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Note

The synthesis of 2-deoxy-DL-*erythro*-pentose (racemic 2-deoxyribose)

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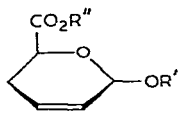
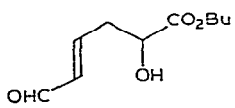
Alkyl 2-alkoxy-5,6-dihydro-2*H*-pyran-6-carboxylates[1] (**1**) can be converted into a variety of monosaccharides *via* suitable functionalisation of the dihydropyran ring[2]. Hitherto, in all of these syntheses, C-2 of the dihydropyran ring bearing the methoxyl group became the anomeric carbon atom and the alkoxycarbonyl group became C-6 of the hexose molecule. However, **1** can be also regarded as an aldonic acid ester derivative, and the alkoxycarbonyl group can be utilised as C-1 of the sugar chain, thereby creating further possibilities for synthesis.

Zamojski *et al.*[1] reported that **1** (R′ = Me, R″ = Bu) easily underwent hydrolysis in dilute mineral acid to give butyl 2,3,4-trideoxy-*aldehydo*-DL-hex-2-enuronate (**2**), to which the *E* configuration was assigned[1]. Compound **2** offers an access to deoxy sugars *via* reduction of the aldehyde group and hydroxylation of the double bond. We now report a new, simple synthesis of 2-deoxy-DL-*erythro*-pentose (**5**) by this general approach; previous syntheses of 2-deoxy-*erythro*-pentose are cited in Ref. 3.

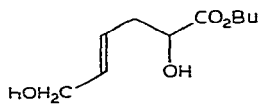
Compound **2** was easily reduced to the diol **3**, which was epoxidized with 3-chloroperoxybenzoic acid to give a mixture of stereoisomeric epoxides **4**. Opening



1

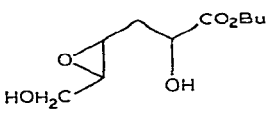


2

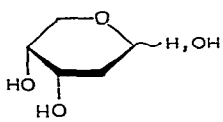


3

R′ = alkyl, sugar moiety
R″ = Bu, *t*-Bu, Et



4



5

of the oxirane ring of **4** with aqueous acetic acid followed by Ruff degradation of the calcium salt of the resulting 3-deoxyhexonic acid gave 2-deoxy-DL-*erythro*-pentose (**5**, 44%). The i.r. spectrum of **5** was indistinguishable from those of the racemic compound obtained by an independent method[3e] and of 2-deoxy-D-*erythro*-pentose.

EXPERIMENTAL

General. — Boiling points refer to air-bath temperatures and are uncorrected. Melting points were determined on a Kofler block and are uncorrected. I.r. spectra were measured for films, with a Unicam SP-200 spectrophotometer. ^{1}H-N.m.r. spectra were recorded for solutions in $CDCl_3$ (internal Me_4Si) with a Jeol JNM-4H-100 (100 MHz) spectrometer. Silica Gel G (Merck) was used for t.l.c., and MN-Kieselgel (100–200 mesh, Macherey Nagel & Co.) for column chromatography.

Butyl *E*-2,3,4-trideoxy-*aldehydo*-DL-hex-2-enuronate (**2**) was prepared by the procedure described earlier[1].

Butyl E-*3,4,5-trideoxy*-DL-*hex-4-enonate* (**3**). — A solution of **2** (10 g, 50 mmol) in tetrahydrofuran–water (1 : 2, 150 ml) was stirred with sodium borohydride (1 g) for 1 h at room temperature, and the mixture was then extracted with chloroform. The extract was dried, filtered, and concentrated *in vacuo* to give **3** (6.0 g, 60%), b.p. 130/0.4 Torr; ν_{max}^{film} 3400 (OH), 1740, and 1210 cm^{-1} (ester). ^{1}H-N.m.r. data: δ 0.96 (t, 3 H, Me), 1.2–1.9 (m, 4 H, -CH_2CH_2-), 2.47 (m, 2 H, H-3,3′), 3.4–4.4 (m, 5 H, -CH_2-, H-2,6,6′), and 5.66 (m, 2 H, H-4,5).

Anal. Calc. for $C_{10}H_{18}O_4$: C, 59.4; H, 9.0. Found: C, 58.9, H, 9.3.

The 2,6-diacetate of **3** had b.p. 130/0.4 Torr; ν_{max}^{film} 1745 and 1230 cm^{-1} (ester). ^{1}H-N.m.r. data: δ 0.95 (t, 3 H, Me), 1.1–1.9 (m, 4 H, -CH_2CH_2-), 2 04 and 2.11 (2 s, 6 H, 2 Ac), 2.50 (m, 2 H, H-3,3′), 4.12 (t, 2 H, -CH_2-), 4.48 (m, 2 H, H-6,6′), 5.00 (t, 1 H, $\sum J$ 12.2 Hz, H-2), and 5.69 (m, 2 H, H-4,5).

Anal. Calc. for $C_{14}H_{22}O_6$: C, 58.7; H, 7.8. Found: C, 58.8; H, 7.9.

Butyl trans-4,5-*anhydro-3-deoxyhexonate* (**4**). — A solution of **3** (4 g, 20 mmol) and 3-chloroperoxybenzoic acid (5 g) in chloroform (20 ml) was left at room temperature for several days. After disappearance of the substrate (t.l.c., light petroleum–ether–methanol, 50 : 45 : 5), the solution was cooled to 0°, filtered, and concentrated to dryness. The oily residue was purified by chromatography on silica gel to give **4** (3.7 g, 86%), b.p. 140/0.4 Torr; ν_{max}^{film} 3500 (OH), 1740, and 1210 cm^{-1} (ester). ^{1}H-N.m.r. data: δ 0.94 (t, 3 H, Me), 1.1–1.9 (m, 4 H, -CH_2CH_2-), 1.99 (m, 2 H, H-3,3′), 3.07 (m, 2 H, H-4,5), 3.59 (dd, 1 H, $J_{5,6}$ 4.5, $J_{6,6'}$ −12.9 Hz, H-6), 3.81 (m, 1 H, $J_{5,6'}$ 3.2, $J_{4,6'}$ 1.3 Hz, H-6′), 4.12 (t, 2 H, -CH_2-), and 4.34 (m, 1 H, H-2).

Samples of **4** obtained from different experiments and purified independently, and which were identical (t.l.c., i.r., and ^{1}H-n.m.r. data), gave inconsistent elemental analyses. However, the data obtained for the 2,6-diacetate of **4** proved the assigned structure.

The 2,6-diacetate of **4** had b.p. 140/0.4 Torr, ν_{max}^{film} 1745 and 1225 cm^{-1} (ester). ^{1}H-N.m.r. data: δ 0 95 (t, 3 H, Me), 1.2–1.9 (m, 4 H, -CH_2CH_2-), 2.10 and 2.17

(2 s, 6 H, 2 Ac), 2.2 (m, 2 H, H-3,3'), 3.00 (m, 2 H, H-4,5), 3.91 (dd, 1 H, $J_{5,6}$ 5.7, $J_{6,6'}$ −12.3 Hz, H-6), 4.15 (t, 2 H, -CH_2-), 4.31 (m, 1 H, $J_{5,6'}$ 3.4, $J_{4,6'}$ 1.5 Hz, H-6'), 5.12 (m, 1 H, H-2),

Anal. Calc. for $C_{14}H_{22}O_7$: C, 55.6; H, 7.3. Found: C, 55.5; H, 7.5.

2-Deoxy-DL-erythro-*pentose* (**5**). — A solution of **4** (0.8 g, 2.2 mmol) in 60% aqueous acetic acid (5 ml) was boiled under reflux for 6 h, and then concentrated under diminished pressure. A solution of the oily residue in water (5 ml) was treated with barium diacetate (0.06 g) and calcium carbonate (0.15 g). The mixture was boiled under reflux for 6 h and then cooled to 40°, ferrous sulphate (0.05 g) and 30% hydrogen peroxide (0.5 ml) were added, and the mixture was stirred for 1 h, filtered, and concentrated. The residue was eluted from a column of silica gel with ethyl acetate, to give **5** as a colourless oil which crystallised on the addition of propan-2-ol, affording **5** (0.13 g, 44%), m.p. 81–84° (lit.[3e,d] m.p. 81–84° and 85–91°); ν_{max}^{film} 3400 (OH), 3290, 1350, 1240, (C-H), 1130, 1110, 1070, 1040, 1000, 980 (acetal), 920, 890, 880, and 810 cm^{-1}.

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