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STUDIES ON NITRO SUGARS. V.[1] A NOVEL SYNTHESIS OF METHYL 5-*O*-BENZOYL-2,3-DIACETAMIDO-2,3-DIDEOXY-β-D-RIBOFURANOSIDE

Tetsuyoshi TAKAMOTO, Hozumi TANAKA, and Rokuro SUDOH

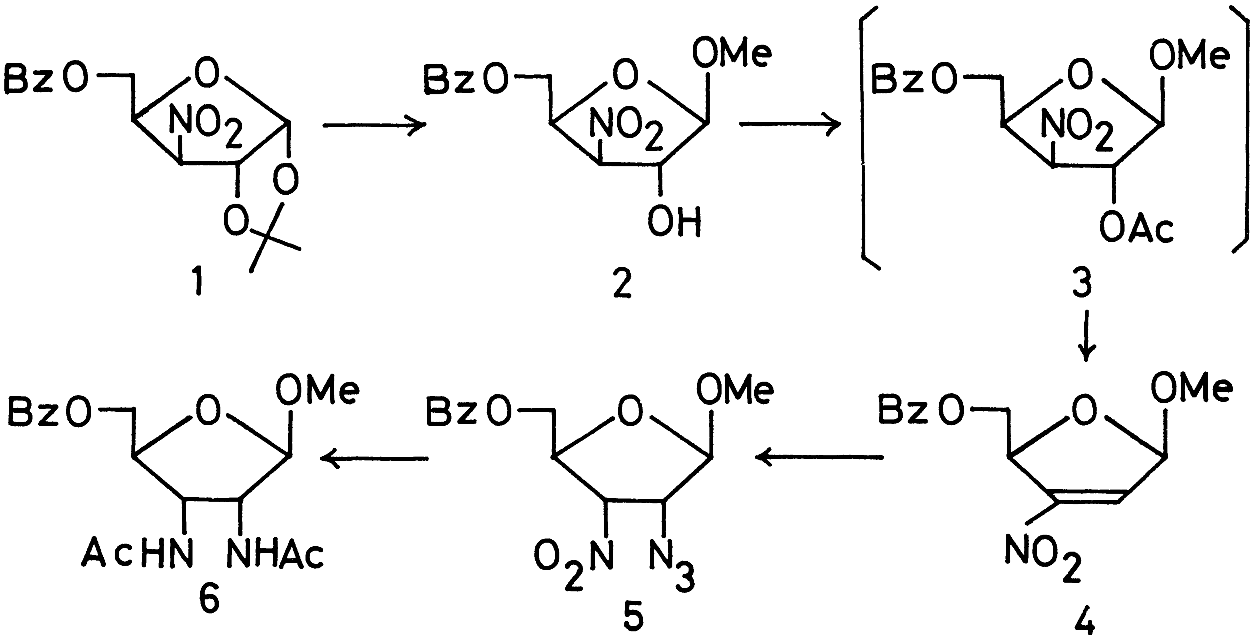
Department of Chemistry, Tokyo Institute of Technology,
O-okayama, Meguro-ku, Tokyo 152, Japan

Treatment of methyl 5-*O*-benzoyl-2,3-dideoxy-3-nitro-β-D-*glycero*-pent-2-enofuranoside (**4**) with hydrazoic acid in chloroform afforded quantitatively methyl 2-azido-5-*O*-benzoyl-2,3-dideoxy-3-nitro-β-D-ribofuranoside (**5**) which was easily led to the corresponding 2,3-diacetamido-ribofuranoside derivative (**6**). Structure of **5** was determined by the specific rotation and its p.m.r. spectrum data.

In the field of carbohydrate chemistry, it has been well known that pyranosides bearing a nitro group at C-3 position are important intermediates for the syntheses of polyamino-,[2] branched-chain sugars,[3] and 2'-nucleosides.[4] However, the synthesis of furanoses bearing a nitro group at C-3 or C-2 position has never been reported. Recently, we have reported[5] a new synthetic method of 3-deoxy-3-nitro-α-D-furanose derivatives, which could be converted to the corresponding nitroolefins, by the oxidation of the sugar oximes with trifluoroperacetic acid.

We now describe a novel synthesis of 2,3-diacetamido-2,3-dideoxy-β-D-ribofuranoside derivative from 5-*O*-benzoyl-3-deoxy-1,2-*O*-isopropylidene-3-nitro-α-D-xylofuranose (**1**)[5] via the corresponding nitroolefin since the reaction of furanoside involving nitroolefin structure with some nucleophilic reagents may also offer interesting problems especially in the field of stereochemistry.

Methanolysis of **1** in the presence of concentrated sulfuric acid as a catalyst at 40°C for 16 hr afforded methyl 5-*O*-benzoyl-3-deoxy-3-nitro-β-D-xylofuranoside (**2**), mp 96-97°C, in 80% yield. Under such mild condition, solvolysis of 5-*O*-benzoyl group can be avoided. Assignment of β-anomeric configuration to **2** is based on its specific rotation $\{[\alpha]_D^{20}$ $-57.8°$ (c 0.6, $CHCl_3$)$\}$,[6] and coupling constant between H-1 and H-2 ($J_{1,2}=0$ Hz) in view of the general data[7-9] with respect to *cis*- (>4.0 Hz) and *trans*-relationship (<1.9 Hz) in a furanoid system.



Treatment of **2** with acetic anhydride in a mixture of pyridine and benzene at room temperature for 12 hr, followed by elimination reaction of acetic acid10) gave in 93% yield a sirup of methyl 5-*O*-benzoyl-2,3-dideoxy-3-nitro-β-D-*glycero*-pent-2-enofuranoside (**4**), $[\alpha]_D^{20}$ -55.8° (c 1, $CHCl_3$), which was characterized by a specific absorption band at 1520 cm^{-1} (olefinic nitro group) in its i.r. spectrum. Further evidences for the structural assignment of **4** are as follows: the long-range coupling between H-1 and H-4 ($J_{1,4}$=1.3 Hz), and between H-2 and H-4 ($J_{2,4}$=1.6 Hz) are observed11) (Fig. 1). The mass spectrum showed $(M+1)^+$ and $(M-NO_2)^+$ peak at m/e 280 and 233, respectively.

According to our results,12) **4** was treated with hydrazoic acid13) in chloroform at room temperature for 4 hr to afford in 92% yield methyl 2-azido-5-*O*-benzoyl-2,3-dideoxy-3-nitro-β-D-ribofuranoside (**5**), mp 61-62°C, which showed absorption bands at 2100 cm^{-1} (azide) and 1555 cm^{-1} (nitro group) in the i.r. spectrum.

The structural assignment of *ribo*-configuration to **5** was done on the basis of the following manner. The specific rotation $\{[\alpha]_D^{20}$ -69.3° (c 1, $CHCl_3$)$\}$ indicates the retention of the anomeric configuration of **4**. As seen from its p.m.r. spectrum (Fig. 2), $J_{1,2}$ (≃0 Hz) means the dihedral angle ($\phi_{1,2}$) to be 80∼100°, i.e., H-1 and H-2 are in a *trans*-relationship each other. On the basis of $\phi_{1,2}$ (80°), $J_{2,3}$ (5.5 Hz) and $J_{3,4}$ (7.8 Hz) should mean $\phi_{2,3}$ and $\phi_{3,4}$ to be ∼30° and ∼170°, respectively. All the data, consequently, support the above structural assignment, i.e., **5** has not

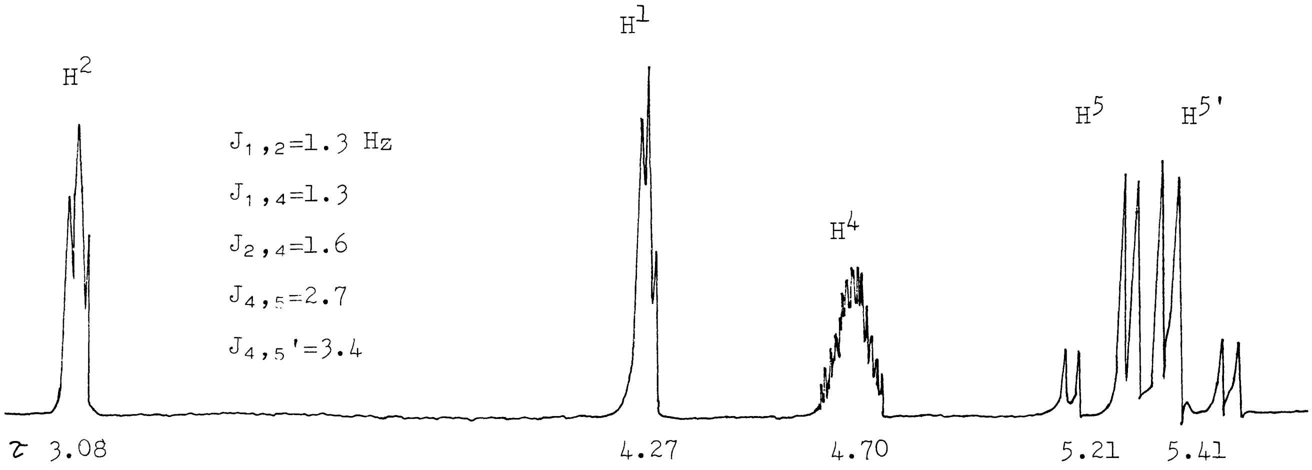


Fig. 1. P.m.r. spectrum of **4** in the region of $\tau 3\sim 6$ at 100 MHz in $CDCl_3$.

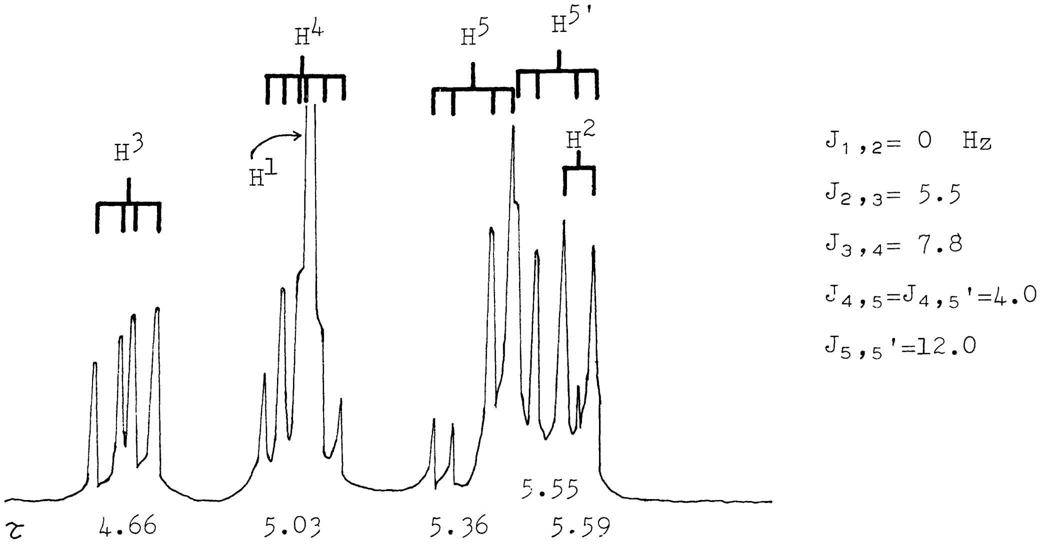


Fig. 2. P.m.r. spectrum of **5** in the region of $\tau 4\sim 6$ at 100 MHz in $CDCl_3$.

xylo- but *ribo*-configuration. The questions with respect to this highly selective formation should be further investigated.

Finally, hydrogenolysis of **5** on Pd-C, followed by *N*-acetylation, gave in 75% yield methyl 5-*O*-benzoyl-2,3-diacetamido-2,3-dideoxy-β-D-ribofuranoside (**6**), mp 183°C (dec), which showed two singlets of *N*-acetyl protons at τ7.93 and 8.03 in the p.m.r. spectrum (in $CDCl_3$) and an absorption band (ν_{N-H}) at 3240 cm^{-1} in the i.r. spectrum.

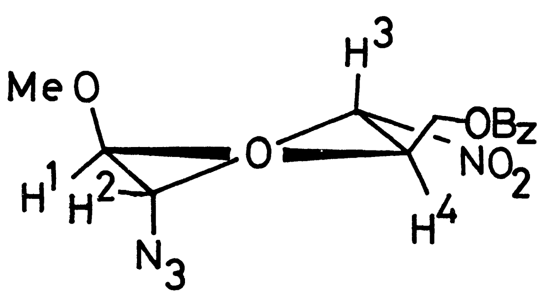


Fig. 3. $^3T_2$ conformation in **5**.

References and Notes

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5) T.Takamoto, R.Sudoh, and T.Nakagawa, Tetrahedron Lett., 2053 (1971); After our report, Kavář and Baer described the synthesis of 3-deoxy-1,2-O-isopropylidene-3-nitro-α-D-xylofuranose in 16% over-all yield through acetonation, partial hydrolysis, periodate oxidation, and reduction from 3-deoxy-3-nitro-D-glucose. (J.Kovář and H.H.Baer, Can. J. Chem., 49, 3238 (1971)).

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10) Nitro acetate **3** has a tendency to eliminate acetic acid, therefore this reaction gave a mixture of **3** and **4**.

11) A similar observation with respect to methyl 5-O-benzoyl-2,3-dideoxy-β-D-*glycero*-pent-2-enofuranoside has been reported. (R.U.Lemieux, K.A.Watanabe, and A.A.Pavia, Can. J. Chem., 47, 4413 (1969)).

12) When phenyl 4,6-O-benzylidene-2,3-dideoxy-3-nitro-β-D-*erythro*-hex-2-enopyranoside was treated with hydrazoic acid at room temperature for 3 hr, phenyl 2-azido-4,6-O-benzylidene-2,3-dideoxy-3-nitro-β-D-glucopyranoside was obtained quantitatively. (T.Sakakibara, R.Sudoh, and T.Nakagawa, J. Org. Chem., In contribution.)

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