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Note

Facile 1-*O*-deacylation of per-*O*-acylaldoses

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Acylated aldoses having the anomeric hydroxyl group free are versatile synthetic intermediates. Various attempts[1–3] have been made for their preparation. Hydrolysis of acetylated glycosyl bromides[4] with silver carbonate in aq. acetone, or of *N*-*p*-tolylaldopyranosylamine acetates[5] with formic acid, are standard procedures for the preparation of such acetylated aldoses.

Preparative methods of such acylated sugars have recently been reported in which per-*O*-acylaldoses were selectively deprotected at the anomeric position by using appropriate solvents and either alkali, Lewis acid, or organic tin oxides, including hydrazine acetate[6], potassium hydroxide[2], potassium cyanide[2], sodium methoxide[7], benzylamine[8], ammonia[9], alumina[10], stannic chloride[11], bis(tributyltin)oxide[2,15], and tributyltin methoxide[15].

As a mild reagent for the selective 1-*O*-deacylation of per-*O*-acylaldoses, we have found ammonium carbonate to give good results.

An initial attempt to deacylate per-*O*-acetyl-α-D-glucopyranose with this agent in methanol caused additional deacetylation under the conditions used (30°, 2 h). Other solvents then examined included acetonitrile, tetrahydrofuran (THF), acetone, 1-methoxy-2-propanol, pyridine and *N*,*N*-dimethylformamide (DMF). The last one (DMF) gave good results; the others were ineffective because reaction times were too long. Thus per-*O*-acetyl-α- and -β-D-gluco (**1** and **2**) and -D-galactopyranoses (**3** and **4**), -α-D-mannopyranose (**5**), and -β-D-xylopyranose (**6**) were selectively deacetylated at the anomeric position with ammonium carbonate in DMF in good yields to the corresponding acylated aldopyranoses (**7**, **8**, **9**, and **10**). Per-*O*-benzoyl-α-D-glucopyranose (**11**) was also effectively converted into 2,3,4,6-tetra-*O*-benzoyl-D-glucopyranose (**12**) with ammonium carbonate in a THF–methanol mixture.

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EXPERIMENTAL

General methods. — ^{1}H-N.m.r. spectra were recorded with a Jeol GSX-270W spectrometer for solutions in $CDCl_3$ with Me_4Si as the internal standard. Melting points were determined in a Shimazu Seisakusho Co. apparatus and are uncorrected. Optical rotations were measured with a Horiba SEPA-200 polarimeter. Column chromatography was performed with EtOAc and hexane as eluent on a column of silica gel CPS-HS-221 (22 mm × 100 mm × 2). Reactions were monitored by t.l.c. on silica gel (plastic plates, $60F_{254}$, Merck) with 2:3 EtOAc–hexane. Detection was performed by spraying with 8% aq. H_2SO_4 followed by heating at 110°. Per-*O*-acetyl-D-aldoses and per-*O*-benzoyl-D-glucopyranose used as starting materials were from Sigma Chemical Co. and Aldrich Chemical Co., respectively. Ammonium carbonate (lump) was purchased from Nakarai Chemicals Co.

2,3,4,6-Tetra-O-acetyl-D-glucopyranose (**7**) *(typical preparation for 2,3,4,6-tetra-O-acetyl-D-hexopyranoses).* — To a solution of **1** (1 g) in dry DMF (6 mL) was added ammonium carbonate (0.5 g; powdered just before use). The mixture was stirred for 20 h at 30°. The reaction generated CO_2 and the turbid solution gradually became clear. After the addition of $CHCl_3$ (20 mL) the mixture was poured with stirring into ice-cooled M HCl (20 mL). The organic layer was removed and the aq. solution was extracted with $CHCl_3$ (30 mL × 2). The combined mixture was washed with saturated $NaHCO_3$ solution (20 mL) and water (15 mL), and evaporated *in vacuo* <40° with additions of butanol–water to the residue for azeotropic removal of DMF. The syrup was dissolved in CH_2Cl_2 and dried with anhydrous Na_2SO_4. After evaporation *in vacuo* the residue was dissolved in a little EtOAc for purification by column chromatography (2:1 hexane–EtOAc). The resultant material was treated[14] with pyridine–Ac_2O to give a mixture of per-*O*-acetylated-α- and -β-D-glucopyranoses.

Compounds **7** derived from **1** and **2** were syrups (respective yields: 74–79 and 87%); from **1** $[\alpha]_{\mathrm{D}}^{23}$ +71.6° (*c* 0.55, $CHCl_3$), from **2**, $[\alpha]_{\mathrm{D}}^{23}$ +104.4° (*c* 0.81, $CHCl_3$); lit.[2]: $[\alpha]_{\mathrm{D}}^{15}$ +71° (*c* 1.14, $CHCl_3$); lit.[9]: anomer (α:β 4:1), $[\alpha]_{\mathrm{D}}^{20}$ +75° (*c* 1, $CHCl_3$); lit.[11]: m.p. 126–129°, $[\alpha]_{\mathrm{D}}$ +96° (*c* 1.5, $CHCl_3$); lit.[11]: m.p. 107–110°, $[\alpha]_{\mathrm{D}}$ +48° (*c* 1.5, $CHCl_3$); lit.[6]: $[\alpha]_{\mathrm{D}}^{20}$ +74° (*c* 1.95, $CHCl_3$); lit.[12]: α anomer, m.p. 113°, $[\alpha]_{\mathrm{D}}$ + 142 → +80.3° ($CHCl_3$), β anomer, m.p. 120°, $[\alpha]_{\mathrm{D}}$ +2.2 → +82.7° ($CHCl_3$); ^{1}H-n.m.r.: δ 2.02–2.09 (3 s, 12 H, 4 Ac), 3.7–4.3 (m, 3 H, H-5,6,6′), and 4.7–5.6 (m, 5 H, H-1,2,3,4, and OH).

Anal. Calc. for $C_{14}H_{20}O_{10}$: C, 48.27; H, 5.80. Found: C, 48.35; H, 5.69 (derived from **1**), C, 48.16; H, 5.88 (derived from **2**).

2,3,4,6-Tetra-O-acetyl-D-galactopyranose (**8**). — Compounds **8** obtained from **3** and **4** were syrups (respective yields; 75 and 78%), from **3**, $[\alpha]_{\mathrm{D}}^{23}$ +104.8° (*c* 0.65, $CHCl_3$), from **4**, $[\alpha]_{\mathrm{D}}^{23}$ +93.4° (*c* 0.64, $CHCl_3$); lit.[2]: m.p. 103–108° (Et_2O), $[\alpha]_{\mathrm{D}}^{15}$ +74° (*c* 1.09, $CHCl_3$); lit.[11]: m.p. 136–138°, $[\alpha]_{\mathrm{D}}$ +133° (*c* 1.9, $CHCl_3$); m.p. 139–140°, $[\alpha]_{\mathrm{D}}$ +139° (*c* 2.4, $CHCl_3$); lit.[12]: α anomer, m.p. 133°, $[\alpha]_{\mathrm{D}}$ +144° ($CHCl_3$), β anomer, m.p. 112°, $[\alpha]_{\mathrm{D}}$ +31.1° → +79.9° ($CHCl_3$); lit.[13b]: α anomer, m.p. 143–

146°, $[\alpha]_D^{22}$ +135° → +69.5° (c 2.0, aq. EtOH, 48 h); ^{1}H-n.m.r.: δ 2.01–2.18 (4 s, 12 H, 4 Ac), 3.8–5.6 (m, 8 H, H-1,2,3,4,5,6,6′, and OH).

Anal. Calc. for $C_{14}H_{20}O_{10}$: C, 48.27; H, 5.80. Found: C, 48.19; H, 5.88 (derived from **3**), C, 48.14; H, 5.71 (derived from **4**).

*2,3,4,6-Tetra-O-acetyl-*D*-mannopyranose* (**9**). — Compound **9** obtained from **5** was a powder (yield; 95%), m.p. 88–89°, $[\alpha]_D^{23}$ +24.6° (c 0.5, $CHCl_3$); lit.[2]: m.p. 94.5–97.5° (Et_2O), $[\alpha]_D^{15}$ +22° (c 1.0, $CHCl_3$); lit.[9]: α anomer, m.p. 92° (Et_2O), $[\alpha]_D^{20}$ +21° (c 1, $CHCl_3$); lit.[11]: m.p. 95–96°, $[\alpha]_D$ +30° (c 1.7, $CHCl_3$); lit.[12]: α anomer, m.p. 93°, $[\alpha]_D$ +26.3° ($CHCl_3$), β anomer, m.p. 160°, $[\alpha]_D$ −24.2° ($CHCl_3$), m.p. 124°, $[\alpha]_D$ −13.6° → −12.0° ($CHCl_3$); lit.[13a]: α anomer, m.p. 93–94°, $[\alpha]_D^{25}$ +22.8° (c 2.2, $CHCl_3$), β anomer, m.p. 105–110°, $[\alpha]_D^{21}$ −12° (c 10, $CHCl_3$); ^{1}H- n.m.r.: δ 2.00–2.15 (4 s, 12 H, 4 Ac), 4.1–4.3 (m, 3 H, H-5, 6,6′), and 5.2–5.5 (m, 5 H, H-1,2,3,4, and OH).

Anal. Calc. for $C_{14}H_{20}O_{10}$: C, 48.27; H, 5.80. Found: C, 48.25; H, 5.77.

*2,3,4-Tri-O-acetyl-*D*-xylopyranose* (**10**). — The deacetylation of **6** was performed as already described except that the reaction was performed for 39 h at 25°. Compound **10** was obtained as powdery crystals (yield; 63%), m.p. 129–132°, $[\alpha]_D^{23}$ +59.6° (c 0.5, $CHCl_3$); lit.[2]: m.p. 137–139° (Et_2O), $[\alpha]_D^{15}$ +63° (c 1.35, $CHCl_3$); lit.[6]: α anomer m.p. 160°, $[\alpha]_D^{20}$ +94° → +64° (c 1, pyridine, 24 h), $[\alpha]_D^{20}$ +67° (c 1.25, $CHCl_3$) → +33.5° ($CHCl_3$ + a trace of CF_3CO_2H); lit.[12]: α anomer, m.p. 138°, $[\alpha]_D$ +70.1° → +40.8°, β anomer, m.p. 142°, $[\alpha]_D$ −20.0° ($CHCl_3$); ^{1}H-n.m.r.: δ 2.04, and 2.09 (2 s, 9 H, 3 Ac), 3.8–3.9 (m, 2 H, H-5,5′), 4.8–5.6 (m, 5 H, H-1,2,3,4, and OH).

Anal. Calc. for $C_{11}H_{16}O_8$: C, 47.82; H, 5.85. Found: C, 47.87; H, 5.82.

*2,3,4,6-Tetra-O-benzoyl-*D*-glucopyranose* (**12**). — To a solution of **11** (1 g) in dry THF (10 mL) was added dry MeOH (20 mL). Into the mixture $(NH_4)_2CO_3$ (1.5 g; powdered just before use) was dispersed. The suspension (sometimes turbid but becoming clear during the reaction with the evolution of CO_2) was stirred for 30 h at 30°. Dichloromethane (30 mL) was added to the mixture and the solution was evaporated to ~30 mL *in vacuo* <30°. Further evaporation was performed three times with additional $CHCl_3$ (30 mL each). The final mixture (~30 mL) was poured into ice–water (20 mL) and the organic layer was washed with water (20 mL × 3) followed by evaporation to a syrup *in vacuo* below 40°. The residue was dissolved in little EtOH and refrigerated overnight. Residual **11** was filtered off and washed with cooled EtOH. The filtrate was evaporated to dryness and the residue recyrstallized from Et_2O and hexane.

Compound **12** was obtained as fibrous crystals (yield; 60%), m.p. 91–92°, $[\alpha]_D^{23}$ +66.0° (c 0.5, $CHCl_3$); lit.[2]: m.p. 89–92° (Et_2O), $[\alpha]_D^{15}$ +65° (c 1.21, $CHCl_3$); lit.[9]: α anomer, m.p. 112° (Et_2O and hexane), $[\alpha]_D^{20}$ +71° (c 1, $CHCl_3$); ^{1}H-n.m.r.: δ 4.4–5.1 (m, 4 H, H-5,6,6′, and OH), 5.6–6.1 (m, 2 H, H-2,4), 6.25 (t, 1 H, H-3), 7.2–8.2 (m, 20 H, 4 Bz).

Anal. Calc. for $C_{34}H_{28}O_{10}$: C, 68.44; H, 4.74. Found: C, 68.36; H, 4.85.

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