The Photochemistry of Carbohydrate Derivatives. Part IV.[1] Photochemical Rearrangement of 4,6-*O*-*o*-Nitrobenzylideneglycopyranosides

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Methanolic solutions of methyl 4,6-*O*-*o*-nitrobenzylideneglycopyranosides rearranged upon irradiation with u.v. light into mixtures of the corresponding amorphous glycopyranoside 4- and 6-*o*-nitrosobenzoates. Trifluoroperacetic acid converts these photoproducts into the corresponding 4- and 6-*o*-nitrobenzoates, which have been separated. The conditions used for this oxidation have been shown not to cause migration of the nitrobenzoyl groups.

The 2,3-di-*O*-acetyl derivatives [(12) and (13)] of methyl α- and β-D-galactoside gave the corresponding galactoside 4- and 6-nitrobenzoates [(14) and (15), and (16) and (17)], both in *ca.* 7 : 3 ratios whereas the diacetates of methyl α- and β-D-glucoside [(1) and (2)] and α-D-mannoside (18) gave 4- and 6-nitrobenzoates [(6) and (7), (8) and (9), and (19) and (20)], all in *ca.* 3 : 7 ratios. Similar rearrangements were observed with methyl 4,6-*O*-*o*-nitrobenzylidene-α-D-glucosides in which the 2- and 3-positions were either unprotected (4), tosylated (5), or methylated (3), and also with the corresponding 2,3-anhydro-α-D-alloside derivative (26). Methyl 2,3-di-*O*-acetyl-4,6-*O*-(2,4-dinitrobenzylidene)-α-D-glucoside (24) gave upon similar treatment the corresponding 4- and 6-dinitrobenzoates also in a *ca.* 3 : 7 ratio. Methyl 2,3 : 4,6-bis-(*O*-*o*-nitrobenzylidene)-α-D-mannoside (29) gave methyl mannopyranoside 2,6-bis-(*o*-nitrobenzoate) (31) and 2,4-bis-(*o*-nitrobenzoate) (30) as the major products.

In the preceding paper [1] we reported the photochemistry of 2,3- and 3,4-*O*-*o*-nitrobenzylidene pyranosides. We now describe the photochemistry of 4,6-*O*-*o*-nitrobenzylidenehexopyranosides.

U.v. irradiation ($\lambda > 290$ nm) of methanolic solutions of methyl 2,3-di-*O*-acetyl-4,6-*O*-*o*-nitrobenzylidene-D-glycopyranosides rapidly gave quantitative yields of compounds that were assumed to be methyl 2,3-di-*O*-acetyl-D-hexopyranoside nitrosobenzoates from their i.r. spectra and by analogy with the results of earlier studies.[2,3] Attempts to raise the m.p.s of these materials by fractional crystallisation were without success. This failure was attributed to the tendency of nitroso-compounds to dimerise.[4] Oxidation of these crude nitrosobenzoates with trifluoroperacetic acid gave a product containing two compounds, which in most cases were separated. These were characterised as methyl di-*O*-acetyl-D-hexopyranoside nitrobenzoates from elemental analyses, and i.r. and n.m.r. spectra. In particular all the n.m.r. spectra showed signals arising from four aromatic protons, one exchangeable hydroxy-proton, and three methyl groups (two from the acetoxy-residues and one from the aglycone). There were also

[1] Part III, P. M. Collins and N. N. Oparaeche, preceding paper.

[2] I. Tanasescu, *Bull. Soc. Sci. Cluj.*, 1924, **2**, 111 (*Chem. Abs.*, 1925, **19**, 2932); I. Tanasescu, A. Otea, *Studio Univ. Babes-Bolyai, Ser. Chem.*, 1972, **17**, 113; E. Bamberger and F. Elger, *Annalen*, 1909, **370**, 319.

[3] G. Ciamician and P. Silber, *Ber.*, 1901, **34**, 2040.

[4] P. A. S. Smith, 'Open Chain Nitrogen Compounds,' Benjamin, New York, 1966, vol. 2, p. 356.

signals for seven hexosyl protons, which in many cases were completely analysed by first-order methods as recorded in Table 1. The splitting patterns yielded vicinal coupling constants which revealed [5] that the transformations of all these derivatives had occurred

side (1) [6] gave two nitrosobenzoates which upon oxidation gave the isomeric nitrobenzoates (6) and (7). These were shown by h.p.l.c. to be present in a ratio 34 : 66, which agreed with the estimate made from the intensity of their t.l.c. spots at R_F 0.5 and 0.63. The isomer

TABLE 1

N.m.r. parameters (δ values; J in Hz) for methyl *O*-acetyl-D-hexopyranoside *o*-nitrobenzoates in $CDCl_3$ [a]

Compound	H-1	H-2	H-3	H-4	H-5	H-6	H-6′	OMe	Blocking groups	OH
(6) [b]	4.95—5.05 (d) $J_{1,2}$ 3.5	5.85—5.05 (q) $J_{2,3}$ 10.5	5.35 (t) $J_{3,2}$ 9.0 $J_{3,4}$ 9.0	5.65 (m) $J_{4,5}$ 9.0	3.84—4.1 (m)	3.7—3.9 (m)		3.42 (s)	2.07 (s)	8.6—8.9
(7) [b]	4.87 (d) $J_{1,2}$ 3.5	4.76 (q) $J_{2,3}$ 10.5	5.23 (q) $J_{3,4}$ 9.0	3.55 (oct) [d] $J_{4,5}$ 10.0	3.86 (oct) $J_{5,6'}$ 2.0	4.40 (q) $J_{6,5}$ 5.3	4.62 (q) $J_{6',6}$ 12.0	3.34 (s)	2.05 (s)	5.76 (d) [e] J 5.8
(10) [c,f]	4.69 (d) $J_{1,2}$ 3.5	3.6—4.1		5.43 (t) $J_{4,5}$ 9.5 $J_{4,3}$ 9.5		2.9—4.1		3.50 (s)	3.21 (s) 3.13 (s)	2.2—2.5
(11) [c,f]	4.69 (d) $J_{1,2}$ 3.5	3.80—4.20				4.7—4.9		3.63 (s)	3.26 (s) 3.23 (s)	
(14) [b]	5.03 (d) $J_{1,2}$ 3.0	5.22 (q) $J_{2,3}$ 11.0	5.53 (q) $J_{3,4}$ 2.5	5.80 (q) $J_{4,5}$ *ca.* 1	4.1—4.4 (m)	3.5—4.0		3.45 (s)	2.08 (s) 2.12 (s)	2.6—2.8
(15) [b]	4.80 (d)	5.05—5.20 (m)		3.9—4.2 (m)		4.35 (q) $J_{6,6'}$ 11.0 $J_{6,5}$ 3.0	4.48 (q) $J_{6',5}$ 3.5	3.26 (s)	2.02 (s) 2.00 (s)	
(16) [c]	5.1—5.3		4.4—4.6	5.71 (q) J 1 and 1.5		3.6—4.0		3.50 (s)	2.07 (s)	2.5—2.8
(17) [b]	4.45 (d) $J_{1,2}$ 7.5	5.25 (q) $J_{2,3}$ 10.0	4.98 (q) $J_{3,4}$ 3.0	4.11 (q) $J_{4,5}$ 1.0	3.99 (sex) $J_{5,6}$ 6.5	4.55 (q) $J_{6,6'}$ 11.5	4.66 (q) $J_{6',5}$ 5.5	3.53 (s)	2.10 (s) 2.05 (s)	2.3—2.7
(19) [b]	4.82 (d) $J_{1,2}$ 1.8	5.41 (q) $J_{2,3}$ 3.0	5.5—5.7			3.8—4.1		3.46 (s)	2.10 (s) 2.22 (s)	2.2—2.6
(20) [c]	4.5—4.8	5.0—5.4		3.7—4.1		4.5—4.8		3.39 (s)	2.07 (s) 2.10 (s)	2.8—3.1
(30) [b]	5.00 (d) $J_{1,2}$ 1.5	5.50 (q)	4.40 (q) $J_{3,2}$ 4.0 $J_{3,4}$ 10.0	5.44 (m)		3.7—4.1		3.46 (s)		3.2—3.4
(31) [b]	4.90 (d) $J_{1,2}$ *ca.* 1	5.44 (q) $J_{2,3}$ *ca.* 2		3.6—4.4		4.6—4.8		3.38 (s)		3.2—3.6

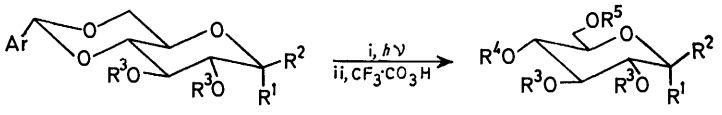
[a] There were signals for aromatic protons in all spectra. [b] 100 MHz. [c] 60 MHz. [d] Irradiation causes quartet at 5.23 to collapse to a doublet (J 10.5) and doublet at 5.76 to collapse to a singlet. [e] Irradiation causes octet at 3.55 to collapse to a quartet (J 10 and 9). [f] Solvent C_6D_6.

with retention of configuration at the pyranosyl ring carbon atoms.

The isomeric ratios of nitrobenzoates in the crude products were estimated from the intensities of product spots on t.l.c. and the intensities of the two aglycone

distribution was confirmed by the intensities of the n.m.r. methoxy-signals and by quantitative separation on column chromatography of a small sample of the crude product.

The major component, which crystallised from the



(1) R^1 = OMe, R^2 = H, R^3 = Ac
(2) R^1 = H, R^2 = OMe, R^3 = Ac
(3) R^1 = OMe, R^2 = H, R^3 = Me
(4) R^1 = OMe, R^2 = H, R^3 = H
(5) R^1 = OMe, R^2 = H, R^3 = Ts
(6) R^1 = OMe, R^2 = H, R^3 = Ac, R^4 = ArCO, R^5 = H
(7) R^1 = OMe, R^2 = H, R^3 = Ac, R^4 = H, R^5 = ArCO
(8) R^1 = H, R^2 = OMe, R^3 = Ac, R^4 = ArCO, R^5 = H
(9) R^1 = H, R^2 = OMe, R^3 = Ac, R^4 = H, R^5 = ArCO
(10) R^1 = OMe, R^2 = H, R^3 = Me, R^4 = ArCO, R^5 = H
(11) R^1 = OMe, R^2 = H, R^3 = Me, R^4 = H, R^5 = ArCO

methoxy-signals in the n.m.r. spectra. In some experiments the ratios of isomeric products were confirmed by high pressure liquid chromatographic (h.p.l.c.) analysis and by quantitative column chromatographic separation of the two components.

After irradiation with u.v. light, the α-D-glucopyrano-

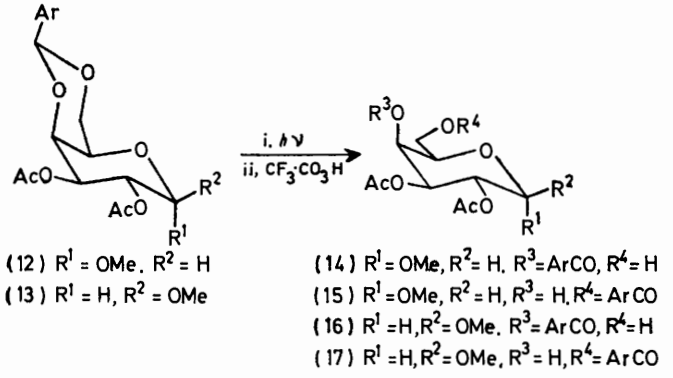
crude reaction mixture in 48% yield, was shown to be the 6-nitrobenzoate (7) because the n.m.r. signals for the C-6 methylene protons were at a relatively low-field

[5] M. Karplus, *J. Amer. Chem. Soc.*, 1963, **85**, 2870.
[6] P. M. Collins and N. N. Oparaeche, *Carbohydrate Res.*, 1974, **33**, 35.

position (δ 4.62 and 4.40) compared with the chemical shift of these protons in the starting material. Also the signal for H-4 was at relatively high field. These results suggested that O-6 was esterified and that O-4 was not, a conclusion confirmed by double-resonance studies which showed that H-4 was coupled to the 4-OH (see Table 1).

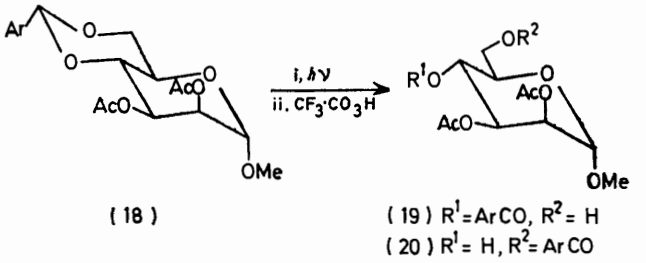
The minor product was freed from (7) by chromatography and since it was also a methyl di-*O*-acetyl-D-hexopyranoside nitrobenzoate, it was assigned the alternative 4-nitrobenzoate structure (6). This was confirmed by the n.m.r. signals (see Table 1) of the C-6 methylene protons, which were at relatively high field, and by the low-field position of the H-4 signal.

Both these products gave methyl α-D-glucopyranoside upon deacylation, thus confirming that the hexose skeleton had not altered during the transformation.



(12) R^1 = OMe, R^2 = H
(13) R^1 = H, R^2 = OMe

(14) R^1 = OMe, R^2 = H, R^3 = ArCO, R^4 = H
(15) R^1 = OMe, R^2 = H, R^3 = H, R^4 = ArCO
(16) R^1 = H, R^2 = OMe, R^3 = ArCO, R^4 = H
(17) R^1 = H, R^2 = OMe, R^3 = H, R^4 = ArCO



(18)

(19) R^1 = ArCO, R^2 = H
(20) R^1 = H, R^2 = ArCO

The 4- and 6-nitrobenzoates (16) and (17), which were obtained by similar treatment of the methyl β-D-galactopyranoside derivative (13), had t.l.c. R_F values of 0.5 and 0.6, and h.p.l.c. t_R values of 13 and 6.4 min. The intensities of the peaks showed that the mixture comprised 66% of (16) and 34% of (17), and this was confirmed by the n.m.r. spectrum. The minor isomer (17) could be crystallised directly from the crude product in low yield (10%); alternatively both (16) and (17) could be obtained pure in 48 and 17% yield, respectively, by column chromatography. These structural assignments were made from the relative chemical shifts of H-4 and H-6 and -6′ for each isomer (see Table 1).

[7] P. de Mayo and S. T. Reid, *Quart. Rev.*, 1961, **15**, 414; D. C. Neckers, 'Mechanistic Organic Photochemistry,' Reinhold, New York, 1967, p. 207.

[8] I. Tanasescu and E. Macouski, *Bull. Soc. chim. France*, 1929, **45**, 1022.

The mixture obtained when the photoproduct from the α-D-galactoside derivative (12) was oxidised contained two compounds in the ratio 3 : 7. The minor component, R_F 0.64, crystallised in low yield leaving a syrup containing almost exclusively the major compound, R_F 0.45. The chemical shifts of H-4 and H-6 and -6′ (see Table 1) showed that the minor product was the 6-nitrobenzoate (15) and the major one the 4-nitrobenzoate (14).

The two isomeric products present in the ratio 3 : 7 in the oxidised photolysate of the mannoside derivative (18) were separated chromatographically. The major component, R_F 0.4, isolated in 53% yield, was the 6-nitrobenzoate (20); the minor one, isolated in 28% yield, R_F 0.3, was the 4-nitrobenzoate (19). Although the n.m.r. spectrum of neither isomer was completely analysed, sufficient information was obtained (see Table 1) to permit structural assignments.

The β-D-glucopyranoside (2) when subjected to this reaction sequence also produced two nitrobenzoates, but on this occasion an attempt was not made to isolate them. However the more mobile component gave a t.l.c. spot twice as intense as that produced by the slower moving component. T.l.c. properties of the products formed from the four other glycoside derivatives [(1), (12), (13), and (18)] indicated that all the 6-nitrobenzoates had greater mobilities than the 4-nitrobenzoates; a reasonable observation, since compounds possessing free primary hydroxy-groups should be less sterically hindered, and therefore more strongly adsorbed by the silica gel, than those possessing a free secondary hydroxy-group. Consequently it has been assumed that compound (2) afforded 4- and 6-nitrobenzoates (8) and (9) in a *ca.* 3 : 7 ratio.

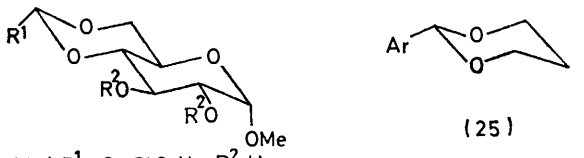
Acetyl groups are not the only substituents stable to the conditions used in this reaction sequence. Successful transformations with compounds (3), (5), and (26) show that methoxy-, tosyl, and anhydro-groups are also unaffected. Therefore the method offers a route to partially protected hexopyranosides possessing one hydroxy-group free at C-6 or C-4. The photorearrangement can also be effected with compound (4) in which the 2- and 3-hydroxy-groups are unprotected.

The reactions probably occur by the mechanism [7] depicted in the Scheme, which is the same as that proposed for the dioxolan ring openings.[1] There are some experimental facts to support this proposal. For example, the photolytic stability of the *O-o*-chlorobenzylidene derivative (21) and the *O-o*-methoxybenzylidene derivative (22) implicates the nitro-group in these reactions,[7,8] and the importance of the intramolecular hydrogen atom abstraction [9] is demonstrated by the failure of the *p*-nitrobenzylidene derivative (23) to react (see also refs. 2, 7, and 10) compared, for

[9] G. Wettermark, E. Black, and L. Digliotti, *J. Amer. Chem. Soc.*, 1962, **84**, 3658; H. Morrison and B. M. Migdalof, *J. Org. Chem.*, 1965, **30**, 3996.

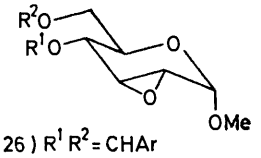
[10] J. A. Barltrop, P. J. Plant, and P. Schofield, *Chem. Comm.*, 1966, 822; A. Patchornik, B. Amit, and R. B. Woodward, *J. Amer. Chem. Soc.*, 1970, **92**, 6333; I. Tanasescu, *Bull. Soc. chim. France*, 1926, **38**, 1443.

example, with the 2,4-dinitrobenzylidene derivative (24) which rearranges readily into 4-*O*- and 6-*O*-(4-nitro-2-nitrosobenzoyl)glucosides (also in a *ca.* 3 : 7 ratio).

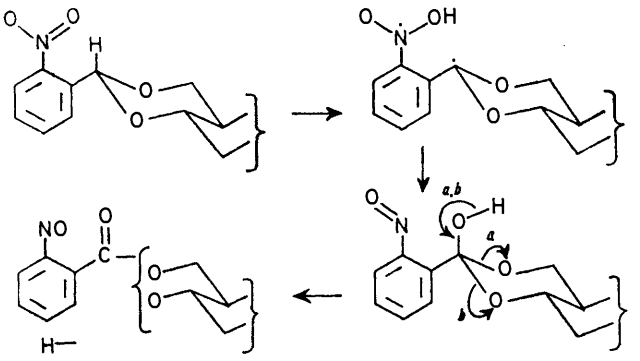


(21) R^1 = 2-ClC_6H_4, R^2 = H
(22) R^1 = 2-$MeO{\cdot}C_6H_4$, R^2 = H
(23) R^1 = 4-$O_2N{\cdot}C_6H_4$, R^2 = H
(24) R^1 = 2,4-$(NO_2)_2C_6H_3$, R^2 = Ac

(25)



(26) R^1R^2 = CHAr
(27) R^1 = OH, R^2 = COAr
(28) R^1 = COAr, R^2 = H



SCHEME

The intermediacy of orthoacids in this mechanistic scheme is speculative, since attempts to trap them with diazomethane in irradiations of compounds (3) and (25) carried out at −180 and −50 °C failed. However their involvement is suggested, since they would readily breakdown into primary and secondary esters [11] with retention of configuration at C-4 as is found in all experiments (see also refs. 7 and 10). The direction of ring opening, which is probably determined at this stage since compounds (6) and (7) did not isomerise even in the acid medium used for the oxidation, showed no apparent dependence upon changes in configuration at carbon atoms remote from the sites of reaction. The C-2 epimeric glycosides (1) and (18) gave 4- and 6-nitrobenzoates in similar proportions (see Table 2) and the ratios of the esters formed from the anomeric glucosides (1) and (2) did not differ significantly. The anomeric pair of galactosides (12) and (13) also gave 4- and 6-nitrobenzoates in similar ratios.

Although the configuration at C-1 and C-2 did not influence the proportions of products, a change in configuration at C-4 might, by analogy with the dioxolan derivatives, be expected to show an effect. A relationship between the ring openings in the latter class of compounds and the orientation of the oxygen atoms has been put forward by King and Allbutt [12] in terms of steric and stereoelectronic effects, but application of this theory to these dioxan derivatives reveals that the ring could open equally well in either direction, since the equatorial lone pair orbitals on both oxygen atoms of the dioxan ring could participate in ring opening without incurring any unfavourable deformation in the chair conformation. However there does appear to be a slight dependence upon the orientation of O-4 in some derivatives. For example, the galactosides (12) and (13), both of which adopt the $^4C_1$ conformation and therefore possess an axially disposed oxygen atom at C-4, gave preponderantly 4-nitrobenzoate derivatives, whereas the three glucosides (1), (2), and (24) and the mannoside (18), which have their oxygen atoms at C-4 equatorially orientated, gave predominantly products in which the primary position is esterified (see Table 2). Great significance cannot be placed upon this observation since the isomer distribution was influenced by blocking groups, as illustrated by the di-*O*-methyl-D-glucoside (3), which gave the secondary and primary esters (10) and (11) in a proportion similar to the 7 : 3 ratio. Because of the divergent results obtained with the *gluco*-derivatives, the effect of neighbouring groups is being studied further.

Methyl 2,3:4,6-bis-*O*-*o*-nitrobenzylidene-α-D-mannopyranoside (29) has also been studied, but since both the *O*-*o*-nitrobenzylidene residues can rearrange in this derivative a complex mixture of products could be formed. However chromatography of the oxidised photolysates afforded only two products in substantial

TABLE 2

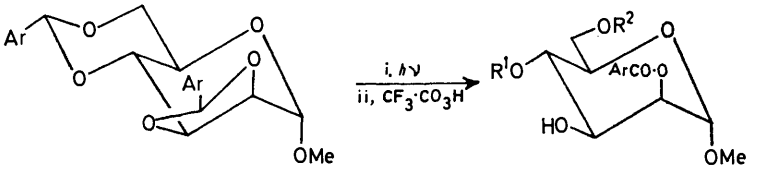
Proportions (%) of primary (1y) and secondary (2y) *o*-nitrobenzoates formed from *O*-*o*-nitrobenzylidene derivatives

O-*o*-Nitrobenzylidene derivative	Glucoside (1)	Glucoside (2)	Glucoside (24)	Galactoside (12)	Galactoside (13)	Mannoside (18)	Glucoside (3)
2y ester	(6) 34 [a]	(8) 30 [b]	(6) [c] 25	(14) 70	(16) 66 [a]	(19) 30	(10) 63 [a]
1y ester	(7) 66 [a]	(9) 70 [b]	(7) [c] 75	(15) 30	(17) 34 [a]	(20) 70	(11) 37 [a]

[a] Confirmed by h.p.l.c. [b] Approximate estimation from t.l.c. [c] Where Ar = 2,4-$(NO_2)_2C_6H_3$.

[11] R. H. De Wolfe, 'Carboxylic Ortho Acid Derivatives,' Academic Press, New York, 1970, p. 139; E. H. Cordes, *Progr. Phys. Org. Chem.*, 1967, **4**, 1.
[12] J. F. King and A. D. Albutt, *Canad. J. Chem.*, 1970, **48**, 1754.

amounts. These were bis-*O*-nitrobenzoyl derivatives and they were isolated in 32 and 45% yields. Examination of the hexosyl proton signals in their n.m.r. spectra showed that the minor component [see (30) in Table 1] exhibited two signals downfield from that of H-1 at δ 5.50 and 5.44 (H-2 and H-4, respectively). The signals for H-6 and -6′ appeared at relatively high field (δ 3.7—4.1). On the other hand, in the spectrum of the major compound [see (31) in Table 1] there was only one signal at lower field than the resonance for H-1. This appeared at δ 5.44 and was assignable to



(29)

(30) R^1 = ArCO, R^2 = H

(31) R^1 = H, R^2 = ArCO

H-2. The signals from H-6 and -6′ were at relatively low field. Therefore the former derivative (30) was the 2,4-diester and the latter derivative (31) the 2,6-diester. The formation of only two isomers in significant amounts both esterified at C-2 is consistent with the rearrangement we observed [1] with methyl 2,3-*O*-*o*-nitrobenzylidene-α-L-rhamnopyranoside, which gave almost exclusively the 2-ester. Our result with compound (29) differs from that of Tanasescu,[13] in which a compound stated to be (29) (see ref. 6) was claimed to undergo rearrangement only in the 4,6-*O*-*o*-nitrobenzylidene residue to give one product.

EXPERIMENTAL

The general procedures were the same as those employed in the preceding paper.[1] Solvents used for chromatography were ethyl acetate–benzene mixtures (*A*, 1 : 3; *B*, 1 : 2; *C*, 1 : 1; *D*, 3 : 2; and *E*, 8 : 3). Unless stated otherwise all the oxidised photoproducts exhibited $\nu_{max.}$ *ca.* 3 500 and 1 530 cm^{-1} (OH and $ArNO_2$, respectively). High pressure liquid chromatography (h.p.l.c.) was carried out with a Waters instrument model ALC 202, on 1 ft × 0.375 in of Micro Porasil (10 μ), using a u.v. detector (254 nm) and, unless stated otherwise, butan-2-ol–iso-octane (1 : 4) at a flow rate of 2 ml min^{-1}.

Sequential U.v. Irradiation and Oxidation of Methyl 4,6-O-o-*Nitrobenzylideneglycopyranosides*.—Unless stated otherwise compounds dissolved in methanol were irradiated under nitrogen, through Pyrex as previously described,[1] either (*a*) in a conventional photolysis well for solutions whose volumes were 100 ml or greater, or (*b*) in tubes situated *ca.* 25 mm from the centre of the lamp, for solutions with volumes less than 50 ml.

(i) *The* 2,3-*di*-O-*acetyl*-α-D-*glucoside* (1). Compound (1), as a pale yellow 2.4% solution (100 ml), was irradiated for 0.5 h. Evaporation of the green solution formed gave a pale yellow solid (2.1 g, 89%), which after several attempted recrystallisations from benzene gave an amorphous mixture of nitrosobenzoates (1.9 g), m.p. 91—100°, $\nu_{max.}$ 3 450 cm^{-1} (OH). The n.m.r. spectrum showed signals for the protons of the protecting groups but the signals from the hexosyl protons were poorly resolved (Found: C, 52.3; H, 5.6. Calc. for $C_{18}H_{21}NO_{10}$: C, 52.6; H, 5.2%).

The nitrosobenzoates (1.9 g) were oxidised with trifluoroperacetic acid to yield a gum (2.0 g, 98%) which contained two products, R_F 0.63 and 0.51 (solvent *D*), present in the ratio *ca.* 7 : 3, as shown by the intensity of the methoxy-signals in the n.m.r. spectrum. H.p.l.c. showed two peaks, t_R 5.9 and 9.4 min, with areas 66 and 34%, respectively. An ethanolic solution of this crude material yielded crystals (1.2 g, 48%) which were supplemented by a further 0.1 g obtained by preparative t.l.c. of the mother liquor, and these were shown to be the 6-*nitrobenzoate* (7) (1.3 g), R_F 0.63, m.p. 129—130° (from ethanol), $[\alpha]_D$ +47° (*c* 0.6 in MeOH) (n.m.r. parameters in Table 1) (Found: C, 50.4; H, 5.0; N, 3.4. $C_{18}H_{21}NO_{11}$ requires C, 50.6; H, 4.9; N 3.3%).

The chromatographed mother liquor, which was homogeneous on t.l.c. gave, after evaporation, the syrupy 4-*nitrobenzoate* (6), $[\alpha]_D$ +79° (*c* 0.7 in MeOH) (n.m.r. parameters in Table 1) (Found: N, 3.2%).

A sample of the crude product (0.62 g) was chromatographically separated on a column into (7) (0.34 g) and (6) (0.16 g).

(ii) *The* 2,3-*di*-O-*acetyl*-β-D-*glucoside* (2). The β-D-glucoside (2) was irradiated as a 0.5% solution (35 ml) for 45 min. The product isolated upon concentration was oxidised in the usual way to give, in 96% yield, a syrupy mixture of nitrobenzoates assumed to be compounds (8) and (9), R_F 0.60 and 0.69 (solvent *D*), and relative intensities *ca.* 3 : 7. Separation of these products was not attempted nor was further characterisation.

(iii) *The* 2,3-*di*-O-*acetyl*-α-D-*galactoside* (12). Compound (12), as a 0.5% solution (25 ml) gave, after 0.75 h irradiation and the usual oxidation and work-up, a gum (0.51 g, 95%). This comprised two products, R_F 0.45 and 0.64 (solvent *C*), in the ratio 7 : 3 as estimated by n.m.r. spectroscopy. An ethanolic solution of the mixture gave, in low yield, the 6-*nitrobenzoate* (15), R_F 0.64, m.p. 80—82° (n.m.r. parameters in Table 1) (Found: C, 50.1; H, 4.9; N, 3.3. $C_{18}H_{21}NO_{11}$ requires C, 50.6; H, 4.9; N, 3.3%). The residual gum contained mainly the 4-nitrobenzoate (14) (n.m.r. parameters in Table 1).

A sample of the crude product (0.50 g) was separated on a short column into (14) (0.25 g) and (15) (0.10 g).

(iv) *The* 2,3-*di*-O-*acetyl*-β-D-*galactoside* (13). When a 2% solution of compound (13) in methanol (85 ml) and dichloromethane (15 ml) was treated as described in (i) it gave two nitrobenzoates (1.8 g, 92%), with h.p.l.c. t_R values of 6.4 and 13.0 min and peak areas in the ratio

[13] I. Tanasescu and M. Ionescu, *Bull. Soc. chim. France*, 1936, 1511; I. Tanasescu and E. Craciunescu, *ibid.*, p. 581.

34 : 66. The n.m.r. spectrum gave a similar ratio of 3 : 7 for the two products. The minor product crystallised from ethanol (0.2 g). Preparative t.l.c. (solvent *E*) of the mother liquor gave more of the same crystals (0.16 g) which were found to be the 6-*nitrobenzoate* (17) (total 0.36 g, 17%), R_F 0.6, m.p. 137—138°, $[\alpha]_D$ +27° (*c* 0.6 in MeOH) (n.m.r. parameters in Table 1) (Found: C, 50.5; H, 5.1; N, 3.6. $C_{18}H_{21}NO_{11}$ requires C, 50.6; H, 4.9; N, 3.3%). The other product (R_F 0.5) obtained by chromatography was the 4-*nitrobenzoate* (16) (1.0 g, 48%) (n.m.r. parameters in Table 1).

Column chromatography of 1.0 g of the crude product gave 0.50 and 0.23 g of the 4- and 6-nitrobenzoates (16) and (17) respectively.

(v) *The* 2,3-*di*-O-*acetyl*-α-D-*mannoside* (18). The usual treatment of 50 ml of a 0.48% solution of the mannoside (18) gave a syrup (0.25 g, 98%) comprising two nitrobenzoates in the ratio *ca.* 3 : 7 as indicated by the methoxy-signals in the n.m.r. spectrum. The mixture was fractionated by p.l.c. (solvent *A*) into the 6-*nitrobenzoate* (20) (0.13 g, 53%), R_F 0.4, $[\alpha]_D$ +47° (*c* 0.2 in $CHCl_3$) (n.m.r. spectrum in Table 1) (Found: C, 50.3; H, 5.1; N, 3.3. $C_{18}H_{21}NO_{11}$ requires C, 50.6; H, 4.9; N, 3.3%), and the 4-*nitrobenzoate* (19) (0.07 g, 28%), R_F 0.3, $[\alpha]_D$ +24° (*c* 0.7 in $CHCl_3$) (n.m.r. spectrum in Table 1) (Found: C, 50.7; H, 5.2; N, 3.1%).

The crude product (0.25 g) was chromatographed on a small column to give unchanged (18) (0.03 g) and compounds (20) (0.13 g) and (19) (0.07 g).

(vi) *The* 2,3-*di*-O-*methyl*-α-D-*glucoside* (3). When 100 ml of a 1% solution of compound (3) was treated in the usual way it gave a crude product (1.0 g, 98%). H.p.l.c. revealed two peaks with t_R 8.75 and 6.4 min in the ratio 63 : 37. Fractional crystallisation from ethanol yielded the 4-*nitrobenzoate* (10) (0.43 g, 40%), R_F 0.55, m.p. 125—126°, $[\alpha]_D$ +65° (*c* 0.5 in $CHCl_3$) (see Table 1 for n.m.r. parameters) (Found: C, 51.4; H, 5.3; N, 3.8. $C_{16}H_{21}NO_9$ requires C, 51.8; H, 5.7; N, 3.8%).

The syrupy mother liquor (0.53 g) was shown by t.l.c. and n.m.r. spectroscopy to be composed of 4 parts of (10) and 6 parts of the 6-nitrobenzoate (11), R_F 0.50 (see Table 1 for n.m.r. parameters).

(vii) *The* 2,3-*di*-O-p-*tolylsulphonyl*-α-D-*glucoside* (5). When 100 ml of a 0.5% solution of compound (5) was treated as described in (i), a gummy mixture of nitrobenzoates was produced (0.54 g, 96%), $\nu_{max.}$ 1 740 cm^{-1} (ester), $[\alpha]_D$ +20° (*c* 0.7 in $CHCl_3$) (Found: C, 51.2; H, 4.8. $C_{28}H_{29}NO_{13}S_2$ requires C, 51.6; H, 4.5%). The poorly resolved 100 MHz n.m.r. spectrum ($CDCl_3$) showed only δ 2.32 (s, $MeC_6H_4SO_3$), 3.14 (s, OMe), 7.0—7.7 (m, 12 aromatic protons), and 3.34—5.20 (complex m, 7 hexosyl protons).

(viii) *The* 2,3-*anhydro*-α-D-*alloside* (26). When a 0.2% solution (50 ml) of the anhydride (26) was irradiated for 50 min and the photoproduct oxidised in the usual way, a mixture of nitrobenzoates (27) and (28) was formed with $[\alpha]_D$ +62° (*c* 0.7), δ ($CDCl_3$) 5.42 (m, *ca.* 30% intensity of H-4 of the 4-nitrobenzoate), 3.2—5.2 (m, hexosyl protons), 7.4br (s, OMe), and 7.5—8.1 (m, aromatic). The two components were not separated.

(ix) *The* 2,3:4,6-*bis*-O-*o*-*nitrobenzylidene*-α-D-*mannoside* (29). When a 1% solution of methyl 2,3:4,6-bis-*O*-*o*-nitrobenzylidene-α-D-mannoside (29) in a mixture of methanol (85 ml) and dichloromethane (15 ml) was irradiated for 40 min and then worked-up in the usual way a mixture of two nitrobenzoates (1.2 g, 96%) was obtained. P.l.c. in solvent *B* gave the 2,6-*bis*-O-*o*-*nitrobenzoyl derivative* (31) (0.42 g, 45%), R_F 0.17, $[\alpha]_D$ +20° (*c* 0.2) (n.m.r. parameters in Table 1) (Found: C, 52.0; H, 4.4; N, 5.5. $C_{21}H_{20}N_2O_{12}$ requires C, 51.2; H, 4.1; N, 5.7%), and the 2,4-*bis*-O-*o*-*nitrobenzoylmannoside* (30), R_F 0.23 (0.3 g, 32%), $[\alpha]_D$ −16° (*c* 0.2) (n.m.r. parameters in Table 1) (Found: C, 51.0; H, 4.5; N, 5.4%).

Sequential U.v. Irradiation and Oxidation of Methyl 2,3-*Di*-O-*acetyl*-4,6-O-(2,4-*dinitrobenzylidene*)-α-D-*glucopyranoside* (24).—Compound (24) (2.0 g) in methanol (100 ml) was irradiated for 2 h and the photoproduct oxidised in the usual way to give a syrup (1.9 g) from which unchanged (24) (0.2 g) crystallised. The residual syrup contained the 4- and 6-(2,4-dinitrobenzoates) of methyl 2,3-di-*O*-acetyl-α-D-glucopyranoside. This material gave an elongated spot on t.l.c. in solvents *B*—*D* and an n.m.r. spectrum which exhibited resolved signals for the blocking groups but not for the seven hexosyl protons. H.p.l.c. [iso-octane–chloroform (2 : 3) at 2 ml min^{-1}] revealed two components with t_R 9.9 and 11.6 min in the ratio 25 : 75, whereas in iso-octane–propan-2-ol (4 : 1) the t_R values were 13.2 and 10.7 min, respectively.

U.v. Irradiation of the 4,6-O-o-*Chloro-*, o-*Methoxy-, and* p-*Nitro-benzylidene Derivatives of Methyl* 2,3-*Di*-O-*acetyl*-α-D-*glucopyranoside* (21)—(23).—Compounds (21)—(23) as 0.5% solutions were irradiated in the usual way for 5 h, but t.l.c. analysis revealed that they had undergone no change. This was confirmed by recovery of the starting materials in high yields.

U.v. Irradiation of Methyl 4,6-O-o-*Nitrobenzylidene*-α-D-*glucopyranoside* (4).—Compound (4) (1.0 g) as a 1% solution in methanol was irradiated for 20 min to give, after concentration, a mixture of methyl α-D-glucopyranoside 4- and 6-nitrosobenzoates (0.9 g), $\nu_{max.}$ 1 740 and 3 450 cm^{-1} (ester CO and OH). The n.m.r. spectrum in D_2O showed signals for the protons in the protecting groups but the signals for the hexosyl and hydroxy-protons were unresolved (Found: C, 51.3; H, 5.2; N, 4.3. Calc. for $C_{14}H_{17}NO_8$: C, 51.4; H, 5.2; N, 4.3%).

Attempts to Trap Orthoacid Intermediates.—(a) Methyl 2,3-di-*O*-methyl-4,6-*O*-*o*-nitrobenzylidene-α-D-glucopyranoside (3) (100 mg) in 5 : 5 : 2 diethyl ether–isopentane–ethanol (EPA) at *ca.* −180 °C was irradiated for 4 h, and then ethereal diazomethane was added. The mixture was warmed to room temperature and the solvent evaporated off, but this yielded only unchanged (3).

(*b*) The experiment was repeated at −50 °C; the product had $\nu_{max.}$ 1 520, 1 750, and 3 450 cm^{-1} (ArNO, C=O, OH), and singlets in the n.m.r. spectrum at δ 3.53, 3.60, 3.46, 3.63, and 3.70, all arising from methoxy-groups. The first three were due to compound (3) and the last three presumably to the methyl di-*O*-methylglucoside nitrosobenzoates (10) and (11) (where Ar = C_6H_4NO).

(*c*) 2-*o*-Nitrophenyl-1,3-dioxan (25) (50 mg) was treated as described in (*b*). This gave a solid (48 mg) which was partially soluble in $CDCl_3$. The soluble fraction was unchanged (25); the insoluble portion was preponderantly propane-1,3-diol 1-nitrosobenzoate, $\nu_{max.}$ 1 525, 1 700, and 3 470 cm^{-1} (ArNO, CO, and OH), δ [$(CD_3)_2SO$] 4.28 (q, ^4J 5.5 Hz, H-1 and -1′), 4.75 (m, H-2 and -2′), and 3.35br (s exchangeable with D_2O,OH) (no MeO signal).

Methyl 4,6-O-o-*Nitrobenzylidene*-2,3-*di*-O-p-*tolylsulphonyl*-α-D-*glucopyranoside* (5).—Methyl 4,6-*O*-*o*-nitrobenzylidene-α-D-glucopyranoside (3 g) and toluene-*p*-sulphonyl chloride

(8 g) were dissolved in pyridine (25 ml) and heated at 100 °C for 2.5 h. The usual work-up gave *compound* (5) (5.4 g, 90%), m.p. 164—166° (from ethanol–dichloromethane), $[\alpha]_D$ +67° (*c* 0.2), $\nu_{max.}$ 1 530 cm^{-1} ($ArNO_2$), δ ($CDCl_3$) 4.98 (d, $J_{1,2}$ 3.5 Hz), 4.41 (q, $J_{2,3}$ 9.5 Hz), 5.14 (t, $J_{3,4}$ 10.0 Hz), 3.48—4.3 (m, H-4, -5, -6, and -6′), 5.99 (s, ArC*H*), 2.25 and 2.42 (2s, 2 × $MeC_6H_4{\cdot}SO_3$), 3.38 (s, OMe), and 6.9—8.0 (m, 12 aromatic protons) (Found: C, 53.2; H, 4.6; N, 2.4; S, 10.0. $C_{28}H_{29}NO_{12}S_2$ requires C, 52.9; H, 4.6; N, 2.2; S, 10.1%).

Methyl 2,3-*Anhydro*-4,6-O-o-*nitrobenzylidene*-α-D-*allopyranoside* (26).—The glucoside ditosylate (5) (1.5 g) was treated with sodium methoxide (0.3 g) in dichloromethane (15 ml) and methanol (10 ml) for 5 days at 0 °C followed by 2 days at 20 °C. The usual work-up gave the *anhydride* (26) (0.74 g, 98%), m.p. 200—201° (from ethanol–dichloromethane), $[\alpha]_D$ +169° (*c* 0.2), $\nu_{max.}$ 1 530 cm^{-1} ($ArNO_2$), δ ($CDCl_3$) 4.95 (t, H-1, *J* 1.5 and 1.0 Hz), 3.5—4.5 (m, H-2, -3, -4, -5, -6, and -6′), 6.3 (s, ArC*H*), 3.54 (s, OMe), and 7.5—8.2 (m, C_6H_4) (Found: C, 54.2; H, 4.9; N, 4.7. $C_{14}H_{15}NO_7$ requires C, 54.4; H, 4.9; N, 4.5%).

Methyl 4,6-O-o-*Chlorobenzylidene*-α-D-*glucopyranoside* (21).—Methyl α-D-glucopyranoside (3.5 g) was vigorously stirred at 20 °C with *o*-chlorobenzaldehyde (10 ml) and sulphuric acid (2 ml) for 40 min. The usual work-up gave *compound* (21) (4 g, 72%), m.p. 175—176°, $[\alpha]_D$ +40° (*c* 1.0) (Found: C, 52.7; H, 5.4; Cl, 11.0. $C_{14}H_{17}ClO_6$ requires C, 53.1; H, 5.4; Cl, 11.2%).

Methyl 4,6-O-p-*Nitrobenzylidene*-α-D-*glucopyranoside* (23).—Compound (23) was prepared by the same method in 82% yield; m.p. 201—202°, $[\alpha]_D$ +8° (*c* 1.0) (Found: C, 51.5; H, 5.1; N, 4.3. $C_{14}H_{17}NO_8$ requires C, 51.4; H, 5.2; N, 4.3%).

Methyl 4,6-O-o-*Methoxybenzylidene*-α-D-*glucopyranoside* (22).—Compound (22) was prepared in the usual way in 96% yield; m.p. 187—189°, $[\alpha]_D$ +48° (*c* 0.2) (Found: C, 56.9; H, 6.1. $C_{15}H_{20}O_7$ requires C, 57.7; H, 6.4%).

Attempted Isomerisation of the 6- *and* 4-O-*Nitrobenzoates* (7) *and* (6).—A pure sample of (7) (100 mg) and a sample of (6) contaminated with 20% of (7) (100 mg) were separately treated with trifluoroperacetic acid in dichloromethane for 2 h. The h.p.l.c. traces of the recovered samples (*ca.* 90 mg) were identical with those of the starting materials.

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