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A FACILE PREPARATION OF *O*-ACYLATED β-D-RIBOFURANOSYL CYANIDE, AN IMPORTANT INTERMEDIATE OF C-NUCLEOSIDE SYNTHESIS

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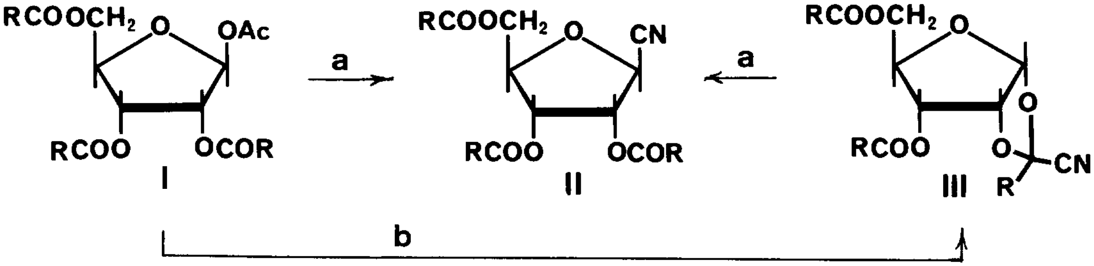
Abstract — Tri-*O*-benzoyl and tri-*O*-acetyl derivatives of the title compound are obtained from the corresponding 1-*O*-acetates in good yields by treatment with cyanotrimethylsilane.

2,3,5-Tri-*O*-benzoyl-β-D-ribofuranosyl cyanide [II (R = Ph)] has been used as a versatile intermediate for the synthesis of C-nucleoside antibiotics[1,2] and its preparation from D-ribose was accomplished by the reaction of the corresponding bromide with mercuric cyanide.[3] This paper describes an efficient and simple procedure for the preparation of 2,3,5-tri-*O*-benzoyl and tri-*O*-acetyl-β-D-ribofuranosyl cyanide [II (R = Ph, Me)] from easily accessible 1-*O*-acetates I (R = Ph, Me) by means of cyanotrimethylsilane.

A mixture of 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose [I (R = Ph), 1.09 g, 2.16 mmol], cyanotrimethylsilane (1.2 ml, 9.3 mmol), and $SnCl_2$ (87 mg, 0.46 mmol) was heated at 70°C for 2 h. The reaction mixture was worked up with aq. $NaHCO_3$ and extracted with ether. The ethereal solution was washed (sat. NaCl), dried (Na_2SO_4), and concentrated. Column chromatography (silica gel) of the residue gave 2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl cyanide [II (R = Ph), 860 mg, 85% yield].[3,4,5]



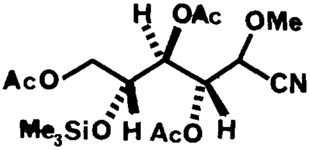
a. Me_3SiCN, $SnCl_2$, 70°C (R = Ph); Me_3SiCN, $BF_3 \cdot OEt_2$, r.t. (R = Ph, Me).
b. Me_3SiCN, $SnCl_2$, r.t. (R = Ph, Me)

[Dedicated to Professor Hitosi Nozaki on the occasion of his 60th birthday]

When the above described mixture was stirred for 2 h at room temperature, 3,5-di-*O*-benzoyl-1,2-*O*-(1-cyanobenzylidene)-D-ribofuranose [III (R = Ph)] was obtained in 45% yield (96% of the consumed starting material) along with 53% of the recovered I. The resulting III was converted to the cyanide II (R = Ph) by treatment with cyanotrimethylsilane at 70°C in the presence of $SnCl_2$. Application of $BF_3\cdot OEt_2$, in place of $SnCl_2$, gave the same cyanide II in 85% yield from I after stirring at room temperature for 2 h.

Acetylated cyanide II (R = Me) was also obtained in 64% yield in addition to the intermediate III (R = Me, 29% yield) by the reaction of I (R = Me) with cyanotrimethylsilane under the catalytic action of $BF_3\cdot OEt_2$ at room temperature. The reaction catalyzed by $SnCl_2$ at room temperature gave III (R = Me, 96% yield) which was recovered unchanged after treatment with cyanotrimethylsilane and $SnCl_2$ at 70°C. Transformation of III (R = Me) into II (R = Me) was successful by treatment with cyanotrimethylsilane under catalytic action of $BF_3\cdot OEt_2$ at room temperature.

Reaction of 2,3,5-tri-*O*-acetyl-1-*O*-methyl-β-D-ribofuranose gave IV[6] as the main product (34%, $SnCl_2$; 71%, $BF_3\cdot OEt_2$) and the formation of II (R = Me) could not be observed.



IV

The above described results are examples of successful application of a novel cyanation by means of cyanotrimethylsilane to carbohydrates.[7]

REFERENCES AND NOTES

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5. Recrystallization from EtOH gave a crystalline product, mp 77.5-78.0°C (lit.[3] mp 78.5-80°C).
6. Structure was determined by ir, ^{1}H-nmr, and ^{13}C-nmr.
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