SOME FURTHER REACTIONS OF CARBOHYDRATE EPIMINES

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ABSTRACT

N-Formylation and *N*-alkylation reactions of methyl 4,6-*O*-benzylidene-2,3-dideoxy-2,3-epimino-α-D-allopyranoside were studied as a route to 3-dimethylamino sugars. Attempts to prepare an *N*-formyl derivative were unsuccessful, but a stable adduct of the epimine and chloral was obtained. An *N*-methylepimine and a quaternary *N*,*N*-dimethylepimmonium salt (**13**) were prepared. Ring-opening reactions of these derivatives were investigated; reaction of **13** with sodium thiocyanate or sodium azide gave dimethylamino-thiocyanato (**15**) and dimethylamino-azido derivatives, respectively. Attempts to prepare a 3-dimethylamino-2,3-dideoxy derivative by desulphurisation of the thiocyanate **15** were unsuccessful, elimination occurring to give methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside.

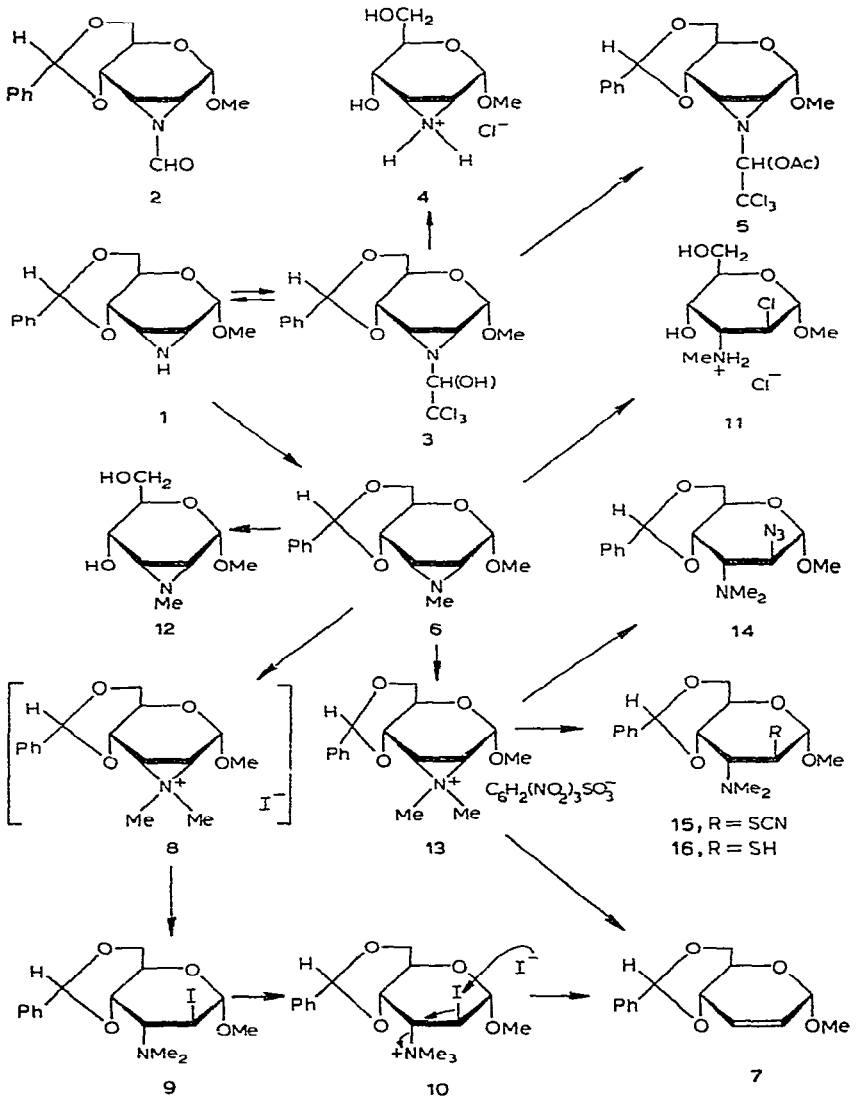
INTRODUCTION

Carbohydrate epimines are useful precursors of various amino sugars by ring-opening reactions[1,2]. *N*-Acylepimines, in particular, have been shown to undergo stereoselective ring-opening, giving preponderantly one product, normally that resulting from *trans*-diaxial ring-opening. The preparation and subsequent ring-opening of *N*-alkyl or *N*-formyl derivatives has been studied with a view to the synthesis of methylamino and dimethylamino sugars, such as are found as constituents of some antibiotics[3].

DISCUSSION

Treatment of methyl 4,6-*O*-benzylidene-2,3-dideoxy-2,3-epimino-α-D-allopyranoside (**1**) with boiling methyl formate[4], with or without the addition of triethylamine, led to no reaction, probably due to the weakly basic character of the epimine. An alternative method of formylation by treatment with chloral[5] in chloroform solution was unsuccessful at room temperature, but a reaction occurred under reflux. The major product was methyl 4,6-*O*-benzylidene-2,3-dideoxy-2,3-(2,2,2-trichloro-1-hydroxyethyl)epimino-α-D-allopyranoside (**3**), resulting from addition of the epimine across the carbonyl group of the aldehyde. Ohshiro *et al.*[6] observed a similar type of reaction between ethyleneimine and various aldehydes. A minor, amorphous

product, probably the required *N*-formylepimine, showed a sharp carbonyl absorption in the infrared at 1700 cm^{-1}. The adduct **3** did not melt sharply, and g.l.c. of the trimethylsilyl ether showed a mixture of two components, with relative peak intensities of 5:8, indicating that **3** is probably a mixture of diastereoisomers formed by the creation of a new asymmetric centre at C-1′. A slow mutarotation of **3** was observed in chloroform; the addition of triethylamine at equilibrium caused a further gradual decrease in optical rotation, but only starting material could be recovered after evaporation of the solvent. The adduct **3** was further characterised by acetylation to give methyl 2,3-(1-acetoxy-2,2,2-trichloroethyl)epimino-4,6-*O*-benzylidene-2,3-dideoxy-α-D-allopyranoside (**5**).



Treatment of the adduct **3** with sodium methoxide did not cause elimination of chloroform to give the required *N*-formylepimine (**2**) but gave the unsubstituted epimine **1**. Hydrochloric acid in acetone did not cause ring opening[2], but gave methyl 2,3-dideoxy-2,3-epimino-α-D-allopyranoside hydrochloride[2] (**4**).

Attention was then turned to direct alkylation of the epimine **1**. Simple ethylepimines react with methyl iodide at low temperature to give unstable quaternary immonium iodides[7] which, on treatment with silver 2,4,6-trinitrobenzenesulphonate (silver picrylsulphonate), yield quaternary immonium picrylsulphonates that are stable because of the low nucleophilicity of the picrylsulphonate ion. The stability of the quaternary epimmonium iodide derivatives of cycloalkenes depends on the ring size of the cycloalkane. Thus, cycloalkane derivatives containing 7, 8, 10, or 12 carbon atoms in the ring give quaternary salts which are stable and crystalline[8], whereas the cyclohexane derivative is not stable and undergoes ring opening to *trans*-2-iodo-*N*,*N*-dimethylcyclohexylamine[9]. The epimine **1** in methanol reacted slowly with methyl iodide and sodium carbonate at room temperature to give, initially, methyl 4,6-*O*-benzylidene-2,3-dideoxy-2,3-(methylepimino)-α-D-allopyranoside (**6**) which reacted further to give methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (**7**) and iodine. The formation of the unsaturated compound probably occurs *via* the quaternary epimmonium iodide **8**, followed by ring opening to give the dimethylamino-iodo derivative **9**. Further methylation of **9** to the quaternary methiodide **10** and subsequent attack by iodide would cause an E_2 elimination to give the unsaturated product **7**, together with iodine and triethylamine. Helmkamp and Pettit[10] have suggested an analogous mechanism for the desulphurisation of episulphides with methyl iodide.

When the epimine **1** in methanol was treated with methyl iodide in the presence of silver carbonate it gave methyl 4,6-*O*-benzylidene-2,3-dideoxy-2,3-(methylepimino)-α-D-allopyranoside (**6**) without further reaction. The n.m.r. spectrum of **6** was consistent with the assigned structure; the H-2 and H-3 signals appeared at unusually high field (τ 8.05). The *N*-methylepimine (**6**) did not readily undergo ring-opening reactions. With an excess of hydrochloric acid in boiling acetone, **6** gave, albeit in poor yield, methyl 2-chloro-2,3-dideoxy-3-methylamino-α-D-altropyranoside hydrochloride (**11**). The *altro* configuration was assigned from a comparison of the specific rotation (+74°) with those[2] of methyl 3-amino-2-chloro-2,3-dideoxy-α-D-altropyranoside hydrochloride (+72°) and methyl 2-amino-3-chloro-2,3-dideoxy-α-D-glucopyranoside (+156°). Catalytic hydrogenation of the *N*-methylepimine **6** removed the benzylidene residue without rupture of the epimine ring, giving methyl 2,3-dideoxy-2,3-methylepimino-α-D-allopyranoside (**12**).

The synthesis of the quaternary salt, namely methyl 4,6-*O*-benzylidene-2,3-dideoxy-2,3-(dimethylepimmonium)-α-D-allopyranoside picrylsulphonate (**13**) was achieved by treating the *N*-methylepimine **6** in acetonitrile with methyl iodide and 1 mol. of silver picrylsulphonate. The n.m.r. spectrum of **13**, although not fully interpretable, was consistent with the proposed structure. A 2-proton singlet at τ 1.7 was assigned to the picrylsulphonate ion, 3 3-proton signals at τ 6.4, 6.5, and 6.8 were

assigned to the *O*-methyl and *N*-methyl groups, and a 2-proton signal at τ 8.0 was assigned to H-2 and H-3, by comparison with the spectrum of the *N*-methylepimine (**6**).

The quaternary salt **13** was very reactive towards nucleophiles and reducing agent. When treated with a variety of metal halides in various solvents at room temperature, a mixture was usually formed consisting of the *N*-methylepimine **6** and the product resulting from ring opening. Potassium thiocyanate in *N*,*N*-dimethylformamide caused ring opening of **13** to give, exclusively, methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-dimethylamino-2-thiocyanato-α-D-altropyranoside (**15**). The *altro* configuration of **15** was assigned from the n.m.r. spectrum on the basis that *trans* ring-opening occurred. Of the two possible *trans* configurations, *gluco* and *altro*, only the latter was consistent[11] with the small coupling constants $J_{2,3}$ and $J_{3,4}$. The assignments were checked by spin-decoupling where possible. A doublet at τ 5.28 was first assigned to H-1, and a quartet at 6.14, assigned to H-2, collapsed to a doublet (J 3.6 Hz) on irradiation of H-1. A partly resolved quartet at τ 6.86 was assigned to H-3 and collapsed to a doublet (J 5 Hz) on irradiation of H-2. An unsymmetrical quartet at τ 6.0 was assigned to H-4 and collapsed to a doublet (J 9 Hz) on irradiation of H-3. The assignments are summarised in the Experimental.

Treatment of the thiocyanate **15** with Raney nickel in boiling ethanol resulted in elimination to form methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (**7**). As an alternative, the thiocyanate **15** was first hydrolysed with sodium methoxide to give the thiol **16**, but with Raney nickel this also gave the unsaturated product **7**.

Treatment of the quaternary salt **13** with sodium ethanethiolate in methanol gave the unsaturated compound **7** directly, as did treatment with potassium hydroxide in 2-methoxyethanol.

Ring opening of the quaternary salt **13** occurred with sodium azide in *N*,*N*-dimethylformamide at room temperature to give a dimethylamino-azido derivative, namely, methyl 2-azido-4,6-*O*-benzylidene-2,3-dideoxy-3-dimethylamino-α-D-altropyranoside (**14**). The n.m.r. spectrum of the azide **14** was similar to that of the thiocyanate **15**.

EXPERIMENTAL

Melting points were determined on a Kofler micro-heating stage, and are uncorrected. Optical rotations were determined at 20° on a Perkin–Elmer 141 polarimeter. Thin-layer chromatography (t.l.c.) was carried out on Silica Gel G (Merck), with detection by ethanolic 5% sulphuric acid at 120°.

Action of chloral on methyl 4,6-O-benzylidene-2,3-dideoxy-2,3-epimino-α-D-allopyranoside (**1**). — (*a*) To a solution of the epimine **1** (26 mg) in chloroform (0.5 ml) was added chloral[3] (16.5 mg), and the mixture was stored overnight at room temperature. After evaporation of the solvent and addition of ether, starting material was recovered.

(*b*) A solution of the epimine (1 g) and chloral (1 g) in chloroform (5 ml) was refluxed for 2 h and then evaporated to a syrup which was partitioned between water and chloroform. The organic layer was washed with water, dried ($CaCl_2$), and evaporated to a syrup which crystallised on the addition of ether. Attempted recrystallisation from ethyl acetate–light petroleum yielded a small amount of a highly insoluble, amorphous solid, m.p. >300°, ν_{max}^{Nujol} 1700 cm^{-1} (C=O), which probably was impure methyl 4,6-*O*-benzylidene-2,3-dideoxy-2,3-formylepimino-α-D-allopyranoside (Found: C, 61.1; H, 5.7. $C_{15}H_{17}NO_5$ calc.: C, 61.8; H, 5.9%).

The mother liquors were evaporated to a crystalline residue which was recrystallised from ethyl acetate–light petroleum to yield methyl 4,6-*O*-benzylidene-2,3-dideoxy-2,3-(2,2,2-trichloro-1-hydroxyethyl)epimino-α-D-allopyranoside (**3**; 750 mg, 50%), m.p. 120–130°, $[\alpha]_D$ +86 (10 min)→ +93° (4 h) (*c* 3.0, chloroform) (Found: C, 46.3; H, 4.25; Cl, 25.8; N, 3.4. $C_{16}H_{18}Cl_3NO_5$ calc.: C, 46.75; H, 4.4; Cl, 25.9; N, 3.4%). Recrystallisation from ethyl acetate–light petroleum yielded a sample with m.p. 150–155°, after partial melting and crystal transition at 120°. The mass spectrum did not show a molecular ion, nor any multiplets having a pattern of three chlorine isotopes. Addition of triethylamine to a solution of the adduct **3** in chloroform caused a rapid fall in optical rotation, followed by a slight rise, but recovery of the product by evaporation and crystallisation yielded apparently unchanged material. G.l.c. of the trimethylsilyl derivative of **3** revealed two components in the ratio of 5:8. Treatment of **3** with pyridine for 6 h caused no reaction (t.l.c. and i.r. spectrum of recovered solid); hence the g.l.c. result did not arise during the silylation procedure by partial reaction of the adduct with pyridine.

Acetylation of the adduct **3** (200 mg) with acetic anhydride (2 ml) and pyridine (10 ml) yielded, on crystallisation from ethanol, methyl 2,3-(1-acetoxy-2,2,2-trichloroethyl)epimino-4,6-*O*-benzylidene-2,3-dideoxy-α-D-allopyranoside (**5**; 65 mg, 30%), m.p. 180–190° (decomp.), $[\alpha]_D$ +31° (*c* 1.0, chloroform) (Found: C, 47.9; H, 4.3; N, 3.2. $C_{18}H_{20}Cl_3NO_6$ calc.: C, 47.7; H, 4.4; N, 3.1%). No mutarotation was observed.

A solution of the adduct **3** (0.5 g) in acetone (10 ml) was treated with conc. hydrochloric acid (0.2 ml). The solution clouded and then crystals separated, which were collected after 1 h to yield methyl 2,3-dideoxy-2,3-epimino-α-D-allopyranoside hydrochloride, m.p. 116–123°, which was identical (i.r. spectrum and mixed m.p.) with the compound obtained by the action of hydrochloric acid on the epimine[2] **1**.

Action of methyl iodide and sodium carbonate on methyl 4,6-O-benzylidene-2,3-dideoxy-2,3-epimino-α-D-allopyranoside (**1**). — (*a*) To a solution of the epimine **1** (100 mg) in ethanol (5 ml), methyl iodide (2 ml) and sodium carbonate (50 mg) were added, and the mixture was shaken at room temperature. After 24 h, t.l.c. (chloroform–ether, 1:1) indicated the presence of starting material and a faster-moving compound, in equal proportions. After a further 48 h, both these components were present, in addition to a second product, which was thought to be unsaturated from its high mobility on t.l.c. and because it charred rapidly with sulphuric acid.

(*b*) A mixture of **1** (1 g), sodium carbonate (0.5 g), and methyl iodide (2 ml)

was refluxed for 2 h. The black solution was evaporated, and the residue was fractionated on a column of silica gel with chloroform and chloroform–ether. The major product crystallized from isopropyl alcohol–light petroleum to yield methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (**7**), m.p. 120–121°, identical (mixed m.p. and i.r. spectrum) with an authentic sample. Another crystalline product was identical (t.l.c. and i.r. spectrum) with methyl 4,6-*O*-benzylidene-2,3-dideoxy-2,3-(methylepimino)-α-D-allopyranoside (**6**) described below.

Methyl 4,6-O-benzylidene-2,3-dideoxy-2,3-(methylepimino)-α-D-allopyranoside (**6**). — A solution of the epimine **1** (10 g) in methanol (50 ml) was mixed with silver carbonate (10 g) and methyl iodide (20 ml) and stirred for 3 h. After filtration, the colourless solution was evaporated, and the residue was crystallised from isopropyl alcohol–light petroleum to yield the *N*-methylepimine **6** (6.5 g, 62%), m.p. 146–147°, $[\alpha]_D$ +140° (*c* 1.7, chloroform); further recrystallisation raised the m.p. to 147–149° (Found: C, 64.85; H, 6.7; N, 5.0. $C_{15}H_{19}NO_4$ calc.: C, 65.0; H, 6.9; N, 5.0%).

Methyl 4,6-O-benzylidene-2,3-dideoxy-2,3-(dimethylepimmonium)-α-D-allopyranoside picrylsulphonate (**13**). — To a solution of methyl 4,6-*O*-benzylidene-2,3-dideoxy-2,3-(methylepimino)-α-D-allopyranoside (4 g, 14.4 mmoles) in acetonitrile (160 ml) was added silver picrylsulphonate[12] [6.27 g (14.4 mmoles) of silver picrylsulphonate $(MeCN)_2$] and methyl iodide (16 ml), and the mixture was left at room temperature for 2 days. The precipitated silver iodide was removed, and the filtrate was evaporated to a syrup which was then extracted several times with boiling ether to leave an amorphous, yellow powder. Crystallisation from acetonitrile–ether or chloroform–ether yielded the quaternary epimmonium picrylsulphonate **13** (5.6 g, 66%), m.p. 170–190° (decomp.) after partial melting and resolidification at 117–120°, $[\alpha]_D$ +31.2° (*c* 1, chloroform) (Found: C, 45.2; H, 4.4. $C_{22}H_{24}N_4O_{13}S$ calc.: C, 45.2; H, 4.1%).

Action of hydrochloric acid in acetone on methyl 4,6-O-benzylidene-2,3-dideoxy-2,3-methylepimino-α-D-allopyranoside (**6**). — Conc. hydrochloric acid (2 ml) was added to a solution of the *N*-methylepimine (1 g) in acetone (40 ml), and the mixture was refluxed for 10 min. The acetone was evaporated, and water was distilled from the residue (to remove benzaldehyde) followed by ethanol. The resulting syrup crystallised on the addition of isopropyl alcohol, to yield methyl 2-chloro-2,3-dideoxy-3-methylamino-α-D-altropyranoside hydrochloride (**11**; 430 mg, 45%). Recrystallisation from ethanol–light petroleum afforded granular crystals, m.p. 183–190° (decomp.), $[\alpha]_D$ +74° (*c* 1.5, water) (Found: C, 36.7; H, 6.5. $C_8H_{17}Cl_2NO_4$ calc.: C, 36.6; N, 6.5%).

Catalytic hydrogenation of methyl 4,6-O-benzylidene-2,3-dideoxy-2,3-(methylepimino)-α-D-allopyranoside (**6**). — A solution of **6** (1 g) in ethanol (5 ml) was hydrogenated at atmospheric pressure in the presence of Raney nickel. T.l.c. (chloroform–methanol, 4:1) indicated that reaction was complete after 2 weeks, giving a single, slower-moving product. The catalyst was filtered off on a pad of Hyflo Supercel, and the solution was evaporated. The crystalline residue was triturated with ether and recrystallised from ethyl acetate, to yield methyl 2,3-dideoxy-2,3-(methylepimino)-α-D-allopyranoside (**12**; 0.46 g, 67%), m.p. 124–125°, $[\alpha]_D$ +176° (*c* 0.8 chloroform) (Found: C, 50.5; H, 8.0; N, 7.4. $C_8H_{15}NO_4$ calc.: C, 50.8; H, 7.9; N, 7.4%).

Action of metal halides on methyl 4,6-O-benzylidene-2,3-dideoxy-2,3-dimethylepimmonium-α-D-allopyranoside picrylsulphonate (**13**). — (*a*) *Sodium iodide in acetonitrile.* To a solution of the quaternary epimmonium picrylsulphonate (**13**, 100 mg) in acetonitrile (0.5 ml) was added sodium iodide (100 mg). T.l.c. (chloroform–ether, 1:1) indicated a rapid reaction at room temperature. After 1 h, the mixture was evaporated to dryness, and the residue was extracted with chloroform. The extract was passed through a short column of silica gel to remove any ionic material and was then evaporated to a yellow syrup. T.l.c. (di-isopropyl ether–ethyl methyl ketone, 6:1) showed the presence of two products, in approximately equal amounts, the slower being coincident with methyl 4,6-*O*-benzylidene-2,3-dideoxy-2,3-(methylepimino)-α-D-allopyranoside (**6**).

(*b*) Sodium chloride or potassium chloride in acetonitrile similarly gave approximately equal amounts of the *N*-methylepimine **6** and a faster-moving product, as indicated by t.l.c.

(*c*) Sodium chloride or potassium iodide in *N,N*-dimethylformamide gave similar mixtures, but with a higher proportion of the unidentified, faster-moving product.

Methyl 4,6-O-benzylidene-2,3-dideoxy-3-dimethylamino-2-thiocyanato-α-D-altropyranoside (**15**). — A solution of methyl 4,6-*O*-benzylidene-2,3-dideoxy-2,3-(dimethylepimmonium)-α-D-allopyranoside picrylsulphonate (**13**) (5 g) in *N,N*-dimethylformamide (50 ml) was used with potassium thiocyanate (3 g), and the mixture was left for 24 h at room temperature. The red solution was evaporated, and the residue was extracted with chloroform. The chloroform extract was passed through a column of silica gel, and the eluate was evaporated to a thin syrup which, after repeated concentration with ethanol, gave a crystalline residue. This was triturated with light petroleum, collected, and recrystallised from isopropyl alcohol–light petroleum, to give **15** (1.7 g, 57%), m.p. 99–101°, $[\alpha]_D$ +62° (*c* 1, chloroform) (Found: C, 58.6; H, 6.4; N, 7.9; S, 9.1. $C_{17}H_{22}N_2O_4S$ calc.: C, 58.3; H, 6.3; N, 8.0; S, 9.1%). N.m.r. data (100 MHz, $CDCl_3$): H-1, τ 5.28 ($J_{1,2}$ 2 Hz); H-2, 6.14 ($J_{2,3}$ 3.6 Hz); H-3, 6.86 ($J_{3,4}$ 5 Hz); H-4, 6.0 ($J_{4,5}$ 9 Hz); Ph, *ca.* 2.7; PhC*H*, 4.57; OMe, 6.62; NMe_2, 7.50.

Methyl 2-azido-4,6-O-benzylidene-2,3-dideoxy-3-dimethylamino-α-D-altropyranoside (**14**). — A solution of **13** (700 mg) in *N,N*-dimethylformamide (4 ml) was treated with sodium azide (300 mg) for 4 days at room temperature. The solvent was evaporated, and the residue was partitioned between water and chloroform. The chloroform solution was dried (Na_2SO_4), filtered, and concentrated. The residue was separated on a column of silica gel, using chloroform as eluent. The fraction containing the main component was evaporated to a crystalline residue which was recrystallised from isopropyl alcohol–light petroleum to yield **14** (90 mg, 22%), m.p. 97–98°, $[\alpha]_D$ +85° (*c* 1.5 chloroform) (Found: C, 57.7; H, 6.6; N, 16.9. $C_{16}H_{22}N_4O_4$ calc.: C, 57.5; H, 6.6; N, 16.7%). N.m.r. data: H-1, τ 5.50 ($J_{1,2}$ 1.7 Hz); H-2, 6.01 ($J_{2,3}$ 3.2 Hz); H-3, 7.20 ($J_{3,4}$ 3.8 Hz); H-4, 6.03 ($J_{4,5}$ 9.0 Hz), Ph, *ca.* 2.7; PhC*H*, 4.60; OMe, 6.64; NMe_2, 7.52.

Desulphurisation of methyl 4,6-O-benzylidene-2,3-dideoxy-3-dimethylamino-2-

thiocyanato-α-D-altropyranoside (**15**.)—(*a*) Raney nickel suspended in ethanol was degassed by heating under reflux overnight. A solution of the thiocyanate **15** (50 mg) in ethanol was mixed with this Raney nickel and refluxed for 1 h, and t.l.c. then indicated that a faster-moving compound was formed. After filtration and evaporation of the solvent, the residue was eluted from a column of silica gel with chloroform to give a crystalline product (5 mg) which was identical with methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (**7**) (m.p., i.r., and t.l.c.).

(*b*) The thiocyanate **15** (1 g) was treated at room temperature with M methanolic sodium methoxide for 10 min, and t.l.c. (chloroform–ether, 1:1) then indicated that reaction was complete. The solution was passed through a column of Amberlite IR-120 (H^+) resin, and the basic eluate was evaporated to the syrupy thiol **16** (Found: N, 4.2. $C_{16}H_{23}NO_4$ calc.: N, 4.3%). Treatment of **16** with Raney nickel in boiling ethanol as above yielded methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (**7**).

Action of sodium ethanethiolate on methyl 4,6-O-benzylidene-2,3-dideoxy-2,3-(dimethylepimmonium)-α-D-allopyranoside picrylsulphonate (**13**). — Reaction of **13** (60 mg) with M methanolic sodium methoxide (1 ml) and ethanethiol (0.2 ml) was very rapid. After a few min, the solution was evaporated, and the residue was partitioned between water and chloroform. The chloroform solution was washed with water, dried ($CaCl_2$), and evaporated to a syrup, which crystallised on the addition of isopropyl alcohol, to yield the unsaturated compound **7** (9 mg), which was identical with an authentic sample (m.p., i.r., and t.l.c.).

Action of potassium hydroxide on methyl 4,6-O-benzylidene-2,3-dideoxy-2,3-(dimethylepimmonium)-α-D-allopyranoside picrylsulphonate (**13**). — Potassium hydroxide (100 mg) was dissolved in 2-methoxyethanol (3 ml), **13** (200 mg) was added slowly, and the mixture was stored overnight. The red solution was then added to water to precipitate the product, which was collected, dissolved in warm isopropyl alcohol, filtered through cotton wool, and then evaporated to dryness. Crystallisation from isopropyl alcohol yielded the unsaturated compound **7** (10 mg).

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