A Ready Route to Hex-3-enopyranosides

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Summary The synthesis of some hex-3-enopyranosides and hex-3-enopyranosiduloses using a variety of readily accessible *cis*- and/or *trans*-3,4-di-*O*-sulphonylated precursors is described.

WORK in progress in this laboratory requires the availability of various unsaturated carbohydrate molecules,[1-3] and we have therefore developed routes to some hex-3-enopyranosides. The synthetic sequence is applicable to a range of differently protected precursors and may be operated on the kilogram scale. Hence these biologically important olefins are readily available for investigation along lines already explored in analogous olefins.[2–4]

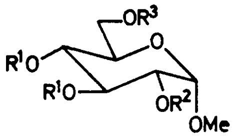
The most accessible hex-3-enopyranoside, the *erythro*-compound (1), originates with methyl α-D-glucopyranoside, (2). Partial benzoylation[5] of the latter afforded the crystalline 2,6-di-*O*-benzoate (3) in 50—60% yield and methanesulphonylation gave (4) as an amorphous solid. Reductive elimination of (4), using the zinc (copper)/sodium iodide/dimethylformamide method[6] applied in the hex-2-enopyranoside case,[1] was complete in 3 h to give a mixture of dibenzoate (5) and monobenzoate (6). Debenzoylation of the mixture afforded (1) (48% overall yield) as an oil characterizable as the di-*O*-*p*-nitrobenzoate (7),† m.p. 152—153°; $[\alpha]_D^{23}$ $-57{\cdot}7°$ (*c* 5·0 in $CHCl_3$).

The size of J_{12} in the 60 MHz n.m.r. spectra of (1) and (7) (4·0 Hz in both) implies the *erythro*-arrangement since in the *threo*-alternative, (8), (*vide infra*) the value of J_{12} is 1 Hz.[7] Hence, the partial deacylation which invariably accompanies eliminations in acylated substrates‡ does not affect the stereochemistry at the allylic position.

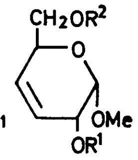
The *threo*-olefin (8) could conceivably be obtained by inverting the C-2 oxygen of (1).[8] However, it was instructive to see how *cis*-sulphonyloxy-groups would fare in the elimination, and hence precursor (9) was synthesized.

Treatment of methyl 4,6-*O*-benzylidene-α-D-altropyranoside with *N*-benzoylimidazole[9] in chloroform for 10 h gave a single product, methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-altropyranoside,[10] in 85% yield based on unrecovered starting material. The benzylidene group of the 2-*O*-benzoyl compound was removed by hydrogenolysis, and the resulting triol tritylated and, without isolation, sulphonated to give (9) in 56% yield.

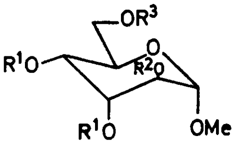
The subjection of (9) to the elimination procedure[1] for 6 h gave partially debenzoylated material (*vide supra*) which was completely debenzoylated to give (10) in 70% yield. Hence, the elimination procedure[1] works equally well for either *cis*- or *trans*-vicinal sulphonyloxy-groups on the pyranoside ring.



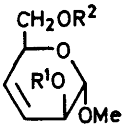
	R¹	R²	R³
(2)	H	H	H
(3)	H	PhCO	PhCO
(4)	MeSO₂	PhCO	PhCO



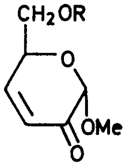
	R¹	R²
(1)	H	H
(5)	PhCO	PhCO
(6)	H	PhCO
(7)	*p*-$O_2NC_6H_4CO$	*p*-$O_2NC_6H_4CO$
(11)	H	Ph_3C



	R¹	R²	R³
(9)	MeSO₂	PhCO	Ph₃C



	R¹	R²
(8)	H	H
(10)	H	Ph₃C



(12) R = Ph₃C
(13) R = H

The *threo*- and *erythro*-olefins were correlated by oxidation of their 6-*O*-trityl derivatives, (10) and (11), respectively, to the same αβ-unsaturated ketone (12),† m.p. 127·5—128°; $[\alpha]_D^{23}$ $-15{\cdot}86°$ (*c* 5·75 in $CHCl_3$). Detritylation using $CHCl_3$–HCl[12] afforded the free ketone (13),†§ (m.p. 60·5–61°; $[\alpha]_D^{23}$ $+54{\cdot}65$; *c* 5·0 in $CHCl_3$) alternatively available by manganese dioxide oxidation of (1).

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† This compound gave correct elemental analysis and spectroscopic data.

‡ See also ref. 1.

§ The n.m.r. parameters of compound (1) agree with those reported for the 6-*O*-methyl[13] and 6-*O*-benzoyl[14] derivatives.

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