Carbohydrate Research, 26 (1973) 441–447

Note

Chromium trioxide–dipyridine complex as an oxidant for partially protected sugars; preparation of aldehydo and certain keto sugar derivatives*†

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(Received October 4th, 1972)

Oxidation of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**7**) by use of *N*,*N*′-dicyclohexylcarbodiimide and methyl sulfoxide[1] affords the corresponding 6-aldehyde[2,3] **8**, a precursor that has been used in this laboratory[2–5] and elsewhere[6] in chain-extension reactions for synthesis of higher-carbon sugars. A route[7] to such aldehydes that is an alternative and that has wide versatility[8] involves photolysis of primary azido derivatives of sugars. In the search for a direct oxidative procedure having greater manipulative convenience, we have evaluated the chromium trioxide–dipyridine complex[9] prepared *in situ* in dichloromethane[10] as an oxidant for partially protected sugars. The present report shows that this reagent provides a convenient and preparatively useful method for oxidizing **7** to **8**, and it was found equally effective for transforming methyl 2,3-*O*-isopropylidene-β-D-ribofuranoside (**5**) into the corresponding 5-aldehyde **6**, and 2,3:4,5-di-*O*-isopropylidene-β-D-fructopyranose (**1**) into the corresponding 1-aldehyde **2**. A protected aldose hemiacetal (**9**) was oxidized by the reagent to the corresponding lactone **10**, and the exocyclic secondary alcohol group of a 6-deoxyhexofuranose derivative (**11** or **16**) gave the corresponding ketone **12**. However, the reagent was not a satisfactory oxidant for three sugar derivatives (**13**, **14**, and **15**) containing endocyclic, "isolated", secondary alcohol groups.

Preparation of the $CrO_3 \cdot 2C_5H_5N$ complex *in situ*[10] by adding chromium trioxide to a solution of the calculated amount of pyridine in dichloromethane was found superior to the procedure employing the preformed complex[9], and maximum yields were achieved in the oxidation reactions by using a 12:1 molar ratio of oxidant to substrate, instead of the 6:1 ratio that had been used[9] for oxidizing hydrocarbon alcohols. Prolonged contact of an excess of the oxidant with the product is to be avoided as decreased yields result, and it is essential to exclude moisture rigorously

*Dedicated to Professor V. Deulofeu, in honor of his 70th birthday.
†Supported, in part, by the National Institutes of Health, U. S. Public Health Service, Department of Health, Education, and Welfare, Bethesda, Maryland 20014, Grant No. GM-11976 (The Ohio State University Research Foundation Project 1820).
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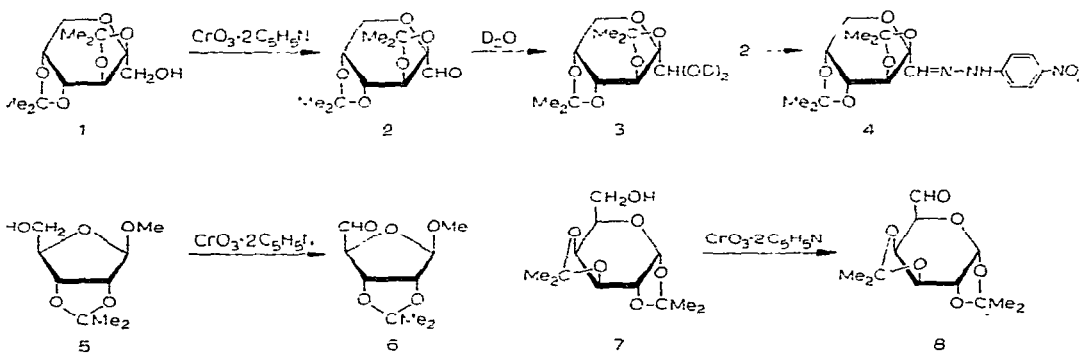
from the system. Isolation of the oxidized product is a simple operation, requiring only conventional washing of the dichloromethane phase (from which chromium reduction-products had precipitated) with sodium hydrogen carbonate, followed by evaporation of the dried organic layer.

The oxidation procedure was applied with 2,3:4,5-di-*O*-isopropylidene-β-D-fructopyranose (**1**) to afford the corresponding 1-aldehyde **2** as a syrup in 53% yield; it was chromatographically homogeneous, and was characterized by n.m.r. and mass spectrometry (see Experimental). Classical characterization was provided by preparation of a crystalline (*p*-nitrophenyl)hydrazone **4**, whose structure was entirely supported by analytical and n.m.r.-spectral data. It is noteworthy that 2,3:4,5-di-*O*-isopropylidene-*aldehydo*-β-D-*arabino*-hexosulo-2,6-pyranose (**2**) exists to the extent of ~90% as the aldehydrol form **3** in a 3:7 mixture of deuterium oxide and tetrahydrofuran. In an earlier, comparative study[11] of aldehydo sugar derivatives in this solvent mixture, it was shown that the aldehydrol form exhibits high stability (73–93% in a series of 5 examples), even in this medium that is more organic than aqueous. The aldehyde **2** is of interest as a starting material for the synthesis of extended-chain sugars.

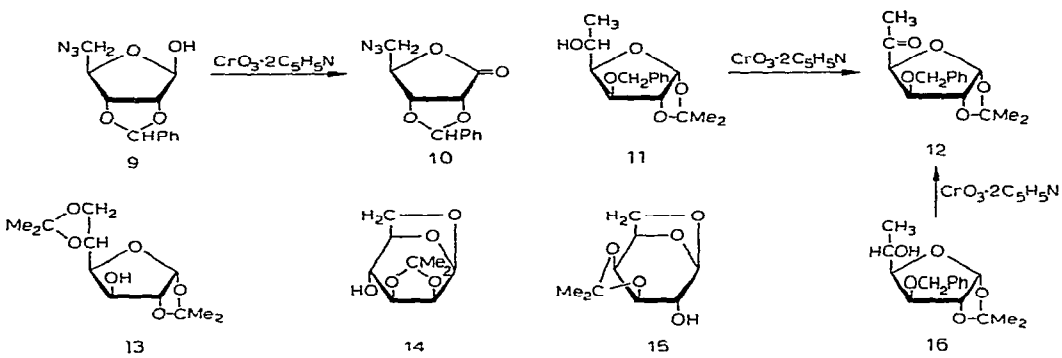
When applied with methyl 2,3-*O*-isopropylidene-β-D-ribofuranoside (**5**), the oxidant gave a 75% yield of the crystalline aldehyde[12] **6**, further characterized as the (*p*-nitrophenyl)hydrazone. The procedure was judged to be preparatively more convenient than other methods of direct oxidation[12,13] and than the route[14] involving photolysis of the 5-azido-5-deoxy derivative of **5**. Other direct-oxidation methods only gave syrupy **6** after extensive column-chromatography and distillation to remove side-products[13], or gave crystalline **6** after sublimation and recrystallization at low temperature[12].



Similarly, the oxidation procedure described here provided a convenient preparative route to 1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-hexodialdo-1,5-pyranose (**8**), obtained in 62% yield from the precursor alcohol **7**. The method offers considerable procedural simplification over the oxidation route first applied[2,3] for this synthesis; it is also superior, in involving fewer steps, to the route[15] involving photolysis of a 6-azido-6-deoxy precursor.

The successful preparation of the three aldehydes **2**, **6**, and **8** suggests that the reagent may be of general utility for the conversion of a primary hydroxymethyl group into an aldehyde group in otherwise protected sugar derivatives. It offers experimental advantages over the methyl sulfoxide–*N*,*N*′-dicyclohexylcarbodiimide method[1], and involves fewer steps than the azide photolysis method; the latter procedure is, however, particularly useful when unsubstituted or partially substituted derivatives are employed[8]. Used as described, the reagent behaves quite differently from the reagent of Sarett[16] (chromium trioxide in pyridine as the solvent).

A protected hemiacetal examined, namely, 5-azido-2,3-*O*-benzylidene-5-deoxy-β-D-ribofuranose (**9**), was oxidized by $CrO_3 \cdot 2C_5H_5N$ to the corresponding 1,4-lactone **10** in 88% yield; application of the Sarett[16] procedure to **9** gave[17] **10** in 80% yield. The Sarett procedure has been shown[18] to afford the 5-keto sugar **12** in ~50% yield from 3-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (**11**) or its L-*ido* analog (**16**) after three successive treatments. However, in the present study, it was found that yields of ~90% of the ketone **12** from either **11** or **16** can be achieved in a single operation by use of $CrO_3 \cdot 2C_5H_5N$ in dichloromethane. Oxidation of these



exocyclic, secondary alcoholic groups having an adjacent methyl group is, however, particularly facile, and the $CrO_3 \cdot 2C_5H_5N$ reagent does not appear to be of general value for oxidizing "isolated" secondary alcohol groups. Thus 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**13**) and 1,6-anhydro-3,4-*O*-isopropylidene-β-D-galactopyranose (**15**) are essentially inert toward the reagent, and 1,6-anhydro-2,3-*O*-isopropylidene-β-D-mannopyranose (**14**) gave a mixture of products. In contrast, the three compounds **13**, **14**, and **15** are successfully oxidized to the corresponding ketones by the methyl sulfoxide–acetic anhydride reagent evaluated in an early, comparative study[19]. In that work, evaluation of another reagent, namely, lead tetraacetate–pyridine, as an oxidant showed it to be generally ineffective with secondary alcohol derivatives; hemiacetals react to give mixtures of lactone and the acetic ester. The lead tetraacetate–pyridine reagent[20] appears to be selective regarding the alcohol precursors; the primary alcohol **7** gives a mixture of aldehyde **8**, starting alcohol **7**, and its 6-acetate[21], whereas the fructose derivative **1** is unreactive. As a preparative route to protected aldehydo sugars, this limited applicability of lead

tetraacetate–pyridine contrasts with the apparent generality of usefulness of the $CrO_3 \cdot 2C_5H_5N$ reagent employed here.

EXPERIMENTAL

General methods. — Melting points were determined with a Thomas–Hoover capillary apparatus, and are uncorrected. Solutions were evaporated *in vacuo* at ~45°. I.r. spectra were recorded with a Perkin–Elmer Model 137 spectrophotometer. N.m.r. spectra were recorded at 100 MHz with a JEOL MH-100 instrument, for solutions in chloroform-*d* containing ~5% of tetramethylsilane as the internal standard and lock signal. Chemical shifts are given on the τ scale, and the J values recorded are first-order spacings. Optical rotations were determined in 1-dm tubes with a Perkin–Elmer Model 141 recording polarimeter. Mass spectra were recorded by C. R. Weisenberger with an AEI MS-902 double-focusing, high-resolution spectrometer at an ionizing potential of 70 eV and an accelerating potential of 8 kV; the source temperature (direct-inlet system) was 150°. Microanalyses were performed by W. N. Rond. X-Ray powder diffraction data give interplanar spacings in Å for CuKα radiation (camera diameter 114.59 mm). Relative intensities were estimated visually: m, moderate; s, strong; v, very; w, weak. The three strongest lines are numbered (1, strongest). T.l.c. was performed on 0.25-mm layers of Silica Gel G (Merck), activated at 110°. G.l.c. was performed on a Beckman GC-5 dual-column instrument, with columns (3 mm × 1.5 m) of 3% SE-30 Chromosorb P (Applied Science Laboratories, State College, Pennsylvania), and helium at a flow-rate of 50 ml per min as the carrier gas.

Chromium trioxide (J. T. Baker, reagent grade) was weighed under nitrogen, and was stored in sealed vials prior to use. Dichloromethane (Matheson, Coleman and Bell, reagent grade) was used as supplied. Pyridine (reagent grade) was distilled from barium oxide, and was stored over Linde 4-A molecular sieves before use.

Oxidation procedure. — Chromium trioxide (12 moles per mole of the alcohol to be oxidized) was added to a solution of dry pyridine (2 moles per mole of CrO_3) in sufficient dichloromethane to give a solution ~10% (w/v) in the $CrO_3 \cdot 2C_5H_5N$ complex. The mixture was stirred, with exclusion of moisture, for 15–20 min at ~25° to afford a deep-red solution. A solution in dichloromethane of the alcohol to be oxidized was added in one portion, with stirring at ambient temperature, to the solution of the oxidant; a tarry deposit of chromium reduction-products formed at once. The mixture was stirred for a further 15–20 min at ~25°, and the supernatant solution was decanted into a separatory funnel containing an equal volume of ice-cold, saturated, aqueous sodium hydrogen carbonate. The tar was extracted with a little ether, and the extract was added to the contents of the separatory funnel; this was thoroughly agitated at 0°, and the organic layer was separated, washed with water, dried (magnesium sulfate), and evaporated to give the crude carbonyl derivative. Toluene was several times evaporated, at ~5 torr, from the residue, to remove traces of pyridine and afford either a syrupy or a crystalline residue, which was analyzed by

g.l.c. or t.l.c., and distilled or recrystallized to give an analytically pure product. The data given were obtained from experiments that were all performed at least twice with concordant results.

2,3:4,5-Di-O-isopropylidene-aldehydo-β-D-arabino-*hexosulo-2,6-pyranose* (**2**). — 2,3:4,5-Di-*O*-isopropylidene-β-D-fructopyranose[22] (**1**, 1.0 g, 3.85 mmol) in dichloromethane (5 ml) was oxidized by the foregoing procedure with a solution of chromium trioxide (4.7 g, 47 mmol) and pyridine (7.4 ml, 94 mmol) in dichloromethane (115 ml), to afford the aldehyde **2** as a syrup; yield 0.54 g (53%), homogeneous by t.l.c., but migrating at the same rate as **1**; retention time 1.76 min by g.l.c. at 135° (a second peak having ~1% of the area of that for **2** had a retention time of 3.33 min and corresponded to the starting alcohol **1**). Distillation at 0.04 torr gave analytically pure **2**, b.p. 79–80°, $[\alpha]_D$ −72° (*c* 1.2, chloroform); λ_{max}^{film} 5.70 (C=O), 7.24 μm (CMe_2); n.m.r. data: τ 0.49 (1-proton singlet, H-1), 5.36 (doublet of doublets, $J_{4,5}$ 7.6 Hz, H-4), 5.51 (doublet, $J_{3,4}$ 2.5 Hz, H-3), 5.72 (width 15.5 Hz, multiplet, H-5), 5.96, 6.16 (AB of ABX system, $J_{5,6}$ 2.0 Hz, $J_{5,6'}$ 1.0 Hz, $J_{6,6'}$ 13.0 Hz, H-6,6'), 8.44, 8.56, 8.58, and 8.65 (3-proton singlets, 2 CMe_2); *m/e* (relative intensities and probable assignments given in parentheses): 243 (55, $M^+ - \cdot CH_3$), 229 (51, $M^+ - \cdot CHO$), 201 (3, $M^+ - \cdot CH_3 - C_2H_2O$), 185 (6), 171 (62, $M^+ - \cdot CH_3 - C_2H_2O - H_2CO$), 143 (28), 125 (21), 113 (29), 97 (8), 85 (45), 83 (7), 69 (44), 59 (55), and 57 (23).

Anal. Calc. for $C_{12}H_{18}O_6$: C, 55.80; H, 7.03. Found: C, 55.97; H, 7.11.

For an uncharacterized oil prepared by oxidizing **1** with methyl sulfoxide and sulfur trioxide–pyridine, an n.m.r. signal at τ 0.46 has been reported[23].

Aldehyde–aldehydrol equilibrium of compound **2** *in 3:7 water–tetrahydrofuran.* — A solution (~10%) of **2** in 3:7 deuterium oxide–tetrahydrofuran was kept for 6.5 h at ~25° to establish equilibrium. The n.m.r. spectrum (internal tetramethylsilane as the standard) showed the signal for H-1 of the aldehydo form **2** at τ 0.70, and a singlet at τ 5.21 ascribed to H-1 of the aldehydrol form **3**, in the relative intensities of ~1:10.

2,3:4,5-Di-O-isopropylidene-aldehydo-β-D-arabino-*hexosulo-2,6-pyranose* (p-*nitrophenyl*)*hydrazone* (**4**). — A solution of the aldehyde **2** (530 mg, 2.06 mmol) and (*p*-nitrophenyl)hydrazine (330 mg, 2.16 mmol) in methanol (10 ml) was boiled for 15 min under reflux, and then evaporated. The residue was dissolved in benzene, and the solution was washed successively with ice-cold 10% sulfuric acid, aqueous sodium hydrogen carbonate, and water, dried (magnesium sulfate), and evaporated; the dark-red residue was recrystallized from 4:1 ethanol–benzene, to afford orange needles of analytically pure **4**; yield 521 mg (65%), m.p. 176–177°, $[\alpha]_D^{25}$ −121° (*c* 1, chloroform); λ_{max}^{KBr} 3.08 (NH), 6.25 (C=N), 6.68 (asym. NO_2), 7.27 (sym. NO_2), 11.91, and 12.34 μm (aryl); n.m.r. data: τ 1.93 (1-proton singlet, disappears on deuteration, NH), 2.04, 3.14 (4-proton AA'BB' pattern, J_{AB} 10.0 Hz, aryl protons), 2.83 (singlet, H-1), 5.35 (doublet, $J_{3,4}$ 2.4 Hz, H-3), 5.48 (doublet of doublets, $J_{4,5}$ 8.0 Hz, H-4), 5.87 (broad doublet, width 10.5 Hz, H-5), 6.15, 6.37 (AB of ABX system, $J_{5,6}$ 1.8 Hz, $J_{5,6'}$ 0.7 Hz, $J_{6,6'}$ 12.8 Hz, H-6,6'), 8.59, 8.67, 8.76, and 8.82 (3-proton singlets, 2 CMe_2); X-ray powder diffraction data: 16.35 vw, 9.84 s (2),

7.93 s, 7.05 w, 5.67 vs (1), 5.27 s (3), 4.96 s, 4.54 s, 4.18 m, 3.94 w, 3.74 m, 3.57 s, and 3.28 m.

Anal. Calc. for $C_{18}H_{23}N_3O_7$: C, 54.96; H, 5.89; N, 10.68. Found: C, 54.97; H, 5.99; N, 10.46.

*Other aldehydo sugar derivatives. — A. Methyl 2,3-*O*-isopropylidene-β-*D*-ribo-pentodialdo-1,4-furanoside* (**6**). Methyl 2,3-*O*-isopropylidene-β-D-ribofuranoside[24] (**5**, 0.50 g, 2.45 mmol) was oxidized by the general procedure, and the product was recrystallized from cold 1:1 ether–petroleum ether (b.p. 30–60°) to afford **6** as white needles; yield 0.38 g (75%), m.p. 60–61°, $[\alpha]_D^{22}$ −220° (*c* 1, chloroform) {lit.[12] m.p. 60–61°, $[\alpha]_D$ −214° (*c* 0.1, chloroform)}; homogeneous (>99%) by g.l.c., T_R 0.69 (relative to **5** = 1.00) at 125°; X-ray powder diffraction data: 9.02 s (3), 8.05 s, 6.28 m, 5.52 m, 4.73 vs (1), 4.64 m, 4.29 m, 4.19 s (2), 3.75 w, 3.66 w, 3.38 w, 3.24 w, and 3.13 m.

The (*p*-nitrophenyl)hydrazone of **6** had m.p. 149–150° (lit.[13] m.p. 151–152°); X-ray powder diffraction data: 10.39 s, 7.82 vs (1), 5.98 m, 5.63 s (2), 5.08 s (3), 4.46 w, 3.76 s, 3.52 m, 3.22 s, and 2.83 m.

Repetition of the procedure, with a 20-min period of reaction at ~25° and with 6:1, 9:1, and 12:1 molar ratios of oxidant to substrate **5**, followed by g.l.c. analysis of the product for residual starting-material, showed that 71, 76, and 99%, respectively, of the starting material **5** had reacted.

*B. 1,2:3,4-Di-*O*-isopropylidene-α-*D*-galacto-hexodialdo-1,5-pyranose* (**8**). Oxidation of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose[3] (**7**, 12 g, 46.5 mmol) gave the aldehyde **8** as a syrup, homogeneous (~99%) by g.l.c., T_R 0.69 (relative to **7** = 1.00); yield 7.4 g (62%). An analytical sample was prepared by short-path distillation; b.p. 105°/0.05 torr, $[\alpha]_D^{28}$ −111° (*c* 2.3, chloroform) {lit.[3] b.p. 104–105°/0.5 torr, $[\alpha]_D$ −131° (*c* 0.9, chloroform)}; n.m.r. data identical with those reported[3]. The (*p*-nitrophenyl)hydrazone had m.p. 213–215°, $[\alpha]_D^{22}$ −102° (*c* 1, chloroform) {lit.[3] m.p. 214–215°, $[\alpha]_D$ −84° (*c* 1, chloforom)}; X-ray powder diffraction data identical with those published[3]. A sample of the original preparation[3] was found to have $[\alpha]_D^{22}$ −102° (*c* 0.7, chloroform).

*Oxidation of 5-azido-2,3-*O*-benzylidene-5-deoxy-β-*D*-ribofuranose* (**9**) *to 5-azido-2,3-*O*-benzylidene-5-deoxy-*D*-ribono-1,4-lactone* (*10*). The hemiacetal **9** (0.45 g, 1.71 mmol) gave the crystalline lactone **10**, which was recrystallized from 1:1 ether–petroleum ether (b.p. 30–60°); yield 0.39 g (88%), m.p. 145–146°, $[\alpha]_D^{22}$ −17° (*c* 0.7, acetone) {lit.[17] m.p. 146–147°, $[\alpha]_D$ −13° (*c* 0.7, acetone)}; homogeneous by t.l.c.

*Oxidation of secondary alcohol derivatives to ketones. — A. Oxidation of 3-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene-α-*D*-glucofuranose*[18] (**11**) *and the β-*L*-ido-analog*[25] (**16**). By the standard oxidation procedure, the α-*D*-*gluco* derivative[18] **11** (1.0 g, 3.40 mmol) gave 3-*O*-benzyl-6-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranos-5-ulose[18] (**12**); yield 0.91 g (91%), homogeneous by t.l.c.; R_F 0.78 (1:1 dichloromethane–ether). Recrystallization from 1:1 ether–petroleum ether (b.p. 30–60°) gave analytically pure **12**; yield 0.78 g (78%), m.p. 56–57°, $[\alpha]_D^{22}$ −88° (*c* 1, chloroform) {lit.[18] m.p. 55–56°, $[\alpha]_D$ −89° (*c* 1.5, chloroform)}; X-ray powder diffraction data: 13.85 m, 10.10 s (2), 8.26 s, 5.74 s, 5.13 vs (1), 4.69 s (3), 4.54 s, 4.35 w, 4.14 w, and 3.97 m.

Repetition of the experiment with the β-L-*ido* derivative[25] **16** (150 mg, 0.51 mmole) as the starting material gave the ketone **12** (131 mg, 87%), identical in all respects with the preceding product.

Behavior of endocyclic, secondary alcohol derivatives on treatment with chromium trioxide–pyridine. — Under the standard oxidation conditions, 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**13**) was recovered unchanged in >90% yield. Similarly, treatment of 1,6-anhydro-3,4-*O*-isopropylidene-β-D-galactopyranose (**15**) with the $CrO_3 \cdot 2C_5H_5N$ reagent led to recovery of 93% of the original mass, which was shown by i.r. and t.l.c. to contain only a small proportion of the 2-ketone[26]. Treatment of 1,6-anhydro-2,3-*O*-isopropylidene-β-D-mannopyranose with the oxidation reagent led to much decomposition of the sugar, affording only a low yield (~20%) of a product judged (by i.r. and t.l.c.) to be only partially oxidized to the 4-ketone[19].

ACKNOWLEDGMENTS

The authors thank Mr. Paul Rosso of this Department, and Dr. Roger Westland of Parke, Davis and Co., Ann Arbor, Michigan, for helpful suggestions.

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