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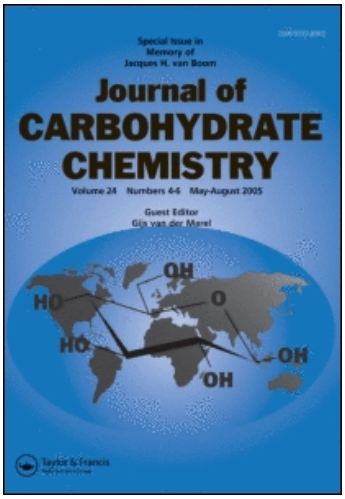

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A GENERAL SYNTHESIS OF DITERMINAL DIAMINODIDEOXYALDITOLS AND 1-AMINO-1-DEOXYALDITOLS USING TRIMETHYLMSILYL PROTECTING GROUPS[1]

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ABSTRACT

General syntheses of diterminal diaminodideoxyalditols and 1-amino-1-deoxyalditols from aldoses are described. Borane-THF reduction of O-trimethylsilylaldaramides, followed by methanolic HCl workup, leads to diaminodideoxyalditol dihydrochlorides. Similar treatment of O-trimethylsilylaldonamides yields aminoalditol hydrochlorides. The general reaction sequence was used to synthesize six diaminoalditols and five monoaminoalditols. The method is generally applicable to both classes of title aminoalditols and is independent of the chain length and stereochemistry of the starting aldose.

INTRODUCTION

The goal of this research was the development of a convenient, general synthesis of diterminal diaminodideoxyalditols. Earlier specific syntheses of terminal diaminodideoxyalditols have been centered around two strategies: 1) introduction of the amine functions or potential amine functions by nucleophilic displacment reactions,[4-7] and 2) introduction of the amine functions through a reduction step.[8-11] We chose to follow the second strategy, but in particular to generate the

amine functions by chemical reduction of hydroxyl protected, organic solvent soluble aldaramides.

The preceding paper[3] describes a model study using this approach, the target being 1,6-diamino-1,6-dideoxgalactitol dihydrochloride (22). Borane-THF reduction of partially O-tert-butyldimethylsilylated galactaramides, a key step in the synthesis, followed by methanolic HCl workup yielded directly the desired final product. However, we have now found that the synthesis of 22 is greatly improved when the trimethylsilyl (TMS) group is substituted for the tert-butyldimethylsilyl (TBDMS) group. This improvement has led to a general synthesis of both diterminal diaminodideoxyalditols (Scheme 1) and 1-amino-1-deoxyaminoalditols (Scheme 2).

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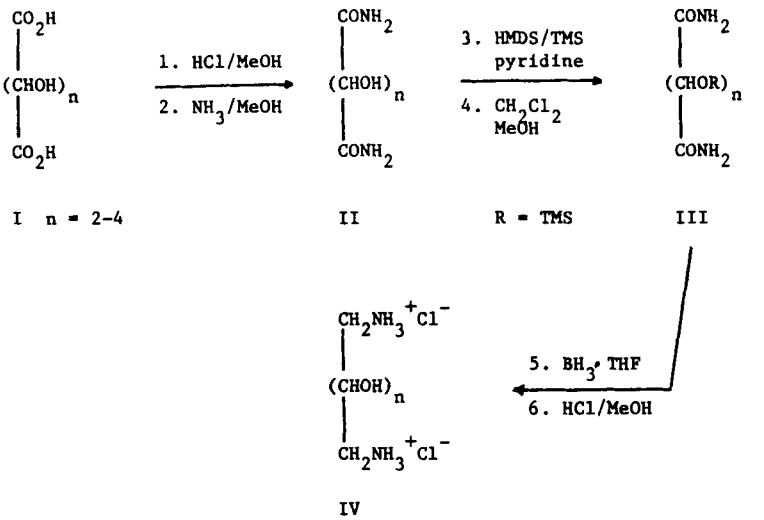
RESULTS AND DISCUSSION

Synthesis of the diterminal diaminodideoxyalditols originated from the aldaric acids (I, Scheme 1), prepared by nitric acid oxidation of the corresponding aldoses. The acids were then esterified with methanolic HCl to yield the crude dimethyl aldarates and/or methyl ester lactones. The crystalline aldaramides (II) were prepared by ammonolysis of the crude esterification products in methanol solution, and pertrimethylsilylation of the aldaramides was done at room temperature with trimethylchlorosilane (TMCS) and hexamethyldisilazane (HDMS) in pyridine.[12,13] Attempts at reducing the silylated products with borane-THF, followed by methanolic HCl workup and deprotection, gave only the starting aldaramides. These results suggested that terminal amido TMS groups on the aldaramides were sterically preventing reduction from occurring. Since amido TMS groups are known to be easily deprotected by alcohols,[14] a routine procedure was employed for selectively removing these groups in the presence of O-TMS groups.

The initial deprotection experiments were carried out in ^{1}H NMR tubes. A drop of methanol-d_4 containing a trace of water was added to crude pertrimethylsilylated aldaramide in chloroform-d ($CDCl_3$). The deprotection was then monitored by ^{1}H NMR. Generally, the spectra of the crude pertrimethylsilylated aldaramides initially contained several N-H peaks, but deprotection for 18 hours generated spectra with the

Scheme 1



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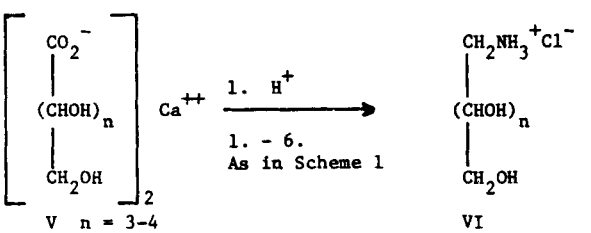
Scheme 2



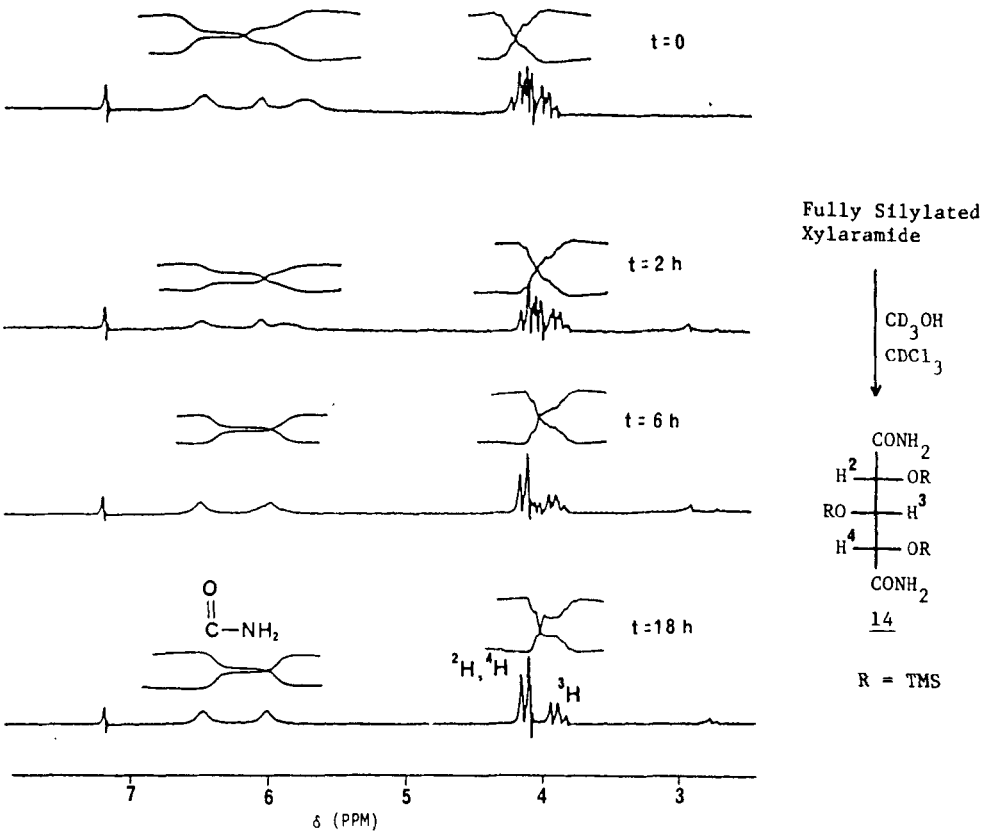


Figure 1. 90 MHz ^{1}H NMR monitoring of amido TMS deprotection of fully silylated xylaramide.

two broad signals characteristic of a primary amide. Quite likely these multiple peaks represent mixtures of amido N-TMS and amido O-TMS compounds. A typical deprotection monitoring experiment is shown in Fig. 1.

The selective amide deprotection of the pertrimethylsilylated aldaramides was readily scaled up for preparative purposes, with dichloromethane and methanol being substituted for the deuterated solvents. The O-TMS aldaramides (III, Scheme 1) were then reduced with borane-THF, and the diamines isolated as their dihydrochlorides (IV). Although borane-THF is commercially available, the best results were

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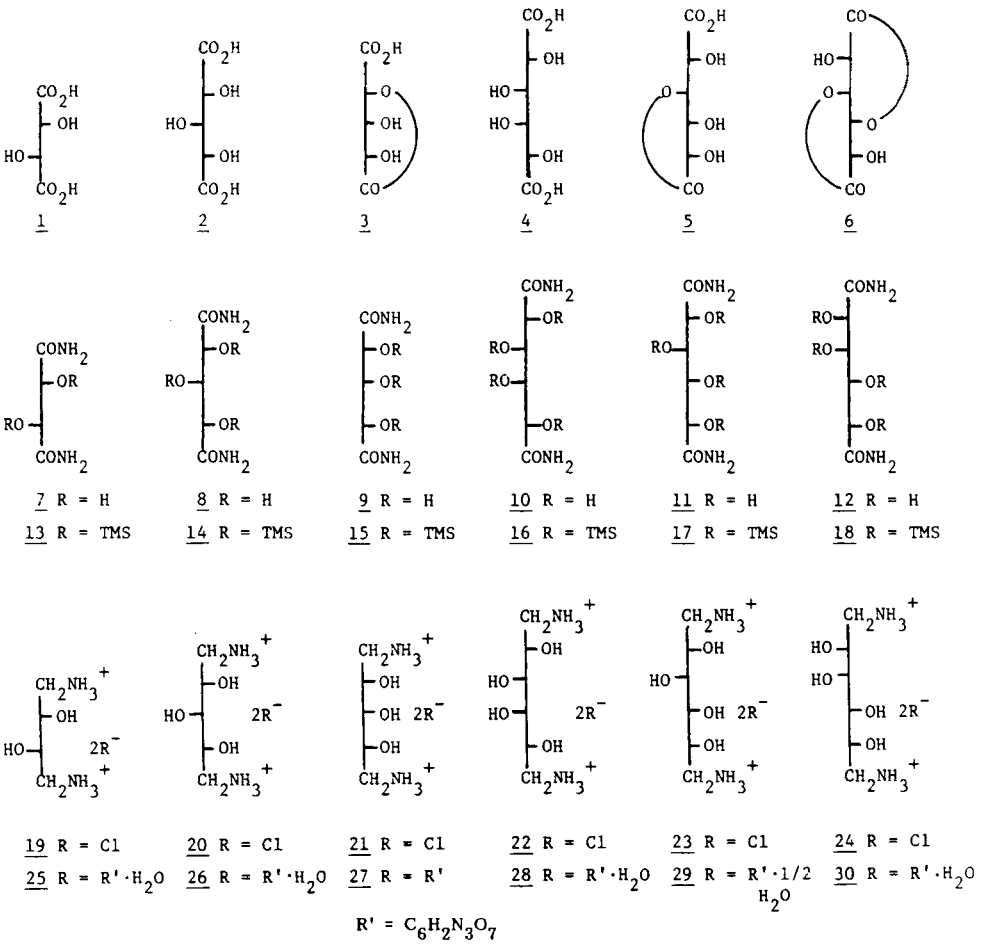

Figure 2. Synthesized diterminal diaminodideoxyalditol salts and precursors.

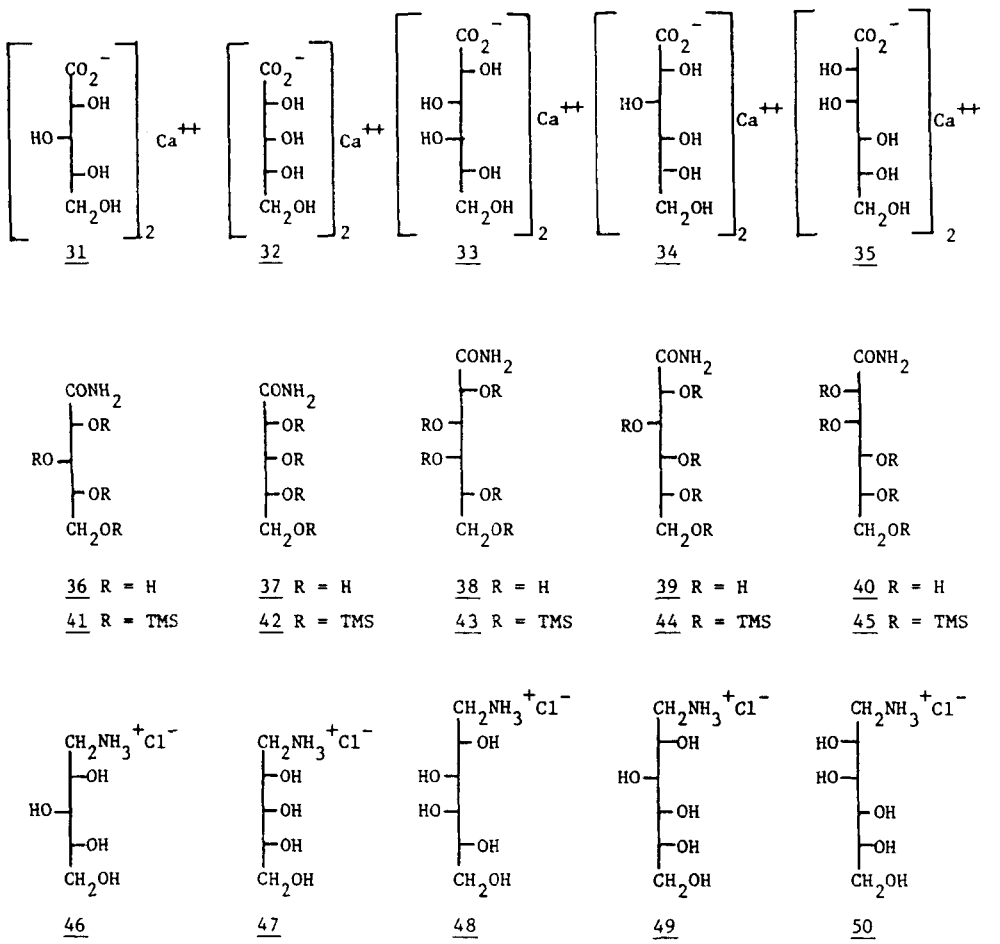

Figure 3. Synthesized 1-amino-1-deoxyalditol hydrochlorides and precursors.

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achieved using reagent freshly prepared from iodine and sodium borohydride. To underscore the general applicability of this sequence, a four carbon, two five-carbon, and three six-carbon diterminal diaminodideoxyalditol dihydrochlorides of the following configurations were prepared; L-threo (19), xylo (20), ribo (21), galacto (22), D-gluco (23), and D-manno (24). The five carbon diamine dihydrochlorides were found to be very hygroscopic and difficult to manipulate, thus accounting for their lower yields. However, both of the parent diamines gave nicely crystalline dipicrates (26 and 27), as did the other diamines (picrates 25, 28, 30 and 30).

A number of general synthetic approaches to 1-amino-1- deoxyalditols have been reported which employ reduction of a nitrogenous precursor.[15] Since aldonic acids are conveniently prepared by electrolytic oxidation of aldoses,[16] we undertook the synthesis of five 1-amino-1-deoxyalditols according to the reaction sequence successfully employed for the diaminoalditols. The aldonic acid/aldonolactone prepared from acidification of the corresponding calcium aldonate (V) was esterified with methanolic HCl, and the crude was product treated with methanolic ammonia to give the aldonamides (Scheme 2). Pertrimethylsilylation of the aldonamides, followed by amide deprotection, gave the O-(trimethylsilyl)aldonamides which were then reduced to yield the 1-amino-1-deoxyalditol hydrochlorides (VI).

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EXPERIMENTAL

Melting points were determined on a Fischer-Johns melting point apparatus and are uncorrected. Solutions were concentrated at reduced pressure on a rotary evaporator. ^{1}H NMR spectra were recorded at 90 or 60 MHz (Varian EM-390 or EM-360 spectrometers) in chloroform-d with tetramethylsilane as an internal standard. IR spectra were obtained using a Beckman Acculab-4 spectrometer. Elemental analyses were performed by Atlantic Microlabs, P. O. Box 80569, Atlanta, GA 30366.

Aldaric acids by nitric acid oxidation of aldoses. Galactaric acid (4),[17] xylaric acid (2);[18] D-glutaric acid, as D-glucaro-6,3-lactone (5);[19] ribaric acid, as ribaro-1,4-lactone (3);[20,21] and mannaric acid; as mannaro-1,4:6,3-dilactone,6);[22] were prepared according to litera-

ture procedures. L-tartaric acid (1) was purchased from Eastman Chemical Company.

Aldonic Acids by Electrolytic Oxidation of Aldoses. Aldonic acids, isolated as their calcium salts, 31 to 35, were prepared as described by Frush and Isbell.[16] Filtering the reaction mixture and concentrating the aqueous filtrate gave the calcium aldonate as a syrup which sometimes crystallized on standing at room temperature overnight. For those salts that did not crystallize, addition of methanol (100 mL) to the syrup and stirring the resultant mixture at room temperature gave the solid product, which was then washed with deionized cold water and dried. The yields of salts ranged from 74% for calcium ribonate (32) to 96% for calcium mannonate (35). Acidification of the calcium aldonates was accomplished by passing 0.06-0.10 moles of the salt in 250-300 mL of deionized water through a column containing 250 mL of Amberlite IR-120 (H^+) resin. The effluent was passed through the column twice more to ensure good exchange. After solvent removal, the crude acid/lactone was used directly in the esterification step.

Esterification of the aldaric and aldonic acids. Conversion of aldararic acids to dimethyl aldarates and/or methyl aldarolactones was carried out in methanolic HCl. Acetyl chloride was added to cold (5 °C) reagent grade methanol for in situ HCl generation. The solution was brought to room temperature, and to it was added the aldaric or aldonic acid. The reaction mixture was then boiled under reflux overnight, and the resultant solution was concentrated to a syrup. Decolorization of the syrup in methanol with activated charcoal was commonly carried out at this stage. As a final step, residual water was removed azeotropically at reduced pressure with toluene. Detailed examples of this procedure have been reported.[23] The same esterification procedure was applied to aldonic acids.

Ammonolysis of aldaric acid and aldonic acid esterification products. The crude esterification products were used directly for conversion to aldonamides and aldaramides. In a typical ammonolysis experiment, the crude esterification product (0.1 mol based on starting aldonic or aldaric acid) in reagent grade methanol (50 mL) was added dropwise to a cold (5 °C) solution of methanol (150 mL) saturated with ammonia. Ammonia was bubbled through the solution during the addi-

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tion and 1 h after the addition was complete. The reaction mixture was then kept open to the atmosphere in a fumehood overnight. The aldonamide or aldaramide usually crystallized directly from the reaction mixture and was removed by filtration. The percent yields (based on crude ester and lactone) and mp's (°C) are as follows: 7 (81%, 195-197), 8 (94%, 178-180), 9 (50%, 154-157), 10 (98%, 225-230), 11 (78%, 169-170), 12 (79%, 186-189), 37 (83%, 136-138), 38 (70% ,174-176), 39 (79%, 144-147) and 40 (80%, 170-172). Xylonamide (36). The preparation of previously unreported xylonamide (36) was carried out according to the general procedure described for the preparation of aldonamides. However, the syrupy product resisted crystallization until it was observed that stirring the syrup with methanol at room temperature for several hours rendered crystalline 36; 9.5 g (88% based on ester/-lactone), mp 80-85 °C. Trituration of the crude product with methanol gave an analytical sample, mp 83-85 °C; IR (Nujol) 1650 cm^{-1} (amide C=0); $[\alpha]_D^{25}$ +51.42° (c 1.2, DMSO).

Anal. Calcd for $C_5H_{10}N_2O_5$: C, 36.36; H, 6.71; N, 8.48. Found: C, 36.15; H, 6.74; N, 8.40.

Trimethylsilylation and amide deprotection of aldonamides and aldaramides. The silylation procedure was based on that of Sweeley and co-workers[12] but was carried out at room temperature according to Loewus.[13] The following trimethylsilylation procedure for ribaramide is representative. To a 250-mL Erlenmeyer flask, with a standard tapered opening, was added pyridene (100 mL), hexamethyldisilazane (32 mL), and trimethylchlorosilane (12 mL) in that order. Ribaramide (9, 3.56 g, 20 mmole) was added to the silylation reagent, the flask was stoppered, and the reaction mixture was stirred at room temperature for 24 h. The highly turbid reaction mixture was vacuum filtered through a fine fritted, sintered glass funnel, and the filtrate was concentrated to a clear syrup. The syrup was dissolved in dry hexanes (75 mL), the slightly turbid mixture was filtered, and the hexane solution was concentrated to a clear, colorless syrup (10.65 g). The syrup was then dissolved in dichloromethane (100 mL) containing methanol (5 mL). The reaction mixture was left overnight at room temperature and then vacuum filtered to remove a small amount of colored precipitate. The clear filtrate was concentrated to give tris-O-(trimethylsilyl)ribaramide (15,

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7.8 g, 99%) as a white solid. The O-TMS aldaramides and aldonamides were either white solids or viscous liquids.

After ^1H NMR verification that selective deprotection was complete, the compounds were used in the reduction step without further purification or attempted recrystallization. The yields of the O-TMS aldonamides and aldaramides were generally about 90%.

Typical diborane reduction of an O-(trimethylsilyl)aldaramide. The synthesis of 1,6-diamino-1,6-di-deoxymannitol dihydrochloride (24). The glassware assembly for the generation of diborane was patterned after that described by Brown,[24] although Brown's procedure employed BF_3 etherate and sodium borohydride to generate diborane. To an ice bath cooled, round bottom flask containing sodium borohydride (22.3 g, 590 mmol) suspended in diglyme (120 mL), was added dropwise a solution of iodine (74.2 g, 292 mmol) in diglyme (240 mL). A slow stream of nitrogen through the system carried the diborane as it was generated to the collection flask which contained tetrakis-O-(trimethylsilyl)mannaramide (18, 9.0 g, 18.1 mmol) and sodium borohydride (40 mg) in THF (300 mL). The nitrogen flow was continued for 1 h after all the iodine solution was added to the diborane generation flask. The collection flask was then removed from the assembly, fitted with a reflux condenser and drying tube, and the reaction mixture was refluxed overnight. The reaction mixture was then cooled (ice-bath), and to it was slowly added methanol (40 mL), and then methanolic HCl (160 mL, 5M). The white turbid mixture was refluxed for 1h, the mixture cooled to room temperature, and the crude powdery amine hydrochloride (24) was collected by vacuum filtration. The product was then washed with ethanol and dried in vacuo; yield 4.08 g (89%); mp 207-210 °C. Trituration with hot ethanol gave a mp of 238 °C, lit.[25] mp 238-241 °C.

For those amine dihydrochlorides that did not crystallize directly from the THF-methanol solution, the solvents were removed at reduced pressure, the residue was stirred with absolute ethanol at room temperature, the white solid dihydrochlorides remaining undissolved. The solid products were then removed by vacuum filtration and washed with absolute ethanol as described. The percent yields of the diaminoalditol hydrochlorides, based on starting per-O-(trimethylsilyl)aldaramides are given in Table 2.

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Table 1

Elemental Analysis Data and Melting Points From Diaminodideoxyalditol Dipicrates and Dihydrochlorides

Compound	Formula	mp °C	Analysis (C, H, N)					
			Calcd (%)			Found (%)		
19	$C_4H_{14}Cl_2N_2O_2$	210-212	24.88	7.26	14.52	24.97	7.28	14.52
25	$C_{16}H_{18}N_8O_{16}\cdot H_2O$	210-212	32.22	3.38	18.78	32.60	3.51	18.90
26	$C_{17}H_{20}N_8O_{17}\cdot H_2O$	235-236	32.60	3.54	17.89	32.37	3.77	17.45
27	$C_{17}H_{20}N_8O_{17}$	205-208	33.56	3.31	18.42	33.61	3.48	18.16
22	$C_6H_{18}Cl_2N_2O_4$	> 240	28.47	7.16	11.07	28.46	7.16	11.07
28	$C_{18}H_{22}N_8O_{18}\cdot H_2O$	240-241	32.94	3.38	17.07	32.81	3.55	16.85
23	$C_6H_{18}Cl_2N_2O_4$	185-189	28.47	7.16	11.07	28.63	7.16	11.03
29	$C_{18}H_{22}N_8O_{18}\cdot 1/2H_2O$	201-202	33.40	3.42	17.31	33.38	3.80	17.17
24	$C_6H_{18}Cl_2N_2O_4$	232	28.47	7.16	11.07	28.51	7.14	11.01
30	$C_{18}C_{22}N_8O_8\cdot H_2O$	199-200	32.91	3.66	17.06	33.15	3.71	17.23

Table 2

Yields of Diamino and Monoaminoalditol Hydrochlorides Based on Starting Per-O-Trimethylsilylaldaramides and Aldonamides

O-TMS Amide	Amine Hydrochloride	Percent Yield
13	19	90
14	20[a]	46
15	21[a]	67
16	22	94
17	23	54
18	24	89
41	46	88
42	47	49
43	48	92
44	49	75
45	50	72

a. Hygroscopic solid.

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Dipicrates 25, 26, 27, 28, 29 and 30. To a concentrated aqueous solution of the alditoldiamine dihydrochloride at room temperature was added an excess of a saturated ethanol-picric acid solution. The dipicrate which crystallized directly from the reaction mixture was crystallized from water for analysis (Table 1).

Typical diborane reduction of an O-(trimethylsilyl)aldonamide. The synthesis of 1-amino-1-deoxy-D-galactitol hydrochloride (48). Crude pentakis-O-(trimethylsilyl)galactonamide (43, 12.6 g, 22.7 mmol, mp 64-66 °C) was prepared by N-deprotection of fully trimethylsilylated galactonamide (14.9 g) in a solution of dichloromethane (100 mL) and methanol (5 mL) at room temperature for 24 h. To an ice bath cooled, round bottom flask (500 mL), containing sodium borohydride (9.0 g, 240 mmol) suspended in diglyme (45 mL), was added dropwise a solution of iodine (30 g, 118 mmol) in diglyme (30 mL). The diborane generated was flushed with nitrogen into a flask containing 43 in THF (150 mL).

The nitrogen flow was continued for 1 h after addition of the iodine solution was complete, and the reaction mixture refluxed overnight. Methanol (10 mL) and methanolic HCl solution (70 mL, 5 M) were then added successively to the cooled (ice-bath) reaction mixture. The acidified reaction mixture was refluxed for 1 h and then concentrated to a syrup. Methanol (15 mL), then methanolic HCl solution (80 mL, 5 M) were added to the crude syrupy product, and the resultant solution brought just to boiling. The mixture was brought to room temperature, the solvents were removed, and the syrupy product was added to abs. ethanol (40 mL). The mixture was stirred overnight to give 1-amino-1-deoxy-D-galactitol hydrochloride (48), mp 141-142 °C, (lit.[26] 143-145 °C), 4.5 g (92%).

1-Amino-1-deoxy-D-xylitol hydrochloride (46), 1-amino-1-deoxy-D-ribitol hydrochloride (47), 1-amino-1-deoxy-D-glucitol hydrochloride (49), and 1-amino-1-deoxy-D-mannitol hydrochloride (50). The 1-amino-1-deoxyalditol hydrochlorides 46, 47, 49 and 50 were prepared using the procedure described for the preparation of 48; 46 mp 108-113 °C (lit.[27] mp 139-140 °C), 47 mp 128-133 °C (lit.[28] mp 129 °C), 49 mp 114-119 °C (lit.[26] 122-126 °C), and 50 mp 156-158 °C(lit.[29]161.5-162.5 °C). The percent yields of these hydrochlorides, based upon per-O-trimethylsilylaldonamides, are given in Table 2.

Each of the 1-amino-1-deoxyalditols was converted to its peracetate in acetic anhydride-pyridine (1:1) and subjected to gas chromatography-mass spectrometry (GC/MS) analysis. The analyses were performed on a Hewlett Packard 5985A system programmed from 50-300 °C at 30 °C/min using a 25 m, 0.1 mm i.d. SE-54 fused silica glass capillary column. The peracetates derived from the crude 1-amino-1-deoxyalditol hydrochlorides were all of 90% or higher purity, with the separate peracetates having retention times in the range of 8-9 min. The spectra from the peracetyl derivatives of the aminopentitols 46 and 47 (mass 361) were virtually identical, consistent with the assigned structures, and displaying peaks at m/e 302 (M - OAc), 289 (M - CH_2NHAc) and 259 (M - OAc - Ac). The spectra from the peracetyl derivatives of aminoglucitol 49 and aminomannitol 50 (mass 433) were indistinguishable below m/e 331 (M - OAc - Ac). However, an m/e 374 (M - OAc) was observed for peracetylated 1-amino-1-deoxyglucitol. A major peak in

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both spectra was m/e 313 (M - 2HOAc). The spectrum from peracetylated 1-amino-1-deoxy-D-galactitol also contained the m/e 331 and 313 peaks. The highest m/e was 361, which can be assigned to (M - CH_2NHAc), a fragmentation not observed with either the aminoglucitol or aminomannitol derivatives.

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