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Note

Photochemical addition of 1,3-dioxolane and of 2-propanol to D-xylal diacetate*

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Recently, we reported the photochemical addition-reaction of 1,3-dioxolane to 3,4,6-tri-*O*-acetyl-D-glucal, 2-acetoxy-3,4,6-tri-*O*-acetyl-D-glucal, and methyl 2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside[1], and of 2-propanol and of acetone to 3,4,6-tri-*O*-acetyl-D-glucal[2]; these reactions were found to be induced with high stereoselectivity and to give products in good yields. We now report the photochemical addition-reactions of 3,4-di-*O*-acetyl-D-xylal (**1**), which was used as a typical species of 1,5-anhydro-pent-1-enitol derivative.

Irradiation of **1** in 1:50 acetone–1,3-dioxolane with a high-pressure mercury-lamp for 85 h at room temperature, followed by chromatographic separation of the resulting mixture on a column of silica gel, gave the ethylene acetal (**2**) of 4,5-di-*O*-acetyl-2,6-anhydro-3-deoxy-*aldehydo*-D-*xylo*-hexose aldehydrol (29% yield) and the ethylene acetal (**3**) of 4,5-di-*O*-acetyl-2,6-anhydro-3-deoxy-*aldehydo*-D-*lyxo*-hexose aldehydrol (10% yield), together with a 1:1 mixture of **2** and **3** (2% yield), and 5,6-di-*O*-acetyl-3,7-anhydro-1,4-dideoxy-2-*C*-methyl-D-*xylo*-heptitol (**4**) (9% yield); 33% of **1** was recovered unchanged. Compound **4** may be regarded as arising from the addition of the (1-hydroxy-1-methylethyl) radical to C-1 of **1**. Moreover, irradiation of **1** in 1:50 acetone–2-propanol, followed by chromatographic separation, afforded **4** (57% yield) and a mixture of **4** and its isomer (**5**) (8% yield), and 18% of **1** was recovered unchanged. The structures of **2**, **3**, and **4** were respectively confirmed by the n.m.r. spectroscopic evidence shown in Table I. The 3-deoxy-D-*xylo* configuration of **2** was assigned from the data for H-2 (δ 3.49; $J_{2,3a}$ 11.7, $J_{2,3e}$ 2.3 Hz), H-3*a* (δ 1.62; $J_{3a,4}$ 11.3 Hz), H-3*e* (δ 2.22), and the acetyl methyl signals that appeared in the equatorial region[3] (δ 2.02 and 2.03). The 3-deoxy-D-*lyxo* configuration of **3** was shown by the data for H-2 (δ 3.65; $J_{2,3a}$ 13.5 Hz), H-3*a* and H-3*e* (δ 1.8–2.2), and the acetyl methyl signal that appeared in the axial region[3] (δ 2.10), which shows

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*Part XII of a series: Synthetic Studies of Carbohydrate Derivatives by Photochemical Reactions. For Part XI, see ref. 4.

TABLE I

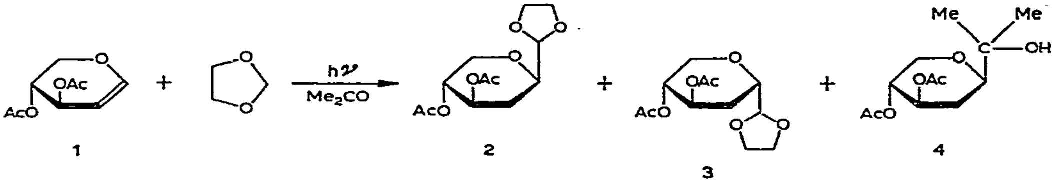
N.M.R.-SPECTRAL DATA FOR COMPOUNDS **2**, **3**, AND **4**[a]

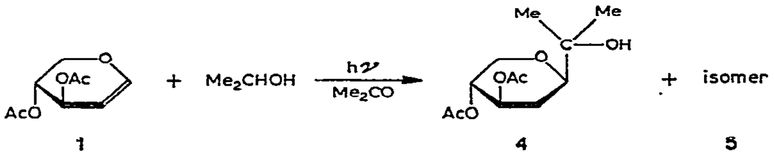
2	**3**	*Assignment*	**4**	*Assignment*
p.p.m.	*p.p.m.*		*p.p.m.*	
4.85 (d)	4.85 (d)	H-1		
3.49 (ddd)	3.65 (ddd)	H-2	3.24 (dd)	H-3
1.62 (td)	1.8 –2.2 (m)	H-3*a*	1.55 (q)	H-4*a*
2.22 (ddd)		H-3*e*	2.17 (ddd)	H-4*e*
5.04 (m)	4.97–5.17 (m)	H-4	5.04 (td)	H-5
4.92 (m)	4.60–4.72 (m)	H-5	4.86 (td)	H-6
3.25 (t)	3.8 –4.0 (m)	H-6*a*	3.23 (t)	H-7*a*
4.14 (dd)	4.17 (dd)	H-6*e*	4.13 (dd)	H-7*e*
3.94 (bs)	3.96 (bs)	$-CH_2CH_2-$	1.13 (s), 1.15 (s)	$C-CH_3$
2.02 (s)	2.10 (s)	$OCOCH_3$	2.06 (s)	OH
2.03 (s)			2.02 (s)	$OCOCH_3$

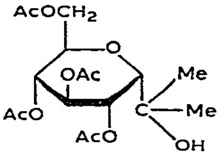
Coupling constants	**2**	**3**	*Coupling constants*	**4**
	(Hz)	*(Hz)*		*(Hz)*
$J_{1,2}$	4.2	4.2		
$J_{2,3a}$	11.7	13.5	$J_{3,4a}$	11.7
$J_{2,3e}$	2.3	7.5	$J_{3,4e}$	2.3
$J_{3a,3e}$	12.8	—	$J_{4a,4e}$	12.8
$J_{3a,4}$	11.3	—	$J_{4a,5}$	11.0
$J_{3e,4}$	5.0	3.0	$J_{4e,5}$	5.0
$J_{4,5}$	10.2	—	$J_{5,6}$	11.0
$J_{5,6a}$	10.2	—	$J_{6,7a}$	11.0
$J_{5,6e}$	5.0	3.0	$J_{6,7e}$	5.0
$J_{6a,6e}$	11.3	10.2	$J_{7a,7e}$	11.0

[a] These data were obtained for solutions in deuteriochloroform, with tetramethylsilane as the internal standard.

that **3** is in the $^1C_4$(D) conformation. Interestingly, the specific rotations of **2** and **3** are −31.4° and −31.2°, respectively; these values are probably attributable to the conformational aspect. The $^1C_4$(D) conformation of **3** may arise from the bulkiness of the 1,3-dioxolan-2-yl group introduced; a similar phenomenon has been observed for 4,5,6,8-tetra-*O*-acetyl-3,7-anhydro-1-deoxy-2-*C*-methyl-D-*glycero*-D-*ido*-octitol (**6**), which has the bulky (1-hydroxy-1-methylethyl) group at C-3, and the equilibrium between the $^4C_1$ and $^1C_4$ conformations of which was assumed to tend toward the latter[4], *i.e.*, its three acetoxyl and one acetoxymethyl groups are axially oriented and its (1-hydroxy-1-methylethyl) group is equatorially oriented. Moreover, the ethylene acetal (**7**) of 4,5,7-tri-*O*-acetyl-2,6-anhydro-3-deoxy-*aldehydo*-D-*manno*-heptose aldehydrol, obtained by the reaction of 3,4,6-tri-*O*-acetyl-D-glucal with 1,3-dioxolane, has been confirmed to be in the $^4C_1$(D) conformation[1b]; interestingly, there is a distinct







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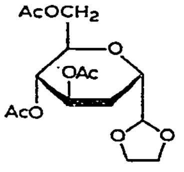

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difference between the bulkiness of the 1,3-dioxolan-2-yl and (1-hydroxy-1-methylethyl) groups, as a consequence of which, **3** assumes the $^1C_4$ conformation, whereas **7**, which cannot do that, is in the $^4C_1$(D) conformation. The 1,4-dideoxy-D-*xylo* configuration of **4** was assigned from the n.m.r. data: for H-3 (δ 3.24; $J_{3,4a}$ 11.7, $J_{3,4e}$ 2.3 Hz), H-4*a* (δ 1.55), and H-4*e* (δ 2.17), which are similar to those of **2**. A structure could not be assigned to **5**, as it was obtained as only trace (in admixture with **4**). However, it may be assumed that **5** is the 3-epimer of **4**, *viz.*, 5,6-di-*O*-acetyl-3,7-anhydro-1,4-dideoxy-2-*C*-methyl-D-*lyxo*-heptitol (having the same configuration as **3**) on the basis of its chromatographic behavior (very similar to that of **4**), the tendency of the (1-hydroxy-1-methylethyl) radical to attack the electron-deficient site of unsaturated sugar derivatives[2], and its n.m.r.-spectral pattern (which is similar to that of **3**).

The 1-enitol **1** was even less reactive than 3,4,6-tri-*O*-acetyl-D-glucal, which had been found to be the least reactive among several unsaturated sugar derivatives[1b], by monitoring the reactions by t.l.c. and g.l.c. The photochemical additions described herein may be assumed to take place by attack of 1,3-dioxolan-2-yl or (1-hydroxy-1-methylethyl) radicals at the electron-deficient site, to give intermediary radicals whose stereochemical stability presumably fixes the stereochemistry of favored products.

In the present work, the ratio (1:50) of acetone to 1,3-dioxolane or to 2-propanol was considerably decreased as compared with the ratios of 1:9 or 1:5 used earlier (see refs. 1 and 2). Application of this smaller proportion of acetone should be disadvantageous, because acetone behaves as a photosensitizer or hydrogen abstractor, or both, in the reaction[2]. However, side reactions of acetone (to give, for example, the corresponding pinacol derivatives) were successfully prevented by use of such a small proportion of acetone. The reaction of such less-reactive 1-enitol species as **1** tends to enhance the formation of by-products, so that isolation of the main product may have been facilitated by utilization of the smaller proportion of acetone*.

Furthermore, the cycloaddition of acetone to **1** in 9:1 acetone–2-propanol under irradiation with a high-pressure mercury-lamp gave a product in good yield.

EXPERIMENTAL

General. — Solvents were purified before use. Solvent ratios are all v/v. 1,3-Dioxolane was prepared from ethylene glycol and paraformaldehyde by use of concentrated sulfuric acid as the catalyst[5], and 3,4-di-*O*-acetyl-D-xylal (**1**) was synthesized according to the Weygand method[6]. Irradiations were conducted externally in a Pyrex-glass tube at a distance of ~5 cm from a 450-W, high-pressure, mercury lamp (Ushio Electric Inc.), the lamp and tubes being cooled with running water during the irradiation. The reaction mixture was placed in the tube, which was stoppered after passing argon gas for 30 min. T.l.c. was performed on Merck TLC aluminum sheets coated with silica gel 60 F_{254}, with 9:1 benzene–acetone as the developer. N.m.r. spectra were recorded with a Varian EM-390 instrument for solutions in deuteriochloroform, with tetramethylsilane as the internal standard, and the spectra obtained were analyzed by the double-resonance or the INDOR technique. G.l.c. was performed with a Hitachi Model K-53 instrument on a column of 10% of SE-30 on Chromosorb-W (60–80 mesh), with nitrogen at 1.0 atm. as the carrier gas; oven temperature, 185°, and injection temperature, 300°. Retention times are given with reference to that of **1** as unity. Specific rotations were determined with a Carl Zeiss Photoelectric Precision Polarimeter (±0.005°), and $[\alpha]_D$ was calculated from α_{546} and α_{578} by the Drude equation.

Ethylene acetal (**2**) *of 4,5-di-*O*-acetyl-2,6-anhydro-3-deoxy-*D-xylo-*hexose aldehydrol and ethylene acetal* (**3**) *of 4,5-di-*O*-acetyl-2,6-anhydro-3-deoxy-*D-lyxo-*hexose aldehydrol.* — A solution of **1** (400 mg) in acetone (0.2 mL)–1,3-dioxolane (10 mL) in a tube was irradiated for 85 h. The solutions in five tubes were combined, and evaporated *in vacuo* to a syrup; chromatographic separation on a column (3 × 30 cm) of silica gel (Wakogel C-300) by successive use of 99:1 (1 L), 49:1 (2.5 L), and 19:1 benzene–acetone (500 mL) as eluants gave, in turn, **1** (649 mg, 33% recovery), **2** (800 mg, 29% yield), 1:1 mixture of **2** plus **3** (50 mg, 2% yield), **3** (276 mg, 10% yield), and **4** (245 mg, 9% yield). R_F values of **2**, **3**, **1**, and **4** in t.l.c.: 0.66, 0.60, 0.88, and 0.44, respectively. Retention times of **2** and **3** (relative to **1**) in g.l.c.: 6.5 and 5.5, respectively. N.m.r.-spectral data are summarized in Table I. The syrupy **2** crystallized on being allowed to stand; m.p. 80.5–81.5°, $[\alpha]_D^{22}$ of **2**, −31.2° (*c* 1.0, acetone); $[\alpha]_D^{22}$ of **3**, −31.4° (*c* 1.0, acetone).

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[*] It has also been confirmed that, in the reaction of more-reactive, unsaturated sugar derivatives, it is advantageous to use a solvent system containing only a small proportion of acetone (*e.g.*, 1 part in 50), although it is then necessary to prolong the time of reaction.

Anal. Calc. for $C_{12}H_{18}O_7$: C, 52.55; H, 6.62. Found: for **2**, C, 52.76; H, 6.65; for **3**, C, 52.60; H, 6.64.

*5,6-Di-O-acetyl-3,7-anhydro-1,4-dideoxy-2-C-methyl-*D-xylo-*heptitol* (**4**). — A solution of **1** (400 mg) in acetone (0.2 mL)–2-propanol (10 mL) was irradiated as just described, and the resulting solutions, in five tubes, were combined, and evaporated *in vacuo*. The syrup thus obtained was chromatographed on a column of silica gel by use, in turn, of 999:1 (800 mL), 997:3 (800 mL), 199:1 (1 L), and 124:1 (2 L) benzene–methanol as eluants, to give **4** (1.474 g, 57%) and a 1:7 mixture of **4** and **5** (213 mg, 8%); the starting material **1** was recovered in 18% yield (362 mg). The R_F values of **4** and **5** in t.l.c. were both 0.44; the retention times of **4** and **5** in g.l.c. (relative to **1**) were 2.8 and 2.5, respectively. Compound **4** had $[\alpha]_D^{22}$ −43.8° (*c* 1.0, acetone).

Anal. Calc. for $C_{12}H_{20}O_6$: C, 55.37; H, 7.75. Found: C, 55.78; H, 7.96.

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