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SYNTHETIC STUDIES OF CARBOHYDRATE DERIVATIVES WITH PHOTOCHEMICAL REACTION. V.[1)] PHOTOCHEMICAL REACTION OF D-GLUCAL AND 2-HYDROXY-D-GLUCAL ACETATES WITH LACTONITRILE

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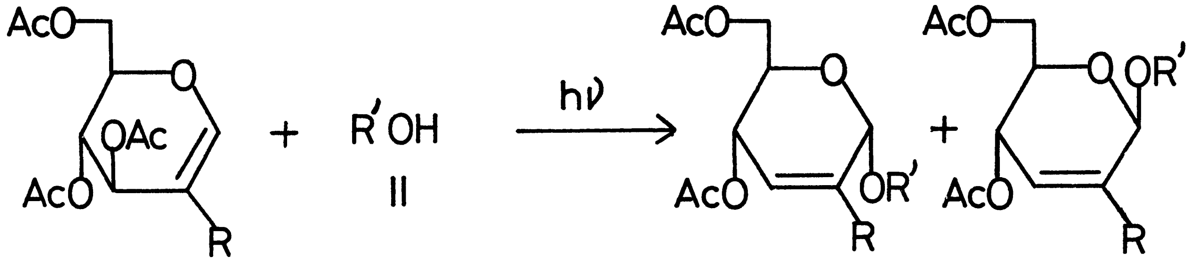
3,4,6-Tri-O-acetyl-D-glucal and 2,3,4,6-tetra-O-acetyl-2-hydroxy-D-glucal were found to give the corresponding 1′-cyanoethyl 4,6-di-O-acetyl-2,3-dideoxy- and 2,4,6-tri-O-acetyl-3-deoxy-D-*erythro*-hex-2-enopyranosides in high yields in the photochemical reaction with lactonitrile accompanied by the elimination of acetic acid and the rearrangement of their double bond.

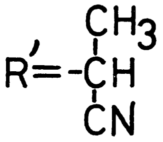
In the preceding paper,[1)] the authors have reported that the photochemical addition reaction of several secondary alcohols to enoses gives the corresponding branched-chain sugar derivatives involving tertiary alcohol substituents. In this communication, the authors wish to report on a new photochemical glycosidation reaction of D-glucal and 2-hydroxy-D-glucal acetates in lactonitrile being attended by an allylic rearrangement.

A solution of 3,4,6-tri-O-acetyl-D-glucal(I)(1.00 g) in lactonitrile(II)(12 ml) was irradiated with ultraviolet light[2)] under nitrogen atmosphere at room temperature for 27 hr, and the volatiles were evaporated *in vacuo*. A silica gel column chromatography of the resultant sirup by the use of a solvent system of benzene-acetone(98 : 2) for the elution gave the sirup of 1′-cyanoethyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside(IIIa)[3)] as a fraction following after that of the corresponding β-anomer(IIIb)[3)] in 37 and 47% yield, respectively {IIIa: $[\alpha]_D^{22}$ +49.4°(c 1.0, acetone); IIIb: $[\alpha]_D^{22}$ +78.2°(c 1.0, acetone)}. Interesting to state, no formation of such tertiary alcohol derivatives was observed



I: R=H

IV: R=OAc


$R' = -CH(CH_3)CN$

IIIa: R=H   IIIb: R=H

Va: R=OAc   Vb: R=OAc

TABLE I. NMR SPECTRAL DATA

Protons	IIIa	IIIb	Va	Vb
H-1'	δ 4.47 ppm	δ 4.72 ppm	δ 4.47 ppm	δ 4.68 ppm
H-1	5.23	5.34	5.30	5.34
H-2	6.06	6.05	——	——
H-3	5.85	5.89	5.87	5.89
H-4	5.44	5.40	5.57	5.55
H-5	4.23	4.09	4.23	4.16
H-6,6'	4.3 – 4.5	4.2 – 4.3	4.3 – 4.4	4.2 – 4.3
$-CH_3$	1.64	1.64	1.66	1.66
$-OCOCH_3$	2.13(6H)	2.11(6H)	2.13(6H) and 2.19(3H)	2.12(6H) and 2.24(3H)
$J_{1,2}$	1Hz >	0.5Hz >	——	——
$J_{1,3}$	2.5	1 >	——	——
$J_{2,3}$	10	10.5	——	——
$J_{2,4}$	1 >	1 >	——	——
$J_{3,4}$	1.5	2	2.3Hz	2.0Hz
$J_{4,5}$	9.5	9.5	9.5	10
$J_{5,6}$	2.5	2.2	——	1 >
$J_{5,6'}$	3.5	3.5	——	3.5
J_{1',CH_3}	7.0	7.0	7.0	7.0

These spectral data were obtained with Varian XL-100 spectrometer in $CDCl_3$ by the use of TMS as an internal standard.

as expected from the fact[1] that ordinary secondary alcohols give the corresponding tertiary alcohol derivatives in the photochemical addition reaction to some enoses. A similar treatment of 2,3,4,6-tetra-O-acetyl-2-hydroxy-D-glucal(IV) in II gave 1′-cyanoethyl 2,4,6-tri-O-acetyl-3-deoxy-α-D-*erythro*-hex-2-enopyranoside(Va) and the corresponding β-anomer(Vb) in 40 and 40% yield, respectively {Va: $[\alpha]_D^{22}$ +95.2° (c 0.6, acetone); Vb: $[\alpha]_D^{22}$ +25.0°(c 1.0, acetone)}.[3] The eluting-out order of these products was the same as observed between IIIa and IIIb.

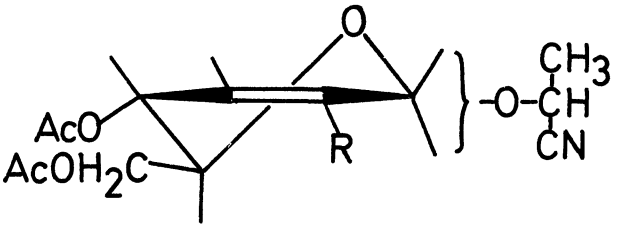
The structural determination of IIIa, IIIb, Va, and Vb was successfully accomplished by their NMR spectra(cf. Table I) to give a conclusion that IIIa and Va are the α-anomers, and IIIb and Vb are the β-anomers of the corresponding D-*erythro*-hex-2-enopyranosides, respectively. This conclusion was derived from the following evidences:

(1) The signals of the anomeric proton of 2,3-dideoxy- and 3-deoxy-α-D-*erythro*-hex-2-enopyranosides are generally known to appear in the higher field comparing with those of the corresponding β-anomers.[4] The anomeric proton signals of IIIa, IIIb, Va, and Vb were observed at δ 5.23, 5.34, 5.30, and 5.34 ppm, respectively.

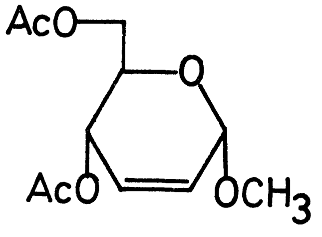
(2) The difference in the chromatographic behavior between IIIa and IIIb was entirely the same as that between Va and Vb. Retention volumes of IIIa, IIIb, Va, and Vb in GLC[5] were 2.1, 1.7, 4.8, and 4.0, respectively. In the column chromatography, IIIb and Vb were eluted faster than IIIa and Va, respectively.

NMR spectroscopy(cf. Table I) showed that all the D-*erythro*-hex-2-enopyranosides of this series adopt *H1* conformation(VI) with $J_{3,4}$ and $J_{4,5}$ values of ca. 2 and ca. 10Hz, respectively, indicative of quasi-axial and axial protons at *C*-4 and *C*-5, respectively.[4]

It is of much interest to notice the preferable formation of the β-anomer in the reaction of I in view of the acid-catalyzed reaction of I with alcohols which favored the formation of the α-anomers.[6] Thus, I was treated with II under the



VI



VII

acidic condition, which was applied to the reaction of I with ordinary alcohols,[4b)] to give IIIa and IIIb in the ratio of 41 : 59.[5)] The ratio was in good agreement with that(44 : 56[5)]) obtained in its photochemical reaction, and hence these results were ascribed to the unusual properties of II. Moreover, starting materials were completely recovered in the dark reaction in the case of the reaction with I and IV, respectively. On the basis of these results, the above photochemical reactions were conceivable to proceed *via* the mechanism involving a radical on the oxygen atom of II which was formed by ultraviolet light, and the nucleophilic attack of the radical on I or IV which resulted in the formation of III or V accompanied by the allylic rearrangement. This reaction is the first case involving an O-radical arisen from alcohol in the field of the carbohydrate chemistry.

In addition to the photochemical reaction of I and IV respectively with II, it is noteworthy to state that methyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside(VII) also gave IIIa and IIIb in 40 and 47% yield, respectively, with the recovery of the starting material in 3% yield in the photochemical reaction with II. Namely, a photochemical transglycosidation reaction seems to be occurred. The mechanism of this reaction is now under investigation in our laboratory.

References

1) K. Matsuura, Y. Araki, Y. Ishido, and S. Satoh, Chem. Lett., 849(1972).

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

3) Analytical data were consistent with the expected structure. Mass spectral data were also consistent with those with respect to hex-2-enopyranosyl derivatives reported by Ferrier *et al.*[R. J. Ferrier, N. Vethaviyasar, O. S. Chizov, V. I. Kadentsev, and B. M. Zolotarev, Carbohyd. Res., 13, 269(1970)].

4) a) R. J. Ferrier, N. Prasad, and G. H. Sankey, J. Chem. Soc. (C), 1969, 587 and preceding papers. b) R. J. Ferrier and M. M. Ponpipon, ibid., 1971, 560. c) R. U. Lemieux and R. J. Bose, Can. J. Chem., 44, 1855(1960).

5) GLC were taken with Hitachi K-53[Column: 1% of SE-30 on Chromosorb-W(60 – 80 mesh); Carrier gas: Nitrogen under 1.5 Atm; Oven temperature: 200°C; Injection temperature: 300°C.]. Retention volume of I and IV were 1.00 and 2.3, respectively. In the acid-catalyzed reaction, some by-products(ca. 20%) were detected other than IIIa and IIIb.

6) R. J. Ferrier and N. Prasad, J. Chem. Soc. (C), 1969, 570.

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