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Note

β-Elimination in aldonolactones: a convenient synthesis of 2-deoxy-D-*erythro*-pentose

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We have recently reported[1] the preparation of 2,4,6-tri-*O*-benzoyl-3-deoxy-D-*arabino*-hexono-1,5-lactone (**1**), in two steps from D-glucono-1,5-lactone in 90% overall yield. We now describe the use of compound **1** for the synthesis of 2-deoxy-D-*erythro*-pentose.

Debenzoylation of **1** with sodium methoxide, followed by removal of cations, afforded a syrup which analysed for a 3-deoxyaldohexonolactone (**2**). The i.r. absorption spectrum of **2** showed a carbonyl band at 1760 cm^{-1}, which indicates the presence of a δ-lactone; however, this value is also close to the range found for γ-lactones[2]. The specific rotation corresponds to the value reported[3] for 3-deoxy-D-*arabino*-hexono-1,4-lactone. Oxidative degradation of **2** with ceric sulfate in M sulfuric acid at 37° gave 2-deoxy-D-*erythro*-pentose isolated as the anilide (40.8% yield from compound **1**). The reagent has been previously used[4,5] for the decarboxylation of α-keto acids. Schiwara and Domagk[6] used ceric sulfate for structural determination of 2-keto-3-deoxyaldohexonic acids. After reduction with borohydride and decarboxylation with ceric sulfate, they proved the formation of a 2-deoxypentose by the Dische reaction[7]. The reagent has not been used hitherto for the synthesis of 2-deoxy sugars. The method described herein is simple, the starting material (D-glucono-1,5-lactone) is inexpensive, and the overall yield is good.

EXPERIMENTAL

2-Deoxy-D-erythro-*pentose*. — 2,4,6-Tri-*O*-benzoyl-3-deoxy-D-*arabino*-hexono-1,5-lactone (**1**) was prepared from D-glucono-1,5-lactone, in 90% yield, as previously reported[1]. Compound **1** (1.18 g) was debenzoylated with sodium methoxide in methanol; after 2 h, the solution was decationized by stirring with Amberlite IR-120(H^+) resin, filtered, and evaporated to a syrup under diminished pressure. The syrup was dissolved in water, the solution was extracted with benzene to remove

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methyl benzoate, and the aqueous phase was evaporated to a syrup (yield, 400 mg; 99%). After several days of drying in a *vacuum* desiccator, the product had $[\alpha]_D^{20}$ +7.7° (*c* 1, water), ν_{max}^{Nujol} 1760 cm^{-1} (lactone C=O). Wood and Fletcher[3] reported $[\alpha]_D^{20}$ +6.4° for crystalline 3-deoxy-D-*arabino*-hexono-1,4-lactone.

Anal. Calc. for $C_6H_{10}O_5$: C, 44.44; H, 6.17. Found: C, 44.36; H, 6.47.

The lactone was treated with a freshly prepared solution of ceric sulfate (1.7 g) in M sulfuric acid (26 ml). After 22 h at 35–37°, the mixture was stirred with an excess of barium carbonate and filtered. Paper chromatography (6:4:3, butan-1-ol–pyridine–water) gave only one spot having the same R_F value as an authentic sample of 2-deoxy-D-*erythro*-pentose, when detected with silver nitrate–sodium hydroxide[8] and with aniline hydrogen phthalate[9]. The Dische (diphenylamine) reaction[7] for 2-deoxypentoses gave an 85% yield calculated from **1**. The calibration curve was prepared from a 2-deoxy-D-*erythro*-pentose solution standardized by titration with alkaline hypoiodite[10].

The sugar solution was concentrated *in vacuo* to a few ml, and salts were precipitated by addition of methanol. The filtrate was concentrated to 5 ml and treated with a solution of aniline (0.4 ml) in ethanol (10 ml). After four days at 0°, the anilide was filtered off; yield, 212 mg (40.8% from **1**); m.p. and mixture m.p. 169–171°. Hardegger[11] reported m.p. 172–173° for 2-deoxy-*N*-phenyl-D-*erythro*-pentosylamine. 2-Deoxy-D-*erythro*-pentose was obtained[11] from the anilide; it crystallized as a mixture of α and β anomers, m.p. 72–76°, $[\alpha]_D^{22}$ −55° (equil.; *c* 0.5, water), lit.[11] m.p. 78–82° (for the mixture of anomers), $[\alpha]_D$ −57° (at equilibrium).

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