CHEMISTRY LETTERS, pp.849-852, 1972. Published by the Chemical Society of Japan

SYNTHETIC STUDIES OF CARBOHYDRATE DERIVATIVES WITH PHOTOCHEMICAL REACTION. IV.1)

PHOTOCHEMICAL ADDITION REACTION OF SECONDARY ALCOHOLS TO METHYL 4,6-DI-*O*-ACETYL-2,3-DIDEOXY-α-*D*-*erythro*-HEX-2-ENOPYRANOSIDE

Kazuo MATSUURA, Younosuke ARAKI, Yoshiharu ISHIDO, and Shiro SATOH*
Department of Chemistry, Faculty of Science, Tokyo Institute of Technology,
O-okayama, Meguro-ku, Tokyo
*The Application Laboratory, Nippon Electric Varian, Iikura-cho, Azabu, Tokyo

Photochemical addition reaction of 2-propanol to methyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-*D*-*erythro*-hex-2-enopyranoside was found to give methyl 4,6-di-*O*-acetyl-2,3-dideoxy-2-*C*-(1-hydroxy-1-methylethyl)-α-*D*-*erythro*-*D*-*glycero*-hexopyranoside in 66% yield. A series of secondary alcohols were also found to give such addition products in the photochemical reaction.

In the previous papers,1,2) the authors have reported the photochemical addition reactions of mercaptans, 1,3-dioxolane, and acetone to some enoses. A recent report of Rosenthal and Shudo3) on such reaction of 2-propanol to 3-deoxy-1,2;-5,6-di-*O*-isopropylidene-α-*D*-*erythro*-hex-3-enofuranoside in the presence of acetone prompts us to report on the results of an investigation on the photochemical addition reaction of secondary alcohols to methyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-*D*-*erythro*-hex-2-enopyranoside(I) which was undertaken in view of the photochemical addition of secondary alcohols to olefins,4) and with an expectation that this reaction may serve as an unique procedure for the preparation of branched-chain sugar derivatives involving tertiary alcohols.

A solution of I(500 mg)5) in 2-propanol(II)(12 ml) was irradiated with an ultraviolet lamp6) in a quartz glass test tube under nitrogen atmosphere at room temperature for 60 hr, and the volatile was evaporated *in vacuo*. The resultant sirup was subsequently chromatographed on a column of silica gel by the use of a solvent system of benzene-acetone(95 : 5) for the elution to give the sirup of methyl 4,6-di-*O*-acetyl-2,3-dideoxy-2-*C*-(1-hydroxy-1-methylethyl)-α-*D*-*erythro*-*D*-

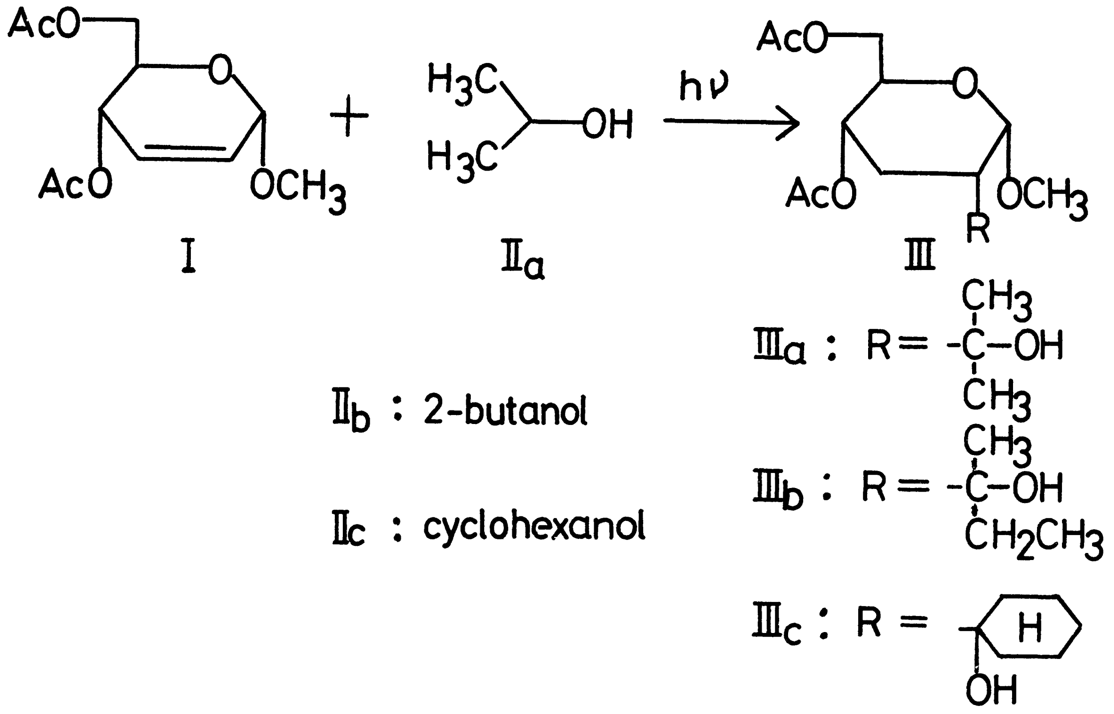

TABLE I. NMR SPECTRAL DATA OF IIIa[a)]

Proton	Chemical Shift(δ value in ppm)	Coupling Constant(Hz)
H-1	4.85	$J_{1,2}$ = 4.2
H-2	1.87	
H-3	1.87	$[J_{2,3} + J_{2,3'}]$ = $14^{b,c)}$
H-3'	1.87	$J_{3,3'}$ = $14^{b)}$
H-4	5.13	$J_{3,4}$ = $J_{3',4}$ = 4.5
H-5	3.94	$J_{4,5}$ = 8.3
H-6 and H-6'	4.25	$J_{5,6}$ = $J_{5,6'}$ = 4.4
$-OCH_3$	3.44	
$=C\langle^{CH_3}_{CH_3}$	1.25 1.27	
$-OCOCH_3$	2.07 and 2.10	

a) The spectrum was taken with Varian HA-100 spectrometer in $CDCl_3$ by the use of TMS as an internal standard.

b) These constants were measured by the addition of $Eu(DPM)_3$ as a shift reagent.

c) $J_{2,3}$ and $J_{2,3'}$ were approximated as 9Hz and 5Hz, respectively.

glycero-hexopyranoside(IIIa)(410 mg, 66% yield).[7] This chromatography gave, in addition, I in 10% recovery yield and an unidentified product(60 mg).

The structural assignment of IIIa was successfully accomplished by its NMR spectrum to give a conclusion that C-1 of 1-hydroxy-1-methylethyl group should link to C-2 of the pyranosyl ring with (S)-configuration and pseudo-equatorial conformation. This conclusion was derived from the following evidences:
(1) Eleven per cent of NOE[8] was observed in the signal of H-1(δ 4.85 ppm) on irradiation at one of the methyl signals of δ 1.27 ppm, and no effect was observed on irradiation at that of 1.25 ppm. (2) The signal of H-4 was observed as a quartet when the signal of H-5(δ 3.94 ppm) was irradiated. (3) The addition of $Eu(DPM)_3$ to the sample together with an irradiation at H-4 proved the signals of H-2, H-3, and H-3′ to be in the typical relation of ABX pattern, and the geminal coupling constant between H-3 and H-3′ 14Hz which is in good agreement with those reported with respect to deoxy sugar derivatives.[9] The magnitude of the observed shifts by the addition of the reagent was in the order of the hydroxy proton, H-2, H-3, and H-3′. Based on these facts, 1-hydroxy-1-methylethyl group was confirmed to link to C-2 of the pyranosyl ring. (4) The acetyl methyl signals were observed in the equatorial acetyl region of the spectrum. (5) All the signals of H-2, H-3, and H-3′ were together observed with an equal chemical shift of δ 1.87 ppm. (6) The coupling constant between H-1 and H-2 was 4.2Hz.[10] These facts can be considered to suggest that the pyranosyl ring may considerably be strained, and thus 1-O-methyl group may occupy a pseudo-axial conformation.

Similar addition reactions were observed in the cases of other secondary alcohols, e. g., 2-butanol(the recovery of I: 11%, the yield of IIIb: 52%[11] and an isomer of IIIb: 15%[12]), cyclohexanol(the recovery of I: 14% and the yield of IIIc: 64%[11]), and 2- and 3-pentanol in which the corresponding products were obtained in a relatively poor yield and were found to be complicated becuase of the concomitant formation of some by-products. On the other hand, I was completely recovered in the cases of the reaction with primary alcohols(methanol, ethanol, and 1-propanol), cyclopentanol, and t-butyl alcohol, respectively. Moreover, ethyl glycoside homologue of I also gave the corresponding addition product(IV) in 60% yield[11] in the same reaction with II.

These reactions also proceeded in the presence of such photosensitizer as acetone, however, the yields of each reaction were lowered on account of the competitive addition of 2-propanol, which was arisen from the photoreduction of acetone, except in the case of 2-propanol.

The reaction described in this communication may be generalized to proceed via the mechanism involving a radical on the carbon atom adjacent to hydroxyl group which may preferably attack on the more electron-sufficient C-2 of I.

Such addition reaction of 1,3-dioxolane and tetrahydrofuran respectively with I were found to proceed via the same mechanism and to give the corresponding 1 : 1 adduct in good yield which will be published elsewhere.

References

1) K. Matsuura, Y. Araki, and Y. Ishido, Bull. Chem. Soc. Japan, 45, No. 11(1972), to be published.

2) K. Matsuura, Y. Araki, Y. Ishido, and T. Murai, Tetrahedron Lett., 1970, 2869.

3) A. Rosenthal and K. Shudo, J. Org. Chem., 37, 1608(1972).

4) G. J. Fonken, " Organic Photochemistry " Vol. 1, ed. by O. L. Chapman, Marcell Dekker Inc., New York, N. Y.(1970), p 197.

5) Prepared by the procedure of Ferrier and Prasad[R. J. Ferrier and N. Prasad, J. Chem. Soc. (C), 1969, 570.].

6) A low pressure mercury lamp(30 W) of Riko Kagaku Co. Ltd. was used in the experiment.

7) The analytical data of this sample were consistent with the expected structure. $[\alpha]_D^{22}$ +86.0°(c 1.0, acetone). The specific absorption band of hydroxyl group was observed at about 3500 cm^{-1}.

8) The value of NOE was obtained under non-degassed condition.

9) S. Hanessian, " Advances in Carbohydr. Chem. " ed. by M. L. Wolfrom, Academic Press, New York, N. Y., Vol. 21 p 143(1966).

10) $J_{1,2e}$ and $J_{1,2a}$ of methyl 2,6-dideoxy-α-D-arabino-hexopyranoside in $CDCl_3$ were reported as 1.5Hz and 3.5Hz, respectively, by Nakanishi et al.[M. Miyamoto, Y. Kawamatsu, M. Shinohara, K. Nakanishi, Y. Nakadaira, and N. S. Bhacca, Tetrahedron Lett., 1964, 2371.].

11) IIIb, IIIc, and IV were the same configuration as IIIa on the basis of their NMR spectral pattern.

12) The NMR spectrum demonstrated the product to be an isomer of IIb.

(Received July 24, 1972)