Tin- and Indium-Mediated Allylation in Aqueous Media: Application to Unprotected Carbohydrates

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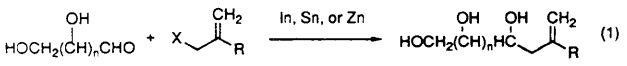
The convenient and efficient indium- and tin-mediated allylation method for extending the carbon chain of unprotected carbohydrates is illustrated by preparation of **4–6** and **9–10**. Various 2-deoxyaldoses can be synthesized by the allylation of aldoses. Indium-mediated reactions between ethyl 2-(bromomethyl)acrylate and aldoses provide access to 2-keto-3-deoxyulosonic acids. These reactions are diastereoselective; the major product contains a *threo* relationship between the newly generated hydroxyl group and the C-2 hydroxyl group of the starting carbohydrate. Results obtained from reactions involving authentic organotin and organoindium reagents and from the corresponding heterogeneous reactions are similar.

Carbohydrate synthesis lacks a repertoire of efficient and versatile C–C bond forming reactions that can be carried out on unprotected carbohydrates in protic media. This paper reports the addition of allyl anion equivalents to the carbonyl group of unprotected carbohydrates mediated by metals such as indium, tin, and zinc (eq 1). The



(1)

double bond of the product homoallylic alcohols can be transformed to carbonyl or other functional groups. In preliminary experiments, the allylation showed high diastereoselectivity.[1] This methodology might be exploited in the preparation of a range of sugars, including heptoses, octoses, and other higher sugars.

The carbohydrate allylation methodology is an extension of procedures originally developed and applied to nonsugar aldehydes and ketones by Luche,[2-5] Nokami,[6] Benezra,[7] and others.[8] The method was extended to unprotected carbohydrates by Schmid and Whitesides.[1] The work of Li and Chan[9a] established the utility of indium in aqueous media. Recently, Mosset and co-workers reported an indium-mediated allylation of aldimines.[9b]

The characteristics of organometallic reactions that are useful in the chemistry of *unprotected* carbohydrates are that (a) they can be carried out in protic media, (b) the experimental protocol is straightforward, (c) they are both regio- and stereoselective, and (d) they are applicable to large-scale (multigram) preparations. In this paper, we describe the exploration and use of In and Sn in the elaboration of carbohydrates, compare the efficiencies and reactivities of these metals, and examine the hypothesis that organometallic reagents are intermediates in these transformations. The results reported here are the product of exploratory work, and the reactions were not optimized; therefore, inferences regarding the limitations of these protocols might be inappropriate.

Results and Discussion

Stereochemistry and Regioselectivity. The configuration at the new stereocenter of the product homoallylic alcohols was unambiguously assigned by transforming adducts **1–3**, derived from D-arabinose, D-ribose, and D-glucose, respectively, to the corresponding peracetylated heptose and octose derivatives **4–6** (Scheme I). Analysis of the ^{1}H NMR spectra of pyranoses **4–6** allowed assignment of the relative stereochemistry at the newly generated stereocenter. In each case, we observed a *threo* relationship between the newly generated hydroxyl group and the C-2 hydroxyl group of the starting carbohydrate.

The same strategy was used to assign the stereochemistry of the newly generated stereocenter in reactions involving a more complex allyic halide. Indium-mediated reactions of ethyl 2-(bromomethyl)acrylate with D-arabinose and D-ribose, followed by ozonolysis, yielded **9** and **10** (Scheme II). Li and Chan reported an indium-mediated reaction of methyl 2-(bromomethyl)acrylate and a nonsugar aldehyde in an aqueous medium and that this reaction could be used to synthesize 2-ketooctulonate derivatives.[9a] Once again, the ^{1}H NMR spectra of these pyranoses indicated a *threo* relationship between the newly generated stereocenter and the C-2 hydroxyl group of the starting carbohydrate. This sequence can be used to synthesize 2-keto-3-deoxyoctulonate derivatives.[10]

Limited experience suggests that only the most reactive carbonyl group reacts with allyl halides when multiple carbonyl groups are present; products from reduction or multiple addition are not observed. For example, D-glucurono-6,3-lactone (**11**) reacted with allyl bromide, under the standard conditions, to give **12**,[11] derived from selective

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(1) Schmid, W.; Whitesides, G. M. *J. Am. Chem. Soc.* **1991**, *113*, 6674–6675.
(2) Einhorn, C.; Einhorn, J.; Luche, J. L. *Synthesis* **1989**, 787–813.
(3) Luche, C. J.; Damiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7926–7927.
(4) Petrier, C.; Luche, J. L. *J. Org. Chem.* **1985**, *50*, 912–915.
(5) Petrier, C.; Einhorn, J.; Luche, J. L. *Tetrahedron Lett.* **1985**, *26*, 1449–1452.
(6) Nokami, J.; Otera, J.; Sudo, T.; Okawara, R. *Organometallics* **1983**, *2*, 191–193.
(7) Mattes, H.; Benezra, C. *Tetrahedron Lett.* **1985**, *26*, 5697–5698.
(8) Wilson, S. R.; Guazzaroni, M. E. *J. Org. Chem.* **1989**, *54*, 3087–3091.
(9) (a) Li, C.; Chan, T. *Tetrahedron Lett.* **1991**, *32*, 7017–7020; Chan, T.; Li, C. *J. Chem. Soc., Chem. Commun.* **1992**, 747. (b) Beuchet, P.; Le Marrec, N.; Mosset, P. *Tetrahedron Lett.* **1992**, *33*, 5959–5960.

(10) (a) 3-Deoxy-D-*manno*-octulonate, also known as KDO, is not the major product of the reaction between D-arabinose and ethyl α-(bromomethyl)acrylate. (b) Recently (+)-KDO has been synthesized using indium: Chan, T. H.; Li, C. J. *Abstracts of Papers*, 203rd National Meeting of the American Chemical Society, San Francisco, CA; American Chemical Society: Washington, DC, April, 1992; Abstract ORGN435.
(11) The stereochemistry of **12** has not been established unambiguously, but we infer the same *threo* relationship between the newly generated vicinal diols.

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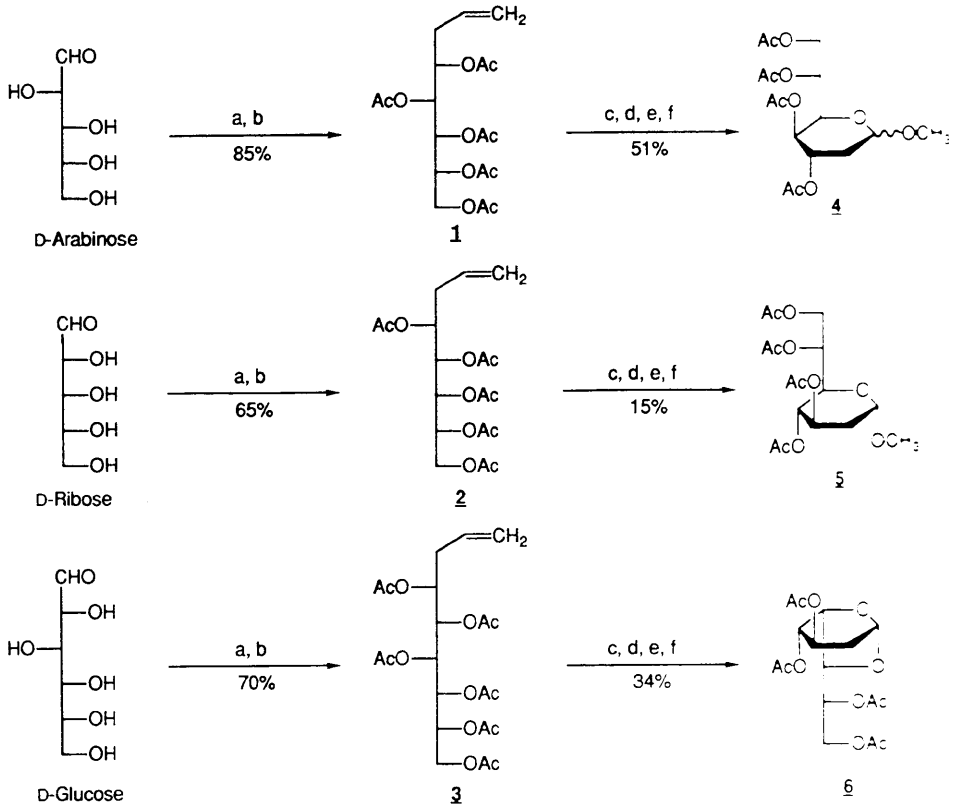
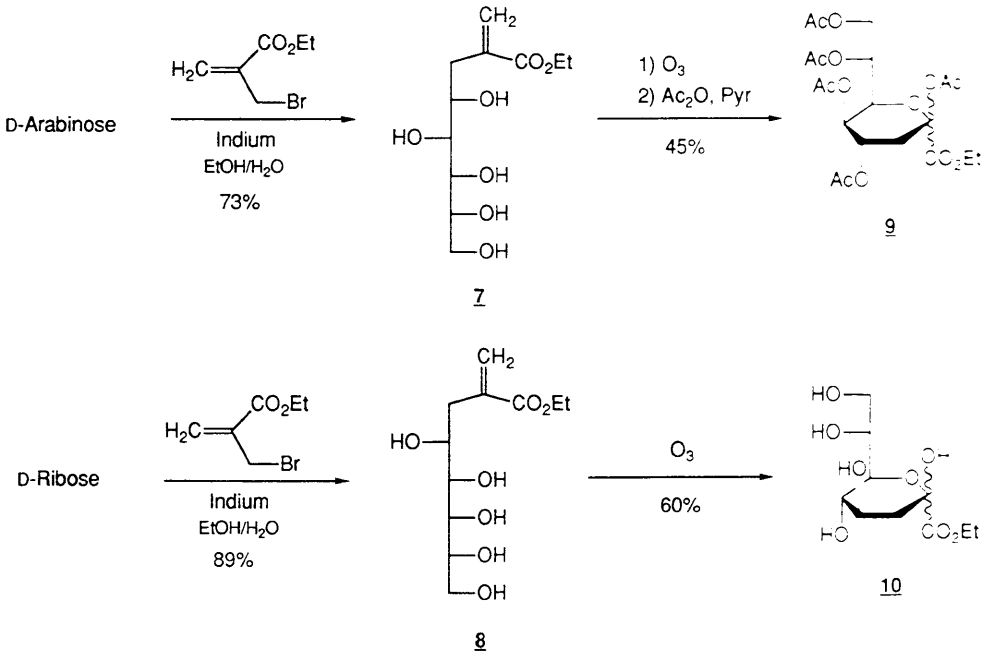
Scheme I[a]



[a] (a) Allyl bromide, Sn, EtOH/H_2O; (b) Ac_2O, pyr, DMAP; (c) NaOMe, MeOH; (d) O_3, MeOH/CH_2Cl_2, −70 °C; (e) MeOH, H^+; (f) Ac_2O, pyr.

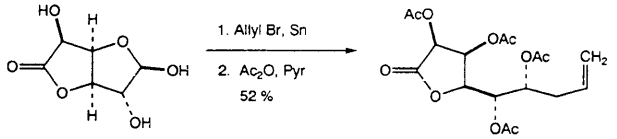
Scheme II



allylation of the aldehyde group (Scheme III). No products resulting from allylation of the lactone were recovered.

Tin-Mediated Reactions. We previously described the use of tin metal in the addition of allyl anion equivalents to aldoses.[1] We have since explored a number of procedures for the reaction: the most convenient procedure involves heating a suspension of allylic bromide, tin powder, and aldose in a polar organic solvent containing enough water to dissolve the sugar. The yield and diastereoselectivity of the reaction are largely independent of solvent, with the exception of the dioxane/water system where the diastereoselectivity was diminished (Table I). Rates of reaction are influenced by the solvent system: the rate of reaction in THF/H_2O is only about one-fifth that in EtOH/H_2O. For a given solvent system, the rate of the reaction is qualitatively proportional to the mole

Scheme III



11 12

Table I. Diastereoselectivity of the Tin-Mediated Reaction[a] of Allyl Bromide with D-Arabinose in Various Solvent Systems

organic cosolvent	organic/H_2O (v/v)	diastereomeric ratio[b] (*threo/erythro*)	yield (%)[c]
EtOH	9:1	5.5[d]	81
THF	1:1	5	69
	5:1	4	96
CH_3CN	1:1	3	95
	5:1	6	74
	10:1	7	90
	20:1	7	59
1,4-dioxane	1:1	2	89
	5:1	3	54
1-propanol	1:1	5	52
	5:1	4	65
	10:1	6	64
MeOH	1:1	4	73
	5:1	4	53
DME	5:1	6	66
	10:1	7	90
	20:1	7	59
pyridine	1:1	no reaction	
	5:1	no reaction	
CH_3NO_2	1:1	no reaction	
	5:1	no reaction	

[a] Reactions promoted by ultrasonication. [b] Diastereomeric ratio determined by ^1H NMR. [c] Isolated yield after peracetylation and chromatography. [d] Reference 1.

fraction of organic solvent in the mixture; however, there must be sufficient water in the reaction mixture to dissolve the sugar.

When stirred at room temperature, tin-mediated reactions proceed too slowly to be useful, but ultrasonication significantly increases the rate. Although both heating and ultrasonication accelerate the allylation reaction, heating is more convenient and gives greater acceleration. The allylation of D-arabinose requires 2 h under reflux and 16–20 h when ultrasonicated.[12] The yield and diastereoselectivity obtained under both sets of conditions are similar.

The rates of reaction increase with increasing surface area of tin, other conditions being equal. Agitation of the tin with powdered glass or glass beads (≤100 mesh) also increases the rate of reaction. The reaction under reflux with powdered glass is completed in less than 1 h, and no loss of diastereoselectivity is observed, although the yield is slightly diminished. No special pretreatment of the metal is required, although finely powdered metal reacts more rapidly than coarsely granulated metal.

Indium-Mediated Reactions. Indium metal has been used in the allylation of carbonyl compounds[9,13,14] and in the Reformatsky reaction.[15–17] The use of indium in carbohydrate chemistry has been sparse. Indium is more

(12) Stirring at rt with broken glass or glass beads affords the same results, but at much slower rate than either ultrasonication or heating at reflux.

(13) For the synthetic use of indium metal, see (a) Araki, S.; Katsumura, N.; Ito, H.; Butsugan, Y. *Tetrahedron Lett.* **1989**, *30*, 1581. (b) Araki, S.; Butsugan, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 1286.

Table II. In- and Sn-Mediated Allylation and Allenylation of Carbohydrates

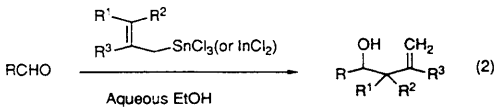
starting sugar	halide[a]	product	yield, % (ratio)[b] In[c]	Sn[d]
D-erythrose	A	13		52 (4:1)
D-arabinose	A	1	74 (7:1)	85 (4:1)
	MA	7	73 (4:1)	
	P	14	35 (>13:1)	
	C	15	78 (8:1)	69 (5:1)
	B	18		46 (10:1)
D-ribose	A	2	60 (6:1)	65 (6:1)
	MA	8	89 (5:1)	
	B	16	65 (8:1)	
D-glucose	A	3	63 (5:1)	70 (7:1)
D-mannose	A	20	72 (5:1)	90 (6:1)
D-fructose	A	17		60 (6:1)
11	A	12		52 (6:1)

[a] A = allyl bromide; B = 1-bromo-2-butyne; C = crotyl bromide; MA = ethyl 2-(bromomethyl)acrylate; P = prenyl bromide. [b] Diastereomeric ratio (*threo/erythro*) determined by ^1H NMR. [c] Stirred at rt in EtOH/H_2O (10:1) with In (150 mesh). [d] Ultrasonicated in EtOH/H_2O (10:1) with Sn (100 mesh).

reactive toward allylic halides than tin,[9] while still being incapable of reducing the aldehyde function. Reactions using indium, unlike those involving tin, proceed smoothly at room temperature with vigorous stirring.[18] The rate of a reaction mediated by indium at room temperature is faster than that mediated by tin using ultrasonication and is comparable to that of a tin-mediated reaction carried out at reflux. The stereoselectivity and yield of indium- and tin-mediated reactions are similar.

Zinc-Mediated Reactions. A mixture of zinc powder and allyl bromide in ethanol/water (10/1) does not yield an allylation product after ultrasonication. Following reaction conditions described by Luche[2–5] and Reissig,[19] we used a solution of THF (or EtOH) and saturated aqueous NH_4Cl, but very little sugar dissolves in these solutions, and no reaction was observed.

Reactions with Organometallic Reagents. The direct addition of organometallic reagents, generated separately, to a solution of a sugar in a protic solvent gives homoallylic alcohols (eq 2). This strategy has been successfully applied



(2)

to non-sugar aldehydes, ketones, and acetals for the addition of allyl[20–22] and propargyl/allenyl[23,24] groups in

(14) For the synthetic use of organoindium compounds, see (a) Chao, L.; Reike, R. *J. Org. Chem.* **1975**, *40*, 2253. (b) Maeda, T.; Tada, H.; Yasuda, K.; Okawara, R. *J. Organomet. Chem.* **1971**, *27*, 13.

(15) (a) Araki, S.; Shimizu, T.; Johar, P.; Jin, S.; Butsugan, Y. *J. Org. Chem.* **1991**, *56*, 2538–2542. (b) Araki, S.; Ito, H.; Butsugan, Y. *J. Org. Chem.* **1988**, *53*, 1831.

(16) Araki, S.; Ito, H.; Butsugan, Y. *Synth. Commun.* **1989**, *18*, 453.

(17) Araki, S.; Ito, H.; Katsumura, N.; Butsugan, Y. *J. Organomet. Chem.* **1989**, *369*, 291.

(18) Replacement of the aqueous phase with 0.1 N HCl increases the rate of the reaction and, in some cases, enhances the efficiency.

(19) Kunz, T.; Reissig, H. *Leibigs Ann. Chem.* **1989**, 891–893.

(20) Gambaro, A.; Boaretto, A.; Marton, D.; Tagliavini, G. *J. Organomet. Chem.* **1983**, *254*, 293–304, and refs therein.

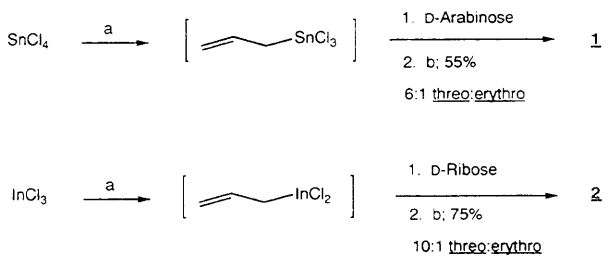
(21) Gambaro, A.; Marton, D.; Peruzzo, V.; Tagliavini, G. *J. Organomet. Chem.* **1982**, *226*, 149–155.

(22) Gambaro, A.; Peruzzo, V.; Plazzogana, G.; Tagliavini, G. *J. Organomet. Chem.* **1980**, *162*, 32.

(23) Boaretto, A.; Marton, D.; Tagliavini, G.; Gambaro, A. *J. Organomet. Chem.* **1985**, *286*, 9.

(24) Boaretto, A.; Marton, D.; Tagliavini, G. *J. Organomet. Chem.* **1985**, *297*, 149–153.

Scheme IV[a]



[a] (a) Allylmagnesium bromide/ether; (b) Ac_2O, pyr, DMAP.

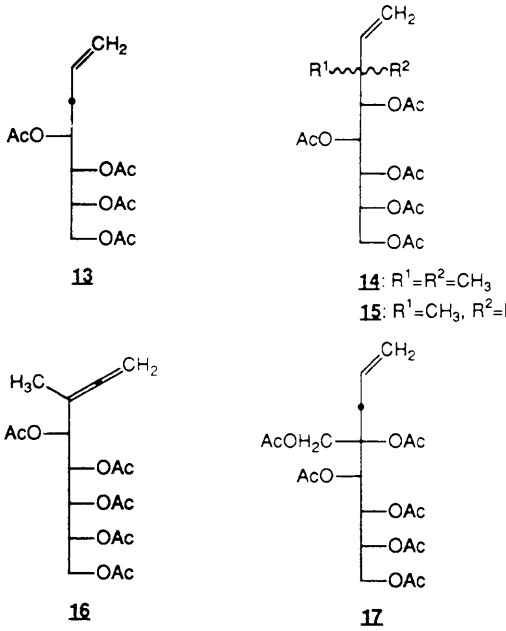
aprotic media such as CH_2Cl_2 or THF. Reaction of allyltrichlorotin with D-arabinose in $EtOH/H_2O$ occurred very rapidly and yielded, after acetylation, 1 (Scheme IV). The diastereomeric ratio was similar to that observed in the reaction with metallic tin and allyl bromide. An allylindium reagent gave similar results, although the diastereoselectivity was improved. The reaction between allyldichloroindium and the aldose, in $EtOH/H_2O$, was essentially instantaneous at room temperature.

Organometallic species are good donors of allenyl groups. It appears that transmetalation proceeds with γ attack of the electrophile in accordance with an S_E2' mechanism.[25,26] The formation of 18 is consistent with an S_E2' mechanism (Scheme V). Allyltri(*n*-butyl)tin does not add to D-arabinose under our reaction conditions, although similar tin compounds are reported to add an allyl moiety to non-sugar aldehydes and ketones in THF and CH_2Cl_2.[27,28] It seems that an electron-deficient organotin reagent must be used: allyltrichlorotin is more reactive than allyltrialkyltin;[29] the low solubility of the latter compound in aqueous media may also contribute to its lack of reactivity. We surveyed a number of organotin compounds prepared by reaction of alkyl, vinyl, propargyl, and allenyl magnesium halide compounds with $SnCl_4$ or $ClSnBu_3$ (Table III). Under the conditions we explored, only a few organometallics were successful participants in the addition reaction.

Reactions between the preformed organometallic reagents and sugars are faster, and easier to workup, than the heterogeneous reactions. The transmetalation reaction between Grignard reagents and tin or indium halides is also simple and rapid. In contrast, no allyl addition is observed if $ZnCl_2$ is used in place of $SnCl_4$ or $InCl_3$.[30] On the basis of similarity between the homogeneous and heterogeneous reactions, we postulate that the heterogeneous reactions proceed through organometallic intermediates.[31]

Variation of Allylic Halides. Various allyic halides have been used in indium- and tin-mediated reactions.[29] The reactions we report proceeded with allyl chloride, bromide, and iodide; the bromide gave the best combination of reactivity and stability toward solvolysis.

Crotyl bromide participated in a tin-mediated reaction with D-arabinose and generated 14 as the major product, an adduct that is formally formed by an S_E2' process.[25] Two new stereocenters are generated in this process, and four stereoisomers are possible. When the crude product is purified by chromatography, two isomers are isolated in 5:1 ratio; the major product contained a 1:1 mixture of two epimers at C-6 of the product. Prenyl bromide reacted with an aldose in the presence of indium in an S_E2' process as observed in 15, albeit in low yield, perhaps due to steric hindrance.



1-Bromo-2-butyne reacted smoothly with aldoses and yielded allene-containing products 16 and 18; alkyne-containing products were not observed. Propargyl bromide has been reported to react with non-sugar aldehydes, in the presence of tin metal,[32] to yield both allene- and alkyne-containing products but failed to react with aldoses under our reaction conditions using either tin or indium.

Sugars. In general, pentoses react more readily than hexoses, and aldoses react more readily than ketoses. D-Fructose reacted with allyl bromide in a tin-mediated reaction to generate 17. D-Glucosamine did not react under the usual reaction conditions or at higher temperatures. Various *N*-protected derivatives of D-glucosamine and D-mannosamine did not participate in either tin- or indium-mediated reactions. Aldose oximes and gluconic acids were also unreactive. The allyl addition products can be converted into higher aldoses via ozonolysis of their double bonds (Scheme II). They can also be converted to ketoses using a palladium-catalyzed oxidation[34] (Scheme VI). The terminal double bond can conceivably be used in other transformations.

Conclusions

The unoptimized tin- and indium-mediated addition of allyl anion equivalents to unprotected carbohydrates is

(25) (a) Gambaro, V.; Marton, D.; Peruzzo, V.; Tagliavini, G. *J. Organomet. Chem.* **1981**, *204*, 191. (b) Peruzzo, V.; Tagliavini, G.; Gambaro, A. *Inorg. Chim. Acta* **1979**, *34*, L263.

(26) Marshall, R.; Young, D. *Tetrahedron Lett.* **1992**, *33*, 2369–2370.

(27) Keck, G.; Abbott, D.; Wiley, M. *Tetrahedron Lett.* **1987**, *28*, 139–142.

(28) Baldwin, J.; Adlington, R.; Sweeney, J. *Tetrahedron Lett.* **1986**, *27*, 5423.

(29) (a) Tagliavini, G.; Peruzzo, V.; Plazzogana, G; Marton, D. *Inorg. Chim. Acta* **1977**, *24*, L47. (b) Tagliavini, G.; Peruzzo, V.; Marton, D. *Inorg. Chim. Acta* **1978**, *26*, L41. (c) Peruzzo, V.; Tagliavini, G. *J. Organomet. Chem.* **1978**, *162*, 32.

(30) When allylmagnesium bromide is added to the suspension of $ZnCl_2$ in ether, the solution turned dark and precipitated a black allylzinc chloride.

(31) Allyltributyltin fails to react with carbohydrates. A reactive organotin reagent seems necessary for this reaction to occur in aqueous conditions.

(32) Wu, S.; Huang, B.; Gao, X. *Synth. Commun.* **1990**, *20*, 1279–1286.

(33) Prevost, C.; Gaudemar, M.; Honigberg, C. *Acad. Sci. (Paris)* **1950**, *230*, 1186.

(34) (a) Tsuji, J. *Synthesis* **1984**, 369. (b) Poss, A.; Belter, R. *Synth. Commun.* **1988**, *18*, 417–423.

Scheme V

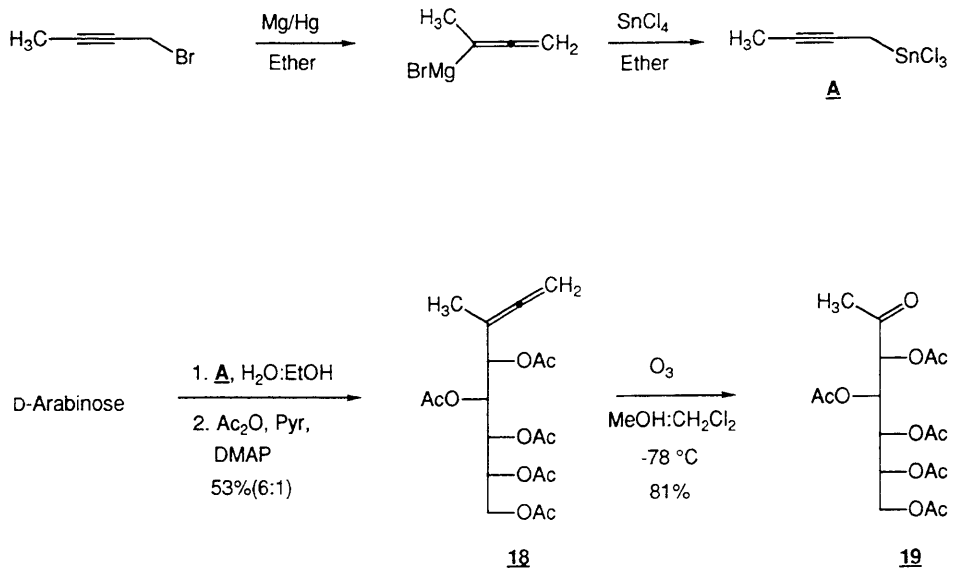
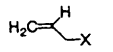
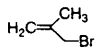
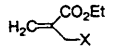
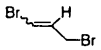
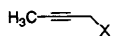
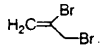
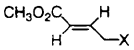
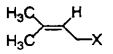
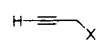
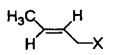
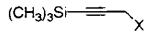
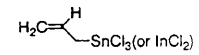
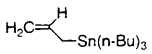
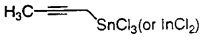
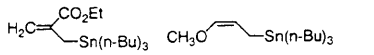
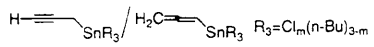
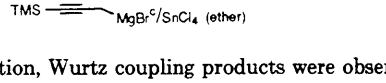


Table III. Summary of Organic Halides and Organometallic Reagents

A. Organic Halides

successful	metals (unsuccessful)	unsuccessful	metals used
	In, Sn, (Zn)		In, Sn
	In, Sn[a]		In, Sn
	In, Sn		In, Sn
			Sn
	In, Sn		In, Sn
	In, Sn		Sn
			In, Sn[b]
			In, Sn

B. Organometallic Reagents

successful	unsuccessful
	
	
	
	MeMgBr; EtMgBr/$SnCl_4$ (THF) benzylMgCl/$SnCl_4$ (THF, ether) phenylMgBr; ethynylMgBr/$SnCl_4$ (THF) vinylMgBr/$SnCl_4$ (THF) allenylMgBr[c]/$SnCl_4$ (ether)
	

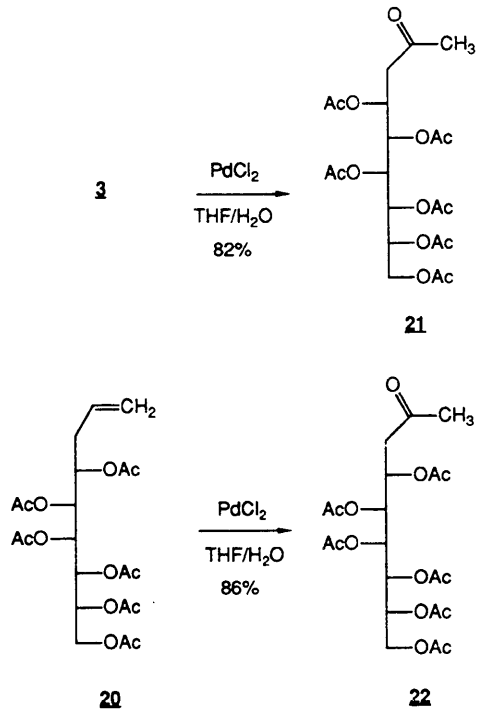
[a] Sn mediates the reaction much more poorly than In. [b] Under ultrasonication, Wurtz coupling products were observed. [c] Reference 33.

versatile, convenient, and efficient. This methodology provides access to various 2-deoxyaldoses. The use of authentic organotin and organoindium reagents gave outcomes essentially identical to those obtained under heterogeneous conditions, implying common reactive species. Indium metal is superior to tin in most applications due to its increased reactivity. Indium-mediated reactions produce fewer byproducts and are more diastereoselective than the corresponding tin-mediated reactions.

Experimental Section

General Procedure A: Addition of Allyl Groups to Carbohydrates Using Tin Metal. To a solution of 1 mmol of the carbohydrate in 25 mL of ethanol/water (9/1) were added 2

Scheme VI



mmol of tin powder (Alfa, 99.999%, 100 mesh), and 3 mmol of allyl bromide. The suspension was sonicated (in a stoppered Pyrex flask immersed in a ultrasound cleaning bath) or heated to reflux until the reaction was complete, as judged by consumption of the carbohydrate (checked by TLC: butanol/acetone/water (4/5/1); usually complete after 12–16 h). The solution was neutralized with 6 N NaOH and filtered through a bed of Celite. The solvent was removed *in vacuo* and the residue was redissolved in 5 mL of pyridine. Acetic anhydride (3 mL) and (dimethylamino)pyridine (DMAP, 10 mg) were added. After the reaction mixture was stirred for 18 h at room temperature, the solvent was removed *in vacuo*, and the diastereomers were separated by SiO_2 chromatography (eluent: hexanes/acetone = 3/1).

General Procedure B: Addition of Allyl Groups to Carbohydrates Using Indium Metal. To a solution of 1 mmol of the carbohydrate in 25 mL of ethanol/water (10/1) were added 2 mmol of indium powder (Aldrich, 99.99%, 150 mesh), and 3 mmol of allyl bromide. The suspension was stirred at rt until the reaction was complete, as judged by consumption of the carbohydrate (checked by TLC: butanol/acetone/water (4/5/1); usually complete after 24–48 h). Some reactions required the use of 0.1 N HCl in place of water. The product was elaborated, processed, and purified as described in general procedure A.

General Procedure C: Addition of Allyl Groups to Carbohydrates Using Preformed Organoindium or Organotin Reagents. To a solution of 3 mmol of tin(IV) tetrachloride (or a suspension of indium(III) trichloride) in 10 mL of dry ether under N_2 was added an ether solution of allylmagnesium bromide (4 mL, 1 M). After being stirred for 5 min, the mixture was added to 2 mmol of the carbohydrate in 44 mL of ethanol/water (10/1). The homogeneous reaction mixture was stirred at room temperature until completion, as determined by consumption of the carbohydrate (checked by TLC: butanol/acetone/water (4/5/1); usually complete after 10 min to 2 h). The product was elaborated, processed, and purified as in general procedure A.

1,2,3,4,5-Penta-*O*-acetyl-6,7,8-trideoxy-L-*gulo*-7,8-octenitol (1). The product was prepared using general procedure A from 150 mg of D-arabinose: yield 341 mg (85%), colorless glass; $[\alpha]^{24}_D$ +2.96° (*c* 12.3, acetone); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.68 (m, 1H, -CH=), 5.38 (dd, 1H, *J* = 4.22 and 7.00 Hz, H_3), 5.26 (dd, 1H, *J* = 4.17 and 6.61 Hz, H_4), 5.08 (m, 2H, =CH_2), 5.03 (m, 1H, H_5), 5.01 (m, 1H, H_2), 4.20 (dd, 1H, *J* = 3.39 and 12.41 Hz, H_{1a}), 4.08 (dd, 1H, *J* = 5.44 and 12.41 Hz, H_{1b}), 2.39–2.28 (m, 2H, -CH_2-vinyl), 2.09, 2 × 2.03, 2.02, 2.01 (4s, 15H, 5 × Ac); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.43, 170.13, 169.84, 169.75, 131.96, 118.92, 70.63, 70.29, 68.78, 68.58, 61.42, 35.11, 20.80, 20.71, 20.64, 20.50; HRMS (FAB) calcd for $C_{18}H_{26}O_{10}$ 403.1604, found 403.1620. Anal. Calcd C, 53.73; H, 6.47. Found: C, 53.93; H, 6.91.

1,2,3,4,5-Penta-*O*-acetyl-6,7,8-trideoxy-D-*talo*-7,8-octenitol (2). The product was prepared using general procedure A from 150 mg of D-ribose: yield 260 mg (65%); colorless glass; $[\alpha]^{24}_D$ +7.92° (*c* 8.4, acetone); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.67 (m, 1H, -CH=), 5.23 (m, 2H, H_3, H_4), 5.18 (m, 1H, H_5), 5.13 (m, 1H, H_2), 5.04 (m, 2H, =CH_2), 4.31 (dd, 1H, *J* = 3.27 and 12.07 Hz, H_{1a}), 4.13 (dd, 1H, *J* = 7.66 and 12.06 Hz, H_{1b}), 2.26 (m, 2H, -CH_2-vinyl), 2.16, 2.03, 2.02, 2.01, 1.99 (5s, 15H, 5 × Ac); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.60, 170.28, 169.98, 169.50, 132.21, 118.80, 70.47, 69.95, 69.70, 68.77, 61.64, 35.40, 20.80, 20.67; HRMS (FAB) calcd for $C_{18}H_{26}O_{10}$ 403.1604, found 403.1589. Anal. Calcd C, 53.73; H, 6.47. Found: C, 54.10; H, 7.01.

1,2,3,4,5,6-Hexa-*O*-acetyl-7,8,9-trideoxy-D-*glycero*-L-*gulo*-8,9-nonenitol (3). The product was prepared using general procedure A from 180 mg of D-glucose: yield 332 mg (70%), colorless glass; $[\alpha]^{24}_D$ +16.94° (*c* 14.1, acetone); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.65 (m, 1H, -CH=), 5.39 (dd, 1H, *J* = 2.55 and 8.30 Hz, H_3), 5.28 (m, 2H, H_4, H_6), 5.05 (m, 3H, H_5, =CH_2), 4.95 (m, 1H, H_2), 4.19 (dd, 1H, *J* = 2.68 and 12.55 Hz, H_{1a}), 4.09 (dd, 1H, *J* = 4.72 and 12.54 Hz, H_{1b}), 2.24 (m, 2H, -CH_2-vinyl), 2.11, 2.09, 2.06, 2.04, 2.02, 2.01 (6s, 18H, 6 × Ac); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.62, 170.12, 169.91, 169.74, 169.66, 132.10, 118.81, 70.42, 70.01, 68.40, 68.19, 67.92, 61.30, 35.40, 20.68, 20.59, 20.51, 20.42; HRMS (FAB) calcd for $C_{21}H_{30}O_{12}$ 475.1816, found 475.1804. Anal. Calcd C, 53.16; H, 6.33. Found: C, 52.59; H, 6.37.

Methyl 3,4,6,7-Tetra-*O*-acetyl-2-deoxy-D-*glycero*-D-*gulo*-heptopyranoside (4). To a solution of 230 mg (0.57 mmol) of **1**, in 10 mL of dry methanol, 23 mmol of sodium were added. The reaction mixture was stirred at room temperature for 2 h and then quenched by the addition of solid CO_2 until the solution was neutral. The precipitate formed was removed by filtration and the filtrate concentrated *in vacuo*. The residue was redissolved in dichloromethane (15 mL) and methanol (3 mL). The solution was cooled to −70 °C, and ozone was bubbled through it for 10 min at −70 °C. Sodium sulfite (50 mg) was added to the reaction mixture at −70 °C, and the mixture was allowed to warm to rt over 1 h and then stirred at rt for 18 h. The mixture was filtered, and the filtrate concentrated *in vacuo*. The residue was dissolved in 5 mL of dry pyridine and 3 mL of acetic anhydride, and 10 mg of DMAP were added. After stirring for 18 h at rt, the solvents were removed *in vacuo*. The residue was purified by SiO_2 chromatography (eluent: hexanes/acetone = 3/1): yield 110 mg (51%, mixture of the two anomers, α/β = 2:3, not separated); ^{1}H NMR (α-anomer, $CDCl_3$, 400 MHz) δ 5.11 (ddd, 1H, *J* = 2.30, 5.00, and 9.90 Hz, H_6), 4.86 (dd, 1H, *J* = 1.15 and 3.18 Hz, H_4), 4.78 (m, 1H, H_3), 4.73 (dd, J_1 = J_2 = 2.60 Hz, H_1), 4.48 (dd, 1H, *J* = 2.29 and 12.20 Hz, H_{7a}), 4.15 (m, 2H, H_5, H_{7b}), 3.28 (s, 3H, OCH_3), 2.06–2.00 (4s, m, 14H, 4 × Ac, $H_{2ax,eq}$); ^{1}H NMR (β-anomer, $CDCl_3$, 400 MHz) δ 5.18 (ddd, 1H, *J* = 2.38, 4.74, and 9.74 Hz, H_6), 5.02 (m, 1H, H_3), 4.78 (m, 1H, H_4), 4.57 (dd, 1H, *J* = 2.24 and 9.80 Hz, H_1), 4.39 (dd, 1H, *J* = 2.38 and 12.26 Hz, H_{7a}), 4.27 (dd, 1H, *J* = 4.79 and 12.27 Hz, H_{7b}), 3.96 (dd, 1H, *J* = 1.36 and 9.74 Hz, H_5), 3.46 (s, 3H, OCH_3), 2.10, 2.05, 2.04, 1.99 (4s, 12H, 4 × Ac), 1.93 (ddd, 1H, *J* = 1.90, 2.24, and 14.30 Hz, H_{2eq}), 1.82 (ddd, 1H, *J* = 3.23, 9.80, and 14.30 Hz, H_{2ax}); HRMS (FAB) calcd for $C_{21}H_{30}O_{12}Na$ 399.1267, found 399.1275.

Methyl 3,4,6,7-Tetra-*O*-acetyl-2-deoxy-α-D-*glycero*-D-*gluco*-heptopyranoside (5). The product was prepared from 80 mg (0.2 mmol) of **2** using the procedure described for **4**: yield 12 mg (15%) and 48 mg (α + β mixture not further purified); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.23 (ddd, 1H, *J* = 5.30, 9.70, and 11.60 Hz, H_3), 5.19 (ddd, 1H, *J* = 2.62, 3.73, and 7.70 Hz, H_6), 4.95 (dd, 1H, J_1 = J_2 = 9.70 Hz, H_4), 4.79 (dd, 1H, *J* = 1.32 Hz and 3.65 Hz, H_1), 4.35 (dd, 1H, *J* = 3.73 and 12.00 Hz, H_{7a}), 4.19 (dd, 1H, *J* = 7.70 and 12.00 Hz, H_{7b}), 3.94 (dd, 1H, *J* = 2.62 and 10.28 Hz, H_5), 2.19 (ddd, 1H, *J* = 1.32, 5.30, and 13.00 Hz, H_{2eq}), 2 × 2.07, 2.02, 1.98 (4s, 12H, 4 × Ac), 1.74 (ddd, 1H, *J* = 3.65, 11.60, and 13.00 Hz, H_{2ax}); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 97.73, 70.15, 69.91, 69.15, 69.08, 61.84, 54.78, 34.70, 20.95, 20.87, 20.80; HRMS (FAB) calcd for $C_{21}H_{30}O_{12}Na$ 399.1267, found 399.1283.

1,6-Anhydro-3,4,7,8-tetra-*O*-acetyl-2-deoxy-β-D-*erythro*-L-*gulo*-octopyranose (6). The product was prepared from 170

mg of 3 using the procedure described for 4, and the reaction mixture was heated to reflux for 50 min during the acetylation step: yield 45 mg (34%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.54 (dd, 1H, J = 1.40 and 1.94 Hz, H_1), 5.19 (ddd, J = 7.06, 8.91, and 10.09 Hz, H_3), 4.98 (dd, 1H, J = 4.32 and 8.91 Hz, H_4), 4.84 (ddd, 1H, J = 2.79, 5.13, and 7.36 Hz, H_7), 4.43 (dd, 1H, J = 2.78 and 12.33 Hz, H_{8a}), 4.39 (d, 1H, $J_{4,5}$ =4.31, $J_{5,6}$ < 1 Hz, H_5), 4.25 (d, 1H, J = 7.36 Hz, H_6), 4.07 (dd, 1H, J = 5.12 and 12.33 Hz, H_{8b}), 2.37 (ddd, 1H, J = 1.95, 7.07, and 13.20 Hz, H_{2eq}), 2.07, 2.06, 2.02, 2.01 (4s, 12H, 4 × Ac), 1.65 (ddd, 1H, J = 1.40, 10.09, and 13.20 Hz, H_{2ax}); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.65, 170.22, 169.93, 169.80, 101.35, 74.18, 73.79, 70.95, 70.74, 67.78, 61.85, 36.95, 20.95, 20.78; HRMS (FAB) calcd for $C_{21}H_{30}O_{12}Na$ 397.1111, found 397.1133.

Ethyl 2,3-Dideoxy-2-methylidene-D-*gluco*-octulonate (7). The product was prepared using general procedure B with 150 mg of D-arabinose and 2 mmol of ethyl (2-bromomethyl)acrylate. The product was purified by SiO_2 chromatography (eluent: $MeOH/CH_2Cl_2$ 1/10 gradient to 1/3): yield 193 mg (73%), white powder; ^{1}H NMR (CD_3OD, 500 MHz) δ 6.25 (d, 1H, J = 1.1 Hz, $=CH_2$), 5.78 (d, 1H, J = 1.1 Hz, $=CH_2$), 4.20 (q, 2H, J = 7.1 Hz, OCH_2), 3.93 (m, 1H, H_4), 3.77 (dd, 1H, J = 3.44 and 11.18 Hz, H_{8a}), 3.74 (dd, 1H, J = 1.84 and 3.80 Hz, H_5), 3.71 (m, 1H, H_7), 3.67 (dd, 1H, J = 1.84 and 7.78 Hz, H_6), 3.64 (dd, 1H, J = 11.18 and 5.43 Hz, H_{8b}), 2.63 (dd, 1H, J = 4.1 and 14.1 Hz, CH_{2a}), 2.50 (dd, 1H, J = 8.85 and 14.1 Hz, CH_{2b}), 1.23 (t, 3H, J = 7.0 Hz, CH_3); ^{13}C NMR (CD_3OD, 125 MHz) δ 169.19, 138.42, 128.91, 74.03, 73.20, 72.28, 64.38, 62.26, 37.38, 14.47; HRMS (FAB) calcd for $C_{11}H_{20}O_7Na$ 287.1107, found 287.1105.

Ethyl 2,3-Dideoxy-2-methylidene-D-*altro*-octulonate (8). The product was prepared using general procedure B with 150 mg of D-ribose and 2 mmol of ethyl (2-bromomethyl)acrylate. The product was purified by SiO_2 chromatography (eluent: $MeOH/CH_2Cl_2$ 1/10 gradient to 1/3): yield 235 mg (89%), white powder; ^{1}H NMR (CD_3OD, 500 MHz) δ 6.20 (d, 1H, J = 1.5 Hz, $=CH_2$), 5.76 (d, 1H, J = 1.5 Hz, $=CH_2$), 4.17 (q, 2H, J = 7.1 Hz, OCH_2), 4.17 (m, 1H, H_4), 3.98 (m, 1H, H_7), 3.86 (dd, 1H, J = 5.52 and 10.1 Hz, H_{8a}), 3.83 (dd, 1H, J = 4.18 and 9.42 Hz, H_6), 3.79 (dd, 1H, J = 1.92 and 10.2 Hz, H_{8b}), 3.27 (m, 1H, H_5), 2.63 (dd, 1H, J = 8.02 and 14.0 Hz, CH_{2a}), 2.55 (dd, 1H, J = 5.64 and 13.8 Hz, CH_{2b}), 1.23 (t, 3H, J = 7.0 Hz, CH_3); ^{13}C NMR (CD_3OD, 125 MHz) δ 169.26, 138.57, 128.79, 74.36, 72.98, 72.43, 69.94, 63.89, 62.26, 37.33, 14.47; HRMS (FAB) calcd for $C_{11}H_{20}O_7Na$ 287.1107, found 287.1107.

Ethyl 2,4,5,7,8-Penta-*O*-acetyl-3-deoxy-D-*gluco*-oct-2-ulopyranosonate (9). A solution of 100 mg of 7 in CH_2Cl_2 (15 mL) and MeOH (5 mL) was cooled to −78 °C before ozone was bubbled through it for 15 min. After addition of dimethyl sulfide (0.5 mL) at −78 °C, the reaction mixture was warmed to rt over 1 h. Stirring continued for 18 h at rt, and then the solvents were removed *in vacuo*. The residue was dissolved in 5 mL of dry pyridine and 3 mL of acetic anhydride, and 10 mg of DMAP were added. After stirring for 18 h at rt, the solvents were removed *in vacuo*. The residue was purified by SiO_2 chromatography (eluent: hexanes/acetone = 3/1): yield 81 mg (45%), colorless glass; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.20 (m, 1H, H_7), 5.03 (m, 1H, H_4), 4.92 (dd, 1H, J = 1.64 and 5.02 Hz, H_5), 4.89 (dd, 1H, J = 1.68 and 9.62 Hz, H_6), 4.49 (dd, 1H, J = 2.37 and 12.27 Hz, H_{8a}), 4.25 (dd, 1H, J = 5.86 and 12.28 Hz, H_{8b}), 4.19 (q, 2H, J = 7.15 Hz, OCH_2), 2.42 (dd, 1H, J = 3.12 and 14.20 Hz, H_{3a}), 2.20 (dd, 1H, J = 3.49 and 14.95 Hz, H_{3b}), 2.08, 2.07, 2.06, 2.03, 2.00 (5s, 15H, 5 × Ac), 1.29 (t, 3H, J = 7.21 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.06, 169.71, 168.85, 168.05, 167.99, 94.75, 70.28, 68.05, 66.76, 63.75, 62.76, 61.79, 31.58, 22.65, 20.90, 20.76, 20.71, 14.11; HRMS (FAB) calcd for $C_{20}H_{28}O_{13}Na$ 499.1428, found 499.1441.

Ethyl 3-Deoxy-D-*altro*-oct-2-ulopyranosonate (10). The product was prepared using the procedures for 9, starting from 200 mg (0.79 mmol) of 8, except the product was not peracetylated and purified by SiO_2 chromatography (eluent: $MeOH/CH_2Cl_2$ 1/10 gradient to 1/3), without further elaboration: yield 121 mg (60%), white powder; ^{1}H NMR (CD_3OD, 500 MHz) δ 4.36 (q, 2H, J = 7.13 Hz, OCH_2), 4.16 (m, 1H, H_7), 4.11 (dd, 1H, J = 4.51 and 10.15 Hz, H_6), 4.01 (dd, 1H, J = 2.07 and 11.36 Hz, H_{8a}), 3.95 (m, 1H, H_4), 3.82 (dd, 1H, J = 3.23 and 11.24 Hz, H_{8b}), 3.46 (dd, 1H, $J_1 = J_2$ = 9.50 Hz, H_5), 2.36 (dd, 1H, J = 4.93 and 13.18 Hz, H_{3a}), 1.77 (dd, 1H, J = 11.61 and 13.09 Hz, H_{3b}), 1.33 (t, 3H, J = 7.10 Hz, CH_3); ^{13}C NMR (CD_3OD, 125 MHz) δ 174.23, 96.64, 75.21, 73.81, 70.58, 69.75, 64.94, 62.53, 40.02, 14.14; HRMS (FAB) calcd for $C_{10}H_{18}O_8Na$ 289.0899, found 289.0887.

2,3,5,6-Tetra-*O*-acetyl-7,8,9-trideoxy-D-*glycero*-L-*gulo*-8,9-nonenonic Acid 1,4-Lactone (12). The product was prepared using general procedure A with 176 mg of 11: yield 167 mg (52%), colorless glass; $[\alpha]^{24}_D$ +2.16° (*c* 2.0, acetone); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.71–5.61 (m, 3H, H_2, H_3, -CH=), 5.49 (dd, 1H, J = 1.85 and 8.31 Hz, H_5), 5.13–5.06 (m, 2H, $=CH_2$), 4.89 (m, 1H, H_6), 4.60 (dd, 1H, J = 3.12 and 11.29 Hz, H_4), 2.26 (m, 2H, CH_2), 2.16, 2.11, 2 × 2.08 (3s, 12H, 4 × Ac); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.21, 169.59, 169.06, 168.80, 131.72, 119.48, 76.63, 70.19, 69.30, 69.23, 67.81, 35.11, 20.80, 20.28, 20.02; HRMS (FAB) calcd for $C_{17}H_{22}O_{10}Na$ 409.1111, found 409.1124.

1,2,3,4-Tetra-*O*-acetyl-5,6,7-trideoxy-D-*lyxo*-6,7-heptenitol (13). The product was prepared using general procedure A from 120 mg of D-erythrose: yield 172 mg (52%), colorless glass; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.64 (m, 1H, -CH=), 5.25 (dd, 1H, J = 8.62 and 2.62 Hz, H_3), 5.15 (m, 1H, H_4), 5.08 (m, 1H, H_2), 5.03 (m, 2H, $=CH_2$), 4.17 (dd, 1H, J = 2.61 and 12.56 Hz, H_{1a}), 4.07 (dd, 1H, J = 4.84 and 12.50 Hz, H_{1b}), 2.22 (m, 2H, $-CH_2$-vinyl), 2.09, 2.01, 2.00, 1.99 (4s, 12H, 4 × Ac); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.53, 170.16, 169.81, 169.71, 132.27, 118.60, 70.01, 69.66, 68.29, 61.85, 35.39, 20.73, 20.61; HRMS (FAB) calcd for $C_{15}H_{22}O_8$ 331.1391, found 331.1377. Anal. Calcd C, 54.54; H, 6.67. Found: C, 54.48; H, 6.83.

1,2,3,4,5-Penta-*O*-acetyl-6,7,8-trideoxy-6,6-dimethyl-L-*gulo*-7,8-octenitol (14). The product was prepared using general procedure B with 1 mmol of D-arbinose and 2 mmol of prenyl bromide: yield 150 mg (35%); colorless glass; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.88 (dd, 1H, J = 10.88 and 17.46 Hz, =CH-), 5.28 (m, 2H, H_3, H_4), 5.05 (m, 1H, H_2), 5.00 (dd, 1H, J = 10.88 and 1.07 Hz, $=CH_2$), 4.96 (dd, 1H, J = 17.46 and 1.07 Hz, $=CH_2$), 4.85 (d, 1H, J = 3.87 Hz, H_5), 4.24 (dd, 1H, J = 3.38 and 12.33 Hz, H_{1a}), 4.05 (dd, 1H, J = 5.99 and 12.33 Hz, H_{1b}), 2.11, 2.06, 2.03, 1.99, 1.97 (5s, 15H, 5 × Ac), 1.04, 0.99 (2s, 6H, 2 × CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.41, 170.20, 170.01, 169.62, 169.52, 142.98, 112.61, 74.61, 70.41, 69.31, 67.79, 61.49, 40.65, 23.53, 23.38, 2 × 20.64, 2 × 20.62, 20.55; HRMS (FAB) calcd for $C_{20}H_{30}O_{10}Na$ 453.1735, found 453.1751.

6-Methyl-1,2,3,4,5-penta-*O*-acetyl-6,7,8-trideoxy-L-*gulo*-7,8-octenitols (15). The product was prepared using general procedure B with 150 mg of D-arabinose and 2 mmol of crotyl bromide. The products are isolated as a mixture of two diastereomers (1:1) at C_6: yield 287 mg (69%), colorless glass; $[\alpha]^{24}_D$ +2.84° (*c* 4.6, acetone); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.75 (m, 1H, -CH=), 5.42 (dd, 1H, J = 3.65 and 7.30 Hz, H_3), 5.37 (dd, J = 4.43 and 8.10 Hz, 1H, H_4), 5.13 (m, 1H, $=CH_2$), 5.05 (m, 1H, $=CH_2$), 5.03 (m, 1H, H_2), 5.01 (dd, 1H, J = 4.52 and 7.36 Hz, H_5), 4.25 (2dd, 1H, J = 3.48 and 7.05 Hz, H_{1a}), 4.13 (2dd, 1H, J = 3.12 and 5.67 Hz, H_{1b}), 2.55 (m, 1H, H_6), 2.15, 2.12, 2.10, 2.08, 2.04 (5s, 15H, 5 × Ac), 0.99 (2d, 3H, J = 6.83 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.35, 170.25, 169.81, 169.68, 169.65, 138.67 and 137.97 ($2C_7$), 116.78 and 116.01 ($2C_8$), 73.51, 73.09, 69.90, 69.43, 69.29, 68.98, 68.54, 68.61, 68.54, 61.50 and 61.44 ($2C_1$), 39.18 and 38.40 ($2C_6$), 20.68, 20.64, 20.61, 20.57, 20.52, 17.45 and 14.20 (2 × CH_3); HRMS (FAB) calcd for $C_{19}H_{28}O_{10}Na$ 439.1580, found 439.1600.

6-Methyl-1,2,3,4,5-penta-*O*-acetyl-6,7,8-trideoxy-D-*talo*-7,8-octadienitol (16). The product was prepared using general procedure B with 150 mg of D-ribose and 2 mmol of 1-bromo-2-butyne: yield 269 mg (65%), colorless glass; $[\alpha]^{24}_D$ +0.64° (*c* 8.5, acetone); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.39 (dd, 1H, J = 4.9 and 6.7 Hz, H_4), 5.35 (dd, 1H, J = 4.2 and 6.6 Hz, H_3), 5.32 (d, 1H, J = 2.9 Hz, H_5), 5.26 (m, 1H, H_2), 4.80 (m, 2H, $=CH_2$), 4.37 (dd, 1H, J = 3.2 and 12.2 Hz, H_{1a}), 4.16 (dd, 1H, J = 7.1 and 12.1 Hz, H_{1b}), 2.13, 2.09, 2.07, 2.06, 2.05 (5s, 15H, 5 × Ac), 1.74 (t, 3H, J = 3.2 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 206.8, 170.42, 169.65, 169.56, 169.28, 95.14, 77.02, 71.38, 69.64, 69.43, 69.02, 61.68, 20.73, 20.63, 2 × 20.56, 20.42, 14.98; HRMS (FAB) calcd for $C_{19}H_{26}O_{10}Na$ 437.1424, found 437.1438.

2-Allyl-hexa-*O*-acetyl-D-*gluco*-hexanitol (17). The product was prepared using general procedure A with 180 mg of D-fructose: yield 284 mg (60%), colorless glass; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.81 (m, 1H, -CH=), 5.72 (d, 1H, J = 3.28 Hz, H_3), 5.57 (dd, 1H, J = 3.28 and 7.24 Hz, H_4), 5.09 (m, 3H, $=CH_2$; H_5),

4.53 (d, 1H, J = 12.22 Hz, H_{1a}), 4.36 (d, 1H, J = 12.34 Hz, H_{1b}), 4.26 (dd, 1H, J = 2.79 and 12.43 Hz, H_{6a}), 4.09 (dd, 1H, J = 5.88 and 12.38 Hz, H_{6b}), 2.87 (dd, 1H, J = 7.57 and 14.81 Hz, -CH_{2a}-vinyl) 2.68 (dd, 1H, J = 6.66 and 14.84 Hz, -CH_{2b}-vinyl), 2.12, 2.08, 2.06, 2 × 2.05, 2.01 (6s, 18H, 6 × Ac); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.31, 169.90, 169.75, 169.35, 169.32, 169.24, 131.18, 119.19, 83.16, 69.66, 69.14, 68.18, 63.56, 61.50, 36.26, 21.62, 20.71, 20.61, 20.50, 20.47, 20.41; HRMS (FAB) calcd for $C_{21}H_{30}O_{12}Na$ 497.1635, found 497.1652.

6-Methyl-1,2,3,4,5-penta-*O*-acetyl-6,7,8-trideoxy-L-*gulo*-6,7-octadienitol (18). The product was prepared using general procedure C with 150 mg of D-arabinose and 2 mmol of 1-bromo-2-butyne: yield 190 mg (46%), colorless solid; $[\alpha]^{24}_D$ +3.44° (*c* 3.5, acetone); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.47 (dd, 1H, J = 2.82 and 8.25 Hz, H_4), 5.35 (dd, 1H, J = 2.78 and 7.70 Hz, H_3), 5.31 (d, 1H, J = 8.28 Hz, H_5), 5.07 (m, 1H, H_2), 4.81 (m, 2H, =CH_2), 4.25 (dd, 1H, J = 3.23 and 12.36 Hz, H_{1a}), 4.07 (dd, 1H, J = 5.84 and 12.38 Hz, H_{1b}), 2.11, 2.09, 2.08, 2.07, 2.05 (5s, 15H, 5 × Ac), 1.75 (t, 3H, J = 3.19 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 207.58, 170.38, 169.78, 169.69, 169.66, 169.45, 94.06, 76.64, 72.85, 69.00, 68.64, 68.52, 68.48, 61.73, 21.04, 20.75, 20.68, 20.57, 20.46, 14.37; HRMS (FAB) calcd for $C_{19}H_{26}O_{10}Na$ 437.1424, found 437.1424.

1-Deoxy-3,4,5,6,7-penta-*O*-acetyl-L-*gulo*-2-heptulose (19). Ozone was bubbled through a solution of 70 mg of **18** in 15 mL of dichloromethane and 5 mL of MeOH at −78 °C for 10 min. After addition of dimethyl sulfide (0.5 mL), the reaction mixture was warmed to room temperature and stirred for 18 h. The mixture was concentrated *in vacuo*, the residue was dissolved in 5 mL of dry pyridine and 3 mL of acetic anhydride, and 10 mg of DMAP was added. After being stirred at ambient temperature for 18 h, the reaction mixture was concentrated *in vacuo*, and the residue was purified by SiO_2 chromatography (eluent: hexanes/ethyl acetate = 1/1): yield 55 mg (81%), colorless glass; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.62 (dd, 1H, J = 3.77 and 4.98 Hz, H_4), 5.48 (dd, 1H, J = 6.34 and 5.00 Hz, H_5), 5.27 (d, 1H, J = 3.76 Hz, H_3), 5.07 (m, 1H, H_6), 4.33 (dd, 1H, J = 3.61 and 12.34 Hz, H_{7a}), 4.12 (dd, 1H, J = 5.69 and 12.36 Hz, H_{7b}), 2.22 (s, 3H, CH_3), 2.09, 2.08, 2.07, 2.06, 2.05 (5s, 15H, 5 × Ac); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 201.04, 170.48, 169.83, 169.71, 169.54, 169.51, 69.34, 68.70, 68.58, 68.18, 61.50, 26.89, 20.68, 20.63, 20.52, 20.46, 20.37; HRMS (FAB) calcd for $C_{17}H_{24}O_{11}Na$ 427.1216, found 427.1219.

1,2,3,4,5,6-Hexa-*O*-acetyl-7,8,9-trideoxy-L-*glycero*-D-*manno*-8,9-nonenitol (20). The product was prepared using general procedure A with 180 mg of D-mannose: yield 427 mg (90%), colorless glass; $[\alpha]^{24}_D$ +5.93° (*c* 12.2, acetone); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.64 (m, 1H, -CH=), 5.43 (dd, 1H, J = 1.93 and 10.00 Hz, H_4), 5.29 (dd, 1H, J = 1.89 and 8.83 Hz, H_3), 5.13 (dd, 1H, J = 1.89 and 10.02 Hz, H_5), 5.01 (m, 2H, =CH_2), 4.93 (m, 2H, H_2, H_6), 4.16 (dd, 1H, J = 2.85 and 12.50 Hz, H_{1a}), 3.97 (dd, 1H, J = 5.36 and 12.50 Hz, H_{1b}), 2.17 (m, 2H, -CH_2-vinyl), 2.08, 2.04, 2 × 2.02, 2.00, 1.99 (5s, 18H, 6 × Ac); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.50, 170.33, 170.00, 169.78, 169.59, 132.50, 118.40, 69.49, 68.98, 68.04, 67.37, 66.86, 61.83, 35.61, 20.91, 20.87, 20.78, 20.64, 20.57; HRMS (FAB) calcd for $C_{21}H_{30}O_{12}$ 475.1816, found 475.1800. Anal. Calcd: C, 53.16; H, 6.33. Found: C, 52.86; H, 6.46.

Large-Scale Preparation of 20. To a solution of 10 mmol (1.8 g) of D-mannose in 200 mL of ethanol/water (9/1), 15 mmol (1.78 g) of tin powder and 15 mmol of allyl bromide were added. The suspension was sonicated for 72 h and then neutralized by the addition of 1 N NaOH. The precipitate formed was removed by centrifugation, the solvent was removed *in vacuo*, and the residue was redissolved in 25 mL of pyridine. After the addition of acetic anhydride (15 mL) and 5 mg of DMAP, the solution was stirred at rt for 18 h. The solvent was removed and the residue purified by SiO_2 chromatography (eluent: hexanes/acetone 4/1 gradient to 1/1). Yield: 2.6 g (55%).

4,5,6,7,8,9-Hexa-*O*-acetyl-1,3-dideoxy-D-*glycero*-D-*ido*-2-nonulose (21). To a solution of 100 mg (0.21 mmol) of **3** in 11 mL of THF/water (10/1) was added 45 mg (0.25 mmol) of $PdCl_2$ in one portion. The suspension was stirred at room temperature until TLC (hexanes/ethyl acetate = 2/1) showed completion of the reaction (3 h; R_f = 0.2). The reaction mixture was filtered through a bed of Celite, and the filtrate was concentrated *in vacuo*. The residue was purified by SiO_2 chromatography (eluent: hexanes/ethyl acetate 1/1): yield 85 mg (82%), colorless glass; $[\alpha]^{24}_D$ +1.52° (*c* 3.4, acetone); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.50 (m, 1H, H_4), 5.45 (dd, 1H, J = 2.10 and 8.35 Hz, H_7), 5.35 (dd, 1H, J = 2.03 and 8.91 Hz, H_6), 5.17 (dd, 1H, J = 1.67 and 8.81 Hz, H_5), 5.00 (m, 1H, H_8), 4.20 (dd, 1H, J = 2.77 and 12.50 Hz, H_{9a}), 4.08 (dd, 1H, J = 5.10 and 12.37 Hz, H_{9b}), 2.61 (m, 2H, $H_{3a,3b}$), 2.21, 2.08, 2.07, 2.05, 2.04, 2 × 2.02 (6s, 21H, 7 × Ac); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 203.95, 170.67, 170.13, 170.09, 169.83, 169.79, 71.08, 2 × 68.44, 67.78, 67.09, 61.59, 43.89, 29.92, 20.70, 20.50; HRMS (FAB) calcd for $C_{21}H_{30}O_{13}Na$ 513.1584, found 513.1605.

4,5,6,7,8,9-Hexa-*O*-acetyl-1,3-dideoxy-D-*glycero*-D-*galacto*-2-nonulose (22). The product was prepared and purified, using the procedure described for **21**, from 100 mg of **20**: yield 89 mg (86%), colorless glass; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.45 (dd, 1H, J = 1.96 and 10.09 Hz, H_6), 5.35 (dd, 1H, J = 1.93 and 9.06 Hz, H_7), 5.20 (m, 1H, H_4), 5.10 (dd, 1H, J = 1.55 and 10.13 Hz, H_5), 4.99 (m, 1H, H_8), 4.16 (dd, 1H, J = 2.69 and 12.53 Hz, H_{9a}), 4.00 (dd, 1H, J = 5.12 and 12.53 Hz, H_{9b}), 2.55 (m, 2H, $H_{3a,3b}$), 2.10, 2 × 2.06, 2 × 2.03, 2.02, 2.01 (5s, 21H, 7 × Ac); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 204.16, 170.52, 170.18, 169.87, 68.72, 67.96, 67.34, 66.69, 61.85, 43.48, 29.99, 20.86, 20.80, 20.66, 20.59; HRMS (FAB) calcd for $C_{21}H_{30}O_{13}Na$ 513.1584, found 513.1598.

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Supplementary Material Available: Copies of ^{13}C NMR-spectra of **7–10**, **12**, **14–19**, **21**, and **22** (14 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.