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Note

A simple preparation of 2,3,4,6-tetra-*O*-acetyl-1-*S*-acetyl-1-thio-*α*-D-glucopyranose*

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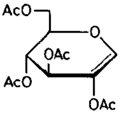
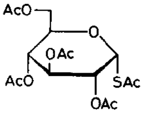
2,3,4,6-Tetra-*O*-acetyl-1-*S*-acetyl-1-thio-*α*-D-glucopyranose (**2**) has been obtained (46% and 36% yield, respectively) by reaction of tetra-*O*-acetyl-*β*-D-glucopyranosyl chloride with either the tetrabutylammonium salt of thioacetic acid in toluene[2] or potassium thioacetate in hexamethylphosphoramide[3]. The photochemical or peroxide-induced addition of thiols to unsaturated carbohydrates has been reported[4-8], and the possibility of obtaining **2** by addition of thioacetic acid to tetra-*O*-acetyl-1,5-anhydro-D-*arabino*-hex-1-enitol (**1**) was investigated.



1



2

Photochemical addition of ethanethiol and propanethiol to **1** proceeded smoothly to yield, exclusively, ethyl and propyl 1-thio-*α*-D-glucopyranoside, respectively[7]. Furthermore, both light- and peroxide-induced addition of thioacetic acid to 3,4,6-tri-*O*-acetyl-D-glucal gave two isomeric 2-*S*-acetyl-1,5-anhydro-2-thio-polyol derivatives[5,6].

Illumination of mixtures of **1** and thioacetic acid with a high-pressure mercury lamp gave only small amounts of addition products. However, as found for 3,4,6-tri-*O*-acetyl-D-glucal[6], *tert*-butyl or cumene hydroperoxide catalysed the addition of thioacetic acid to **1** at room temperature, giving almost exclusively the *α*-D-*gluco* product **2**. When the reactions were monitored by ^{13}C-n.m.r. spectroscopy, it was found that *tert*-butyl hydroperoxide and cumene hydroperoxide were equally efficient catalysts,

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*Stereoselective Thioglycoses Synthesis, Part XII. For Part XI, see ref. 1.

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whereas di-*tert*-butyl peroxide was ineffective even at 80° and ~1 mol of hydroperoxide, added in portions during ~48 h, was necessary in order to complete the reaction. Thus, although the addition probably involves a chain reaction, the chain is apparently short, possibly because of combination of thioacetyl radicals. This inference was confirmed by the formation of large amounts of thioacetyl-disulphide. Therefore, an excess of thioacetic acid is necessary.

When the addition reaction was performed without a solvent, by-products were formed, but, on the addition of acetone, a clean reaction took place and a 60–70% yield of **2** was obtained.

The addition of thiols to alkenes can be reversible[8], but prolonged treatment of **2** with the hydroperoxides in acetone led to no change as seen from ^{13}C-n.m.r. spectra. Attempts to use dichloromethane or benzene as solvent were unsuccessful.

EXPERIMENTAL

Melting points are uncorrected. ^{13}C-N.m.r. spectra were recorded on a Bruker AM-250 instrument and, when reactions were monitored, the instrument was operated without deuterium lock. *tert*-Butyl and cumene hydroperoxides were commercial products, which were dried ($MgSO_4$) before use. The thioacetic acid was distilled (b.p. ~80°).

*2,3,4,6-Tetra-*O*-acetyl-1-*S*-acetyl-1-thio-α-*D*-glucopyranose* (**2**). — To a solution of tetra-*O*-acetyl-1,5-anhydro-D-*arabino*-hex-1-enitol[9,10] (**1**, 5.0 g) in acetone (15 mL) was added thioacetic acid (9 mL). Cumene hydroperoxide (4 mL) was then added in four portions during 36 h whilst the mixture was kept at 20°. A ^{13}C-n.m.r. spectrum of the mixture obtained 12 h after the last addition of hydroperoxide showed the presence of 85% of **2** and 15% of **1**. Concentration of the mixture at 20° and crystallization of the residue from ether–pentane gave **2** (4.15 g, 66%), m.p. 122–124°. Recrystallization from ethanol yielded material (3.85 g) with m.p. 123–125°, $[\alpha]_D$ +143.5° (*c* 1.95, chloroform); lit.[2] m.p. 124–126°, $[\alpha]_D$ +140°. ^{13}C-N.m.r. data ($CDCl_3$): δ 80.2 (C-1), 71.4, 71.0, 68.9, 67.8 (C-2–5), 61.5 (C-6).

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