Photolysis of Dimethylthiocarbamates as a Route to Deoxy-sugars

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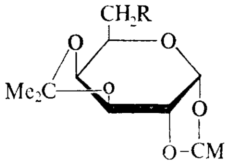
WE are concerned with photochemical techniques in synthetic carbohydrate chemistry.[1,2] We report the photolysis of some dimethylcarbamate esters of sugar derivatives[3] and show that a one-step, preparative conversion of the ester into a deoxy-sugar derivative can be achieved.

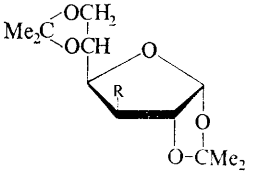
Photolysis of a methanolic solution of the 6-dimethylthiocarbamate[3] (I) of 1,2 : 3,4-di-*O*-isopropylidene-α-D-galactopyranose (III), with a 450 w mercury-arc lamp for 200 hr., gave a 25% yield of 6-deoxy-1,2 : 3,4-di-*O*-isopropylidene-α-D-galactopyranose (II), m.p. 30—35°, identical by n.m.r. spectrum and *X*-ray powder diffraction pattern to an authentic sample[4] of (II). A second product, isolated in 35% yield was identical to an authentic sample of the alcohol (III). The latter could be reconverted[3] into (I) in high yield. Thus, on re-cycling the product (III), conversion of the ester (I) into the deoxy-derivative (II), could be obtained with yields in the range 35—45%.

Similarly, photolysis of the 3-dimethylthiocarbamate[3] (IV) of 1,2 : 5,6-di-*O*-isopropylidene-α-D-glucofuranose (VI) gave 21% of syrupy 3-deoxy-1,2 : 5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranose (V), which gave an n.m.r. spectrum identical to that of an authentic sample[5] of (V) that had been prepared by desulphurization of bis-(1,2 : 5,6-di-*O*-isopropylidene-α-glucofuranose) disulphide[6] with hydrogen-saturated Raney nickel. Together with (V) was isolated 25% of the crystalline alcohol

(VI), which could be reconverted into the ester (IV), so that conversion yields of (IV) into (V) of 30—35% were feasible.

Photolysis of 1,6-anhydro-4-*O*-dimethylthiocarbamoyl-2,3-*O*-isopropylidene-*β*-D-mannopyranose[3] (VII) gave 26% of a new deoxy-sugar,† m.p. 126°, $[\alpha]_D$ $-22 \pm 3°$ (*c* 0·8, chloroform), formulated as 1,6-anhydro-4-deoxy-2,3-*O*-isopropylidene-*β*-D-*lyxo*-hexopyranose (VIII) by analogy with the foregoing reactions; it showed n.m.r. resonances (100 MHz, $CDCl_3$) at τ 7·70 and 7·92 for the 4-methylene group, $J_{4e,4a}$ 16 Hz. Also isolated from the photolysis reaction was the crystalline alcohol[7] (IX), yield 29%, which could be converted into the deoxy-sugar (VIII) by way of the dimethylthiocarbamate (VII); conversion yields of (VII) into (VIII) were 30—40%.

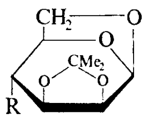


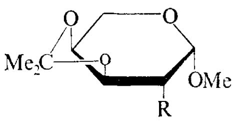


(I) R=OC(S)NMe$_2$ (IV)

(II) R=H (V)

(III) R=OH (VI)





(VII) R=OC(S)NMe$_2$ (X)

(VIII) R=H (XI)

(IX) R=OH (XII)

The photolysis of the 2-dimethylthiocarbamate[3] (X) of methyl 3,4-*O*-isopropylidene-*β*-L-arabinopyranoside[8] (XII) was likewise studied, and the 2-deoxy-derivative (XI) was isolated, together with the parent alcohol (XII).

The process leading from the dimethylthiocarbamate to the deoxy-derivative appears to involve rearrangement to an intermediate, the *S*-dimethylcarbamoyl derivative of a deoxythiosugar, which subsequently undergoes C–S homolysis with capture of a hydrogen atom from the solvent to give the product; a concurrent process involves simple cleavage of the *O*-dimethylthiocarbamoyl group to give the alcohol.

Since the dimethylthiocarbamate esters of "isolated" alcohol groups in carbohydrate derivatives are readily prepared in high yield,[3] the photochemical procedure described here furnishes a useful preparative route to deoxy-sugar derivatives.

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† All compounds described in this paper were homogeneous by t.l.c., gave satisfactory elemental analyses, i.r. and n.m.r. spectra were consistent with the structures assigned.

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