Studies on the Chemical Decomposition of Simple Sugars. XVIII. The Synthesis of D-*ribo*-3-Hexulose Pentaacetate*

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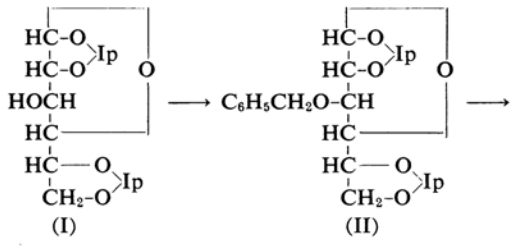
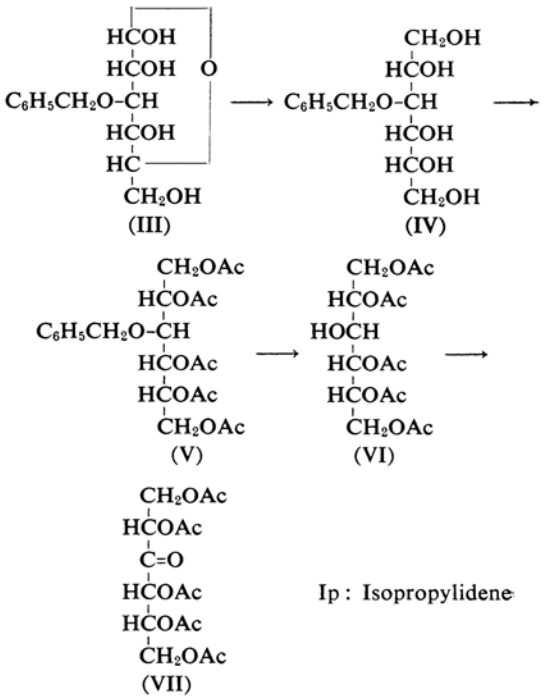
Although some 3-hexuloses have been synthesized,[1-3] their chemical properties have been received only limited attention. In the mechanism posturated by Hayami[4] for the acetol formation from monosaccharides in a concentrated phosphate buffer solution, 3-hexulose might play an important role as an intermediate. However, there has been no unequivocal experimental evidence. In the present paper, a synthesis of D-*ribo*-3-hexulose pentaacetate, a new 3-hexulose derivative, and its rapid conversion to acetol in a phosphate buffer solution will be described.





The treatment of diacetone-D-glucose (I) with sodium hydride and benzyl bromide in

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1) J. K. N. Jones, *J. Am. Chem. Soc.*, **78**, 2855 (1956).
2) J. M. Sugihara and G. U. Yuen, ibid., **79**, 5780 (1957).
3) G. U. Yuen and J. M. Sugihara, *J. Org. Chem.*, **26**, 1598 (1961).
4) J. Hayami, This Bulletin, **34**, 927 (1961).

ether gave 3-*O*-benzyl-1,2; 5,6-di-*O*-isopropylidene-D-glucofuranose (II).[5,6] The hydrolysis of II with sulfuric acid in aqueous methanol yielded 3-*O*-benzyl-D-glucopyranose (III),[6] 38%, m. p. 141.5—142.5°C. Compound III consumed 1.01 mol. of sodium metaperiodate per mole of substrate. The sodium borohydride reduction of III in water gave a thick syrup of 3-*O*-benzyl-D-sorbitol (IV) which, on acetylation with acetic anhydride and pyridine, gave a syrupy 3-*O*-benzyl-D-sorbitol pentaacetate (V) in a 83% yield. The removal of the benzyl group of V by catalytic hydrogenolysis with palladium black in acetic acid gave 1,2,4,5,6-penta-*O*-acetyl-D-sorbitol (VI) quantitatively as a slightly yellow syrup, b. p. 164—167°C/0.1 mmHg, $[\alpha]_D^{10}+8.2°$ (ethanol), ν_{OH} 3550 cm^{-1}. Found: C, 49.01; H, 6.10. Calcd. for $C_{16}H_{24}O_{11}$: C, 48.98, H, 6.17%. D-*ribo*-3-Hexulose 1,2,4,5,6-pentaacetate (VII) was obtained by the chromium trioxide oxidation of VI in acetic acid, 54%; pale yellow syrup, b. p. 138—139°C/0.05 mmHg, $[\alpha]_D^{10}-18.2°$ (ethanol), $\nu_{C=O}$ 1756 cm^{-1}, λ_{max} 273 mμ, ε_{max} 109 (ethanol). Found: C, 49.11; H, 5.91. Calcd. for $C_{16}H_{22}O_{11}$: C, 49.23; H, 5.68%.

The treatment of VII with a concentrated phosphate buffer solution (pH 9.0) gave an acetol more quickly than when D-glucose or β-D-glucose pentaacetate was used. This behavior of the 3-hexulose derivative might prove that 3-hexulose or its ene-diolate ion is an intermediate in an acetol formation from monosaccharides; it might also support the mechanism proposed by Hayami.[4] Further investigations are in progress, and additional details will be published later.

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5) A. S. Meyer and T. Reichstein, *Helv. Chim. Acta*, **29**, 152 (1946).
6) K. Freudenberg et al., *Chem. Ber.*, **58**, 666 (1925).