Synthetic Studies of Carbohydrate Derivatives with Photochemical Reactions. IX.[1] The Photochemical Addition of 1,3-Dioxolane to Several Enoses

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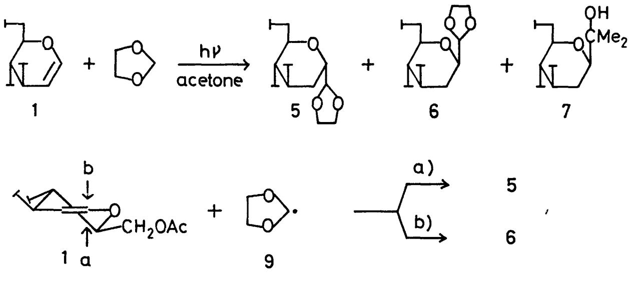
The photochemical addition reactions of 1,3-dioxolane to enoses with an endocyclic or exocyclic double bond, such as 3,4,6-tri-*O*-acetyl-D-glucal, 2,3,4,6-tetra-*O*-acetyl-2-hydroxy-D-glucal, methyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside, and methyl 5-deoxy-2,3-*O*-isopropylidene-β-D-*erythro*-pent-4-enofuranoside, were studied. It was found that the addition of 1,3-dioxolane to the enoses proceeds with great ease, thus affording the corresponding 1,3-dioxolan-2-yl derivatives in excellent yields, and with a considerable regiospecificity and stereoselectivity. The reactions of tetrahydrofuran with the enoses were also studied.

In this series of investigations, the photochemical reaction of sugar derivatives has been studied mainly from a synthetic standpoint of view.[2] Rosenthal and Elad[3] have reported that an acetone-sensitized photochemical addition of 1,3-dioxolane to a terminal olefinic compound affords 2-substituted dioxolane derivatives as the main products, plus its 4-substituted isomers as the minor products. This reaction has also been shown to be applicable to enoses; *i. e.*, 5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hex-5-enofuranose and 3-deoxy-1,2; 5,6-di-*O*-isopropylidene-3-methylene-α-D-*ribo*-hexfuranose, which have a terminal and an exocyclic double bond respectively, thus giving the corresponding equimolar adducts with 1,3-dioxolane in 45 and 55% yields respectively.[4]

In the field of carbohydrate chemistry, it is now an essential problem to obtain an excellent method of synthesizing sugar derivatives with a branched-aldehyde structure; such derivatives can conceivably be derived from such a photochemical addition of 1,3-dioxolane to enoses involving an endocyclic double bond, followed by acid-catalyzed hydrolysis under mild conditions, since the functional group can be converted into a hydroxymethyl group by reduction or into a heterocyclic structure by an appropriate set of reactions, *etc.* In a previous paper,[2a] the present authors briefly reported on the acetone-sensitized photochemical addition of 1,3-dioxolane to 3,4,6-tri-*O*-acetyl-D-glucal (**1**) and 2,3,4,6-tetra-*O*-acetyl-2-hydroxy-D-glucal (**2**); in that study, though, the final structural determination was not achieved. The photochemical additions of **1**, **2**, methyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (**3**), and methyl 5-deoxy-2,3-*O*-isopropylidene-β-D-*erythro*-pent-4-enofuranoside (**4**) will be described in this article.

Results and Discussion

An acetone-sensitized photochemical addition of 1,3-dioxolane to **1** was carried out by irradiating it with a high-pressure mercury lamp in 1,3-dioxolane under a nitrogen atmosphere. The subsequent chromatographic separation of the sirup obtained by the concentration of the reaction mixture on a column of silica gel afforded 4,5,7-tri-*O*-acetyl-2,6-anhydro-3-deoxy-D-*arabino*-L-*glycero*-heptose ethylene acetal (**5**) and 4,5,7-tri-*O*-acetyl-2,6-anhydro-3-deoxy-D-*arabino*-D-*glycero*-heptose ethylene acetal (**6**) in 37 and 37% yields respectively, along with 5,6,8-tri-*O*-acetyl-3,7-anhydro-1,4-dideoxy-2-*C*-methyl-D-*arabino*-D-*glycero*-octitol (**7**)[2f] (24% yield). **7** was produced by the nucleophilic attack of the 2-propanol-2-yl radical (**8**), which had been formed from acetone by the abstraction of a hydrogen atom from 1,3-dioxolane, on the C-1 of **1**. The structural assignments of **5** and **6** were made on the basis of their NMR data, shown in Table 1. In the spectrum of **5**, the signals of H-2, H-3a, and H-3e are observed as multiplets at δ 4.01, 1.79, and 2.22 ppm respectively, while $J_{2,3a}$, $J_{2,3e}$, and $J_{3a,3e}$ have been determined to be 6.0, 4.0, and 14.0 Hz respectively. In the spectrum of **6**, on the other hand, the signals of H-2, H-3a, and H-3e are observed at δ 3.56 as an octet, and those at 1.61 and 2.19 ppm, as multiplets, while $J_{2,3a}$, $J_{2,3e}$, and $J_{3a,3e}$ were determined to be 11.5, 2.2, and 11.5 Hz respectively. The 1,3-dioxolan-2-yl groups at C-2 in **5** and **6** were concluded to be in axial and equatorial orientations respectively, on the basis of the above assignments for H-2s in **5** and **6** being in equatorial and axial orientations respectively. Consequently, the photochemical addition of 1,3-dioxolan-2-yl radical (**9**) to **1** can conceivably



(—| = OAc)

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[1] Part VIII: K. Matsuura, Y. Araki, and Y. Ishido, This Bulletin, **46**, 2261 (1973).

[2] a) K. Matsuura, S. Maeda, Y. Araki, Y. Ishido, and A. Murai, *Tetrahedron Lett.*, **1970**, 2869; b) K. Matsuura, S. Maeda, Y. Araki, and Y. Ishido, This Bulletin, **44**, 292 (1971); c) K. Matsuura, Y. Araki, and Y. Ishido, *ibid.*, **45**, 3496 (1972); d) K. Matsuura, Y. Araki, Y. Ishido, and S. Sato, *Chem. Lett.*, **1972**, 849; e) K. Matsuura, Y. Araki, Y. Ishido, and M. Kainosho, *ibid.*, **1972**, 853; f) K. Matsuura, Y. Araki, Y. Ishido, K. Kushida, and A. Murai, *Carbohyd. Res.*, in press; g) Y. Araki, K. Matsuura, Y. Ishido, and K. Kushida, *Chem. Lett.*, **1973**, 383.

[3] I. Rosenthal and D. Elad, *J. Org. Chem.*, **33**, 805 (1968), and the preceding papers.

[4] J. S. Jewell and W. A. Szareck, *Tetrahedron Lett.*, **1969**, 43.

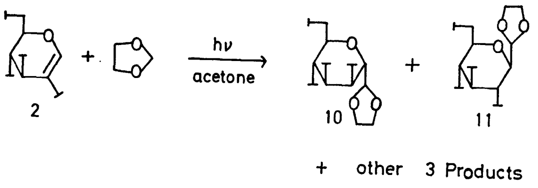
Table 1. NMR spectral data of **5**, **6**, **10**, and **11**

Protons	Chemical shifts in δ value			
	5	**6**	**10**	**11**
H-1	5.01	4.88	5.01	5.04
H-2	4.01	3.56	3.57	3.58
H-3a	1.79	1.61	—	5.0—5.3
H-3e	2.22	2.19	5.66	—
H-4	5.31	4.85—5.1	5.11	5.09
H-5	4.90		5.35	5.0—5.3
H-6	3.8—4.4	3.6	3.73	3.6—3.7
H-7,7′		4.06, 4.25	4.2—4.4	4.15—4.4
O-(CH$_2$)$_2$-O	3.8—4.1	3.8—4.1	3.8—4.1	3.8—4.1
O-COCH$_3$	2.02, 2.04, 2.07	2.01, 2.02, 2.06	2.00, 2.06, 2.12, 2.17 (ax.)	2.03, 2.06, 2.07, 2.10
Coupling constants in Hz				
H-1—H-2	4.0	3.6	5.8	3.0
H-2—H-3a	6.0	11.5	—	9.1
H-2—H-3e	4.0	2.2	1.3	—
H-3a—H-3e	14.0	11.5	—	—
H-3a—H-4	9.5	11.5	—	9.2
H-3e—H-4	5.0	3.0	3.2	—
H-4—H-5	8.0		9.8	9.2
H-5—H-6			9.8	
H-6—H-7		4.5	2.4	
H-6—H-7′		2.5	4.9	
H-7—H-7′		12.0	12.2	

These data were obtained in CDCl$_3$ by the use of tetramethylsilane as the internal standard.

take place regiospecifically at the C-1 of **1** from both the α- and β- sides of the 1-enopyranosyl ring, without any configurational selectivity, thus giving **5** and **6** in a relative ratio of 1 : 1.

The treatment of **2** under similar conditions afforded 3,4,5,7-tetra-*O*-acetyl-2,6-anhydro-D-*glycero*-D-*talo*-heptose ethylene acetal (**10**) and 3,4,5,7-tetra-*O*-acetyl-2,6-anhydro-D-*glycero*-D-*gulo*-heptose ethylene acetal (**11**) in 17 and 42% yields respectively. Much as in the previous reaction, three products, which are the adducts with **8**, were concomitantly afforded in this case.[5] The NMR spectral evidence for the structural determination of **10** and **11** is demonstrated in Table 1. In the spectrum of **10**, the signals of H-2 and H-3 are observed at δ 3.57 (quartet) and 5.66 (quartet) ppm respectively, and $J_{2,3}$ and $J_{3,4}$ were determined to be 1.3 and 3.2 Hz respectively. Moreover, only one of the four acetyl signals is observed at δ 2.17 ppm.



In the spectrum of **11**, on the other hand, the signal of H-2 is observed at δ 3.58 (quartet) ppm, $J_{2,3}$ and $J_{3,4}$ were determined to be 9.1 and 9.2 Hz respectively, and all the acetyl signals are observed in the equatorial region. In **10**, the 1,3-dioxolan-2-yl group and the *O*-acetyl group are concluded to occupy the axial orientation at C-2 and C-3 respectively. In **11**, on the other hand, they are in the equatorial orientation at C-2 and C-3 respectively. The addition of the **9** radical may take place on the C-1 of **2** from the α- and β-sides of the 2-hydroxy-1-enopyranosyl ring, thus giving **10** and **11** respectively; this reaction was thus established to involve the *cis*-addition-type mechanism.

Subsequently, the photochemical addition of 1,3-dioxolane to **3** and **4** respectively under the irradiation of a low-pressure mercury lamp was investigated.[6]

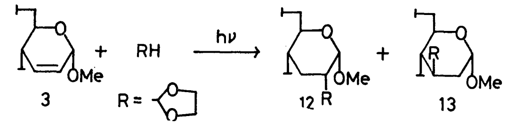


Table 2. NMR spectral data of **12** and **13**

Protons	**12**	Peotons	**13**
H-1	4.77	H-1	4.80
H-2	2.1	H-2a	1.68
H-3a	2.1	H-2e	1.96
H-3e	1.9	H-3	2.42
H-4	4.99	H-4	5.01
H-5	3.9	H-5	3.9
H-6	4.13	H-6	4.03
H-6′	4.22	H-6′	4.25
H-2′	4.97	H-3′	4.75
O-(CH$_2$)$_2$-O	3.8—4.1	O-(CH$_2$)$_2$-O	3.8—4.1
O-CH$_3$	3.40	O-CH$_3$	3.37
O-COCH$_3$	2.04, 2.08	O-COCH$_3$	2.04, 2.08
Coupling constants in Hz			
H-1—H-2	4.0	H-1—H-2a	3.3
H-2—H-2′	6.0	H-1—H-2e	1.5
H-3a—H-4	9.0	H-2a—H-2e	14.0
H-3e—H-4	5.3	H-2a—H-3	12.6
H-4—H-5	9.0	H-2e—H-3	4.3
H-5—H-6	3.5	H-3—H-3′	4.8
H-5—H-6′	5.2	H-3—H-4	10.5
H-6—H-6′	11.8	H-4—H-5	10.5
		H-5—H-6	5.5
		H-5—H-6′	2.8
		H-6—H-6′	12.5

These data were determined in CDCl$_3$ by the use of tetramethylsilane as the internal standard.

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5) Gas Chromatographic examination elucidated the relative ratio of the three products to be 1 : 2 : 1, and the major product to be 4,5,6,8-tetra-*O*-acetyl-3,7-anhydro-1-deoxy-2-*C*-methyl-D-*glycero*-D-*gulo*-octitol. Details with respect to these results will be published elsewhere.

6) It is natural and advantageous to irradiate the reaction mixture with a low pressure mercury lamp in the absence of acetone as the photosensitizer on account of the concomitant formation of the adduct with acetone, by which the yield of the expected product is directly affected, when the reaction was carried out under the irradiation of a high pressure mercury lamp in the presence of acetone. However, the irradiation of **1** or **2** in pure 1,3-dioxolane afforded no product and resulted in the complete recovery of the corresponding starting materials.

The irradiation of **3** afforded methyl 4,6-di-*O*-acetyl-2,3-dideoxy-2-*C*-(1,3-dioxolan-2-yl)-α-D-*erythro*-D-*glycero*-hexopyranoside (**12**) and methyl 4,6-di-*O*-acetyl-2,3-dideoxy-3-*C*-(1,3-dioxolan-2-yl)-α-D-*arabino*-hexopyranoside (**13**) in 39 and 39% yields respectively. The structural determination of **12** and **13** was accomplished by the use of their NMR spectral data (Table 2). In the spectrum of **12**, H-2, H-3a, and H-3e signals are observed at δ *ca.* 2.1 (multiplet), *ca.* 2.1 (multiplet), and *ca.* 1.9 (multiplet) ppm respectively, and $J_{1,2}$ is found to be 4.0 Hz. In the spectrum of **13**, on the other hand, H-2a, H-2e, and H-3 signals are observed at δ 1.68, 1.96, and 2.42 ppm respectively, and $J_{2a,3}$, $J_{2e,3}$, and $J_{3,4}$ are found to be 12.6, 4.3, and 10.5 Hz respectively. On the basis of this evidence, **12** and **13** were concluded to involve a 1,3-dioxolan-2-yl group at C-2 and C-3 respectively in equatorial orientations. It can thus be stated that this reaction affords the thermodynamically more stable stereoisomers selectively in a relative ratio of 1 : 1, since no product with an axial substituent is formed.

Incidentally, similar products could be obtained by carrying out the irradiation with a high-pressure mercury lamp in the presence of acetone as the photosensitizer. However, the reaction was inevitably accompanied by the formation of methyl 4,6-di-*O*-acetyl-2,3-dideoxy-2-*C*-(1-hydroxy-1-methylethyl)-α-D-*erythro*-D-*glycero*-hexopyranoside, which had previously been shown to be formed by the addition of the **8** resulting from acetone to **3**,[2d] in a 10% yield.

The irradiation of **4** with a low-pressure mercury lamp under the conditions employed for **3** was, on the other hand, found by tlc and glc to afford at least six products.

Among these products, only methyl 5-deoxy-2,3-*O*-isopropylidene-β-D-*ribo*-hex-dialdofuranoside 6-ethylene acetal (**14**) was isolated in a 10% yield from the reaction mixture. The structure of **14** was confirmed by its NMR spectral data (Table 3). Such a formation of several products in this case, in contrast with the cases of the other enoses employed in the present study, may be due to the high reactivity of the exocyclic double bond, as is generally accepted,[7] and also to a potential photoisomerization of the photoaddition product once formed.[8]

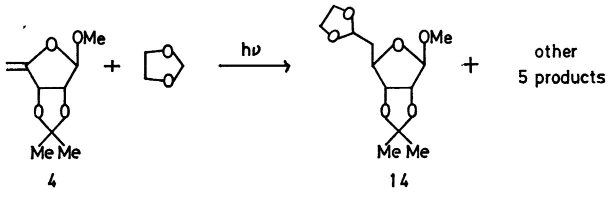
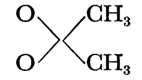


Table 3. NMR spectral data of **14**

Chemical shifts		Coupling constants	
Protons	δ value	Protons	Hz
H-1	4.86	H-1—H-2	0
H-2	4.54	H-2—H-3	6.0
H-3	4.66	H-3—H-4	3.5
H-4	4.11	H-4—H-5(5′)	7.0
H-5,5′	2.11	H-5(5′)—H-6	5.0
H-6	5.05		
O-$(CH_2)_2$-O	3.94[a]		
O-CH_3	3.31		
	1.32, 1.45		

These data were obtained in $CDCl_3$ by the use of tetramethylsilane as the internal standard.

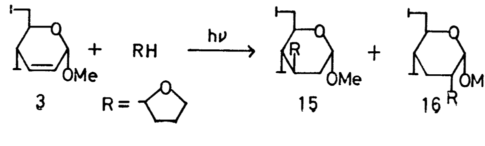
a) These signals appeared centering in the vicinity of this chemical shift.

The photochemical addition of 1,3-dioxolane to the enoses, as far as it has been examined, may be summarized as follows:

1) In the reaction of such enoses as **1**, the addition takes place regiospecifically at C-1 from both the α- and β-sides of the 1-enopyranosyl ring, thus giving the corresponding equimolar adducts, such as **5** and **6** in high yields in a relative ratio of 1 : 1. In the reaction of such enoses as **2**, which have a substituent at their C-2 position, on the other hand, the preferential formation of an isomer such as **11**, which is thermodynamically more stable than a configurational isomer such as **10**, is observed. 2) In the reaction of such 2-enoses as **3**, isomers with thermodynamically stable (*i. e.*, equatorial) substituents, such as **12** and **13**, are produced, although no regioselectivity is observed. 3) The reaction of 4-enoses involving an exocyclic double bond such as **4** proceeds with great ease in comparison with those of the other enoses, although such a reaction lacks regio- and stereoselectivity. 4) On the basis of the results obtained by the reaction of **2**, it can be considered that these reactions proceed in part at least by means of a *cis*-addition mechanism.

In addition to the photochemical addition reaction of 1,3-dioxolane, similar photochemical addition of tetrahydrofuran(THF) to enoses was investigated in view of the reactivity of 1,3-dioxolane, the location of the 2-yl radical of which is established by the adjacent two oxygen atoms.

The irradiation of **3** in THF by means of a low-pressure mercury lamp gave methyl 4,6-di-*O*-acetyl-2,3-dideoxy-3-*C*-(2-tetrahydrofuranyl)-α-D-*arabino*-hexopyranoside (**15**) and methyl 4,6-di-*O*-acetyl-2,3-dideoxy-2-*C*-(2-tetrahydrofuranyl)-α-D-*erythro*-D-*glycero*-hexopyranoside (**16**) in 15 and 32% yields respectively. In this case, 44% of the starting material was recovered. The structure of **15** and **16** were confirmed by com-



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[7] Exocyclic double bonds have generally accepted to have higher reactivities than endocyclic double bonds in the free radical addition reaction of thio radicals to double bonds; *cf.* M. Fukuyama, "Yuhriki-no-Kagaku (Chemistry of Free Radicals)," ed. by H. Sakurai and K. Tokumaru, Nanko-do, Tokyo (1967), p. 219.

[8] D. Elad and R. D. Youssefyeh, *Tetrahedron Lett.*, **1963**, 2189: in this paper, acetone-induced photoisomerization of 2-substituted 1,3-dioxolanes into the corresponding esters has been reported.

paring their NMR spectra with those of **13** and **12** respectively (*cf.* Table 1).

In the photochemical addition of **4** in place of **3**, the formation of at least five products and the recovery of no starting material were detected by tlc and glc, although their structures could not be determined. **1** was, moreover, recovered quantitatively by treating it under the same conditions. Furthermore, the irradiation of **2** in THF in the presence of acetone as the photosensitizer was carried out by means of a high-pressure mercury lamp to give a mixture of two products, **17a** and **17b**(1 : 1), in a 27% yield.[9] The NMR spectra of these products showed that all the acetyl groups are in an equatorial orientation, and the integration curve demonstrated that these are the corresponding equimolar adducts of **2** with THF, which may correspond to two of the three structures shown in Fig. 1, although their structures could not be confirmed. On the basis of these results, the order of the reactivity of the enoses to THF may be concluded to be (**4**>) **3**>**2**(>**1**).

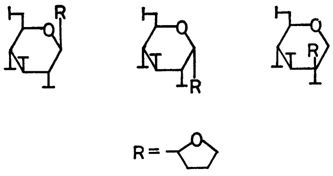

Fig. 1.

In contrast with the cyclic ethers described above, the reactivity of tetrahydropyran was found to be remarkably lower; it gave only a trace of products[10] in reactions with **2** and **3** respectively, and they were recovered almost quantitatively.

Moreover, an acyclic ether such as diethyl ether gave no product at all in spite of a variety of examinations with respect to the potential dependence on the concentration, the effect of the variation in the photosensitizer(such as acetone, 2-butanone, acetophenone, or benzophenone), and irradiation by means of a low-pressure mercury lamp or a high-pressure one in the presence of photosensitizers in reactions with the enoses.

It may thus be concluded with respect to the reactivity of the ethers employed herein that:

1,3-Dioxolane>THF>THP>Diethyl Ether

Experimental

The solvents used for the experiment were purified in the usual manner prior to use. Irradiations were carried out with a high-pressure mercury lamp (450 W) of Ushio Electric, Inc., in a Pyrex-glass tube at a distance of about 5 cm, or with a low-pressure mercury lamp (30 W) of Riko Kagaku Co., Ltd., in a quartz test tube, and with one (6 W) of Ushio Electric, Inc., under a nitrogen atmosphere at room temperature. The tlc's were carried out by the use of Wakogel B-5, and the solvent system of benzene–methanol (9 : 1 v/v) was used for the development. The NMR spectra were taken with a Varian HA-100 apparatus in deuterochloroform using tetramethylsilane as the internal standard. The glc data were obtained with a Hitachi K-53 model; Column: 10% SE-30 on Chromosorb W (60—80 mesh); carrier gas: nitrogen under 1.5 Atm unless otherwise noticed; oven temperature: 200 °C, and injection temperature: 300 °C. The mass spectra were taken with a Hitachi RMU 6E model spectrometer.

*4,5,7-Tri-*O*-acetyl-2,6-anhydro-3-deoxy-*D*-arabino-*L-glycero-*heptose Ethylene Acetal (**5**) and 4,5,7-Tri-*O*-acetyl-2,6-anhydro-3-deoxy-*D-arabino-D-glycero-*heptose Ethylene Acetal (**6**)*: A solution of 3,4,6-tri-*O*-acetyl-D-glucal (**1**) (1.00 g) in a solvent system composed of acetone (2 ml) and 1,3-dioxolane (10 ml) was irradiated by means of a high-pressure mercury lamp for 73 hr, after which the reaction mixture was concentrated *in vacuo*.

The residual sirup was chromatographed on a column of silica gel (Mallinckrodt Silica Gel, 100-mesh) by the use of a solvent system of benzene–acetone, whose relative content ratio was changed in turn to 99 : 1 (800 ml), 98 : 2 (800 ml). and 97 : 3 (800 ml) v/v for the elution. **5** (500 mg, 37%), **6** (500 mg, 37%), and 5,6,8-tri-*O*-acetyl-3,7-anhydro-1,4-dideoxy-2-*C*-methyl-D-*arabino*-D-*glycero*-octitol (**7**) (255 mg, 21%) were eluted out in turn separately. The retention volumes of **1**, **5**, **6**, and **7** in glc were 1, 4.4, 4.6, and 2.5 respectively. The specific rotations of these products were as follows; **5**: $[\alpha]_D^{22}$ +28.0 ° (*c* 1.0, Me_2CO), **6**: $[\alpha]_D^{22}$ +8.0° (*c* 1.0, Me_2CO). Found: C, 52.39 (**5**), and 52.08 (**6**); H, 6.71 (**5**) and 6.60 (**6**)%. Calcd for $C_{15}H_{22}O_9$: C, 52.02; H, 6.40%. The NMR data of **5** and **6** are demonstrated in Table 1.

*3,4,5,7-Tetra-*O*-acetyl-2,6-anhydro-*D-glycero-D-talo-*heptose Ethylene Acetal (**10**) and 3,4,5,7-Tetra-*O*-acetyl-2,6-anhydro-*D-glycero-D-gulo-*heptose Ethylene Acetal (**11**)*. A solution of 2,3,4,6-tetra-*O*-acetyl-2-hydroxy-D-glucal (**2**) (1.00 g) in a solvent system composed of acetone (2 ml) and 1,3-dioxolane (10 ml) was irradiated by means of a high-pressure mercury lamp for 54 hr, after which the reaction mixture was concentrated *in vacuo*. The resultant sirup was chromatographed on a column of silica gel by the use of a solvent system of benzene–acetone, whose relative content ratio was changed in turn to 96.5 : 3.5 (1000 ml), 96 : 4 (800 ml), 95 : 5 (800 ml), and acetone (100 ml) v/v, for the elution; this afforded **10** (210 mg, 17%), **11** (510 mg, 42%), and three by-products[5] (equimolar adducts of **2** with acetone, 225 mg, 19%). The retention volumes of **2**, **10**, **11**, and the by-products in glc were, respectively, 2.1, 7.7, 8.1, 3.7, 4.4, and 5.0. Mass spectrum of **11**: m/e=404 (M^+), 344[$(M-60)^+$], and 331 [$(M-73)^+$]. Specific rotations: **10**: $[\alpha]_D^{22}$ +22.3° (*c* 1.0, Me_2CO), **11**: $[\alpha]_D^{22}$ −2.0° (*c* 1.0, Me_2CO). Found: C, 50.52 (**10**) and 51.01 (**11**): H, 6.04 (**10**) and 6.04 (**11**)%. Calcd for $C_{17}H_{24}O_{11}$: C, 50.49; H, 5.98%. The NMR data of these products are shown in Table 1.

*Methyl 4,6-Di-*O*-acetyl-2,3-dideoxy-2-*C*-(1,3-dioxolan-2-yl)-α-*D-erythro-D-glycero-*hexopyranoside (**12**) and Methyl 4,6-Di-*O*-acetyl-2,3-dideoxy-3-*C*-(1,3-dioxolan-2-yl)-α-*D-arabino-*hexopyranoside (**13**)*. A) A solution of methyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (**3**) (1.00 g) in 1,3-dioxolane (25 ml) was irradiated by means of a low-pressure mercury lamp (30 W) for 115 hr, after which the reaction mixture was concentrated *in vacuo*. The residual sirup was chromatographed on a column of silica gel by the use of a solvent system of benzene–acetone, whose relative content ratio was changed in turn to 99 : 1 (1000 ml), 98 : 2 (500 ml), 97 : 3 (500 ml), 9 : 1 (200 ml) v/v, for the elution; this afforded **3** (115 mg, 12% recovery), **12** (510 mg, 39%),

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[9] Two peaks corresponding to **17a** and **17b** were detected in glc with retention volumes of 8.3 and 8.9, respectively, and their chromatographic separation has not yet been accomplished.

[10] The amounts of the corresponding products in the reaction with **2** or **3** were determined as less than 10% yields by means of glc.

and **13** (510 mg, 39%). The retention volumes of **3**, **12**, and **13** in glc were, respectively, 0.8, 2.2, and 2.2. The specific rotations of **12** and **13** were $[\alpha]_D^{22}$ +84.5° (*c* 1.0, Me_2CO) and $[\alpha]_D^{22}$ +55.7° (*c* 1.0, Me_2CO) respectively. Found: C, 52.62 (**12**) and 52.91 (**13**): H, 7.05 (**12**) and 7.12 (**13**)%. Calcd for $C_{14}H_{22}O_8$: C, 52.82; H, 6.97%. The NMR spectral data of these products are shown in Table 2. B) A similar treatment of **3** (1.00 g) in a solvent composed of 1,3-dioxolane (9 ml) and acetone (1 ml) under irradiation with a high-pressure mercury lamp (450 W) for 14 hr, and a similar chromatographic treatment of the sirup obtained by the concentration of the reaction mixture, afforded **12** (420 mg, 32%) and **13** (410 mg, 31%), in addition to methyl 4,6-di-*O*-acetyl-2,3-dideoxy-2-*C*-(1-hydroxy-1-methylethyl)-α-D-*erythro*-D-*glycero*-hexopyranoside[2d] (60 mg, 10%).

*Methyl 5-Deoxy-2,3-*O*-isopropylidene-β-*D-ribo-*hexo-dialdofuranoside 6-Ethylene Acetal (**14**).* A solution of methyl 5-deoxy-2,3-*O*-isopropylidene-*β*-D-*erythro*-pent-4-enofuranoside (**4**) (1.00 g) in 1,3-dioxolane (180 ml) was irradiated by means of a low-pressure mercury lamp (6 W) for 51 hr, after which the reaction mixture was concentrated *in vacuo*. The residual sirup was chromatographed on a column of silica gel by the use of a solvent system of benzene–acetone, whose relative content ratio was changed in turn to 99 : 1 (1000 ml), 98 : 2 (500 ml), and 97 : 3 (500 ml), for the elution, thus affording **14** (140 mg, 10%). Its retention volume in glc was 5.4 with reference to that of **4** (1.0) under 0.8 Atm of nitrogen gas. $[\alpha]_D^{22}$ −70.8° (*c* 1.0, Me_2CO). Found: C, 55.78; H, 7.53%. Calcd for $C_{12}H_{20}O_6$: C, 55.37; H, 7.75%. The NMR data of this product are shown in Table 3.

*Methyl 4,6-Di-*O*-acetyl-2,3-dideoxy-3-*C*-(2-tetrahydrofuranyl)-*α-D-arabino-*hexopyranoside (**15**) and Methyl 4,6-Di-*O*-acetyl-2,3-dideoxy-2-*C*-(2-tetrahydrofuranyl)-*α-D-erythro-D-glycero-*hexopyranoside (**16**).* A solution of **3** (0.500 g) in THF (25 ml) was irradiated by means of a low-pressure mercury lamp (30 W) for 210 hr, after which the reaction mixture was concentrated *in vacuo*. The residual sirup was chromatographed on a column of silica gel by the use of a solvent system of benzene–acetone (98 : 2 v/v, 1000 ml) for the elution, thus affording **3** (220 mg, 44% recovery), **15** (95 mg, 15%), and **16** (205 mg, 32%). The retention volumes of **15** and **16** in glc were 3.2 and 3.4 respectively. The specific rotations of **15** and **16** were as follows: $[\alpha]_D^{22}$ +78.5 (*c* 1.0, Me_2CO) and +66.1° (*c* 1.0, Me_2CO) respectively. The NMR spectral data of **15** and **16** are almost superimposable with those of **13** and **12** respectively, except that the singals of the tetrahydrofuranyl-ring protons are observed at δ *ca.* 1.8—2.0 (4H) and 3.8—4.0 (3H) ppm in both cases. Moreover, these were concluded, on the basis of the relative ratios of the integration curves of their NMR spectra, to be equimolar adducts of **2** with THF.

*Irradiation of 2,3,4,6-Tetra-*O*-acetyl-2-hydroxy-*D*-glucal (**2**) in Tetrahydrofuran–Acetone with a High-pressure Mercury Lamp.* A solution of **2** (1.00 g) in a solvent system composed of tetrahydrofuran (22.5 ml) and acetone (2.5 ml) was irradiated with a high-pressure mercury lamp for 150 hr, after which the reaction mixture was concentrated *in vacuo*. The residual sirup was chromatographed on a column of silica gel by the use of the solvent system of benzene–acetone, whose relative content ratio was changed in turn to 97 : 3 (1500 ml) and 91 : 9 (1000 ml) v/v for the elution, thus affording **2** (110 mg, 11% recovery), a mixture of the corresponding equimolar adducts **17a** and **17b** (330 mg, 27%), and the same three by-products (equimolar adducts of **2** with acetone,[5] 460 mg, 40%) as have been described in the second example of this section.

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