Synthetic Studies of Carbohydrate Derivatives with Photochemical Reaction. II.[1] Photochemistry of Benzylidene Sugar Derivatives

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The acetone-sensitized photochemical conversion of cyclic acetals to the corresponding carboxylic esters[2] suggests the possibility that the reaction may serve as an unique procedure for the preparation of deoxy sugars from cyclic acetals of sugars. A study on the photochemistry of sugar cyclic acetals has been carried out and part of the results will be described in the present communication.

A solution of methyl 2,3-*O*-benzylidene-β-D-ribofuranoside[3] (I)(0.02M) in a mixture of *t*-butyl alcohol and acetone (9:1) was irradiated[4] at room temperature under nitrogen atmosphere[5] for 60 hr, and the volatiles were evaporated *in vacuo*. The residue was subsequently chromatographed on a silica gel column by elution with benzene - acetone (95 : 5) to give I (recovery : 34%) as the first fraction and methyl 2(or 3)-*O*-benzoyl-β-D-ribofuranoside (II)[6] (58% yield) as the second fraction. Contrary to expectation, the corresponding deoxy sugar was not produced. Variation of the molar concentration of I to 0.08 and 0.40 resulted in a stepwise decrease of the yield of II, and in an increase of that of recovered I. These results are summarized in Table 1. The correlation between the molar concentration of I and the results is now under investigation especially with respect to the effect of oxygen[7] which is slightly contained in commercial nitrogen. It is of interest that the content ratios of *endo*- and *exo*-benzylic proton isomers in each recovered I were considerably varied as compared with that of I applied as the starting material. This leads to the conclusion that *endo-exo* photoisomerization of the isomers actually took place along with the unexpected photooxygenation reaction of I. The reaction may be generalized to proceed *via* the benzylic radical(III) which is convertible into all the species mentioned above as follows:

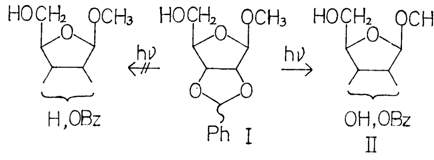


Table 1. Photochemical reaction of methyl 2,3-*O*-benzylidene-β-D-ribofuranoside (I)

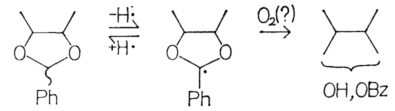
Run	Conc. of I[a] (mol)	Recovery of I Yield (%)	 *exo*-H/*endo*-H	Yield of II (%)
1	0.02	34	0.25,[b] 0.20[c]	58[c]
2	0.08	67	0.27[c]	28[c]
3	0.40	100	0.75[c]	—

All the reactions were carried out in *t*-butyl alcohol - acetone (9 : 1) for 60 hr under irradiation.[4]

a) *exo*-H/*endo*-H of the isomers in the starting material was NMR spectroscopically 1.5, and gas chromatographically 2.0, and also refers to b and c.

b) Calcd by NMR[*exo*-H 4.29 τ, *endo*-H 4.03 τ (CDCl$_3$)]; These assignments were done by reference to 8).

c) Calcd by glc[Column: SE 30 1% on Chromosorb W, injection temp. 270°C, column temp. 200°C, carrier gas: N$_2$ 150 m*l*/min, retention time (min): *exo*-H-I 5.2, *endo*-H-I 5.6 and II 9.8].



III

A similar treatment of 3,5-*O*-benzylidene-1,2-*O*-isopropylidene-α-D-xylofuranose[6] also gave the corresponding 3- and 5-*O*-monobenzoate of 1,2-*O*-isopropylidene-α-D-xylofuranose[6] in good yield. Detailed results with other sugar derivatives will be published elswhere.

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[1] K. Matsuura, S. Maeda, Y. Araki, and Y. Ishido, *Tetrahedron Lett.*, **1970**, 2869.

[2] D. Elad and R. D. Youssefyeh, *ibid.*, **1963**, 2189.

[3] G. R. Baker and T. M. Noone, *J. Chem. Soc.*, **1955**, 1327.

[4] A Pyrex-glass mercury lamp (450 W) of Ushio Electric Inc. was used.

[5] Commercial nitrogen was used without further purification.

[6] Analytical, NMR, and mass spectral data were consistent with the expected structure.

[7] H. E. Seyfarth, A. Rieche, and A. Hesse, *Chem. Ber.*, **100**, 624 (1967).

[8] N. Baggett, K. W. Buck, A. B. Foster, and J. W. Webber, *J. Chem. Soc.*, **1965**, 3401 and the preceding papers.