CHEMISTRY LETTERS, pp. 871-872, 1978. Published by the Chemical Society of Japan

SYNTHESIS AND CONFORMATION OF 1,2,4-TRI-O-ACETYL-5,6-DIDEOXY-3-O-METHYL-5-C-[(S)-PHENYLPHOSPHINYL]-β-D-GLUCOPYRANOSE

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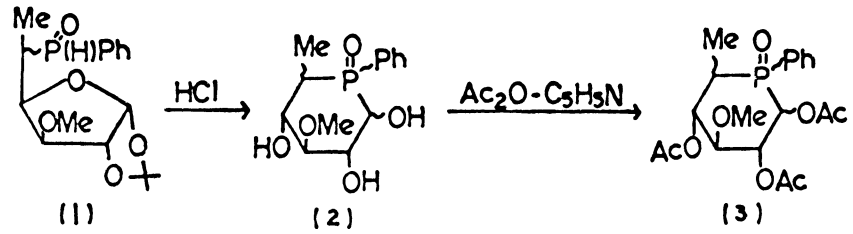
Hydrolysis of phenylphosphinyl derivative of hexofuranose (1) followed by acetylation gave two compounds. The X-ray analysis of one component revealed the structure to be 1,2,4-tri-O-acetyl-5,6-dideoxy-3-O-methyl-5-C-[(S)-phenylphosphinyl]-β-D-glucopyranose (3a) which had a $^4C_1$ (D) conformation.

We reported a synthetic method to prepare sec-alkanephosphonates from ketones via hydrazones.[2] Attempts were successful to obtain sugar derivatives having a phosphorus-carbon bond.[3]

Hydrolysis of (5RS)-5,6-dideoxy-1,2-O-isopropylidene-5-C-(phenylphosphinyl)-3-O-methyl-α-D-xylo-hexofuranose (1)[3] with 0.5N hydrochloric acid at 90-100° for 5 h afforded a syrup (2) in 75% yield. The material was then treated with acetic anhydride in pyridine. Two crystalline compounds (mp 304-306° and 164-165°) were isolated from the ethanol solution of the resulting crude material (crude yield 70%). Both compounds had molecular ion peaks at m/e 412. This suggests that the compounds should be isomers either on C_1 or C_5 carbon atom, or phosphorus atom.

The synthetic procedure implies an occurrence of D-gluco- and/or L-ido-pyranose derivatives containing a phosphorus atom in the hemiacetal ring, however, X-ray crystallographic analysis of the high mp compound[4] (16% yield) showed D- or L-glucopyranose derivative. Therefore, the compound was determined to be 1,2,4-tri-O-acetyl-5,6-dideoxy-3-O-methyl-5-C-[(S)-phenylphosphinyl]-β-D-glucopyranose (3a) with $^4C_1$ (D) conformation.



(1) (2) (3)

1-Phenyl-4,4-dimethylphosphorinane has a chair conformation with the phenyl group on its axial position.[5] Axial preference of a phenyl group has also been reported for the chair form of a six-membered ring phenylphosphonite.[6]

The length of phosphorus-carbon bonds is longer than that of carbon-carbon bonds of the hemiacetal ring by a factor of 1.4. This observation consists with the reported ratio of 1.2.[5,7] The compound described here (3a) is the first sugar derivative, whose ring heteroatom is phosphorus, being subjected to X-ray analysis.

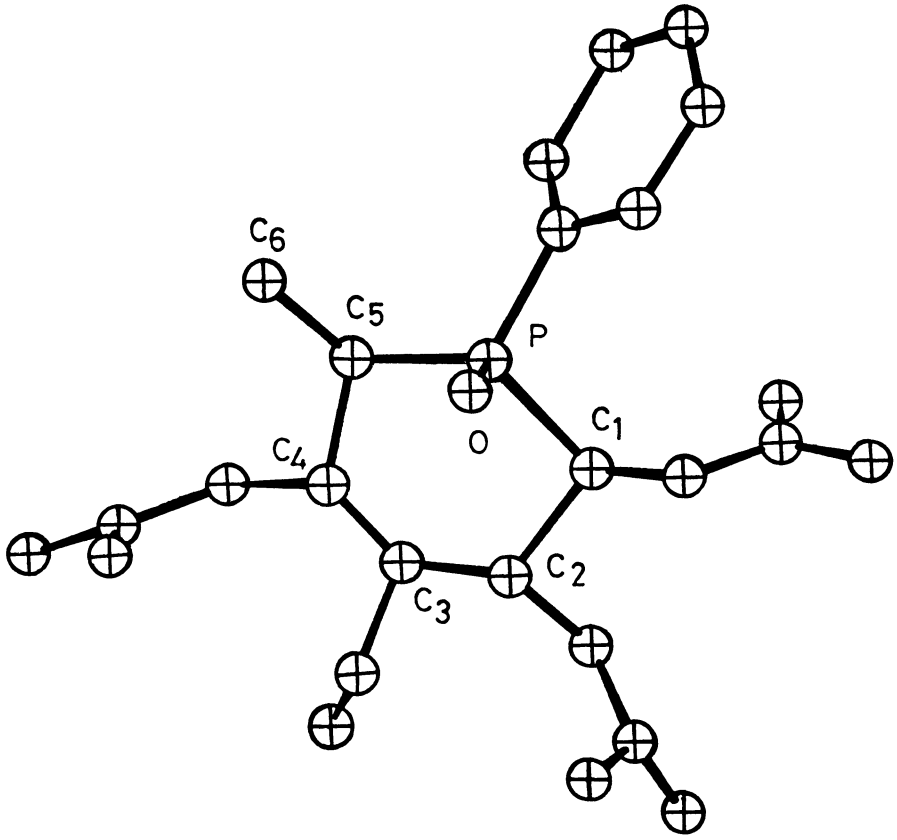


Figure. Computer-generated drawing[8] of 1,2,4-tri-O-acetyl-5,6-dideoxy-3-O-methyl-5-C-[(S)-phenylphosphinyl]-β-D-glucopyranose

References and Notes

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(Received April 26, 1978)