

FORMATION OF FURANONES FROM 5-Q-METHYLALDOSES

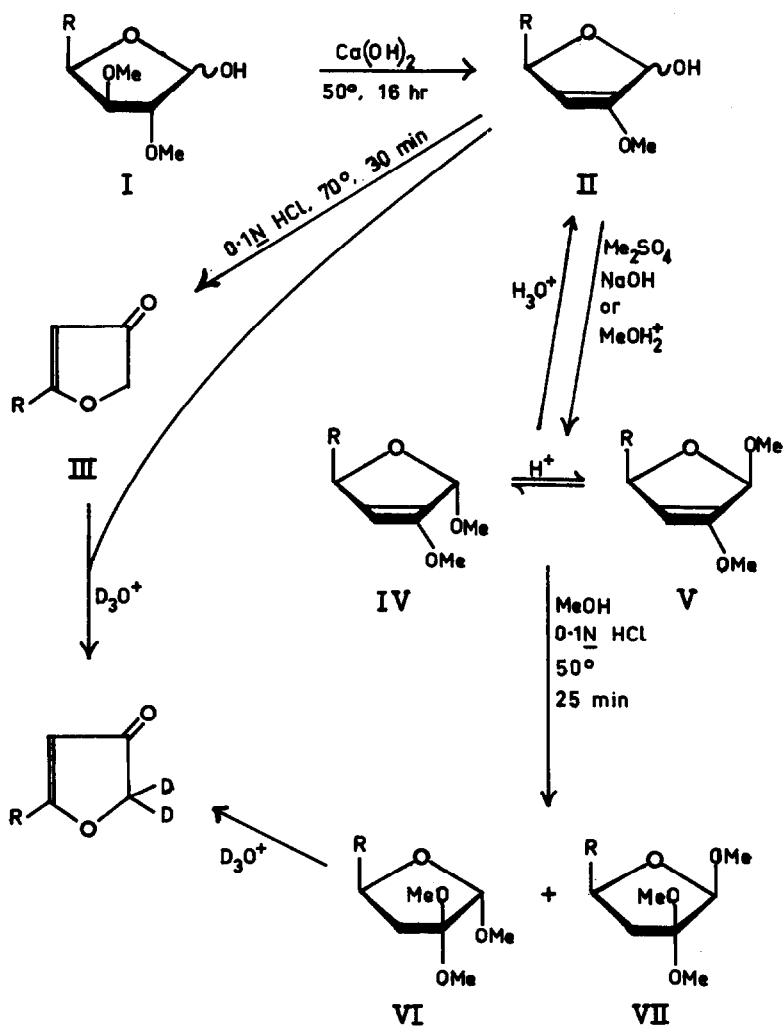
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Bott and Hirst<sup>1</sup> reported that 2,3,4- and 2,3,5-trimethyl ethers of D-xylose and L-arabinose yielded 2-furaldehyde on acid treatment. I have been able to confirm their results on the pyranose derivatives but have been unable to detect any trace of 2-furaldehyde from the furanose forms, either by their phloroglucinol method or from the absorption at 277 m $\mu$ .

Since it is believed that acid causes the elimination of the C-3 substituent of an aldose to yield a 3-deoxyglyc-2-ene<sup>2</sup> it was of interest to investigate the reactions of the furanose forms of these intermediates, such as II; the pyranose forms (3-deoxy-2-Q-methylglyc-2-enopyranoses) have been shown to yield 3,4-dideoxyglyc-3-enopyranosuloses and then 2-furaldehydes.<sup>2,3</sup> The present study reveals that the action of acid on II does not yield 2-furaldehydes but 3(2H)-furanones III. A 3(2H)-furanone had previously been reported to be formed by the acid treatment of 6-deoxy-D-lyxo-hex-5-ulonic acid.<sup>4</sup>



The glycenofuranose\* II was prepared from 2,3,5,6-tetra-O-methyl-D-glucose (I) by the action of lime-water, as reported for the glycenopyranoses.<sup>3</sup> Methylation of the product II,  $[\alpha]_D^{25} + 35^\circ \rightarrow +9.6^\circ$  (30 min) ( $c$  1, water), gave the anomeric glycosides: IV, isolated by gas-liquid chromatography (g.l.c.),  $[\alpha]_D^{25} + 33^\circ$  ( $c$  0.4, water), and V, isolated by crystallization from pentane, m.p.  $30^\circ$ ,  $[\alpha]_D^{25} + 13^\circ$  ( $c$  0.5, water). The PMR spectra of II, IV, and V were similar to those reported for the furanose forms of II ( $R = -CHOHCH_2OH$ ),<sup>3</sup> in particular only the  $\beta$ -D anomers had large values (3.0-4.0 cps) for  $L_{1,4}$ . The infrared spectrum of each of these glycenoses showed a very strong band between  $1668-1670\text{ cm}^{-1}$  ( $C=C-OCH_3$ ).

The first action of acid on the glycosides IV and V was to yield the anomeric mixture. In aqueous solution the glycosides were then hydrolysed to II, as indicated by g.l.c. and by the PMR spectra. With methanol as solvent, addition took place at the double bond to yield the "osone" derivatives VI and VII, which were isolated by g.l.c.,  $[\alpha]_D^{25} + 93^\circ$  and  $-69^\circ$  ( $c$  2,  $CHCl_3$ ). The PMR spectra of VI and VII each showed an octet at  $\delta \sim 1.9$  ( $C-CH_2-C$ ), five methoxyl groups at  $\delta \sim 3.3$ , and a singlet at  $\delta \sim 4.4$  (H-1), all of correct intensity.

The 3(2H)-furanone III was formed in aqueous acid solution from II, IV, and V in 70% yield or, more slowly, in poor yield from VI and VII. This furanone rapidly polymerized in non-aqueous solvents containing traces of acid. It was obtained after distillation and recrystallization

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\* Satisfactory analytical data were obtained for compounds I-VI.

as a low melting solid, m.p. 27-27.5°,  $[\alpha]_D^{25} + 107.6^\circ$  (c 1, water), intense bands at 1700  $\text{cm}^{-1}$  (C=O) and 1602  $\text{cm}^{-1}$  (C=C-C=O),

$\lambda_{\text{H}_2\text{O}}$  187  $\mu$  and 262  $\mu$  ( $\epsilon$  2,400 and 12,800), changing after max.

30 min in 0.01N sodium hydroxide to  $\lambda_{\text{max}}$  296  $\mu$  ( $\epsilon$  17,200). The PMR spectra in carbon tetrachloride, with internal tetramethylsilane ( $\delta$  0) as reference, showed four singlets at  $\delta$  3.37 (OMe), 3.44 (OMe), 4.49 ( $\text{H}_2$ -2), and 5.64 (H-4), a doublet at  $\delta$  3.62 ( $\text{H}_2$ -2') and a triplet at  $\delta$  4.14 (H-1'), with intensities of 3:3:2:1:2:1 ( $J_{1',2}$ , 4.5 cps). When formed in deuterium oxide the furanones did not show the band at  $\delta$  4.49; C-2 was therefore fully deuterated. These properties correspond to those reported for 3(2H)-furanones.<sup>5</sup>

With 2,3,5-tri-O-methyl-L-arabinose the same series of reactions took place. The products II and III ( $\text{R} = \text{MeOCH}_2$ -) did not give any 2-furaldehyde when subjected to the acid treatment of Bott and Hirst.<sup>1</sup>

#### References

- <sup>1</sup> H.G. Bott and E.L. Hirst, J. Chem. Soc. **1932**, 2621 (1932)
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