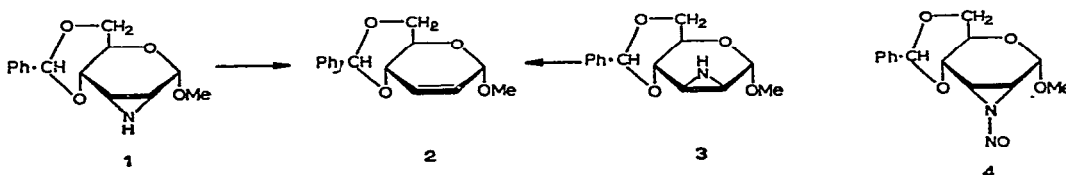


Nitrogen-containing carbohydrate derivatives

Part XII*. Reaction of epimino sugars with nitrous acid

From previous work on the nitrous acid deamination of simple alkyl aziridines¹, and of steroid epimines², to the corresponding alkenes, it would be expected that epimino sugars would give unsaturated sugars. Deaminations of methyl 4,6-*O*-benzylidene-2,3-dideoxy-2,3-epimino- α -D-alloside (1) and the corresponding mannoside (3) have both given good yields of methyl 4,6-*O*-benzylidene-2,3-dideoxy- α -D-erythro-hex-2-enopyranoside (2).



In the case of the epimino alloside (1), it was possible to isolate the intermediate yellow *N*-nitrosoepimine (4), having an ultraviolet spectrum which corresponded well with that recorded¹ for *N*-nitroso-*trans*-2,3-dimethylaziridine. The spectrum also showed a band due to contaminating unsaturated glycoside (2). The *N*-nitrosoepimino mannoside was too unstable for isolation.

This facile reaction provides a ready method of characterising epimino sugars and may, in some cases, provide a method of preparing unsaturated sugars inaccessible by other routes.

EXPERIMENTAL

Deaminations

(a) *Methyl 4,6-O-benzylidene-2,3-dideoxy-2,3-epimino- α -D-alloside* (1). The epimino alloside (1)³ (263 mg; 0.001 mole) was dissolved in aqueous acetic acid (50%; 10 ml). Sodium nitrite (103 mg; 0.0015 mole), dissolved in water (4 ml), was added. A yellow paste formed; this was diluted with water (20 ml), and the mixture was processed in two ways.

(i) The mixture was rapidly filtered, and the yellow precipitate was washed with a small volume of water and dissolved in methanol (100 ml), with shaking at room temperature. The methanol solution was filtered and cooled to -20° , and the yellow methyl 4,6-*O*-benzylidene-2,3-dideoxy-2,3-*N*-nitrosoepimino- α -D-alloside (4) (28%) (Found: C, 57.8; H, 5.5; N, 9.2. $C_{14}H_{16}N_2O_5$ calc. C, 57.9; H, 5.5; N, 9.6%) was collected in a pre-cooled filter and dried in a pre-cooled desiccator (P_2O_5). The product, which could be kept for a few days at -20° , had ν_{\max} 1510 cm^{-1} (N=O), λ_{\max}^{MeOH} 217, 257, and 451 $m\mu$ (ϵ_{\max} not recorded, because of the compound's instability);

*Part XI. G. J. F. CHITTENDEN AND R. D. GUTHRIE, *J. Chem. Soc.*, 1966 (c) 1508.

Clark and Helmkamp¹ reported $\lambda_{\text{max}}^{\text{MeOH}}$ 254 and 457 m μ for *N*-nitroso-*trans*-2,3-dimethylaziridine. Methyl 4,6-*O*-benzylidene-2,3-dideoxy- α -D-*erythro*-hex-2-enopyranoside has $\lambda_{\text{max}}^{\text{MeOH}}$ 217 m μ .

The *N*-nitrosoepimine was thermally unstable and became colourless after storage for about 4 h at room temperature. In an attempted m.p. determination, the compound turned colourless at 60–70°; continued heating gave m.p. 115–116° (the unsaturated glycoside **2** has m.p. 119–120°).

(ii) The mixture was made alkaline by addition of 2N sodium hydroxide, and then extracted with chloroform. The extracts were dried (Na₂SO₄) and evaporated. The crystalline residue (249 mg) was recrystallised from ethanol to give methyl 4,6-*O*-benzylidene-2,3-dideoxy- α -D-*erythro*-hex-2-enopyranoside (**2**) (81%), m.p. 118–119°, $[\alpha]_{\text{D}}^{26} + 129^\circ$ (c 0.2, chloroform) (Lit.⁴, m.p. 119–120°, $[\alpha]_{\text{D}}^{20} + 129^\circ$).

(b) Methyl 4,6-*O*-benzylidene-2,3-dideoxy-2,3-epimino- α -D-mannoside. This compound* was treated as in (a) above. Procedure (i) gave a very unstable, yellow product, presumed to be the *N*-nitrosoepimine. Procedure (ii) gave the unsaturated glycoside (**2**), in 78% yield, m.p. 119–120°.

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*This epimine, usually made from the diaxial methyl 2-azido-4,6-*O*-benzylidene-2-deoxy- α -D-altroside 3-methanesulphonate³, has also been synthesised from the corresponding diequatorial 3-azido-D-glucoside 2-methanesulphonate by using the same conditions. The epimine was isolated, in 71% yield, as its *N*-acetyl derivative. (This experiment was carried out by D. Murphy.)