat lamp for 0.5 h, followed by processing of the mixture as described for **8**. Crystallization from ether–pentane provided 580 mg (90%) of **21**: mp 113–116 °C; $[\alpha]^{20}_D$ +174° (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 3.85 (m, 1 H, H-5), 4.58 (t, 1 H, H-4), 5.12 (d, 1 H, H-1′), 5.56 (t, 1 H, H-4′), 5.59 (dd, 1 H, H-2′), 5.81 (t, 1 H, H-3′), 6.58 (d, 1 H, H-3), 7.2–8.2 (7 C_6H_5, H-1), 4.1–4.8 (other protons); $J_{1',2'}$ = 8.0, $J_{2',3'} = J_{3',4'} = J_{4',5'}$ = 9.8, $J_{3,4} = J_{4,5}$ = 9.3 Hz. Anal. Calcd for $C_{61}H_{48}BrNO_{17}$: C, 63.88; H, 4.22; N, 1.22. Found: C, 64.01; H, 4.19; N, 1.19.

3,6-Di-*O*-benzoyl-2-(benzoyloximino)-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl)-α-D-*arabino*-hexopyranosyl Bromide (22). A mixture of benzoyloxime **19a** (0.72 g, 0.67 mmol) and *N*-bromosuccinimide (0.13 g, 0.74 mmol) in ethanol-free tetrachloromethane (20 mL) was irradiated with a 450-W heat lamp for 0.5 h, followed by processing of the mixture as described for **8**. Crystallization from ether–pentane provided 0.74 g (96%) of **22**: mp 111–113 °C; $[\alpha]^{20}_D$ +173° (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 5.42 (dd, 1 H, H-2′), 5.74 (t, 1 H, H-4′, 5.92 (d, 1 H, H-1′), 6.16 (dd, 1 H, H-3′), 6.35 (d, 1 H, H-3), 7.2–8.1 (H-1, 7 C_6H_5), 4.3–4.9 (other protons); $J_{1',2'}$ = 3.8, $J_{2',3'}$ = 10.3, $J_{3',4'} = J_{4',5'}$ = 9.8, $J_{3,4}$ = 7.5 Hz. Anal. Calcd for $C_{61}H_{48}BrNO_{17}$: C, 63.88; H, 4.22; N, 1.22. Found: C, 63.86; H, 4.16; N, 1.20.

Methyl 3,6-Di-*O*-benzoyl-2-oximino-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-β-D-*arabino*-hexopyranoside (23). A mixture of β-glycoside **24** (150 mg, 0.14 mmol) and hydrazine hydrate (0.05 mL, 1.1 mmol) in 90% aqueous ethanol (4 mL) was stirred at room temperature for 2 h, whereupon TLC showed absence of educt. The mixture was neutralized with 1 N HCl and the resulting precipitate was filtered, washed with ethanol and was subsequently purified by elution from a short silica gel column with benzene–ethyl acetate (5:1). Concentration of the major fraction followed by crystallization from ether–pentane gave 105 mg (77%) of **23**: mp 105–107 °C; $[\alpha]^{21}_D$ +47.2° (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 3.49 (s, 3 H, OMe), 3.92 (m, 1 H, H-5), 4.52 (dd, 1 H, H-4), 5.14 (d, 1 H, H-1′), 5.57 (dd, 1 H, H-3′), 5.64 (s, 1 H, H-1), 5.80 (dd, 1 H, H-2′), 5.93 (br d, 1 H, H-4′), 6.14 (d, 1 H, H-3), 7.2–8.0 (6 C_6H_5), 8.38 (s, 1 H, NOH, exchangeable on deuteration), 4.3–4.5 (other protons); $J_{3,4}$ = 4.5, $J_{4,5}$ = 7.3, $J_{1',2'}$ = 8.0, $J_{2',3'}$ = 10.3, $J_{3',4}$ = 3.5, $J_{4',5'} \simeq$ 1 Hz. Anal. Calcd for $C_{55}H_{47}NO_{17}$: C, 66.46; H, 4.77; N, 1.41. Found: C, 66.37; H, 4.66; N, 1.34.

Methyl 3,6-Di-*O*-benzoyl-2-(benzoyloximino)-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-β-D-*arabino*-hexopyranoside (24). Oximinoglycosyl bromide **8** (6.0 g, 5.2 mmol) was added to a mixture of methanol (2.2 mL, 52 mmol), silver carbonate (4.33 g, 15.7 mmol), and iodine (1.33 g, 5.2 mmol) in dry dioxane (60 mL) with molecular sieves (3 Å, 3 g, powder). The mixture was stirred in the dark at room temperature for 30 h, whereafter all the educt had been consumed (TLC), followed by dilution with dichloromethane (200 mL), and filtered through celite. The filtrate was washed with 0.1 N aqueous $Na_2S_2O_3$ (100 mL), water (100 mL), saturated aqueous $NaHCO_3$ (100 mL), and water (3 × 100 mL). Drying (Na_2SO_4) and evaporation on a rotatory evaporator gave a yellowish syrup, which was eluted through a silica gel column with toluene–ethyl acetate (10:1). The major fraction was concentrated and crystallized from ether to furnish 4.48 g (79%) of **24** as colorless crystals: mp 116–118 °C; $[\alpha]^{18}_D$ +40.2° (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 3.60 (s, 3 H, OMe), 3.99 (dt, 1 H, H-5), 4.56 (dd, 1 H, H-4), 5.14 (d, 1 H, H-1′), 5.59 (dd, 1 H, H-3′), 5.76 (s, 1 H, H-1), 5.82 (dd, 1 H, H-2′), 5.97 (br d, 1 H, H-4′), 6.37 (d, 1 H, H-3), 7.2–8.1 (7 C_6H_5), 4.3–4.5 (other protons); $J_{3,4}$ = 4.3, $J_{4,5}$ = 7.0, $J_{5,6}$ = 4.5, $J_{1',2'}$ = 8.0, $J_{2',3'}$ = 10.5, $J_{3',4'}$ = 3.5, $J_{4',5'} \simeq$ 1.5 Hz. Anal. Calcd for $C_{62}H_{51}NO_{18}$: C, 67.82; H, 4.68; N, 1.28. Found: C, 67.86; H, 4.58; N, 1.24.

Benzyl 3,6-Di-*O*-benzoyl-2-(benzoyloximino)-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-β-D-*arabino*-hexopyranoside (25). A mixture of benzyl alcohol (0.07 mL, 0.70 mmol), silver carbonate (57.6 mg, 0.21 mmol), and oximinoglycosyl bromide **8** (80 mg, 0.07 mmol) in dry dioxane (1 mL) with molecular sieves (3 Å, 100 mg, powder) was stirred in the dark at room temperature for 2 days. The resulting mixture was diluted with dichloromethane (10 mL), filtered through Celite, and washed with water, saturated aqueous $NaHCO_3$, and water. After drying (Na_2SO_4), the solvent was removed in vacuo to give a syrup, which was eluted through a silica gel column with benzene–ethyl acetate (10:1). Concentration of the major fraction (eluted first), followed by crystallization of the residue from ether–pentane, provided 67 g (82%) of **25**: mp 96–98 °C; $[\alpha]^{17}_D$ +27.8° (*c* 0.58, $CHCl_3$); ^1H NMR (100 MHz, $CDCl_3$) δ 4.03 (m, 1 H, H-5), 4.71 and 4.92 (two 1 H-d, benzyl-H_2), 5.15 (d, 1 H, H-1′), 5.59 (dd, 1 H, H-3′), 5.84 (dd, 1 H, H-2′), 5.95 (s, 1 H, H-1), 5.98 (d, 1 H, H-4′), 6.38 (d, 1 H, H-3), 7.1–8.1 (7 C_6H_5), 4.3–4.6 (other protons); $J_{3,4}$ = 4.0, $J_{1',2'}$ = 8.0, $J_{2',3'}$ = 10.5, $J_{3',4'}$ = 3.5 Hz. Anal. Calcd for $C_{68}H_{55}NO_{18}$: C, 69.56; H, 4.72; N, 1.19. Found: C, 69.16; H, 4.63; N, 1.11.

Cyclohexyl 3,6-Di-*O*-benzoyl-2-(benzoyloximino)-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-β-D-*arabino*-hexopyranoside (26). A mixture of cyclohexanol (0.075 mL, 0.7 mmol), silver carbonate (115 mg, 0.42 mmol), molecular sieves (3 Å, 100 mg), and oximinoglycosyl bromide **8** (80 mg, 0.07 mmol) in dry dioxane (1 mL) was stirred in the dark at room temperature for 3 days. Workup of the mixture as described for **24** and crystallization of the residue from ether–pentane gave 63 mg (77%) of **26**: mp 103–105 °C; $[\alpha]^{18}_D$ +38.8° (*c* 0.5, $CHCl_3$); ^1H NMR (100 MHz, $CDCl_3$) δ 1.7–1.9 (m, cyclohexyl-H), 5.16 (d, 1 H, H-1′), 5.61 (dd, 1 H, H-3′), 5.84 (dd, 1 H, H-2′), 5.99 (s, 1 H, H-1), ca. 6.02 (m, 1 H, H-4′), 6.33 (d, 1 H, H-3), 7.1–8.1 (6 C_6H_5), 3.8–4.5 (other protons); $J_{3,4}$ = 3.5, $J_{1',2'}$ = 8, $J_{2',3'}$ = 10.5, $J_{3',4'}$ = 3.5 Hz. Anal. Calcd for $C_{67}H_{59}NO_{18}$: C, 69.01; H, 5.10; N, 1.20. Found: C, 68.62; H, 4.85; N, 1.19.

Methyl 2-Acetamido-3,6-di-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-2-deoxy-β-D-mannopyranoside (27). A solution of methyl β-glycoside **24** (500 mg, 0.46 mmol) in tetrahydrofuran (5 mL) was treated at −10 °C with a 1 M solution of diborane in tetrahydrofuran (5.5 mL) and the mixture was stirred for 30 min at −10 °C and 2 h at ambient temperature. Excess reductant was decomposed by the addition of methanol (4 mL) followed by addition of acetic anhydride (2 mL) for N-acetylation (1 h, 25 °C), passing of the solution through a basic ion exchanger (OH^1 form), and washing with methanol. The eluate was taken to dryness and the residue was purified by fast elution from a silica gel column (2 × 15 cm) with benzene–ethyl acetate (2:1). On concentration of the main fraction, dissolution of the residue in ether–ethyl acetate (2:1), and addition of *n*-pentane **27** crystallized: 428 mg (92%); mp 123–125 °C; $[\alpha]^{19}_D$ +47° (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 1.94 (s, 3 H, NAc), 3.43 (s, 3 H, OMe), 3.81 (dt, 1 H, H-5), 4.16 (dd, 1 H, H-4), 4.64 (d, 1 H, H-1), 4.88 (dt, 1 H, H-2), 4.98 (d, 1 H, H-1′), 5.49 (dd, 1 H, H-3), 5.51 (dd, 1 H, H-3′), 5.71 (d, 1 H, NH), 5.75 (dd, 1 H, H-2′), 5.84 (br d, 1 H, H-4′); $J_{1,2}$ = 1.5, $J_{2,3}$ = 4.0, $J_{2,NH}$ = 8.5, $J_{3,4} = J_{4,5}$ = 9.0, $J_{1',2'}$ = 8.0, $J_{2',3'}$ = 10.5, $J_{3',4'}$ = 3.5, $J_{4',5'} \simeq$ 1 Hz.

The analytical sample had to be dried over P_4O_{10} at 56 °C to afford acceptable values. Without that, **27** analyzed for a monohydrate. Anal. Calcd for $C_{57}H_{51}NO_{17}$: C, 66.99; H, 5.03; N, 1.37. Found: C, 66.83; H, 4.95; N, 1.32.

A minor fraction eluted from the above silica gel column following **27** comprised, on removal of the solvent, 16 mg (4%) of the 3-de-O-benzoylated derivative of **27**, as evidenced by ^1H NMR (300 MHz, $CDCl_3$) of the product (amorphous, $[\alpha]^{20}_D$ +64° in chloroform) obtained on acetylation (pyridine/acetic anhydride, 2 h at 25 °C): δ 1.96 (s, 3 H, NAc), 2.11 (s, 3 H, OAc), 3.37 (s,

3 H, OMe), 3.74 (td, 1 H, H-5), 4.02 (t, 1 H, H-4), 4.52 (d, 1 H, H-1), 4.69 (dt, 1 H, H-2), 4.99 (d, 1 H, H-1'), 5.18 (dd, 1 H, H-3), 5.59 (dd, 1 H, H-3'), 5.63 (d, 1 H, NH), 5.78 (dd, 1 H, H-2'), 5.98 (br d, 1 H, H-4'), 7.2–8.2 (5 C_6H_5), 4.2–4.8 (other protons); $J_{1,2}$ = 1.5, $J_{2,3}$ = 4.0, $J_{2,NH}$ = 8.5, $J_{3,4}$ = $J_{4,5}$ = 9.3, $J_{1',2'}$ = 8.0, $J_{2',3'}$ = 10.5, $J_{3',4'}$ = 3.5, $J_{4',5'}$ = 1 Hz.

Methyl 2-Acetamido-2-deoxy-4-*O*-(β-D-galactopyranosyl)-β-D-mannopyranoside (28). A solution of **27** (205 mg, 0.2 mmol) in 0.05 M methanolic sodium methoxide (5 mL) was stirred at room temperature for 16 h and was subsequently neutralized with a dry acidic resin (Amberlite IR-120, H^+ form) and filtered. The filtrate was evaporated to dryness and the residue was partitioned between dichloromethane (15 mL) and water (15 mL). The aqueous layer was separated and washed with dichloromethane (2 × 20 mL), and the combined organic solutions were taken to dryness. The residue crystallized from methanol/ether: 68 mg (86%) of **28** as colorless crystals of mp 274–276 °C dec; $[\alpha]^{22}_D$ = −23° (*c* 0.5, water); ^{1}H NMR (300 MHz, D_2O) δ 2.07 (s, 3 H, NAc), 3.52 (s, 3 H, OMe), 4.46 (d, 1 H, H-1'), 4.56 (dd, 1 H, H-2), 4.73 (d, 1 H, H-1); $J_{1,2}$ = 1.5, $J_{1',2'}$ = 7.7, $J_{2,3}$ = 4.0 Hz; ^{13}C NMR (D_2O) δ 175.3 (s, NHC=O), 103.0 (d, C-1'), 100.3 (d, C-1), 76.0, 75.3, and 75.2 (d each, C-4, C-5, C-5'), 72.4, 70.9, and 70.6 (d, each, C-3', C-2', C-3), 68.5 (d, C-4'), 61.0 (t, C-6'), 59.8 (t, C-6), 56.8 (q, OMe), 52.1 (d, C-2), 21.9 (q, Ac-CH_3). Anal. Calcd for $C_{15}H_{27}NO_{11}$: C, 45.34; H, 6.84; N, 3.52. Found: C, 45.26; H, 6.77; N, 3.44.

Isopropyl Hexa-*O*-benzoyl-β-D-lactosuloside [Isopropyl 3,6-Di-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-β-D-*arabino*-hexopyranosid-2-ulose] (29). Lactosulosyl bromide **7** (514 mg, 0.5 mmol) was added to a stirred mixture of silver carbonate (165 mg, 0.6 mmol), molecular sieves (3 Å, 0.5 g), and dry isopropyl alcohol (0.05 mL, 0.6 mmol) in dichloromethane (5 mL), and stirring at room temperature was continued overnight. Subsequent filtration and removal of the solvent gave **29** as an amorphous solid (450 mg, 90%) of $[\alpha]^{20}_D$ +43° (*c* 1, $CHCl_3$) and R_f 0.4–0.5 in dichloromethane–ethyl acetate (10:1), i.e., the usual tailing observed for ulosides: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18 and 1.22 (2 d, 3 H each, isopropyl-CH_3), 4.67 (dd, 1 H, H-4), 4.94 (d, 1 H, H-1'), 5.04 (s, 1 H, H-1), 5.48 (dd, 1 H, H-3'), 5.75 (dd, 1 H, H-2'), 5.86 (d, 1 H, H-3), 5.82 (br d, 1 H, H-4'), 7.2–8.1 (6 C_6H_5); $J_{3,4}$ = 9.5, $J_{4,5}$ = 7.9, $J_{1',2'}$ = 8.0, $J_{2',3'}$ = 10.4, $J_{3',4'}$ = 3.4 Hz. Anal. Calcd for $C_{57}H_{50}O_{17}$: C, 59.64; H, 8.35. Found: C, 59.50; H, 8.31.

Isopropyl 4-*O*-(β-D-Galactopyranosyl)-β-D-mannopyranoside (30). A solution of uloside **29** (400 mg, 0.39 mmol) in dioxane (5 mL) containing 0.5 mL of water was cooled to 0 °C followed by the addition of sodium borohydride (19 mg, 0.5 mmol).[50] After 2 h at ambient temperature the reaction was quenched by acetic acid (0.02 mL) and the mixture was taken to dryness, affording 400 mg of a colorless amorphous solid containing two products in an approximate 4:1 ratio (R_f 0.39 and 0.46, respectively, TLC in dichloromethane–ethyl acetate, 10:1). The major fraction eluted second with the same solvent combination from a silica gel column was taken to dryness and debenzoylated with 0.05 M methanolic sodium methoxide (16 mL) at 0 °C for 12 h. Neutralization with Amberlite IR 120 (H^+ form), filtration, and evaporation left a homogeneous (R_f 0.41 in *n*-pentane–ethyl acetate–water, 7:1:1) syrup which gave an amorphous solid on trituration with ethanol: 110 mg (72%) of **30**; $[\alpha]^{22}_D$ −22° (*c* 1, water); ^{1}H NMR (300 MHz, D_2O) δ 1.21 and 1.25 (2 d, 3 H each, isopropyl-CH_3), 4.15 (qq, 1 H, isopropyl-CH), 4.46 (d, 1 H, H-1'), 4.82 (d, 1 H, H-1); $J_{1,2}$ < 1, $J_{1',2'}$ = 7.8 Hz; ^{13}C NMR (D_2O) δ 104.2 (d, C-1'), 101.6 (d, C-1), 79.9 (d, isopropyl-C, C-1), 79.9 (d, OCH), 76.6, 76.0, 75.8 (d each, C-3, C-4, C-5'), 74.5, 74.2, 73.8 (d each, C-2, C-5, C-3'), 72.3 (d, C-2'), 69.8 (d, C-4'), 62.3, 61.5 (t each, C-6, C-6'), 23.6 and 22.3 (2 q, 2 isopropyl-CH_3). Anal. Calcd for $C_{15}H_{28}O_{11}$: C, 46.87; H, 7.34. Found: C, 46.80; H, 7.22.

3,6-Di-*O*-benzoyl-2-nitroso-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-1,5-anhydro-D-*arabino*-hex-1-enitol (31). To a solution of oximinoglycosyl bromide **8** (80 mg, 0.07 mmol) and iodine (20 mg, 0.08 mmol) in dry *N*,*N*-dimethylformamide (1 mL) was added *s*-collidine (0.01 mL, 0.08 mmol), and the mixture was stirred at room temperature for 20 h. Subsequent dilution with dichloromethane, washing with 0.1 N aqueous $Na_2S_2O_3$, water, 0.1 N HCl, and again water was followed by drying (Na_2SO_4) and removal of the solvent in vacuo. The resulting syrup was purified by elution from a silica gel column with benzene–ethyl acetate (10:1 → 5:1 gradient). The major fraction (eluted second) was concentrated to a syrup which crystallized from ether–pentane: 45 mg (67%) of presumably dimeric **31** as a colorless, microcrystalline solid of mp 118–121 °C and $[\alpha]^{17}_D$ +64.2° (*c* 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.05 (d, 1 H, H-1'), 5.49 (dd, 1 H, H-3'), 5.77 (dd, 1 H, H-2'), 5.82 (br d, 1 H, H-4'), 6.42 (m, 2 H, H-1, H-3), 7.2–8.3 (6 C_6H_5), 3.9–4.7 (other protons); $J_{3,4}$ = 3.5, $J_{1',2'}$ = 8.0, $J_{2',3'}$ = 10.3, $J_{3',4'}$ = 3.5, $J_{4',5'}$ = 1.0 Hz. Anal. Calcd for $C_{54}H_{43}NO_{16}$: C, 67.43; H, 4.51; N, 1.46. Found: C, 67.13; H, 4.50; N, 1.37.

Methyl Hexa-*O*-benzoyl-α-D-lactosuloside Oxime [Methyl 3,6-Di-*O*-benzoyl-2-oximino-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-α-D-*arabino*-hexopyranoside] (32). A. By Selective Debenzoylation of 33 with Hydrazine. A mixture of α-glycoside **33** (150 mg, 0.14 mmol) and hydrazine hydrate (0.05 mL, 1.1 mmol) in 90% aqueous ethanol (4 mL) was stirred at ambient temperature for 2 h, whereupon TLC indicated absence of educt. The mixture was neutralized with 1 N HCl, and the resulting precipitate was filtered, washed with ethanol, and subsequently purified by elution from a short silica gel column with benzene–ethyl acetate (5:1). Concentration of the major fraction followed by crystallization from ether–pentane gave 108 mg (79%) of **32**: mp 118–120 °C; $[\alpha]^{20}_D$ +75° (*c* 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.42 (s, 3 H, OMe), 4.37 (t, 1 H, H-4), 4.65 (dd, 1 H, H-5'), 5.01 (d, 1 H, H-1'), 5.48 (dd, 1 H, H-3'), 5.75 (dd, 1 H, H-2'), 5.83 (br d, 1 H, H-4'), 5.86 (s, 1 H, H-1), 6.18 (d, 1 H, H-3), 7.2–8.2 (6 C_6H_5), 8.10 (s, 1 H, NOH, exchangeable on deuteration), 3.9–4.5 (other protons); $J_{3,4}$ = $J_{4,5}$ = 9.5, $J_{1',2'}$ = 8.0, $J_{2',3'}$ = 10.5, $J_{3',4'}$ = 3.5, $J_{4',5'}$ ≃ 1.5 Hz; IR (KBr) 3420 cm^{-1} (NOH). Anal. Calcd for $C_{55}H_{47}NO_{17}$: C, 66.46; H, 4.77; N, 1.41. Found: C, 66.26; H, 4.75; N, 1.40.

B. By Methanolysis of 8. A solution of **8** (160 mg, 0.14 mmol) in dry methanol (4 mL) was refluxed for 3 h, whereafter TLC indicated absence of educt. The mixture was taken to dryness and the residue was purified by elution from a silica gel column with benzene–ethyl acetate (10:1 → 5:1 gradient). The major fraction was concentrated and the residue was crystallized from ether–pentane: 95 mg (62%) of **32**, identical with the product described under A.

Methyl 3,6-Di-*O*-benzoyl-2-(benzoyloximino)-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-α-D-*arabino*-hexopyranoside (33). A mixture of **8** (1.15 g, 1 mmol), molecular sieves (3 Å, 1.0 g), 1,1,3,3-tetramethylurea (0.25 mL, 2 mmol), *s*-collidine (0.15 mL, 1.1 mmol), iodine (250 mg, 1 mmol), methanol (0.2 mL, 5 mmol), and dry dioxane (10 mL) was stirred under an atmosphere of nitrogen at ambient temperature for 2 days, was subsequently diluted with dichloromethane (50 mL) and filtered through Celite. The filtrate was washed with 0.1 N $Na_2S_2O_3$ (20 mL), water (30 mL), 0.1 N HCl (20 mL), water (30 mL), saturated aqueous $NaHCO_3$ (20 mL), and water (3 × 30 mL). After drying (Na_2SO_4), the solvent was removed in vacuo to give a syrup comprising an approximate 12:1 mixture (^{1}H NMR) of **33** and its β-anomer. Elution from a silica gel column with benzene–ethyl acetate (10:1), concentration of the major fraction, and crystallization of the residue from ether–pentane afforded 930 mg (84%) of **33**: mp 117–119 °C; $[\alpha]^{18}_D$ +72.4° (*c* 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.53 (s, 3 H, OMe), 4.51 (t, 1 H, H-4), 4.69 (dd, 1 H, H-5'), 5.05 (d, 1 H, H-1'), 5.49 (dd, 1 H, H-3'), 5.78 (dd, 1 H, H-2'), 5.83 (br d, 1 H, H-4'), 5.95 (s, 1 H, H-1), 6.39 (d, 1 H, H-3), 7.2–8.4 (7 C_6H_5), 3.9–4.7 (other protons); $J_{3,4}$ = $J_{4,5}$ = 9.3, $J_{1',2'}$ = 8.0, $J_{2',3'}$ = 10.5, $J_{3',4'}$ = 3.3, $J_{4',5'}$ ≃ 1.5 Hz. Anal. Calcd for $C_{62}H_{51}NO_{18}$: C, 67.82; H, 4.68; N, 1.28. Found: C, 67.72; H, 4.67; N, 1.31.

Benzyl 3,6-Di-*O*-benzoyl-2-(benzoyloximino)-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-α-D-*arabino*-hexopyranoside (34). Treatment of **8** with benzyl alcohol (5 molar equiv) and *s*-collidine (1.1 molar equiv) in a manner analogous to the conversion **8** → **33** gave **34** in 82% yield: mp 106–108 °C (from ether–pentane); $[\alpha]^{19}_D$ +99.4° (*c* 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.51 (t, 1 H, H-4), 4.64 (dd, 1 H, H-5'), 4.68 and 4.83 (two 1 H-d, benzyl-H_2), 5.04 (d, 1 H, H-1'),

(50) Conditions adapted from a procedure previously used by Lemieux et al.[40] for similar glycobiosulosides.

5.47 (dd, 1 H, H-3′), 5.77 (dd, 1 H, H-2′), 5.81 (br d, 1 H, H-4′), 6.06 (s, 1 H, H-1), 6.45 (d, 1 H, H-3), 7.2–8.3 (8 C_6H_5), 3.9–4.5 (other protons); $J_{3,4} = J_{4,5} = 9.0$, $J_{1',2'} = 8.0$, $J_{2',3'} = 10.5$, $J_{3',4'} = 3.5$, $J_{4',5'} = 1.5$ Hz. Anal. Calcd for $C_{68}H_{55}NO_{18}$: C, 69.56; H, 4.72; N, 1.19. Found: C, 69.47; H, 4.62; N, 1.13.

Cyclohexyl 3,6-Di-*O*-benzoyl-2-(benzoyloximino)-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-α-D-*arabino*-hexopyranoside (35). Subjection of **8** to treatment with cyclohexanol (8 molar equiv) and *s*-collidine (1.1 molar equiv) in dioxane (2 days, 25 °C) and processing of the mixture as described for **33** furnished **35** in 78% yield: mp 112–114 °C; $[\alpha]^{22}_D$ +91.4° (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 1.2–1.8 (m, 10 H, cyclohexyl-H_2), 4.65 (br d, 1 H, H-5′), 5.04 (d, 1 H, H-1′), 5.47 (dd, 1 H, H-3′), 5.77 (dd, 1 H, H-2′), 5.80 (br d, 1 H, H-4′), 6.18 (s, 1 H, H-1), 6.40 (d, 1 H, H-3), 7.2–8.3 (7 C_6H_5), 3.7–4.5 (other protons); $J_{3,4} = 8.3$, $J_{1',2'} = 10.3$, $J_{3',4'} = 3.3$, $J_{4',5'} \simeq 1$ Hz. Anal. Calcd for $C_{67}H_{59}NO_{18}$: C, 69.01; H, 5.10; N, 1.20. Found: C, 68.65; H, 5.06; N, 1.16.

Methyl 2-Acetamido-3,6-di-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-2-deoxy-α-D-glucopyranoside [Methyl *N*-Acetylhexa-*O*-benzoyl-α-D-lactosaminide] (36). A 1 M solution of diborane in tetrahydrofuran (4.4 mL) was added to a stirred solution of oximino glycoside **33** (400 mg, 0.36 mmol) in tetrahydrofuran (4 mL) at −10 °C under an atmosphere of nitrogen. The mixture was stirred for 0.5 h at −10 °C and then allowed to warm to room temperature with further stirring for 2 h, whereafter all the educt had been consumed (TLC). Excess diborane was decomposed by the addition of methanol (4 mL) and then acetic anhydride (2 mL) was added for N-acetylation (1 h, 25 °C). The resulting mixture was eluted through a basic resin (Merck ion exchanger III, OH^- form) with methanol. The eluate was concentrated in vacuo and the residue was purified by being passed over a silica gel column with a 2:1 → 1:2 gradient of benzene/ethyl acetate. The major fraction eluted first was concentrated and the residue was crystallized by being dissolved in a 2:1 mixture of ether/ethyl acetate followed by addition of pentane: 280 mg (75%) of **36**; mp 130–132 °C; $[\alpha]^{21}_D$ +84.6° (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 1.86 (s, 3 H, NAc), 3.38 (s, 3 H, OMe), 4.20 (dd, 1 H, H-4), 4.51 (td, 1 H, H-2), 4.75 (d, 1 H, H-1), 4.92 (d, 1 H, H-1′), 5.41 (dd, 1 H, H-3′), 5.64 (dd, 1 H, H-3), 5.71 (dd, 1 H, H-2′), 5.77 (br d, 1 H, H-4′), 5.85 (d, 1 H, NH); $J_{1,2} = 3.5$, $J_{2,3} = 11.0$, $J_{2,NH} = 9.8$, $J_{3,4} = 9.3$, $J_{4,5} = 9.8$, $J_{1',2'} = 8.0$, $J_{2',3'} = 10.5$, $J_{3',4'} = 3.5$, $J_{4',5'} = 3.8$ Hz.

The analytical sample required drying over P_4O_{10} at 56 °C for 12 h to give acceptable values. Anal. Calcd for $C_{57}H_{51}NO_{17}$: C, 66.99; H, 5.03; N, 1.37. Found: C, 66.89; H, 4.93; N, 1.36.

The fraction eluted next was treated as above to give 20 mg (6%) of the 3-de-O-benzoylated derivative of **36** as evidenced by ^1H NMR (300 MHz, $CDCl_3$): δ 1.96 (s, 3 H, NAc), 3.33 (s, 3 H, OMe), 4.25 (td, 1 H, H-2), 4.69 (d, 1 H, H-1), 5.05 (d, 1 H, H-1′), 5.60 (dd, 1 H, H-3′), 5.62 (d, 1 H, NH), 5.91 (dd, 1 H, H-2′), 5.98 (br d, 1 H, H-4′); $J_{1,2} = 3.5$, $J_{2,3} = 10.5$, $J_{2,NH} = 9.0$, $J_{1',2'} = 8.0$, $J_{2',3'} = 10.5$, $J_{3',4'} = 3.5$, $J_{4',5'} \sim 1$ Hz.

Benzyl 2-Acetamido-3,6-di-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-2-deoxy-α-D-glucopyranoside (Benzyl Hexa-*O*-benzoyl-*N*-acetyl-α-D-lactosaminide) (37). A solution of benzyl α-glycoside **34** (500 mg, 0.43 mmol) in tetrahydrofuran (5 mL) was cooled (−10 °C) and a 1 M solution of diborane in tetrahydrofuran (5.1 mL) was added followed by stirring for 30 min at −10 °C and 2 h at ambient temperature. Excess reductant was decomposed by methanol (4 mL) and N-acetylation was effected by the addition of acetic anhydride (2 mL) and 1 h of stirring. The resulting mixture was passed through a basic ion exchanger (OH^- form) with methanol as the eluant. Removal of the solvent, purification of the residue by fast elution from a silica gel column (2 × 15 cm) with benzene–ethyl acetate (2:1 → 1:2 gradient), concentration of the main fraction to dryness, dissolution in ether–ethyl acetate (2:1), and addition of *n*-pentane resulted in crystallization: 375 mg (80 %) of **37**; mp 110–112 °C; $[\alpha]^{20}_D$ +81.6° (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 1.80 (s, 3 H, NAc), 4.22 (dd, 1 H, H-4), 4.51 (td, 1 H, H-2), 4.52 and 4.71 (two 1 H-d, benzyl-H_2), 4.91 (d, 1 H, H-1′), 4.95 (d, 1 H, H-1), 5.40 (dd, 1 H, H-3′), 5.66 (dd, 1 H, H-3), 5.71 (dd, 1 H, H-2′), 5.76 (br d, 1 H, H-4′), 5.82 (d, 1 H, NH), 7.2–8.3 (7 C_6H_5), 3.8–4.5 (other protons); $J_{1,2} = 3.5$, $J_{2,3} = 11.0$, $J_{2,NH} = 9.5$, $J_{3,4} = 9.3$, $J_{4,5} = 9.5$, $J_{1',2'} = 8.0$, $J_{2',3'} = 10.5$, $J_{3',4'} = 3.5$, $J_{4',5'} \simeq 1$, $J_{gem(benzyl\text{-}H_2)} = 12$ Hz. The analytical sample had to be dried over P_4O_{10} at 50 °C to give satisfactory values. Anal. Calcd for $C_{66}H_{55}NO_{17}$: C, 68.91; H, 4.97; N, 1.28. Found: C, 68.78; H, 5.13; N, 1.25.

Methyl 2-Acetamido-2-deoxy-4-*O*-(β-D-galactopyranosyl)-α-D-glucopyranoside (Methyl *N*-Acetyl-α-D-lactosaminide) (38). A solution of **36** (200 mg) in 0.05 M methanolic sodium methoxide (5 mL) was kept for 15 h at room temperature and the mixture was subsequently processed as described for **27** → **28** to provide 66 mg (79%) of **38** as colorless crystals (from methanol–ether); mp 216–218 °C; $[\alpha]^{22}_D$ −83.0° (*c* 0.5, water); ^1H NMR (300 MHz, D_2O) δ 2.04 (s, 3 H, NAc), 3.40 (s, 3 H, OMe), 4.48 (d, 1 H, $J_{1',2'} = 7.7$ Hz, H-1′), 4.79 (H-1, partly overlapped with D-OH signal); ^{13}C NMR (D_2O) δ 174.2 (NHCO), 102.7 (d, C-1′), 97.6 (d, C-1), 78.4 (d, C-4), 75.2 (d, C-5′), 72.4 (d, C-5), 70.8, 70.2, and 69.5 (d each, C-2′, C-3, C-3′), 68.4 (d, C-4′), 60.6 (t, C-6′), 59.8 (t, C-6), 55.1 (q, OCH_3), 53.1 (d, C-2), 21.7 (q, Ac-CH_3). Anal. Calcd for $C_{15}H_{27}NO_{11}\cdot H_2O$: C, 43.37; H, 7.03; N, 3.37. Found: C, 43.24; H, 6.93; N, 3.29.

For the β-methyl analogue of **38** rotations of −17°[51] and −23°,[52] in water at 22 °C, have been reported.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft for an operational grant (Li 95/35), the Humboldt Foundation for awarding a fellowship (to E.K.), and the Fonds der Chemischen Industrie for a Doktoranden-Stipendium (to S.W.).

Registry No. **6**, 87760-36-9; **7**, 87760-37-0; **8**, 97523-39-2; **9**, 41545-58-8; **9** (β-anomer), 41093-36-1; **10**, 61198-91-2; **11**, 97523-40-5; **12**, 97589-70-3; **13**, 97523-41-6; **14**, 97523-42-7; **15**, 97550-79-3; **16a**, 97523-43-8; **16b**, 18311-30-3; **17a**, 75414-17-4; **17b**, 97589-71-4; **18a**, 97589-72-5; **18b**, 97589-73-6; **19a**, 97523-44-9; **19b**, 97523-45-0; **20**, 87713-49-3; **21**, 97523-46-1; **22**, 97523-47-2; **23**, 97523-48-3; **24**, 97523-49-4; **25**, 97523-50-7; **26**, 97523-51-8; **27**, 97523-52-9; **27** (3-de-O-benzoylated deriv), 97523-53-0; **27** (3-O-acetyl deriv), 97523-66-5; **28**, 97523-54-1; **29**, 97523-55-2; **29** (2α-hydroxy deriv), 97523-64-3; **29** (2β-hydroxy deriv), 97523-65-4; **30**, 97523-56-3; **31**, 97523-57-4; **32**, 97523-58-5; **33**, 97523-59-6; **34**, 97523-60-9; **35**, 97523-61-0; **36**, 97523-62-1; **36** (3-de-O-benzoylated deriv), 97523-62-1; **37**, 97523-63-2; **38**, 85193-95-9; lactose, 63-42-3; *p*-cyanobenzoyl chloride, 6068-72-0; octa-*O*-benzoyl-β-D-maltose, 14200-60-3; octa-*O*-benzoyl-β-D-cellobiose, 4710-82-1; cyclohexanol, 108-93-0.

(51) Takamura, T.; Chiba, T.; Tejima, S. *Chem. Pharm. Bull.* **1981**, *29*, 2270.

(52) Kuhn, R.; Kirschenlohr, W. *Liebigs Ann. Chem.* **1956**, *600*, 135.