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Note

A convenient, one-step oxidation of glycals to lactones using pyridinium chlorochromate

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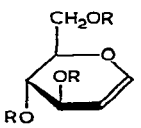
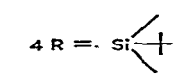
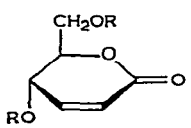
Pyridinium chlorochromate (PCC) is a cheap and stable reagent which can oxidise primary and secondary alcohols to carbonyl compounds[1]. Piancatelli *et al.*[2] reported that PCC could effect high-yielding oxidation of linear and cyclic enol ethers to esters and lactones. We now report on applications of PCC in the carbohydrate field.

When 3,4,6-tri-*O*-acetyl-1,5-anhydro-2-deoxy-D-*arabino*-hex-1-enitol (3,4,6-tri-*O*-acetyl-D-glucal, **1**) was added, at room temperature, to a suspension of PCC in dichloroethane, no reaction took place, but at 80°, **1** was converted (~80%) into the known 4,6-di-*O*-acetyl-2,3-dideoxy-D-*erythro*-hex-2-enono-1,5-lactone[3–5] (**5**). Similarly, tri-*O*-benzoyl-D-glucal[6] (**2**) was converted into the lactone **6**. 2,3-Dideoxy-hex-2-enono-1,5-lactones, previously prepared by various routes[3,4,7], are of potential interest because numerous natural products contain α,β-unsaturated lactone structures[8].

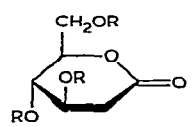


1 R = Ac
2 R = Bz
3 R = Bzl





5 R = Ac
6 R = Bz



7 R = Bzl

The extent of oxidation with PCC depends on the nature of the protecting groups of the glucal. Thus, treatment of tri-*O*-benzyl-D-glucal[9] (**3**), at room tempera-

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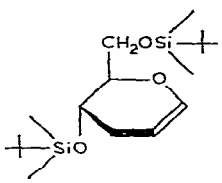
ture, with PCC in dichloroethane gave 60% of the known 3,4,6-tri-*O*-benzyl-2-deoxy-D-*arabino*-hexono-1,5-lactone[5] (**7**). Using similar conditions, 3,4,6-tri-*O*-*tert*-butyldimethylsilyl-D-glucal[10] (**4**) was converted into a 4:1 mixture (determined by n.m.r. spectroscopy) of saturated and α,β-unsaturated lactones, from which the saturated lactone **8** was isolated, crystalline.

For the glucal derivative **9** (ref. 10), where no elimination is possible, ~70% of the lactone **10** was easily isolated. Tri-*O*-benzyl-D-galactal[11] (**11**) was oxidised at room temperature by PCC to the lactone **12**.



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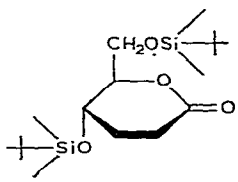

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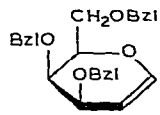

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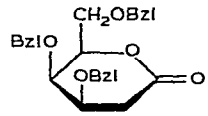

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Gouedard *et al.*[7] have reported the oxidation of 3,4,6-tri-*O*-acetyl-D-glucal (**1**) with a palladium complex (Li_2PdCl_4), to give a mixture of saturated and unsaturated lactones in moderate yields.

The reactions with PCC reported here allow a convenient conversion of glycals into lactones.

EXPERIMENTAL

General. — Melting points were determined with a Büchi apparatus. Optical rotations were determined at 22–24° with a Perkin–Elmer model 141 polarimeter. I.r. spectra were recorded with a Jouan-Jasco IRA-1 spectrometer. ^{1}H-N.m.r. spectra were recorded for solutions in $CDCl_3$ (internal standard, Me_4Si) unless otherwise stated. Purity of products was determined by t.l.c. on Kieselgel $60F_{254}$ (Merck) with detection by charring with sulphuric acid. Column chromatography was performed on Kieselgel 60 (Merck, 0.063–0.200 mm). Pyridinium chlorochromate was purchased from Aldrich Europe (19,014-4) and used without further purification. Microanalyses were performed by the Service Central d'Analyse du C.N.R.S. (Vernaison).

4,6-Di-O-acetyl-2,3-dideoxy-D-erythro-*hex-2-enono-1,5-lactone* (**5**). — A mixture of pyridinium chlorochromate (PCC, 500 mg, 2 equiv.) and 3,4,6-tri-*O*-acetyl-D-glucal (**1**, 306 mg) was stirred in 1,2-dichloroethane (5 mL) for 17 h at 80°, and then cooled and poured onto a column of silica gel (10 g) prepared in hexane. Elution with hexane–ethyl acetate (3:2) gave **5** (78%) in nearly pure form, and the ^{1}H-n.m.r. data agreed with those published[4]. Further chromatography and then distillation gave **5**, b.p. 130–135°/0.5 mmHg, $[\alpha]_D$ +119.5° (*c* 3.25, chloroform); lit.[3–5] $[\alpha]_{578}$ +129°, $[\alpha]_D^{25}$ +158° (chloroform), $[\alpha]_D^{20}$ −106° (ethanol).

Anal. Calc. for $C_{10}H_{22}O_6$: C, 52.63; H, 5.30. Found: C, 52.67; H, 5.05.

4,6-Di-O-benzoyl-2,3-dideoxy-D-erythro-*hex-2-enono-1,5-lactone* (**6**). — A mixture of PCC (228 mg, 2 equiv.) and 3,4,6-tri-*O*-benzoyl-D-glucal (**2**, 240 mg) was stirred in 1,2-dichloroethane (5 mL) for 24 h at 80°, and then cooled and poured onto a column of silica gel (10 g) prepared in hexane. Elution with hexane–ethyl acetate (7:3) gave **6** as a syrup (120 mg, 65%), $[\alpha]_D$ +193° (*c* 0.35, chloroform), ν_{max}^{film} 1750 cm^{-1} (C=O). ^{1}H-N.m.r. data: δ 8.0 (m, 4 H, Ph), 7.3–7.6 (m, 6 H, Ph), 6.90 (dd, 1 H, $J_{2,3}$ 9, $J_{3,4}$ 3 Hz, H-3), 6.15 (dd, $J_{2,4}$ 1.5 Hz, H-2), 5.85 (dq, 1 H, $J_{4,5}$ 6 Hz, H-4), 4.95 (m, 1 H, H-5), and 4.58 (d, 2 H, H-6,6').

Anal. Calc. for $C_{20}H_{16}O_6$: C, 68.17; H, 4.58. Found: C, 68.30; H, 4.63.

3,4,6-Tri-O-benzyl-2-deoxy-D-arabino-*hexono-1,5-lactone* (**7**). — A mixture of PCC (109 mg, 2 equiv.) and 3,4,6-tri-*O*-benzyl-D-glucal (**3**, 105 mg) was stirred in 1,2-dichloroethane (7 mL) for 40 h at room temperature, and then poured onto a column of silica gel (10 g) prepared in hexane. Elution with hexane–ethyl acetate (7:3) and crystallisation from ethanol gave **7** (65 mg, 60%), m.p. 82–83°, $[\alpha]_D$ +47° (*c* 0.65, ethanol); lit.[5] m.p. 83°, $[\alpha]_D^{25}$ +48° (ethanol).

3,4,6-Tri-O-benzyl-2-deoxy-D-lyxo-*hexono-1,5-lactone* (**12**). — A solution of 3,4,6-tri-*O*-benzyl-D-galactal (**11**, 93 mg) in 1,2-dichloroethane (5 mL) was oxidised with PCC (96 mg, 2 equiv.) during 24 h. Work-up, as described for **7**, gave **12** as a syrup (61 mg, 63%), b.p. 250–260°/0.5 mmHg, $[\alpha]_D$ +4.5° (*c* 0.6, chloroform), ν_{max}^{film} 1750 cm^{-1} (C=O). ^{1}H-N.m.r. data: δ 7.2–7.4 (m, 15 H, 3 Ph), 4.77 (AB system, 2 H, CH_2Ph), 4.53 and 4.44 (2 s, 4 H, 2 CH_2Ph), and 2.87 (m, H-2,2').

Anal. Calc. for $C_{27}H_{28}O_5$: C, 74.98; H, 6.53. Found: C, 74.93; H, 6.38.

3,4,6-Tri-O-tert-butyldimethylsilyl-2-deoxy-D-arabino-*hexono-1,5-lactone* (**8**). — A mixture of PCC (300 mg, 2 equiv.) and 3,4,6-tri-*O-tert*-butyldimethylsilyl-D-glucal (**4**, 338 mg) was stirred in 1,2-dichloroethane (6 mL) for 48 h at room temperature. Elution of the mixture from a column of silica gel (10 g, prepared in hexane) with hexane–ethyl acetate (9:1) gave a 4:1 mixture of **8** and its α,β-unsaturated analogue.

A solution of the mixture in ethyl acetate was hydrogenated in the presence of 10% Pd/C. The product was eluted from a column of silica gel (30 g) with hexane–ethyl acetate (9:1), to give **8** (190 mg, 54%), m.p. 84–85° (from pentane), $[\alpha]_D$ +21.5° (*c* 1, chloroform), ν_{max}^{film} 1750 cm^{-1} (C=O).

Anal. Calc. for $C_{24}H_{52}O_5Si_3$: C, 57.09; H, 10.38. Found: C, 56.89; H, 10.23.

4,6-Di-O-tert-butyldimethylsilyl-2,3-dideoxy-D-erythro-*hexono-1,5-lactone* (**10**). — A mixture of PCC (210 mg, 2 equiv.) and 4,6-di-*O-tert*-butyldimethylsilyl-3-deoxy-D-glucal (**9**, 174 mg) was stirred in 1,2-dichloroethane (5 mL) for 24 h at room temperature. The reaction mixture was poured onto a column of silica gel (10 g) prepared in hexane. Elution with hexane–ethyl acetate (4:1) gave **10** (125 mg, 71%), b.p. 170–175°/12 mmHg, m.p. 36–38°, $[\alpha]_D$ +29° (*c* 1, chloroform), ν_{max}^{film} 1740 cm^{-1} (C=O).

Anal. Calc. for $C_{18}H_{38}O_3Si_2$: C, 57.70; H, 10.22. Found: C, 57.67; H, 10.10.

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