Chain Extensions from C-1 and C-5 of D-Xylopyranose Derivatives

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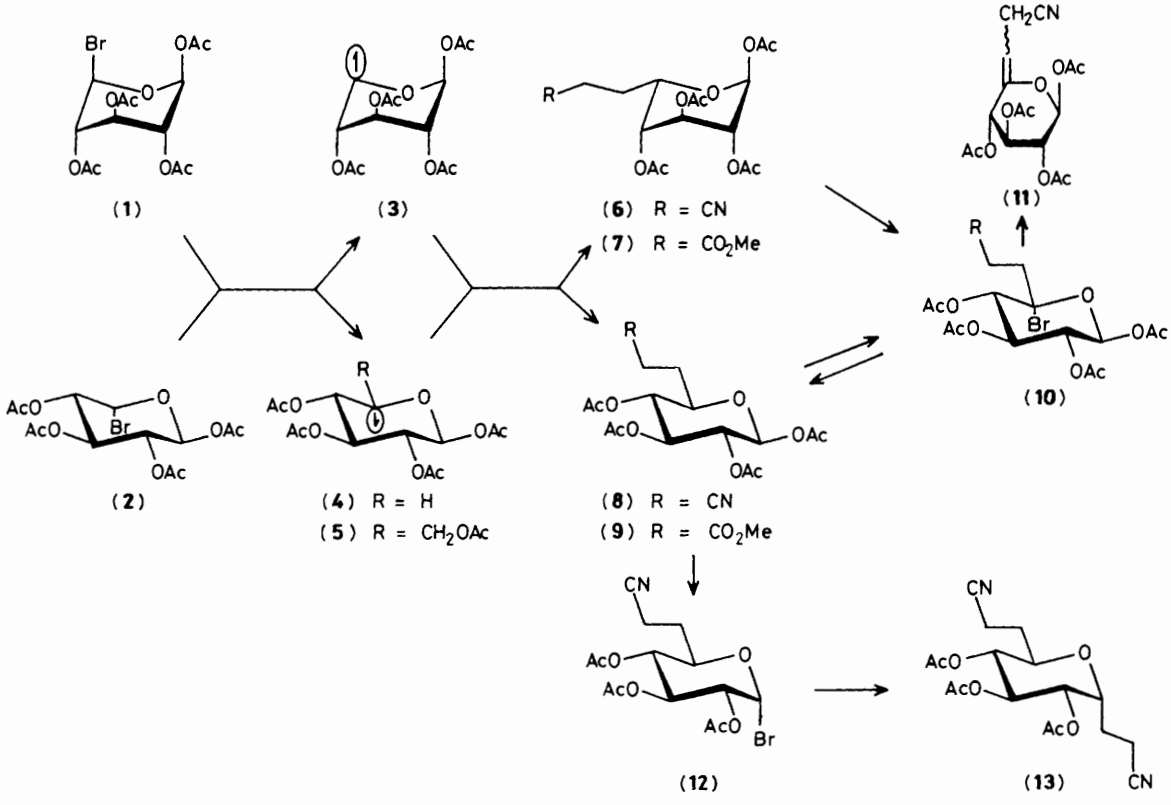
Free radicals produced successively at C-5 and C-1 from corresponding D-xylopyranose-based bromides add to acrylonitrile and methyl acrylate to give products with β-propionitrile or β-propionate substituents at these positions; some steric control can be achieved in the reactions, and the 4,8-anhydroundecanose derivative (**13**) is produced with good selectivity.

We have previously described the photobromination of tetra-*O*-acetyl-β-D-xylopyranose and the epimeric 5-bromo-products (**1**) and (**2**) from which the major (5*S*) isomer (**2**) can be isolated directly by crystallisation.[1,2] Treatment of this compound in refluxing diethyl ether with tributyltin hydride added slowly under visible light and in the presence of



acrylonitrile is now reported to give the L-*ido*-adduct (**6**) (23%) by direct crystallisation and further quantities (total 38%) were isolated, together with the D-*gluco*-isomer (**8**) (35%) and β-D-xylopyranose tetra-acetate, following flash column chromatography. Similar results were obtained, but the overall yields from D-xylose tetra-acetate were enhanced, when the reaction was carried out with the unfractionated (5*S*,*R*) bromide mixture (**1,2**). In similar fashion, the L-*ido*- and D-*gluco*-6,7-dideoxyoctopyranuronate derivatives (**7**) and (**9**) were isolated in 38 and 31% yield, respectively, when methyl acrylate was used as the radical trapping reagent.† These additions were notably non-stereoselective, whereas previously reported related reactions involving radicals derived from D-glucopyranosyl halides showed good selectivity in giving axial adducts,[3,4] and we ascribe this significant variation to the relative conformational instability of the pentos-5-yl radical intermediate. This, like tetra-*O*-acetyl-β-D-xylopyranose,[5] is likely to exist in solution in both chair conformations (**3**) and (**4**) (or in modifications of them which are flattened near C-5)[6] and to react preferentially in these forms, while the tetra-*O*-acetyl-D-glucopyranos-1-yl radical will exist (as does penta-*O*-acetyl-α-D-glucopyranose) and react[7] preferentially in the $^4C_1$ α-form (or in flattened modification of it[6]).

We have reported that penta-*O*-acetyl-β-D-glucopyranose and its 5-epimer, penta-*O*-acetyl-α-L-idopyranose, both undergo efficient radical bromination at C-5 to give the 5-bromide of the former following, it is assumed, reaction of the common, sterically and stereoelectronically preferred axial $^4C_1$ radical (**5**) with bromine.[8] In related fashion the epimeric nitriles (**6**) and (**8**) gave the same bromide (**10**) which, on reduction with tributyltin hydride in diethyl ether, afforded the D-*gluco*-nitrile (**8**) in 58% isolated yield together with 18% of the alkene (**11**). It is therefore possible to isomerise the L-*ido*-adduct (**6**) to the D-*gluco*-compound (**8**) with modest efficiency and thereby increase the overall yield of the latter to about 60% from the bromides (**1**) and (**2**) [without considering the alkene (**11**) as a further source].

Compound (**8**), treated with hydrogen bromide in acetic acid, gave the crystalline glycosyl bromide (**12**) in 83% yield, and from this, by further reaction with tributyltin hydride under light in the presence of acrylonitrile, the crystalline dinitrile (**13**) was isolated in 70% yield. This approach therefore offers a means of introducing carbon chains at C-2 and C-6 of tetrahydropyranyl rings to give compounds of potential value in the synthesis of a range of natural products having *C*-glycosidic constituents.[9]

We thank the Wellington Medical Research Foundation for providing financial support.

Received, 2nd January 1987; Com. 001

† All new compounds gave satisfactory elemental analyses and were characterised by ^1H n.m.r. spectroscopic methods. The conformations illustrated represent (at least approximately) those adopted in solution.

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