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Synthetic Studies of Carbohydrate Derivatives with Photochemical Reaction. III.[1] Solvent Effects on the Photocycloaddition of Acetone to 3,4,6-Tri-*O*-acetyl-D-glucal

Kazuo Matsuura, Younosuke Araki, and Yoshiharu Ishido
Department of Chemistry, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo

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In a previous paper,[2] the present authors reported the photochemical reaction of mercaptans or 1,3-dioxolane with enoses in the presence of acetone (**1**) as a photosensitizer. In the present paper, we wish to report the photocycloaddition of **1** to 3,4,6-tri-*O*-acetyl-D-glucal (**2**); this resulted in the formation of an oxetane derivative, *i.e.*, 5,6,8-tri-*O*-acetyl-2,4;3,7-dianhydro-1-deoxy-2-*C*-methyl-D-*glycero*-D-*ido*-octitol (**3**), and there were interesting solvent effects on the reaction. According to a recent paper,[3] incidentally, the photocycloaddition of **1** to **2** without the utilization of any solvent gave **3** in a 33% yield; this yield was calculated on the basis of the amount of **2** consumed (recovery yield=47%), and the structure of **3** was deduced by deriving **3** into some derivatives.

Results and Discussion

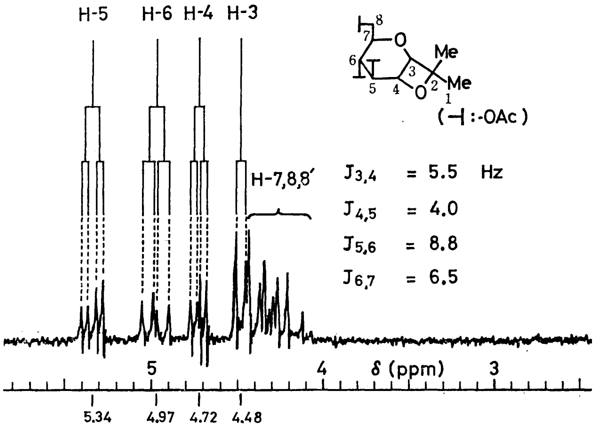

Fig. 1. 100 MHz NMR spectrum of 5,6,8-tri-*O*-acetyl-2,4; 3,7-dianhydro-1-deoxy-2-*C*-methyl-D-*glycero*-D-*ido*-octitol (**3**) in $CDCl_3$ with TMS as the internal standard. (δ 2.5—5.8 ppm)

The irradiation of **2** in **1**—2-propanol (100: 1) with an ultraviolet lamp under nitrogen at room temperature for 100 hr gave **3** in a good yield. The structure of **3**, especially with respect to the stereochemistry in the mutual fusion of its pyranose and oxetane rings at C-3 and C-4 of **3**, was examined as follows.

i) The NMR spectrum of **3**, whose signals were assigned by the double-resonance technique, shows (*cf.* Fig. 1) that the H-3 and H-4 signals give a doublet at δ 4.48 ($J_{3,4}$=5.5 Hz) and a quartet at 4.72 ppm ($J_{4,5}$=4.0 Hz), respectively. Consequently, the facts lead to the conclusion that the carbonyl oxygen of **1** links to C-2, and the carbonyl carbon to C-1 of the

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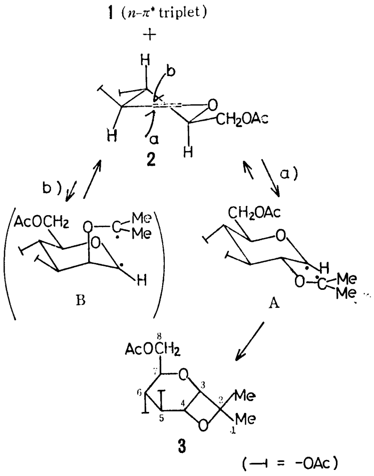
[1] K. Matsuura, S. Maeda, Y. Araki, and Y. Ishido, This Bulletin, **44**, 292 (1971).

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

[3] Khong-Seng Ong and R. L. Whistler, *J. Org. Chem.*, **37**, 572 (1972).

pyranose ring of **2**.[4] The coupling constants of H-6—H-7 (6.5 Hz) and H-5—H-6 (8.8 Hz) indicate that H-6 and H-7 are not in a true diaxial *trans* correlation; hence, the pyranose ring of **3** can be considered to be strained to some extent.

ii) The addition of piperylene as a quencher to the system resulted in no formation of **3**, and the reaction was confirmed to involve the addition of the n—π^* triplet acetone to **2**. It is well known[5] that the carbonyl oxygen in the n—π^* triplet state is electron-deficient. Thus, the attack of the carbonyl oxygen should take place at the more electron-sufficient C-2 of **2**, and the resultant radical at C-1 should be stabilized by the resonance with the pyranose ring oxygen. Moreover, the general mode of the oxetane ring formation in the photochemistry is considered to involve the biradical intermediate.[6] On the basis of the above considerations, the mechanism of this reaction may be formulated as below. The selective formation of **3** with the chirality of *S* at C-4 may be explained by comparing the stereochemical stability between the biradical intermediates, A and B. This conclusion agrees with that reported by Ong and Whistler.[3]



Subsequently, the solvent effects on this reaction were examined; the results are summarized in Table 1. Interestingly, the addition of solvents (about 1%) to **1** promoted the formation of **3**, whereas the addition of 100 times of a solvent to **1** brought about no formation of **3** and a quantitative recovery of **2**; this is in contrast with the addition of 2-propanol, which resulted in the formation of two new products detected gas-chromatographically with retention volumes of 2.5 and 2.6 (observed as a shoulder on the preceding peak), and the recovery of **2** in a 5% yield.[7]

Table 1. The examination of sovent effects on the photocycloaddition reacion[a)]

Solvent added[b)]	Yield of the Octitol (**3**), %[c)]
2-Propanol	99
2-Propanol–Piperylene[d)]	0
Ethanol	70
Diethyl Ether	46
Tetrahydrofuran	30
1,4-Dioxane	87
Cyclohexane	25
Benzene	26
Toluene	52
Pyridine	24

a) All the reactions were carried out by the use of **2** (35 mg), acetone (10 m*l*) under nitrogen at room temperature by the irradiation with an ultraviolet lamp (450 W) for 32 hr.

b) Zero point one m*l* of the solvents were added, respectively, and, on the other hand, the addition of a large excess amount of them other than 2-propanol resulted in no reaction.

c) All the yields were calculated from glc. *cf.* Without any solvent, the reaction gave the product in 17% yield.[3)]

d) The addition of piperylene (0.5 and 0.1 m*l*, respectively) resulted in quntitative recoveries of **2**.

Similar phenomena were found in the same reactions of the other enoses; those investigations are now in progress in our laboratory.

Experimental

The solvents applied in the experiments were purified in the usual manner before use. Irradiations were carried out with a high-pressure mercury lamp (450W) of Ushio Electric, Inc., in a Pyrex-glass test tube at the distance of about 5 cm. The TLC was carried out by the use of Wakogel B-5 and the solvent system of benzene–methanol (9: 1 v/v) for the development. The NMR spectra were taken with Varian XL-100 in $CDCl_3$ by the use of tetramethylsilane (TMS) as the internal standard, while a mixture of $CDCl_3$-CD_3CN (1: 1) was used for the improvement of the resolution of the spectrum. The glc was done with a Hitachi K-53 apparatus; column: 1% of SE-30 on Chromosolb W(60—80 mesh), carrier gas: N_2 under 1.5 atm, oven temperature: 200°C, and injection temperature: 300°C. MS was taken with a Hitachi RMU-6E apparatus.

*Irradiation of 3,4,6-Tri-*O*-acetyl-*D*-glucal (2) with Acetone (1).* A solution of **2** (1.00 g) in a mixture of **1** (10 m*l*) and 2-propanol (0.1 m*l*) was irradiated under a nitrogen atmosphere at room temperature for 100 hr, and then the volatiles were evaporated *in vacuo*. The residue was subsequently chromatographed on a silica gel column by the use of benzene–acetone (19: 1 v/v) as an eluting solvent system; this gave a chromatographically-pure syrup of **3** (330 mg, 27% yield[9)]). $[\alpha]_D^{25}$ +49.5° (c 1.0 Me_2CO) $[\alpha]_D^{25}$ +54.1° (c 1.0, $CHCl_3$)[3)]. NMR ($CDCl_3$) δ 4.48 (H-3, d, $J_{3,4}$=5.5 Hz), 4.72 (H-4, q, $J_{4,5}$=4.0 Hz), 5.34 (H-5, q, $J_{5,6}$=8.8 Hz), 4.97 (H-6, q, $J_{6,7}$=6.5 Hz), 4.4—4.1 (H-7,8,8′, m), 1.43 and 1.45 ($2CH_3$), and 2.06, 2.08, and 2.11 ppm ($3CH_3CO$), and NMR ($CDCl_3$-CD_3CN=1: 1) δ 4.47 (H-3), 4.69 (H-4), 5.30 (H-5), 4.93 (H-6), 4.45—4.10 (H-7,8,8′), 1.40 and 1.43 ($2CH_3$), and

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[4] *cf.* H. Sakurai, K. Shima, and S. Toki, *Nippon Kagaku Zasshi*, **89**, 537 (1968).

[5] A. Padwa, *Tetrahedron Lett.*, **1964**, 3465.

[6] D. R. Arnold, "Advances in Photochemistry," Vol. 6, Interscience Publishers, New York, (1968), p. 301.

[7] More detailed investigation is necessary to make a decisive discussion on the solvent effect in this reaction. In addition, the reaction in water gave 4,6-di-*O*-acetyl-*psudo*-D-glucal[8)] (39% yield), and that in tetrachloromethane the adduct of **2** with the solvent, respectively. No formation of **3** was observed in both cases.

[8] E. Fischer. *Ber.*, **47**, 196 (1914).

[9] Prior to the column chromatography, the yield of **2** and **3** were calculated from glc as 13 (recovery) and 71% yield, respectively.

2.04, 2.07, and 2.07 ppm ($3CH_3CO$). IR: no absorption of OH group was observed. glc: retention volume=2.4 (**2**: 1.00). Found: C, 54.52; H, 6.66%. Calcd for $C_{15}H_{22}O_8$: C, 54.54; H, 6.71%. MS: *m/e*=329[$(M-1)^+$].

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