JOC Article

Intramolecular Hydrogen Abstraction Reaction Promoted by Alkoxy Radicals in Carbohydrates. Synthesis of Chiral 2,7-Dioxabicyclo[2.2.1]heptane and 6,8-Dioxabicyclo[3.2.1]octane Ring Systems

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The reaction of specifically protected anhydroalditols with (diacetoxyiodo)benzene or iodosylbenzene and iodine is a mild and selective procedure for the synthesis of chiral 6,8-dioxabicyclo[3.2.1]octane and 2,7-dioxabicyclo[2.2.1]heptane ring systems under neutral conditions. This reaction can be considered to be an intramolecular glycosidation that goes through an intramolecular hydrogen abstraction promoted by an alkoxy radical followed by oxidation of the transient *C*-radical intermediate to an oxycarbenium ion. This methodology is useful not only for the preparation of chiral synthons but also for the selective oxidation of specific carbons of the carbohydrate skeleton, constituting a good procedure for the synthesis of protected uloses.

The most representative examples of the 2,7-dioxabicyclo[2.2.1]heptane and 6,8-dioxabicyclo[3.2.1]octane systems are the 1,5-anhydrofuranoses, 1,4-anhydropyranoses, and 1,6-anhydropyranoses, a series of anhydrosugars to which the trivial name *glycosans* was given.[1] 1,6-Anhydropyranoses are generally formed by acid treatment of the corresponding carbohydrates, by thermal depolymerization of some polysaccharides, and by specific intramolecular glycosidation reactions by *O*-6 nucleophilic attack of a good leaving group at the anomeric center. In this latter case the opposite reaction, displacement of a 6-leaving group by the anomeric oxygen, may also be possible.[2] 1,5-Anhydrofuranoses and 1,4-anhydropyranoses, both possessing a 2,7-dioxabicyclo-[2.2.1]heptane ring system, are more strained compounds and require a more specific synthesis.[3]

These compounds are considered intramolecular glycosides and are important building blocks in synthetic organic chemistry for the preparation of enantiomerically pure non-carbohydrate compounds,[4] and also for the synthesis of complex oligosaccharides[5] and *C*-disaccharides.[6] The ether bridge locks the conformation of the carbohydrate ring and simultaneously protects two of the hydroxylic groups, which may be important features in a synthetic process.[7] Of special interest are the acid-catalyzed transformation of the 6,8-dioxabicyclo[3.2.1]-octane into the 2,8-dioxabicyclo[3.2.1]octane ring system present in the core of zaragozic acids,[8] and the synthesis of oxepanes by stereoselective reduction of the acetal group.[9]

Furthermore, 6,8-dioxabicyclo[3.2.1]octane structural units are widespread in bioactive natural products. These compounds can have relatively simple structures such as the pheromones frontalin,[10] multistriatin, and *exo*-brevicomin[11] or can be very complex substances isolated

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(9) (a) Ishihara, K.; Mori, A.; Yamamoto, H. *Tetrahedron* **1990**, *46*, 4595−4612. (b) Fujiwara, K.; Amano, A.; Tokiwano, T.; Murai, A. *Tetrahedron* **2000**, *56*, 1065−1080.

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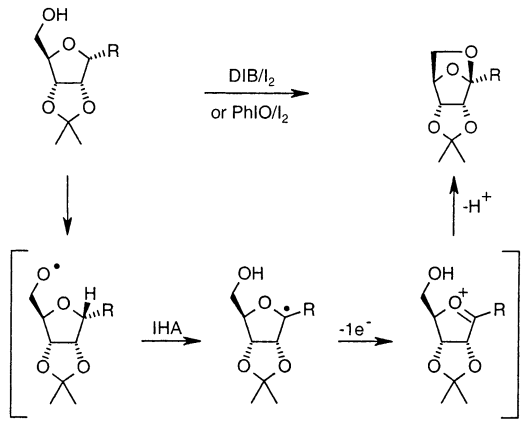
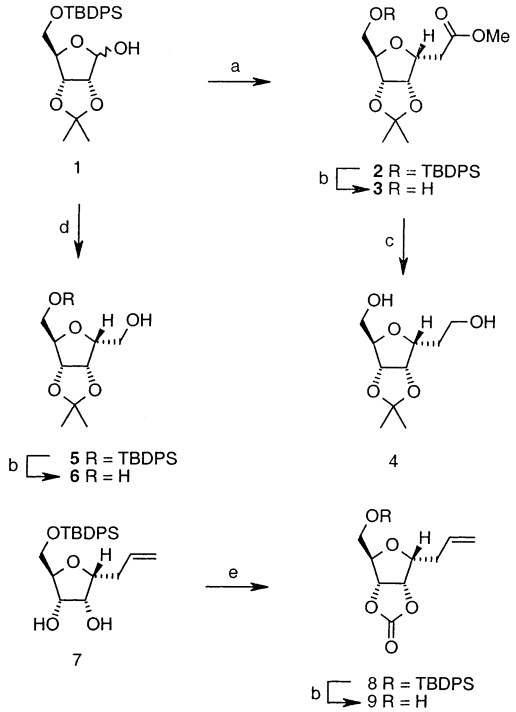
SCHEME 1



from marine organisms such as palytoxin,[12] pinnatoxin A,[13] didemniserinolipid A,[14] and cyclodidemniserinol.[15] On the other hand, the system 2,7-dioxabicyclo[2.2.1]heptane is also present in natural products such as isogosterone,[16] loukacinol B,[17] and salpichrolide J.[18]

The general route for the preparation of these dioxabicyclo[*n*.2.1]alkane ring systems during the synthesis of these natural products is the acid-catalyzed cyclization of the corresponding keto diols. Here we report on an alternative methodology for the synthesis of chiral 2,7-dioxabicyclo[2.2.1]heptane and 6,8-dioxabicyclo[3.2.1]-octane ring systems, under neutral conditions, using an intramolecular hydrogen abstraction (IHA) reaction.[19] The reaction was triggered by alkoxy radicals generated in situ by reaction of alcohols with (diacetoxyiodo)benzene (DIB) or iodosylbenzene in the presence of iodine. The *C*-radical generated by the IHA is subsequently oxidized with an excess of reagent to give an oxycarbenium ion that is then internally trapped by the nucleophilic alcohol (Scheme 1). In a previous communication, we described some preliminary results obtained,[20] and we now disclose herein full details of these experiments. The reaction was tested in the pentose and hexose series of carbohydrates

SCHEME 2. Substrates for the 2,7-Dioxabicyclo[2.2.1]heptane Series[a]



[a] Key: (a) methyl (triphenylphosphoranylidene)acetate, MeCN, rt, overnight, 83%; (b) Bu_4NF, THF, rt; (c) $LiAlH_4$, THF, rt, 1 h, 98%; (d) NaH, trimethylsulfoxonium iodide, DMSO, rt, 2 h, 23%; (e) triphosgene, CH_2Cl_2/Py, −70 °C, 96%.

by using models in pyranose and furanose forms as depicted in Schemes 2 and 3.

Synthesis of Substrates and Results. The aldonic ester **3** and 2,5-anhydro-alditols **4** and **6** were prepared from 2,3-*O*-isopropylidene-D-ribofuranose[21] by using a well-established method for the *C*-glycosidation of carbohydrates (Scheme 2).[22] The Wittig reaction with methyl (triphenylphosphoranylidene)acetate and subsequent cyclization left the tether preferentially on the α-side of the molecule, due to the presence of the bulky TBDPS-protecting group (**2**α/**2**β, 5.5:1).[23] The reaction of the free lactol with trimethylsulfoxonium ylide afforded exclusively the required α-isomer **5**.[24] Reaction of the known[25] diol **7** with triphosgene[26] afforded the cyclic carbonate **8** that was subsequently desilylated to give the desired alcohol **9**. 3,6-Anhydro-1,2:4,5-di-*O*-isopropylidene-D-*glycero*-D-*manno*-heptitol (**10**) was prepared from D-mannose as previously described (Table 1, entry 5).[24]

We have also prepared a number of *C*-glycosides of the tetrahydropyran group in order to extend the IHA

(11) Recent synthesis of multistriatin and *exo*-brevicomin: Taniguchi, T.; Ohnishi, H.; Ogasawara, K. *J. Chem. Soc., Chem. Commun.* **1996**, 1477−1478.

(12) Synthesis of palytoxin: Armstrong, R. W.; Beau, J.-M.; Cheon, S. H.; Christ, W. J.; Fujioka, H.; Ham, W.-H.; Hawkins, L. D.; Jin, H.; Kang, S. H.; Kishi, Y.; Martinelli, M. J.; McWhorter, W. W., Jr.; Mizuno, M.; Nakana, M.; Stutz, A. E.; Talamas, F. X.; Taniguchi, M.; Tino, J. A.; Ueda, K.; Uenishi, J.; White, J. B.; Yonaga, M. *J. Am. Chem. Soc.* **1989**, *111*, 7525−7530.

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(19) Recent reviews: (a) Majetich, G.; Wheless, K. *Tetrahedron* **1995**, *51*, 7095−7129. (b) Feray, L.; Kuznetsov, N.; Renaud P. In *Radicals in Organic Synthesis*; Renaud, P., Sibi, M. P., Eds.; Wiley-VCH: Weinheim, Germany, 2001; Vol. 2, pp 246−278. (c) Robertson, J.; Pillai, J.; Lush, R. K. *Chem. Soc. Rev.* **2001**, *30*, 94−103.

(20) Francisco, C. G.; Herrera, A. J.; Suárez, E. *Tetrahedron Lett.* **2000**, *41*, 7869−7873.

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(22) Levy, D. E.; Tang, C. *The Chemistry of C-Glycosides*; Pergamon Press: Oxford, UK, 1995.

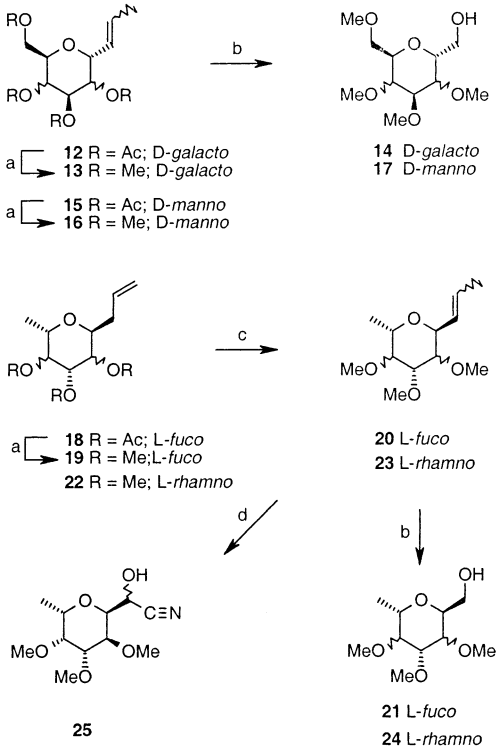
(23) Ohrui, H.; Jones, G. H.; Moffatt, J. G.; Maddox, M. L.; Christensen, A. T.; Byram, S. K. *J. Am. Chem. Soc.* **1975**, *97*, 4602−4613.

(24) Fréchou, C.; Dheilly, L.; Beaupère, D.; Uzan, R.; Demailly, G. *Tetrahedron Lett.* **1992**, *33*, 5067−5070.

(25) (a) Bennek, J. A.; Gray, G. R. *J. Org. Chem.* **1987**, *52*, 892−897. (b) McDevitt, J. P.; Lansbury, P. T. *J. Am. Chem. Soc.* **1996**, *118*, 3818−3828.

(26) Burk, R. M.; Roof, M. B. *Tetrahedron Lett.* **1993**, *34*, 395−398.

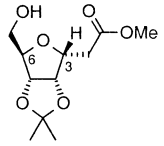
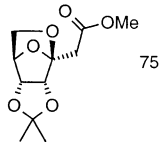
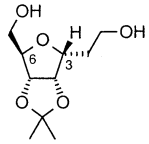
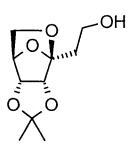
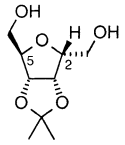
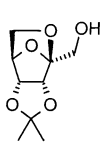
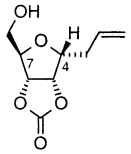
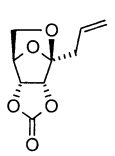
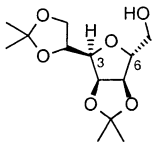
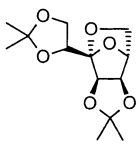
SCHEME 3. Substrates for the 6,8-Dioxabicyclo[3.2.1]octane Series[a]



[a] Key: (a) (i) KOH, MeOH, rt, 1 h; (ii) NaH, MeI, DMF, rt; (b) (i) O_3, CH_2Cl_2/MeOH, −78 °C; (ii) Me_2S, $NaBH_4$, rt; (c) $(PhCN)_2PdCl_2$, PhH, reflux, 24 h, 60%; (d) (i) O_3, CH_2Cl_2/MeOH, −78 °C; (ii) Me_2S, Et_2AlCN, toluene, 0 °C, 10 min, 56.4% overall. The terms D-*galacto*, D-*manno*, L-*fuco*, and L-*rhamno* refer to the starting sugar.

reaction to the synthesis of anhydrosugars of the 6,8-dioxabicyclo[3.2.1]octane type. The first substrate, 2,6-anhydro-1,3,4,5-tetra-*O*-benzyl-D-*glycero*-L-*gulo*-heptitol (**11**) (Table 2, entry 1), was synthesized from D-glucose by using the Wittig-oxymercuration process developed by Sinaÿ et al.[27] Several other models of 2,6-anhydroheptitols **14**, **17**, **21**, **24**, and **25** were prepared starting from suitable derivatives of D-galactose, D-mannose, L-fucose, and L-rhamnose, respectively (Scheme 3). The syntheses were efficiently accomplished by using a three-step protocol: Lewis acid catalyzed *C*-glycosidation with allyltrimethysilane,[28] treatment with bis(benzonitrile) dichloropalladium(II) in refluxing benzene in order to promote the isomerization of the olefin,[29] and ozonolysis followed by reductive workup with $NaBH_4$. The allylation reaction proceeded in all cases with good stereoselectivity to give the required α-isomer, while the olefin isomerization gave an unseparated *E*/*Z* mixture. The mixture of cyanohydrins **25** was prepared by ozonolysis of olefin **20** and in situ reaction of the aldehyde with diethylaluminum cyanide.[30]

TABLE 1. Synthesis of Anhydrosugars of the 2,7-Dioxabicyclo[2.2.1]heptane Type[a]

entry	substrate	iodine (mmol)	time (h)	product	yield (%)
1	 **3**	0.5	2	 **26**	75
2	 **4**	1	0.5	 **27**	66
3	 **6**	0.5	0.75	 **28**	70
4[b]	 **9**	1	0.75	 **29**	88
5[b,c]	 **10**	0.5	1.5	 **30**	86[d]

[a] All reactions were performed at room temperature under nitrogen containing (diacetoxyiodo)benzene (DIB) (1.1 mmol) and iodine per mmol of substrate in the solvents specified in the Experimental Section. [b] Under irradiation with two 80-W tungsten filament lamps. [c] DIB (2 mmol) was used. [d] 1-*O*-Acetyl-2,3:3,6-di-*O*-isopropylidene-α-D-mannofuranose (7%) was also obtained.

The IHA reaction of alcohol **3** gave exclusively the 3,7-anhydro-heptonate **26** by selective abstraction of the hydrogen at C3 (Table 1, entry 1). In principle, the primary *O*-radical could abstract either of the hydrogen atoms at C3 or C4, both through a six-membered transition state (TS). Indeed, a study of the rotation of the H−C6−C7−O dihedral angle gave conformations of minimum energy for distances of approximately 3 Å between the oxygen and either H−C3 or H−C4.[31] Notwithstanding, the TS energy should favor the abstraction

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(29) (a) Brooks, G.; Edwards, P. D.; Hatto, J. D. I.; Smale, T. C.; Southgate, R. *Tetrahedron* **1995**, *51*, 7999−8014. (b) Wilcox, C. S.; Long, G. W.; Suh, H. *Tetrahedron Lett.* **1984**, *25*, 395−398.

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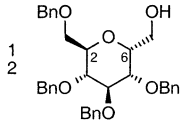
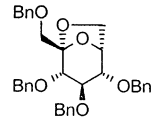
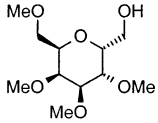
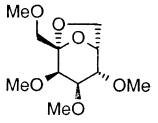
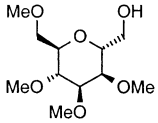
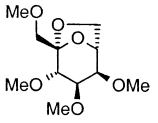
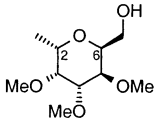
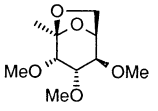
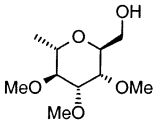
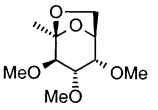
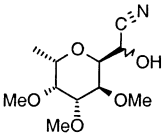
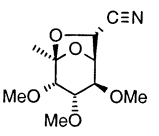
(31) Molecular mechanics calculations were performed with the AMBER* all-atom force field and the GB/SA solvation model for $CHCl_3$ as implemented in version 7.0 of the MacroModel and BatchMin packages.

TABLE 2. Synthesis of Anhydrosugars of the 6,8-Dioxabicyclo[3.2.1]heptane Type[a]

entry	substrate	PhIO (mmol)	time (h)	product	yield (%)
1	 **11**	2	1	 **31**	60
2		1[b]	1		54
3	 **14**	2	2	 **32**	65[c]
4	 **17**	2	2	 **33**	76
5	 **21**	2	0.5	 **34**	85[d]
6		2	0.5		69
7	 **24**	2	1.5	 **35**	90[e]
8		1.1[b]	0.75		83[e]
9	 **25**	1.5[b]	6	 **36**	28[e,f]

[a] All reactions were performed at room temperature under nitrogen containing iodosylbenzene and iodine (1 mmol) per mmol of substrate in the solvent specified in the Experimental Section and under irradiation with two 80-W tungsten filament lamps. [b] DIB was used. [c] A catalytic amount of $BF_3{\cdot}EtO_2$ was added. [d] A catalytic amount of camphorsulfonic acid was added. [e] Irradiation was omitted. [f] 1-*O*-Acetyl-6-deoxy-2,3,4-tri-*O*-methyl-L-galactopyranose (37%) was also obtained.

of H−C3 over the bicyclo[3.3.0] bridgehead hydrogen at C4, and this may be the reason for the observed regioselectivity.

As may be expected, diol **4** cyclized through the most favorable six-membered TS to give exclusively 2-deoxy-D-*ribo*-hept-3-ulose **27**; no products derived from the alternative *O*-radical at C1 were detected in the crude reaction mixture (Table 1, entry 2). The IHA reaction of D-altritol derivative **6** occurred on the *β*-side of the molecule to give the 2,5-anhydro-*β*-D-psicopyranose **28** as the sole product of the reaction. The alternative hydrogen atom transfer of the H−C5 promoted by the alkoxy radical at C1 is inhibited by the isopropylidene group that hinders the α-side of the molecule (Table 1, entry 3). This simple transformation of a ribose derivative into 2,5-anhydro-*β*-D-psicopyranose **28**, a protected ketose with one more carbon, is worth noting. The carbonate **9** was synthesized in order to have a method to deprotect the 5,6-diol under basic conditions compatible with the 2,7-dioxabicyclo[2.2.1]heptane, the reaction proceeding smoothly to give the anhydro derivative **29** in good yield (Table 1, entry 4).

The IHA reaction of D-*glycero*-D-*manno*-heptitol **10**, easily prepared from 2,3:5,6-di-*O*-isopropylidene-D-mannofuranose, took place by the α-side of the molecule to yield L-*altro*-hept-3-ulose **30** (Table 1, entry 5). The yield of this reaction was 86% and was amenable to scale-up (13 mmol) with only a nominal decrease in yield (80%). In addition to **30**, the side product 1-*O*-acetyl-2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose, a compound coming from a *β*-fragmentation of the alkoxy radical, was formed in low yield (7%).

The 6,8-dioxabicyclo[3.2.1]octane system can also be obtained from conveniently functionalized carbohydrate precursors (Table 2). Thus, the D-*glycero*-L-*gulo*-heptitol derivative **11** reacted with iodosylbenzene and iodine to give the D-*ido*-hept-2-ulopyranose derivative **31** (Table 2, entry 1).[32] In this series iodosylbenzene gave somewhat better yields than DIB (compare entries 1−2 and 7−8); the acetate group in the latter may act as an external nucleophile and compete with the primary alcohol during the cyclization reaction. The IHA reaction occurred under a more stable $^4C_1$ chair conformation, allowing a 1,3-diaxial interaction between the involved substituents, the hydrogen atom at C2, and the hydroxymethyl group at C6. We were unable to detect any compound arising from the geometrically possible abstraction of the axial hydrogen at C4 in this or any other example of this series. Probably steric and stereoelectronic factors favor the abstraction at C2 over C4.[33] Comparison of the IHA reaction of compounds **14** and **17** shows that changes in the stereochemistries of the nearby carbons 3 and 5 do not significantly influence the course and yield of the reaction (Table 2, entries 3 and 4). Under similar conditions the L-*glycero*-D-*galacto*-heptitol **21** afforded *β*-L-*gulo*-hept-2-ulopyranose derivative **34**. In this substrate the hydrogen transfer occurred with the pyranose ring under a $^1C_4$ chair conformation, which allowed the maximum approximation between the alkoxy radical and the hydrogen at C2. A small amount of camphorsulfonic acid that may catalyze the intramolecular glycosidation increased notably the yield of the reaction (Table 2, compare entries 5 and 6). In the case of the L-*glycero*-L-*manno*-heptitol derivative **24** irradiation was unnecessary, the reaction occurring smoothly in excellent yield only with ambient light (Table 2, entry 7). Once more, the use of DIB as oxidant gave an inferior result (entry 8). It is worth noting that compounds **34** and **35** were obtained in better yields than their pseudoenantiomers **32** and **33**, respectively, with which the only difference

(32) Recently the DIB/I_2 system has been used for the deprotection of carbohydrate benzyl ethers in the presence of a suitably located hydroxyl group. We have not detected debenzylation or formation of benzylidene to an appreciable extent in this case (Madsen, J.; Viuf, C.; Bols, M. *Chem. Eur. J.* **2000**, *6*, 1140−1146).

(33) For studies on stereoelectronic effects in intermolecular hydrogen abstraction reactions see: (a) Malatesta, V.; Ingold, K. U. *J. Am. Chem. Soc.* **1981**, *103*, 609−614. (b) Beckwith, A. L. J.; Easton, C. J. *J. Am. Chem. Soc.* **1981**, *103*, 615−619.

is the 1-methoxy group. Probably the presence of a supplementary β-oxygen could deactivate to some degree the hydrogen abstraction at C2.[34]

The cyanohydrins **25** were prepared in order to test the stability of this grouping (Table 2, entry 9). Unfortunately, we were unable to separate both isomers completely, but a reaction performed with the mixture (1:1) allowed us to reach the following conclusions: the **25**-*R* isomer cyclized efficiently to give **36** with the cyano group in the exo position in an estimated yield of 60%; on the other hand, the **25**-*S* isomer, which should leave the cyano group in the endo position, only gave 1-*O*-acetyl-6-deoxy-2,3,4-tri-*O*-methyl-L-galactopyranose coming from the β-fragmentation of the alkoxy radical. This was confirmed since pure **25**-*S* gave exclusively fragmented material in 52% yield. The possible transfer of the cyano group to C2 was not observed. Probably the oxidation of the *C*-radical was too fast, preventing the radical addition to the nitrile.[35]

These examples demonstrate the utility of the IHA reaction in the synthesis of dioxabicyclic[*n*.2.1]alkane (*n* = 2, 3) systems. The synthesized compounds could be of interest as chiral synthons in the preparation of more complex natural products. It is noteworthy that the reaction conditions are sufficiently mild as to be compatible with the sensitive 1,2-isopropylidene group of the mannofuranose **10**. Consequently, common protective groups should be compatible and this should increase the usefulness of this methodology.[36] The reaction also may be useful for the selective oxidation of specific carbons of the carbohydrate skeleton and constitute a mild procedure for the preparation of protected uloses which are not readily accessible by conventional synthetic methods.

Experimental Section

General Methods. Melting points were determined with a hot-stage apparatus. Optical rotations were measured at the sodium line at ambient temperature in $CHCl_3$ solutions. IR spectra were obtained as a thin film smeared onto NaCl plates unless otherwise stated. NMR spectra were determined at 500 MHz for ^{1}H and 125.7 MHz for ^{13}C in $CDCl_3$ unless otherwise stated, in the presence of TMS as internal standard. Mass spectra were determined at 70 eV. Merck silica gel 60 PF (0.063−0.2 mm) was used for column chromatography. Circular layers of 1 mm of Merck silica gel 60 PF_{254} were used on a Chromatotron for centrifugally assisted chromatography. Commercially available reagents and solvents were analytical grade or were purified by standard procedures prior to use. "Usual workup" means aqueous treatment, extraction with CH_2Cl_2, washing with 10% aqueous sodium thiosulfate, drying with Na_2SO_4, filtration, and evaporation in vacuo. All reactions involving air- or moisture-sensitive materials were carried out under a nitrogen atmosphere. The spray reagent for TLC analysis was 0.5% vanillin in H_2SO_4−EtOH (4:1) and further heating until development of color.

Methyl 2-Deoxy-3,6:3,7-dianhydro-4,5-*O*-isopropylidene-D-*ribo*-heptonate (26). A solution of the alcohol **3** (84 mg, 0.34 mmol) in a mixture of CH_2Cl_2−cyclohexane (4 mL, 1:1) containing (diacetoxyiodo)benzene (DIB) (120 mg, 0.37 mmol) and iodine (43 mg, 0.17 mmol) was stirred at room temperature under nitrogen for 2 h. The usual workup followed by chromatotron chromatography of the residue (hexanes−EtOAc, 85:15) afforded the anhydrosugar **26** (62 mg, 0.25 mmol, 75%) as a colorless oil: $[\alpha]_D$ −62 (*c* 0.72); IR 2985, 2901, 1747, 1372, 1208 cm^{-1}; ^{1}H NMR δ 1.27 (3H, s), 1.41 (3H, s), 2.93 (1H, d, J = 15.5 Hz), 3.1 (1H, d, J = 15.5 Hz), 3.39 (1H, d, J = 7.4 Hz), 3.53 (1H, dd, J = 7.2, 3.8 Hz), 3.70 (3H, s), 4.38 (1H, d, J = 5.5 Hz), 4.44 (1H, d, J = 5.5 Hz), 4.6 (1H, d, J = 3.9 Hz); ^{13}C NMR δ 25.4 (CH_3), 25.9 (CH_3), 33.8 (CH_2), 51.9 (CH_3), 64.6 (CH_2), 77.8 (CH), 80.1 (CH), 81.5 (CH), 105.9 (C), 112.3 (C), 168.8 (C); MS (EI) *m*/*z* (rel intensity) 244 (M^+, 1), 243 (8), 229 (22), 213 (31); HRMS calcd for $C_{11}H_{16}O_6$ 244.094678, found 244.090878. Anal. Calcd for $C_{11}H_{16}O_6$: C, 54.09; H, 6.60. Found: C, 54.16; H, 6.81.

3,7-Anhydro-2-deoxy-4,5-*O*-isopropylidene-D-*ribo*-hept-3-ulofuranose (27). A solution of the alcohol **4** (43 mg, 0.197 mmol) in CH_2Cl_2 (2 mL) containing DIB (70 mg, 0.217 mmol) and iodine (51 mg, 0.2 mmol) was stirred at room temperature under nitrogen for 0.5 h. The usual workup followed by column chromatography (hexanes−EtOAc, 6:4) afforded the anhydrosugar **27** (28 mg, 0.13 mmol, 66%) as a colorless oil: $[\alpha]_D$ −68 (*c* 0.116); IR 3500, 2938, 2898, 1742, 1373, 1058 cm^{-1}; ^{1}H NMR δ 1.29 (3H, s), 1.45 (3H, s), 2.20 (1H, ddd, J = 15.1, 6.2, 3.9 Hz), 2.28 (1H, ddd, J = 15.3, 7.1, 4.2 Hz), 3.4 (1H, d, J = 7.4 Hz), 3.55 (1H, dd, J = 7.1, 3.9 Hz), 3.88 (2H, m), 4.2 (1H, d, J = 5.6 Hz), 4.41 (1H, d, J = 5.4 Hz), 4.66 (1H, d, J = 3.8 Hz); ^{13}C NMR δ 25.2 (CH_3), 25.9 (CH_3), 30.7 (CH_2), 58.2 (CH_2), 64.3 (CH_2), 77.9 (CH), 80.2 (CH), 81.9 (CH), 108.6 (C), 112.2 (C); MS (EI) *m*/*z* (rel intensity) 201 (M^+ − Me, 23), 171 (11), 158 (8); HRMS calcd for $C_9H_{13}O_5$ 201.076290, found 201.083736. Anal. Calcd for $C_{10}H_{16}O_5$: C, 55.54; H, 7.46. Found: C, 55.41; H, 7.31.

2,6-Anhydro-3,4-*O*-isopropyliden-D-*ribo*-hex-2-ulofuranose (2,5-Anhydro-3,4-*O*-isopropylidene-β-D-psicopyranose) (28). A solution of the alcohol **6** (40 mg, 0.196 mmol) in dry MeCN (3 mL) containing DIB (97 mg, 0.3 mmol) and iodine (36 mg, 0.137 mmol) was stirred at room temperature, under nitrogen, for 0.75 h. The usual workup followed by column chromatography (hexanes−EtOAc, 1:1) afforded the anhydrosugar **28** (28 mg, 0.14 mmol, 70%) as a crystalline solid: mp 118−119 °C (from *n*-hexanes−EtOAc); $[\alpha]_D$ −58 (*c* 0.228); IR ($CHCl_3$) 3601, 2983, 2900, 1734, 1602, 1384 cm^{-1}; ^{1}H NMR δ 1.28 (3H, s), 1.45 (3H, s), 3.42 (1H, d, J = 7.2 Hz), 3.56 (1H, dd, J = 3.8, 7.2 Hz), 4.03 (1H, dd, J = 6.6, 12.5 Hz), 4.07 (1H, dd, J = 5.9, 12.5 Hz), 4.29 (1H, d, J = 5.5 Hz), 4.42 (1H, d, J = 5.5 Hz), 4.69 (1H, d, J = 3.8 Hz); ^{13}C NMR δ 25.2 (CH_3), 25.9 (CH_3), 59.1 (CH_2), 64.4 (CH_2), 78.3 (CH), 80.3 (CH), 81.2 (CH), 107.1 (C), 112.6 (C); MS (EI) *m*/*z* (rel intensity) 201 (M^+ − H, 7), 187 (16); HRMS calcd for $C_9H_{13}O_5$ 201.076290, found 201.071293. Anal. Calcd for $C_9H_{14}O_5$: C, 53.46; H, 6.98. Found: C, 53.68; H, 6.62.

4,8-Anhydro-1,2,3-trideoxy-5,6-*O*-(oxomethylene)-D-*ribo*-oct-1-en-4-ulofuranose (29). A solution of alcohol **9** (102 mg, 0.51 mmol) in dry CH_2Cl_2 (5 mL) containing DIB (197 mg, 0.612 mmol) and iodine (91 mg, 0.357 mmol) was irradiated with one 80-W tungsten-filament lamp at room temperature under nitrogen for 0.75 h. The usual workup followed by chromatotron chromatography (hexanes−EtOAc, 70:30) afforded the anhydrosugar **29** (90 mg, 0.45 mmol, 88%) as a crystalline solid: mp 93.5 °C (from *n*-hexanes−EtOAc); $[\alpha]_D$ −70 (*c* 0.39); IR 2915, 1791, 1157, 1091 cm^{-1}; ^{1}H NMR δ 2.79 (2H, d, J = 7.2 Hz), 3.59 (1H, d, J = 7.8 Hz), 3.69 (1H, dd, J = 3.8, 7.8 Hz), 4.63 (1H, d, J = 6.0 Hz), 4.86 (1H, d, J = 3.8

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(35) (a) Kalvoda, J.; Botta, L. *Helv. Chim. Acta* **1972**, *55*, 356−366. (b) Freerksen, R. W.; Pabst, W. E.; Raggio, M. L.; Sherman, S. A.; Wroble, R. R.; Watt, D. S. *J. Am. Chem. Soc.* **1977**, *99*, 1536−1542.

(36) For the use of this methodology with carbohydrates possessing sensitive protecting groups see: (a) González, C. C.; Kennedy, A. R.; León, E. I.; Riesco-Fagundo, C.; Suárez, E. *Angew. Chem., Int. Ed.* **2001**, *40*, 2326−2328. (b) Francisco, C. G.; Freire, R.; González, C. C.; León, E. I.; Riesco-Fagundo, C.; Suárez, E. *J. Org. Chem.* **2001**, *66*, 1861−1866. (c) Armas, P.; Francisco, C. G.; Suárez, E. *J. Am. Chem. Soc.* **1993**, *115*, 8865−8866.

Hz), 4.89 (1H, d, J = 6.0 Hz), 5.20 (1H, d, J = 9.1 Hz), 5.28 (1H, d, J = 15.1 Hz), 5.86 (1H, m); ^{13}C NMR (50.4 MHz) δ 32.1 (CH_2), 65.1 (CH_2), 78.3 (CH), 78.9 (CH), 79.4 (CH), 107.6 (C), 119.8 (CH_2), 129.8 (CH), 154.1 (C); MS (EI), m/z (rel intensity) 198 (M^+, 15), 154 (2); HRMS calcd for $C_9H_{10}O_5$ 198.0528165, found 198.057854. Anal. Calcd for $C_9H_{10}O_5$: C, 54.54; H, 5.09. Found: C, 54.84; H, 4.70.

3,7-Anhydro-1,2:4,5-di-*O*-isopropylidene-D-*allo*-hept-3-ulofuranose (30). A solution of the alcohol **10**[24] (105 mg, 0.38 mmol) in CH_2Cl_2 (3 mL) containing DIB (244 mg, 0.76 mmol) and iodine (48 mg, 0.19 mmol) was irradiated with two 80-W tungsten-filament lamps at room temperature under nitrogen for 1.5 h. The usual workup followed by column chromatography (hexanes−EtOAc, 7:3) afforded the anhydrosugar **30** (89 mg, 0.327 mmol, 86%) and 1-*O*-acetyl-2,3:3,6-di-*O*-isopropylidene-α-D-mannofuranose (8 mg, 0.026 mmol, 7%). The reaction is also amenable to scale-up (3.5 g, 13 mmol) with only nominal decrease in yield (80%). Compound **30**: colorless oil; $[\alpha]_D$ −59.4 (*c* 0.16); IR ($CHCl_3$) 3014, 2992, 2938, 2900, 1383, 1371, 1228 cm^{-1}; ^{1}H NMR δ 1.27 (3H, s), 1.37 (3H, s), 1.43 (3H, s), 1.45 (3H, s), 3.44 (1H, d, J = 7.3 Hz), 3.54 (1H, dd, J = 7.3, 3.9 Hz), 4.09 (1H, dd, J = 8.3, 7.0 Hz), 4.14 (1H, dd, J = 8.5, 5.3 Hz), 4.37 (1H, d, J = 5.5 Hz), 4.39 (1H, d, J = 5.5 Hz), 4.61 (1H, dd, J = 6.9, 5.3 Hz), 4.64 (1H, d, J = 3.9 Hz); ^{13}C NMR δ 25.1 (2 × CH_3), 25.8 (CH_3), 25.9 (CH_3), 64.6 (CH_2), 64.6 (CH_2), 71.4 (CH), 78.4 (CH), 80.1 (CH), 81.2 (CH), 107.0 (C), 110.0 (C), 112.3 (C); MS (EI) m/z (rel intensity) 257 (M^+ − Me, 49), 214 (11), 199 (73); HRMS calcd for $C_{12}H_{17}O_6$ 257.102503, found 257.09977. Anal. Calcd for $C_{13}H_{20}O_6$: C, 57.34; H, 7.40. Found: C. 57.04; H, 7.49. 1-*O*-Acetyl-2,3:3,6-di-*O*-isopropylidene-α-D-mannofuranose: $[\alpha]_D$ +76 (*c* 0.42); IR 2988, 2939, 1748, 1374, 1231 cm^{-1}; ^{1}H NMR δ 1.33 (3H, s), 1.37 (3H, s), 1.45 (3H, s), 1.47 (3H, s), 2.06 (3H, s), 4.02 (1H, dd, J = 4.2, 8.5 Hz), 4.04 (1H, d, J = 6.2 Hz), 4.085 (1H, dd, J = 6.2, 8.9 Hz), 4.39 (1H, ddd, J = 4.3, 6.2, 7.9 Hz), 4.69 (1H, d, J = 5.9 Hz), 4.84 (1H, dd, J = 3.6, 5.9 Hz), 6.11 (1H, s); ^{13}C NMR (50.3 MHz) δ 21.0 (CH_3), 24.6 (CH_3), 25.0 (CH_3), 25.9 (CH_3), 26.9 (CH_3), 66.8 (CH_2), 72.8 (CH), 79.3 (CH), 82.2 (CH), 85.0 (CH), 100.7 (CH), 109.3 (C), 113.2 (C), 169.4 (C); MS (EI) m/z (rel intensity) 287 (M^+ − Me, 100), 243 (7), 229 (51); HRMS calcd for $C_{13}H_{19}O_7$ 287.113066, found 287.109016. Anal. Calcd for $C_{14}H_{22}O_7$: C, 55.62; H, 7.33. Found: C, 55.68; H, 6.94.

2,7-Anhydro-1,3,4,5-tetra-*O*-benzyl-β-D-*ido*-hept-2-ulopyranose (31). Method A: A solution of the alcohol **11**[27] (61 mg, 0.11 mmol) in a mixture of CH_2Cl_2−cyclohexane (1:1) (8 mL) containing DIB (39 mg, 0.12 mmol) and iodine (28 mg, 0.11 mmol) was irradiated with two 80-W tungsten-filament lamps at room temperature under nitrogen for 1 h. The usual workup followed by column chromatography (hexanes−EtOAc, 85:15) afforded the anhydrosugar **31** (32 mg, 0.06 mmol, 54%) as an oil: $[\alpha]_D$ −10.5 (*c* 1.49); IR ($CHCl_3$) 3064, 3031, 2902, 1455, 1072 cm^{-1}; ^{1}H NMR δ 3.46 (1H, d, J = 10.3 Hz), 3.74 (1H, dd, J = 7.3, 5.5 Hz), 3.83 (1H, m), 3.92 (1H, d, J = 10.4 Hz), 4.17 (1H, d, J = 7.9 Hz), 4.44 (1H, dd, J = 4.3, 4.3 Hz), 4.52 (1H, d, J = 11.6 Hz), 4.61 (1H, d, J = 11.6 Hz), 4.62 (1H, d, J = 12.2 Hz), 4.68 (1H, d, J = 11.0 Hz), 4.71 (1H, d, J = 12.2 Hz), 4.78 (1H, d, J = 11.6 Hz), 4.81 (1H, d, J = 11.6 Hz), 4.89 (1H, d, J = 11.0 Hz), 7.21−7.31 (20H, m); ^{13}C NMR δ 65.9 (CH_2), 69.2 (CH_2), 72.9 (CH_2), 73.6 (CH_2), 74.2 (CH), 74.7 (CH_2), 75.3 (CH_2), 79.8 (CH), 81.3 (CH), 83.2 (CH), 107.5 (C), 125.9−128.5 (20 × CH), 137.6 (C), 138.0 (C), 138.3 (C), 138.6 (C); MS (EI) m/z (rel intensity) 461 (M^+ − Bn, 15), 369 (5), 355 (17), 91 (100); HRMS calcd for $C_{35}H_{36}O_6$ 552.251170, found 552.245819. Anal. Calcd for $C_{35}H_{36}O_6$: C, 76.06; H, 6.57. Found: C, 75.99; H, 6.59. **Method B:** A solution of the alcohol **11**[27] (25 mg, 0.05 mmol) in a mixture of CH_2Cl_2−cyclohexane (1:1) (3 mL) containing iodosylbenzene (22 mg, 0.10 mmol) and iodine (15 mg, 0.059 mmol) was irradiated with two 80-W tungsten-filament lamps at room temperature under nitrogen for 50 min. The usual workup followed by column chromatography (hexanes−EtOAc, 85:15) afforded the anhydrosugar **31** (15 mg, 0.03 mmol, 60%).

2,7-Anhydro-1,3,4,5-tetra-*O*-methyl-β-D-*gulo*-hept-2-ulopyranose (32). A solution of the alcohol **14** (20 mg, 0.08 mmol) in a mixture of CH_2Cl_2−cyclohexane (1:1) (3 mL) containing iodosylbenzene (35 mg, 0.16 mmol), iodine (20 mg, 0.08 mmol), and BF_3·OEt (0.01 mL, 0.08 mmol) was irradiated with two 80-W tungsten-filament lamps at reflux temperature under nitrogen for 2 h. The usual workup followed by column chromatography (hexanes−EtOAc, 25:75) afforded the anhydrosugar **32** (13 mg, 0.052 mmol, 65%) as a colorless oil: $[\alpha]_D$ +20 (*c* 0.52); IR 2904, 2828, 1452, 1195, 1105, 1052 cm^{-1}; ^{1}H NMR δ 3.38 (1H, d, J = 9.9 Hz), 3.41 (1H, dd, J = 4.4, 4.1 Hz), 3.43 (3H, s), 3.46 (3H, s), 3.49 (3H, s), 3.52 (3H, s), 3.55 (1H, dd, J = 9.2, 4.1 Hz), 3.67 (1H, dd, J = 7.6, 4.8 Hz), 3.74 (1H, d, J = 4.4 Hz), 3.77 (1H, d, J = 10.0 Hz), 3.95 (1H, d, J = 7.6 Hz), 4.46 (1H, dd, J = 4.4, 4.4 Hz); ^{13}C NMR δ 58.3 (CH_3), 58.7 (CH_3), 59.5 (CH_3), 60.8 (CH_3), 64.9 (CH_2), 71.8 (CH_2), 72.7 (CH), 76.2 (CH), 78.5 (CH), 80.2 (CH), 106.8 (C); MS (EI) m/z (rel intensity) 248 (M^+, <1), 233 (<1), 217 (<1), 187 (<1); HRMS calcd for $C_{11}H_{20}O_6$ 248.125976, found 248.128181. Anal. Calcd for $C_{11}H_{20}O_6$: C, 53.21; H, 8.12. Found: C, 53.01; H, 8.48.

2,7-Anhydro-1,3,4,5-tetra-*O*-methyl-β-D-*altro*-hept-2-ulopyranose (33). A solution of the alcohol **15** (80 mg, 0.32 mmol) in a mixture of CH_2Cl_2–cyclohexane (2:1) (3 mL) containing iodosylbenzene (141 mg, 0.64 mmol) and iodine (81 mg, 0.32 mmol) was irradiated with two 80-W tungsten-filament lamps at room temperature under nitrogen for 2 h. The usual workup followed by column chromatography (hexanes−EtOAc, 6:4) afforded the anhydrosugar **33** (60 mg, 0.242 mmol, 76%) as a colorless oil: $[\alpha]_D$ −112 (*c* 0.79); IR 2902, 2831, 1454, 1365, 1268, 1112, 1026 cm^{-1}; ^{1}H NMR δ 3.40 (3H, s), 3.41 (1H, d, J = 10.6 Hz), 3.44 (1H, dd, J = 8.8, 4.4 Hz), 3.45 (3H, s), 3.48 (3H, s), 3.51 (3H, s), 3.51 (1H, d, J = 8.8 Hz), 3.56 (1H, dd, J = 4.3, 2.6 Hz), 3.66 (1H, d, J = 7.9 Hz), 3.76 (1H, d, J = 10.6 Hz), 3.81 (1H, dd, J = 7.9, 5.7 Hz), 4.74 (1H, dd, J = 5.5, 1.8 Hz); ^{13}C NMR δ 57.5 (CH_3), 57.8 (CH_3), 59.5 (CH_3), 60.6 (CH_3), 65.8 (CH_2), 71.0 (CH_2), 73.8 (CH), 76.8 (CH), 80.3 (CH), 80.81 (CH), 107.6 (C); MS (EI) m/z (rel intensity) 247 (M^+ − H, 1), 233 (54), 201 (12); HRMS calcd for $C_{11}H_{19}O_6$ 247.118152, found 247.118824. Anal. Calcd for $C_{11}H_{20}O_6$: C, 53.21; H, 8.12. Found: C, 53.33; H, 8.16.

2,7-Anhydro-1-deoxy-3,4,5-tri-*O*-methyl-β-L-*gulo*-hept-2-ulopyranose (34). Method A: A solution of the alcohol **21** (13 mg, 0.059 mmol) in dry MeCN (3 mL) containing iodosylbenzene (26 mg, 0.118 mmol), iodine (15 mg, 0.059 mmol), and camphorsulfonic acid (7 mg, 0.03 mmol) was irradiated with two 80-W tungsten-filament lamps at reflux temperature under nitrogen for 25 min. The usual workup followed by column chromatography (hexanes−EtOAc, 25:75) afforded the anhydrosugar **34** (11 mg, 0.05 mmol, 85%) as a colorless oil: $[\alpha]_D$ −27 (*c* 0.53, CH_2Cl_2); IR 2918, 2829, 1746, 1455, 1382, 1230, 1106 cm^{-1}; ^{1}H NMR δ 1.52 (3H, s), 3.42 (1H, dd, J = 10.7, 4.1 Hz), 3.44 (1H, dd, J = 4.1, 8.8 Hz), 3.47 (3H, s), 3.51 (3H, s), 3.54 (1H, ddd, J = 8.8, 4.3, 4.3 Hz), 3.58 (3H, s), 3.68 (1H, dd, J = 7.2, 4.8 Hz), 3.91 (1H, d, J = 7.2 Hz), 4.45 (1H, dd, J = 4.3, 4.3 Hz); ^{13}C NMR δ 20.6 (CH_3), 58.5 (CH_3), 58.7 (CH_3), 61.5 (CH_3), 64.8 (CH_2), 73.1 (CH), 78.4 (CH), 80.6 (CH), 80.9 (CH), 107.4 (C); MS (EI) m/z (rel intensity) 218 (M^+, <1), 203 (1); HRMS calcd for $C_{10}H_{19}O_5$ 218.115424, found 218.105984. Anal. Calcd for $C_{10}H_{18}O_5$: C, 55.03; H, 8.31. Found: C, 55.18; H, 8.62. **Method B:** A solution of the alcohol **21** (57 mg, 0.259 mmol) in dry MeCN (7 mL) containing iodosylbenzene (114 mg, 0.518 mmol) and iodine (49 mg, 0.194 mmol) was stirred at room temperature, under nitrogen, for 35 min. Workup analogously afforded compound **34** (39 mg, 0.179 mmol, 69%).

2,7-Anhydro-1-deoxy-3,4,5-tri-*O*-methyl-α-L-*altro*-hept-2-ulopyranose (35). Method A: A solution of the alcohol **24** (18 mg, 0.082 mmol) in CH_2Cl_2 (1.5 mL) containing iodosylbenzene (35 mg, 0.16 mmol) and iodine (20 mg, 0.08 mmol) was stirred at room temperature under nitrogen for 40 min. The usual workup followed by column chromatography (hex-

anes−EtOAc, 25:75) afforded the anhydrosugar **35** (16 mg, 0.073 mmol, 90%) as a colorless oil: $[\alpha]_D$ +122 (*c* 0.42); IR 2939, 2829, 1238, 1123, 1000 cm^{-1}; ^1H NMR δ 1.49 (3H, s), 3.24 (1H, d, J = 8.6 Hz), 3.38 (1H, dd, J = 8.6, 4.6 Hz), 3.45 (3H, s), 3.50 (3H, s), 3.53 (3H, s), 3.55 (1H, dd, J = 4.5, 2.7 Hz), 3.62 (1H, d, J = 7.9 Hz), 3.83 (1H, dd, J = 7.9, 5.8 Hz), 4.65 (1H, dd, J = 5.6, 2.3 Hz); ^{13}C NMR δ 19.8 (CH_3), 57.8 (CH_3), 57.8 (CH_3), 61.0 (CH_3), 65.9 (CH_2), 73.6 (CH), 77.1 (CH), 80.3 (CH), 84.5 (CH), 107.9 (C); MS (EI) *m*/*z* (rel intensity) 218 (M^+, <1), 203 (5), 187 (43), 88 (100); HRMS calcd for $C_{10}H_{18}O_5$ 218.115413, found 218.117867. Anal. Calcd for $C_{10}H_{18}O_5$: C, 55.03; H, 8.31. Found: C, 55.18; H, 8.62. **Method B:** A solution of the alcohol **24** (24 mg, 0.109 mmol) in CH_2Cl_2 (2 mL) containing DIB (39 mg, 0.12 mmol) and iodine (28 mg, 0.11 mmol) was stirred at room temperature under nitrogen for 40 min. The usual workup followed by column chromatography (hexanes−EtOAc, 25:75) afforded the anhydrosugar **35** (19 mg, 0.09 mmol, 83%).

(7*S*)-2,7-Anhydro-7-*C*-cyano-1-deoxy-3,4,5-tri-*O*-methyl-*β*-L-*gulo*-hept-2-ulopyranose (36). A solution of the cyanohydrins mixture **25** (26 mg, 0.106 mmol, 1:1) in CH_2Cl_2/cyclohexane (2 mL, 1:1) containing DIB (53 mg, 0.164 mmol) and iodine (28 mg, 0.11 mmol) was stirred at room temperature under nitrogen for 6 h. The usual workup followed by chromatotron chromatography (hexanes−EtOAc, 6:4) afforded the anhydrosugar **36** (7 mg, 0.03 mmol, 28%) and acetyl 6-deoxy-2,3,4-tri-*O*-methyl-*β*-L-galactopyranoside (6 mg, 0.024 mmol, 22%) and acetyl 6-deoxy-2,3,4-tri-*O*-methyl-α-L-galactopyranoside (4 mg, 0.016 mmol, 15%). Compound **36** $[\alpha]_D$ −30.5 (*c* 0.22); IR ($CHCl_3$) 2936, 2832, 2359, 1744, 1463, 1386, 1125, 1104, 1058 cm^{-1}; ^1H NMR δ 1.63 (3H, s), 3.26 (1H, dd, J = 8.9, 4.3 Hz), 3.42 (1H, d, J = 4.4 Hz), 3.50 (6H, s), 3.57 (3H, s), 3.58 (1H, dd, J = 8.9, 4.3 Hz), 4.66 (1H, s), 4.67 (1H, d, J = 4.4 Hz); ^{13}C NMR δ 20.5 (CH_3), 58.7 (CH_3), 59.0 (CH_3), 61.6 (CH_3), 63.3 (CH), 77.1 (CH), 77.6 (CH), 79.8 (CH), 80.1 (CH), 110.5 (C), 117.6 (C); MS (EI) *m*/*z* (rel intensity) 244 (M^+ + H, 4), 217 (8), 212 (3); HRMS calcd for $C_{11}H_{18}NO_5$ 244.118486, found 244.120144. Anal. Calcd for $C_{11}H_{17}O_5N$: C, 54.31; H, 7.04; N, 5.76. Found: C, 54.38; H, 7.19; N, 5.39. Acetyl 6-deoxy-2,3,4-tri-*O*-methyl-*β*-L-galactopyranoside: $[\alpha]_D$ −31 (*c* 0.48); IR 2984, 2937, 2833, 1748, 1372, 1230, 1089 cm^{-1}; ^1H NMR δ 1.30 (3H, d, J = 6.4 Hz), 2.12 (3H, s), 3.22 (1H, dd, J = 9.9, 3.0 Hz), 3.39 (1H, d, J = 3.0 Hz), 3.46 (1H, dd, J = 10.3, 8.6 Hz), 3.53 (3H, s), 3.54 (3H, s), 3.60 (3H, s), 3.62 (1H, q, J = 6.3 Hz), 5.42 (1H, d, J = 8.2 Hz); ^{13}C NMR δ 16.4 (CH_3), 21.1 (CH_3), 58.3 (CH_3), 60.7 (CH_3), 61.8 (CH_3), 71.2 (CH), 78.1 (CH), 79.1 (CH), 84.2 (CH), 94.2 (CH), 159.6 (C); MS (EI) *m*/*z* (rel intensity) 189 (M^+ − OAc, 4), 173 (1); HRMS calcd for $C_9H_{17}O_4$ 189.112674, found 189.11454. Anal. Calcd for $C_{11}H_{20}O_6$: C, 53.21; H, 8.12. Found: C, 53.27; H, 8.01. Acetyl 6-deoxy-2,3,4-tri-*O*-methyl-α-L-galactopyranoside: $[\alpha]_D$ −122 (*c* 0.4); IR 2983, 2937, 2830, 1747, 1372, 1234, 1136, 1108 cm^{-1}; ^1H NMR δ 1.23 (3H, d, J = 6.9 Hz), 2.10 (3H, s), 3.43 (3H, s), 3.48 (1H, d, J = 2.5 Hz), 3.50 (1H, dd, J = 10.2, 2.5 Hz), 3.51 (3H, s), 3.58 (3H, s), 3.70 (1H, dd, J = 10.0, 3.5 Hz), 3.94 (1H, q, J = 6.7 Hz), 6.33 (1H, d, J = 3.4 Hz); ^{13}C NMR δ 16.5 (CH_3), 21.1 (CH_3), 58.1 (CH_3), 59.0 (CH_3), 61.8 (CH_3), 68.9 (CH), 76.7 (CH), 78.8 (CH), 80.2 (CH), 90.1 (CH), 169.6 (C); MS (EI) *m*/*z* (rel intensity) 248 (M^+, <1), 189 (5), 173 (1). Anal. Calcd for $C_{11}H_{20}O_6$: C, 53.21; H, 8.12. Found: C, 53.26; H, 8.38. In the same conditions pure **25**-*S* (25 mg, 0.1 mmol) in CH_2Cl_2/cyclohexane (5 mL, 1:1) containing DIB (38 mg, 0.12 mmol) and iodine (25 mg, 0.1 mmol) afforded the above-mentioned L-galactopyranosides (13 mg, 0.052 mmol, 52%, α−*β*, 52:42).

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Supporting Information Available: A complete description of experimental details and characterization data for compounds **2**−**9**, **12**−**17**, and **19**−**25**. This material is available free of charge via the Internet at http://pubs.acs.org.

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