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Note

β-Elimination in aldonolactones: a convenient synthesis of 2,4,6-tri-*O*-benzoyl-3-deoxy-D-*arabino*-hexono-1,5-lactone

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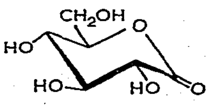
The formation of unsaturated derivatives on benzoylation of aldono-1,4-lactones has been reported[1,2], and we now describe a comparable reaction of D-glucono-1,5-lactone (**1**).

Benzoylation of **1** for 90 min at room temperature afforded 2,3,4,6-tetra-*O*-benzoyl-D-glucono-1,5-lactone[3], but with a large excess of benzoyl chloride and pyridine for 16 h, crystalline 2,4,6-tri-*O*-benzoyl-3-deoxy-D-*erythro*-hex-2-enono-1,5-lactone (**2**) was obtained (97%). Treatment of 4-*O*-benzyl-D-*glycero*-D-*gulo*-heptono-1,5-lactone with pyridine–acetic anhydride gave[4] 2,6,7-tri-*O*-acetyl-4-*O*-benzyl-3-deoxy-D-*arabino*-hept-2-enono-1,5-lactone.



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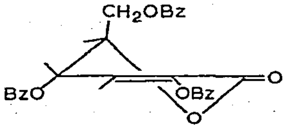

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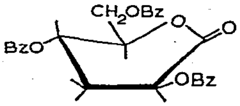

3

Compound **2** had $\lambda_{\max}^{\mathrm{MeOH}}$ 234 nm, and a similar absorption (232 nm) was reported for the α,β-unsaturated 1,4-lactone obtained on benzoylation of D-*glycero*-D-*gulo*-heptono-1,4-lactone. The shift in the lactone carbonyl absorption, with respect to the saturated lactone[3], and the n.m.r. data are in agreement with the assigned structure. Compound **2** had $J_{3,4}$ and $J_{4,5}$ values similar to those of the analogous acetyl derivative obtained[5] as a syrup by treatment of 2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranose, or the *manno* isomer, with methyl sulphoxide–triethylamine–sulphur trioxide, indicating that it exists mainly in the $^{5}H_{\mathrm{O}}$ conformation. Such a conformation would be stabilized by an allylic ester effect[6].

Catalytic hydrogenation of **2** was stereoselective and gave crystalline 2,4,6-tri-*O*-benzoyl-3-deoxy-D-*arabino*-hexono-1,5-lactone (**3**, 96%). If **2** reacted in the $^{5}H_{\mathrm{O}}$

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conformation, the bulky exocyclic group in the quasi-axial orientation would prevent attack from above the ring. The $J_{2,3}$ and $J_{2,3'}$ values (8.5 and 10 Hz) of **3** suggest a distorted-boat conformation. Boat and half-chair conformations have been proposed[7,8] for δ-lactones, both of which satisfy the constraints due to the planarity of the $\rangle C{=}O$ moiety. The half-chair conformation of **3** would be destabilised by the *ax* BzO-2 group.

The configuration of **3** was established by debenzoylation with sodium methoxide and conversion of the product into 3-deoxy-D-*arabino*-hexonic acid phenylhydrazide[9]. The ease of formation and high yield of 2,4,6-tri-*O*-benzoyl-3-deoxy-D-*arabino*-hexono-1,5-lactone suggests its use in the synthesis of 3-deoxy-D-*arabino*-hexose by reduction with a dialkylborane[10].

EXPERIMENTAL

Melting points were determined with a Fisher–Johns apparatus and are uncorrected. I.r. spectra were recorded with a Perkin–Elmer Infracord spectrophotometer, and u.v. spectra with a Beckman DK-2A instrument. N.m.r. spectra were determined with a Varian A-60 spectrometer for solutions in chloroform-*d* with tetramethylsilane as the internal reference. T.l.c. was performed on Silica gel G (Merck), using benzene–ethyl acetate (98:2) and detection with iodine vapour.

*2,4,6-Tri-O-benzoyl-3-deoxy-*D-erythro-*hex-2-enono-1,5-lactone* (**2**). — D-Glucono-1,5-lactone (2 g) was suspended in anhydrous pyridine (40 ml), and benzoyl chloride (20 ml) was slowly added. The mixture was shaken for 16 h at room temperature and then poured with stirring into 300 ml of ice–water. After 90 min, the product was extracted with chloroform, and the extract was washed successively with saturated, aqueous sodium hydrogen carbonate and water, dried (Na_2SO_4), and evaporated *in vacuo* with the addition of toluene to remove the pyridine. Benzoic acid was then removed by sublimation at 80° under diminished pressure, and the residue was crystallized from ether and recrystallized from ethanol to give **2** (5.13 g, 97%), m.p. 111–112°, $[\alpha]_D$ +105° (*c* 0.8, chloroform), R_F 0.78, λ_{max}^{MeOH} 234 nm (ε 53,000), ν_{max}^{Nujol} 1730–1710 (α,β-unsaturated 1,5-lactone and benzoate C=O), 1680 and 1640 cm^{-1} (C=C–C=O). N.m.r. data: τ 1.8–2.8 (*m*, 3BzO), 3.2 (*d*, $J_{3,4}$ 4.5 Hz, H-3), 3.85 (*q*, $J_{3,4}$ 4.5, $J_{4,5}$ 5.5 Hz, H-4), 4.7–5.05 (*m*, H-5), 5.3 (*m*, H-6,6′).

Anal. Calc. for $C_{27}H_{20}O_8$: C, 68.64; H, 4.27. Found: C, 68.36; H, 4.30.

*2,4,6-Tri-O-benzoyl-3-deoxy-*D-arabino-*hexono-1,5-lactone* (**3**). — A solution of **2** (1.74 g) in ethyl acetate (100 ml) was hydrogenated over 5% palladium–charcoal (300 mg) at atmospheric pressure and 0°. The filtered solution was evaporated under diminished pressure and the residue crystallized from ethanol to give **3** (1.68 g, 96%), m.p. 158–160° (from ethanol–acetone, 5:3), $[\alpha]_D^{20}$ +27° (*c* 0.8, 90% acetone), R_F 0.24, ν_{max}^{Nujol} 1750 (1,5-lactone), 1720 cm^{-1} (benzoate C=O). N.m.r. data: τ 1.8–2.7 (*m*, 3BzO), 4.0 (*q*, $J_{2,3}$ 8.5, $J_{2,3'}$ 10 Hz, H-2), 4.2–4.5 (*m*, H-4), 4.8–5.1 (*m*, H-5), 5.3 (*m*, H-6,6′), 7.1–7.5 (*m*, H-3,3′).

Anal. Calc. for $C_{27}H_{22}O_8$: C, 68.36; H, 4.64. Found: C, 68.08; H, 4.73.

Compound **3** was debenzoylated with sodium methoxide in methanol to give a syrup, b.p. 90°/0.001 mmHg, which on paper chromatography (1-butanol–pyridine–water, 6:4:3) migrated as one spot detected with silver nitrate–sodium hydroxide[11] and with hydroxylamine–ferric chloride[12].

Treatment of the foregoing product with an equal amount of phenylhydrazine gave 3-deoxy-D-*arabino*-hexonic acid phenylhydrazide, m.p. 124–126° (from methanol–ether), $[\alpha]_D^{20}$ $-45°$ (*c* 0.6, methanol); lit.[9] m.p. 128–129°, $[\alpha]_D^{13}$ $-46.7 \pm 2°$ (*c* 1.2, methanol).

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