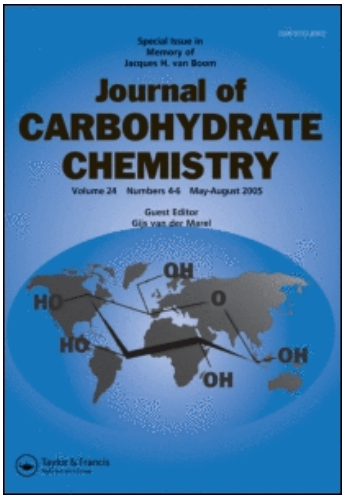

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SYNTHESIS OF 3-DEOXY DERIVATIVES OF 2-AMINO-2-DEOXY-D-GLUCOSE

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ABSTRACT

Methyl 2-acetamido-2,3-dideoxy-α-D-glucopyranosides have been obtained by an elimination reaction of the corresponding 3-O-mesylallopyranoside with NaH or DBU followed by hydrogenation over Pd/C. Reaction of 2-acetamido-2-deoxy-3-O-mesylallopyranosides with inorganic azides under phase transfer reaction conditions afforded 2-acetamido-3-azido-2,3-dideoxy-glucopyranoses which after hydrogenation over Pd/C gave 2-acetamido-3-amino-2,3-dideoxy-D-glucopyranoses.

INTRODUCTION

In relation to aminoglycoside antibiotics,[1] removal of the hydroxyl group at C-3 of aminosugars is of interest due to the marked activities of 3'-deoxy derivatives against resistant bacteria. These 3'-deoxy compounds include both natural antibiotics such as lividomycin,[2] tobramycin,[3] and istamycin,[4] and semi-synthetic antibiotics, e.g. 3'-deoxykanamycins[5] and 3'-deoxybutyrosins.[5] Chemical deoxygenations at C-3' have been carried out by radical-type reactions[6] and by S_N2 processes.[7-10] In this paper we describe an efficient method for deoxygenation at C-3 which involves the

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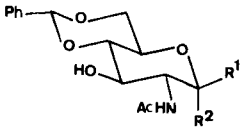
selective E2 elimination of a sulfonyloxy group at that position and hydrogenation of the resulting unsaturated sugar. We also report the selective S_N2 displacement of the C-3 methanesulfonyloxy group under phase transfer reaction conditions which gives easy access to biologycally important 3-substituted derivatives, such as 2,3-diamino-2,3-dideoxypyranoses.[11]

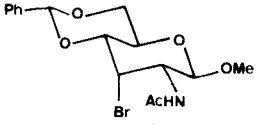
RESULTS AND DISCUSSION

Suitable starting compounds for the E2 and S_N2 reactions being studied were allopyranose derivatives having good leaving groups at C-3. Attempts to prepare the 3-haloallosamine derivative 6 by reaction of the glucosamine derivative 1 with triphenylphosphine and triphenylphosphite halogenation reagents ($(C_6H_5)_3P/CCl_4$, $(C_6H_5O)_3P/Br_2$, $(C_6H_5O)_3P/I_2$)) were unsucessful, presumably due to the presence of the axially oriented 1-O-Me group which hindered the approach of the nucleophile to C-3.[12] In contrast, formation of the 3-bromo-β-D-allo-pyranoside 3 did occur by reaction of the corresponding methyl β-D-glucopyranoside 2 with $(C_6H_5O)_3P/Br_2$. The allo configuration of 3 was established by ^1H NMR spectroscopy since H-3

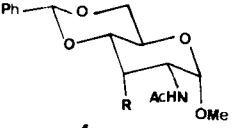


1, $R^1 = H$; $R^2 = OMe$

2, $R^1 = OMe$; $R^2 = H$



3



4 . R = OH

5 . R = OMs

6 . R = halogen.

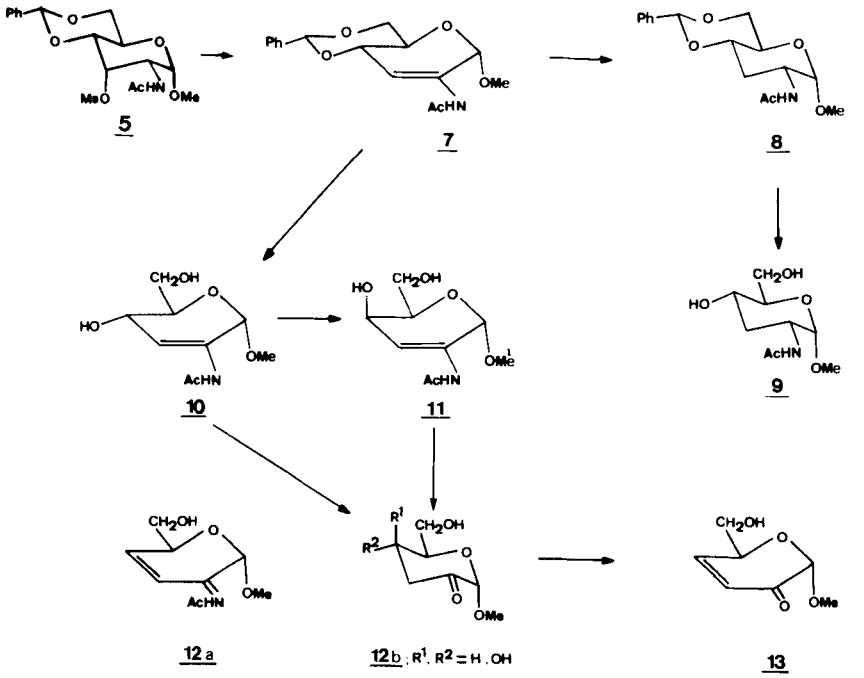
appeared as a doublet of doublets with values of $J_{2,3}$ and $J_{3,4}$ of 1.6 and 2.0 Hz. The β-anomeric configuration was shown by $J_{1,2}$= 8 Hz. Due to the low yield of 3 (36%),

the 3-O-mesyl-N-acetyl-α-D-allosamine derivative 5[13] was used as starting material. Compound 5 was obtained in 3 steps and 61% total yield from the readily accesible methyl 2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (1).

Elimination of the axially oriented 3-O-mesyl group was accomplished by treatment of 5 with strong bases such as sodium hydride, in 1,2-dimethoxyethane, or 1,5-diazabicyclo [5.4.0] undec-5-ene (DBU), in dimethylformamide, and afforded the 2,3-unsaturated glucosamine 7 in 97% and 83% yield, respectively. The presence of the olefinic double bond of 7 was deduced by ^{1}H NMR and confirmed by reduction of the double bond. Catalytic hydrogenation of 7 over 10% palladium on charcoal afforded the reduced compound 8 in 78% yield. The use of higher temperatures and hydrogen pressures in this hydrogenation reaction induced hydrogenolysis of the 4,6-O-benzylidene group to give methyl 2-acetamido-2,3-dideoxy-α-D-*ribo*-hexopyranoside 9. The configuration of the new asymmetric center at C-2 was determined by ^{1}H NMR and confirmed by comparison with published data from 8[8-10,14] and 9.[7-9] The stereoselective reduction of 7 to 8 is in agreement with hydrogenation occurring from the less hindered face of the double bond, opposite to the axially oriented 1-O-methyl group.

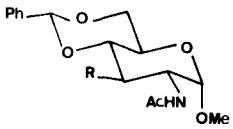
Treatment of 7 with hot aqueous acetic acid afforded mixtures of compounds from which methyl 2-acetamido-2,3-dideoxy-α-D-*erythro*- and -*threo*-hex-2-enopyranosides 10 and 11 and methyl 3,4-dideoxy-α-D-*glycero*-hex-3-enopyranos-2-uloside 13 were identified. TLC and ^{1}H NMR monitoring of this reaction indicated the initial formation of 10 followed by the appearance of 11 and then 13. Enone 13 was the only detectable

compound after 30 min of acidic treatment. Compound 11



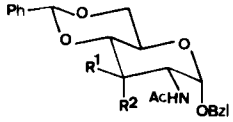
resulted from the acid catalyzed epimerization of the allylic quasi-equatorial 4-OH of the erythro compound 10 to the thermodynamically more stable quasi-axial orientation.[15] The stereochemistry at C-4 of 10 and 11 was determined from the ^{1}H NMR spectra of the compounds. The olefinic H-3 protons appeared as doublets, $J_{3,4}$= 2 Hz for 10 and $J_{3,4}$= 6.0 Hz for 11, indicating the quasi-axial and quasi-equatorial relationship of H-4 in 10 and 11, respectively. The formation of 13 can be explained by hydrolysis of 10 or 11 in the aqueous medium to the ketone 12b, followed by a dehydration step. The formation of similar

enone pyranosides from ketosugar derivatives, under acid conditions, has been described.[16] Nevertheless, the formation of 13 could also be explained by an inverse sequence of reactions, i.e. first dehydration of 10 or 11 to give enimide 12a followed by hydrolysis to afford 13.



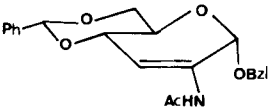
14 . R = N_3

15 . R = NH_2



16 . R^1 = H ; R^2 = OMs

17 . R^1 = N_3 ; R^2 = H



18

Several attempts were made to prepare methyl and benzyl 2-acetamido-3-azido-2,3-dideoxy-α-D-glucopyranosides 14[13] and 17[17] by treatment of the corresponding 3-O-mesyl-α-D-allopyranosides 5 and 16 with sodium azide in various organic solvents; N,N-dimethylformamide[17a] (DMF), dimethylsulfoxide[17b] (DMSO), hexamethylphosphoric triamide[13] (HMPT), acetonitrile, and 1,2-dimethoxyethane. However, in our hands displacement and elimination products were formed in aproximately equal amounts, with overall product recovery only 60-70%. Thus, a method more selective to displacement was investigated.

Methyl 3-azido-α-D-glucopyanoside 14 was prepared in 81% yield by reaction of 5 with sodium azide under phase transfer catalysis conditions, using tetrabutylammonium hydrogensulfate in 1,2-dimethoxyethane/water. The use of other catalysts such as tetraethylammonium bromide, benzyltrimethylammonium bromide or benzyltriethylammonium chloride required longer reaction times, but also gave good yields. Similarly, reaction of 16 with lithium azide in acetonitrile in the presence of tetrabutylammonium hydrogensulfate afforded benzyl 3-azido-α-D-glucopyranoside 17 in 70% yield.

Catalytic hydrogenation of the azide 14 over 10% palladium on charcoal gave methyl 2-acetamido-3-amino-4,6-O-benzylidene-2,3-dideoxy-α-D-glucopyranoside, 15, in 79% yield.

EXPERIMENTAL

Melting points were measured with a Kofler hot-stage apparatus and are uncorrected. ^{1}H NMR spectra were recorded with Varian EM-390 (90 MHz) and Bruker WM 360 (360 MHz) spectrometers using Me_4Si as an internal standard. UV absorption spectra were taken with a Perkin-Elmer 402 spectrophotometer. IR spectra were recorded with a Perkin-Elmer 257 spectrophotometer. Analytical TLC was performed on aluminium sheets coated with a 0.2 mm layer of silica gel 60 F_{254} purchased from Merck and preparative TLC on glass plates coated with a 2 mm layer of silica gel PF_{254} (Merck). Compounds were detected with a UV light (254 nm) or by spraying the plate with a ethanol-sulfuric acid (3:7) mixture and heating.

Methyl 2-acetamido-4,6-O-benzylidene-3-bromo-2,3-dideoxy-β-D-allopyranoside (3). A cooled (ice bath) mixture of methyl 2-acetamido-4,6-O-benzylidene-2-deoxy-β-D-glucopyranoside (1 g, 3.1 mmol), triphenylphosphite (1.24 g, 4 mmol) and 1,2-dimethoxyethane (15 mL) was treated with bromine (0.3 mL, 6 mmol). The reaction mixture was stirred at room temperature for two h, and then passed through an Amberlite IR-45 (10 g) column. The eluate was concentrated at reduced pressure to give a syrup which was purified by preparative TLC using EtOAc: hexane (5:2) to give 3 (0.43 g, 36%): mp 160 °C (from n-propanol); $[\alpha]_D$ - 44.7° (c 1, chloroform); ^{1}H NMR data [$(CD_3)_2SO$]: δ 1.90 (s, 3H, NAc), 3.41 (s, 3H, OMe), 3.70 - 4.35 (m, 5H, H-2, H-4, H-5, H-6), 4.69 (d, 1H,

H-1, $J_{1,2}$= 8 Hz), 4.85 (dd, 1H, H-3, $J_{2,3}$, $J_{3,4}$= 1.6, 2.0 Hz), 5.75 (s, 1H, CH-Ph), 7.43 (m, 5H, C_6H_5), 8.23 (d, 1H, NH, $J_{NH,2}$= 7.5 Hz).

Anal. Calcd for $C_{16}H_{20}BrNO_5$: C, 49.70; H, 5.21; Br, 20.18; N, 3.62. Found: C, 49.69; H, 5.35; Br, 19.74; N, 3.57.

Methyl 2-acetamido-4,6-O-benzylidene-2-deoxy-3-O-methylsulfonyl-α-D-allopyranoside (5). A solution of 4 (0.65 g, 2 mmol) in dry pyridine (15 mL) was treated with mesyl chloride (0.4 g, 5 mmol) with cooling (ice bath) and the solution was kept in the refrigerator overnight. The reaction mixture was poured on a water: ice (2:1) mixture (100 mL) and extracted with chloroform. The organic extracts were washed rapidly with diluted sulfuric acid, an aqueous solution of $NaHCO_3$ and water. The chloroform solution was dried over Na_2SO_4, filtered and concentrated to give (5) (0.61 g, 76%): mp 184 - 185 °C (from EtOAc - hexane);$[\alpha]_D$+ 22° (c 1, chloroform); lit.[13] mp 179 - 181.5 °C,$[\alpha]_D$+ 17° (c 0.5, chloroform); ^1H NMR data [$(CD_3)_2SO$]:δ 1.91 (s, 3H, NAc), 3.06 (s, 3H, CH_3SO_3), 3.38 (s, 3H, OMe), 3.60 - 4.40 (m, 5H, H-2, H-4, H-5, H-6), 4.65 (d, 1H, H-1, $J_{1,2}$ = 4 Hz), 4.98 (dd, 1H, H-3, $J_{2,3}$ and $J_{3,4}$ = 1.5 and 2.4 Hz), 5.68 (s, 1H, CH-Ph), 7.38 (m, 5H, C_6H_5), 7.60 (d, 1H, NH, $J_{NH,2}$ = 8.5 Hz)

Methyl 2-acetamido-4,6-O-benzylidene-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (7). a) A mixture of 5 (0.2 g, 0.5 mmol), sodium hydride (10 mg) and 1,2-dimethoxyethane (10 mL) was stirred for 12 h at room temperature. The solvent was removed at reduced pressure and the residue, dissolved in $CHCl_3$ (10 mL), was washed twice with 10 mL of water. The organic phase was dried over Na_2SO_4, and concentrated to give 7 (0.15 g, 97%) as a solid: mp 170-171 °C (from EtOAc-hexane);$[\alpha]_D$+ 45°

(c 1, chloroform); UV λ_{max} (MeOH) = 235 nm (ε 8620); ^{1}H NMR data [$(CD_3)_2SO$]: δ 1.97 (s, 3H, NAc), 3.40 (s, 3H, OMe), 3.50 - 4.30 (m, 4H, H-4, H-5, H-6), 4.88 (s, 1H, H-1), 5.64 (s, 1H, CH - Ph), 6.42 (d, 1H, H-3, $J_{3,4}$ = 1.5 Hz), 7.38 (m, 5H, C_6H_5), 9.16 (broad s, 1H, NH).

Anal. Calcd for $C_{16}H_{19}NO_5$: C, 62.95; H, 6.23; N, 4.59. Found: C, 62.59; H, 6.00; N, 4.56.

b) A solution of 5 (2 g, 4.9 mmol), and DBU (0.91 g, 6 mmol) in DMF (15 mL) was heated to reflux for 24 h and then the solvent was removed. A chloroform solution of the residue was washed with water, dried over Na_2SO_4 and concentrated at reduced pressure. The product 7 was obtained in 83% yield (1.24 g) after preparative TLC using EtOAc as the eluent.

Methyl 2-acetamido-4,6-O-benzylidene-2,3-dideoxy-α-D-ribo-hexopyranoside (8). To a solution of 7 (2 g, 6.5 mmol) in EtOAc (50 mL) was added 10% Pd/C (1 g), and the mixture was hydrogenated at 30 psi and 25 °C for 24 h. The catalyst was removed by filtration and the filtrate concentrated to give a solid which was purified by preparative TLC using EtOAc as eluent to afford 8 (1.57 g, 78%): mp 242 - 243 °C (dec.) (from n-propanol-EtOAc); $[\alpha]_D$ + 52° (c 1, chloroform); lit.[8] mp 232 °C (dec.), $[\alpha]_D$ + 51.1° (c 0.86); lit.[9] mp 245 °C (subl.), $[\alpha]_D$ + 55.5° (c 0.95); lit.[10] mp 264 °C, $[\alpha]_D$ + 52° (c 1); lit.[14] mp 224 °C, $[\alpha]_D$ + 53.7° (c 1); ^{1}H NMR data [$(CD_3)_2SO$, 360 MHz]: δ 1.81 (q, 1H, H-3a, $J_{3a,3e}$= 11.4 Hz, $J_{3a,2}$= $J_{3a,4}$= 11.6 Hz), 2.00 (s, 3H, NAc), 2.19 (dt, 1H, H-3e, $J_{3e,2}$= 4.4 Hz, $J_{3e,4}$= 5.0 Hz), 3.42 (s, 3H, OMe), 3.60 - 3.80 (m, 3H, H-5, H-6), 4.26 (dt, 1H, H-4, $J_{4,5}$= 11.5 Hz), 4.31 (m, 1H, H-2, $J_{1,2}$= 3.5 Hz, $J_{2,NH}$= 8.3 Hz), 4.60 (d, 1H, H-1), 5.74 (d, 1H, NH), 7.35 - 7.49 (m, 5H, C_6H_5).

Anal. Calcd for $C_{16}H_{24}NO_5$: C, 62.54; H, 6.84; N,

4.56. Found: C, 62.90; H, 7.21; N, 4.35.

Methyl 2-acetamido-2,3-dideoxy-α-D-ribo-hexopyranoside (9). A mixture of 7 (0.5 g, 0.16 mmol), EtOAc (25 mL) and 10% Pd/C (0.5 g) was hydrogenated at 45 psi and 35 °C for 30 h. The catalyst was removed by filtration and the filtrate concentrated to give 9 (0.262 g, 73%): mp 210 - 211 °C (from ethanol); $[\alpha]_D$ + 138° (c 1, water); lit.[7] mp 211 - 212 °C, $[\alpha]_D$ + 138° (c 1, water); lit.[8] mp 214 - 215 °C; lit[9] mp 208 - 210 °C, $[\alpha]_D$ + 139° (c 1, water).

Treatment of 7 with aqueous acetic acid. A mixture of 7 (1 g, 3.28 mmol) in 70% aqueous acetic acid (30 mL) was refluxed for 20 min and then poured on a saturated solution of $NaHCO_3$ (200 mL). The resulting mixture was extracted with chloroform and the organic phase dried over Na_2SO_4, concentrated under reduced pressure and purified by preparative TLC using EtOAc - hexane (3:1) as the eluent, to give 13 (0.2 g, 40%): mp 60 - 61 °C (from diethyl ether-hexane), $[\alpha]_D$ + 52° (c 1, chloroform); lit.[19] mp 60.5 - 61 °C, $[\alpha]_D$ + 54.65° (c 5, chloroform).

When a mixture of compound 7 (0.5 g, 1.64 mmol) in 70% aqueous acetic acid (25 mL) was heated to 95 °C for 5 min and worked up as before, a (2:1) mixture of 10 and 11 (0.14 g, 39%) was obtained: ^{1}H NMR data for 10 [$(CD_3)_2SO$]: δ 1.92 (s, 3H, NAc), 3.31 (s, 3H, OMe), 3.20 - 4.13 (m, 4H, H-4, H-5, H-6), 4.80 (s, 1H, H-1), 6.21 (d, 1H, H-3, $J_{3,4}$= 2.1 Hz), 6.60 and 7.25 (2 broad s, 2H, OH), 8.98 (s, 1H, NH) and ^{1}H NMR data for 11 [$(CD_3)_2SO$]: δ 1.90 (s, 3H, NAc), 3.30 (s, 3H, OMe), 3.10 - 4.0 (m, 4H, H-4, H-5, H-6), 5.32 (s, 1H, H-1), 6.52 (d, 1H, H-3, $J_{3,4}$= 6.0 Hz), 9.15 (broad s, 1H, NH).

Methyl 2-acetamido-3-azido-4,6-O-benzylidene-2,3-dideoxy-α-D-glucopyranoside (14). A mixture of 5 (2 g, 5 mmol)), sodium azide (0.97 g, 15 mmol), and tetrabutylammonium hydrogensulfate (1.7 g, 5 mmol) was

dissolved in a 1,2-dimethoxyethane-water (1:1) solution (20 mL). The mixture was refluxed for 48 h with vigorous stirring. The precipitate which appeared was removed by filtration and crystallized from acetonitrile to give 14 (1.39 g, 81%) as white needles: mp 255 - 256 °C; $[\alpha]_D$ + 38.7° (c 1, chloroform); lit.[10] mp 253 - 255 °C, $[\alpha]_D$ + 36° (c 1, chloroform); IR (KBr) 2120 cm^{-1} (N_3); ^1H NMR data [$(CD_3)_2SO$]: δ 1.88 (s, 3H, NAc), 3.34 (s, 3H, OMe), 3.57 - 4.25 (m, 6H, H-2, H-3, H-4, H-5, H-6), 4.62 (d, 1H, H-1, $J_{1,2}$ = 3.5 Hz), 5.70 (s, 1H, CH-Ph), 7.40 (m, 5H, C_6H_5), 8.19 (d, 1H, NH, $J_{NH,2}$ = 8.5 Hz).

Similarly, a mixture of 5 (0.1 g, 0.25 mmol), sodium azide (0.1 g, 1.5 mmol), a tetraalkylammonium salt (0.5 mmol), 1,2-dimethoxyethane (2 mL) and water (2 mL) was refluxed with vigorous stirring for several days and worked up as before to give 14 with variable yields. The mixture, when refluxed for 5 days with tetraethylammonium bromide, afforded 0.07 g (80%) of 14, with benzyltrimethylammonium bromide for 8 days gave 0.065 g (75%) of 14, and with benzyltriethylammonium chloride for 3 days gave 0.07 g (80%) of 14.

Methyl 2-acetamido-3-amino-4,6-O-benzylidene-2,3-dideoxy-α-D-glucopyranoside (15). A mixture of 14 (2 g, 8 mmol), methanol (100 mL) and 10% Pd/C (1 g) was hydrogenated at 40 psi and 35 °C for 10 h. The catalyst was removed by filtration and the clear solution concentrated to leave solid 15, which was crystallyzed from methanol (1.46 g, 79%): mp 261 - 262 °C; $[\alpha]_D$ + 49° (c 1, chloroform); IR (KBr) 3300 cm^{-1} (NH_2); ^1H NMR data [$(CD_3)_2SO$]: δ 1.87 (s, 1H, NAc), 3.30 (s, 1H, OMe), 3.02 (m, 1H, H-3), 3.36 - 4.17 (m, 5H, H-2, H-4, H-5, H-6), 4.58 (d, 1H, H-1, $J_{1,2}$ = 4.5 Hz), 5.58 (s, 1H, CH-Ph), 7.36 (m, 5H, C_6H_5), 7.82 (d, 1H, NH, $J_{NH,2}$ = 8.5 Hz).

Anal. Calcd for $C_{16}H_{22}N_2O_5$: C, 59.62; H, 6.83; N, 8.69. Found: C, 59.31; H, 7.07; N, 8.58.

Benzyl 2-acetamido-3-azido-4,6-O-benzylidene-2,3-dideoxy-α-D-glucopyranoside (17). A mixture of benzyl 2-acetamido-4,6-O-benzylidene-2-deoxy-3-O-methanesulfonyl α-D-allopyranoside[17] 16 (0.47 g, 1 mmol), lithium azide (0.55 g, 10 mmol), tetrabutylammonium hydrogensulfate (0.339 g, 1 mmol) and acetonitrile (20 mL) was refluxed for 5 days. The mixture was poured on a water/ice mixture (50 mL) and the solid which precipitated was removed by filtration dried and recrystallyzed from ethanol to give 17 (0.3 g, 70%): mp 246 - 247 °C; $[\alpha]_D$ + 106° (c 1, dimethyl sulfoxide); lit.[17a,b] mp 244 - 245 °C, $[\alpha]_D$ + 97° (c 1, dimethyl sulfoxide).

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