The Photochemistry of Carbohydrate Derivatives. Part III.[1] Photochemical Rearrangements of 2,3- and 3,4-*O*-*o*-Nitrobenzylideneglycopyranosides

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When irradiated with u.v. light, methanolic solutions of fully protected 2,3- and 3,4-*O*-*o*-nitrobenzylideneglycopyranosides rearrange to give the corresponding glycoside *o*-nitrosobenzoates. Oxidation of these products with trifluoroperacetic acid gives glycoside *o*-nitrobenzoates. Since each of these transformations gives almost exclusively one isomer in high yield, the reactions constitute a good synthesis of partially protected pyranose derivatives.

The 2,3-*O*-*o*-nitrobenzylidene derivatives [(1) and (7)] of methyl 4-*O*-acetyl-α-L-rhamnoside and methyl 4,6-di-*O*-methyl-β-D-alloside gave respectively the 2- and the 3-*o*-nitrobenzoates [(3) and (9)]. The 3,4-*O*-*o*-nitrobenzylidene derivatives (10) and (16) of methyl 2-*O*-acetyl-α-L-fucoside and methyl 2-*O*-acetyl-β-L-arabinoside gave the 4-*O*-*o*-nitrobenzoyl derivatives (12) and (18), and the corresponding derivative (13) of 1,6-anhydro-2-*O*-mesyl-β-L-galactose gave the 3-*O*-*o*-nitrobenzoyl derivative (15). In all the reactions the minor positional isomer constituted less than 5% of the total product. The 3-*O*-*o*-nitrobenzoyl-rhamnoside (5) and -arabinoside (20) were the only ones detectable by n.m.r. spectroscopy.

Oxidation of the *o*-nitrobenzoates (3) and (18) with ruthenium tetraoxide afforded methyl 4-*O*-acetyl-6-deoxy-2-*O*-*o*-nitrobenzoyl-α-L-*arabino*-hexopyranoside-3-ulose (6) and methyl 2-*O*-acetyl-4-*O*-*o*-nitrobenzoyl-β-L-*threo*-pentopyranoside-3-ulose (21), respectively.

THERE is a need in synthetic carbohydrate chemistry for protecting groups which are stable to a wide variety of reagents but which can be removed under mild conditions in the presence of other functional groups. Light-sensitive blocking groups offer great potential in this respect, but few reports have appeared [2-4] since Tanasescu and his co-workers [5] commenced their pioneering work in which they extended the photochemical reactions of *o*-nitrobenzaldehyde.[6,7] They irradiated *o*-nitrobenzylidene polyol derivatives and showed, for example, that the ethylene glycol derivative gave 2-hydroxyethyl *o*-nitrosobenzoate.[8]

Their later work [9-11] with the corresponding sugar derivatives was complicated for several reasons. The derivatives studied were bis- or tris-*O*-*o*-nitrobenzylidene compounds and consequently the structures were sometimes uncertain.[10] The nitroso-photoproducts they obtained were not easy to handle, and the stereochemistry of the products was often difficult to determine. All these problems were acentuated by the lack of good separatory methods and spectroscopic techniques available at the time the work was done. Their studies with compounds which were thought to be 2,3: 4,6-bis-*O*-*o*-nitrobenzylidene derivatives of the glycosides of D-glucose, D-galactose, and D-mannose also suffered similar drawbacks.[10] This problem was recently discussed by us in connection with the structure these authors proposed for the last-mentioned derivative.[12]

Prompted by our interest in the application of photochemical methods to synthetic carbohydrate chemistry [1,13] we have undertaken a study of the photorearrangement of several new mono-*O*-*o*-nitrobenzylideneglycopyranosides.[14] The compounds discussed here contain a 2-*o*-nitrophenyl-1,3-dioxolan system and those reported in the following paper possess a 2-*o*-nitrophenyl-1,3-dioxan system.

RESULTS AND DISCUSSION

Irradiation of a mixture of the *endo*- and *exo*-forms of methyl 6-deoxy-2,3-*O*-*o*-nitrobenzylidene-α-L-mannoside 4-acetate [(1*en*) and (1*ex*)] [12] as a *ca.* 1% solution in methanol with light ($\lambda > 290$ nm) from a 450 W mercury arc afforded, after evaporation, a quantitative yield of a pale yellow-green amorphous powder. This compound, which was assumed to be a hydroxy-nitrosobenzoate by analogy with the results of earlier workers [5-7] and from its $\nu_{max.}$ values (1 510 and 3 450 cm^{-1}), was difficult to characterise, probably owing to the tendency of nitroso-compounds to dimerise.[15] Consequently it was oxidised with trifluoroperacetic acid in dichloromethane at 0 °C to a readily crystallised compound in 95% overall yield. This product had i.r. absorption bands corresponding to ester, hydroxy-, and aromatic nitro-groups and an

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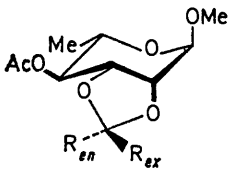
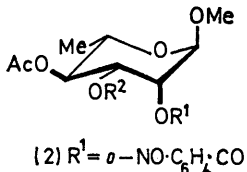
elemental analysis consistent with it being a methyl 4-*O*-acetyl-6-deoxyhexopyranoside nitrobenzoate. The 6-deoxy-α-L-*manno*-structure could be assigned since



(1*en*) R_{en} = *o*-$NO_2C_6H_4$, R_{ex} = H

(1*ex*) R_{en} = H, R_{ex} = *o*-$NO_2C_6H_4$

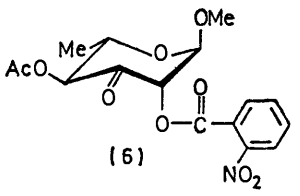


(2) R^1 = *o*-$NO{\cdot}C_6H_4{\cdot}CO$, R^2 = H

(3) R^1 = *o*-$NO_2C_6H_4{\cdot}CO$, R^2 = H

(4) R^1 = H, R^2 = *o*-$NO{\cdot}C_6H_4{\cdot}CO$

(5) R^1 = H, R^2 = *o*-$NO_2C_6H_4{\cdot}CO$



(6)

upon deacylation it afforded methyl α-L-rhamnopyranoside. The n.m.r. spectrum confirmed the gross structure, exhibiting signals for four aromatic protons, three methyl groups (arising from the aglycone, the acetate, and the C-5 methyl group), a hydroxy-group, and five ring hydrogen atoms. These ring proton resonances were analysed as follows. The signal at δ 4.92 was readily assigned to the anomeric proton because it was the only signal at the correct chemical shift that was a doublet. Furthermore $J_{1,2}$ (1.3 Hz) was acceptable for equatorial protons at C-1 and C-2 on a pyranoid ring. The mutual splitting patterns of the remaining protons then permitted assignments as shown in the Table. The couplings $J_{1,2}$ 1.3, $J_{2,3}$ 3.5, $J_{3,4}$ 10.0, and $J_{4,5}$ 10.0 Hz are in agreement with the α-L-rhamnopyranoside structure in the $^1C_4$ conformation. The low-field chemical shifts of H-2 and H-4 (δ 5.60 and 5.17) in comparison with that of H-3 (δ 4.25) show that the acyl groups are attached to O-2 and O-4. Therefore this product must be the 4-*O*-acetyl-2-*o*-nitrobenzoyl derivative (3). This was corroborated by oxidising compound (3) with ruthenium tetraoxide to the pyranosidulose (6), the n.m.r. spectrum of which showed signals assignable to H-2 and -4 as doublets, thus indicating that the free carbonyl group was at C-3. The pure *endo*- and *exo*-rhamnoside derivatives (1*en*) and (1*ex*) [12] gave the same products when similarly irradiated and oxidised.

The presence of the 3-*O*-*o*-nitrobenzoyl isomer (5) in the peroxy-acid-oxidised photoproduct was indicated by the n.m.r. spectrum of the mother liquor which remained after 63% of crystalline (3) had been removed. The spectrum revealed signals that could be assigned to all the protons of compound (5) (see Table). Particularly significant were the chemical shifts of H-2 and -3 *vis-à-vis* those of the corresponding protons in compound (3). The differences in chemical shift clearly indicated that in compound (5) the hydroxy-group at C-3 was esterified whereas that at C-2 was not. It was estimated, from the intensities of the signals for the two isomers, that prior to isomer enrichment the oxidised photolysate contained *ca.* 95% of the 2-*o*-nitrobenzoate (3) and 5% of the 3-*o*-nitrobenzoate (5).

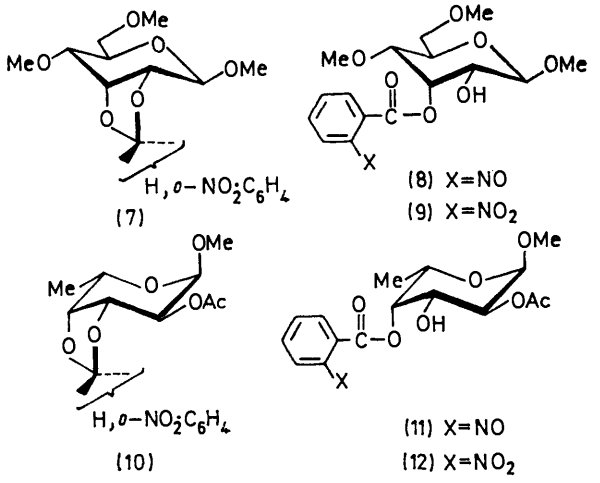
Another 2,3-*O*-*o*-nitrobenzylidene derivative (7) [12] which was irradiated was prepared from methyl 4,6-di-*O*-methyl-β-D-allopyranoside. Oxidation of the photoproduct gave crystalline material in 93% yield, the n.m.r. spectrum of which (see Table) showed that one isomer (9) comprised more than 95% of the product. As expected for a di-*O*-methyl derivative of a pyranoside monoester only two of the hexose proton resonances were at low field, *i.e.* δ 4.65 and 6.00, and thus clearly resolved. The signal at higher field was readily assigned

N.m.r. (100 MHz) parameters (δ values; J in Hz) of pyranoside *o*-nitrobenzoates in perdeuteriobenzene

Compound	H-1	H-2	H-3	H-4	H-5	H-6 and -6′ or H-5′	OMe(s)	$MeCO_2$(s)	OH
(3)	4.92 (d) $J_{1,2}$ 1.3	5.60 (q) $J_{2,3}$ 3.5	4.25 (q) $J_{3,4}$ 10.0	5.17 (t) $J_{4,5}$ 10.0	3.78 (oct) $J_{5,6}$ 6.0	1.26 (d) $J_{6Me,5}$ 6.0	3.06	1.84	2.7br (s)
(5)	4.62 (d) $J_{1,2}$ 1.3	4.32 (m) Narrow	5.67 (q) $J_{3,2}$ 3.5	5.48 (t) $J_{4,3}$ 10.0 $J_{4,5}$ 10.0	3.6—4.0	1.30 (d)	3.10	1.90	2.7br (s)
(9)	4.65 (d) $J_{1,2}$ 7.5	3.8—4.1 region	6.0br (t) $J_{3,2}$ {3.0 $J_{3,4}$ {3.5	3.84—4.1 region	3.45—3.7 (3H)		3.19 3.22 3.39 (3 × OMe)		
(12)	4.90 (d) $J_{1,2}$ 3.5	5.33 (q) $J_{2,3}$ 10.3	4.29 (q) $J_{3,4}$ 3.5	5.50 (q) $J_{4,5}$ 1.0	3.72 (m) $J_{5,6}$ 6.5	1.26 (d) $J_{6Me,5}$ 6.5	3.00	1.79	
(15) [a]	4.55 (d) $J_{1,2}$ 1.5	5.50 (t) $J_{2,3}$ 1.5	5.39 (q) $J_{3,4}$ 5.0	4.48 (t) $J_{4,5}$ 5.0	*ca.* 3.6 (m)	4.0—4.3 (2 H)		3.35 (OMs)	
(18)	4.91 (d) $J_{1,2}$ 3.5	5.26 (q) $J_{2,3}$ 10.0	4.29 (q) $J_{3,4}$ 3.5	5.43 (q) $J_{4,5}$ 1.8	3.80 (q) $J_{5,5'}$ 13.0	3.62 (d) $J_{5',4}$ 1.0	3.07	1.80	3.15br (s)
(18) [b]	5.04 (d) $J_{1,2}$ 3.0	5.10 (q) $J_{2,3}$ 10.0	4.36 (q) $J_{3,4}$ 4.0	5.60 (m)	3.96—4.04 (2 H)		3.47	2.20	2.60br (s)
(20)	5.00 (d) $J_{1,2}$ 3.0	5.57 (q) $J_{2,3}$ *ca.* 10	5.67 (q) $J_{3,2}$ 10.0 $J_{3,4}$ 3.0	4.17 (q) $J_{4,5}$ *ca.* 2	3.80—3.62 (2 H)		3.10	1.89	3.15 region
(20) [b]	4.96 (d) $J_{1,2}$ 3.5	5.28 (q) $J_{2,3}$ 10.5	5.52 (q) $J_{3,4}$ 3.0	4.34br (oct) $J_{4,5}$ 1.5	3.96 (q) $J_{5,5'}$ 12.5	3.73 (q) $J_{5',4}$ 2.0	3.42	2.10	2.3br (s)

[a] Solvent $(CD_3)_2SO$. [b] Solvent $CDCl_3$.

to the anomeric proton, because it was a doublet split by 7.5 Hz and the other signal was assigned to the proton attached to the carbon atom carrying the nitrobenzoate residue. This signal, which was a broad triplet split by 3.5 and 3.0 Hz must be due to H-3 because this proton



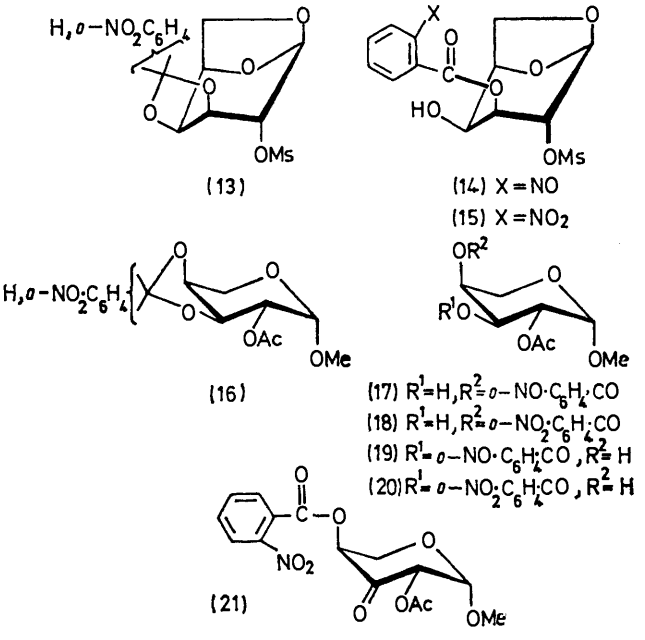
is the only one flanked by two *cis*-hydrogen atoms. Therefore the product was the 3-nitrobenzoate (9).

A pair of 3,4-*O*-*o*-nitrobenzylidenehexopyranosides was then studied. Compound (10),[12] derived from methyl 2-*O*-acetyl-α-L-fucopyranoside was similarly treated, but the nitrobenzoate product obtained in 86% yield was, on this occasion, non-crystalline. However the n.m.r. spectrum, which was analysed by first-order means, as recorded in the Table, showed that the gum comprised more than 95% of one fucoside isomer. This material was assigned the 2-*O*-acetyl 4-nitrobenzoate structure (12) because the proton signals due to H-2 and -4 (δ 5.33 and 5.50) were at lower field than that of H-3 (δ 4.29).

Irradiation and sequential oxidation of the other 3,4-*O*-*o*-nitrobenzylidenehexose (13) [12] prepared from 1,6-anhydro-β-D-galactopyranose 2-mesylate gave a crystalline nitrobenzoate (15) in 89% yield, the n.m.r. spectrum of which clearly showed two signals at low field: a triplet at δ 5.50 (two splittings of 1.5 Hz) and a quartet at δ 5.39 (split by 1.5 and 5.0 Hz). These signals must arise from protons attached to the carbon atoms carrying mesylate and nitrobenzoate groups (*i.e.* C-2 and C-3 or C-4). The lower field signal must be due to H-2 because the H-1 signal was also split by 1.5 Hz, and the higher field signal was assigned to H-3 because it was coupled to H-2. Another signal, at fairly high field (δ 4.48), showed coupling to H-3 and must therefore be due to H-4. This indicated that the 4-OH was unsubstituted and that the product was 1,6-anhydro-2-*O*-mesylgalactose 3-*o*-nitrobenzoate (15). Signals attributable to any of the protons of the 4-*o*-nitrobenzoyl isomer could not be detected in the n.m.r. spectrum of the crude product. Consequently its presence was assumed to be less than 5%.

The only pentopyranoside studied was compound (16) [12] and this was also a 3,4-*O*-*o*-nitrobenzylidene derivative. It gave, after sequential photolysis and oxidation, crystalline methyl 2-*O*-acetylarabinoside nitrobenzoates which afforded, upon deacylation, a high yield of methyl β-L-arabinopyranoside. The major isomer, which was readily purified by recrystallisation, was shown by n.m.r. spectroscopy (see Table) to be the 4-nitrobenzoate (18). The H-2 and -4 signals appeared at relatively low field, *i.e.* δ 5.26 and 5.43, and consequently the two ester residues were at the 2- and 4-positions. This structural assignment was confirmed by converting (18), with ruthenium tetraoxide, into the pyranosidulose derivative (21), which was shown, by the multiplicities of the n.m.r. signals for H-2 and -4, to possess the carbonyl group at C-3.

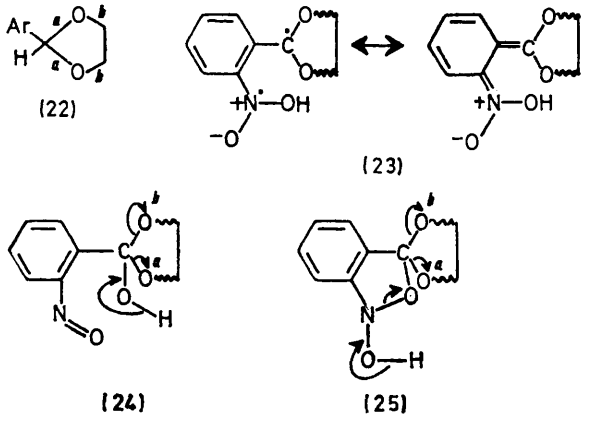
The n.m.r. spectrum of the residue obtained from the mother liquor from which (18) had crystallised showed signals that were assigned to the aglycone and acetyl methyl groups, and H-1, -3, and -4 of the 3-nitrobenzoate (20) (see Table). Signals for the remaining protons for this isomer were obscured by those of the major isomer (18). It was calculated from the intensity of the signals in this spectrum that the original crude



product must have contained *ca.* 95% of the 4-nitrobenzoate (18) and 5% of the 3-nitrobenzoate (20).

The transformations of the five derivatives all occurred stereospecifically, giving products with the same configuration as the original sugar derivative. Therefore the dioxolan ring probably opened at the benzylidene carbon atom [*a* in (22)] rather than the alternative carbon atoms [*b* in (22)], since the latter mode of cleavage could, in principle, give rise to some inverted products. These results and the observation that the photorearrangements could not be induced with either *meta*- or

para-nitrobenzylidene derivatives,[6,8,16] are consistent with the mechanism set out below, which is based upon proposed mechanisms for the photochemical reactions of several *o*-nitrobenzene derivatives which possess benzylic hydrogen atoms.[17,18] The initial step probably involves intramolecular hydrogen atom abstraction [19] to give the intermediate (23),[17] which then probably undergoes a hydroxy-group migration [4-6,17,20] to yield an orthoacid



(24). This would readily rearrange to give a hydroxy-nitrosobenzoate [21] with retention of configuration at the pyranosyl carbon atoms. Alternatively (23) could yield the intermediate (25) which could also rearrange to a hydroxy-nitrosobenzoate. The final rearrangement in this sequence could however occur in two ways as shown by the arrows *a* and *b* in (24) [or (25)]. Since the reactions were all highly regiospecific the dioxolan rings must be cleaved preferentially in one direction. This preference does not correlate directly with the site of fusion to the hexopyranose ring. For example, compounds (1) and (7), both 2,3-*O*-*o*-nitrobenzylidene derivatives, gave the 2-nitrosobenzoate (2) and the 3-nitrosobenzoate (8) respectively, whereas the 3,4-*O*-*o*-nitrobenzylidene derivatives (10), (16), and (13) yielded the 4-nitrosobenzoates (11) and (17) and the 3-nitrosobenzoate (14), respectively.

The direction of these cleavages can however be rationalised in conformational terms, since it can be seen by inspection of the major products in their preferred chair conformations that they all possess the newly formed free hydroxy-group in an equatorial disposition and the ester function in an axial orientation.

Acyl migration often occurs with *cis*-vicinal cyclic diol monoesters,[22] particularly under acidic or basic conditions. Therefore an experimental check was made to determine if the isomer distribution reported in this work resulted from this secondary ground state process. Arabinoside esters were selected for examination, because the product mixture from the *O*-nitrobenzylidene derivative (16) was shown to contain some of the minor isomer. Pure samples of the 4-nitrobenzoate (18) and the 3-nitrobenzoate (20) (the latter being prepared by selective nitrobenzoylation of methyl arabinopyranoside) were separately subjected to the usual irradiation–oxidation sequence. The n.m.r. spectra of the materials recovered from these treatments were examined. Although both spectra were slightly less well resolved than those of the initial pure samples, neither contained signals which could be attributed to the other positional isomers. Therefore the conditions used for the oxidation and irradiation reactions did not cause the nitrobenzoyl groups to migrate and it is probable that the nitrosobenzoyl groups would behave similarly.

There is a similarity between these photochemical transformations and the hydrolysis of orthoesters. Hydroxy-esters are formed in both reactions and furthermore it has been noted that hydrolyses of orthoesters derived from six-membered cyclic vicinal diols yield hydroxy-esters in which the hydroxy-group is equatorially oriented on the six-membered ring and the ester function axially disposed.[23] For example, Buchanan and Fletcher [24] found that 1,3-dioxolan-2-ylium ions formed in the hydrolysis of epoxy-pyranoside acetate derivatives were converted into pyranoside acetates in which the ester residue was axial. King and Albutt [23] proposed that the regioselectivity, in this, and in other examples derived from cyclohexanediols, was attributable to steric and stereoelectronic effects. They claimed that cleavage was facilitated by overlap from an orbital of a lone pair from one of the dioxolan ring oxygen atoms. Furthermore they showed that for steric reasons assistance from the *exo*-lone pair on the axial oxygen atom was favoured. Therefore the bond to the equatorially orientated oxygen atom was the one that would be cleaved. These same requirements could be invoked in the present case to explain the breakdown of the orthoacid (24).

Although some of the steps in the mechanistic sequence are still only speculative, sufficient is now known about the reaction of this class of derivatives to predict the structure of the product. Therefore this photochemical rearrangement now constitutes a useful method for preparing, in high yield, partially protected hexopyranose derivatives possessing an unblocked equatorial hydroxy-group, and it also affords a way of removing an arylmethylene residue without recourse to acid. Consequently it should find uses in carbohydrate synthesis.

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EXPERIMENTAL

I.r. spectra were measured for solids dispersed in potassium bromide discs and for gums smeared on sodium chloride plates, with a Perkin-Elmer Infracord 137 instrument; unless stated otherwise, optical rotations were measured for solutions in chloroform with a Bellingham and Stanley polarimeter. N.m.r. spectra at 60 and 220 MHz were measured with Varian A60D and HA220 instruments, respectively, and at 100 MHz with a JEOL-MH-100 instrument. Unless stated to the contrary the reported spectra were measured for solutions in $CDCl_3$ at 60 MHz. For t.l.c. and p.l.c., plates coated with Kieselgel G_{254} (Merck) were employed with benzene–ethyl acetate mixtures (*A* 2 : 1; *B* 4 : 1) and the compounds were located either with an anisaldehyde–sulphuric acid–ethanol spray at elevated temperatures or under u.v. light.

General Reaction Procedure.—Solutions (0.5—2.0%) of the *o*-nitrobenzylidene sugar derivatives in methanol, sometimes containing dichloromethane, were irradiated with light from a 450 W Hanovia medium-pressure mercury arc which had been filtered through Pyrex ($\lambda > 290$ nm). Irradiations were carried out either (*a*) in the annular cavity formed between a water-cooled immersion well (o.d. 52 mm) and an outer vessel, or (*b*) in tubes attached to the surface of the water-cooled well. The latter method was used for solutions with volumes less than 80 ml. The irradiations were monitored by t.l.c. in solvent *A* and when all the starting material had reacted the photolysates were evaporated. The nitrosobenzoates so obtained were usually oxidised [25] directly at 0 °C during 0.5 h as 2% solutions in dichloromethane with trifluoroperacetic acid (1.1 mol. equiv.), which had been prepared by treating trifluoroacetic anhydride in dichloromethane with hydrogen peroxide (86%). Water was then added and after a further 10 min the organic layer was separated. This was washed with water and aqueous sodium hydrogen carbonate, dried, and evaporated to give crude nitrobenzoates.

Sequential Irradiation and Oxidation of Pyranose o-*Nitrobenzylidene Derivatives.*—(a) *Methyl* 4-O-*acetyl*-2,3-O-o-*nitrobenzylidene*-α-L-*rhamnoside* (1). The pure *endo*-nitrobenzylidene rhamnoside [12] (1*en*) (0.55 g) in methanol (50 ml) was irradiated by method (*b*) for 30 min and then evaporated to give a pale yellow green solid which was oxidised [25] to give crude rhamnoside nitrobenzoates (0.54 g, 94%), R_F 0.50 (solvent *A*). Recrystallisation of this material gave pure *rhamnoside 2-nitrobenzoate* (3) (0.34 g), m.p. 101—102°, $[\alpha]_D$ +95° (*c* 1.0 in MeOH) (Found: C, 51.7; H, 5.2; N, 3.5. $C_{16}H_{19}NO_9$ requires C, 52.0; H, 5.2; N, 3.8%) (for δ and *J* values see Table). Evaporation of the mother liquor gave material (0.20 g) which was fractionated into unchanged (1) (25 mg), decomposition products (50 mg), and rhamnoside nitrobenzoates (0.12 g). The n.m.r. spectrum of the last fraction showed that it comprised mainly the 2-nitrobenzoate (3) with a little methyl 4-*O*-acetyl-α-L-rhamnoside 3-*o*-nitrobenzoate (5), the n.m.r. parameters of which are recorded in the Table.

The pure *exo*-isomer (1*ex*) [12] (0.15 g) gave, after irradiation and oxidation, a similar mixture of nitrobenzoates (0.15 g, 96%) and an *endo–exo* mixture behaved similarly.

(b) *Methyl* 4,6-*di*-O-*methyl*-2,3-O-o-*nitrobenzylidene*-β-D-*alloside* (7). Compound (7) [12] (0.14 g) was irradiated according to method (*b*) in methanol (35 ml) for 20 min and then oxidised [25] to give the 3-*nitrobenzoate* (9) (0.14 g, 93%), R_F 0.23 (solvent *A*), m.p. 120—121° (from diethyl ether), $[\alpha]_D$ +43° (*c* 0.2) (for δ and *J* values see Table) (Found: C, 51.9; H, 5.5; N, 3.8. $C_{16}H_{21}NO_9$ requires C, 51.8; H, 5.7; N, 3.8%). It was estimated that the 2-nitrobenzoate isomer constituted less than 5% of the crude product as determined from the intensity of a weak n.m.r. multiplet at δ 6.24. This signal might be due to H-2 of this isomer but there was no corroborative evidence for this assignment.

(c) *Methyl* 2-O-*acetyl*-3,4-O-o-*nitrobenzylidene*-α-L-*fucoside* (10). The *endo–exo*-nitrobenzylidene fucoside mixture (10) [12] (0.27 g) was irradiated in methanol (25 ml) for 40 min as described in (*b*) and then oxidised.[25] The 10% unchanged (10), R_F 0.6 (solvent *A*), was removed from the crude syrup by column chromatography on silica gel to give the 4-*nitrobenzoate* (12) (0.23 g, 86%), R_F 0.36, $[\alpha]_D$ −59° (*c* 1.0) (Found: C, 51.2; H, 5.4; N, 3.6. $C_{16}H_{19}NO_9$ requires C, 52.0; H, 5.2; N, 3.8%) (δ and *J* values in Table). There were no n.m.r. signals that could be attributed with certainty to the 3-nitrobenzoate. However, a weak multiplet at δ 5.1 was present which had an intensity of *ca.* 0.05H.

(d) 1,6-*Anhydro*-2-O-*methylsulphonyl*-3,4-O-o-*nitrobenzylidene*-β-D-*galactose* (13). The title compound [12] (0.59 g) was irradiated for 25 min in methanol (100 ml) by method (*a*), and then oxidised [25] to give the 3-*nitrobenzoate* (15) (0.56 g, 89%), R_F 0.30 (solvent *A*), m.p. 163—165° [from methanol–light petroleum (b.p. 40—60°)], $[\alpha]_D$ +43° (*c* 0.2) (δ and *J* values in Table) (Found: C, 42.9; H, 4.0; N, 3.3. $C_{14}H_{15}NSO_{10}$ requires C, 43.2; H, 3.9; N, 3.6%). All the signals in the n.m.r. spectrum of the crude product could be assigned to compound (15). It was concluded that the 4-nitrobenzoate constituted less than 5% of the total product.

(e) *Methyl* 2-O-*acetyl*-3,4-O-o-*nitrobenzylidene*-β-L-*arabinoside* (16). The syrupy *endo–exo*-mixture (16) [12] (1.2 g) in methanol (100 ml) was irradiated according to method (*a*) for 15 min. The nitrosobenzoates (1.1 g, 92%) obtained were oxidised [25] to give a crystalline mixture [R_F 0.3 (solvent *A*)] of 4- and 3-nitrobenzoates (18) and (20) (1.1 g, 96%). Deacylation of a portion of this product with sodium methoxide in methanol afforded, in high yield, a chromatographically homogeneous specimen of methyl β-L-arabinopyranoside.

Recrystallisation of the crude oxidised photoproduct from benzene gave the 4-*nitrobenzoate* (18), m.p. 163—164°, $[\alpha]_D$ +52° (*c* 0.5) (δ and *J* values in Table) (Found: C, 51.1; H, 4.9; N, 4.0. $C_{15}H_{17}NO_9$ requires C, 50.7; H, 4.8; N, 3.9%). The n.m.r. parameters for the 3-nitrobenzoate (20), which were abstracted from the spectrum of the crude mixture of (18) and (20) remaining in the mother liquor, are recorded in the Table. The intensity of the signals indicated that the initial product contained 95% of the 4-nitrobenzoate (18).

Crystalline specimens of compound (16) were not very soluble in methanol. Therefore in a typical irradiation experiment compound (16) (1 g) was dissolved in 1 : 1 dichloromethane–methanol (200 ml) and then treated according to method (*a*).

Stabilities of the Isomeric Esters (18) *and* (20).—Compounds (18) and (20) (75 mg each) were separately dissolved in dichloromethane (4 ml) and treated with trifluoroperacetic acid in the usual way for 2 h. The esters were recovered by the standard procedure and their n.m.r. spectra measured at 100 MHz.

[25] W. D. Emmons and A. F. Ferris, *J. Amer. Chem. Soc.*, 1953, **75**, 4623; W. D. Emmons, *ibid.*, 1954, **76**, 3468.

Compounds (18) and (20) (75 mg) were dissolved in 1 : 1 dichloromethane–methanol (20 ml) and irradiated for 45 min as described in method (*b*). The recovered compounds were oxidised and the n.m.r. spectra of both samples were measured at 100 MHz.

Methyl 4-O-*Acetyl*-2-O-o-*nitrobenzoyl*-α-L-arabino-*hexopyranosid*-3-*ulose* (6).—The rhamnoside derivative (3) (0.53 g) was oxidised [26] in carbon tetrachloride (50 ml) by the standard procedure with ruthenium tetraoxide [from ruthenium dioxide (0.5 g)]. The usual work-up gave the *pyranosid*-3-*ulose* (6) (0.5 g, 92%), m.p. 119—120°, $[\alpha]_D$ +65° (*c* 0.2), δ (C_6D_6) 5.04 (d, $J_{1,2}$ 1.5 Hz), 5.42 (d, $J_{2,1}$ 1.5 Hz), 5.40 (d, $J_{4.5}$ 9.0 Hz), 4.12 (octet, $J_{5,6}$ 6.0 Hz), 1.26 (d, CMe), 1.84 (s, Ac), 3.05 (s, OMe), and 7.0—7.6 (m, $NO_2C_6H_4$) (Found: C, 52.4; H, 4.8; N, 4.0. $C_{16}H_{17}NO_9$ requires C, 52.3; H, 4.7; N, 3.8%).

Methyl 2-O-*Acetyl*-4-O-o-*nitrobenzoyl*-β-L-threo-*pentopyranosid*-3-*ulose* (21).—The arabinoside 4-nitrobenzoate (18) (0.1 g) was oxidised as described above to give the *pyranosid*-3-*ulose* (21) (0.08 g, 82%), δ (C_6D_6) 4.87 (d, $J_{1,2}$ 4.0 Hz), 5.79 (d, $J_{2.1}$ 4.0 Hz), 5.39 (q, $J_{4.5}$ 2.0, $J_{4.5'}$ 2.5 Hz), 3.92 (q, $J_{5.5'}$ 13.0 Hz), 3.70 (q, $J_{5'.5}$ 13.0 Hz), 1.70 (s, Ac), 2.91 (s, OMe), and 6.6—7.4 (m, $NO_2C_6H_4$) (Found: C, 50.7; H, 4.5; N, 3.9. $C_{15}H_{15}NO_9$ requires C, 51.0; H, 4.3; N, 4.0%).

Methyl 2-O-*Acetyl*-3-O-o-*nitrobenzoyl*-β-L-*arabinopyranoside* (20).—Methyl 2-*O*-acetyl-β-L-arabinopyranoside (4 g) was treated with *o*-nitrobenzoyl chloride (3.6 g) in pyridine at 20 °C for 24 h. The usual work-up afforded a yellow syrup (6 g) which was fractionated by chromatography on silica gel with dichloromethane–benzene (1 : 1) into a fast-moving sample of the 3,4-di-*O*-*o*-nitrobenzoyl derivative (*ca.* 2.0 g) and a less mobile sample of compound (20) (3.8 g, 55%), $\nu_{max.}$ 1 530, 1 740, and 3 500 cm^{-1} (NO_2, Ac, and OH) (Found: C, 50.5; H, 5.1; N, 3.8. $C_{15}H_{17}NO_9$ requires C, 50.7; H, 4.8; N, 3.9%) (for n.m.r. parameters in $CDCl_3$ see Table).

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[26] P. J. Beynon, P. M. Collins, P. T. Doganges, and W. G. Overend, *J. Chem. Soc.* (*C*), 1966, 1131.