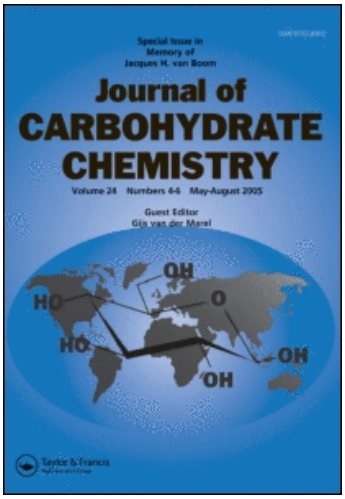

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DIBORANE REDUCTION OF O-(TERT-BUTYLDIMETHYLSILYL)GALACTARAMIDES. A MODEL STUDY FOR AMINOALDITOL SYNTHESIS[1]

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ABSTRACT

Tert-butyldimethylsilylation of dimethyl galactarate (1) with tert-butylchlorodimethylsilane/imidazole/N,N-dimethylformamide at 25 °C gave dimethyl 2,5-bis-O-(tert-butyldimethylsilyl)galactarate (2) as the principal product, with methyl 2,3,5-tris-O-(tert-butyldimethylsilyl)-D,L-galactarate-1,4-lactone (3) and methyl 2,3-bis-O-(tert-butyldimethylsilyl)-D,L-galactarate-1,5-lactone (4) as minor products. When the reaction was carried out at 65 °C, the only product was the 1,4-lactone, 3. Ammonolysis of 2 in methanol gave 2,5-bis-O-(tert-butyldimethylsilyl)-galactaramide (5, 94%), which was conveniently reduced with borane-THF to 1,6-diamino-1,6-dideoxygalactitol, isolated as its dihydrochloride 9. Ammonolysis of 3 in methanol gave a mixture of 5; 2,3,4-tris-O-(tert-butyldimethylsilyl)-D,L-galactaramide (6), 2,3,5-tris-O-(tert-butyldimethylsilyl)-D,L-galactaramide (7), and 2,3,5-tris-O-(tert-butyldimethylsilyl)-D,L-1,4-lactonogalactaramide (8). Borane-THF reduction of a mixture of 6 and 7 also yielded 9. This study served as a model for the use of O-silylated carbohydrate amides in the preparation of aminodeoxyalditols.

INTRODUCTION

Terminal diaminodideoxyalditols are not known to be naturally occurring compounds, but a number of them and their derivatives have been synthesized.[1-11] Derivatives of diaminodideoxyalditols have been used as chelating agents[4] and as the diamine monomers in the synthesis of Nylon-type polymers.[5,12] N-substituted diaminodideoxyalditols have

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also been employed as antitumor and antileukemia agents.[13-15] Interest in this laboratory in aldaric acid chemistry prompted us to pursue a general synthesis of diaminodideoxyalditols from aldaric acid diamides (aldaramides). Two features of the proposed synthesis that were deemed of particular importance were; (1) use of a hydroxyl protecting group that was independent of the length and stereochemistry of aldaramide, and (2) employment of an efficient and convenient amide reducing agent. This report represents a model study for the proposed general synthesis, with 1,6-diaminodideoxygalactitol dihydrochloride (9) as the target compound, the tert-butyldimethylsilyl (TBDMS) group serving as a hydroxyl protector, and borane-THF acting as the reducing agent.

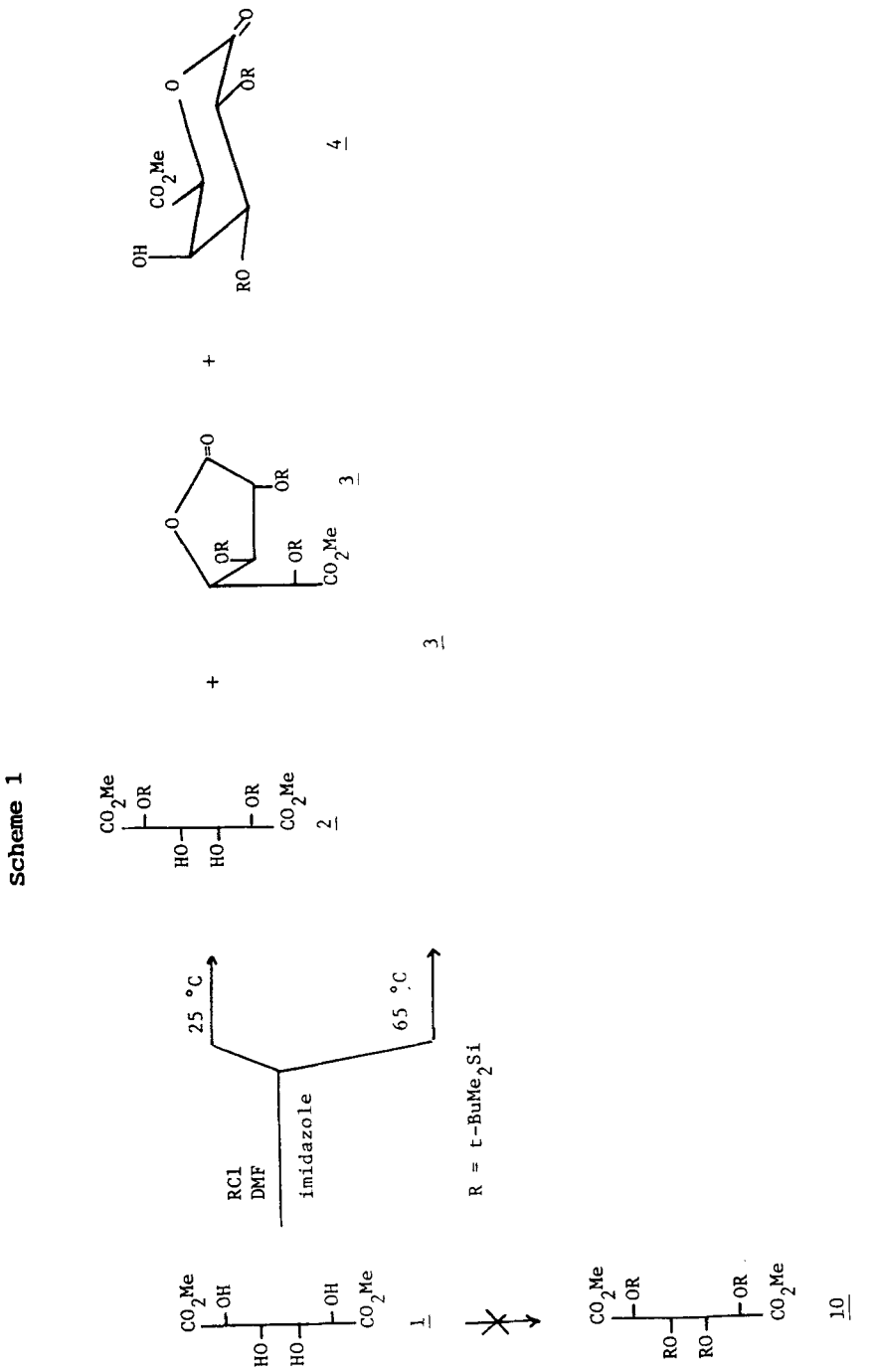
RESULTS AND DISCUSSION

The planned four-step synthesis of 1,6-diamino-1,6-dideoxygalactitol dihydrochloride (9) from dimethyl galactarate (1) was patterned after a synthesis of 9 reported by Morgan and Wolfrom.[10] In the Morgan and Wolfrom synthesis, the four hydroxyl groups were protected as di-O-isopropylidene ketals, and the amide reducing agent was lithium aluminum hydride. In our designed synthesis, the TBDMS group was chosen to protect the hydroxyl functions, with borane-THF to be used for amide reduction.

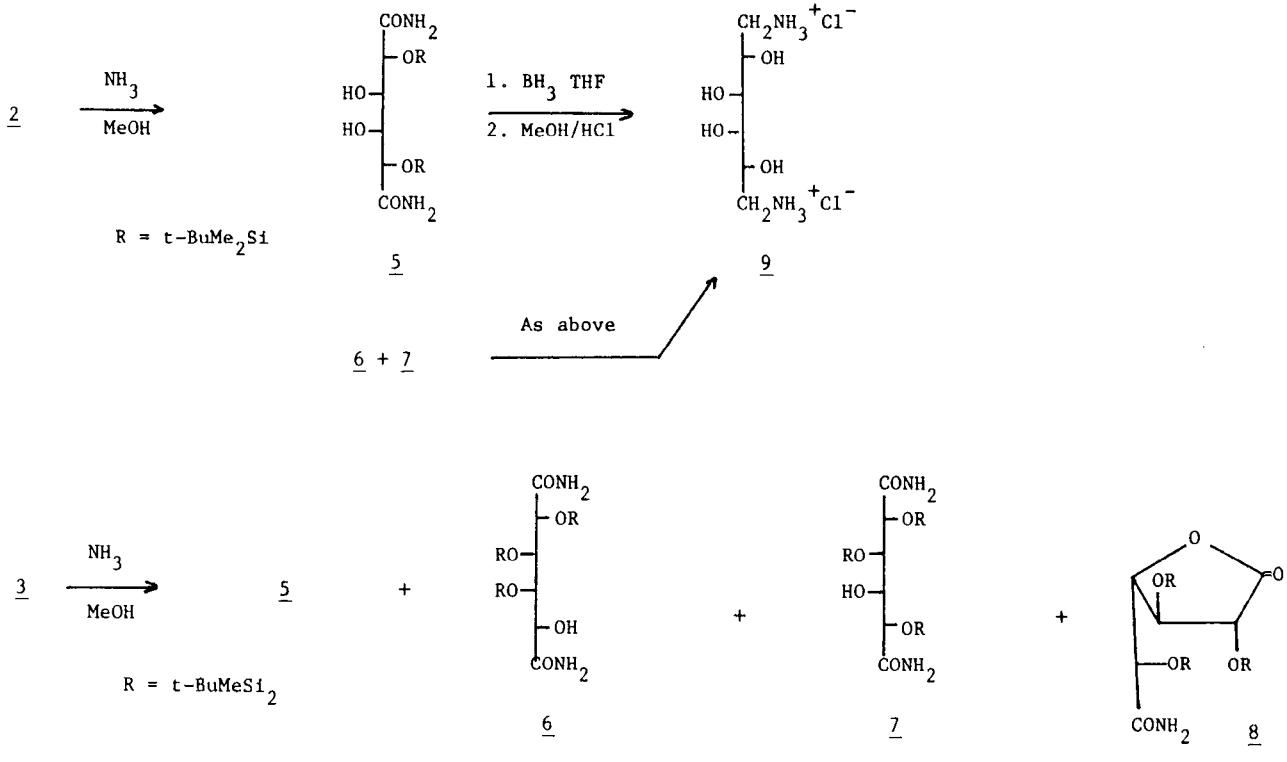
Tert-butyldimethylsilylation of Dimethyl Galactarate

It was anticipated that the reaction of 1 with tert-butylchlorodimethylsilane in DMF containing imidazole[16] would give acyclic dimethyl tetrakis-O-(tert-butyldimethylsilyl)galactarate (10, Scheme 1). However, when dimethyl galactarate (1) was tert-butyldimethylsilylated at room temperature, three products were formed. The major product formed in the reaction was dimethyl 2,5-bis-O-(tert-butyldimethylsilyl)-galactarate (2). The two minor products were methyl 2,3,5-tris-O-(tert-butyldimethylsilyl)-D,L-galactarate-1,4-lactone (3) and methyl 2,3-bis-O-(tert-butyldimethylsilyl)-D,L-galactarate-1,5-lactone (4). Trituration of the crude semisolid product mixture with pentane yielded insoluble 2 (36%) and a residue which was purified by silica gel flash chromatography to give 3 (11 %), 4 (11 %) and additional 2 (5 %).

Scheme 1



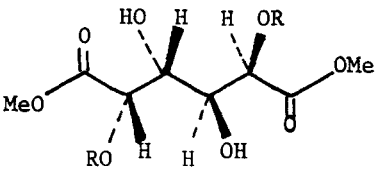
Scheme 2



Carrying out the reaction at 65 °C for 24 hours gave only 3, isolated as an oil.

The location of the two TBDMS groups on 2 was deduced from its ^{1}H NMR spectrum in $CDCl_3$. Equivalent H-2 and H-5, the most deshielded protons on 2, were observed as a singlet (4.65 ppm), indicating that the hydroxyl groups on C-2 and C-5 were protected as their TBDMS ethers. In contrast, the signal from the more shielded H-3 and H-4 protons (3.78 ppm) was split, although partially obscured by the methyl ester singlet. Also split was the signal from the C-3 and C-4 hydroxyl protons (2.55 ppm), this signal disappearing upon addition of D_2O to the sample. The singlet nature of these backbone protons was rationalized after a consideration of the conformations of some model compounds previously described in the literature.

Acyclic galactose derivatives strongly prefer extended zig-zag conformations in solution, as determined from NMR studies on the penta-O-acetyl derivatives of galactononitrile,[17] galactose dimethyl acetal,[18] and galactose diethyl dithioacetal.[18] The extended conformation is favored since it lacks conformationally destabilizing interactions between parallel 1,3-substituents. The same extended zig-zag conformational preference was also noted for galactaric acid in the solid state.[19] That the ^{1}H NMR signals of the backbone protons of 2 should appear as two broadened singlets after deuterium (D_2O) exchange of OH supports an extended zig-zag conformation for this compound in $CDCl_3$. In this conformation (Fig.1) compound 2 has an alternating axis of symmetry between C-3 and C-4. Consequently, H-3 and H-4 are magnetically equivalent protons[20] and would not show mutual coupling. Furthermore, relative to the model compounds described,[17-18] very small coupling between the gauche protons H-2, H-3 and H-5, H-4 of 2 is expected. Interestingly, the torsional angle H-2, C-2, C-3, H-3 for symmetrical crystalline galactaric acid is 83.4°,[19] an angle if maintained in solution would have approximately zero coupling according to the Karplus rule.[21] This angular relationship does in fact carry over into solution as H-2, H-5 and H-3, H-4 of galactaric acid in D_2O are each observed as slightly broadened singlets (4.56 and 4.09 ppm), as are H-2, H-5 and H-3, H-4 of dimethyl galactarate (4.58 and 4.08 ppm). These latter compounds, as well as 2, adopt a fully extended zig-zag conformation in solution.



R = tert-$BuMe_2Si$

Figure 1. Extended conformation for 2.

The two minor products from the room temperature reaction were both methyl ester lactones, 3, a 1,4-lactone, and 4, a 1,5-lactone. The IR spectrum of 3 contained two distinct carbonyl absorbances, an ester carbonyl at 1760 cm^{-1} and the 1,4-lactone at 1800 cm^{-1}. A single peak (1760 cm^{-1}) for both the methyl ester and 1,5-lactone carbonyls was observed in the IR spectrum of 4. In the ^1H NMR spectrum of 3, each of the H-2 to H-5 resonances was cleanly separated and readily assigned using proton decoupling techniques. However, the corresponding proton signals from 4 were tightly clustered (4.30-4.45 ppm) and assigned only with the aid of spectral simulation. The simulated spectrum of 4 (H-2 to H-5) was compared to the portion of the recorded spectrum wherein the coupling contribution from the single OH (doublet at 2.68 ppm) was eliminated by D_2O exchange.

Ammonolysis of 2 and 3

The ammonolysis of the major product from the room temperature tert-butyldimethylsilylation of acyclic 2 proceeded rapidly in ammonia saturated methanol to give insoluble 2,5-bis-O-(tert-butyldimethylsilyl)-galactaramide (5, 91%). Determining the structure of 5 was complicated by the fact that this high melting compound (mp 305 °C) was insoluble in organic solvents and its ^1H-NMR spectrum could not be obtained. However, the assigned structure for 5 was supported by an appropriate amide carbonyl IR absorption (1670 cm^{-1}), a correct elemental analysis, and an electron impact direct probe mass spectrum with M - tert-butyl and M/2 peaks. Since the TBDMS groups on 2 were located at C-2 and C-5, these groups must be located on the same carbons of 5.

Ammonolysis of 3 in methanol at room temperature and atmospheric pressure was ineffective, whereas ammonolysis in a pressure tube at room temperature and 40 psi (four days) gave four products. A high melting solid (305 °C), determined to be 5, crystallized from the reaction mixture as the reaction proceeded. After workup of the filtrate, a solid mixture of two isomeric TBDMS protected galactaramides was isolated; 2,3,4-tris-O-(tert-butyldimethylsilyl)-D,L-galactaramide (6) and 2,3,5-tris-O-(tert-butyldimethylsilyl)-D,L-galactaramide (7). Fractional crystallization of this mixture gave the individual products. The pressure ammonolysis experiment was repeated several times and in each instance 5 was the predominant crystalline product, with 6 and 7 being minor products.

Unlike 5, the tris-O-TBDMS galactaramides 6 and 7 were readily soluble in organic solvents. Consequently, the location of the free hydroxyl group on each molecule was ascertained from the corresponding ^{1}H NMR spectrum in $CDCl_3$. For 6, the C-5 proton was observed as a doublet of doublets which collapsed to a doublet after deuterium (D_2O) exchange with the lone hydroxyl proton. However, the multiplet from the C-4 proton of 7 changed to a doublet of doublets after deuterium exchange of the hydroxyl proton.

After fractional crystallization of 5, 6, and 7, the crude amorphous residue obtained was determined to be 2,3,5-tris-O-(tert-butyldimethylsilyl)-D,L-1,4-lactonogalactonamide (8). The IR spectrum of 8 had both amide and 1,4-lactone carbonyl absorptions (1690 and 1790 cm^{-1}). The ^{1}H NMR spectrum contained the characteristic broad doublet for 1^o amide protons (6.45 and 6.05 ppm) and integrated correctly for three TBDMS groups. This compound was not used for further purposes.

It was noted that while the acyclic diester 2 underwent ammonolysis readily, the lactone-ester 3 reacted slowly with ammonia. The reactivity of 2 is consistent with Hoagland's anchimeric assistance model[22] for the aminolysis of diethyl galactarate, as compared to the aminolysis of diethyl adipate. Drawing upon his own work and that of Ogata and co-workers,[23] Hoagland has shown that aminolysis of diethyl galactarate is anchimerically assisted by the C-4 OH group in forming a reactive 1,4-lactone intermediate. When the lactone cannot be formed, as is the case when the hydroxyl groups of diethyl galactarate are

protected as their isopropylidene derivatives, the aminolysis rate is significantly depressed. Using the Hoagland model, both ester functions of 2 can be converted to amides through successive 1,4-lactone intermediates. Although the order of steps in the ammonolysis of 3 to the product mixture 5-8 is not clear, solvolysis of one TBDMS group from 3 is required to give 5. Compound 6, with contiguous TBDMS groups at C-2, C-3, and C-4 results from the migration of a TBDMS group from C-5 to C-4 on some acyclic intermediate. Migrations of TBDMS groups to available hydroxyl groups have been previously observed.[24]

Borane-THF Reduction of 5-7

Borane-THF was chosen as the reducing agent for the amides 5-7 because of its appreciable reactivity and because workup with methanolic HCl is simple and also removes the TBDMS protecting groups. Isolated yields of 9 were 83% from 5, and 66% from a mixture of 6 and 7.

Conclusions

A synthesis of 9 from dimethyl galactrate utilizing TBDMS protecting groups and borane-THF as an amide reducing agent was carried out. While the reaction sequence used here to prepare 9 produced a number of new and interesting partially TBDMS protected derivatives of galactaric acid, it was complicated by the formation of multiple products at the tert-butyldimethylsilylation stage. However, the synthesis of 9 did serve as a model that led to the use of the trimethylsilyl (TMS) group as a hydroxyl protector in a procedure (as described in the following paper) for the general preparation of diterminal diaminodideoxyalditols and 1-amino-1-deoxyalditols.

EXPERIMENTAL

General Methods. Melting points were determined with a Fisher-Johns melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded at 90 MHz (Varian Model 390 spectrometer), 270 and/or 300 MHz (Nicolet Fourier-transform NMR spectrometers. Simulated ^{1}H NMR spectra were generated with a Nicolet NMCSIM spectral simulation program using a Nicolet NMC-1280 computer. Simulations for

a four-spin system required 4 K of data. IR spectra were recorded with a Beckman Acculab 4 spectrometer. MS analyses were carried out with a Hewett-Packard 5985 system. Solutions were concentrated under reduced pressure. Elemental analyses were performed by Atlantic Microlabs, P.O. Box 80569, Atlanta, GA 30366.

Tert-butyldimethylsilylation of Dimethyl Galactarate.

a. Tert-butylchlorodimethylsilane (3.2 g, 21 mmol) was added to an ice cold suspension of dimethyl galactarate[25] (1.19 g, 5 mmol) and imidazole (1.38 g, 20 mmol) in N,N-dimethylformamide (50 mL). The reaction mixture was allowed to come to room temperature (ca. 1 h), stirred for 16 h, diluted with ice cold water (50 mL) and extracted with dichloromethane (2 x 75 mL). The organic layer was dried ($MgSO_4$), concentrated, and pentane was added to the residue. Dimethyl 2,5-bis-O-(tert-butyldimethylsilyl)galactarate (2), 840 mg (36%), separated as crystals, mp 120-122 °C; IR (KBr) 3500 (OH) and 1750 cm^{-1} (ester C=0); ^1H NMR ($CDCl_3$, 90 MHz) δ 4.65 (2, s, H-2 & H-5), 3.78 (6, s, OCH_3; m, 2, H-3 & H-4), 2.55 (2, m, OH at C-3 & C-4), 0.95 (18, s, t-butyl), and 0.15 and 0.10 ppm (each s, each 6, $SiMe_2$).

Anal. Calcd for $C_{20}H_{42}O_8Si_2$ (466.72): C, 51.48; H, 9.09. Found: C, 51.59; H, 9.14.

The filtrate from crystallizing 2 was concentrated and subjected to flash chromatography on silica using toluene-acetone (19 : 1) as the eluent. The ester-lactone methyl 2,3,5-tris-O-(tert-butyldimethylsilyl)--D,L-galactarate-1,4-lactone (3) was obtained as an oil (312 mg, 11.4%); ^1H NMR ($CDCl_3$, 270 MHz) δ 4.49 (t, 1, H-3, $J_{2,3}$ = 5.13 Hz, $J_{3,4}$ = 3.66 Hz), 4.43 (d, 1, H-2), 4.37 (t, 1, H-4, $J_{4,5}$ = 5.13 Hz), 4.25 (d, 1, H-5), 3.78 (s, 3, OCH_3), 0.88 -0.97 (27, three s, tert-butyl) and 0.10-0.21 (18, 6s, SiMe). The spectrum of H-2 to H-5 was simulated using a spectrometer frequency of 270 MHz, a spectrum width of 350 Hz, an offset of 950 Hz, and a line width of 1.2 Hz. IR (neat) 1760 (ester C=O) and 1800 cm^{-1} (1,4-lactone C=O).

Anal. Calcd for $C_{25}H_{52}Si_3O_7$ (548.95): C, 54.70; H, 9.54. Found: C, 54.99; H, 9.83.

A second major fraction was obtained from the column chromatography as a mixture of two components (R_f = 0.35-0.45). This fraction was rechromatographed on silica gel using toluene-acetone (49:1) as the

eluent to give as pure materials, 2 (111 mg, 4.8%, total yield 2 = 41%) and methyl 2,3-bis-O-(tert-butyldimethylsilyl)-D,L-galactarate-1,5-lactone (4, 255 mg, 11.7%), mp 126-128 °C; IR 1760 cm^{-1} (ester and 1,5-lactone C=O); ^1H NMR ($CDCl_3$, 300 MHz) δ 4.398 (1, H-2, $J_{2,3}$ = 4.5 Hz) 4.396 (1, H-5, $J_{4,5}$ = 2.0 Hz), 4.340 (1, H-4, $J_{3,4}$ = 2:4 Hz), 4.330 (1, H-3), 2.777 (1, d, 4-OH, $J_{OH,H-4}$ = 2.7 Hz), 3.950 (3, s, OCH_3), 0.915, 0.940 (ea 9, ea s, tert-butyl) and 0.200, 0.165, 0.135, 0.115 ppm (ea 3, ea s, SiMe). Simulation of the H-2 to H-5 region of the spectrum after OH to OD exchange was calculated using a spectrometer frequency of 300 MHz, spectrum width of 185 Hz, an offset of 1080 Hz, and a line width of 1.0 Hz.

Anal. Calcd for $C_{19}H_{38}Si_2O_7$ (434.68): C, 52.50; H, 8.81. Found: C, 52.27; H, 8.81.

b. When the tert-butyldimethylsilylation of dimethyl galactarate was carried out at 65 °C for 24 h, methyl 2,3,5-tris-O-(tert-butyldimethylsilyl)-D,L-galactarate-1,4-lactone (3) was obtained as an oil, and as the only product (>90% isolated yield).

Ammonolysis of methyl 2,3,5-tris-O-(tert-butyldimethylsilyl)-D,-L-galactarate-1,4-lactone (3). A solution of 3 (2.55 g, 4.65 mmol) in methanol (5 mL) was diluted with cold (5 °C) anhydrous ammonia saturated methanol (30 mL). The reaction mixture was kept at room temperature and 40 psi of ammonia in a 100 mL pressure tube for four days. During the course of the reaction 2,5-bis-O-(tert-butyldimethylsilyl)-D,L-galactaramide crystallized (5, 0.47g, 23%), mp 305 °C after subliming above 295 °C. Compound 5 was insoluble in common polar and nonpolar organic solvents; IR (KBr) 3450, 3390 (amide NH) and 1670, 1635 cm^{-1} (amide C=O); direct probe electron impact mass spectrum 379 (M - tert-butyl), and 218 (M/2).

Anal. Calcd for $C_{18}H_{40}N_2O_6Si_2$ (436.70): C, 49.51; H, 9.23; N, 6.41. Found: C, 49.67; H, 9.27; N, 6.35.

The ammoniacal methanol solution was added to water (10 mL), and the turbid mixture was extracted with pentane (3 x 30 mL). The combined pentane extracts were gravity filtered through phase separating paper (Whatman #1, P/S), and allowed to concentrate to a smaller volume in an open flask in a fumehood.
2,3,4-Tris-O-(tert-butyldimethylsilyl)-D,L-galactaramide (6, 0.45 g,

17.5%) precipitated from the solution as cubes. The crude product was observed to be contaminated with a very small amount of a filamentous crystalline material (7). An analytical sample of 6 was crystallized from ethyl acetate, mp 194-195 °C; IR (KBr) 3380 (amide NH) and 1695 cm^{-1} (amide C=O); ^1H NMR ($CDCl_3$, 90 MHz) δ 6.65 and 6.30 (2, each broad s, $CONH_2$), 5.46 (2, broad s, $CONH_2$), 4.50 (1, s, H-2), 4.35 (1, dd, H-5, $J_{4,5}$ = 1.2 Hz, $J_{5,5\text{-OH}}$ = 3.6 Hz), 4.1 (1, d, H-3, $J_{3,4}$ = 4.8 Hz), 4.0 (1, dd, H-4, $J_{4,5}$ = 1.8 Hz), 0.80-0.75. (27, 3s, tert-butyl) and 0.1 ppm (18, s, $SiMe_2$).

Anal. Calcd for $C_{24}H_{54}O_6N_2Si_3$ (550.97): C, 52.32; H, 9.88; H, 5.08. Found: C, 52.09; H, 9.82; N, 5.05.

Futher evaporation of the pentane gave 2,3,5-tris-O-(tert-butyldimethylsilyl)-D,L-galactaramide (7, 0.2g, 4.6%) as filaments, mp 160-163 °C; IR (KBr) 3380 (amide NH) and 1695 cm^{-1} (amide C=O); ^1H NMR ($CDCl_3$, 90 MHz) δ 6.42 and 6.20 (2, each broad s, $CONH_2$), 5.9 (2, broad s, $CONH_2$), 4.45 (1, d, H-2, $J_{2,3}$ = 1.5 Hz), 4.20 (1, d, H-5, $J_{4,5}$ = 1.8 Hz), 4.0 (1, dd, H-3, $J_{3,4}$ = 8.1 Hz), 3.65 (1, m, H-4, $J_{4\text{-4OH}}$ = 9.6 Hz), 2.75 (1, d, 4-OH), 0.9 (27, 2s, tert-butyl) and 0.1 ppm (18, s, $SiMe_2$).

Anal. Calcd for $C_{24}H_{54}O_6N_2Si_3$ (550.97); C, 52.32; H, 9.88; N, 5.08. Found: C, 52.09; H, 9.88; N, 5.05.

Ammonolysis of 2. A solution of dimethyl 2,5-bis-O-(tert-butyldimethylsilyl)galactarate (2, 0.140 g, 0.30 mmol) in methanol (4 mL) was added to ammonia saturated methanol (2 mL). Ammonia was bubbled slowly through the methanol solution for 25 min during which time the product precipitated. The product was removed by filtration, washed with a little methanol, dried, and identified as 5 from its IR spectrum and mmp with material derived from 3; yield, 0.123 g (94%).

1,6-Diamino-1,6-dideoxygalactitol dihydrochloride (9).

From 5. Borane-THF (20. mL, 1 M BH_3 in tetrahydrofuran, Aldrich Chemical Co.) and tetrahydrofuran (30 mL) were added through a rubber septum under a nitrogen atmosphere to a 100-mL three-neck flask held in an ice bath and fitted with a reflux condenser carrying a drying tube and a gas inlet tube. The solid 5 (1.10 g, 2.51 mmol) was then added all at once to the cooled borane-THF solution with the reaction mixture effervescing as the solid dissolved. The resultant

solution was boiled under reflux overnight, cooled to 5 °C and treated carefully with methanolic HCl (31.5 mL of 4.15 M HCl). The amine salt 9 that precipitated was removed by filtration to give 0.53 g (83%), mp above 240 °C (decomp.), lit. mp above 220 °C (decomp.)[10]

From 6 & 7. The reduction procedure was the same as that described for 5 but was carried out on 6 (1.0 g, 1.8 mmol), slightly contaminated with 7. The reduction was done using borane-THF, (15 mL, 1 M, Aldrich Chemical Co.) in tetrahydrofuran (30 mL). The dihydrochloride 9 was obtained (0.305g, 66%), mp above 240 °C (decomp).

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References and Footnotes

1. For preliminary reports see a) J. L. Navia and D. E. Kiely, Abstr. Papers Am. Chem. So. Mtg., 179 (1980) Houston, CARB 27, b) J. L. Navia, Diss. Abstr. Int., B 1982, 42(7) 2840.

2. W. N. Haworth, R. L. Heath, and L. F. Wiggins, J. Chem. Soc., 155 (1944).

3. K. Butler and W. A. W. Cummings, J. Chem. Soc., 636 (1956).

4. O. I. Samoilova, I. A. Seliverstova, N. M. Dyatlova, and V. G. Yashnunskii, Zh. Obshch Khim., 43, 365 (1973); Chem. Abstr., 78, 148165p (1973).

5. T. P. Bird, W. A. P. Black, E. T. Dewar, and J. B. Hare, J. Chem. Soc., 1208 (1963).

6. G. S. Skinner, L. A. Henderson, C. G. Custafson, Jr., J. Am. Chem. Soc., 80, 3788 (1958).

7. O. I. Samoilova, V. M. Plakhotnik and V. G. Yashunkic: USSR Patent 306118 (C1. C07c) June 11, 1971; Chem. Abstr., 75 , 98156b (1971).

8. M. L. Wolfrom, F. Shafizadeh, J. O. Wehrmuller, and R. K. Armstrong, J. Org. Chem., 23, 571 (1958).

9. T. Horvath, P. Sohar, and G. Abraham, Carbohydr. Res., 73, 277 (1979).

10. J. W. W. Morgan and M. L. Wolfrom, J. Org. Chem., 78, 2496 (1956).

11. F. I. Carroll, J. Org. Chem., 31, 366 (1966).

12. T. P. Bird, W. A. P. Black, E. T. Dewar, and J. B. Hare, J. Chem. Soc., 3389 (1963).

13. T. Horvath and L. Vargha, Magy. Kem. Lapja, 27, 361 (1972); Chem. Abstr., 78, 66994u (1973).

14. L. Vargha, T. Horvath, M. Halasz, E. Csanyi, and B. Dumbovich, Canadian Patent 984401 (Cl. 260-464.4), February 24, 1976; Chem. Abstr., 84, 180556b (1976).

15. T. Horvath, E. Csanyi, S. Eckhardt, and E. Kiraly, Belgian Patent 868988 (Cl. C07C) January 15, 1979; Chem. Abstr., 91, 175668e (1979).

16. E. J. Corey and A. Venkateswarlu, J. Am. Chem. Soc., 94, 6190 (1972).

17. L. M. Sweeting, B. Coxon, and R. Varma, Carbohydr. Res., 72, 43 (1979).

18. M. Blanc-Muesser, J. Defaye and D. Horton, Carbohydr. Res., 87, 71 (1980).

19. G. A. Jeffrey and R. A. Wood, Carbohydr. Res., 108, 205 (1982).

20. "Spectrometric Identification of Organic Compounds", R. M. Silverstein, G. C. Bassler, and T. C. Morrill, 4th Ed., John Wiley & Sons, New York, NY, 1981, pp. 201-202.

21. a) M. Karplus, J. Chem. Phys., 30, 11 (1959); b) M. Karplus, J. Am. Chem. Soc., 85, 2870 (1963).

22. P. D. Hoagland, Carbohydr. Res., 98, 203 (1981).

23. N. Ogata, K. Sanui, Y. Hosoda, and H. Nakamara, J. Polym. Sci., Polym. Chem. Ed., 14, 783 (1976).

24. K. K. Ogilvie and D. W. Entwistle, Carbohydr. Res., 89, 203 (1981).

25. B. A. Lewis, F. Smith and H. M. Stephen in: "Methods in Carbohydrate Chemistry", Vol. 2; R. L. Whistler and M. L. Wolfrom, Eds.; Academic Press, New York, NY, 1963, p. 38.