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Note

p-Diazoacetylbenzyl 1-thio-β-D-xylopyranoside

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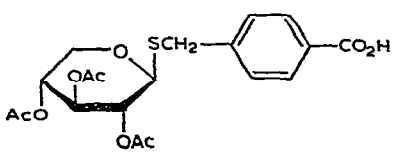
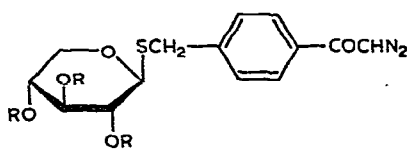
We recently described[1] the preparation of some azidophenyl glycosides. The nitrenes photolytically generated from these azido compounds are useful agents for labelling the active site of glycosidases. The carbenes formed from the light-induced decomposition of diazoketones are also potential photo-affinity reagents. The preparation of some diazoketo derivatives of glycosylamines and phenyl glycosides has been reported by Thomas[2]. We now describe the synthesis of a diazoacetylbenzyl 1-thioxylopyranoside (**3**) by a simple route that should be of general applicability.



1



2 R = Ac
3 R = H

EXPERIMENTAL

Melting points were determined with a Mettler FP-2 instrument and are uncorrected. Optical rotations were measured with a Perkin–Elmer Model 141 polarimeter. The purity of the products was tested by t.l.c. on Silica Gel G (Merck) with acetic acid–water–ethyl acetate (1:1:3) for the glycosides, and ethyl acetate–benzene (3:7) for the acetates. Detection was effected with 5% of sulphuric acid in ethanol (10 min at 120°). I.r. spectra were recorded for dispersions in Nujol with a Perkin–Elmer grating spectrometer, using CsI discs. U.v. spectra were recorded with a Beckman DBG spectrophotometer.

p-Carboxybenzyl 2,3,4-tri-O-acetyl-1-thio-β-D-xylopyranoside (**1**). — To 2,3,4-tri-*O*-acetyl-1-thio-β-D-xylopyranose[3] (3 g), dissolved in acetone (10 ml), a solution of α-bromotoluic acid (2.16 g) and potassium carbonate (3.2 g) in water (10 ml) was added. The mixture was stirred at room temperature for 20 min, acidified with glacial acetic acid, and extracted with chloroform (40 ml). Concentration of the

extract and trituration of the residue with methanol gave **1** (4.1 g, 61%), m.p. 143–145°, $[\alpha]_D^{22}$ −99° (*c* 0.4, chloroform), λ_{max}^{MeOH} 230 nm (ε 10^4), ν_{max} 1690 cm^{-1} (COOH).

Anal. Calc. for $C_{19}H_{22}O_9S$: C, 53.5; H, 5.2. Found: C, 53.0; H, 5.3.

p-*Diazoacetylbenzyl 2,3,4-tri-*O*-acetyl-1-thio-β-*D*-xylopyranoside* (**2**). — A solution of **1** (0.84 g) in dry benzene (10 ml) was refluxed (30 min) with freshly distilled thionyl chloride (1 ml). Excess of thionyl chloride and benzene were removed *in vacuo* (<40°), and the residue was dissolved in dry ether (10 ml). A cold (0°) solution of diazomethane in ether (0.2 g in 10 ml; prepared from *N*-methyl-*N*-nitroso-*p*-toluenesulphonamide[4]) was then added to the cooled solution. Evaporation of the solvent and crystallisation of the residue from methanol gave **2** (0.5 g, 51%), m.p. 102–104°, $[\alpha]_D^{22}$ −120° (*c* 0.4, chloroform), ν_{max} 2100 cm^{-1} (CHN_2). The u.v. spectrum showed an absorption maximum at 245 nm (ε 1.5×10^4) and a shoulder at 300 nm.

Anal. Calc. for $C_{20}H_{22}N_2O_8S$: C, 53.9; H, 4.9. Found: C, 53.9; H, 5.2.

p-*Diazoacetylbenzyl 1-thio-β-*D*-xylopyranoside* (**3**). — Conventional deacetylation[5] of **2** gave **3** (0.1 g, 70%), m.p. 158–159°, $[\alpha]_D^{22}$ −15° (*c* 0.3, water), ν_{max} 2100 cm^{-1} (CHN_2). The u.v. spectrum showed an absorption maximum at $\lambda_{max}^{H_2O}$ 245 nm (ε 1.5×10^4) and a shoulder at 300 nm, which disappeared upon irradiation (Mineralight UVS 11, 4-watt lamp, 257 nm).

Anal. Calc. for $C_{13}H_{16}N_2O_5S$: C, 50.0; H, 5.1. Found: C, 49.8; H, 5.1.

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