Photochemical Rearrangement of Some *o*-Nitrobenzylidene Carbohydrate Derivatives. A Route to Partially Protected Sugars

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Summary Photochemical rearrangement of *o*-nitrobenzylidene glycosides to *o*-nitrosobenzoates and the oxidation of these products to give partially protected carbohydrate *o*-nitrobenzoates are described.

IT has been known[1,2] for many years that *o*-nitrobenzaldehyde rearranges to *o*-nitrosobenzoic acid upon photolysis and that its diethyl acetal rearranges[3] to ethyl *o*-nitrosobenzoate and ethanol. Tanasescu and his co-workers[4] have also shown that cyclic acetals, derived from this aldehyde and diols, behave similarly giving hydroxy-nitrosobenzoates, and that[5] the di-*o*-nitrobenzylidene derivatives they obtained by condensing aldoses and pyranosides with this aldehyde undergo photolytic rearrangement to nitrobenzylidene nitrosobenzoates; however, the structures of these carbohydrate derivatives proved difficult to determine.

We have examined this photochemical rearrangement with mono-nitrobenzylidene glycosides and have overcome the problem of characterising the nitroso photo-products by oxidizing them to nitrobenzoates. This procedure has permitted the regiospecificity and stereospecificity of the reaction to be ascertained.

These photolyses offer a useful route to partially protected sugar esters (*cf.* ref. 6) and represents a novel method for removing an acetal residue without acid.

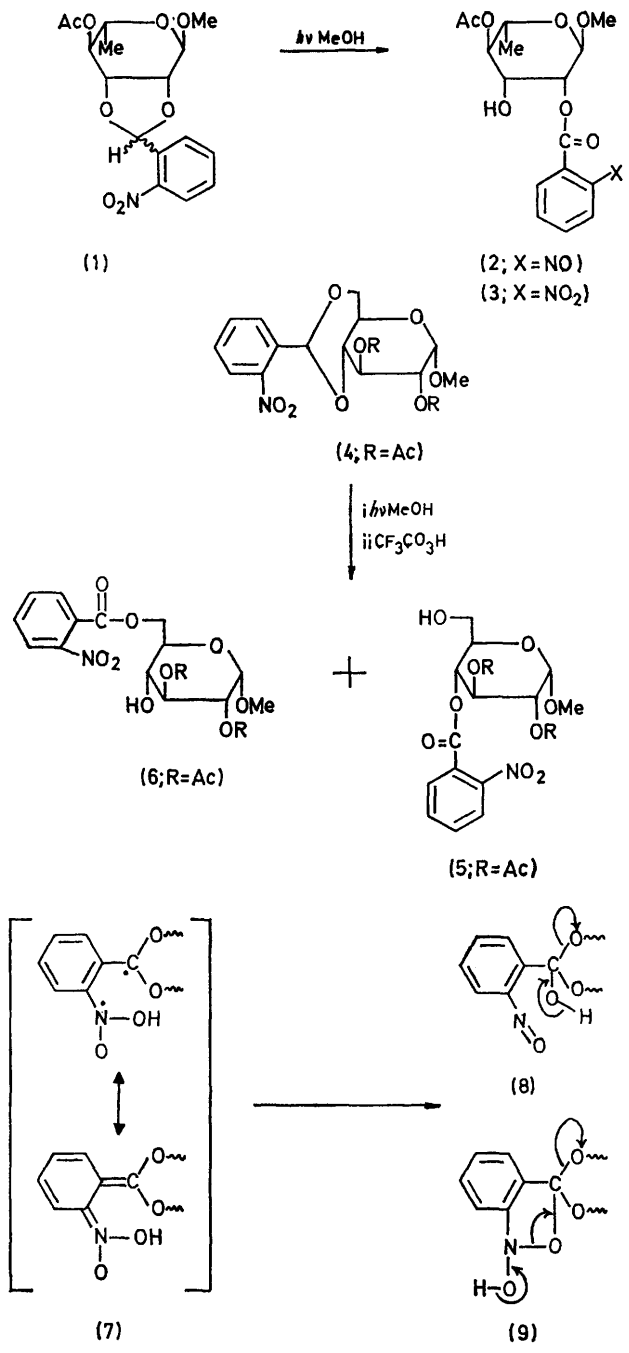
Irradiation† of a 1% (w/v) methanolic solution of a 1:2 *endo–exo*-mixture[7] of the pyranoside‡ (**1**) (prepared by standard procedures in 70% yield from methyl L-rhamnoside) rapidly gave the *o*-nitrosobenzoate (**2**). Compound (**2**) (probably dimeric) could only be obtained as an amorphous solid, but after oxidation with peroxytrifluoroacetic acid gave crystals of the L-rhamnoside (**3**), (88%), m.p. 101—102°, $[\alpha]_D$ + 95°,§ ν_{max} 3495 (OH) cm^{-1}. The n.m.r. spectrum [τ (C_6D_6) 4·4 (q, $J_{2,1}$ 1·3, $J_{2,3}$ 3·5 Hz), 4·85 (t, $J_{4,5}$ 10, $J_{4,3}$ 10 Hz), 5·10 (d, 1-H), 5·65 (q, 3-H), 6·23 (o, $J_{5,6}$ 6 Hz), and 8·8 (d, 5-Me)] was consistent only with the *rhamno*-configuration, the nitrobenzoyl substituent being at the 2-position, and the free hydroxy-group at position 3. These conclusions were confirmed by deacylation[8] of (**3**) to give methyl α-L-rhamnopyranoside and by oxidation of (**3**) with ruthenium tetroxide[9] to the 2,4-diester of methyl α-L-*lyxo*-hexopyranosid-3-ulose. No 3-*O*-*o*-nitrobenzoate, which would be formed from the product obtained by the alternative photochemical opening of the dioxolan ring, was found in the oxidized photolysate mixture.

Photochemical cleavage also occurred under similar conditions with 1,3-dioxan derivatives. The α-D-glucopyranoside (**4**) (obtained in 75% yield from methyl glucoside) upon sequential photolysis and oxidation gave a 3:7 mixture of 4- and 6-*o*-nitrobenzoates (**5**) and (**6**) (90%). Frac-

† Medium pressure mercury arc 450 W lamp, through Pyrex.

‡ Pure samples of the *endo*- and *exo*-isomers yielded identical products.

§ Optical rotations were measured on methanol solutions. All the nitrobenzoates reported gave satisfactory elemental analyses.



tional crystallization of the crude product gave the 6-nitrobenzoate (**6**) (60%), m.p. 128—129°, $[\alpha]_D$ + 47°; ν_{max} 3500 cm^{-1}; τ [$(CD_3)_2SO$, 100 MHz] 5·13 (d, $J_{1,2}$ 3·3), 5·24 (q, $J_{2,3}$ 10 Hz), 4·74 (q, $J_{3,4}$ 8·8 Hz), 6·45 (o, $J_{4,5}$ 10, $J_{4,OH}$ 6·0 Hz), 6·14 (o, $J_{5,6'}$ 5·3 Hz), 5·38 (q, $J_{6,5}$ 1·8 Hz), 5·6 (q, $J_{6',6}$ 11·6 Hz), and 4·25 (d, J 6·0, OH) and chromatography (SiO_2) of the mother liquors gave more (**6**), (R_f 0·63), (*ca.* 2%) and the 4-*o*-nitrobenzoate (**5**), (R_f 0·51) as a syrup (25%), ν_{max} 3500 cm^{-1}; $[\alpha]_D$ 79°; τ ($CDCl_3$; 100 MHz) 5·01 (1-H), 5·05 (2-H), 4·65 (t, $J_{3,2}$ 9·0, $J_{3,4}$ 9·0 Hz), 4·35 (t, $J_{4,5}$ 9·0 Hz), and 5·9—6·4 (5-, 6-, and 6'-H). Nitrobenzoates (**5**) and (**6**) both gave methyl α-D-glucopyranoside upon deacylation.[8]

Other similar high-yield transformations include the conversion of methyl 2-*O*-acetyl-3,4-*O*-*o*-nitrobenzylidene-β-L-arabinoside into a mixture of 8 parts of the 4-*O*-*o*-nitrobenzoyl- and 2 parts of the 3-*O*-*o*-nitrobenzoyl-arabinoside acetates, and the conversion of the α- and the β-anomers of methyl 2,3-di-*O*-acetyl-4,6-*O*-*o*-nitrobenzylidene-D-galactopyranosides into a mixture of 7 parts of the 4-*O*-*o*-nitrobenzoyl- and 3 parts of the 6-*O*-*o*-nitrobenzoyl-galactoside diacetates. Molecules containing free hydroxy-groups (*e.g.* **4**; R = H), methyl ether residues (**4**; R = Me) and tosyloxy-groups *e.g.* (**4**; R = $SO_2C_6H_4Me$-*p*) also undergo the photochemical reaction.

There are some similarities between this photochemical acetal ring cleavage and the Hanessian–Hullar[10,11] *N*-bromosuccinimide (NBS) reaction, but their mechanisms appear to be different. The NBS reaction affords bromobenzoates, in which the stereochemistry at the newly formed non-acylated carbon atom (C–Br) is thought to be inverted; in the absence of participating groups however, the stereochemistry at the non-acylated carbon atom (C–OH) is retained in the hydroxy-nitrosobenzoate formed photochemically. Thus photochemical cleavage of the dioxolan or dioxan rings occurs between an oxygen atom and the benzylic carbon atom.

Transformation of the kind described could not be induced with either *para*- or *meta*-nitrobenzylidene derivatives, consistent with the current view[12] that the initial step in this type of photochemical reaction is intramolecular hydrogen atom abstraction to give an intermediate of the type (**7**). This intermediate could then yield the nitrosobenzoate either *via* intermediate (**8**) or (**9**).

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