Carbohydrate Research, 95 (1981) 291–298
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

DIRECT FORMATION OF *C*-GLYCOFURANOSYL DERIVATIVES BY THE REACTION OF D-ALDOSES WITH NITROMETHANE AND METHYL NITROACETATE*

TOHRU SAKAKIBARA, TETSUYOSHI TAKAMOTO†, TOSHIHIKO MATSUZAKI, HIROSHI OMI, U. WIN MAUNG‡, AND ROKURO SUDOH

Department of Chemistry, Faculty of Science, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152 (Japan)

(Received September 18th, 1980; accepted for publication in revised form, November 20th, 1980)

ABSTRACT

Under appropriate conditions, condensation of D-ribose (**1**) with nitromethane afforded D-ribofuranosylnitromethanes (**3** and **4**) directly, in high yields. On the other hand, similar reactions of 5-deoxy-D-xylose (**9**) gave acyclic products (**11**), which were readily converted into the cyclized products (**12** and **13**) upon heating in water. Condensation of **9** with methyl nitroacetate, however, furnished a cyclic product (**10**) directly. The stereochemistry of the products is discussed on the basis of chemical reactions as well as instrumental data.

INTRODUCTION

The natural occurrence of a number of *C*-glycosyl compounds has led to considerable synthetic work[1] on the introduction of C–C bonds at the anomeric position of aldoses. In these studies, the intramolecular Michael-type reaction of 1,2-unsaturated alditols[2] is one of the important approaches. Selectivity in ring formation is important for such syntheses. Unprotected 1-deoxy-1-nitro-D-alditols[3,4] are known to give mainly D-aldopyranosylnitromethanes. We have recently synthesized[5] D-furanosyl analogs, having appropriate protecting groups, through dehydration and subsequent cyclization by heating under neutral conditions. The yields in this approach, were unsatisfactory, however, particularly with nitromethane (15–25%), because the reaction is reversible. To improve the overall yields, the equilibrium at the critical addition step needs to be shifted. Our preliminary results, that the condensation products of nitromethane with D-ribose afforded α-D-ribofuranosylnitromethane (**4**) as crystals in 10% overall yield from D-ribose upon heating

*Reported, in part, at the Xth International Symposium on Carbohydrate Chemistry, London, April, 1978.
†Present address: Merck Sharp & Dohme, Tokyo, Japan.
‡UNESCO Student, 1976–1977.

in water for 14 h, suggested favoured formation of the furanose ring without the need for protecting groups.

This paper demonstrates the direct formation of *C*-glycosyl derivatives from D-aldoses.

RESULTS AND DISCUSSION

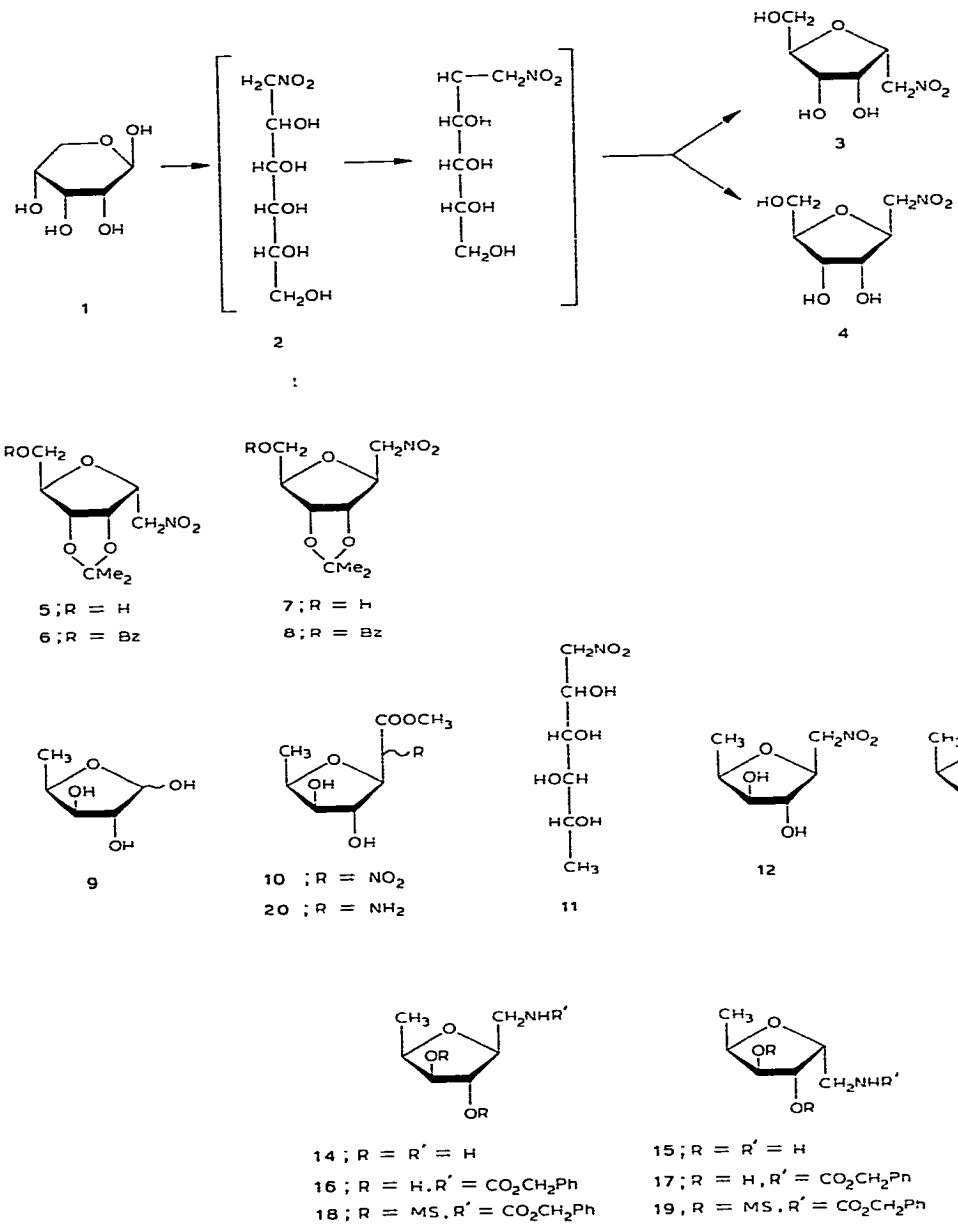
In the condensation of D-ribose (**1**) with nitromethane in methanol, the catalytic effects of various bases were examined and evaluated by t.l.c.*. Pyridine, barium carbonate, sodium and potassium acetates, and calcium oxide, all gave the starting aldose **1**, whereas a mixture of **1**, acyclic **2**, and traces of cyclic products **3** and **4** was observed when sodium methoxide, and sodium, potassium, calcium, barium, and ammonium hydroxides, and triethylamine were used. These results were still unsatisfactory.

When the reaction was performed in the presence of potassium carbonate and 18-crown-6 in tetrahydrofuran, the cyclic derivatives **3** and **4** were formed directly as major products. Polarimetric monitoring of the reaction showed the rate to be dependent on the amount of crown ether up to 0.25 molar equivalent to **1**, and the specific rotation reached $+31.1°$ (*c* 2.1). Although a 69% yield of **3** and **4** (based on **1**) was obtained, simpler conditions were still required because of purification problems caused by contamination with the crown ether. Significant improvement was made by the use of an excess of sodium or potassium carbonate, without any other catalysts. With potassium carbonate in methanol, the α anomer **3** (~17%) crystallized after deionization with Amberlite IR-120 (H^+ form) and removal of the solvent. Almost pure β anomer **4** (~62%) was obtained as a syrup after chromatographic purification. As the β anomer (**4**) is liable to epimerize to **3**, however, no complete purification was successful. The products **3** and **4** were characterized as the known *O*-isopropylidene benzoate derivatives[5] **6** and **8**.

Under the same conditions, however, condensation of 5-deoxy-D-xylose (**9**) with methyl nitroacetate, was complicated. Nevertheless, further efforts led to acceptable results; the cyclic product **10** was isolated in 69% overall yield (based on 5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose as the preparative precursor of **9**) when a catalytic amount of potassium acetate and 5 mol of calcium chloride (as a dehydrating agent) in tetrahydrofuran were employed. No other diastereomers were obtained. Structural assignment of **10** was based on elemental analysis, characteristic i.r. absorption bands at 1750 (CO_2Me) and 1560 cm^{-1} (NO_2), a $J_{3,4}$ coupling constant (1.6 Hz), suggesting a *trans*-relationship between H-3 and H-4, and the following chemical transformations providing firm evidence.

Addition of nitromethane to 5-deoxy-D-xylose in the presence of potassium acetate and 18-crown-6 in tetrahydrofuran selectively gave an epimeric mixture of addition products (**11**), in contrast to the case with D-ribose. This mixture readily

*R_F values: 0.08 for **1**, 0.32 for **2**, and 0.55 for **3** and **4** 10:5:1 in ethyl acetate–acetone–water.



underwent dehydration and subsequent cyclization upon heating in water to give the β and α anomers **12** and **13** (~2:1) in 63% yield. The β anomer **12** was isolated by fractional crystallization. The optical rotations (−53° in acetone for **12** and −17° for a ~1:4 mixture of **12** and **13**) suggested that compounds **12** and **13** had the β and α configuration, respectively[2,6]. Compounds **12** and **13** were hydrogenated with Raney nickel and the products were benzyloxycarbonylated to afford **16** and **17**.

After chromatographic separation, the amino sugars **16** and **17** were converted into the dimethanesulfonates **18** and **19**, respectively.

Chemical shifts in ^{13}C-n.m.r. are often employed for determining the anomeric configuration of *O*-, *N*-, and *C*-glycosyl derivatives. In methyl D-xylofuranosides, the anomeric carbon atom of the α anomer resonates at higher field than that of the β counterpart, because of steric hindrance[7]. For the disulfonates **18** and **19**, most of the signals in the ^{13}C-n.m.r. spectra were assigned by selective proton-decoupling[8]. The C-2 atoms of compounds **18** and **19**, which correspond to the anomeric carbon atom, resonate at 81.97 and 75.04 p.p.m., respectively, indicating that **19** has the α configuration. Assignments of C-1 and C-6 for compounds **3**, **4**, **6**, **12**, **13**, and **16–19** were readily made by chemical-shift reasoning and by off-resonance, broad-band decoupling. It is noteworthy that C-1 of all of the α anomers resonates at higher field than that of the corresponding β anomers.

In order to determine the configuration at C-3 of **10**, direct conversion of **10** into **12** or **13** was attempted. As judged from t.l.c., compound **10** was stable and was recovered on acid treatment with trifluoroacetic acid or *p*-toluenesulfonic acid, whereas the reaction became complicated on treatment with base (sodium methoxide). Catalytic hydrogenation of **10** with palladium-on-carbon followed by pyrolysis afforded the same spot as **14** (and not **15**) in t.l.c., revealing that **10** has the β configuration.

EXPERIMENTAL

General methods. — Melting points are uncorrected. Solutions were evaporated under diminished pressure. Optical rotations were measured with a Carl Zeiss photoelectric polarimeter. I.r. spectra were recorded for potassium bromide discs with a Hitachi 215 i.r. spectrophotometer. ^{1}H-N.m.r. spectra were taken with a Varian EM-360 or a JNM-4H-100 (JEOL) spectrometer with tetramethylsilane as the internal standard. ^{13}C-N.m.r. spectra were recorded with a Varian CFT-20 spectrometer (chemical shifts in p.p.m.). Column chromatography and t.l.c. were performed on silica gel [C-300 (Wakogel, Japan) and GF 254 (E. Merck, Darmstadt)], with the following solvent systems: carbon tetrachloride–acetone (*A*) 1:2 (v/v); (*B*) 20:1; (*C*) 3:1; (*D*) 1:1; (*E*) 2:1; (*F*) 5:2 ethyl acetate–hexane; (*G*) 10:9:1 methanol–chloroform–25% ammonium hydroxide.

*2,5-Anhydro-1-deoxy-1-nitro-*D*-altritol* (**3**) *and* -D-*allitol* (**4**). — (*a*) D-Ribose (15 g, 0.1 mol) was treated with nitromethane (40 mL, 0.74 mol) in methanol (90 mL) in the presence of M sodium methoxide (45 mL, 0.045 mol) for 3 h at room temperature with stirring. After deionization with cation-exchange resin (Amberlite IR-120, H^+), the filtrate was evaporated and the residue dissolved in water (80 mL). The aqueous solution was heated for 14 h at 70–80° and then evaporated. The residue was purified by column chromatography with ethyl acetate as eluant. Fractions having R_F 0.5 (*A*) were combined and evaporated to give a mixture of **3** and **4**, from which crystalline **3** was separated. Recrystallization from isopropyl alcohol afforded 1.93 g (10%)

of **3**; m.p. 139–140°, $[\alpha]_D^{22}$ +79° (*c* 1, water); ν_{max} 1550 cm^{-1} (NO_2); ^{13}C-n.m.r. (D_2O): δ 57.16 (C-6), 71.79 (C-1), 67.39, 67.65, 73.05, and 77.97 (C-2–C-5).

Anal. Calc. for $C_6H_{11}NO_6$: C, 37.31; H, 5.74; N, 7.25. Found: C, 37.47; H, 5.75; N, 7.10.

The mother liquor consisted of **4** (4.84 g, 25%) together with traces of **3**, having $[\alpha]_D^{22}$ −7° (*c* 1.5, water).

(*b*) To a solution of D-ribose (12 g, 0.08 mol), nitromethane (43.2 mL, 0.8 mol), and 18-crown-6 (5.28 g, 0.02 mol) in tetrahydrofuran (500 mL) was added potassium carbonate (550 mg, 5.2 mmol) and the mixture was stirred for 24 h at room temperature. After neutralization with M hydrochloric acid, the mixture was evaporated. The residue was chromatographed with ethyl acetate as eluant and the eluate containing products was roughly divided into two fractions containing or not containing the crown ether. These two fractions were chromatographed again and the eluates having R_F 0.5 (*A*) were combined. Treatment similar to that just described (*a*) afforded **3** (2.47 g, 16%) and **4** (8.18 g, 53%), the latter containing a small amount of **3**. Compound **4** had ^{13}C-n.m.r. (D_2O): 62.17 (C-6), 78.00 (C-1), 71.63, 72.88, 79.42, and 85.50 (C-2–C-5).

(*c*) A solution of D-ribose (15 g, 0.1 mol), nitromethane (6 mL, 0.11 mol), and potassium carbonate (13.8 g, 0.1 mol) in methanol (100 mL) was stirred at room temperature until starting material was no longer detectable in t.l.c. (~6 h). After addition of water, the mixture was deionized. Removal of the resin, and complete evaporation of the filtrate by azeotropic distillation with ethanol, afforded crystalline **3** (3.28 g, 17%, after recrystallization).

The mother liquor was evaporated and the residue was similarly chromatographed to afford 12 g (62%) of **4** containing a small amount of **3**.

*2,5-Anhydro-6-*O*-benzoyl-1-deoxy-3,4-*O*-isopropylidene-1-nitro*-D*-altritol* (**6**). — A solution of **3** (7.90 g, 40.9 mmol) and 2,2-dimethoxypropane (5.5 mL) in tetrahydrofuran (80 mL) in the presence of *p*-toluenesulfonic acid (70 mg) was gently distilled (Vigreux column) at ~60° until compound **3** was no longer detectable in t.l.c. (*A*). The mixture was deionized with the resin and evaporated. The syrup was dissolved in tetrahydrofuran (50 mL) and cooled at 0°. To the solution was added benzoyl chloride (14.3 mL, 0.12 mol) and then slowly pyridine (8.3 mL). The mixture was stirred for 6 h at 0° and evaporated completely. The oily layer obtained was washed several times with water and petroleum ether. Addition of methanol afforded crystals, which were recrystallized from ethanol to give 12.1 g (88%) of **6**, identical (t.l.c., i.r. spectra) with an authentic sample[5].

*2,5-Anhydro-6-*O*-benzoyl-1-deoxy-3,4-*O*-isopropylidene-1-nitro*-D*-allitol* (**8**). — Similar treatment of **4** (6.30 g, 32.6 mmol, contaminated with **3**) to that just described afforded **8** (8.75 g) and **6** (1.5 g) after chromatographic separation (*B*). Recrystallization from ethanol afforded 7.47 g (68%) of **8** and 1.21 g (11%) of **6**, identical (t.l.c., i.r. spectra) with authentic samples.

Methyl 3,6-anhydro-2,7-dideoxy-2-nitro-D-glycero-L-talo-*heptonate or* -D-glycero-L-galacto-*heptonate* (**10**). — 5-Deoxy-1,2-*O*-isopropylidene-α-D-xylose[9] (2.9 g,

~16.7 mmol) was treated with 1% sulfuric acid (45 mL) for 1 h at 80°. The mixture was made neutral with barium hydroxide and the precipitated barium sulfate was filtered off. The filtrate was evaporated to give syrupy **9**, which was used for the next reaction without further purification. A mixture of the syrup, methyl nitroacetate (4.25 g, 35.7 mmol), potassium acetate (83 mg), calcium chloride (10.8 g), and tetrahydrofuran (45 mL) was stirred for 4 days at room temperature. Calcium chloride was filtered off and the filtrate was evaporated. The residue was chromatographed (*C*) to give crystalline **10** (2.7 g, 68.9%). An analytical sample was prepared by recrystallization from dichloromethane–hexane or acetone–hexane; m.p. 110° (dec.), $[\alpha]_D^{20}$ −42° (*c* 1, methanol); R_F 0.50 (*F*); ν_{max} 1750 (CO) and 1560 cm^{-1} (NO_2); ^{1}H-n.m.r. (CD_3OD): δ 5.61 (d, 1 H, $J_{2,3}$ 10 Hz, H-2), 4.43 (q, 1 H, $J_{3,4}$ 1.6 Hz, H-3), 4.23 (d, 1 H, $J_{4,5}$ ~0 Hz, H-4), 3.92 (d, 1 H, $J_{5,6}$ 3.5 Hz, H-5), 4.27 (oct, 1 H, $J_{6,7}$ 7.0 Hz, H-6), 1.23 (d, 3 H, H-7), and 3.87 (s, 3 H, OMe).

Anal. Calc. for $C_8H_{13}NO_7$: C, 40.85; H, 5.57; N, 5.96. Found: C, 40.70; H, 5.31; N, 5.78.

*2,5-Anhydro-1,6-dideoxy-1-nitro-*D*-gulitol* (**12**) *and* -D-*iditol* (**13**). — A mixture of 5-deoxy-D-xylose **9** (3 g, 22 mmol), nitromethane (4 g, 66 mmol), potassium carbonate (0.3 g), 18-crown-6 (0.6 g), and tetrahydrofuran (100 mL) was stirred for 2 days at room temperature. The solvent was evaporated and the residue was chromatographed with ethyl acetate as eluant, giving **11** as a syrup (3.7 g, 85%). The syrup was dissolved in water (50 mL) and the aqueous solution heated for 15 h at 80–90°. The mixture was evaporated and the residue chromatographed with ethyl acetate as eluant to yield a crystalline mixture (2.5 g, 63% from **9**). Fractional crystallization from isopropyl alcohol–diisopropyl ether afforded **12** (796 mg, 20.1%); m.p. 101–102°, $[\alpha]_D^{20}$ −53° (*c* 1, acetone); ν_{max} 1560 cm^{-1} (NO_2); ^{1}H-n.m.r. (CD_3OD + traces of AcOH): δ 4.67 (q, 2 H, $J_{1,2}$ 7.7, $J_{1',2}$ 7.5 Hz, H-1 and H-1'), 4.33 (sex, 1 H, $J_{2,3}$ 2.3 Hz, H-2), 3.95 (q, 1 H, $J_{3,4}$ 1.5 Hz, H-3), 3.87 (q, 1 H, $J_{4,5}$ 3.5 Hz, H-4), 4.22 (oct, 1 H, $J_{5,6}$ 7.0 Hz, H-5), and 1.26 (d, 3 H, H-6); ^{13}C-n.m.r. (CD_3OD): 14.35 (C-6), 78.81 (C-1), 79.29, 79.58, 81.06, and 82.94 (C-2–C-5).

Anal. Calc. for $C_6H_{11}NO_5$: C, 40.68; H, 6.26; N, 7.91. Found: C, 40.75; H, 6.35; N, 7.72.

A 1:4 mixture of **12** and **13** had $[\alpha]_D^{20}$ −17° (*c* 1, acetone); ^{13}C-n.m.r. (CD_3OD) of **13**: δ 14.02 (C-6), 76.60 (C-1), 78.08, 78.08, 78.64, and 79.46 (C-2–C-5).

*2,5-Anhydro-1-benzyloxycarbonylamino-1,6-dideoxy-*D*-gulitol* (**16**) *and* -D-*iditol* (**17**). — A mixture of **12** and **13** (2.32 g, 13.1 mmol) in methanol (10 mL) was hydrogenated in the presence of Raney nickel (510 mg). After stirring overnight at room temperature, the catalyst was filtered off and the filtrate was evaporated. The syrup (1.92 g), which consisted of **14** and **15** [R_F 0.50 and 0.40, respectively, (*G*)], was dissolved in water–methanol (20 mL, 1:1, v/v), and sodium carbonate (1.66 g) and benzyl chloroformate (2.67 g) were gradually added to the solution with stirring at room temperature. After stirring overnight, the mixture was deionized. The residue was chromatographed with dichloromethane–acetone (50:1, v/v) as eluant. Compound **17** was eluted faster than **16** (total yield, 2.75 g). The products were recrystallized

from chloroform–hexane: **16**, 1.31 g (35.5%); m.p. 99–100°, $[\alpha]_D^{20}$ −15° (*c* 1, methanol); R_F 0.36 (*D*); ν_{max} 3300 (NH), 1685 and 1530 cm^{-1} (amide); ^{1}H-n.m.r. (CD_3OD): δ 7.34 (s, 5 H, Ph), ~3.37 (q, 2 H, $J_{1,2}$ 4.5 and $J_{1',2}$ 5.6 Hz, H-1 and H-1'), 3.1–3.9 (m, 3 H, H-2, H-3, and H-4), 4.09 (oct, 1 H, $J_{5,6}$ 6.7 Hz, H-5), 1.23 (d, 3 H, H-6), and 5.10 (s, 2 H, OCH_2Ph); ^{13}C-n.m.r. (CD_3OD): δ 14.16 (C-6), 44.44 (C-1), 67.50 (OCH_2Ph), 78.64, 80.02, 81.53, and 85.21 (C-2–C-5).

Anal. Calc. for $C_{14}H_{19}NO_5$: C, 59.77; H, 6.81; N, 4.98. Found: C, 59.57; H, 6.69; N, 4.89.

Compound **17** (0.82 g, 22.3%) had m.p. 100–101°, $[\alpha]_D^{20}$ +5° (*c* 1, methanol); R_F 0.42 (*D*); ν_{max} 3450 (NH), 1680 and 1540 cm^{-1} (amide); ^{1}H-n.m.r. (CD_3OD): δ 7.33 (s, 5 H, Ph), ~3.37 (d, 2 H, $J_{1,2} = J_{1',2}$ 5.6 Hz, H-1 and H-1'), 4.12 (sex, 1 H, $J_{2,3}$ 2.6 Hz, H-2), 3.31 (q, 1 H, $J_{3,4}$ 1.5 Hz, H-3), 3.89 (q, 1 H, $J_{4,5}$ 3.0 Hz, H-4), 4.24 (oct, 1 H, $J_{5,6}$ 5.2 Hz, H-5), 1.18 (d, 3 H, H-6), and 5.08 (s, 2 H, OCH_2Ph); ^{13}C-n.m.r. (CD_3OD): 14.29 (C-6), 41.21 (C-1), 67.58 (OCH_2Ph), 77.65, 78.37, 79.38, and 80.14 (C-2–C-5).

Anal. Calc. for $C_{14}H_{19}NO_5$: C, 59.77; H, 6.81; N, 4.98. Found: C, 59.50; H, 6.66; N, 5.31.

Similar hydrogenation of **12** afforded **14** [R_F 0.50 (*G*)], which was converted into **16**.

*2,5-Anhydro-1-benzyloxycarbonylamino-1,6-dideoxy-3,4-di-*O*-(methylsulfonyl)-*D*-gulitol* (**18**). — Compound **16** (829 mg, 2.95 mmol) was dissolved in pyridine (5 mL) and the solution was cooled to −18°. To the solution was added methanesulfonyl chloride (880 mg, 7.69 mmol) dropwise with stirring, and the mixture was kept at 0° for 3 h. Crushed ice was added, and the mixture was stirred for 1 h and then extracted with chloroform. The extracts were washed with water, dried (sodium sulfate), and evaporated. Addition and evaporation of ethanol yielded a crystalline material, which was recrystallized from ethanol to give 1.09 g (84.5%) of **18**; m.p. 95–97°, $[\alpha]_D^{20}$ +5° (*c* 1, chloroform); R_F 0.48 (*E*); ν_{max} 3370 (NH), 1680 and 1540 (amide), 1350, 1330, and 1180 cm^{-1} (SO_2); ^{1}H-n.m.r. ($CDCl_3$): δ 7.34 (s, 5 H, Ph), ~3.55 (m, 2 H, $J_{1,2} = J_{1',2}$ 3.7 Hz, H-1 and H-1'), 4.00 (q, 1 H, $J_{2,3}$ 3.7 Hz, H-2), 5.02 (q, 1 H, $J_{3,4} \leq$ 1.0 Hz, H-3), 5.04 (q, 1 H, $J_{4,5}$ 3.7 Hz, H-4), 4.18 (oct, 1 H, $J_{5,6}$ 6.7 Hz, H-5), 1.34 (d, 3 H, H-6), 3.10 (s, 3 H, Ms), 2.06 (s, 3 H, Ms), and 5.12 (s, 2 H, OCH_2Ph); ^{13}C-n.m.r. ($CDCl_3$): δ 13.16 (C-6), 37.93 and 38.48 (Ms), 41.68 (C-1), 67.14 (OCH_2Ph), 76.64 (C-5), 81.97 (C-2), 84.05 and 84.34 (C-3–C-4).

Anal. Calc. for $C_{16}H_{23}NO_9S_2$: C, 43.93; H, 5.30; N, 3.20; S, 14.66. Found: C, 43.79; H, 5.14; N, 3.25; S, 14.72.

*2,5-Anhydro-1-benzyloxycarbonylamino-1,6-dideoxy-3,4-di-*O*-(methylsulfonyl)-*D*-iditol* (**19**). — Treatment of **17** (352 mg, 1.25 mmol) as just described (foregoing) afforded **19** (448 mg, 81.8%); m.p. 97–98°, $[\alpha]_D^{20}$ +2° (*c* 1, chloroform); R_F 0.44 (*E*); ν_{max} 3375 (NH), 1690 and 1535 (amide), 1350–1370 and 1180 cm^{-1} (SO_2); ^{1}H-n.m.r. ($CDCl_3$): δ 7.34 (s, 5 H, Ph), 3.46 (t, 2 H, $J_{1,2} = J_{1',2} = J_{1,NH}$ 6.3 Hz, H-1 and H-1'), 4.31 (sex, 1 H, $J_{2,3}$ 4.5 Hz, H-2), 5.21 (q, 1 H, $J_{3,4}$ 1.1 Hz, H-3), 5.09 (q, 1 H, $J_{4,5}$ 3.7 Hz, H-4), 4.43 (oct, 1 H, $J_{5,6}$ 6.0 Hz, H-5), 1.29 (d, 3 H, H-6), ~5.25 (t, 1 H, NH),

3.12 (s, 6 H, Ms), and 5.16 (s, 2 H, OCH_2PH); ^{13}C-n.m.r. ($CDCl_3$): δ 14.18 (C-6), 38.02 and 38.16 (Ms), 39.76 (C-1), 66.85 (OCH_2Ph), 75.04 (C-2), 77.10 (C-5), 81.35 (C-4), and 83.04 (C-3).

Anal. Calc. for $C_{16}H_{23}NO_9S_2$: C, 43.93; H, 5.30; N, 3.20; S, 14.66. Found: C, 44.01; H, 5.23; N, 3.35; S, 14.89.

T.l.c. study on pyrolysis of hydrogenated **10**. — Palladium-on-carbon was activated by hydrogen in 5:1 methanol–water, and compound **10** (285 mg, 1.21 mmol) was hydrogenated in the presence of M acetic acid (1.25 mL). When 70 mL of hydrogen had been consumed, the mixture was filtered, and the filtrate evaporated to a syrup (280 mg). The syrup (2 mg), upon boiling in 0.1 mL of dimethyl sulfoxide for 5 min, gave the same spot as **14** [R_F 0.50 (*G*)].

REFERENCES

1 S. HANESSIAN AND A. G. PERNET, *Adv. Carbohydr. Chem. Biochem.*, 33 (1976) 111–188.
2 H. OHRUI, G. H. JONES, J. G. MOFFATT, M. L. MADDOX, A. T. CHRISTENSEN, AND S. K. BYRAM, *J. Am. Chem. Soc.*, 97 (1975) 4602–4613.
3 J. C. SOWDEN, C. H. BOWERS, L. HOUGH, AND S. H. SHUTE, *Chem. Ind. (London)*, (1962) 1827–1828.
4 L. HOUGH AND S. H. SHUTE, *J. Chem. Soc.*, (1962) 4633–4637.
5 T. TAKAMOTO, H. OMI, T. MATSUZAKI, AND R. SUDOH, *Carbohydr. Res.*, 60 (1978) 97–103.
6 J. C. SOWDEN AND H. O. L. FISCHER, *J. Am. Chem. Soc.*, 69 (1947) 1048–1050.
7 R. G. S. RITCHIE, N. CYR, B. KORSCH, H. J. KOCH, AND A. S. PERLIN, *Can. J. Chem.*, 53 (1975) 1424–1433.
8 *E.g.*, L. F. JOHNSON, in G. C. LEVY (Ed.), *Topics in Carbon-13 NMR Spectroscopy*, Wiley–Interscience, New York, Vol. 3, pp. 7–15.
9 P. A. LEVENE AND J. COMPTON, *J. Biol. Chem.*, 111 (1935) 325–333.