Use of Allyltrimethylsilane in the Formation of Potential *C*-Nucleoside Precursors[1]

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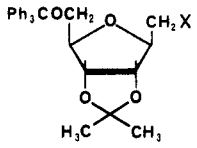
The soft nucleophile allyltrimethylsilane reacted with 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose under Lewis acid catalysis to afford the novel allyl sugar 4,7-anhydro-1,2,3-trideoxy-5,6,8-tri-*O*-benzoyl-D-*altro*-(*allo*)-oct-1-ene (**1**) as an anomeric mixture. Compound **1** was readily oxidized to afford 3,6-anhydro-2-deoxy-4,5,7-tri-*O*-benzoyl-D-heptose (**2**) or 3,6-anhydro-2-deoxy-4,5,7-tri-*O*-benzoyl-D-heptanoic acid (**3**). The chemical versatility of **3** was demonstrated by the facile conversion of **3** into the β-keto ester ethyl 4-(2,3,5-tri-*O*-benzoyl-D-ribofuranosyl)acetoacetate (**6**) and the β-keto nitrile 4-(2,3,5-tri-*O*-benzoyl-D-ribofuranosyl)acetoacetonitrile (**12**). Both compounds (**6** and **12**) underwent diazo coupling reactions, while **6** was also annulated to furnish the homo-*C*-nucleoside 2-amino-6-[(α- and β-D-ribofuranosyl)methyl]pyrimidin-4-one (**10**).

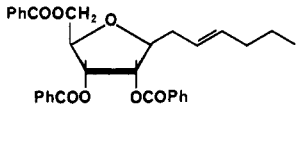
"*C*-Nucleoside" is a term frequently used to classify an ever growing group of both naturally occurring[2] and synthetically derived compounds. Nucleosides are generally considered to be compounds which contain a heterocyclic aglycon and a carbohydrate moiety which are joined together by a nitrogen–carbon bond. *C*-Nucleosides are also compounds composed of a sugar portion and an aglycon (generally heterocyclic in nature); however, *C*-nucleosides differ from the traditional nucleosides in that the bond which joins the sugar and heterocyclic aglycon is a C–C bond instead of a C–N bond. *C*-Nucleosides have become interesting synthetic targets since many of the naturally occurring *C*-nucleosides exhibit a broad spectrum of biological activity.[2]

The nature of the glycosidic bond in *C*-nucleosides is responsible for the development of a wide variety of new synthetic strategies[3] in the nucleoside area. One of the more versatile and popular approaches involves the construction of a suitably functionalized sugar onto which the desired heterocycle can be constructed. Of course the functionalization contained in the sugar is of prime importance since it both dictates and limits the type of heterocycle which may be assembled. Compounds A and B are examples of sugars which have previously been used[4,5] in this approach. Anomeric mixtures (favoring the β anomer)[6] of these sugar derivatives have been synthesized by the condensation of a stabilized ylide with 2,3-*O*-isopropylidene-5-*O*-trityl-D-ribofuranose. Several examples of compounds synthesized from compounds A or B have recently been reported, e.g., pseudouridine,[7] pseudoisocytidine,[7] 2-thiopseudouridine,[7] oxazinomycin,[5] 9-deazainosine,[8] and 9-deazaadenosine.[9]

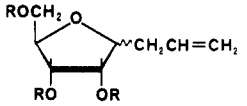


A X = COOEt

B X = CN



C



D R = Acyl

An alternate approach for the synthesis of this type of sugar has been reported[10] and was recently investigated in our laboratories.[11] This procedure involved the stannic chloride catalyzed condensation of 1-hexene and the readily available sugar 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose. We found that the desired β anomer of this reaction, compound C, was obtained in small amounts due to the poor nucleophilic character of 1-hexene and competing side reactions. However, the fact that 1-hexene possessed sufficient nucleophilicity to react at all was enough to suggest that perhaps better and more efficient "soft" nucleophiles could be found. Our search for such an alternative reagent led us to examine the use of allyltrimethylsilane (All-Me_3Si) as the condensing agent in the above reaction.

The mildly nucleophilic nature of All-Me_3Si has been demonstrated,[12] particularly in the presence of Lewis acids such as $TiCl_4$, BF_3, or $AlCl_3$. Also of considerable interest was a recent account[13] which described the reaction of All-Me_3Si with acetals to form substituted allyl ethers in the presence of the Lewis acid trimethylsilyl trifluoromethanesulfonate (Me_3Si triflate). Since the anomeric centers in tetrasubstituted pentose sugars are indeed acetals, it seemed reasonable to assume that suitably substituted sugars might also react under similar condi-

(1) This study was supported by funds from the National Institutes of Health (Training Grant No. 5-T32-GM07767) and the American Cancer Society (Grant CH-133). It was presented in part at the 182nd National Meeting of the American Chemical Society, New York, 1981; Abstract CARB 40.

(2) For a review see: Suhadolnik, R. J.; "Nucleoside Antibiotics", Wiley-Interscience: New York, 1970; Chapters 9 and 10, pp 354–404.

(3) For recent reviews see: (a) Hanessian, S.; Pernet, A. G. *Adv. Carbohydr. Chem.* **1976**, *33*, 111. (b) James, S. R. *J. Carbohydr. Nucleosid. Nucleotid.* **1979**, *6*, 415.

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

(5) DeBernardo, S.; Weigele, M. *J. Org. Chem.* **1977**, *42*, 109.

(6) The term anomeric is not strictly applicable to *C*-glycosides but is used for convenience.

(7) Chu, C. K.; Wempen, I.; Watanabe, K. A.; Fox, J. J. *J. Org. Chem.* **1976**, *41*, 2793.

(8) Lim, M.-I.; Klein, R. S.; Fox, J. J. *Tetrahedron Lett.* **1980**, *21*, 1013.

(9) Lim, M.-I.; Klein, R. S. *Tetrahedron Lett.* **1981**, *22*, 25.

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(11) Cupps, T. L.; Wise, D. S.; Townsend, L. B. submitted for publication in *Carbohydr. Res.*

(12) Hosomi, A.; Endo, M.; Sakurai, H. *Chem. Lett.* **1976**, 941. Ojima, I.; Kumagai, M. *Ibid.* **1978**, 575.

(13) Tsunoda, T.; Suzuki, M.; Noyori, R. *Tetrahedron Lett.* **1980**, *21*, 71.

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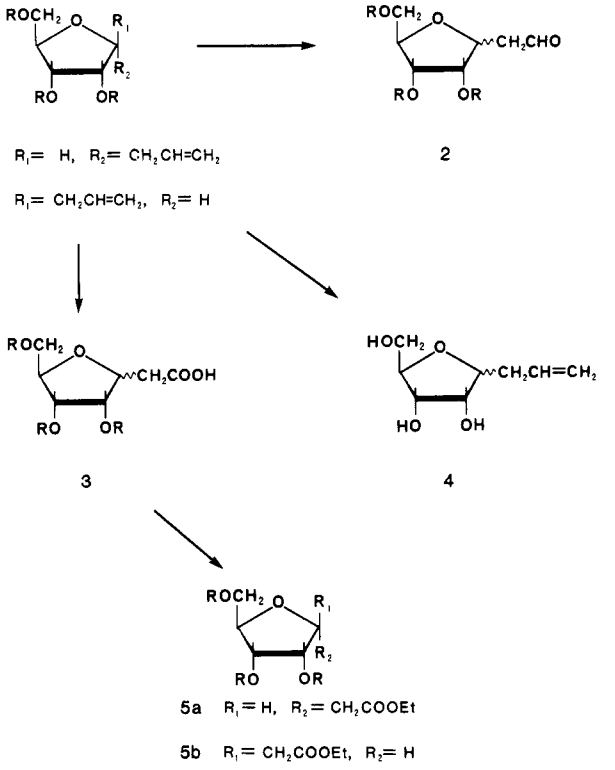
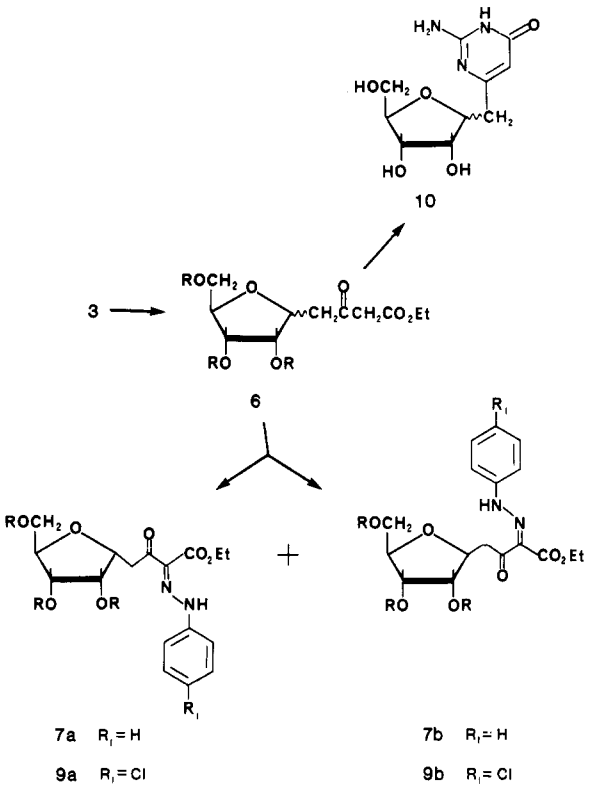
Scheme I[a]



[a] R = COPh.

Scheme II[a]



[a] R = COPh.

tions with All-Me_3Si to form allyl sugar derivatives of the general form shown in compound D. We now report the successful condensation of 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose with All-Me_3Si as well as several chemical transformations which have been carried out on the allyl product to elaborate potential C-nucleoside intermediates.

Results and Discussion

The reaction of All-Me_3Si with 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose, in the presence of excess Me_3Si triflate, formed 4,7-anhydro-1,2,3-trideoxy-5,6,8-tri-*O*-benzoyl-D-*altro*-oct-1-ene (**1a**) and 4,7-anhydro-1,2,3-trideoxy-5,6,8-tri-*O*-benzoyl-D-*allo*-oct-1-ene (**1b**) in a combined yield of 83% and in a 10/1 ratio, respectively (see Scheme I). That **1a** and **1b** were anomers was suggested by their similar ^1H NMR data but differing optical rotation values. However, the unequivocal proof of structure was provided by the following chemical transformations. The anomeric mixture of **1a** and **1b** was treated with ozone in methanol to form an intermediate which was assumed to be the traditional ozonide.[14] Treatment of this intermediate with 30% hydrogen peroxide in 97% formic acid afforded a 91% yield of 3,6-anhydro-1-deoxy-4,5,7-tri-*O*-benzoyl-D-heptanoic acid[10] (**3**) as an inseparable mixture of anomers. Esterification of **3** was accomplished in ethanol containing a trace of *p*-toluenesulfonic acid to produce the known compounds[15] **5a** and **5b**. These compounds possessed optical rotations as well as other spectral data which were in complete agreement with those reported[15] in the literature. Compounds **1a** and **1b** were facilely deblocked to afford a quantitative yield of 4,7-anhydro-1,2,3-tri-deoxy-D-*altro*(*allo*)-oct-1-ene (**4**). Also, a mixture of **1a** and **1b** was readily converted into the previously reported 3,6-anhydro-2-deoxy-4,5,7-tri-*O*-benzoyl-D-heptose (**2**)[11] by ozonolysis followed by a reductive workup with methyl sulfide.

Since one of our areas of research interest involves *C*-nucleosides, we were interested in the synthetic potential of compound **3** as a possible precursor of certain *C*-nucleosides. In particular, we were interested in the ability of **3** to function effectively as a precursor of the pyrimidine "homo-*C*-nucleosides" of the type recently reported[16] by Secrist. Thus, compound **3** was first converted to ethyl 4-(2,3,5-tri-*O*-benzoyl-D-ribofuranosyl)acetoacetate (**6**) by reacting the acid chloride of **3** (generated by using thionyl chloride) with the dilithium salt of ethyl hydrogen malonate according to the reported[17] procedure. Compound **6** was isolated in 86% yield as a 4/1 (α/β) anomeric mixture (Scheme II). Compound **6** was then treated with guanidine in boiling ethanol to produce the isocytosine homo-*C*-nucleoside[16] **10** in 56% yield. However, the condensation of **6** with thiourea, urea, or formamidine did not afford the expected pyrimidine derivatives.

An interesting approach for the synthesis of pyrimidines involves the reported[18] ring closure of an aliphatic β-keto nitrile with guanidine. In order to determine whether or not such a procedure might be applicable to a sugar-containing β-keto nitrile, we synthesized 4-(2,3,5-tri-*O*-benzoyl-D-ribofuranosyl)acetoacetonitrile (**12**). Two different approaches were investigated in our efforts to prepare **12**. In the first approach the isomeric carboxylic acid mixture of **3** was reacted with *tert*-butyl cyanoacetate in the presence of diethyl phosphorocyanidate[19] (DEPC) and triethylamine to form compound **11** (Scheme III), the

(14) March, J., Ed. "Advanced Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1977; p 1090.
(15) Hanessian, S.; Ogawa, T.; Guindon, Y. *Carbohydr. Res.* **1974**, *38*, C12.
(16) Secrist, J. A., III. *J. Org. Chem.* **1978**, *43*, 2925.
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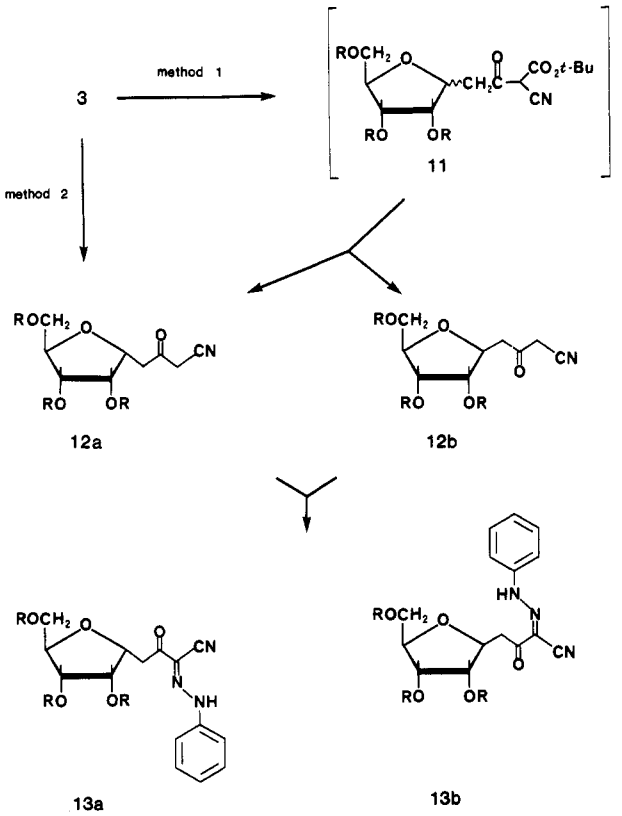
(18) Ito, I.; Oda, N.; Kato, T.; Ota, K. *Chem. Pharm. Bull.* **1975**, *23*, 2104.
(19) Shioiri, T.; Hamada, Y. *J. Org. Chem.* **1978** *43*, 3631. For the preparation of DEPC see: Shioiri, T.; Yokoyama, Y.; Kasai, Y.; Yamada, S. *Tetrahedron* **1976**, *32*, 2211.

Scheme III[a]



[a] R = COPh.

structure of which was confirmed by ^{1}H NMR and IR spectral data. Compound **11** was not isolated but was instead directly treated with a trace amount of *p*-toluenesulfonic acid monohydrate in boiling toluene to afford compound **12** as a mixture of the α and β anomers in about 36% yield from **3**. This low yield prompted us to investigate a second approach to afford **12**. The acid chloride of **3** was reacted with the dilithium salt of cyanoacetic acid[20] to afford pure **12a** as a crystalline product in 41% yield. In contrast, the aforementioned DEPC procedure resulted in the formation of an anomeric mixture which favored **12b** (β anomer) in a ratio of 8:3 as determined by high-performance liquid chromatography (HPLC). Anomeric assignments were made from ^{1}H NMR data (360 MHz). The chemical shift of the anomeric proton in compound **12a** appeared downfield from that of compound **12b** since the β face location of this anomeric proton placed it out of the shielding influence of the 2′-oxygen. This is in agreement with the general trend seen for most nucleoside anomeric pairs.[21]

It has been demonstrated[22] that β-keto esters and β-keto nitriles react with benzenediazonium salts to form α-(phenyldiazo)-β-oxo esters and α-(phenyldiazo)-β-oxo nitriles, respectively, in good yield. The phenyldiazo esters have been used extensively as precursors for the synthesis of 5-(phenyldiazo)pyrimidines.[23] In order to investigate the use of this approach in the synthesis of modified *C*-nucleoside precursors, we applied the diazo-coupling procedure to compound **6**. When the diazonium salt of freshly distilled aniline was reacted with **6**, compounds **7a** and **7b** were isolated in high yield. The structural assignment of **7a** and **7b** was made from ^{1}H NMR data and microanalysis. Although a rigorous anomeric assignment using 60-MHz ^{1}H NMR data was impossible, the assignment was tentatively made by using TLC R_f data which showed two slightly slower moving spots in about the same ratio as that of the starting mixture (**6**). Compound **6** was also readily coupled with *p*-chlorobenzenediazonium chloride, forming the phenylhydrazone **9** as an anomeric mixture. Unfortunately, we were unsuccessful in our attempts to obtain pyrimidine derivatives from **7** using guanidine, formamidine, or thiourea as the annulating reagents. In the case of the β-keto nitriles, the anomeric mixture of **12** was coupled with benzenediazonium chloride to produce the phenylhydrazones **13a** and **13b** in high yield. Attempts to convert compounds **12** and **13** into pyrimidines were unsuccessful.

In summary, the allyl sugars **1a** and **1b** were readily formed by the reaction of All-Me_3Si with 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose. Oxidative cleavage of the olefinic bond led to the formation of the versatile intermediate **3**, which in turn was readily transformed into the β-keto ester **6** or the β-keto nitrile **12**. Phenyldiazo coupling converted **6** into compounds **7** (**a** and **b**) and **9** (**a** and **b**). Similarly, the compound **12** reacted in high yield to form **13** (**a** and **b**). The β-keto ester **6** was also converted to the known homo-*C*-nucleoside **10**. The applicability of the All-Me_3Si condensation reaction with other protected sugars, including 2-deoxyribose and arabinose, is currently being investigated in our laboratories.

Experimental Section

General Methods. Low-pressure column chromatography was performed by using Merck Lobar (silica gel-60) prepacked columns (size A, B, or C) with typical flow rates of 5–10 mL/min. Fractions (15 mL) were collected by using an ISCO Retriever III automatic fraction collector. For compounds which were UV absorbing, fractions containing the requisite compound were detected by using an Altex Model 152 dual wavelength UV detector (254 nm) with a preparative flow cell. Gravity column chromatography was accomplished by using 70–230-mesh Merck silica gel. Thin-layer chromatography (TLC) was accomplished by using SilicAR 7GF (250-μm layer) on prescored glass plates (2.5 × 8 cm) purchased from Analtech, Inc., Newark, DE. The solvent systems used were as follows: (a) hexanes[24]/ethyl acetate (3:1 v/v), (b) hexanes/ethyl acetate (6:1 v/v), (c) hexanes/ethyl acetate (15:1 v/v), (d) benzene/ethyl acetate (85:15 v/v), (e) benzene/ethyl acetate/acetic acid (340:60:1 v/v/v), (f) toluene/ethyl acetate (12:1 v/v), (g) toluene/ethyl acetate (15:1 v/v), (h) chloroform/methanol (9:1 v/v), (i) chloroform/methanol (12:1 v/v), (j) ethyl acetate/methanol (9:1 v/v), (k) ethyl acetate/methanol (20:1 v/v), (l) chloroform/methanol (3:1 v/v), (m) methylene chloride/ethyl acetate (40:1 v/v). Evaporations were carried out with a Buchler flash evaporator with a water aspirator and a room-temperature water bath unless otherwise noted. Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained by using a Varian EM-360 (60 MHz) spectrometer or a Bruker WM 360 (360 MHz) spectrometer. The following abbreviations were used to designate the multiplicity of individual signals: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dt = doublet of triplets, and dq = doublet of quartets. Optical rotations were measured with a Perkin-Elmer Model 141 automatic polarimeter. IR spectra were recorded by using a Perkin-Elmer 281 spectrometer. High-performance liquid chromatography was carried out with a Varian Vista 54 chromatograph using a Whatman ODS-3 10-μm particle size reversed-phase column (4.6 × 250 mm), a Brownlee 10-μm particle size guard column, and a Varian UV-50 variable-wavelength UV detector or a Waters Model 401 refractive

(20) This appears to be a general reaction and is therefore under further investigation for synthetic merit by our laboratory.
(21) Nishimura, T.; Shimizu, B. *Chem. Pharm. Bull.* **1965**, *13*, 803.
(22) For example see: Garg, H. G.; Joshi, S. S. *J. Indian Chem. Soc.* **1960**, *37*, 626.
(23) (a) Brown, D. J. "The Pyrimidines"; Wiley: New York, 1962; Chapter V, p 152. (b) Brown, D. J. "The Pyrimidines, Supplement 1"; Wiley: New York, 1970; Chapter V, p 108.
(24) Hexanes were purchased as such from Mallinckrodt, Inc., St. Louis, MO.

index detector. Retention times (t_r) were measured from the time of injection, and flow rates of 1.0 mL/min were maintained except where noted. Mass spectral data were obtained on a Finnigan Model 4023 GC/MS instrument with electron ionization. Melting points are uncorrected and were determined by using a Thomas-Hoover capillary melting point apparatus. Elemental analyses were obtained from M-H-W Laboratories, Phoenix, AZ.

4,7-Anhydro-1,2,3-trideoxy-5,6,8-tri-*O*-benzoyl-D-*altro*-oct-1-ene (1a) and 4,7-Anhydro-1,2,3-trideoxy-5,6,8-tri-*O*-benzoyl-D-*allo*-oct-1-ene (1b). A solution of 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose (5.04 g, 10 mmol) and trimethylsilyl trifluoromethanesulfonate (Me_3Si triflate; 2.45 mL, 14 mmol) in nitromethane (50 mL) was treated with allyltrimethylsilane (2.38 mL, 15 mmol; purchased from Alfa Chemical Co.) at 0 °C and stirred under a nitrogen atmosphere for 5 h. The solvent and excess volatiles were then removed in vacuo. The stiff syrup was dissolved in ethyl acetate, washed first with a saturated sodium bicarbonate solution (2 × 30 mL) and then with a saturated sodium chloride solution (1 × 30 mL), and finally dried over magnesium sulfate. Filtration and evaporation of the filtrate yielded a syrup which was chromatographed on silica gel (40–50 g; 5 cm i.d. column; eluent 5% ethyl acetate in toluene, v/v). The proper fractions (determined by TLC, solvent system c) were combined and evaporated to yield a mixture of the oils **1a** and **1b** (3.75 g, 83% combined yield) in a ratio of 8:1, respectively. The major component **1a** was separated from **1b** by using low-pressure chromatography (Lobar column, size B; solvent system c).

Compound 1a: R_f 0.10 (solvent system c); $[\alpha]^{23}_D$ +85.0° (*c* 0.8, $CHCl_3$); ^1H NMR (60 MHz, $CDCl_3$) δ 2.51 (m, 2, H-3), 4.2–6.0 (m, 8, H-1a, H-1b, H-2, H-4, H-5, H-6, H-7, H-8), 7.2–8.3 (m, 15, aromatics). Anal. Calcd for $C_{29}H_{26}O_7$: C, 71.59; H, 5.39. Found: C, 71.73; H, 5.27.

Compound 1b. Since **1b** was only a minor constituent, we had some trouble achieving analytical purity as is reflected in the microanalysis data. However, spectral data for **1b** were obtained anyway to allow a comparison of **1b** with **1a**: R_f 0.16 (solvent system c); $[\alpha]^{23}_D$ +39.83° (*c* 1.8, $CHCl_3$); ^1H NMR (60 MHz, $CDCl_3$) δ 2.57 (m, 2, H-3), 4.3–6.2 (m, 8, H-1a, H-1b, H-2, H-4, H-5, H-6, H-7, H-8), 7.1–8.3 (m, 15, aromatic). Anal. Calcd for $C_{29}H_{26}O_7$: C, 71.59; H, 5.39. Found: C, 72.75; H, 5.72.

3,6-Anhydro-2-deoxy-4,5,7-tri-*O*-benzoyl-D-heptose (2). A solution of the mixture of **1a** and **1b** (0.66 g, 1.5 mmol) in methanol (25 mL) was treated with ozone at −70 °C for 5 min and then purged with dry nitrogen for 30 min. While the temperature was maintained at −70 °C, methyl sulfide (0.7 mL) was added, and the resulting solution was allowed to warm to room temperature over a period of 3 h with stirring. After evaporation of the solvent, the yellow oil was chromatographed on silica gel (Lobar, size B), with elution at a flow rate of 4 mL/min with methylene chloride/ethyl acetate (40:1 v/v). The aldehyde-containing fractions [TLC solvent system m, visualized by using a (2,4-dinitrophenyl)hydrazine TLC spray test] were combined and evaporated to yield the aldehyde derivative **2** (0.42 g, 72%) as an inseparable anomeric mixture (α/β ratio, 11:8). Spectral data were identical with those previously obtained[11] for this compound.

3,6-Anhydro-2-deoxy-4,5,7-tri-*O*-benzoyl-D-heptanoic Acid (3). A solution of a mixture of **1a** and **1b** (2.25 g, 5.0 mmol) in methanol (100 mL) was cooled to −70 °C, purged with dry oxygen (10 min), and then treated with ozone to effect a constant blue color. The solution was purged with nitrogen for 30 min, and the methanol was immediately removed in vacuo (bath temperature < 35 °C). The resulting white foam was dissolved in 97% formic acid (10 mL) and then treated with 30% hydrogen peroxide (2–3 mL) dropwise at room temperature. The turbid solution was heated at reflux temperature for 60 min, cooled to room temperature, and then evaporated to afford a colorless glass. This glass was dissolved in ethyl acetate and chromatographed on a silica gel column (60 g, 3-cm i.d.), by elution with solvent system e. Proper fractions (TLC, solvent system e) were collected and evaporated to afford the mixture **3** (2.30 g, 91%) as a glass.

Mixture 3: R_f 0.3 (solvent system e); ^1H NMR (60 MHz, $CDCl_3$) δ 2.93 (d, $J_{2,3}$ = 7 Hz, H-2), 4.4–5.2 (m, 4, H-3, H-6, H-7a, H-7b), 5.5–6.2 (m, 2, H-4, H-5), 7.2–8.3 (m, aromatic), 9.3 (br s, COOH). Anal. Calcd for $C_{28}H_{24}O_9 \cdot 0.25H_2O$: C, 65.56; H, 4.91. Found: C, 65.75; H, 4.79.

4,7-Anhydro-1,2,3-trideoxy-D-*altro*(*allo*)-oct-1-ene (4). Sodium (0.23 g, 10 mmol) was reacted carefully with ethanol (25 mL), and the resulting solution was added to a stirred solution of a mixture of **1a** and **1b** (4.75 g, 11 mmol) in absolute ethanol (35 mL) at room temperature. Stirring was continued for 1 h while the solution was protected from moisture with a calcium sulfate drying tube. The pH of the solution was adjusted to pH 7 with ethanol-washed Dowex 50W-X8 cation-exchange resin (H^+). The resin was collected by filtration and rinsed twice with 25-mL portions of hot ethanol. The combined filtrates were then evaporated to afford a golden syrup. This syrup was purified by filtration through a bed of silica gel (30 g) in a sintered-glass funnel (8-cm i.d.) by eluting first with methylene chloride to remove the ethyl benzoate and then with methylene chloride/methanol (5:1 v/v). The nucleoside-containing fractions (determined by TLC, solvent system j) were combined and evaporated to afford a colorless waxy material. This material was dried in vacuo (0.1 torr, 20 °C, 24 h) to yield compound **4**: 1.84 g (97%); R_f 0.78 (solvent system j), 0.38 (solvent system h); ^1H NMR (60 MHz, Me_2SO-d_6) δ 2.28 (2, m, H-3), 3.2–4.1 (m, 6, H-4, H-5, H-6, H-7, H-8a, H-8b), 5.1 (m, 2, H-1), 5.53–6.20 (m, 1 H-2), 4.5–5.0 (m, 3, OH). Anal. Calcd for $C_8H_{14}O_4$: C, 53.77; H, 8.18. Found: C, 53.93; H, 8.27.

Ethyl 3,6-Anhydro-2-deoxy-4,5,7-tri-*O*-benzoyl-D-*altro*-heptonate (5a) and Ethyl 3,6-Anhydro-2-deoxy-4,5,7-tri-*O*-benzoyl-D-*allo*-heptonate (5b). A solution of **3** (0.10 g, 0.22 mmol) and *p*-toluenesulfonic acid (1 mg) in ethanol (10 mL) was heated at reflux for 16 h and then evaporated to afford a colorless syrup. This syrup was coevaporated six times with absolute ethanol (15-mL portions). Chromatography under low pressure on silica gel (3 cm i.d. × 30 cm column; 17% ethyl acetate in hexanes, v/v) followed by evaporation of appropriate fractions (determined by TLC, solvent system b) afforded the separated, colorless syrups **5a** and **5b** (combined weight of 0.084 g, 80% yield). Spectral data are included below since they did not appear in the original reference[10] for the synthesis of these compounds.

Compound 5a:[10] R_f 0.15 (solvent system b); $[\alpha]^{16}_D$ +63.4° (*c* 1.0, $CHCl_3$); ^1H NMR (60 MHz, $CDCl_3$) δ 1.12 (t, 3, CH_2CH_3), 2.83 (d, 2, $J_{2,3}$ = 7 Hz, H-2), 4.07 (q, 2, CH_2CH_3), 4.5–4.7 (m, 3, H-6, H-7a, H-7b), 4.97 (dt, 1, $J_{3,2}$ = 7 Hz, $J_{3,4}$ = 4 Hz, H-3), 5.7–6.2 (m, 2, H-4, H-5), 7.1–8.3 (m, 15, aromatic). Anal. Calcd for $C_{30}H_{28}O_9$: C, 67.66; H, 5.30. Found: C, 67.89; H, 5.45.

Compound 5b:[10] R_f 0.27 (solvent system b); $[\alpha]^{16}_D$ +27.5° (*c* 1.0, $CHCl_3$); ^1H NMR (60 MHz, $CDCl_3$) δ 1.17 (t, 3, CH_2CH_3), 2.77 (d, 2, $J_{2,3}$ = 7 Hz, H-2), 4.08 (q, 2, CH_2CH_3), 4.4–4.8 (m, 4, H-3, H-6, H-7a, H-7b), 5.4–5.8 (m, 2, H-4, H-5), 7.2–8.3 (m, 15, aromatics). Anal. Calcd for $C_{30}H_{28}O_9$: C, 67.66; H, 5.30. Found: C, 67.84; H, 5.38.

Ethyl 4-(2,3,5-Tri-*O*-benzoyl-D-ribofuranosyl)acetoacetate (6). A solution of the acid **3** (13.80 g, 27.4 mmol) in ether (40 mL), thionyl chloride (40 mL), and DMF (several drops added to catalyze the reaction) was heated at reflux for 3 h. The solvents were removed in vacuo, leaving a residue which was dissolved in and coevaporated twice with dry benzene (30 mL, distilled over sodium). The resulting acid chloride was dried at 35 °C (0.5 mmHg, 2 h), dissolved in dry THF/methylene chloride (50 mL, 5:1 v/v), and then used in the following reaction.

To dry THF (200 mL, distilled over $LiAlH_4$) were added ethyl hydrogen malonate (7.23 g, 54.7 mmol) and 2,2′-bipyridyl (2 mg). The solution was cooled to −65 °C under a nitrogen atmosphere. A solution of *n*-butyllithium (68.4 mL of a 1.6 M solution in dry *n*-hexane) was added dropwise to the solution of ethyl hydrogen malonate until a persistent pink color was achieved (about 33 mL). The solution was then allowed to slowly warm to 0 °C, and additional base was continually added to maintain the pink color. After the permanent pink color was achieved at 0 °C, the solution was recooled (−65 °C), and the acid chloride solution from above was added dropwise over 30 min, while the temperature was maintained at −65 °C. The mixture was allowed to warm to 0 °C after a 2-h reaction time and then quenched by adding it to a well-stirred mixture of ether (400 mL) and 1 N hydrochloric acid (150 mL). The aqueous layer was separated and washed with ether (1 × 100 mL). The organic layers were combined and washed with a saturated sodium bicarbonate solution (3 × 75 mL) and a saturated sodium chloride solution (2 × 75 mL) and dried over magnesium sulfate. Filtration and evaporation of the filtrate

yielded a golden syrup (15.2 g). A portion of this syrup (3.00 g) was chromatographed on silica gel (Lobar, size C) by eluting with hexanes/ethyl acetate (5:1 v/v) at a flow rate of 12 mL/min. Proper fractions (determined by TLC, solvent system a) were pooled and evaporated in vacuo to give the colorless syrup **5** (2.58 g, 86%) in an anomeric ratio of 4:1 (α/β).

Compound 6. R_f 0.25, 0.32 (solvent system a); t_r = 10.6, 10.9 min [Whatman ODS-3; gradient using methanol/acetonitrile/water, 50:30:20 (v/v/v) to 50:50:0 (v/v/v) over 15 min]; ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.12 (m, 3, CH_3), 3.02 (d, 2, H-4), 3.45 (s, 2, H-2), 4.58–6.13 (m, 6, H-1′, H-2′, H-3′, H-4′, H-5′), 7.0–8.2 (m, 15, aromatic). Anal. Calcd for $C_{32}H_{30}O_{10}$: C, 66.89; H, 5.28. Found: C, 66.76; H, 5.35.

Ethyl 4-(2,3,5-Tri-*O*-benzoyl-α-D-ribofuranosyl)-2-(phenyldiazo)acetoacetate (7a) and Ethyl 4-(2,3,5-Tri-*O*-benzoyl-β-D-ribofuranosyl)-2-(phenyldiazo)acetoacetate (7b). A solution of compound **6** (4:1 α/β mixture; 1.31 g, 2.31 mmol) and sodium acetate (0.5 g) in ethanol (75 mL) and water (5 mL) was treated with a 0.44 M solution of benzenediazonium chloride (5.0 mL) dropwise at 5 °C. After 30 min the solution was poured into a mixture of methylene chloride (500 mL) and water (100 mL). The organic layer was separated, washed with 1 N hydrochloric acid (2 × 50 mL), 5% sodium bicarbonate solution (1 × 75 mL), and saturated sodium chloride solution (1 × 50 mL), and then dried over magnesium sulfate. Filtration and evaporation of the filtrate yielded a brown foam which was dissolved in the minimal amount of toluene and chromatographed on silica gel (120 g; column, 3.5-cm i.d.) by eluting with solvent system f. Proper fractions (TLC, solvent system f) were collected and evaporated to afford a yellow foam, 1.52 g (98%) as a mixture of compounds **7a** and **7b**. Separation of a small amount (0.16 g) of the mixture of **7a** and **7b** was accomplished by using low-pressure chromatography on silica gel (Lobar, size A) and eluting with solvent system a.

Compound 7a: 0.12 g; R_f 0.28 (solvent system f); ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.33 (t, 3, CH_2CH_3), 3.52 (d, 2, H-4), 4.32 (q, 2, CH_2CH_3), 4.63–6.32 (m, 6, H-1′, H-2′, H-3′, H-4′, H-5′), 7.0–8.2 (m, 20, aromatic), 12.92 (s, 1, NH). Anal. Calcd for $C_{36}H_{34}N_2O_{10}$: C, 67.25; H, 5.05; N, 4.13. Found: C, 67.39; H, 5.13; N, 3.93.

Compound 7b: 0.03 g; R_f 0.37 (solvent system f); ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.37 (t, 3, CH_2CH_3), 3.43 (d, 2, H-4), 4.32 (q, 2, CH_2CH_3), 4.60–5.97 (m, 6, H-1′, H-2′, H-3′, H-4′, H-5′), 7.0–8.3 (m, 20, aromatic), 12.93 (s, 1, NH). Anal. Calcd for $C_{36}H_{34}N_2O_{10}$: C, 67.25; H, 5.05; N, 4.13. Found: C, 67.13; H, 5.20; H, 3.94.

Ethyl 4-(D-Ribofuranosyl)-2-(phenyldiazo)acetoacetate (8). A solution of the mixture of **7a** and **7b** (0.34 g, 0.5 mmol) in absolute ethanol (10 mL) was cooled to −10 °C and then treated with sodium (0.013 g) dissolved in ethanol (10 mL). The resulting solution was stirred at −5 °C for 16 h and then neutralized to pH 7 with Dowex 50W-X4 cation-exchange resin (H^+). The resin was collected by filtration and washed with hot ethanol (2 × 10 mL). The combined alcohol filtrates were evaporated to give a reddish foam which was dissolved in the minimal amount of ethyl acetate (2 mL) and purified by low-pressure chromatography (Lobar, size B; ethyl acetate/methanol, 40:1 v/v; 4 mL/min). The proper fractions (TLC, solvent system k) were pooled and evaporated to afford a yellow oil. This oil solidified spontaneously to give compound **8** (0.125 g, 81%). Crystallization from hexanes/ethyl acetate yielded an analytical sample.

Compound 8: mp 117–120 °C; R_f 0.2 (solvent system k); $[\alpha]^{23}_D$ −14.5° (*c* 1.4, methanol); ^{1}H NMR (360 MHz, acetone-d_6) δ 1.33 (t, CH_2CH_3), 3.18 (m, H-4a, H-4b), 4.31 (m, CH_2CH_3), 4.30–3.50 (m, H-1′, H-2′, H-3′, H-4′, H-5′a, H-5′b, 2′-OH, 3′-OH, 5′-OH), 7.35 (m, aromatics), 12.26 (s, major NH), 14.51 (s, minor NH). Anal. Calcd for $C_{17}H_{22}N_2O_7$: C, 55.73; H, 6.05; N, 7.65. Found: C, 55.57; H, 6.01; N, 7.48.

Ethyl 2-[(*p*-Chlorophenyl)diazo]-4-(2,3,5-tri-*O*-benzoyl-D-ribofuranosyl)acetoacetate (9). The α/β mixture **6** (2.58 g, 4.5 mmol) was dissolved in ethanol (125 mL) and water (10 mL), and sodium acetate (3.3 g) was then added to the solution. A solution of *p*-chlorobenzenediazonium chloride [generated from *p*-chloroaniline, (0.57 g), sodium nitrite (0.31 g), and 6 N hydrochloric acid (2 mL)] was then added dropwise to the above solution at 5 °C. After 30 min the ice-cold solution was filtered, and the yellow precipitate was washed with water (3 × 20 mL). After air drying, the solid was dissolved in ethyl acetate (75 mL), dried over magnesium sulfate, filtered, and evaporated to afford compound **9** as an orange foam (3.18 g, 99%). This foam was crystallized from hexanes/ethyl acetate.

Compound 9: mp 75–78 °C; R_f 0.36, 0.51 (solvent system a); ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.33 (t, CH_2CH_3), 3.53 (m, H-4a, H-4b), 4.32 (dq, CH_2CH_3), 4.53–5.30 (m, H-1′, H-4′, H-5′a, H-5′b), 5.63–6.20 (m, H-2′, H-3′), 7.20–8.23 (m, 19, aromatic), 12.87 (s, major NH), 14.70 (s, minor NH). Anal. Calcd for $C_{38}H_{33}O_{10}N_2Cl$: C, 64.00; H, 4.66; N, 3.93. Found: C, 63.89; H, 5.00; H, 3.83.

2-Amino-6-[(α- and β-D-ribofuranosyl)methyl]pyrimidin-4-one (10). A mixture of compound **6** (80 mg, 0.14 mmol) and guanidine carbonate (38 mg, 0.21 mmol) in absolute ethanol (5 mL) was stirred at room temperature for 1 h. The mixture was heated at reflux for 3 h and then allowed to stand at room temperature for an additional 48 h. The solution was evaporated and chromatographed on silica gel (10 g, 2.0-cm i.d. column) with ethyl acetate/methanol (3:1 v/v) to remove the ethyl benzoate and then with ethyl acetate/methanol (2:1 v/v) to obtain the product. The proper fractions (TLC, solvent system l) were pooled and evaporated to afford a solid which was lyophilized from water at −70 °C (0.035 torr), yielding compound **10**: 20 mg (56%): mp 225 °C dec; R_f 0.15 (solvent system l); ^{1}H NMR data were in agreement with reported[16] literature values. Anal. Calcd for $C_{10}H_{15}N_3O_5 \cdot {}^1/_3H_2O$: C, 45.63: H, 6.00; N, 15.96. Found: C, 46.06; H, 6.14; N, 15.61.

4-(2,3,5-Tri-*O*-benzoyl-D-ribofuranosyl)acetoacetonitrile (12). Method 1. A solution of **3** (0.15 g, 1.01 mmol; dried by azeotropic coevaporation with benzene) and *tert*-butyl cyanoacetate (0.14 g, 1.01 mmol) in dry DMF (8 mL; 4-Å sieves) was cooled to 0 °C and maintained under a nitrogen atmosphere. Diethyl phosphorocyanidate[19] (0.02 g, 0.2 mL, 1.2 mmol) was added through a septum followed by the addition of triethylamine (0.33 g, 3.2 mmol, 0.45 mL). The solution was stirred at 0 °C for 2 h and then at 25 °C for 40 h. The DMF was evaporated, and the remaining dark brown residue was dissolved in benzene/ethyl acetate (40 mL, 1:1 v/v). After being washed with 10% sulfuric acid (3 × 15 mL), saturated sodium bicarbonate solution (1 × 15 mL), and saturated sodium chloride solution (2 × 15 mL), the solution was dried over magnesium sulfate. Filtration and evaporation of the filtrate yielded a brown syrup which was chromatographed on silica gel (20 g, 3-cm i.d. column) by eluting with diethyl ether. The intermediate (**11**, 0.50 g) was isolated by pooling and evaporating the appropriate fractions (determined by TLC, solvent system d): ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.3 (s, 9, *t*-Bu), 3.0 (m, 2, H-4), 4.4–6.0 (m, 6, sugar protons), 7.2–8.2 (m, 15, aromatic); IR (film) 2224 cm^{-1} (CN).

A solution of crude **11** (0.35 g, 0.6 mmol) and *p*-toluenesulfonic acid monohydrate (80 mg) in dry toluene (30 mL) was heated at reflux for 16 h. The solution was cooled to room temperature, diluted with ethyl acetate (15 mL), washed with saturated sodium bicarbonate solution (1 × 10 mL) and saturated sodium chloride solution (2 × 10 mL), and then dried over magnesium sulfate. Filtration and evaporation of the filtrate yielded a brown syrup which was chromatographed on a silica gel column (2 cm i.d. × 20 cm) by eluting with hexanes/ethyl acetate (25:1 v/v). The proper fractions (TLC, solvent system d) were pooled and evaporated to yield a syrup of **12a** and **12b** as a colorless mixture: 0.16 g (36% from **3**; ratio of **12a**/**12b** was 8:3).

Compounds 12a and 12b: R_f 0.40, 0.46 (solvent system d), 0.10, 0.15 (solvent system a); t_r = 11.91, 12.47 min [Whatman ODS-3; methanol/acetonitrile/water gradient, 30:30:40 (v/v/v) to 40:40:20 (v/v/v) over 10 min; flow rate = 1.5 mL/min]; ^{1}H NMR (360 MHz, $CDCl_3$) for **12b**[25] δ 2.96 (dd, H-4b, $J_{4b,4a}$ = 16 Hz, $J_{4b,1'}$ = 7.8 Hz), 3.06 (dd, H-4a, $J_{4a,1'}$ = 3.8 Hz, $J_{4a,4b}$ = 16 Hz), 3.51 (d, H-2b, $J_{2b,2a}$ = 20 Hz), 3.59 (d, H-2a, $J_{2a,2b}$ = 20 Hz), 4.53 (m, H-5′), 4.58 (m, H-1′), 4.73 (m, H-4′), 5.39 (t, H-3′, J = 6.5 Hz), 5.68 (t, H-2′, J = 5.3 Hz). Anal. Calcd for $C_{30}H_{25}NO_8$: C, 68.31; H, 4.78; N, 2.66. Found: C, 68.02; H, 4.85; N, 2.46.

Method 2. *n*-Butyllithium (5.15 mL, 1.6 M solution in *n*-hexane) was added dropwise to a solution of cyanoacetic acid (dried as a solution in ethyl acetate for 24 h over magnesium

(25) The 360-MHz ^{1}H NMR spectrum was obtained on a mixture of **12a** and **12b**, but since pure **12a** was obtained in the second procedure only, the signals for **12b** are recorded here. See the second procedure which follows for those of **12a**.

sulfate; 0.35 g, 4.1 mmol) and 2,2'-bipyridyl (1 mg) in THF (dry, 50 mL) under a nitrogen atmosphere at -60 °C. During the addition, the solution was allowed to warm to 5 °C. When the permanent pink end point was reached, the solution was recooled to -60 °C. A solution of the acid chloride of **3** (1.04 g, 2.06 mmol of **3**; prepared as usual in ether, thionyl chloride, and DMF and thoroughly dried in vacuo prior to use) in dry methylene chloride (15 mL) was then added dropwise over a period of 10 min. The mixture was stirred at -60 °C for 1 h, allowed to warm to 25 °C, and then poured into a flask containing diethyl ether (100 mL) and 1 N hydrochloric acid (30 mL). The resulting biphasic solution was stirred vigorously for 30 min. The organic layer was separated, washed with a saturated sodium bicarbonate solution (3 × 20 mL) and a saturated sodium chloride solution (3 × 20 mL), and then dried over magnesium sulfate. Filtration and evaporation of the filtrate afforded a residue which was purified by low-pressure chromatography (3 cm i.d. × 30 cm silica column; hexanes/ethyl acetate, 2:1 v/v; flow rate 12 mL/min). The desired fractions (indicated by UV monitoring) were collected and evaporated to a glass. Tritration with hexanes produced compound **12a** (0.45 g, 45%) as a solid which was crystallized from methanol.

Compound 12a: mp 141-141.5 °C; R_f 0.4 (solvent system d); $[\alpha]^{23}_D$ +89.3° (*c* 1.0, $CHCl_3$); IR (KBr) 2250 cm^{-1} (CN); ^1H NMR (360 MHz, $CDCl_3$) δ 2.94 (dd, H-4b, $J_{4b,4a}$ = 17 Hz, $J_{4b,1'}$ = 5.5 Hz), 3.14 (dd, H-4a, $J_{4a,4b}$ = 17 Hz, $J_{4a,1'}$ = 7.8 Hz), 3.51 (s, H-2), 4.53 (dd, H-4', $J_{4',5'}$ = 13 Hz, $J_{4',3'}$ = 6.0 Hz), 4.64 (m, H-5'a,H5'b), 4.90 (ddd, H-1', $J_{1',2'}$ = 4.6 Hz, $J_{1',4b}$ = 5.5 Hz, $J_{1',4a}$ = 7.8 Hz), 5.77 (dd, H-3', $J_{3',2'}$ = 4.6 Hz, $J_{3',4'}$ = 6.0 Hz), 5.91 (t, H-2', *J* = 4.6 Hz), 7.2-8.0 (m, aromatics). Anal. Calcd for $C_{30}H_{25}NO_8$: C, 68.31; H, 4.78; N, 2.66. Found: C, 68.28; H, 4.77; N, 2.58.

2-(Phenyldiazo)-4-(2,3,5-tri-*O*-benzoyl-α-D-ribofuranosyl)acetoacetonitrile (13a) and 2-(Phenyldiazo)-4-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)acetoacetonitrile (13b). Compound **12** (0.13 g, 0.25 mmol) was dissolved in a mixture of ethanol (10 mL), sodium acetate (0.1 g), and water (1 mL). This mixture was cooled to 5 °C and treated dropwise with a 0.44 M of benzenediazonium chloride (0.8 mL). The resulting yellow mixture was stirred for 1 h. Methylene chloride (50 mL) was added to the mixture, and the organic layer was separated, washed with saturated sodium bicarbonate solution (2 × 10 mL) and with a saturated sodium chloride solution (2 × 10 mL), and then dried over magnesium sulfate. Filtration and evaporation of the filtrate afforded a semisolid which was a mixture of compounds **13a** and **13b**, 0.16 g (100%). Column chromatography (silica gel, 30 g, 3 cm i.d. column, solvent system f) was used to separate the anomers **13a** and **13b** which were isolated after pooling and evaporation of the appropriate fractions (TLC, solvent system f). The α/β ratio (**13a**/**13b**) was essentially the same as that of the starting material **12**.

Compound 13a: yellow oil; R_f 0.13 (solvent system g); ^1H NMR (360 MHz, $CDCl_3$) δ 3.29 (m, H-4a, H-4b), 4.47 (m, H-4'), 4.60 (m, H-5'a, H-5'b), 5.01 (m, H-1'), 5.78 (dd, H-3'), 5.94 (dd, H-2'), 7.2-8.0 (m, 19, aromatic), 14.63 (s, NH). Anal. Calcd for $C_{36}H_{29}N_3O_8$: C, 68.46; H, 4.63; N, 6.65. Found: C, 68.56; H, 4.70; N, 6.51.

Compound 13b: yellow needles: mp 159.0-160.5 °C; R_f 0.1 (solvent g); ^1H NMR (360 MHz, $CDCl_3$) δ 3.32 (m, H-4a, H-4b), 4.50-4.69 (m, H-5'a, H-5'b), 4.7-4.8 (m, H-1', H-4'), 5.58 (dd, H-2'), 5.69 (pseudo t, H-3'), 7.2-8.1 (m, 19, aromatic), 14.63 (s, NH). Anal. Calcd for $C_{36}H_{29}N_3O_8$: C, 68.46; H, 4.63; N, 6.65. Found: C, 68.43;, H, 4.89; N, 6.32.

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Registry No. **1a**, 83023-37-4; **1b**, 82921-67-3; α-**2**, 83476-38-4; β-**2**, 83476-39-5; α-**3**, 50907-76-1; β-**3**, 50907-75-0; **3** acid chloride, 83572-02-5; α-**4**, 83476-40-8; β-**4**, 83540-89-0; **5a**, 50907-77-2; **5b**, 50907-78-3; α-**6**, 83486-30-0; β-**6**, 83476-41-9; **7a**, 83476-42-0; **7b**, 83476-43-1; α-**8**, 83476-44-2; β-**8**, 83476-45-3; α-**9**, 83476-46-4; β-**9**, 83476-47-5; α-**10**, 66358-88-1; β-**10**, 66358-89-2; α-**11**, 83476-48-6; β-**11**, 83540-90-3; **12a**, 83476-49-7; **12b**, 83476-50-0; **13a**, 83476-51-1; **13b**, 83542-11-4; 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose, 6974-32-9; allyltrimethylsilane, 762-72-1; guanidine carbonate, 3425-08-9; *tert*-butyl cyanoacetate, 1116-98-9; cyanoacetic acid, 372-09-8; benzenediazonium chloride, 100-34-5.

Secondary α-Deuterium Kinetic Isotope Effects in Solvolyses of Ferrocenylmethyl Acetate and Benzoate in Ethanol[1a]

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Secondary α-deuterium kinetic isotope effects (KIE) in solvolyses of ferrocenyldideuteriomethyl acetate and benzoate were determined in 96% (v/v) ethanol, at 25 °C, as k_H/k_D = 1.24 and 1.26, respectively. The KIEs were also determined in the presence of 0.1 mol dm^{-3} lithium perchlorate: the k_H/k_D values were 1.23 and 1.22 for acetate and benzoate complexes, respectively. The maximum KIE for the C-O bond cleavage of a primary substrate is as large as, or larger than, that of secondary derivatives, which is estimated to be 1.23 per deuterium. The measured KIE of about 12% per D therefore represents a strongly reduced effect relative to its maximum. The solvolyses exhibit "a special salt effect". This effect indicates the presence of solvent-separated ion pairs and the return to tight pairs. As the maximum KIE is expected in solvolyses involving transformation of one type of ion pair into another, the strongly reduced α-D KIE supports the structure involving direct participation of electrons that in the ground state are localized at the iron atom. The alkyl-oxygen cleavage is accompanied by 10-15% acyl-oxygen cleavage.

The structure and stability of the α-ferrocenyl carbocations have been extensively studied,[2,3] but the structure of the ferrocenylmethyl cation ($FcCH_2^+$) is still a subject of debate. The dilemma is whether the electrons involved

(1) (a) Taken from the Ph.D. thesis (in preparation) by D. Šutić, to be submitted to the Faculty of Pharmacy and Biochemistry, University of Zagreb; (b) University of Sarajevo, Sarajevo; (c) University of Zagreb.

(2) Uršič, S.; Ašperger, S. *J. Inorg. Nucl. Chem.* **1979**, *41*, 1329 and references therein.

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