solution of 0.36 mL (5.1 mmol) of dimethyl sulfoxide in 5 mL of dichloromethane. After 15 min, a solution of 1.00 g (2.55 mmol) of the above alcohol (the precursor to the acid **25**) in 8.5 mL of dichloromethane was added to the reaction mixture. After 20 min, the reaction mixture was treated with 1.78 mL (12.7 mmol) of trimethylamine, allowed to warm to room temperature, and then poured into 100 mL of 50% saturated aqueous NaCl. The resulting mixture was extracted with two 150-mL portions of ether, and the combined organic extracts were dried ($MgSO_4$) and then concentrated under reduced pressure. To a stirred solution of the residue in 17 mL of ethanol and 1.30 g (7.64 mmol) of $AgNO_3$ in 1.80 mL of water was added, over 15 min, a solution of 1.01 g (15.28 mmol) of 85% KOH in 16.8 mL of water. After 30 min at room temperature, the solution was filtered and the precipitate was washed with three 10-mL portions of 6% aqueous KOH. The combined filtrates were cooled to 0 °C, 200 mL of ether was added, and the stirred mixture was carefully acidified to pH 2 with concentrated aqueous HCl. The ether phase was separated and the aqueous phase was extracted with two 200-mL portions of ether. The combined organic extracts were dried ($MgSO_4$) and then concentrated under reduced pressure. Chromatography of the residue on 50 g of silica gel with ether afforded 984 mg (95%) of the acid **25** as a viscous, light-yellow oil: $R_f = 0.06$ (silica gel, 4:6 ether/petroleum ether). A portion of this material was treated with excess ethereal diazomethane. Evaporation of solvent at reduced pressure and chromatography of the residue on silica gel with 3:7 ether/petroleum ether afforded the methyl ester of **25** as a colorless oil: $R_f = 0.36$ (silica gel, 4:6 ether/petroleum ether); evaporative distillation 170 °C (0.005 mmHg); $[\alpha]^{27}_D$ +57.6° (*c* 1.83, $CHCl_3$); IR ($CHCl_3$) 3000, 2950, 2880, 1750, 1460, 1385, 1375, 1100, 1070, 1015, 870 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.03 (t, 3 H, CH_3CH_2), 1.12 (d, 3 H, CH_3CH), 1.33, 1.50 (2 s, 6 H, $(CH_3)_2C$), 3.73 (s, 3 H, OCH_3), 3.92 (d, 1 H, $J = 4$ Hz, C(17)–H), 5.07 (s, 1 H, OCHO), 7.33 (s, 5 H, C_6H_5). Anal. Calcd for $C_{23}H_{27}O_7$: C, 65.70; H, 7.67. Found: C, 65.77; H, 7.65. Treatment of this ester with lithium tetrahydridoaluminate in ether at 0 °C produced the starting alcohol.

2(*S*)-Ethyl-2-[5(*S*)-carboxy-3(*S*)-methyl-2(*R*)-tetrahydrofuryl]-3-(*R*),4(*S*)-(dimethylmethylenedioxy)-5(*S*)-(benzloxy)tetrahydrofuran (24) and Methyl Ester. By the procedure described above for the acid **25**, 195 μL (2.24 mmol) of oxalyl chloride in 10 mL of dichloromethane, 211 μL (2.98 mmol) of dimethylsulfoxide in 5.0 mL of dichloromethane, 585 mg (1.49 mmol) of the alcohol (the precursor to the acid **24**), and then dissolution of the crude aldehyde in 10 mL of ethanol, 0.76 g (4.47 mmol) of $AgNO_3$ in 1.1 mL of water, and addition of 0.59 g (8.95 mmol) of 85% KOH in 9.8 mL of water, afforded, after chromatography on 40 g of silica gel with ether, 567 mg (93%) of the acid **24** as a viscous, colorless oil: $R_f = 0.10$ (silica gel, 4:6 ether/petroleum ether). A portion of this material was treated with excess ethereal diazomethane. Evaporation of the solvent at reduced pressure and chromatography of the residue on silica gel with 3:7 ether/petroleum ether afforded the methyl ester of the acid **24** as a colorless oil: $R_f = 0.27$ (silica gel, 4:6 ether/petroleum ether); evaporative distillation 170 °C (0.005 mmHg); $[\alpha]^{23}_D$ +61.9° (*c* 1.46, $CHCl_3$); IR ($CHCl_3$) 3000, 2950, 2880, 1730, 1450, 1440, 1385, 1375, 1270, 1075, 875 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (t, 3 H, $J = 7$ Hz, CH_3CH_2), 1.23 (d, 3 H, $J = 6$ Hz, CH_3CH), 1.33, 1.48 (2 s, 6 H, $(CH_3)_2C$), 3.47 (s, 3 H, OCH_3), 3.98 (d, 1 H, $J = 6$ Hz, C(17)–H), 5.12 (d, 1 H, $J = 2$ Hz, OCHO), 7.32 (s, 5 H, C_6H_5). Anal. Calcd for $C_{23}H_{32}O_7$: C, 65.70; H, 7.67. Found: C, 65.73; H, 7.72. Treatment of this ester with lithium tetrahydridoaluminate in ether at 0 °C produced the starting alcohol.

The Convergent Synthesis of Polyether Ionophore Antibiotics: An Approach to the Synthesis of the Monensin Tetrahydropyran–Bis(tetrahydrofuran) via the Ester Enolate Claisen Rearrangement and Reductive Decarboxylation[1]

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Received September 28, 1984

Abstract: The monensin tetrahydropyran equivalent **22** is prepared from D-fructose and then joined to the monensin bis(tetrahydrofuran) equivalent **24a** via the ester enolate Claisen rearrangement. Methodology for the radical induced, reductive decarboxylation of the resulting acid **26a** is described. Anomeric stabilization of the intermediate tetrahydrofuran-2-yl radical is an important factor in the stereochemical outcome of this process. Reduction of 1-chloro-2,3-*O*-isopropylidene furanoid and pyranoid carbohydrate derivatives with lithium di-*tert*-butylbiphenyl affords the corresponding glycals in high yield.

Through the ester enolate Claisen rearrangement, difficult carbon–carbon bond constructions can be realized intramolecularly after the two reaction partners have been joined intermolecularly in a relatively easy esterification. Application of this inherently convergent process to furanoid and pyranoid carboxylic acids and glycals has led to a toal synthesis of lasalocid A[3] and its enantiomer[4] in sufficient quantities for biological testing. In order to explore this strategy further, we have developed routes ot additional subunits for polyether synthesis as reported in the preceding two papers in this issue. In general, the substitution pattern of the ionophore framework nicely accommodates the functionality engendered by the ester enolate Claisen rearrangement. The resulting olefin can, for example, be hydrogenated or hydroborated, and the carboxyl residue can usually be reduced to a methyl or ethyl group. When this is not the case, the convergent union of

(1) (a) Grateful acknowledgment is made for support of this investigation by NIH (No. HL-23167). Acknowledgment is also made for the use of the Southern California Regional NMR Facility (National Science Foundation Grant CHE-79-16324). (b) The crystallographic analysis was supported in part by grants from the Veterans Administration (No. 5455-01P), the National Institute of Health (AM30579), and the Fannie E. Ripple Foundation. Neil Mandel is a Veterans Administration Associate Research Career Scientist. Acknowledgment is also made for the use of the Southern California Regional NMR Facility (National Science Foundation Grant CHE-79-16324).

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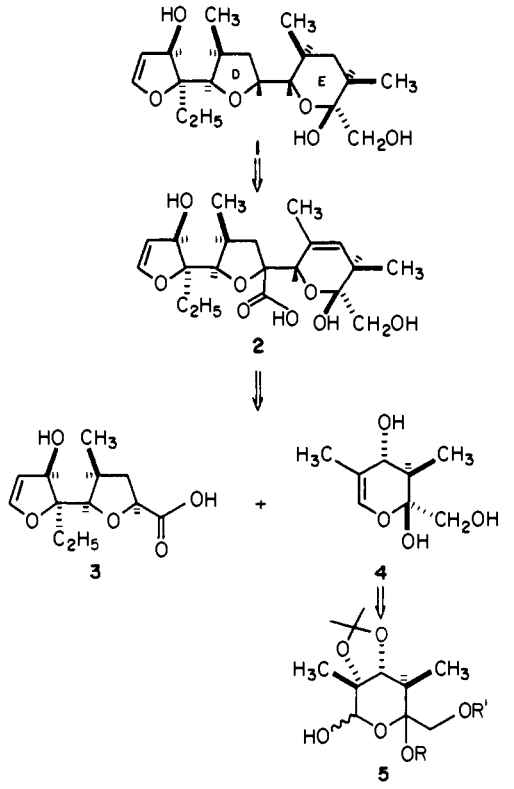
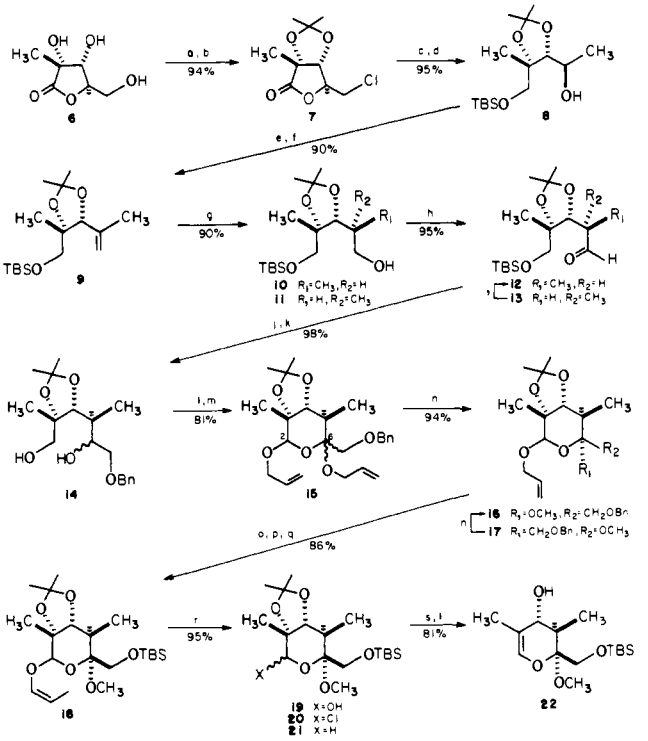
Scheme I. Retrosynthetic Analysis for the Connection of Monensin's D and E Rings



two subunits carries a price: removal of a surplus carbon. Indeed, the bond joining the terminal tetrahydrofuran and tetrahydrofuran rings of a large subclass of polyethers bears vicinal hydrogens. Reductive decarboxylation of γ,δ-unsaturated acids is thus an important goal of our program for polyether synthesis; broader implications exist for the expanded utility of the ester enolate Claisen rearrangement as well.

The connection of monensin's D and E rings depicted in Scheme I is an appropriate setting in which to evaluate this problem. In planning a route to the glycal **4**, our confidence in the procedure developed for the reductive fragmentation of lactol acetonides[5] outweighed our doubts concerning the stability of the hemiacetal ketal **5**. α-D-glucosaccharinic acid γ-lactone (**6**),[6] requiring introduction of an oxygenated two-carbon fragment at C4 and deoxygenation at C5, was therefore a suitable starting material for this subunit (Scheme II). Hydride reduction of the derived[7] chlorolactone **7** accomplished the latter objective, and selective protection[8] of the resulting diol[9] allowed for chain extension at C4 by oxidation to the ketone and Wittig methylenation. Hydroboration[10] of the olefin **9** was studied in some detail. While borane in THF produced a slight 2:1 excess of the desired 4*S* diastereomer **10**, dialkylboranes exhibited a marked preference for production of the 4*R* epimer **11** which increased with the steric bulk of the reagent.[11] Following completion of this work, Midland[12] reported a similar dependency, and the Felkin-type transition state model he proposed can be used to rationalize our results as well. Fortunately, this less than satisfactory stereochemical outcome could be ameliorated by equilibration to a 1:1 mixture of the aldehydes **12** and **13** on silica gel, and after two recycles of the minor aldehyde **13**, the desired aldehyde **12** was obtained in a total yield of 77% from the olefin **9**. The C6 carbon was then introduced in the form of (benzyloxy)methyllithium,[13] and fluoride[14] treatment of the resulting adduct gave a 1:1 mixture of the diols **14** which contain all the atoms of the secoglycal core. Addition of the crude keto aldehyde obtained from dual Swern oxidation[15] to *p*-toluenesulfonic acid in allyl alcohol caused ring closure to a 1:1 mixture of the tetrahydropyrans **15**. Selective ketal exchange in methanol demonstrated that these products were epimeric only at C6 and operationally distinguished this center from the allyl acetal at C2. The proton NMR spectra of the easily separated mixture of methyl ketals **16** and **17** each showed a 9-Hz coupling between the C4 and C5 hydrogens. This confirmed that epimerization had not occurred at the C5 methyl group during either the cyclization or equilibration process.[16] Difference NOE spectra at 500 MHz then established the relative stereochemistry at C6: an enhancement between the C5 methyl group and the

Scheme II. Synthesis of the Monensin E Ring Equivalent, Pyranoid Glycal **22**[a]



[a] (a) H_2SO_4, $(CH_3)_2CO$; (b) DMF, $(COCl)_2$, CH_2Cl_2; (c) LAH, Et_2O; (d) TBSCl, C_5H_5N, CH_2Cl_2; (e) $(i\text{-PrN})_2C$, Cl_2CHCO_2H, Me_2SO, C_6H_6; (f) $(Ph)_3PCH_2$, THF; (g) BH_3, THF; 10% NaOH, 30% H_2O_2; (h) $(COCl)_2$, Me_2SO, Et_3N; (i) SiO_2, petroleum ether, Et_2O; (j) $C_6H_5CH_2OCH_2Sn(n\text{-Bu})_3$, *n*-BuLi, THF; (k) $(n\text{-Bu})_4NF$, THF; (l) $(COCl)_2$, Me_2SO; Et_3N; (m) *p*-TsOH, CH_2CHCH_2OH: (n) $C_6H_5NH^+$-*p*-TsO^-, MeOH; (o) *t*-BuOK, Me_2SO; (p) Li/NH_3, THF; (q) TBSOTf, 2,6-lutidine, CH_2Cl_2; (r) $Hg(OAc)_2$, THF, H_2O; (s) $P(NMe_2)_3$, CCl_4, THF; (t) lithium 4,4'-di-*tert*-butylbiphenyl, THF.

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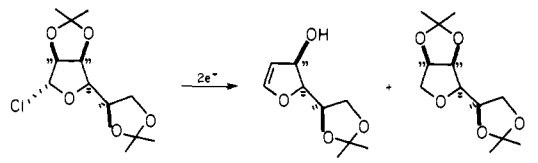
(16) In fact, attempts to equilibrate the parallel 4-epi series from the aldehyde **13** demonstrated that elimination of allyl alcohol from C5 is irreversible.

Table I. Reductive Fragmentation of the Model Furanosyl Chloride **23a**



23a **23b** **23c**

reductant	yield of **23b**	**23b**:**23c**
Li/NH_3[a]	75%	7.9:1
Na/NH_3[a]	77%	10.7:1
K/NH_3[a]	79%	15.0:1
SmI_2[b]	0%	
sodium naphthalene[c]	82%	>50:1
lithium benzophenone[d]	NR[h]	
sodium anthracene[e]	NR	
sodium trimesitylborane[f]	70%	>50:1
lithium 4,4'-di-*tert*-butylbiphenyl[g]	94%	>50:1

[a] 35 eq of metal, 0.5 M, 1:10 THF/NH_3, −78 °C, 30 min, then NH_4Cl. [b] 2 eq, 0.07 M, THF, 25 °C, 3 h. [c] 6 eq, 0.21 M THF, −35 °C, 20 min, then H_2O. [d] 5 eq, 0.50 M THF, 25 °C. [e] 5 eq, 0.25 M THF, 25 °C. [f] 5 eq, 0.25 M THF, −20–0 °C, 1 h, then H_2O. [g] 5 eq, 0.20 M THF, −78 °C, 15 min, then H_2O. [h] No reaction.

C7 methylene hydrogens indicated that these substituents were cis in the more polar ketal **16**; the corresponding enhancement between the C7 and C5 hydrogens in the less polar ketal **17** corroborated this interpretation. Anticipating the need for stereochemical control in the hydrogenation of a future C3,4 olefin, we elected to consolidate the C6 ketals through equilibration in methanol and carry forward the epimer with the benzyloxymethylene substituent axially disposed. The acid-stable benzyl protecting group had served to prevent intramolecular acetalization at C2, but now its incompatibility with the reducing conditions prescribed for glycal formation[5] called for its replacement. Base-catalyzed isomerization of the allyl group,[17] Birch reduction, and low-temperature silylation with TBS-triflate[18] delivered the modified tetrahydropyran **18** in excellent overall yield. Finally, treatment of the *cis*-propenyl ether with mercuric acetate in aqueous THF[17] unmasked the hemiacetal ketal **19** under essentially neutral conditions. Although this lactol slowly unraveled to the corresponding keto aldehyde on standing in deuteriochloroform (half-life: 12 h), its remarkable stability to aqueous workup and chromatography on silica gel allowed the pure oil to be isolated in 95% yield and stored indefinitely at −20 °C.

This straightforward resolution of the most dubious aspect of our synthetic plan casts an ironic light on the unforeseen difficulties we encountered in obtaining useful quantities of the glycal **22**. While proton NMR indicated that Castro's tris(dimethylamino)phosphine/carbon tetrachloride reagent[19] gave the pyranosyl chloride **20** without incident, addition of this material to excess lithium in liquid ammonia at −78 °C according to our standard procedure[5] produced a disconcerting 1:1 ratio of the desired glycal **22** and the tetrahydropyran **21** in a combined yield of only 50%. Nearly quantitative recovery of the isolated glycal from the reducing medium ruled out product decomposition as a cause of the exceptionally low ratio and yield. Equally puzzling was the poor mass balance of the reaction, since TLC did not even show a hint of other byproducts. Frustrated by these results, we were constrained to reinvestigate basic methodology for glycal synthesis from lactol acetonide precursors.

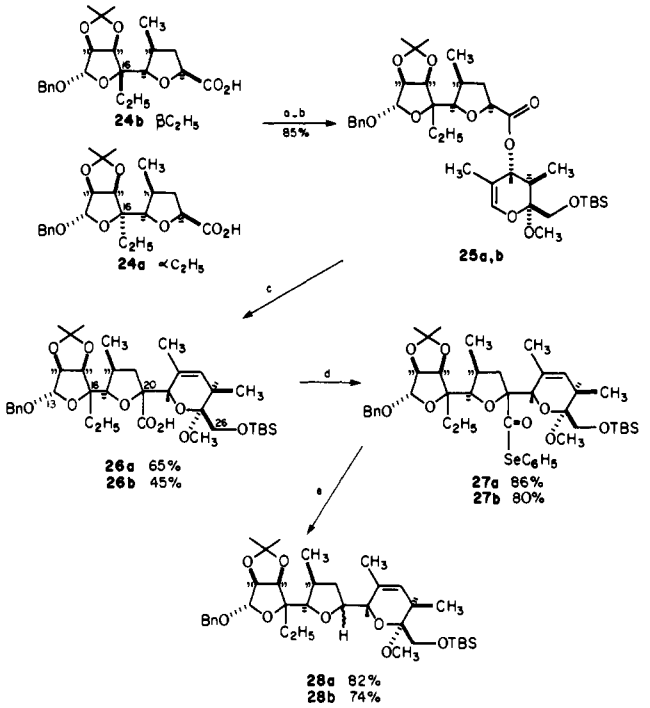
These experiments are summarized in Tables I and II. Products of hydrodehalogenation such as **21** had not been observed previously with pyranoid glycals, but the analogous byproducts (e.g., **23c**) usually accompany furanoid glycals to the extent of 10–20%.[5] If these byproducts arise from protonation of an intermediate carbanion by a relatively acidic lithium cation–ammonia complex, one would expect to observe increasing fragmentation to protonation ratios with decreasing counterion solvation. While this argument is admittedly oversimplified, the furanosyl chloride **23a**[20] did in fact display the expected trend (Table I). However, reduction of the pyranosyl chloride **20** with potassium in liquid ammonia gave results indistinguishable from those obtained with lithium in liquid ammonia (Table II). We therefore turned our attention to aprotic reducing media.

Table II. Reductive Fragmentation of the Pyranosyl Chloride **20**

reductant	yield of **22**	**22**:**21**
Li/NH_3[a]	25%	1.05:1
K/NH_3[a]	27%	1.07:1
sodium naphthalene[b]	31%	>50:1
lithium 4,4'di-*tert*-butylbiphenyl[c]	81%	>50:1

[a] 50 eq of metal, 0.06 M, 1:10 THF/NH_3, −78 °C, 30 min, then NH_4Cl. [b] 12 eq, 0.20 M THF, −78 °C, 30 min, then H_2O. [c] 12 eq, 0.20 M THF, −78 °C, 15 min, then H_2O.

Scheme III. Union of Monensin's E and C + D Ring Subunits (a = α-C_2H_5, b = β-C_2H_5)[a]



[a] (a) $(Ph)_3P$, CCl_4, CH_2Cl_2; (b) 22, DMAP, CH_2Cl_2; (c) 25a, $KN(TMS)_2$, TBSCl, THF; 1 N LiOH; 25b, LDA, TMSCl, THF; H_3O^+; (d) $PhOP(O)Cl_2$, C_6H_5SeH, Et_3N, THF; (e) $(n\text{-}Bu)_3SnH$, AIBN, C_6H_6.

After an initial disappointment with samarium diiodide in THF,[21] a series of radical anions[22] gave promising results with the model furanosyl chloride **23a**. Particularly encouraging was the absence of hydrodehalogenation products. Sodium naphthalene had been previously reported to give the glycal **23b** in 59% yield;[23] in our hands, lowering the reaction temperature to −53 °C raised the chromatographed yield to 82%. Use of Freeman's[24] di-*tert*-butylbiphenyl radical anion was even more rewarding, and

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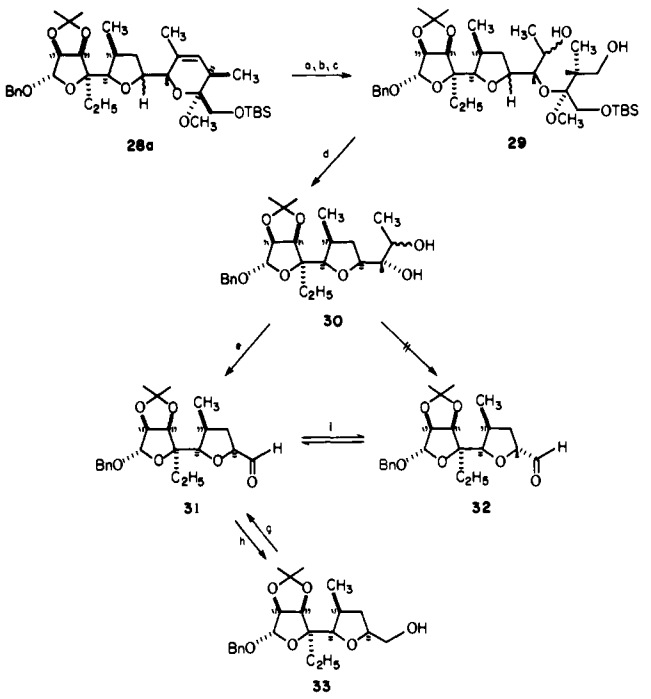
its striking superiority as an electron-transfer reagent became fully apparent with the pyranosyl chloride **20** (Table II). While either base-induced elimination[25] of an incipient aldehyde of fragmentation[26] of the intermediate radical could conceivably be responsible for the poor mass balance observed with both lithium in liquid ammonia and sodium naphthalene, these or other nonproductive pathways are minimized by lithium di-*tert*-butylbiphenyl which reproducibly delivered the pyranoid glycal **22** in 81% chromatographed yield.

With the subunits for monensin's C and D rings already in hand,[27] the stage was now set for joining this E ring equivalent to the polyether backbone (Scheme III). At this point we had been unable to determine the C16[28] configuration of the Claisen epimers **24a** and **24b**, so we planned to carry both carboxylic acids forward until we obtained a crystalline intermediate or derivative. Formation of the acid chlorides with triphenylphosphine/carbon tetrachloride[29] permitted direct addition of the glycal **22** and DMAP to the crude reaction mixtures, and in both cases the acid-sensitive esters **25a** and **25b** could be isolated in 85% yield by chromatography on Activity III alumina. Our initial study of the ester enolate Claisen rearrangement was carried out on the major epimer. Fortunately, enolization with LDA and trapping with TMSCl provided, after thermal rearrangement at 50 °C, a single crystalline carboxylic acid in 45% yield. The result of the X-ray structure analysis[30] (see supplementary material) confirmed the stereochemical assignments we had made[27] on the basis of spectroscopic of chemical inference and established that the minor Claisen epimer **24a** possessed the natural configuration at C16.[28]

Since the relative stereochemistry at this center was expected to have little bearing on the chemistry of the D–E ring juncture, we attacked the major problem of reductive decarboxylation of **26b** while the crystallographic investigation was still in progress.

Of all the methods available for removing unactivated carbonyl groups, only Wilkinson's catalyst,[31] which uniquely avoids radical or carbonium ion intermediates, offers a mechanistically rational basis for achieving decarbonylation with retention of stereochemistry.[32] However, sterically hindered aldehydes undergo the rate-determining oxidative addition to the rhodium center only with extreme difficulty,[33] and the likelihood of side reactions[34] under the forcing conditions anticipated dissuaded us from pursuing this approach. Although nonstereorational, the trialkylstannane-induced decarbonylation of phenyl seleno esters is an attractive alternative.[35] This method would not only provide the noralkane directly, but its compatability with olefin functionality[36] would allow us to ascertain the configuration of the resulting stereocenter through chemical correlation.

Scheme IV. Determination of the C20 Stereochemistry Resulting from Decarboxylation of the Acid 26a[a]



[a] (a) OsO_4, C_5H_5N; aqueous $NaHSO_3$, THF; (b) $NaIO_4$, H_2O, THF; (c) $NaBH_4$, EtOH; (d) 1% HCl, THF; (e) $NaIO_4$, H_2O, THF; (f) K_2CO_3, MeOH; (g) $(COCl_2)$, Me_2SO; Et_3N; (h) LAH, Et_2O.

Preparation of the required phenyl seleno ester **27b** provided an unexpected challenge. The failure of lithium hydroxide in refluxing aqueous THF to saponify the methyl ester of the acid **26b** had alerted us to the extraordinary steric hindrance to nucleophilic attack at the acyl carbon; not surprisingly, the carboxylic acid **26b** was utterly impregnable to reagents which mechanistically rely on the *intermolecular* delivery of a nucleophile for carbonyl activation or phenyl seleno ester formation.[37]

Conceptually, an *intramolecular* esterification process provides an elegant way out of this difficulty. Experimental realization of this concept in preparatively acceptable yield was tortuous but ultimately gratifying, as numerous standard as well as recent procedures were carefully explored before the following reaction sequence was developed.

The hypothesis that nucleophilic displacement at phosphorous proceeds though a pentacovalent oxyphosphorane *intermediate* has been a fruitful concept in the interpretation of the chemical

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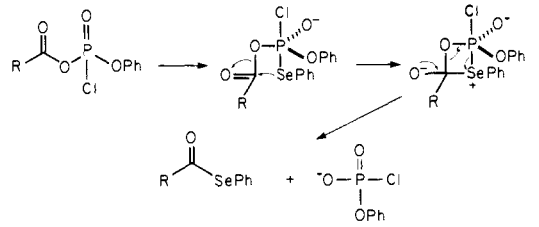
stereochemical behavior of organophosphorous compounds.[38,39] We speculated that such an intermediate might have a lifetime of sufficient duration to allow for an *intramolecular* condensation between phenyl selenide and carboxylate ligands (see below).



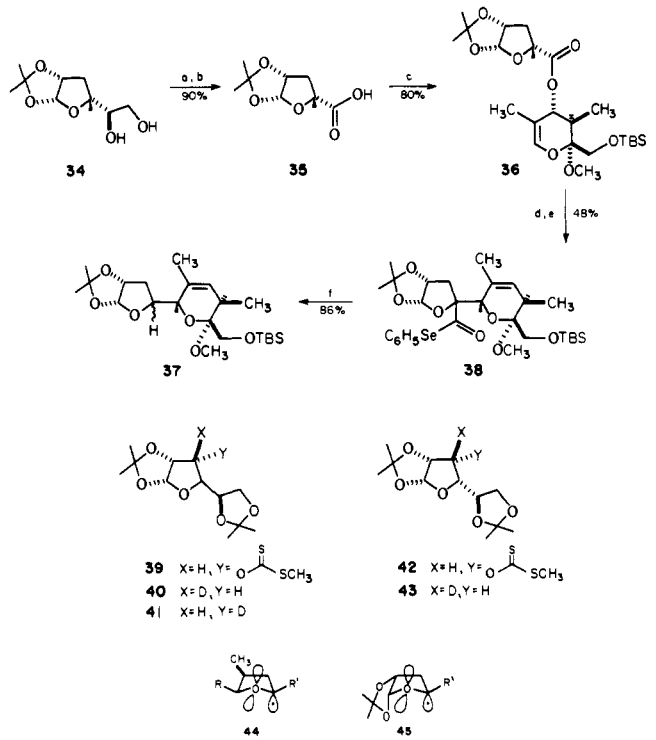
Since alkyl phenylselenyl halophosphates have not been characterized,[40] we elected to add selenophenol to the mixed anhydride between the carboxylic acid **26b** and an alkyl dihalophosphate. In the event, treatment of the triethylamine salt of the acid with phenyl dichlorophosphate[41] in THF at 0 °C for 30 min, followed by the addition of excess triethylamine and selenophenol, produced within minutes an 80% yield of the phenyl seleno ester **27b** and 12% recovered carboxylic acid. While we have no direct evidence for the intermediacy of an oxyphosphorane, this result stands in sharp contrast to the inefficacy of mixed anhydrides with relatively weak electrophilicity at phosphorous.[37]

Decarbonylation of the phenyl seleno ester with tri-*n*-butyltin hydride and a trace of AIBN[35] in refluxing benzene afforded the noralkane **28b** in 74% yield. Intriguingly, 500-MHz NMR indicated that a single C20[28] epimer had been obtained. Since the results of the X-ray crystal structure had demoted this work to model status, we were content to demonstrate the chemical fitness of the decarboxylation methodology and postponed resolution of the stereochemical issue until the correct C16[28] epimer **26a** was in hand.

Reinvestigation of the Claisen rearrangement of the model ester **25b** revealed that the modest yield was due in part to C-silylation of the ester enolate. Enolization by potassium hexamethyldisilazide and trapping with TBSCl eliminated this problem, and use of this reagent combination to generate the silyl ketene acetal of the ester **25a** provided, after thermal rearrangement at room temperature for 48 h, a 5:1 mixture of diastereomeric Claisen products in 65% yield.[42] The mixed chlorophosphate anhydride method again met our expectations, and the resulting phenyl seleno esters were separated by chromatography and individually decarbonylated: significantly, each gave an identical 5:1 mixture of inseparable noralkane epimers. The stereochemical outcome of this process was determined by chemical degradation as outlined in Scheme IV.

Cleavage of the E ring gave a mixture of the diols **29**, and the two major components were separated by chromatography and individually hydrolyzed to the diols **30**. Periodate cleavage of these intermediates would give either aldehyde **31** or **32**. Samples of these epimers were prepared from the alcohol **33**.[27] Reduction of the aldehyde **31** gave back the starting alcohol, and equilibration with potassium carbonate in methanol produced the epimeric aldehyde **32**. In the event, periodate cleavage of the diols **30** gave in each case a product identical with aldehyde **31** and distinct from aldehyde **32** as judged by direct comparison by TLC and 500-MHz NMR. Therefore, the stereochemistry at C20[28] was predominantly incorrect.

Scheme V. Model Study of Decarboxylation Stereochemistry[a]



[a] (a) $NaIO_4$, H_2O; (b) $AgNO_3$, KOH, H_2O, EtOH; (c) $(Ph_3)P$, CCl_4, CH_2Cl_2; **22**, DMAP, CH_2Cl_2; (d) $KN(TMS)_2$, TBSCl, THF; 1 N LiOH; (e) $PhOP(O)Cl_2$, C_6H_5SeH, Et_3N, THF; (f) $(n\text{-}Bu)_3SnH$, AIBN, C_6H_6.

Since the intermediate alkoxy radical generated by decarbonylation is pyramidal and inverting rapidly,[43] the product distribution is controlled, according to the Curtin–Hammett principle,[44] only by the difference between the total free energy of activation for each pathway. It appeared to us that steric interactions between the tri-*n*-butylstannane and the *cis*-alkyl substituents on the tetrahydrofuranyl radical might produce the energy difference decisive against the desired stereoisomer. To test this hypothesis, we prepared the phenyl seleno ester **38** via the known diol **34**[45] and the glycal **22** as outlined in Scheme V.

The steric bias of the bicyclic 1,2-*O*-isopropylidenefuranose system had been amply demonstrated.[46] In the specific case of free radical reactions, treatment of the dithiocarbonate **39** with tri-*n*-butyltin deuteride gave an 85:15 mixture of the deoxy isomers **40** and **41**. Similar treatment of the dithiocarbonate **42** gave only the deoxyfuranose **43** from exclusive exo attack.[47] Thus, if steric effects are indeed decisive in the stereochemical outcome of hydrogen abstraction by tetrahydrofuran-2-yl radicals, the *all-cis*-tetrahydrofuran **37** should predominate in the decarbonylation of phenyl seleno ester **38**. In fact, we obtained **37** as a 1:1 mixture.

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Considering the previous results, the relatively high proportion of hydrogen abstraction by the endo radical is surprising. This outcome can be explained by considering the contribution of a stereoelectronic effect to the total free energy of activation.

Both theoretical and experimental studies have demonstrated that carbon-centered radicals whose orbitals are antiperiplanar to a nonbonded electron pair on an α-oxygen are significantly stabilized by conjugative delocalization.[43,48] The stereoelectronic preference for axial bond formation and cleavage at such centers is a manifestation of this stabilization.[49] Since the activation enthalpy for hydrogen abstraction is rather insensitive to radical stability,[50] differences in the total free energy of activation will arise from the usual conformational factors, stereoelectronic effects, and steric interactions with the reagent. A pseudoequatorial exocyclic side chain and a pseudoaxial C1–O bond are important stabilizing factors in furanosides.[51] In conformer **45** the radical is also quasi-axial, and this stereoelectronic stabilization apparently compensates for steric interactions with the trialkylstannane; the total free energy of activation is therefore competitive with that for unhindered hydrogen abstraction by the exo radical.[52] Reconsidering the decarboxylation of ester **27a**, we see that radical **44** enjoys a pseudoequatorial disposition of its most bulky substituents, a pseudoaxial radical, and unhindered access to hydrogen abstraction. Since no other conformer meets all these criteria, the *all-cis*-tetrahydrofuran predominates. We are currently exploring new avenues to reverse this stereochemical outcome.

Experimental Section

Melting points are uncorrected. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded at 90 MHz except where designated "500 MHz". Data are reported as follows: chemical shift (multiplicity, integrated intensity, coupling constants, assignment). Optical rotations were measured in 1-dm cells of 1-mL capacity; chloroform, when used as a solvent for optical rotations, was filtered through neutral alumina (Activity I) immediately prior to use. Reaction solvents and liquid reagents were purified by distillation or drying shortly before use. Reactions were run under an argon atmosphere arranged with a mercury bubbler so that the system could be alternately evacuated and filled with argon and left under a positive pressure. Reported temperatures were measured externally. Syringes and reaction flasks were dried at least 12 h in an oven (120–140 °C) and cooled in a dessicator over anhydrous $CaSO_4$ prior to use. If feasible, reaction flasks were also flame-dried in vacuo.

2,3-*O*-(1-Methylethylidene)-2-*C*-methyl-5-chloro-D-deoxyribono-1,4-lactone (7). To a stirred solution of 0.28 mL (3.2 mmol) of oxalyl chloride in 10 mL of dichloromethane at 0 °C was added, dropwise over 3 min, 0.26 mL (3.3 mmol) of *N*,*N*-dimethylformamide. The resulting white suspension was allowed to warm to room temperature and after 10 min was recooled to 0 °C and 606 mg (3.0 mmol) of crystalline 2-methyl-2,3-*O*-(1-methylethylidene)-D-ribonic acid γ-lactone was then added in one portion. The resulting solution was heated at reflux for 4.5 h and then cooled to room temperature, poured into 75 mL of saturated aqueous NaCl, and then extracted with two 150-mL portions of ether. The organic extracts were combined and dried ($MgSO_4$). Removal of the solvent under reduced pressure and chromatography of the residue on 50 g of silica gel with 4:6 ether/petroleum ether afforded 660 mg (100%) of the lactone as a white, crystalline solid: mp 78–79 °C; R_f = 0.18 (silica gel, 3:7 ether/petroleum ether); evaporative distillation 70–75 °C (0.001 mmHg); $[\alpha]^{23}_D$ −41.9° (*c* 1.51, $CHCl_3$); IR ($CHCl_3$) 3000, 2940, 1785, 1450, 1375, 1350, 1100, 1000 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.43 (s, 6 H, CH_3), 1.65 (s, 3 H, CH_3), 3.50–3.87 (m, 2 H, CH_2Cl), 4.47 (s, 1 H, C(3)–H), 4.70 (m, 1 H, C(4)–H). Anal. Calcd for $C_9H_{13}O_4$: C, 48.99; H, 5.94. Found: C, 49.09; H, 5.99.

2(*S*)-Methyl-2,3(*R*)-(dimethylmethylenedioxy)-*n*-pentane-1,4(*R*)-diol. To a stirred solution of 58.7 g (0.266 mol) of the lactone **7** in 1.0 L of ether cooled to 0 °C was added, cautiously in several portions, 12.1 g (0.32 mol) of lithium tetrahydridoaluminate. Cooling was then discontinued, and the resulting mixture was stirred at room temperature for 7 h and then recooled to 0 °C and sequentially treated with 12.1 mL of water, 12.1 mL of 15% aqueous sodium hydroxide, 36.3 mL of water, and then 20 g of $MgSO_4$. Filtration and evaporation of the solvent at reduced pressure afforded 50.8 g (100%) of the diol as a white solid, mp 103–104 °C (lit.[9] mp 103–104 °C). Chromatography of a portion of this solid on silica gel with 8:2 ether/petroleum ether provided the analytical sample: mp 105–105.5 °C; R_f = 0.22 (silica gel, 8:2 ether/petroleum ether); $[\alpha]^{23}_D$ −36.1° (*c* 1.56, $CHCl_3$) [lit.[9] $[\alpha]_D$ −36° (*c* 1.0, $CHCl_3$)]; IR ($CHCl_3$) 3495, 3000, 2950, 1385, 1375, 1245, 1100, 1055 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.33 (d, 3 H, *J* = 7 Hz, CH_3CH), 1.37 (s, 6 H, $2CH_3C$), 1.43 (s, 3 H, CH_3C), 3.1–4.2 (m, 6 H). Anal. Calcd for $C_9H_{18}O_4$: C, 56.82; H, 9.54. Found: C, 56.85; H, 9.62.

5-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-4(*S*)-methyl-3(*R*),4-(dimethylmethylenedioxy)-*n*-pentan-2(*R*)-ol (8). To a stirred solution of 50.8 g (0.266 mol) of the above diol in 530 mL of dichloromethane were added 86 mL (1.06 ol) of pyridine and then 48.1 g (0.319 mol) of *tert*-butyldimethylchlorosilane. After 36 h at room temperature, the reaction mixture was diluted with 1.5 L of ether and washed with 500 mL of water, two 500-mL portions of saturated aqueous NaCl, and then dried ($MgSO_4$). Removal of the solvent under reduced pressure and chromatography of the residue on 500 g of silica gel with 2:8 ether/petroleum ether afforded 76.9 g (95%) of the alcohol **8** as a colorless oil: R_f = 0.35 (silica gel, 2:8 ether/petroleum ether); evaporative distillation 85–90 °C (0.005 mmHg); $[\alpha]^{22}_D$ −19.7° (*c* 1.11, $CHCl_3$); IR ($CHCl_3$) 3450, 3000, 2960, 2940, 2875, 1470, 1385, 1375, 1250, 1100, 1075, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.13 (s, 6 H, $(CH_3)_2Si$), 0.92 (s, 9 H, $(CH_3)_3C$), 1.30 (d, 3 H, *J* = 7 Hz, CH_3CH), 1.35 (s, 6 H, $2CH_3C$), 1.40 (s, 3 H, CH_3C), 3.18–4.06 (m, 5 H). Anal. Calcd for $C_{15}H_{32}O_4Si$: C, 59.17; H, 10.59. Found: C, 59.30; H, 10.58.

5-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-4(*S*)-methyl-3(*R*),4-(dimethylmethylenedioxy)-*n*-pentan-2-one. To a stirred solution of 6.13 g (20.1 mmol) of the above alcohol **8** in 11.9 mL of dimethyl sulfoxide and 11.9 mL of benzene at 0 °C were added 0.84 mL (10.1 mmol) of dichloroacetic acid and then, dropwise over 5 min, 6.33 mL (40.4 mmol) of diisopropylcarbodiimide. Cooling was discontinued, and the resulting mixture was stirred for 1.5 h at room temperature. The solution was then diluted with 900 mL of ether, washed with 500 mL of 2% aqueous H_2SO_4 acid, 500 mL of 2% aqueous NaOH, and 500 mL of saturated aqueous NaCl, and then dried ($MgSO_4$). The solvent was evaporated under reduced pressure and to the residue was added 200 mL of petroleum ether. The undissolved urea was removed by filtration. Evaporation of the solvent and flash chromatography of the residue on 250 g of silica gel with 1:9 ether/petroleum ether afforded 5.72 g (94%) of the ketone as a colorless oil: R_f = 0.35 (silica gel, 2:8 ether/petroleum ether); evaporative distillation 75–80 °C (0.005 mmHg); $[\alpha]^{24}_D$ −39.3° (*c* 1.47, $CHCl_3$); IR ($CHCl_3$) 3000, 2860, 1725, 1710, 1475, 1465, 1380, 1375, 1100, 1000, 925 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.03 (s, 6 H, $(CH_3)_2Si$), 0.87 (s, 9 H, $(CH_3)_3C$), 1.37 (s, 3 H, CH_3C), 1.40 (s, 3 H, CH_3C), 1.50 (s, 3 H, CH_3C), 2.26 (s, 3 H, $CH_3C(O)$), 3.33 (d, 1 H, *J* = 11 Hz, $CCHHO$), 3.55 (s, 1 H, *J* = 11 Hz, $CCHHO$), 4.17 (s, 1 H, $CCHC(O)$). Anal. Calcd for $C_{15}H_{30}O_4Si$: C, 59.56; H, 10.00. Found: C, 59.58; H, 10.05.

5-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-4(*S*)-methyl-3(*R*),4-(dimethylmethylenedioxy)-2-methyl-*n*-pent-1-ene (9). To a stirred suspension of 2.43 g (6.81 mmol) of methyltriphenylphosphonium bromide in 20 mL of THF at 0 °C was added dropwise 4.00 mL (6.24 mmol) of a 1.56 M solution of *n*-butyllithium in hexane. Cooling was then discontinued, and the reaction mixture was stirred at room temperature for 30 min and then cooled to −78 °C. A solution of 1.72 g (5.68 mmol) of the above ketone in 8 mL of THF was added over 5 min, and the reaction was then allowed to warm to room temperature. After 50 min, the reaction mixture was cooled to −78 °C, treated with 5 mL of saturated aqueous $NaHCO_3$, allowed to warm to room temperature, poured into 150 mL of saturated aqueous NaCl, and then extracted with three 200-mL portions of petroleum ether. The combined organic extracts were dried ($MgSO_4$) and then evaporated under reduced pressure. Chromatography of the residue on 100 g of silica gel with 1:9 ether/petroleum ether afforded 1.64 g (96%) of the olefin as an oil: R_f = 0.66 (silica gel, 3:7 ether/petroleum ether); evaporative distillation 75–80 °C (0.005 mmHg); $[\alpha]^{23}_D$ −29.5° (*c* 1.84, $CHCl_3$); IR ($CHCl_3$) 3000, 2870, 1465, 1385, 1375, 1250, 1100, 1000, 850 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.03 (s,

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6 H, $(CH_3)_2Si$), 0.88 (s, 9 H, $(CH_3)_3C$), 1.38 (s, 6 H, $2CH_3C$), 1.43 (s, 3 H, CH_3C), 1.80 (s, 3 H, $CH_3C{=}C$), 3.21 (d, 1 H, J = 10 Hz, CC*H*HO), 3.52 (d, 1 H, J = 10 Hz, CCH*H*O), 4.20 (s, 1 H, CCHC=C), 4.88 (br s, 1 H, C=C*H*H), 5.18 (br s, 1 H, C=CH*H*). Anal. Calcd for $C_{16}H_{32}O_3Si$: C, 63.95; H, 10.73. Found: C, 63.81; H, 10.72.

5-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-4(*S*)-methyl-3(*R*),4-(dimethylmethylenedioxy)-2(*R*)- and 2(*S*)-*n*-pentan-1-ol (10 and 11). To a stirred solution of 440 mg (1.46 mmol) of the olefin 9 in 10 mL of THF at 0 °C was added over 1 min 4.4 mL (4.40 mmol) of a 1.0 M solution of BH_3 in THF. After 1.5 h at 0 °C, the reaction mixture was cautiously treated with 1.5 mL of 3 M aqueous NaOH and then allowed to warm to room temperature. When there was no further evidence of H_2 evolution (ca. 15 min), 1.1 mL of 30% aqueous H_2O_2 was added, and the resulting mixture was heated in an oil bath at 50 °C. After 1 h, the solution was allowed to cool, poured into 75 mL of saturated aqueous NaCl, and then extracted with two 150-mL portions of ether. The combined organic extracts were dried ($MgSO_4$), and the solvent was then evaporated under reduced pressure. ^1H NMR of the crude residue indicated the presence of a 2.0:1.0 mixture of diastereomeric alcohols **10** and **11**. Chromatography of this residue on 30 g of silica gel with 35:65 ether/petroleum ether afforded as a colorless oil 420 mg (90%) of the unseparated alcohols: R_f (major diastereomer) = 0.32 (silica gel, 4:6 ether/petroleum ether); R_f (minor diastereomer) = 0.29 (silica gel, 4:6 ether/petroleum ether); evaporative distillation 95–100 °C (0.005 mmHg); IR ($CHCl_3$) 3530, 3400, 2990, 2860, 1470, 1460, 1380, 1370, 1250, 1080 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.08 (s, 6 H, $(CH_3)_2Si$), 0.90 (s, 9 H, $(CH_3)_3C$), 0.93 (d, "1 H", J = 7 Hz, CHCH_3, minor diastereomer), 1.09 (d, "2 H", J = 7 Hz, CHCH_3, major diastereomer), 1.33, 1.37 (2 s, 9 H, $3CH_3C$), 1.85–2.25 (br m, 1 H, CH_3CH). Anal. Calcd for $C_{16}H_{34}O_4Si$: C, 60.33; H, 10.76. Found: C, 60.38; H, 10.77.

5-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-4(*S*)-methyl-3(*R*),4-(dimethylmethylenedioxy)-2(*R*)- and 2(*S*)-methyl-*n*-pentan-1-al (12 and 13). To a stirred solution of 1.01 mL (11.6 mmol) of oxalyl chloride in 60 mL of dichloromethane at −78 °C was added over 5 min a solution of 0.97 mL (13.7 mmol) of dimethyl sulfoxide in 5 mL of dichloromethane. After 15 min, a solution of 3.35 g (10.5 mmol) of a 2:1 mixture of alcohols **10** and **11** in 20 mL of dichloromethane was added over 10 min to the reaction mixture. After 20 min at −78 °C, the reaction mixture was treated with 7.3 mL (53 mmol) of triethylamine, allowed to warm to room temperature, and then poured into 100 mL of saturated aqueous NaCl. This mixture was extracted with two 200-mL portions of ether, and the combined organic extracts were dried ($MgSO_4$). Evaporation of the solvent under reduced pressure and chromatography of the residue on 300 g of silica gel with 20:280 ether/petroleum ether afforded first 2.12 g (64%) of the aldehyde **12** as a colorless oil: R_f = 0.24 (silica gel, 20:280 ether/petroleum ether); evaporative distillation 65–70 °C (0.001 mmHg); IR ($CHCl_3$) 3000, 2940, 1725, 1470, 1385, 1375, 1255, 1090 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.07 (s, 6 H, $(CH_3)_2Si$), 0.89 (s, 9 H, $(CH_3)_3C$), 1.22 (d, 3 H, J = 7 Hz, CH_3CH), 1.30 (s, 3 H, CH_3C), 1.37 (s, 6 H, 2 CH_3C), 2.73–3.13 (m, 1 H, CH_3CH), 3.21 (d, 1 H, J = 10 Hz, CC*H*HO), 3.65 (d, 1 H, J = 10 Hz, CCH*H*O), 4.02 (d, 1 H, J = 10 Hz, CC*H*CH), 9.70 (d, 1 H, J = 1.5 Hz, CHO). Anal. Calcd for $C_{16}H_{32}O_4Si$: C, 60.72; H, 10.19. Found: C, 60.46; H, 10.07.

There was then eluted 1.04 g (31%) of the aldehyde **13** as a colorless oil: R_f = 0.19 (silica gel, 20:280 ether/petroleum ether); evaporative distillation 65–70 °C (0.001 mmHg); IR ($CHCl_3$) 3000, 1725, 1470, 1385, 1375, 1255, 1090 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.07 (s, 6 H, $(CH_3)_2Si$), 0.90 (s, 9 H, $(CH_3)_3C$), 1.15 (d, 3 H, J = 7 Hz, CH_3CH), 1.33 (s, 3 H, CH_3C), 1.36 (s, 6 H, 2 CH_3C), 2.68–3.00 (m, 1 H, CH_3CH), 3.27 (d, 1 H, J = 11 Hz, CC*H*HO), 3.76 (d, 1 H, J = 11 Hz, CCH*H*O), 3.81 (d, 1 H, J = 10 Hz, CC*H*CH), 9.75 (d, 1 H, J = 3 Hz, CHO). Anal. (2:1 mixture of **12** and **13**) Calcd for $C_{16}H_{32}O_4Si$: C, 60.72; H, 10.19. Found: C, 60.46; H, 10.07.

Recycling of the Aldehyde 13. To a stirred solution of 1.04 g (3.28 mmol) of the aldehyde **13** in 20 mL of petroleum ether and 1 mL of ether was added 9.4 g of silica gel, and the resulting slurry was stirred under argon until TLC indicated that a 1:1 mixture of aldehydes **12** and **13** had been produced (ca. 36 h). The mixture was then filtered, and the silica gel was thoroughly rinsed with ether. Evaporation of the solvent and chromatography of the residue on 150 g of silica gel with 20:280 ether/petroleum ether afforded 0.48 g of the aldehyde **12**. Repetition of the above process on the recovered aldehyde **13** afforded an additional 0.22 g of the aldehyde **12**, thus constituting an 85% overall yield from the alcohols **10** and **11**.

6-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-5(*S*)-methyl-4(*R*),5-(dimethylmethylenedioxy)-3(*S*)-methyl-1-(benzyloxy)-*n*-hexan-2(*R*)- and -2(*S*)-ol. To a stirred solution of 3.27 g (9.04 mmol) of (benzyloxymethyl)tributylstannane in 55 mL of THF at −78 °C was added 5.35 mL (8.34 mmol) of a 1.56 M solution of *n*-butyllithium in hexane. After 5 min, a solution of 2.20 g (6.95 mmol) of the aldehyde **12** in 9 mL of THF was added over 6 min. The resulting mixture was stirred 55 min at −78 °C and then treated with 5 mL of saturated aqueous NH_4Cl. The solution was poured into 100 mL of saturated aqueous NaCl and extracted with two 250-mL portions of ether. The combined organic extracts were dried ($MgSO_4$), and the solvent was then evaporated under reduced pressure. Flash chromatography of the residue on 200 g of silica gel with 35:65 ether/petroleum ether afforded 3.01 g (98%) of an unseparated 1.4:1 mixture of the alcohols as a colorless oil: R_f = 0.32 (silica gel, 4:6 ether/petroleum ether); evaporative distillation 145–150 °C (0.005 mmHg); IR ($CHCl_3$) 3580, 2990, 2860, 1465, 1460, 1450, 1380, 1370, 1250, 1085 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.03 (s, 6 H, $(CH_3)_2Si$), 0.87 (s, 9 H, $(CH_3)_3C$), 0.98 (d, "1.25 H", J = 7 Hz, CH_3CH), 1.00 (d, "1.75 H", J = 7 Hz, CH_3CH), 1.30, 1.37 (2 s, 9 H, 3 CH_3C), 4.47, 4.49 (2 s, 2 H, $C_6H_5CH_2$), 7.29 (s, 5 H, C_6H_5). Anal. Calcd for $C_{24}H_{42}O_5Si$: C, 65.71; H, 9.65. Found: C, 65.66; H, 9.60.

2(*S*)-Methyl-2,3(*R*)-(dimethylmethylenedioxy)-4(*S*)-methyl-5(*R*)- and -5(*S*)-hydroxy-6-(benzyloxy)-*n*-hexan-1-ol (14). To a stirred solution of 3.01 g (6.86 mmol) of the above alcohol in 20 mL of THF at room temperature was added 8.0 mL (8.0 mmol) of a 1 M solution of tetra-*n*-butylammonium fluoride in THF. After 20 min, the reaction mixture was poured into 100 mL of 50% saturated aqueous NaCl and extracted with three 100-mL portions of ether. The combined organic extracts were dried ($MgSO_4$), and the solvent was evaporated at reduced pressure. Chromatography of the residue on 200 g of silica gel with 8:2 ether/petroleum ether afforded first 751 mg of a single epimer of the alcohol **14**: R_f = 0.22 (silica gel, 8:2 ether/petroleum ether); evaporative distillation 145–150 °C (0.005 mmHg); $[\alpha]^{23}_D$ −1.7° (c 0.56, $CHCl_3$); IR ($CHCl_3$) 3570, 3450, 2980, 1450, 1375, 1365, 1230, 1100, 900 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.07 (d, 3 H, J = 7 Hz, CH_3CH), 1.40 (s, 6 H, $2CH_3C$), 1.46 (s, 3 H, CH_3C), 3.98 (d, 1 H, J = 8 Hz, CC*H*CH), 4.57 (s, 2 H, $C_6H_5CH_2$), 7.37 (s, 5 H, C_6H_5). Anal. Calcd for $C_{18}H_{28}O_5$: C, 66.64; H, 8.70. Found: C, 66.76; H, 8.72.

There were then eluted 736 mg of mixed fractions and then 743 mg of a single epimer of the alcohol **14**: R_f = 0.14 (silica gel, 8:2 ether/petroleum ether); evaporative distillation 145–150 °C (0.005 mmHg); $[\alpha]^{23}_D$ −15° (c 0.52, $CHCl_3$); IR ($CHCl_3$) 3570, 3430, 2990, 1450, 1375, 1365, 1100, 1030, 925 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.97 (d, 3 H, J = 7 Hz, CH_3CH), 1.37 (s, 6 H, $2CH_3C$), 1.43 (s, 3 H, CH_3C), 3.83 (d, 1 H, J = 7 Hz, CC*H*CH), 4.56 (s, 2 H, $C_6H_5CH_2$), 7.33 (s, 5 H, C_6H_5). Anal. Calcd for $C_{18}H_{28}O_5$: C, 66.64; H, 8.70. Found: C, 66.68; H, 8.78. Total yield of diols **14**: 2.23 g (100%).

2-(Allyloxy)-3(*R*)-methyl-3,4(*R*)-(dimethylmethylenedioxy)-5(*R*)-methyl-6(*R*)- and -6(*S*)-(allyloxy)-6-[(benzyloxy)methyl]tetrahydropyran (15). To a stirred solution of 0.32 mL (3.7 mmol) of oxalyl chloride in 10 mL of dichloromethane at −78 °C was added a solution of 0.28 mL (3.9 mmol) of dimethyl sulfoxide in 4 mL of dichloromethane. After 10 min, a solution of 573 mg (1.76 mmol) of the alcohols **14** in 4 mL of dichloromethane was added to the reaction mixture. After 25 min, the reaction mixture was treated with 1.97 mL (14.1 mmol) of triethylamine, allowed to warm to room temperature, and then poured into 100 mL of saturated aqueous NaCl. The resulting mixture was extracted with two 150-mL portions of ether, dried ($MgSO_4$), and then evaporated under reduced pressure and then further dried under high vacuum for 30 min to afford 565 mg of an oil. To a stirred solution of this material in 5 mL of allyl alcohol and 0.5 mL of a mixture of 2,2-(diallyloxy)propane and 2-(allyloxy)propene (see below) was added 42 mg (0.22 mmol) of *p*-toluenesulfonic acid monohydrate. After 95 min at room temperature, 0.5 mL (3.6 mmol) of triethylamine was added, and then the reaction was evaporated under reduced pressure. Chromatography of the residue on 60 g of silica gel with 2:8 ether/petroleum ether afforded 599 mg (81%) of an oil consisting of a 1:1 mixture of the allyl ketals **15** epimeric at C5: R_f = 0.32, 0.36 (silica gel, 2:8 ether/petroleum ether); evaporative distillation 140–150 °C (0.005 mmHg); IR ($CHCl_3$) 3000, 1450, 1380, 1225, 1110, 995 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.15 (d, "1.5 H", J = 7 Hz, CH_3CH), 1.17 (d, "1.5 H", J = 7 Hz, CH_3CH), 1.37, 1.40, 1.43 (3 s, 9 H, 3 CH_3C), 3.52 (s, "1 H", CCH_2O), 3.57 (s, "1 H", CCH_2O), 4.73 (s, "0.5 H", OCHO), 4.87 (s, "0.5 H", OCHO), 7.33 (s, 5 H, C_6H_5). Anal. Calcd for $C_{24}H_{34}O_6$: C, 68.88; H, 8.18. Found: C, 68.87; H, 8.16.

2,2-(Diallyloxy)propane and 2-(Allyloxy)propene. To a solution of 50 mL (0.41 mol) of dimethoxypropane and 58 mL (0.85 mol) of allyl alcohol was added 250 mg (1 mmol) of pyridinium *p*-toluenesulfonate, the resulting mixture was heated in an oil bath at 110 °C, and methanol was distilled off through a Vigreaux column at 65–70 °C. After 5 h, the oil bath was allowed to cool to 60 °C, and the pressure was gradually reduced to 75 mmHg. The material (25 mL) which distilled between 50 and 55 °C at this pressure consisted of a ca. 1:2 mixture of 2,2-(diallyloxy)propane and 2-(allyloxy)propene and some allyl alcohol. No methanol or methyl ethers were present: IR ($CHCl_3$) 3620, 3480, 3000, 1655, 1610, 1380, 1275, 995 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.32 (s, $(CH_3)_2C$), 1.77 (s, $CH_3C{=}C$).

2-(Allyloxy)-3(*R*)-methyl-3,4(*R*)-(dimethylmethylenedioxy)-5(*R*)-methyl-6(*R*)- and -6(*S*)-methoxy-6-[(benzyloxy)methyl]tetrahydropyran (16 and 17). To a stirred solution of 683 mg (1.63 mmol) of the ketals **15** in 25 mL of dry methanol was added 50 mg (0.2 mmol) of pyridinium *p*-toluenesulfonate, and the mixture was then heated 5 h at 45 °C. The reaction was allowed to cool and then concentrated under reduced pressure. Chromatography of the residue on 50 g of silica gel with 1:9 ether/petroleum ether afforded first 296 mg of the methyl ketal **17** as a colorless oil: R_f = 0.22 (silica gel, 2:8 ether/petroleum ether); evaporative distillation 160–165 °C (0.01 mmHg); $[\alpha]^{22}_D$ −2.7° (*c* 1.06, $CHCl_3$); IR ($CHCl_3$) 2990, 1455, 1380, 1370, 1260, 925, 870 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.07 (d, 3 H, *J* = 6 Hz, CH_3CH), 1.33 (s, 9 H, 3 CH_3C), 2.10–2.47 (m, 1 H, CH_3CH), 3.20 (s, 3 H, OCH_3), 3.50 (s, 2 H, CCH_2O), 3.82 (d, 1 H, *J* = 9 Hz, $CCHCH$), 4.53 (s, 2 H, $C_6H_5CH_2$), 4.70 (s, 1 H, OCHO), 7.33 (s, 5 H, C_6H_5). Anal. Calcd for $C_{22}H_{32}O_6$: C, 67.32; H, 8.22. Found: C, 67.42; H, 8.19.

There was then eluted 304 mg of the methyl ketal **16** as a colorless oil: R_f = 0.16 (silica gel, 2:8 ether/petroleum ether); evaporative distillation 160–165 °C (0.01 mmHg); $[\alpha]^{22}_D$ −55.1° (*c* 0.88, $CHCl_3$); IR ($CHCl_3$) 2990, 1450, 1380, 1370, 940, 870 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17 (d, 3 H, *J* = 6 Hz, CH_3CH), 1.37 (s, 3 H, CH_3C), 1.43 (s, 6 H, $2CH_3C$), 2.00–2.33 (m, 1 H, CH_3CH), 3.33 (s, 3 H, OCH_3), 3.53 (s, 2 H, CCH_2O), 3.90 (d, 1 H, *J* = 9 Hz, $CCHCH$), 4.90 (s, 1 H, OCHO), 7.33 (s, 5 H, C_6H_5). Anal. Calcd for $C_{22}H_{32}O_6$: C, 67.32; H, 8.22. Found: C, 67.08; H, 8.13. Three recycles of the methyl ketal **17** in a manner similar to that described above provided 234 mg of additional methyl ketal **16** representing a total yield of 85%.

2-(1-Oxy-*cis*-propenyl)-3(*R*)-methyl-3,4(*R*)-(dimethylmethylenedioxy)-5(*R*)-methyl-6(*S*)-methoxy-6-[(benzyloxy)methyl]tetrahydropyran. To a stirred solution of 282 mg (0.718 mmol) of the allyl ether **16** in 2.0 mL of Me_2SO was added in one portion 81 mg (0.72 mmol) of potassium *tert*-butoxide, and the resulting mixture was immediately immersed in an oil bath preheated to 80 °C. After 20 min, the dark solution was allowed to cool, poured into 75 mL of brine, and then extracted with two 100-mL portions of ether. The combined organic extracts were dried ($MgSO_4$), and the solvent was evaporated at reduced pressure. Chromatography of the residue on 30 g of silica gel with 1:9 ether/petroleum ether afforded 269 mg (95%) of the *cis*-propenyl ether as a colorless oil: R_f = 0.29 (silica gel, 1:9 ether/petroleum ether); evaporative distillation 170 °C (0.01 mmHg); $[\alpha]^{22}_D$ −37.6° (*c* 1.24, $CHCl_3$); IR ($CHCl_3$) 3000, 2940, 1670, 1450, 1380, 1370, 1010, 870 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.18 (d, 3 H, *J* = 7 Hz, CH_3CH), 1.47 (s, 9 H, $3CH_3C$), 1.67 (dd, 3 H, *J* = 7, *J'* = 2 Hz, $CH_3CH{=}CH$), 2.00–2.37 (m, 1 H, CH_3CH), 3.33 (s, 3 H, OCH_3), 3.53 (s, 2 H, CCH_2O), 5.00 (s, 1 H, OCHO), 7.33 (s, 5 H, C_6H_5). Anal. Calcd for $C_{22}H_{32}O_6$: C, 67.32; H, 8.22. Found: C, 67.22; H, 8.11.

2-(1-Oxy-*cis*-propenyl)-3(*R*)-methyl-3,4(*R*)-(dimethylmethylenedioxy)-5(*R*)-methyl-6(*S*)-methoxy-6-[([(1,1-dimethylethyl)dimethylsilyl]oxy)methyl]tetrahydropyran (18). To a stirred solution of 42 mg (6.1 mmol) of lithium in 30 mL of anhydrous liquid ammonia at −78 °C was added a solution of 257 mg (0.655 mmol) of the above benzyl ether in 3.5 mL of THF over 5 min. After an additional 10 min, 530 mg (10 mmol) of dry NH_4Cl was cautiously added, and the resulting colorless mixture was diluted with 50 mL of ether and allowed to evaporate. The resulting ethereal suspension was treated briefly with $MgSO_4$, filtered, and then concentrated under reduced pressure. The residue was dried under high vacuum for 1 h, dissolved in 2.2 mL of dichloromethane, and cooled to −30 °C. To the resulting, stirred solution were added 0.15 mL (1.31 mmol) of dry 2,6-lutidine and then 0.22 mL (0.98 mmol) of nearly colorless *tert*-butyl(dimethylsilyl) triflate. After 40 min, 0.5 mL of saturated aqueous $NaHCO_3$ was added and the reaction mixture poured into 50 mL of saturated aqueous $NaHCO_3$ and then extracted with two 75-mL portions of ether. The combined organic extracts were dried ($MgSO_4$), and the solvent was then evaporated under reduced pressure. Chromatography of the residue on 30 g of silica gel with 1:9 ether/petroleum ether afforded 248 mg (91%) of the silyl ether **18** as a colorless oil: R_f = 0.29 (silica gel, 1:9 ether/petroleum ether); evaporative distillation 120–130 °C (0.005 mmHg); $[\alpha]^{22}_D$ −36.6° (*c* 1.00, $CHCl_3$); IR ($CHCl_3$) 3990, 2860, 1670, 1460, 1380, 1250, 970, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.10 (s, 6 H, $(CH_3)_2Si$), 0.93 (s, 9 H, $(CH_3)C$), 1.20 (d, 3 H, *J* = 7 Hz, CH_3CH), 1.47 (s, 9 H, 3 CH_3C), 1.67 (dd, 3 H, *J* = 7, *J'* = 2 Hz, $CH_3CH{=}CH$), 2.20 (dq, 1 H, *J* = 8, *J'* = 7 Hz, CH_3CHCH), 3.33 (s, 3 H, OCH_3), 3.95 (d, 1 H, *J* = 8 Hz, $CCHCH$), 4.57 (dq, 1 H, *J* = 7, *J'* = 7 Hz, $CH_3CH{=}CH$), 5.00 (s, 1 H, OCHO), 6.11 (dq, 1 H, *J* = 7, *J'* = 2 Hz, $CH_3CH{=}CH$). Anal. Calcd for $C_{21}H_{40}O_6Si$: C, 60.54; H, 9.68. Found: C, 60.66; H, 9.53.

3(*R*)-Methyl-3,4(*R*)-(dimethylmethylenedioxy)-5(*R*)-methyl-6(*S*)-methoxy-6-[([(1,1-dimethylethyl)dimethylsilyl]oxy)methyl]tetrahydropyran-2-ol (19). To a stirred solution of 936 mg (2.25 mmol) of the *cis*-propenyl ether **18** in 49.3 mL of THF and 12.4 mL of water was added 1.07 g (3.37 mmol) of mercuric acetate. After 30 min at room temperature, the reaction mixture was poured into 300 mL of ether and then washed with 100 mL of saturated aqueous NaCl. The aqueous washing was extracted with 100 mL of ether, and the combined organic phases were dried briefly ($MgSO_4$). Evaporation of the solvent under reduced pressure and chromatography of the residue on 125 g of silica gel with 1:1 ether/petroleum ether afforded 805 mg (95%) of the lactol **19** as a homogeneous colorless oil. R_f = 0.23 (silica gel, 1:1 ether/petroleum ether); ^1H NMR ($CDCl_3$) δ 0.1 (s, 6 H, $(CH_3)_2Si$); 0.93 (s, 9 H, $(CH_3)_3C$), 1.17 (d, 3 H, *J* = 7 Hz, CH_3CH), 1.40 (s, 3 H, CH_3C), 1.45 (s, 6 H, $2CH_3C$), 3.0 (br s, 1 H, OH), 3.32 (s, 3 H, OCH_3), 3.93 (d, 1 H, *J* = 9 Hz), 5.13 (br s, 1 H, $HOCHO$).

3-Methyl-4(*R*)-hydroxy-4,5-dihydro-5(*R*)-methyl-6(*S*)-methoxy-6-[([(1,1-dimethylethyl)dimethylsilyl]oxy)methyl]pyran (22). To a stirred solution of 12.66 g (47.5 mmol) of 4,4′-di-*tert*-butylbiphenyl in 173 mL of THF was added under a blanket of argon 300 mg (43.2 mmol) of lithium wire cut into 15 pieces. Before addition, each piece was dipped briefly in methanol, rinsed in ether, squeezed with forceps, and then added to the THF solution while still wet with ether. After the solution turned deep blue-green (ca. 2 min), the solution was cooled to 0 °C and stirred for 6 h.

Then, to a stirred solution of 761 mg (2.02 mmol) of the lactol **19** and 0.23 mL (2.4 mmol) of CCl_4 in THF at −78 °C was added dropwise 0.39 mL (2.12 mmol) of distilled tris(dimethylamino)phosphine. After 20 min, the solution was allowed to warm to room temperature and then stirred an additional 30 min.

To 102 mL (25 mmol) of a stirred solution of lithium 4,4′-di-*tert*-butylbiphenyl at −78 °C was then added over 5 m the above solution of the pyranosyl chloride **20** in THF. After 10 min, 5 mL of water was added to the reaction mixture. The solution was allowed to warm to room temperature, poured into 300 mL of ether, and then washed with 100 mL of saturated aqueous NaCl. The solution was dried ($MgSO_4$) and then evaporated at reduced pressure. Chromatography of the residue on silica gel with 1:9 ether/petroleum ether afforded first recovered 4,4′-di-*tert*-butylbiphenyl and then 495 mg (81%) of the glycal **22** as a colorless oil: R_f = 0.15 (silica gel, 1:5 ether/petroleum ether); evaporative distillation 85–90 °C (0.001, mmHg); $[\alpha]^{23}_D$ +9.8° (*c* 0.52, $CHCl_3$); IR ($CHCl_3$) 3520, 2990, 2850, 1670, 1470, 1460, 1250, 1135, 1000, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.10 (s, 6 H, $(CH_3)_2Si$), 0.88 (d, 3 H, *J* = 7 Hz, CH_3CH), 0.95 (s, 9 H, $(CH_3)_3C$), 1.73 (d, 3 H, *J* = 1.5 Hz, $CH{=}CCH_3$), 2.45 (q, 1 H, *J* = 7 Hz), 3.23 (s, 3 H, OCH_3), 3.40 (s, 2 H, $CHOH$), 3.43 (d, 1 H, *J* = 11 Hz, $CCHHO$), 3.80 (d, 1 H, *J* = 11 Hz, $CCHHO$), 5.92 (d, 1 H, *J* = 1.5 Hz, $CH{=}CCH_3$). Anal. Calcd for $C_{15}H_{30}O_4Si$: C, 59.56; H, 10.00. Found: C, 59.79; H, 10.06.

2(*R*)-Ethyl-2-[5(*S*)-carboxy-3(*S*)-methyl-2(*R*)-tetrahydrofuryl]-3-(*R*),4(*S*)-(dimethylmethylenedioxy)-5(*S*)-(benzyloxy)tetrahydrofuran Ester with the Glycal 22 (25a). To a stirred solution of 392 mg (0.965 mmol) of the acid **24a** in 2.5 mL of dichloromethane and 2.5 mL of carbon tetrachloride was added 380 mg (1.44 mmol) of triphenylphosphine, and the resulting mixture was heated in an oil bath at 50 °C. After 2 h, an additional 105 mg (0.40 mmol) of triphenylphosphine was added, heating was continued for 20 min, and then the solution was cooled to 0 °C. To this solution were added a solution of 278 mg (0.919 mmol) of the glycal **22** and 337 mg (2.76 mmol) of 4-(dimethylamino)pyridine in 2.0 mL of dichloromethane. The resulting mixture was allowed to warm to room temperature, and after 20 min the reaction mixture was applied directly to a column of 40 g of alumina (Activity III). Elution with 2:8 ether/petroleum ether afforded 541 mg of the ester **25a** as a colorless oil: R_f = 0.20 (silica gel, 2:8 ether/petroleum ether); IR ($CHCl_3$), 2950, 1730, 1670, 1460, 1385, 1375, 1255, 1020, 910, 870, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.11 (s, 6 H, $(CH_3)_2Si$), 0.95 (s, 9 H, $(CH_3)C$), 1.17 (d, 3 H, CH_3CH), 1.38, 1.53 (2 s, 6 H, $(CH_3)_2C$), 1.65 (s, 3 H, $CH_3C{=}CH$), 3.25 (s, 3 H, OCH_3), 3.48 (d, 1 H, *J* = 12 Hz, $CCHHO$), 3.85 (d, 1 H, *J* = 12 Hz, $CCHHO$), 3.93 (d, 1 H, *J* = 5 Hz, C(17)—H), 5.12 (s, 1 H, OCHO), 6.13 (s, 1 H, J < 0.5 Hz, $CH_3C{=}CH$), 7.32 (s, 5 H, C_6H_5).

2(*S*)-[5(*R*)- and -5(*S*)-carboxy-3(*S*)-methyl-2(*R*)-[2(*R*)-ethyl-3-(*R*),4(*S*)-(dimethylmethylenedioxy)-5(*S*)-(benzyloxy)-2-tetrahydrofuryl]-5-tetrahydrofuryl]-3-methyl-5,6-dihydro-5(*R*)-methyl-6(*S*)-methoxy-6-[([(1,1-dimethylethyl)dimethylsilyl]oxy)methyl]-2*H*-pyran (26a). To a stirred solution of 1.02 mmol of potassium hexamethyldisilazide in 6.9 mL of THF at −78 °C was added, dropwise over 5 min, a solution of 352 mg (0.509 mmol) of the ester **25a** in 3.5 mL of THF. After 15 min, 12.7 mL (1.27 mmol) of a 0.10 M solution of *tert*-butyl(dimethylsilyl)chlorosilane in THF (this solution was stored over a mixture of 3-Å and 4-Å sieves) was added over 3 min. The resulting mixture was allowed to stand at room temperature for 48 h, treated with 5.0 mL of 1 M aqueous LiOH for 45 min, diluted with 150 mL of ether, and then washed with 50 mL of saturated aqueous NaCl acidified to pH 2 with dilute aqueous HCl. The organic phase was dried ($MgSO_4$) and con-

centrated under reduced pressure. Chromatography of the residue on 35 g of silica gel with 4:6 ether/petroleum ether afforded 229 mg (65%) of an unseparated 5:1 diastereomeric mixture of the acids **26a** as a colorless oil: R_f = 0.24 (major diastereomer), 0.21 (minor diastereomer) (silica gel, 4:6 ether/petroleum ether); IR ($CHCl_3$) 3220, 2920, 1765, 1455, 1385, 1375, 1255, 1095, 1010, 875, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.13 (s, 6 H, $(CH_3)_2Si$), 0.97 (s, 9 H, $(CH_3)_3C$, 1.33, 1.47 (2 s, "5 H", $(CH_3)_2C$), 1.36, 1.53 (2 s, "1 H", $(CH_3)_2C$), 1.63 (br s "0.5 H", $CH_3C{=}CH$), 1.78 (br s, "2.5 H", $CH_3C{=}CH$), 3.47 (s, 3 H, OCH_3), 5.23 (br s, "0.17 H", $CH_3C{=}CH$), 5.30 (br s, "0.83 H", $CH_3C{=}CH$), 7.33 (s, 5 H, C_6H_5). Anal. Calcd for $C_{37}H_{58}O_{10}Si$: C, 64.32; H, 8.46. Found: C, 64.37; H, 8.34.

2(*S*)-[5(*R*)- and -5(*S*)-carboxy-3(*S*)-methyl-2(*R*)-[2(*R*)-ethyl-3-(*R*),4(*S*)-(dimethylmethylenedioxy)-5(*S*)-(benzyloxy)-2-tetrahydrofuryl]-5-tetrahydrofuryl]-3-methyl-5,6-dihydro-5(*R*)-methyl-6(*S*)-methoxy-6-[([(1,1-dimethylethyl)dimethylsilyl]oxy)methyl]-2*H*-pyran Phenyl Seleno Ester (27a). To a stirred solution of 100 mg (0.145 mmol) of the acids **26a** in 1.8 mL of THF at 0 °C were added 61 μL (0.43 mmol) of triethylamine and then 43 μL (0.29 mmol) of phenyl dichlorophosphate. After 30 min, 100 μL (0.72 mmol) of triethylamine and then 61 μL (0.58 mmol) of selenophenol were added. After 10 min at 0 °C, the mixture was allowed to warm to room temperature, diluted with 100 mL of ether, and then washed with 50 mL of saturated aqueous NaCl. The solvent was dried ($MgSO_4$) and then evaporated under reduced pressure. Chromatography of the residue on 20 g of silica gel with 5:95 ether/petroleum ether afforded first 19 mg (16%) of a seleno ester **27a**: R_f = 0.20 (silica gel, 1:9 ether/petroleum ether); IR ($CHCl_3$) 2950, 2860, 1715, 1460, 1385, 1375, 1250, 1100, 1015, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.00 (s, 6 H, $(CH_3)_2Si$), 0.83 (s, 9 H, $(CH_3)_3C$), 1.30, 1.48 (2 s, 6 H, $(CH_3)_2C$), 1.73 (br s, 3 H, $CH_3C{=}CH$), 3.43 (s, 3 H, OCH_3), 3.67 (s, 2 H, CCH_2O), 5.10 (s, 1 H, OCHO), 5.20 (br s, 1 H, $CH_3C{=}CH$), 7.23–7.57 (m, 10 H, $2C_6H_5$).

There was then eluted 84 mg (70%) of a seleno ester **27a**: R_f = 0.17 (silica gel, 1:9 ether/petroleum ether); IR ($CHCl_3$) 2950, 2860, 1715, 1460, 1385, 1250, 1100, 1015, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.00 (s, 6 H, $(CH_3)_2Si$), 0.88 (s, 9 H, $(CH_3)_3C$), 1.27, 1.43 (2 s, 6 H, $(CH_3)_2C$), 1.88 (br s, 3 H, $CH_3C{=}CH$), 3.30 (s, 3 H, CH_3O), 5.13 (s, 1 H, OCHO), 5.23 (br s, 1 H, $CH_3C{=}CH$), 7.23–7.52 (m, 10 H, $2C_6H_5$).

2(*S*)-[3(*S*)-Methyl-2(*R*)-[2(*R*)-ethyl-3(*R*),4(*S*)-(dimethylmethylenedioxy)-5(*S*)-(benzyloxy)-2-tetrahydrofuryl]-5(*R*)- and -5-(*S*)-tetrahydrofuryl]-3-methyl-5,6-dihydro-5(*R*)-methyl-6(*S*)-methoxy-6-[([(1,1-dimethylethyl)dimethylsilyl]oxy)methyl]-2*H*-pyran (28a). To a stirred solution of 103 mg (0.124 mmol) of the seleno esters **27a** and 200 μL (0.74 mmol) of freshly distilled tri-*n*-butyltin hydride in 6.0 mL of refluxing benzene was added a trace of AIBN. After 120 min, the reaction was allowed to cool to room temperature, and the solvent was evaporated at reduced pressure. Chromatography of the residue on 15 g of silica gel with 1:9 ether/petroleum ether afforded 66 mg (82%) of an inseparable 5:1 (^1H NMR) mixture of noralkanes **28a** as a colorless oil: R_f = 0.17 (silica gel, 1:9 ether/petroleum ether); IR 2960, 2940, 2890, 2860, 1460, 1385, 1375, 1260, 1210, 1095, 1015, 845 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) major diastereomer δ 0.05 (s, 6 H, $(CH_3)_2Si$), 0.88 (s, 9 H, $(CH_3)C$), 0.95 (d, 3 H, J = 7 Hz, CH_3CH), 0.98 (t, 3 H, J = 7.5 Hz, CH_3CH_2), 1.07 (d, 3 H, J = 7 Hz, CH_3CH), 1.28, 1.46 (2 s, 6 H, $(CH_3)_2C$), 1.48 (ddd, 1 H, J = 12, J' = 5.5, J'' = 2.5 Hz, C(19)—H), 1.69 (dt, 1 H, J = 14, J' = 7.5 Hz, CH_3CHH), 1.75 (s, 3 H, J < 0.5 Hz, $CH_3C{=}CH$), 1.92 (dt, 1 H, J = 14, J' = 7.5 Hz, CH_3CHH), 1.99 (dq, 1 H, J = 1.5, J' = 7 Hz, $CH_3CHCH{=}C$), 2.40–2.48, 2.48–2.56 (2 br m, 2 H, C(18)—H, C(19)—α-H), 3.39 (s, 3 H, OCH_3), 3.61 (d, 1 H, J = 11 Hz, $CCHHO$), 3.68 (d, 1 H, J = 4.5 Hz, C(17)—H), 3.73 (d, 1 H, J = 11 Hz, $CCHHO$), 4.10 (ddd, 1 H, J = 10, J' = 5.5, J'' = 5 Hz, C(20)—H), 4.19 (br s, 1 H, C(21)—H), 4.39 (d, 1 H, J = 12 Hz, C_6H_5CHH), 4.55, 4.71 (2 d, 2 H, J = 6 Hz, $OCHCHO$), 4.68 (d, 1 H, J = 12 Hz, C_6H_5CHH), 5.09 (s, 1 H, OCHO), 5.33 (br s, 1 H, J = 1.5, J' < 0.5 Hz, $CH_3{=}CHCH$), 7.25–7.34 (m, 5 H, C_6H_5), minor diastereomer δ 0.06 (s, 6 H, $(CH_3)_2Si$), 1.12 (d, 3 H, CH_3CH), 1.77 (s, 3 H, J < 0.5 Hz, $CH_3C{=}CH$), 2.28 (m, 1 H), 3.36 (s, 3 H, OCH_3), 3.62 (d, 1 H, J = 11 Hz, $CCHHO$), 3.72 (d, 1 H, J = 11 Hz, $CCHHO$), 3.88 (d, 1 H, J = 5 Hz, C(17)—H), 4.40 (d, 1 H, J = 12 Hz, C_6H_5CHHO), 4.58 (d, 1 H, J = 6 Hz, $OCHCHO$), 5.01 (s, 1 H, OCHO), 5.35 (br s, 1 H, $CH_3C{=}CH$). Anal. Calcd for $C_{36}H_{58}O_8Si$: C, 66.84; H, 9.04. Found: C, 66.77; H, 8.88. Decarbonylation of the separated seleno esters **27a** under conditions similar to those described above gave in each case an identical 5:1 mixture of noralkanes.

2(*R*)-Ethyl-2-[5(*S*)-formyl-3(*S*)-methyl-2(*R*)-tetrahydrofuryl]-3-(*R*),4(*S*)-(dimethylmethylenedioxy)-5(*S*)-(benzyloxy)tetrahydrofuran (31). To a stirred solution of 22 μL (0.26 mmol) of oxalyl chloride in 2 mL of dichloromethane at −78 °C was added 24 μL (0.34 mmol) of dimethyl sulfoxide. After 10 min, a solution of 67 mg (0.17 mmol) of the alcohol **33**[27] in 0.5 mL of dichloromethane was added to the reaction mixture. After 15 min, the solution was treated with 120 μL (0.85 mmol) of triethylamine, allowed to warm to room temperature, and then diluted with 50 mL of ether. This mixture was washed with 20 mL of 50% saturated aqueous NaCl, the organic phase was dried ($MgSO_4$), and then the solvent was evaporated under reduced pressure. Chromatography of the residue on 10 g of silica gel with 1:1 ether/petroleum ether yielded 57 mg (85%) of the aldehyde **31** as a colorless oil: R_f = 0.36 (silica gel, 1:1 ether/petroleum ether); ^1H NMR ($CDCl_3$) δ 1.03 (t, 3 H, J = 7 Hz, CH_3CH_2), 1.13 (d, 3 H, J = 7 Hz, CH_3CH), 1.33, 1.52 (2 s, 6 H $(CH_3)_2C$), 3.97 (d, 1 H, J = 4 Hz, C(17)–H), 5.10 (s, 1 H, OCHO), 9.72 (d, 1 H, J = 2 Hz, C(O)H). Treatment of a portion of this aldehyde with LAH in ether at 0 °C produced the alcohol **33** as identified by TLC and ^1H NMR.

2(*R*)-Ethyl-2-[5(*R*)-formyl-3(*S*)-methyl-2(*R*)-tetrahydrofuryl]-3-(*R*),4(*S*)-(dimethylmethylenedioxy)-5(*S*)-(benzyloxy)tetrahydrofuran (32). To a stirred solution of 34 mg (0.087 mmol) of the aldehyde **31** in 3.0 mL of dry methanol was added 200 mg of granular, anhydrous K_2CO_3, and the mixture was heated in an oil bath at 60 °C. After 2 h, the cooled reaction mixture was diluted with 40 mL of ether and washed with 20 mL of water and then 20 mL of saturated aqueous NaCl. The organic phase was dried ($MgSO_4$) and the solution concentrated under reduced pressure. Chromatography of the residue with 3:7 ether/petroleum ether afforded first 12 mg (35%) of the aldehyde **31** and then 14 mg (41%) of the aldehyde **32** as a colorless oil: R_f = 0.28 (silica gel, 1:1 ether/petroleum ether); ^1H NMR ($CDCl_3$) 1.03 (t, 3 H, J = 7 Hz, CH_3CH_2), 1.10 (d, 3 H, J = 6 Hz, CH_3CH), 1.33, 1.50 (2 s, 6 H, $(CH_3)_2C$), 4.02 (d, 1 H, J = 4 Hz, C(17)–H), 5.13 (s, 1 H, OCHO), 9.75 (d, 1 H, J = 2 Hz, C(O)H).

2(*S*)-Ethyl-2-[5(*S*)-carboxy-3(*S*)-methyl-2(*R*)-tetrahydrofuryl]-3-(*R*),4(*S*)-(dimethylmethylenedioxy)-5(*S*)-(benzyloxy)tetrahydrofuran Ester with the Glycal 22 (25b). By the procedure described above for the preparation of ester **25a**, 310 mg (0.763 mmol) of the acid **24b** and 300 mg (1.14 mmol) of triphenylphosphine in 1.5 mL of carbon tetrachloride, 1.5 mL of dichloromethane, and a solution of 279 mg (2.28 mmol) of 4-(dimethylamino)pyridine and 226 mg (0.748 mmol) of the glycal **22** in 2.0 mL of dichloromethane afforded, after chromatography on 35 g of alumina (Activity III) with 2:8 ether/petroleum ether, 439 mg (85%) of the ester **25b** as a colorless oil: R_f = 0.27 (silica gel, 3:7 ether/petroleum ether); IR ($CHCl_3$) 3000, 2935, 2860, 1735, 1670, 1460, 1385, 1375, 1255, 1140, 1095, 1010, 870, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.08 (s, 6 H, $(CH_3)_2Si$), 0.90 (s, 9 H, $(CH_3)_3C$), 1.32, 1.52 (2 s, 6 H, $(CH_3)_2C$), 1.55 (s, 3 H, J < 0.5 Hz, $CH_3C{=}CH$), 3.22 (s, 3 H, OCH_3), 3.42 (d, 1 H, J = 14 Hz, $CCHHO$), 3.80 (d, 1 H, J = 14 Hz, $CCHHO$), 3.97 (d, 1 H, J = 5 Hz, C(17)—H), 5.15 (d, 1 H, J = 1.5 Hz, OCHO), 6.08 (s, 1 H, J < 0.5 Hz, $CH_3C{=}CH$), 7.32 (br s, 5 H, C_6H_5).

2(*S*)-Ethyl-[5(*R*)-carboxy-3(*S*)-methyl-2(*R*)-[2(*S*)-ethyl-3(*R*),4-(*S*)-(dimethylmethylenedioxy)-5(*S*)-(benzyloxy)-2-tetrahydrofuryl]-5-tetrahydrofuryl]-3-methyl-5,6-dihydro-5(*R*)-methyl-6(*S*)-methoxy-6-[([(1,1-dimethylethyl)dimethylsilyl]oxy)methyl]-2*H*-pyran (26b). To a stirred solution of 0.70 mmol of lithium diisopropylamide in 4.0 mL of THF at −78 °C was added, dropwise over 5 min, a solution of 373 mg (0.538 mmol) of the ester **25b** in 1.5 mL of THF. After 10 min, the reaction mixture was treated with 0.19 mL (1.07 mmol Me_3SiCl) of the supernatant centrifugate from a 3:1 mixture of trimethylchlorosilane and triethylamine. The reaction mixture was then heated at 50 °C for 2 h, allowed to cool, diluted with 100 mL of ether, and washed with 40 mL of saturated aqueous NaCl acidified to ~pH 2 with dilute aqueous HCl. The organic phase was dried ($MgSO_4$) and the solvent evaporated under reduced pressure. Chromatography of the residue on 25 g of silica gel with 3:7 ether/petroleum ether afforded 170 mg (45%) of the acid **26b** as a white solid. Recrystallization of a portion of this material from methanol afforded the analytical sample as colorless plates: mp 167–168 °C; R_f = 0.38 (silica gel, 4:6 ether/petroleum ether); IR ($CHCl_3$) 3200, 2930, 2885, 2860, 1755, 1460, 1365, 1275, 1095, 1010, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.08 (s, 6 H, $(CH_3)_2Si$), 0.93 (s, 9 H, $(CH_3)_3C$), 1.35, 1.47 (2 s, 6 H, $(CH_3)_2C$), 1.82 (br s, 3 H, $CH_3{-}C{=}CH$), 3.42 (s, 3 H, OCH_3), 3.95 (d, 1 H, J = 4 Hz, C(17)—H), 4.23 (br s, 1 H, C(21)—H), 5.13 (d, 1 H, J = 1.5 Hz, OCHO), 5.40 (br s, 1 H, $CH_3C{=}CH$). Anal. Calcd for $C_{37}H_{58}O_{10}Si$: C, 64.32; H, 8.46. Found: C, 64.37; H, 8.42.

2(*S*)-Ethyl-[5(*R*)-carboxy-3(*S*)-methyl-2(*R*)-[2(*S*)-ethyl-3(*R*),4-(*S*)-(dimethylmethylenedioxy)-5(*S*)-(benzyloxy)-2-tetrahydrofuryl]-5-tetrahydrofuryl]-3-methyl-5,6-dihydro-5(*R*)-methyl-6(*S*)-methoxy-6-[([(1,1-dimethylethyl)dimethylsilyl]oxy)methyl]-2*H*-pyran Phenyl Seleno Ester (27b). By the procedure described above for the preparation of seleno ester **27a**, 20 mg (0.029 mmol) of the acid **26b**, 12 μL (0.086 mmol) of triethylamine, and 8.6 μL (0.058 mmol) of phenyl dichlorophosphate in 0.4 mL of THF, and then 20 L (0.14 mmol) of triethylamine and 12 μL (0.12 mmol) of selenophenol, afforded, after chromatography on 5 g of silica gel with 1:9 ether/petroleum ether, 19 mg (80%)

of the seleno ester **27b** as a colorless oil: R_f = 0.16 (silica gel, 1:9 ether/petroleum ether); IR ($CHCl_3$) 3000, 2960, 2940, 2890, 2865, 1710, 1465, 1385, 1375, 1260, 1195, 1020, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.08 (s, 6 H, $(CH_3)_2Si$), 0.90 (d, 3 H, J = 7 Hz, CH_3CH), 1.05 (t, 3 H, J = 7 Hz, CH_3CH_2), 1.18 (d, 3 H, J = 7 Hz, CH_3CH), 1.37, 1.55 (2 s, 6 H, $(CH_3)_2C$), 1.98 (br s, 3 H, CH_3C=CH), 3.34 (s, 3 H, OCH_3), 3.58 (s, 2 H, CCH_2O), 4.07 (d, 1 H, J = 5 Hz, C(17)—H), 4.17 (br s, 1 H, $CHC(CH_3)$), 4.57, 4.83 (2 d, 2 H, J = 12 Hz, $C_6H_5CH_2$), 4.85 (br s, 2 H, OC*H*CHO), 5.18 (br s, 1 H, OCHO), 5.30 (br s, 1 H, CH_3C=C*H*).

2(*S*)-[3(*S*)-Methyl-2(*R*)-[2(*S*)-ethyl-3(*R*),4(*S*)-(dimethylmethylenedioxy)-5(*S*)-(benzyloxy)-2-tetrahydrofuryl]-5-tetrahydrofuryl]-3-methyl-5,6-dihydro-5(*R*)-methyl-6(*S*)-methoxy-6-[([(1,1-dimethylethyl)dimethylsilyl]oxy)methyl]-2*H*-pyran (28b). By the procedure described for the preparation of the noralkanes **28a**, 14.0 mg (0.0169 mmol) of the seleno ester **27b**, 70 μL (0.26 mmol) of tri-*n*-butyltin hydride, and a trace of AIBN in 5.0 mL of benzene afforded, after 1 h at reflux and chromatography on 7 g of silica gel with 1:9 ether/petroleum ether, 8.1 mg (74%) of a single noralkane **28b** as a colorless oil: R_f = 0.19 (silica gel, 1:9 ether/petroleum ether); IR ($CHCl_3$) 2960, 2930, 2860, 1465, 1385, 1375, 1255, 1095, 1015, 845 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.03, 0.04 (2 s, 6 H, $(CH_3)_2Si$), 0.87 (s, 9 H, $(CH_3)_3C$), 0.92 (d, 3 H, J = 7.5 Hz, CH_3CH), 1.00 (t, 3 H, J = 8 Hz, CH_3CH_2), 1.19 (d, 3 H, J = 7 Hz, CH_3CH), 1.32, 1.49 (2 s, 6 H, $(CH_3)_2C$), 1.46 (s, 3 H, CH_3C=CH), 3.34 (s, 3 H, OCH_3), 3.56, 3.69 (2 d, 2 H, J = 11 Hz, CCH_2O), 3.77 (d, 1 H, J = 7 Hz, C(17)—H), 3.80 (m, 1 H, C(20)—H), 4.17 (br d, 1 H, J = 6 Hz, $OCHC(CH_3)$), 4.52, 4.75 (2 d, 2 H, J = 12 Hz, $C_6H_5CH_2$), 4.66 (d, 1 H, J = 6 Hz, OCHC*H*C), 4.85 (dd, 1 H, J = 6, J' = 2.5 Hz, OC*H*CHC), 5.15 (d, 1 H, J = 6 Hz, OCHO), 5.30 (br s, 1 H, CH_3C=C*H*).

3-Deoxy-1,2-*O*-(1-methylethylidene)-β-L-*threo*-pentofuranuronic Acid (35) and Methyl Ester. To a stirred solution of 454 mg (2.22 mmol) of the diol **34** in 10.0 mL of water at room temperature was added 475 mg (2.22 mmol) of $NaIO_4$. After 30 min, the solution was extracted with two 100-mL portions of chloroform, and the combined organic extracts were dried ($MgSO_4$) and then concentrated under reduced pressure. The residue was dissolved in 8.7 mL (5.10 mmol) of 0.588 M aqueous silver nitrate, and to the stirred solution at room temperature was added, dropwise over 5 min, 11.2 mL (10.2 mmol) of 0.91 M aqueous KOH. After 20 min, the solution was filtered, and the precipitate was washed with two 10-mL portions of 0.91 M aqueous KOH. The filtrate was cooled to 0 °C, carefully acidified to pH 2 with 6 M aqueous HCl, and then extracted with four 100-mL portions of chloroform. The combined organic extracts were dried ($MgSO_4$) and then concentrated under reduced pressure to afford 376 mg (90%) of the acid **35** as an oil of >95% (^1H NMR) purity; ^1H NMR ($CDCl_3$) δ 1.30, 1.52 (2 s, 6 H, $(CH_3)_2$), 2.32 (ddd, 1 H, J = 14, J' = 9, J'' = 5 Hz, OCHC*H*HCH, β-H), 2.72 (dd, 1 H, J = 14, J' = 1 Hz, OCHCH*H*CH, α-H), 4.63 (dd, 1 H, J = 9, J' = 1 Hz, OCHC(O)), 4.73 (dd, 1 H, J = 4.5, J' = 5 Hz, OCHC*H*O), 5.88 (d, 1 H, J = 4.5 Hz, OCHO), 9.12 (br s, 1 H, CO_2H). A portion of this oil was treated with ethereal diazomethane and the solvent evaporated under reduced pressure. Chromatography of the residue on silica gel with 7:3 ether/petroleum ether afforded the methyl ester of acid **35** as a colorless oil: R_f = 0.20 (silica gel, 7:3 ether/petroleum ether); evaporative distillation 60 °C (0.005 mmHg); $[\alpha]^{22}_D$ −63.6° (*c* 1.12, $CHCl_3$) [lit.[64] $[\alpha]^{20}_D$ −67.1° (*c* 1, $CHCl_3$)]; IR ($CHCl_3$) 2990, 2950, 1750, 1735, 1440, 1385, 1375, 1260, 1160, 1105, 1070, 1035, 855 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30, 1.47 (2 s, 6 H, $(CH_3)_2C$). 2.27 (ddd, 1 H, J = 14, J' = 9, J'' = 5 Hz, OCHC*H*HCH, β-H), 2.68 (d, 1 H, J = 14, J' = 0.5 Hz, OCHCH*H*CH, α-H), 3.42 (s, 3 H, OCH_3), 4.62 (dd, 1 H, J = 9, J' = 0.5 Hz, OCHC(O)), 4.68 (dd, 1 H, J = 5, J' = 4 Hz, OCHC*H*O), 5.83 (d, 1 H, J = 4 Hz, OCHO). Anal. Calcd for $C_9H_{14}O_5$: C, 53.46; H, 6.99. Found: C, 53.59; H, 6.99.

3-Deoxy-1,2-*O*-(1-methylethylidene)-β-L-*threo*-pentofuranuronic Acid Ester with the Glycal 22 (36). By the procedure described for the preparation of ester **25a**, 133 mg (0.707 mmol) of the acid **35**, 370 mg (1.41 mmol) of triphenylphosphine in 1.5 mL of carbon tetrachloride and 1.5 mL of dichloromethane, and a solution of 259 mg (2.12 mmol) of 4-(dimethylamino)pyridine and 203 mg (0.673 mmol) of the glycal **22** in 2.0 mL of dichloromethane afforded, after chromatography on 20 g of alumina (Activity III) with 4:6 ether/petroleum ether, 254 mg (80%) of the ester **36** as a colorless oil: R_f = 0.19 (silica gel, 1:1 ether/petroleum ether); IR ($CHCl_3$) 2970, 2950, 2860, 1750, 1680, 1465, 1385, 1375, 1260, 1140, 1030, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.05 (s, 6 H, $(CH_3)_2Si$), 0.88 (s, 9 H, $(CH_3)C$), 1.28, 1.50 (2 s, 6 H, $(CH_3)_2C$), 1.57 (s, 3 H, CH_3C=CH), 3.20 (s, 3 H, OCH_3), 3.43 (d, 1 H, J = 14 Hz, CC*H*HO), 3.83 (d, 1 H, J = 14 Hz, CCH*H*O), 4.58 (dd, 1 H, J = 6, J' = 2 Hz, OCHC(O)), 4.65 (dd, 1 H, J = 3, J' = 3 Hz, OCHC*H*O), 5.10 (d, 1 H, OC*H*CHCH$_3$), 5.83 (d, 1 H, J = 3 Hz, OCHO), 6.10 (s, 1 H, OC*H*=CCH$_3$, $J \sim$ 0.5 Hz).

2(*S*)-[2-Carboxy-4(*R*),5(*R*)-(dimethylmethylenedioxy)-2-tetrahydrofuryl]-3-methyl-5,6-dihydro-5(*R*)-methyl-6(*S*)-methoxy-6-[([(1,1-dimethylethyl)dimethylsilyl]oxy)methyl]-2*H*-pyran. By the procedure described for the preparation of the acids **26a**, 0.22 mmol of potassium hexamethyldisilazide in 1.5 mL of THF, a solution of 67 mg (0.14 mmol) of the ester **36**, and 2.82 mL (0.282 mmol) of a 1 M solution of *tert*-butyldimethylchlorosilane, provided, after treatment with 1.0 mL of 1 M aqueous LiOH and chromatography on 10 g of silica gel with 1:9 methanol/chloroform, 41 mg (61%) of a single acid as a colorless oil: R_f = 0.27 (silica gel, 1:9 methanol/chloroform); IR ($CHCl_3$) 3400, 2960, 2930, 2860, 1765, 1465, 1380, 1255, 1110, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.08 (s, 6 H, $(CH_3)_2Si$), 0.92 (s, 9 H, $(CH_3)_3C$), 0.96 (d, 3 H, J = 7 Hz, CH_3CH), 1.35, 1.57 (2 s, 6 H, $(CH_3)_2C$), 1.83 (s, 3 H, CH_3C=CH), 3.47 (s, 3 H, OCH_3), 3.73 (s, 2 H, CCH_2O), 5.33 (s, 1 H, CH_3C=C*H*), 6.05 (d, 1 H, J = 3 Hz, OCHO). Anal. Calcd for $C_{23}H_{40}O_8Si$: C, 58.45; H, 8.53. Found: C, 58.09; H, 8.43.

2(*S*)-[2-Carboxy-4(*R*),5(*R*)-(dimethylmethylenedioxy)-2-tetrahydrofuryl]-3-methyl-5,6-dihydro-5(*R*)-methyl-6(*S*)-methoxy-6-[([(1,1-dimethylethyl)dimethylsilyl]oxy)methyl]-2*H*-pyran Phenyl Seleno Ester (38). By the procedure described above for the preparation of seleno ester **27a**, 40 mg (0.084 mmol) of the above acid in 1.0 mL of THF, 25 μL (0.17 mmol) of phenyl dichlorophosphate, and 35 μL (0.25 mmol) of triethylamine, and then 36 μL (0.34 mmol) of selenophenol and 59 μL (0.42 mmol) of triethylamine, provided after chromatography on 10 g of alumina (Activity III) with 1:9 and then 2:8 ether/petroleum ether, 41 mg (79%) of the seleno ester **38** as a light yellow oil: R_f = 0.29 (silica gel, 2:8 ether/petroleum ether); IR ($CHCl_3$) 2960, 1720, 1385, 1375, 1100, 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.05 (s, 6 H, $(CH_3)_2Si$), 0.90 (s, 9 H, $(CH_3)_3C$), 0.95 (d, 3 H, J = 7 Hz, CH_3CH), 1.35 (s, 3 H, CH_3C), 1.74 (s, 6 H, CH_3C, CH_3C=CH), 2.32 (dd, 1 H, J = 14, J' = 2 Hz, CHC*H*HC, α-H), 2.52 (m, 1 H, CH_3CHCH), 2.76 (dd, J = 14, J' = 6 Hz CHCH*H*C, β-H), 3.42 (s, 3 H, OCH_3), 3.67 (s, 2 H, CCH_2O), 4.58 (br s, 1 H, OC*H*C(CH$_3$)), 4.85 (ddd, 1 H, J = 6, J' = 4, J'' = 2 Hz, OCHC*H*O), 5.35 (br s, 1 H, CH_3=C*H*), 5.97 (d, 1 H, J = 4.5 Hz, OCHO), 7.12–7.68 (m, 5 H, C_6H_5).

2(*S*)-[4(*R*),5(*R*)-(Dimethylmethylenedioxy)-2(*R*)- and -2(*S*)-tetrahydrofuryl]-3-methyl-5,6-dihydro-5(*R*)-methyl-6(*S*)-methoxy-6-[([(1,1-dimethylethyl)dimethylsilyl]oxy)methyl]-2*H*-pyran (37). By the procedure described above for the noralkanes **28a**, 30 mg (0.049 mmol) of the seleno ester **38**, 50 L (0.19 mmol) of freshly distilled tri-*n*-butyltin hydride, and a trace of AIBN in 2.0 mL of benzene provided, after 50 min at reflux and chromatography on silica gel with 1:9 and then 2:8 ether/petroleum ether, first 8.8 mg (42%) of a noralkane **37**: R_f = 0.23 (silica gel, 2:8 ether/petroleum ether); IR ($CHCl_3$) 2960, 2860, 1460, 1485, 1475, 1255, 1110, 1030, 850 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.04, 0.05 (2 s, 6 H, $(CH_3)_2Si$), 0.89 (s, 9 H, $(CH_3)_3C$), 0.97 (d, 3 H, J = 7 Hz, CH_3CH), 1.31, 1.56 (2 s, 6 H, $(CH_3)_2C$), 1.83 (s, 3 H, CH_3C=CH), 2.11 (ddd, 1 H, J = 14, J' = 7, J'' = 7 Hz, CHC*H*HCH, β-H), 2.38 (br m, 1 H, CH_3CH), 2.61 (ddd, 1 H, J = 14, J' = 2, J'' = 1 Hz, CHCH*H*CH, α-H), 3.28 (s, 3 H, OCH_3), 3.59, 3.68 (2 d, 2 H, J = 12 Hz, CCH_2O), 4.22 (ddd, 1 H, J = 11, J' = 7, J'' = 2 Hz, $CH_2CHCH(CH_3)$), 4.26 (br d, 1 H, J = 11 Hz, OC*H*CCH$_3$), 4.73 (ddd, 1 H, J = 7, J' = 5, J'' = 1 Hz, OCHC*H*O), 5.43 (br s, 1 H, CH_3C=CH), 5.80 (d, 1 H, J = 5 Hz, OCHO); mass spectrum, m/e 428 (M^+).

There was then eluted 9.3 mg (44%) of a noralkane **37**: R_f = 0.18 (silica gel, 2:8 ether/petroleum ether); IR ($CHCl_3$) 2940, 2870, 1465, 1385, 1375, 1260, 1170, 850 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.04, 0.05 (2 s, 6 H, $(CH_3)_2Si$), 0.87 (s, 9 H, $(CH_3)_3C$), 0.92 (d, 3 H, CH_3CH), 1.32, 1.48 (2 s, 6 H, $(CH_3)_2C$), 1.71 (s, 3 H, CH_3C=CH), 2.01 (dd, 1 H, J = 14, J' = 4 Hz, CHC*H*HCH, α-H), 2.06 (ddd, 1 H, J = 14, J' = 8, J'' = 4 Hz, CHCH*H*CH, β-H), 2.52 (br m, 1 H, CH_3CH), 3.36 (s, 3 H, OCH_3), 3.58, 3.76 (2 d, 2 H, J = 11 Hz, CCH_2O), 4.12 (br s, 1 H, OC*H*CCH$_3$), 4.45 (ddd, 1 H, J = 8, J' = 4, J'' = 4 Hz, $CH_2CHCHC(CH_3)$), 4.74 (dd, 1 H, J = 4, J' = 3 Hz), 5.41 (br s, 1 H, CH_3C=C*H*), 5.81 (d, 1 H, J = 3 Hz, OCHO); mass spectrum, m/e 428 (M^+).

Supplementary Material Available: Atomic positional and thermal parameters are presented in Table I, bond distances in Table II, and bond angles in Table III (8 pages). Ordering information is given on any current masthead page.