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Preliminary communication

β-Elimination in pentofuranuronates to give enol acetals

J. KISS and K. NOACK
Chemical and Physical Research Department, F. Hoffmann–La Roche & Co., Ltd., Basel (Switzerland)
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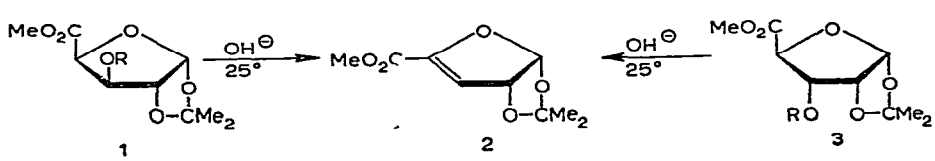
Formation of an enol acetal by β-elimination in some D-gluco and D-galacto-pyranuronate derivatives leads to 4-deoxyhex-4-enopyranuronates, the leaving groups employed being 4-methylsulfonyloxy or 4-D-glucopyranosyloxy groups. These base-catalyzed β-eliminations can be achieved under extremely mild conditions, and we found that the relative stereochemical disposition, on the pyranoid ring, of the substituents that participate directly in the β-elimination (namely, the proton on C-5 and the leaving group on C-4) are not decisive as regards the rate of reaction[1]. These studies served as model experiments that indicated that similar β-eliminations (*a,e* and *a,a*, respectively) occur in Nature in the enzymic degradation of mucopolysaccharides and polyuronates[2].

We have now found that a similar β-elimination giving an enol acetal occurs with pentofuranuronates having the proton on C-4 and the leaving group on C-3 either *cis* or *trans* to each other. We chose as model compounds (*a*) the methyl 1,2-*O*-isopropylidene-α-D-xylofuranuronate derivatives (1) for study of *trans*-elimination, and (*b*) the corresponding D-ribofuranuronates (3) for the *cis*-elimination reaction. Both pentofuranuronates were obtained by catalytic oxidation of the corresponding, protected pentofuranoses with oxygen in the presence of platinum. After formation of the methyl ester of the free acid with diazomethane, the leaving group was introduced onto the 3-hydroxyl group by means of methanesulfonyl chloride or diphenyl phosphorochloridate in pyridine. Compound **1b** had m.p. 80–81°; $[\alpha]_D^{25}$ −28.5° (*c* 0.58, chloroform), and compound **3b** had m.p. 57–59°; $[\alpha]_D^{25}$ +60.5 (*c* 0.56, methanol).



a, R = SO_2Me
b, R = $P(OPh)_2$
O

Treatment of these 3-(diphenyl phosphates) or of the 3-methanesulfonates 1a or 3a with a slight excess of potassium hydroxide in methanol at 25° caused rapid elimination of a molecular proportion of diphenyl hydrogen phosphate or methanesulfonic acid. According to estimates made by monitoring the reaction on t.l.c. plates, there was no appreciable difference in the rate of these β-eliminations, regardless of the *cis* or *trans* disposition of the proton on C-4 relative to the leaving group on C-3. The product, methyl 3-deoxy-1,2-*O*-isopropylidene-α-D-*glycero*-pent-3-enofuranuronate (2) was obtained in excellent yield as a colorless oil, b.p. 70–75° (bath)/0.01 torr (Hickman tube), n_D^{26} 1.4652, $[\alpha]_D^{25}$ −15.7° (*c* 0.70, methanol); ν_{max}^{film} 1747, 1221 (ester), and 1632 cm^{-1} (—C=C—); τ (100 MHz, $CDCl_3$): 3.83 (H-1), 3.93 (H-3), and 4.45 (H-2). As may be seen from Fig.1, the

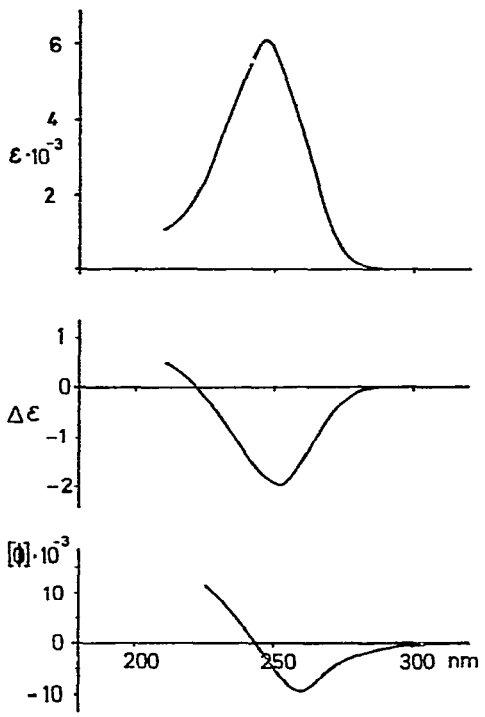


Fig.1. Ultraviolet, o.r.d., and c.d. spectra of compound **2**.

u.v. spectrum has a strong maximum at 247 nm, and the o.r.d./c.d. spectra shows Cotton effects due to the α,β-unsaturated (enol acetal)—carboxylic ester structure.

Compound 2, which contains an endocyclic, enol acetal linkage, is unstable at 25°: spontaneous polymerization occurs during several days, resulting in a white solid. The instability of 2 is presumably attributable to its acrylic ester structure, involved in a furanoid system. It is interesting that the analogous hex-4-enopyranuronates, obtained by a similar β-elimination reaction[3], are stable under the same conditions. Although the phenomenon has not yet been investigated thoroughly, it may be assumed that the

instability of 2 is due to the labilizing effect of the endocyclic, enol acetal double bond in a 5-ring system, not present in the 4,5-unsaturated pyranoid system.

The β-elimination to give enol acetals is also interesting from the viewpoint of the degradation of some pentose conjugates existing in Nature. Todd and co-workers[4a], Jones and Williamson[4b], and Vizsolyi and Tener[4c] described a procedure for stepwise degradation of polyribonucleotides and poly-2′-deoxyribonucleotides in which the terminally linked pentofuranoside residue was oxidized to the corresponding pentofuranosiduronate and the product was treated with alkali, resulting in cleavage of the terminal oxidized residue of the polynucleotide chain.

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