Reactions of Relevance to the Chemistry of Aminoglycoside Antibiotics. Part 12.[1] A Study of Cyclic Iminocarbonates

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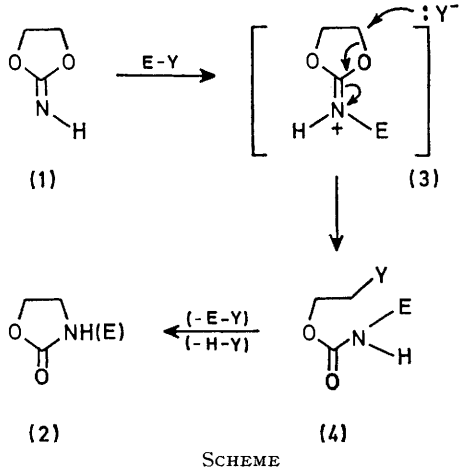
A novel method for the replacement of a carbohydrate hydroxy-group by an amino-function *via* rearrangement of cyclic iminocarbonates has been developed. Several examples from the carbohydrate field illustrate that the overall process is strongly influenced both by the nature of the substituent attached to the nitrogen atom of the iminocarbonate ring, and by stereoelectronic factors inherent in the substrate structure.

WITHIN the last decade, many aminoglycosides of differing structural types have been produced by fermentation and found to possess valuable antibiotic properties. Consequently, much effort has been directed towards the synthesis of carbohydrates in which one or more of the hydroxy groups have been replaced by a nitrogen function.

The most frequently adopted strategies for the introduction of the nitrogenous moiety involve displacement of sulphonyloxy-groups by azide anion, hydrazine, or ammonia, and nucleophilic ring opening of epoxides.[2] In the sugar series however, the use of charged nucleophiles often leads to the stereoelectronic development of unfavourable dipolar interactions,[3] while neutral nucleophiles such as hydrazine tend to function as bases and promote elimination. Intramolecular displacement *via* neighbouring group participation is a much more attractive alternative and has been used for the preparation of *cis*-1,2-amino-sugars.[4] In general, however, several steps are necessary for the separate introduction of the nucleophile and the leaving group.

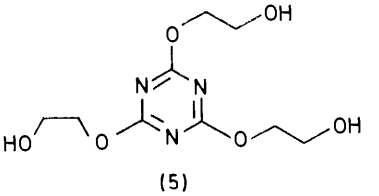
We envisaged that the thermodynamically favourable isomerisation of a cyclic iminocarbonate (1) to an oxazolidin-2-one (2) should lead to a regio- and stereocontrolled interconversion of the hydroxy- and amino-



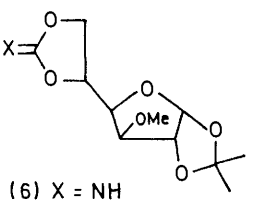
SCHEME

functions (Scheme). Reaction with a reagent $E^{\delta+}-Y^{\delta-}$ (E = electrophile, Y = nucleophile and leaving group) which in the ideal situation functions as a catalyst, leads to concomitant introduction of the nucleophile and the leaving group required for intramolecular displacement. Moreover, the intermediate (3) possesses a positively charged leaving group to facilitate ring-opening.

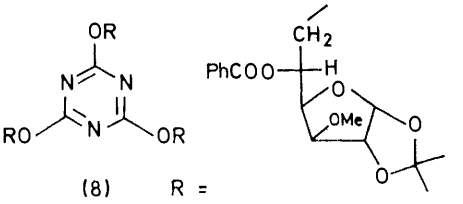
Examination of the literature revealed that the parent ethylene iminocarbonate (1) was a highly labile substance which underwent ring-opening and 'trimerisation' to the cyanurate (5).[5] *N*-Alkyl-, *N*-aryl-, and *N*-halogeno-



(5)



(6) X = NH
(7) X = O



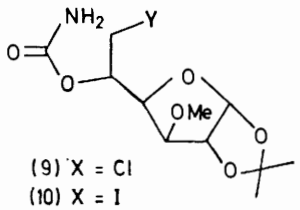
(8) R =

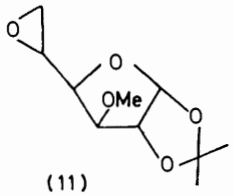
iminocarbonates can, however, be isolated and ring-opening reactions of the type leading to intermediate (4) have been noted.[6] A particularly encouraging observation was made by Addor,[7] who prepared the derived hydrochloride salts by reaction of cyanogen chloride with diols under acidic conditions, and reported facile rearrangement to chlorourethanes. The Lewis-acid-catalysed thermal isomerisation of ethylene *N*-phenyliminocarbonate has also been described.[8]

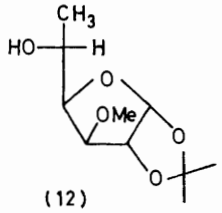
1,2-*O*-Isopropylidene-3-*O*-methyl-α-D-glucofuranose was selected as a suitable model for exploratory studies. Sequential treatment of the diol with butyl-lithium and cyanogen bromide led to the formation of the desired iminocarbonate (6) in essentially quantitative yield. The proposed structure was supported by the expected i.r. absorption at 1 700 cm^{-1} and by acid hydrolysis to the known cyclic carbonate (7).[9] The iminocarbonate system proved to be thermally labile. Benzoylation of the derived product led to the isolation of an amorphous solid whose i.r. spectrum ($\nu_{max.}$ 1 560 cm^{-1}) and molecular weight suggest the cyanurate structure (8).

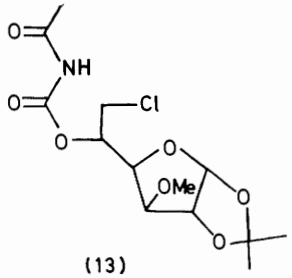
Nevertheless, reaction of freshly prepared imino-

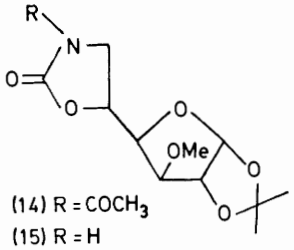
carbonate (6) with anhydrous oxalic acid in the presence of lithium chloride led smoothly and in high yield to the ring-opened chlorourethane (9). The less stable iodo-derivative (10) was also prepared in an analogous manner.

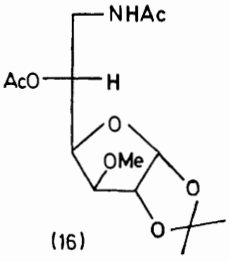


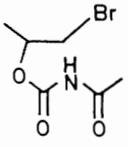


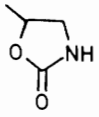


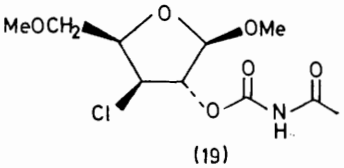


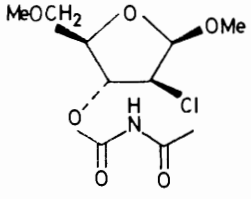


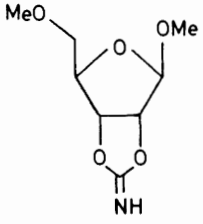


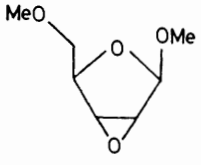


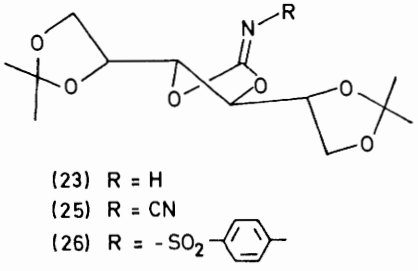


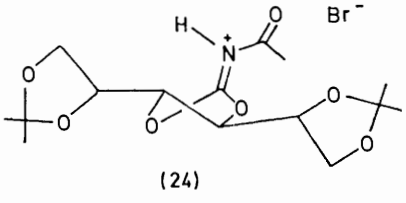


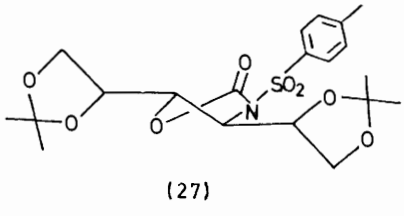


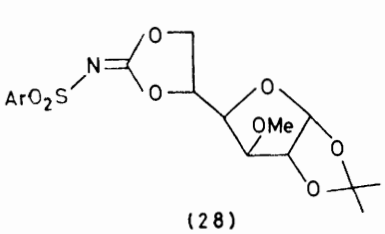


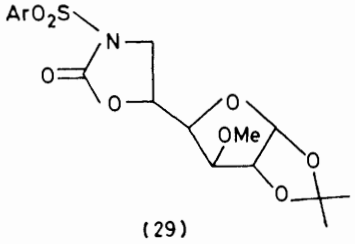


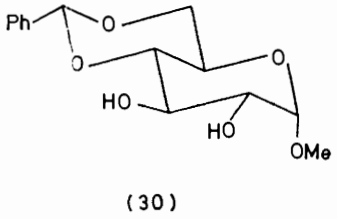












Although the base induced cyclisation of halogeno-carbamates is cited as a general method for the construction of oxazolidin-2-ones,[10] the halogenocarbamates (9) and (10) resisted all attempts to form the crucial carbon–nitrogen bond under a variety of conditions. Elimination of the elements of isocyanic acid and subsequent ring-closure to form the known [11] epoxide (11) was consistently observed. This undesired fragmentation has also been reported by other workers.[12] Silver-ion induced cyclisation led, not unexpectedly, to the cyclic carbonate (7) *via* participation of the ' harder ' oxygen atom of the carbamate. An alternative cyclisation method involving reaction of the chlorourethane with

metallic sodium led to the formation of the known [13] 6-deoxy-derivative (12) in low yield.

The presence of an additional electron-withdrawing substituent on the nitrogen atom would localise the negative charge and hence minimise elimination in the ring-closure step. Freshly prepared iminocarbonate (6) was reacted with an excess of acetyl chloride to furnish the required *N*-acetylchlorourethane (13). Treatment of this substance with sodium hydride in tetrahydrofuran led to formation of the desired carbon–nitrogen bond. The primary product of the reaction was not however the anticipated *N*-acetyloxazolidin-2-one (14) but the parent compound (15), thus implying that cyclisation is followed by loss of keten. The diacetate (16) was prepared by cleavage of the crude cyclisation product with potassium hydroxide and acetylation. The regiospecificity of the sequence was confirmed by an independent synthesis of (16) involving displacement of 1,2-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranose-6-tosylate with azide anion, followed by reduction and acetylation.

From the practical standpoint, isolation of the iminocarbonate is unnecessary. Thus, sequential treatment of readily available propane-1,2-diol with butyl-lithium, cyanogen bromide, and finally freshly distilled acetyl bromide led directly to the isolation of carbamate (17) as a relatively unstable waxy solid in 63% overall yield. Cyclisation of this product with sodium hydride in tetrahydrofuran gave the oxazolidone (18) whose structure was confirmed by comparison with an authentic sample.[14]

We have also successfully prepared the *N*-acetylchlorourethanes (19) and (20) from methyl-5-*O*-methyl-β-D-ribofuranose iminocarborate (21). In this instance, however, opening of the iminocarbonate ring proceeded only at elevated temperature. Moreover, attempted cyclisation of (19) did not lead to oxazolidone formation but to a product whose spectroscopic properties were, once again, in accord with the anhydro-sugar (22).

The cyclic iminocarbonate (23) derived from 1,2;5,6-di-*O*-isopropylidene-D-mannitol occupies a unique position among the iminocarbonates described in this work, inasmuch as it is a beautifully crystalline solid with no observed tendency towards decomposition. The stability of this derivative was also reflected in its reactivity. Thus, reaction with acetyl bromide led to the formation of a quaternary salt (24) which, even on thermolysis, resisted ring-opening to the desired *N*-acetylbromourethane. Nevertheless, this substrate did provide the opportunity to develop an even better leaving group by further modification of the electron-withdrawing substituent attached to the nitrogen atom. Thus, it was possible to prepare the *N*-cyanoiminocarbonate (25) and the *N*-*p*-tolylsulphonyliminocarbonate (26). It was encouraging to observe that the enhanced electron-withdrawing power of these groupings over the parent iminocarbonate was manifest in their spectroscopic properties. The n.m.r. spectra showed a substantial downfield shift of the protons directly attached to the iminocarbonate ring and the i.r. spectra displayed a lowering of the C=N stretch [1 668 (NC–N=C) and 1 638 ($ArSO_2$–N=C) cm^{-1}]. Attempted isomerisation of the *N*-cyanoiminocarbonate (25) with a saturated solution of sodium iodide in acetone was unsuccessful, even at elevated temperature. Rearrangement of the *N*-*p*-tolylsulphonyliminocarbonate (26) under essentially the same conditions, did however lead to a low yield of the desired oxazolidin-2-one (27).

The scope of this latter approach was extended by the preparation of the glucofuranose derivative (28). As expected, rearrangement of this sterically less demanding substrate proceeded under much milder conditions to furnish the oxazolidin-2-one derivative (29) in 73% yield. The sodium-iodide-catalysed isomerisation of *N*-*p*-tolylsulphonyliminocarbonates thus fulfils the criteria set out in the Scheme for the ideal situation in which the isolation of ring-opened intermediates is unnecessary.

Finally, in assessing the viability of the overall sequence, two dominating factors emerge. The first of these, which is subject to experimental control, is the choice of the electron-withdrawing substituent attached to the nitrogen atom of the iminocarbonate ring. The second factor is the wide ranging influence of substrate structure, which determines, in the first instance, the feasibility and subsequent stability of the iminocarbonate. Thus, although the iminocarbonate is almost certainly the kinetically controlled product of an allowed *exo*-cyclisation,[15] ring-opening and subsequent trimerisation of the hydroxycyanate may be favoured on thermodynamic grounds if the ring is strained or the surrounding environment is not sufficiently congested. Thus we were unable to isolate the strained iminocarbonate from the *trans*-2,3-diol (30).

Cyclic iminocarbonates have often been postulated as intermediates in the cyanogen bromide mediated coupling of carbohydrate polymers to polypeptides and similar compounds.[16] We find, however, that the iminocarbonate (23) is stable to cyclohexylamine at room temperature. Thus the reported coupling reactions surely involve the known reaction of the amino-group and the isomeric cyanate function.[17] In any case the polymers used do not contain *cis*-glycol functions of a type which would give iminocarbonates [*cf.* the failure to form an iminocarbonate from (30)].

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 257 spectrometer and u.v. spectra with a Unicam SP 800B spectrometer. ^1H N.m.r. spectra were recorded in deuteriochloroform solution with tetramethylsilane as internal standard on a Varian T-60 instrument. Mass spectra were recorded with an A.E.I. MS 9 instrument. Optical rotations were measured on a Perkin-Elmer 141 polarimeter. All solvents were purified by standard techniques and all evaporations were carried out with a rotary evaporator under vacuum.

1,2-O-*Isopropylidene*-3-O-*methyl*-α-D-*glucofuranose*-5,6-*iminocarbonate* (6).—A solution of butyl-lithium in hexane (1.4 ml, 1.46M) was added dropwise, *via* a syringe, to a

magnetically stirred solution of 1,2-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranose (504.7 mg) in freshly distilled anhydrous tetrahydrofuran (4 ml) under nitrogen and stirring was continued for 1 h at room temperature. After cooling in an ice-bath, a solution of cyanogen bromide (300.4 mg) in tetrahydrofuran (2 ml) was added *via* a syringe and the mixture was allowed to attain room temperature over 1.5 h. The mixture was diluted with water and thoroughly extracted with chloroform. The combined organic extracts were washed with brine, dried (Na_2SO_4), and the solvent removed to yield the title compound (552 mg, 98%) as an unstable foam, $\nu_{max.}$ 3 340 and 1 700 (C=NH) cm^{-1}, τ 4.18 (1 H, d, $J_{1,2}$ 3.8 Hz, H-1), 5.02—5.40 (1 H, m, H-5), 5.48 (1 H, d, $J_{1,2}$ 3.8 Hz, H-2), 5.5—5.8 (4 H, m, 1 H exchanges with D_2O), 6.21 (1 H, d, $J_{3,4}$ 3 Hz, H-3), 6.59 (3 H, s, OMe), and 8.52 and 8.68 (6 H, 2 s, CMe_2).

Thermal Rearrangement of 1,2-O-*Isopropylidene*-3-O-*methyl*-α-D-*glucofuranose*-5,6-*iminocarbonate*.—A freshly prepared sample of the iminocarbonate (6) (310 mg) was heated in an oil-bath maintained at 85 °C for 20 h during which time the complete disappearance of the iminocarbonate stretching frequency at 1 700 cm^{-1} was observed. A solution of freshly distilled benzoyl chloride (0.6 ml) in pyridine (1.4 ml) was then added and the mixture was allowed to stand at room temperature for 36 h. The product was diluted with ether and poured into a mixture of ice and sodium carbonate solution. The ethereal extract was washed with brine, dried (Na_2SO_4), and the solvent removed to give a viscous glass (340 mg). Purification by preparative t.l.c. afforded an amorphous powder (194.5 mg, 45%) which exhibited no sharply defined melting range and could not be induced to crystallise, $\nu_{max.}$ 1 721 (OCOPh) and 1 560 (cyanurate) cm^{-1}; τ 1.95 and 2.60 (5 H, aromatic), 4.08br (1 H, d, $J_{1,2}$ 4.0 Hz), 4.46 (1 H, m, H-5), 5.2—5.8 (4 H, m), 6.22 (1 H, d, $J_{3,4}$ 3.0 Hz, H-3), 6.71 (3 H, s, OMe), and 8.52 and 8.69 (6 H, 2 s, CMe_2) [Found (osmometry): *M*, 1 162. $C_{54}H_{63}O_{21}N_3$ requires *M*, 1 089].

Acid Hydrolysis of 1,2-O-*Isopropylidene*-3-O-*methyl*-α-D-*glucofuranose*-5,6-*iminocarbonate* (6).—To a stirred solution of freshly prepared iminocarbonate (6) (250 mg) in tetrahydrofuran (2.5 ml) under a nitrogen atmosphere was added dropwise, *via* a syringe, a solution of oxalic acid dihydrate (65.2 mg) in tetrahydrofuran (0.5 ml). The reaction mixture was stirred at room temperature for 1.5 h and the resultant turbid solution was poured into sodium carbonate solution and thoroughly extracted with chloroform. The combined organic extract was washed with brine, dried (Na_2SO_4), and the solvent removed to give the corresponding cyclic carbonate (161.4 mg, 64%) as a clear oil, $[\alpha]_D^{20}$ −43° (*c* 6.4, $CHCl_3$) {lit.,[9] $[\alpha]_D^{22}$ −49.4° (*c* 6.4, $CHCl_3$)}; $\nu_{max.}$ 1 800 (C=O) cm^{-1}, τ 4.10 (1 H, d, $J_{1,2}$ 3.2 Hz, H-1), 4.98—5.32 (1 H, m, H-5), 5.38—5.70 (4 H, m), 6.20 (1 H, d, $J_{3,4}$ 2.7 Hz, H-3), 6.60 (3 H, s, OMe), and 8.52 and 8.66 (6 H, 2 s, CMe_2).

5-O-*Carbamoyl*-6-*chloro*-6-*deoxy*-1,2-O-*isopropylidene*-3-O-*methyl*-α-D-*glucofuranose* (9).—A solution of anhydrous oxalic acid (60 mg) in dry tetrahydrofuran (1 ml) was added *via* a syringe to a magnetically stirred solution of anhydrous lithium chloride (220.3 mg) and freshly prepared iminocarbonate (6) (291.2 mg) in dry tetrahydrofuran (3 ml) under nitrogen. The mixture was stirred at room temperature for 20 h and solvent was then removed *in vacuo*. The solid residue was taken up in warm chloroform, filtered to remove inorganic salts, and then concentrated to yield the *title compound* as a solid (290.0 mg, 84%), m.p. 151—151.5 °C (from benzene), $[\alpha]_D^{30}$ −30° (*c* 5.24, $CHCl_3$); $\nu_{max.}$ 3 540 and 3 428 (N–H) and 1 735 (C=O) cm^{-1}; τ 4.06 (1 H, d, $J_{1,2}$ 3.8 Hz, H-1), 4.58—5.0 (3 H, m, 2 H, exchanges with D_2O, H-5 and NH_2), 5.43 (1 H, d, $J_{1,2}$ 3.8 Hz, H-2), 5.53 and 5.83 (1 H, dd, $J_{3,4}$ 3.5, $J_{4,5}$ 9.0 Hz, H-4), 6.0—6.4 (3 H, m, H-3, -6, and -6′), 6.60 (3 H, s, OMe), 8.52 and 8.68 (6 H, 2 s, CMe_2); *m/e* 282/280 (M^+ − 15) (Found: C, 48.8; H, 6.25; N, 4.2; Cl, 11.1. $C_{11}H_{18}ClNO_6 \cdot 1/3C_6H_6$ requires C, 48.55; H, 6.25; N, 4.35; Cl, 11.02%) (benzene ratio confirmed by n.m.r.). By using sodium iodide in place of lithium chloride, the analogous iodourethane derivative was prepared in 76% yield as an unstable waxy solid which turned yellow on standing; $\nu_{max.}$ 3 520 and 3 418 (N–H) and 1 732 (C=O) cm^{-1}; τ 4.08 (1 H, d, $J_{1,2}$ 3.8 Hz, H-1), 4.6—4.9 (3 H, m, 2 H, exchanges D_2O, H-5 + NH_2), 5.40 (1 H, d, $J_{1,2}$ 3.8 Hz, H-2), 5.64 and 5.78 (1 H, dd, $J_{3,4}$ 3.6, $J_{4,5}$ 8.2 Hz, H-4), 6.10—6.50 (3 H, m, H-3, -6, and -6′), 6.58 (3 H, s, OMe), and 8.48 and 8.64 (6 H, 2 s, CMe_2); *m/e* 372 (M^+ − 15).

Attempted Cyclisation Reaction of 5-O-*Carbamoyl*-6-*deoxy*-6-*halogeno*-1,2-O-*isopropylidene*-3-O-*methyl*-α-D-*glucofuranose*.—(A) *Under basic conditions*. Sodium hydride (137.7 mg, 100%) was added all in one portion to a magnetically stirred solution of the chlorourethane (9) (231.2 mg) and imidazole (6 mg) in dry tetrahydrofuran (5 ml) under an atmosphere of nitrogen with cooling in a carbon tetrachloride–solid CO_2 bath. The mixture was allowed to warm to room temperature over 14 h and aqueous tetrahydrofuran was then added to quench excess of hydride. Solvent was removed *in vacuo* and the residue was diluted with water and thoroughly extracted with chloroform. The combined organic extracts were washed with brine, dried (Na_2SO_4), and the solvent removed to give a brown glass (148.2 mg). Purification by column chromatography on silica gel yielded 5,6-anhydro-1,2-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranose (130.2 mg, 77%) as a clear oil, $[\alpha]_D^{22}$ −66° (*c* 1.1, $CHCl_3$) {lit.,[11] $[\alpha]_D^{22}$ −67° (*c* 1.1, $CHCl_3$)}; τ 4.09 (1 H, d, $J_{1,2}$ 3.8 Hz, H-1), 5.43 (1 H, d, $J_{1,2}$ 3.8 Hz, H-2), 3.9—4.4 (2 H, m, H-3 and -4), 6.53 (3 H, s, OMe), 6.76 (1 H, m, H-5), 7.20 (2 H, m, H-6 and -6′), and 8.58 and 8.71 (6 H, 2 s, CMe_2).

Several bases of differing strength and nucleophilicity were also unsuccessfully examined.

(B) *Silver-ion-promoted cyclisation*. A solution of freshly prepared iodourethane (10) (351.5 mg) in dry pyridine (1 ml) was added *via* a syringe to a magnetically stirred solution of silver nitrate (390.3 mg) in pyridine (2 ml) under nitrogen. Aliquot monitoring by t.l.c. revealed unchanged starting material after 14 h at room temperature. The mixture was then heated in an oil-bath maintained at 80 °C for 20 h, cooled, diluted with ether, washed with water, brine, dried (Na_2SO_4), and the solvent removed to give a clear oil (120.2 mg). Purification by p.l.c. afforded 1,2-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranose-5,6-carbonate (93.5 mg, 39%) as the major product, identical with the previously described sample.

(C) *Reaction of chlorourethane* (9) *with metallic sodium*. Sodium metal (130 mg) was added to a solution of the chlorourethane (169.6 mg) in tetrahydrofuran (3 ml) at room temperature under nitrogen and the mixture was stirred for 16 h and then quenched by the careful, dropwise addition of aqueous tetrahydrofuran. Removal of tetrahydrofuran *in vacuo* followed by thorough extraction of the aqueous phase with chloroform, washing with brine, drying (Na_2SO_4), and solvent removal afforded a yellow oil (91.0 mg). Two

major components were separated by preparative t.l.c. The more polar compound (67.0 mg, 50%) proved to be 1,2-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranose by comparison with an authentic sample. The less polar compound (11.7 mg, 9%) was shown to be 6-deoxy-1,2-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranose, $[\alpha]_D^{22}$ −62.6 (*c* 0.86, $CHCl_3$) {lit.,[13] $[\alpha]_D^{20}$ −64° (*c* 0.7, $CHCl_3$)}; $\nu_{max.}$ 3 580—3 500 (OH) cm^{-1}; τ 4.05 (1 H, d, $J_{1.2}$ 3.9 Hz, H-1), 5.39 (1 H, d, $J_{1.2}$ 3.9 Hz, H-2), 3.8—4.2 (3 H, m, H-3, -4, and -5), 4.54 (3 H, s, OMe), 7.4—7.6 (1 H, exchanges with D_2O, OH), 8.54 and 8.71 (6 H, 2 s, CMe_2), and 8.69 (3 H, d, $J_{5.6}$ 6 Hz, CH_3).

5-O-(N-*Acetylcarbamoyl*)-6-*chloro*-6-*deoxy*-1,2-O-*isopropylidene*-3-O-*methyl*-α-D-*glucofuranose* (13).—Acetyl chloride (0.2 ml, freshly distilled from *NN*-dimethylaniline) was added rapidly *via* a syringe to a freshly prepared solution of the cyclic iminocarbonate (6) (267.8 mg) in dry benzene (2 ml) and the mixture was stirred for 22 h at room temperature under nitrogen. Removal of solvent and excess of acetyl chloride *in vacuo* followed by preparative t.l.c. furnished the *title compound* (177.2 mg, 51%) as a clear oil, $[\alpha]_D^{20}$ −25.5° (*c* 10.6, $CHCl_3$); $\nu_{max.}$ 3 386 (NH) and 1 763 and 1 715 (C=O) cm^{-1}; τ 2.30br (1 H, exchanges with D_2O, NH), 4.12 (1 H, d, $J_{1.2}$ 3.8 Hz, H-1), 4.75 (1 H, m, H-5), 5.42 (1 H, d, $J_{1.2}$ 3.8 Hz, H-2), 5.58 and 5.67 (1 H, AB q, $J_{3.4}$ 3.0, $J_{4.5}$ 9.0 Hz, H-4), 6.0—6.4 (3 H, m, H-3, -6, and -6′), 6.62 (3 H, s, OMe), 7.58 (3 H, s, $NCOCH_3$), and 8.55 and 8.68 (6 H, 2 s, CMe_2); *m/e* 324/322 (M^+ − 15) (Found: C, 46.3; H, 6.3; N, 4.35; Cl, 10.3. $C_{13}H_{20}ClNO_7$ requires C, 46.25; H, 5.95; N, 4.15; Cl, 10.5%).

N-*Acetyloxazolidin*-2-*one Derivative of* 6-*Amino*-6-*deoxy*-1,2-O-*isopropylidene*-3-O-*methyl*-α-D-*glucofuranose* (14).—Sodium hydride (22.8 mg) was added all in one portion to a magnetically stirred solution of the *N*-acetylchlorourethane (13) (177.0 mg) in dry tetrahydrofuran (2 ml) under nitrogen at room temperature and stirring was continued for 6 h. The solvent was then removed *in vacuo* and acetic anhydride (3 ml) and sodium acetate (165 mg) were added to the residue. The mixture was then heated in an oil-bath maintained at 80 °C for 18 h. Excess of acetic anhydride and acetic acid were then removed under high vacuum and the residue was taken up in chloroform, filtered, and the solvent evaporated to give a dark yellow oil (143.5 mg). Purification by preparative t.l.c. afforded the *title derivative* (78.9 mg, 50%), m.p. 142—143.5 °C [from ether–light petroleum (b.p. 40—60°)]; $[\alpha]_D^{20}$ −89.95° (*c* 2.04, $CHCl_3$); $\nu_{max.}$ 1 795 and 1 700 (C=O) cm^{-1}; τ 4.10 (1 H, d, $J_{1.2}$ 3.8 Hz, H-1), 5.0—5.35 (1 H, m, H-5), 5.43 (1 H, d, $J_{1.2}$ 3.8 Hz, H-2), 5.57 and 5.68 (1 H, AB q, $J_{3.4}$ 3.8, $J_{4.5}$ 7.0 Hz, H-4), 3.8—4.18 (3 H, m, H-3, -6, and -6′), 6.59 (3 H, s, OMe), 7.49 (3 H, s, $NCOCH_3$), and 8.52 and 8.69 (6 H, 2 s, CMe_2); *m/e* 286 (M^+ − 15) (Found: C, 51.75; H, 6.35; N, 4.55. $C_{13}H_{19}NO_7$ requires C, 51.8; H, 6.35; N, 4.65%).

6-*Acetamido*-5-*acetoxy*-6-*deoxy*-1,2-O-*isopropylidene*-3-O-*methyl*-α-D-*glucofuranose* (16).—A vast excess of sodium hydride (200 mg) was added in portions to a stirred solution of the *N*-acetylchlorourethane (13) (84.0 mg) in dry tetrahydrofuran (5 ml) under nitrogen at room temperature and stirring was continued for 15 h. The mixture was quenched by the addition of wet tetrahydrofuran and all solvents were removed *in vacuo*. The residue was taken up in chloroform and washed with brine, dried (Na_2SO_4), and the solvent removed to give a clear oil (76.0 mg) which was dissolved in ethanol (4 ml) and water (1 ml) containing potassium hydroxide (226.5 mg). The mixture was heated under reflux for 5 h and then all solvent was removed *in vacuo*. The residue was taken up in chloroform, filtered, and the solvent removed to give a brown oil (67 mg) which was dissolved in acetic anhydride (0.5 ml) and pyridine (1.5 ml). After 26 h at room temperature, removal of all solvents under high vacuum gave a brown residue which was chromatographed on a short silica gel column to give the *title compound* as an oil (46.1 mg, 58%), $[\alpha]_D^{20}$ −12.9° (*c* 4.61, $CHCl_3$); $\nu_{max.}$ 3 538 (NH), 1 735 ($OCOCH_3$), and 1 669 ($NHCOCH_3$) cm^{-1}; τ 3.84br (1 H, exchanges with D_2O, NH), 4.07 (1 H, d, $J_{1.2}$ 4.0 Hz, H-1), 4.64—5.0 (1 H, m, H-5), 5.40 (1 H, d, $J_{1.2}$ 4.0 Hz, H-2), 5.68 and 5.84 (1 H, AB q, $J_{3.4}$ 3.0, $J_{4.5}$ 9.1 Hz, H-4), 6.19—6.55 (3 H, m, H-3, -6, and -6′), 6.60 (3 H, s, OMe), 7.93 and 8.03 (6 H, 2 s, $NCOCH_3$ and $OCOCH_3$), and 8.48 and 8.68 (6 H, 2 s, CMe_2); *m/e* 302 (M^+ − 15) (Found: C, 52.9; H, 7.5; N, 4.25. $C_{14}H_{23}NO_7$ requires C, 53.0; H, 7.3; N, 4.4%).

6-*Azido*-6-*deoxy*-1,2-O-*isopropylidene*-3-O-*methyl*-α-D-*glucofuranose*.—Recrystallised toluene-*p*-sulphonyl chloride (2.0 g) was added all in one portion to a stirred solution of 1,2-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranose (2.44 g) in pyridine (20 ml) with cooling in an ice-bath. The reaction mixture was allowed to come to room temperature and stirring was continued for a further 46 h. Pyridine was removed *in vacuo* at room temperature, water was added, and the product was thoroughly extracted with diethyl ether. The combined ethereal extracts were washed with copper sulphate solution, water, brine, and then dried (Na_2SO_4). Removal of solvent gave the monotosylate (2.9 g) as a light yellow oil which was used without further purification. The tosylate (2.9 g) and sodium azide (4.0 g) were dissolved in acetone (25 ml) and water (18 ml) and the clear solution was heated under reflux for a period of 48 h. The solvent was then completely removed *in vacuo*, benzene was added, and the mixture was refluxed in a Dean and Stark water separator for 3 h, filtered to remove inorganic salts, and the filtrate concentrated under reduced pressure to give the *title compound* as a yellow oil (2.3 g, 85%). An analytical sample was prepared by short-path distillation, b.p. 85—90 °C at 5 × 10^{-4} mmHg; $[\alpha]_D^{20}$ −40.54° (*c* 5.4, $CHCl_3$); $\nu_{max.}$ 3 540br (OH) and 2 120 (N_3) cm^{-1}; τ 4.18 (1 H, d, $J_{1.2}$ 4.0 Hz, H-1), 5.45 (1 H, d, $J_{1.2}$ 4.0 Hz, H-2), 5.8—4.3 (3 H, m, H-3, -4, and -5), 4.4—4.5 (2 H, m, H-6 and -6′), 4.58 (3 H, s, OMe), and 7.14br (1 H, exchanges with D_2O, OH) (Found: C, 46.25; H, 6.4; N, 16.05. $C_{10}H_{17}N_3O_5$ requires C, 46.35; H, 6.6; N, 16.2%).

6-*Acetamido*-5-*acetoxy*-6-*deoxy*-1,2-O-*isopropylidene*-3-O-*methyl*-α-D-*glucofuranose*.—Platinum oxide (50 mg) was added to a solution of 6-azido-6-deoxy-1,2-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranose (260 mg) in absolute ethanol (25 ml) and the mixture was hydrogenated at 1 atm with vigorous stirring for 72 h. The mixture was then filtered through a pad of Celite and the solvent removed *in vacuo* to give an oil (250 mg) which was dissolved in acetic anhydride (6 ml) and pyridine (3 ml) and allowed to stand at room temperature for 20 h. Solvent and excess of reagent were removed under high vacuum and the residue was taken up in chloroform and successively washed with sodium hydrogencarbonate solution, water, copper sulphate solution, and brine, and then dried (Na_2SO_4). Removal of solvent and column chromatography on silica gel afforded the diacetate (260.0 mg, 82%) as an oil, $[\alpha]_D^{20}$ −13.1° (*c* 3.8, $CHCl_3$). The spectral properties of this substance were identical in every respect with those of the diacetate prepared by the iminocarbonate route.

1-*Methyl*-2-*bromoethyl* N-*Acetylcarbamate* (17).—Butyl-lithium (4 ml, 2.5M in hexane) was added *via* a syringe to a magnetically stirred mixture of propane-1,2-diol (762.0 mg) in dry benzene (15 ml) under nitrogen at room temperature. After 35 min the mixture was cooled in an ice-bath and a solution of cyanogen bromide (1.497 g) in benzene (10 ml) was added *via* a syringe. The mixture was allowed to attain room temperature over 1.5 h prior to the addition of acetyl bromide (2.5 ml, neat, freshly distilled from *NN*-dimethylaniline) *via* a syringe. The mixture was then stirred at room temperature for 20 h. Solvent and excess of acetyl bromide were then removed *in vacuo* and the residue was taken up in chloroform, and washed with brine. The organic phase was dried (Na_2SO_4) and the solvent evaporated to give a viscous oil (1.93 g). Rapid short-column chromatography on silica gel gave the desired carbamate (1.41 g, 63%) as a relatively unstable waxy solid which was used without further purification, $\nu_{max.}$ 3 280br (NH), and 1 765 and 1 700br (C=O) cm^{-1}; τ 1.78br (1 H, exchanges with D_2O, N–H), 4.87 (1 H, sextet, J_{AB} 6.4, J_{AC} 4.2 Hz, HCO), 6.51 (2 H, d, J_{AC} 4.2 Hz, CH_2Br), 7.54 (3 H, s, CH_3CON), and 8.59 (3 H, d, J_{AB} 6.4 Hz, CH_3CO); *m/e* 225/223 (M^+).

5-*Methyloxazolidin*-2-*one* (18) *by Cyclisation of Carbamate* (17).—Sodium hydride (254.8 mg) was added all in one portion to a stirred solution of the carbamate (17) (360.5 mg) in dry tetrahydrofuran (4 ml) under nitrogen and stirring was continued at room temperature for 18 h. The mixture was quenched by the addition of water and all solvents were removed *in vacuo*. The residue was extracted with warm chloroform, filtered, and the solvent removed to give a dark brown oil (102.5 mg) which was purified by short-path distillation to yield 5-methyloxazolidin-2-one (81.0 mg, 50%) as a liquid, b.p. 98—103 °C at 0.5 mmHg; $\nu_{max.}$ 3 340br (NH) and 1 760br (C=O) cm^{-1}; τ 3.38br (1 H, exchanges with D_2O, NH), 5.25 (1 H, complex sextet, J_{AB} 6, $J_{AC} \simeq J_{AC'}$ = 7 Hz, CHO), 4.33 and 6.81 (2 H, 2 t, $J_{AC} \simeq J_{AC'}$ = 7 Hz, CHH'NH), and 8.58 (3 H, d, J_{AB} 6 Hz, CH_3).

5-*Methyloxazolidin*-2-*one* (18).—An authentic sample was prepared by a literature method [14] involving reaction of cyanuric acid with propylene oxide in dimethylformamide, b.p. 113—118 °C at 1.5 mmHg. The chromatographic and spectral behaviour of this substance was identical with the sample prepared by the carbamate cyclisation above.

Methyl-5-O-*methyl*-α-D-*ribofuranoside*-2,3-*iminocarbonate* (21).—A solution of butyl-lithium in hexane (1.5 ml, 1.58M) was added dropwise *via* a syringe to a magnetically stirred solution of methyl 5-*O*-methyl-α-D-ribofuranoside [18] (411.3 mg) in dry benzene (5 ml) under nitrogen. After 35 min at room temperature, the reaction mixture was cooled in an ice-bath and a solution of cyanogen bromide (313 mg) in benzene (2 ml) was added *via* a syringe. The mixture was maintained at 0 °C for 0.5 h and then at room temperature for 1 h, diluted with benzene, and washed with water. The aqueous phase was extracted with chloroform and the combined organic extracts were washed with brine, dried (Na_2SO_4), and the solvent removed to give the iminocarbonate as an oil (387.4 mg, 83%), $\nu_{max.}$ 3 360 (NH) and 1 700 (C=N) cm^{-1}; τ 4.80br (1 H, exchanges with D_2O, NH), 4.80—5.10 (3 H, m, H-1 and -3), 5.54 and 5.70 (1 H, dd, $J_{4.5}$ 6, $J_{4.5'}$ 6 Hz, H-4), 6.66 and 6.68 (6 H, 2 s, 2 OMe), and 6.55—6.70 (2 H, m, H-5 and -5').

Acid Hydrolysis of Methyl-5-O-*methyl*-α-D-*ribofuranoside*-2,3-*iminocarbonate*. *Preparation of Methyl*-5-O-*methyl*-α-D-*ribofuranoside*-2,3-*carbonate*.—Oxalic acid dihydrate (125 mg) in water (1 ml) was added to a magnetically stirred solution of freshly prepared iminocarbonate (21) (362 mg) in tetrahydrofuran (4 ml) and the mixture was stirred at room temperature for 2.0 h, poured into a dilute solution of sodium hydrogencarbonate, and extracted with benzene (1×) and chloroform (2×). The combined organic extracts were washed with brine, dried (Na_2SO_4), and the solvent removed to give the cyclic carbonate (308.9 mg, 85%) as a clear oil. An analytical sample was prepared by short-path distillation, b.p. 85—90 °C at 5 × 10^{-4} mmHg; $[\alpha]_D^{20}$ −94.4° (*c* 0.61, $CHCl_3$); $\nu_{max.}$ 1 800 (C=O) cm^{-1}; τ 4.80—5.10 (3 H, m, H-1, -2, and -3), 5.45 and 5.60 (1 H, dd, $J_{4.5}$ 6, $J_{4.5'}$ 6 Hz, H-4), 6.63 and 6.65 (6 H, 2 s, 2 OMe), and 6.55—6.70 (2 H, m, H-5 and -5'); *m/e* 172 (M^+ — OMe) (Found: C, 47.2; H, 5.85. $C_8H_{12}O_6$ requires C, 47.05; H, 5.9%).

Ring-opening of Methyl-5-O-*methyl*-α-D-*ribofuranoside*-2,3-*iminocarbonate* (21) *with Acetyl Chloride*.—Acetyl chloride (0.6 ml, freshly distilled from *NN*-dimethylaniline) was added to a solution of freshly prepared iminocarbonate (21) (328 mg) in chloroform (4 ml) and the mixture was sealed under nitrogen in a pressure tube. After 1.5 h at room temperature, the tube was heated at 80 °C for 16 h, cooled, opened, and solvent and excess of acetyl chloride were removed *in vacuo*. Column chromatography on silica gel afforded methyl-5-*O*-methyl-α-D-ribofuranoside-2,3-carbonate (61.5 mg, 19%) and an isomeric mixture of the ring-opened *N*-acetylchlorourethanes (19) and (20) (316 mg, 70%). The isomers could be separated by careful column chromatography on silica gel HF 50 (7 g) by elution with 30% diethyl ether—70% light petroleum (b.p. 40—60°), collecting 10-ml fractions. The less polar isomer (19) (186.2 mg) was an oil; $[\alpha]_D^{20}$ +163.7° (*c* 0.54, $CHCl_3$); $\nu_{max.}$ 3 385 (NH) and 1 765 and 1 715 (C=O) cm^{-1}; τ 1.75br (1 H, exchanges with D_2O, NH), 4.86 (2 H, m, H-1 and -3), 5.53 [2 H, m, H-2(Cl) and H-4], 6.37 (2 H, m, H-5 and -5'), 6.58 and 6.60 (6 H, 2 s, 2 OMe), and 7.58 (3 H, s, $NCOCH_3$); *m/e* 250 (M^+ — OMe). The more polar isomer (20) (130.7 mg) was an oil, $[\alpha]_D^{20}$ −39.4° (*c* 0.17, $CHCl_3$); $\nu_{max.}$ 3 382 (NH) and 1 765 and 1 715 (C=O) cm^{-1}; τ 1.85br (1 H, exchanges with D_2O, NH), 4.75 (1 H, s, H-2), 4.97 (1 H, s, H-1), 5.28—5.77 [2 H, m, H-3(Cl) and H-4], 6.25 (2 H, m, H-5 and -5'), 6.55 and 6.57 (6 H, 2 s, 2 OMe), and 7.53 (3 H, s, $NCOCH_3$); *m/e* 250 (M^+ — OMe). The tentative structural assignments of isomers (19) and (20) are based on chemical-shift and double-irradiation studies. An analytical sample of the isomeric mixture was prepared by short-path distillation, b.p. 150 °C at 3 × 10^{-3} mmHg (Found: C, 42.65; H, 5.85; N, 4.7. Calc. for $C_{10}H_{16}ClNO_6$: C, 42.65; H, 5.7; N, 4.9%).

Attempted Cyclisation of N-*Acetylchlorourethane* (19) *with Sodium Hydride in Tetrahydrofuran*.—A suspension of sodium hydride (33.5 mg) and imidazole (3.6 mg) in dry tetrahydrofuran (0.5 ml) was cooled in an ice-bath while stirring under nitrogen. A solution of the *N*-acetylchlorourethane (52.28 mg) in tetrahydrofuran (4 ml) was added dropwise, *via* a syringe, and the mixture was allowed to warm to room temperature. Aliquot monitoring by analytical t.l.c. revealed the slow formation of a less polar product and the complete absence of starting material after 96 h. The mixture was quenched by the addition of wet tetrahydrofuran and solvent was removed *in vacuo*. The residue was taken up in water (5 ml) and thoroughly extracted with chloroform (5 × 5 ml), washed with brine,

dried (Na_2SO_4), and the solvent removed *in vacuo* to give an oil (24.4 mg, 81%) which was not purified further since the i.r. spectrum displayed no carbonyl absorption.

1,2,5,6-Di-O-isopropylidene-D-mannitol-3,4-iminocarbonate (23).—A solution of butyl-lithium in hexane (3.5 ml, 1.58M) was added slowly *via* a syringe to a stirred solution of 1,2;5,6-di-*O*-isopropylidene-D-mannitol (1.31 g) in dry tetrahydrofuran (10 ml) under nitrogen at room temperature. After 30 min, the mixture was cooled in an ice-bath and a solution of cyanogen bromide (641.8 mg) in tetrahydrofuran (5 ml) was added dropwise *via* a syringe. The mixture was allowed to attain room temperature over 1.5 h, and solvent and excess of cyanogen bromide were removed *in vacuo*. The residue was diluted with water and thoroughly extracted with chloroform. The organic phase was washed with brine, dried (Na_2SO_4), and the solvent removed to yield the *title compound* as a stable solid (1.45 g, 100%), m.p. 133.5—138 °C [from ethyl acetate and light petroleum (b.p. 100—120°)]; $[\alpha]_D^{17}$ −10.65° (*c* 1.69, $CHCl_3$); $\nu_{max.}$ 3 345 (NH) and 1 705 (C=N) cm^{-1}; τ 4.80br (1 H, exchanges with D_2O, NH), 5.40—6.18 (8 H, m, complex), and 8.54 and 8.68 (12 H, 2 s, 2 CMe_2); *m/e* 272 (M^+ − 15) (Found: C, 54.45; H, 7.15; N, 5.15. $C_{13}H_{21}NO_6$ requires C, 54.35; H, 7.4; N, 4.9%).

1,2;5,6-Di-O-isopropylidene-D-mannitol-3,4-carbonate.— A solution of butyl-lithium in hexane (0.7 ml, 1.58M) was added *via* a syringe to a magnetically stirred solution of 1,2;5,6-di-*O*-isopropylidene-D-mannitol (266 mg) in tetrahydrofuran (2 ml) under nitrogen at room temperature. After 30 min, the mixture was cooled in an ice-bath and a solution of cyanogen bromide (128 mg) in tetrahydrofuran (1 ml) was added *via* a syringe. The reaction was allowed to warm to room temperature over 1.5 h, and a solution of oxalic acid dihydrate (75.3 mg) in water (0.5 ml) was added *via* a syringe. Stirring was continued for 1.5 h and solvent was then removed *in vacuo*. The aqueous residue was poured into a solution of sodium hydrogencarbonate and thoroughly extracted with chloroform. The organic extract was washed with brine, dried (Na_2SO_4), and the solvent removed to yield the title compound (219.4 mg, 82%) as a solid, m.p. 144—146 °C [from ethyl acetate–light petroleum (b.p. 60—80 °C)] (lit.,[19] 146.5—147 °C); $[\alpha]_D^{20}$ 13.5° (*c* 1.74, acetone) {lit.,[19] $[\alpha]_D^{20}$ 14.9 (*c* 1.8, acetone)}; $\nu_{max.}$ 1 805 (C=O) cm^{-1}; τ 5.40—6.20 (8 H, m, complex) and 8.54 and 8.63 (12 H, 2 s, 2 CMe_2); *m/e* 288 (M^+).

Reaction of Iminocarbonate (23) *with Acetyl Bromide*.—Freshly distilled acetyl bromide (50 μl) was added to a solution of the iminocarbonate (23) (143 mg) in deuteriochloroform (0.5 ml) and the progress of the reaction was monitored in an n.m.r. tube, which indicated the rapid growth of a new acetyl absorption at τ 7.48. Analytical t.l.c., however, revealed only cyclic carbonate, thus suggesting that salt formation without rearrangement was occurring. Since an earlier experiment had demonstrated that attempted thermolysis at this stage (80 °C, 1.5 h) led to concomitant destruction of the isopropylidene groupings, solvent and excess of acetyl bromide were removed *in vacuo*. The residue was dissolved in dry acetonitrile and heated under reflux. Aliquot monitoring by t.l.c. revealed only cyclic carbonate. No evidence (i.r., n.m.r., and t.l.c.) was obtained for the formation of the desired *N*-acetylbromourethane.

1,2;5,6-Di-O-isopropylidene-D-mannitol-3,4-N-cyanoiminocarbonate (25).—Diphenylamine (84.3 mg), cyanogen bromide (171 mg), and 1,2;5,6-di-*O*-isopropylidene-D-mannitol-2,3-iminocarbonate (155 mg) were dissolved in dry benzene (1 ml) and heated in a sealed tube maintained at 76 °C for 20.5 h. The tube was cooled, opened, and benzene and excess of cyanogen bromide were removed *in vacuo*. The residue was taken up in ether, filtered, and the solvent evaporated to give a crude product (281.6 mg) which was chromatographed on silica gel yielding cyclic carbonate (24.9 mg, 16%) and the *title compound* (54.5 mg, 32%), m.p. 108.5—109 °C [from ethyl acetate–light petroleum (b.p. 100—120°)]; $[\alpha]_D^{23}$ −44.8° (*c* 0.3, $CHCl_3$); $\nu_{max.}$ 2 218 (C≡N) and 1 668 (C=N) cm^{-1}; τ 5.19 (2 H, m, H-3 and -4), 5.42—6.22 (6 H, m), and 8.52 and 8.65 (12 H, 2 s, 2 CMe_2); *m/e* 297 (M^+ − 15) (Found: C, 53.75; H, 6.4; N, 8.9. $C_{14}H_{20}N_2O_6$ requires C, 53.85; H, 6.45; N, 8.95%).

Attempted Isomerisation of 1,2;5,6-Di-O-isopropylidene-D-mannitol-3,4-N-cyanoiminocarbonate with Sodium Iodide in Acetone.—A solution of the *N*-cyanoiminocarbonate (25) (54.5 mg) in [$^2H_6$]acetone (0.5 ml) saturated with sodium iodide (305.4 mg) was heated in a sealed n.m.r. tube maintained at 85 °C for 7 h. The temperature was then raised to 110 °C over 3.5 h and heating was continued for a further 60 h. Monitoring by n.m.r. spectroscopy revealed some breakdown of the isopropylidene groupings but no evidence for the rearranged product. The tube was cooled, opened, and acetone was evaporated. The residue was taken up in chloroform and water and the aqueous phase was thoroughly extracted with chloroform. The combined extracts were washed with brine, dried (Na_2SO_4), and the solvent removed to give a crude product (36.2 mg). I.r. and t.l.c. analysis of this product indicated it to be a mixture of cyclic carbonate and unchanged starting material, $\nu_{max.}$ 2 218, 1 805, and 1 668 cm^{-1}.

1,2;5,6-Di-O-isopropylidene-D-mannitol-3,4-(N-p-tolylsulphonyl)iminocarbonate (26).—Freshly recrystallised toluene-*p*-sulphonyl chloride (383.2 mg) was added all in one portion to a solution of the iminocarbonate (23) (571.6 mg) in dry pyridine (3 ml) and the mixture was swirled to effect dissolution and allowed to stand at room temperature for 65.5 h. The bulk of the pyridine was removed *in vacuo* and the residue was taken up in chloroform and water, washed with brine, dried (Na_2SO_4), and the solvent removed to give a crude solid product (1.0013 g) which was purified by short-column silica gel chromatography and finally by recrystallisation to yield the *title compound* (610 mg, 70%), m.p. 119.5—120 °C [from ethyl acetate–light petroleum (b.p. 100—120°)]; $[\alpha]_D^{17}$ −21.62° (*c* 0.74, $CHCl_3$); $\nu_{max.}$ 1 638 (C=NTs) cm^{-1}; τ 2.2 and 2.75 (4 H, AB, aromatic), 5.42 (2 H, m, H-3 and -4), 5.72—6.22 (6 H, m), 7.58 (3 H, s, CH_3), and 8.61 and 8.72 (12 H, 2 s, 2 CMe_2); *m/e* 441 (M^+) and 426 (M^+ − 15) (Found: C, 54.4; H, 6.1; N, 3.35; S, 7.35. $C_{20}H_{27}NO_8S$ requires C, 54.4; H, 6.15; N, 3.15; S, 7.25%).

N-p-Tolylsulphonyloxazolidin-2-one Derivative of 3-Amino-3-deoxy-1,2;5,6-di-O-isopropylidene-D-mannitol (27).—Sodium iodide (487.7 mg), the tosyliminocarbonate (26) (106.3 mg), and [$^2H_6$]acetone (0.6 ml) were heated in a sealed n.m.r. tube at a temperature of 115 °C for 72 h. The tube was cooled, opened, and solvent was removed *in vacuo*. The residue was taken up in chloroform and water, and the aqueous phase was thoroughly extracted with chloroform. The combined organic extracts were washed with brine, dried (Na_2SO_4), and the solvent removed to give a viscous glass (101.3 mg). Preparative t.l.c. yielded a fraction (32.6 mg) from which cyclic carbonate (14 mg) was separated by fractional crystallisation from ethyl acetate–light

petroleum (b.p. 100—120°). Concentration of the mother liquors yielded the rearranged derivative (32) (18 mg, 17%) as an oil; $[\alpha]_D$ −28.6° (*c* 0.56, EtOAc); $\nu_{max.}$ 1 785 (C=O) cm^{-1}; τ 2.12 and 2.70 (4 H, AB q, aromatic), 5.18—4.26 (8 H, m), 7.54 (3 H, s, CH_3), and 8.52, 8.60, 8.65, and 8.72 (12 H, 4 s, 2 CMe_2); *m/e* 426 (M^+ − 15) (Found: C, 54.3; H, 6.1; N, 3.05. $C_{20}H_{27}NO_8S$ requires C, 54.4; H, 6.15; N, 3.15%).

1,2-O-*Isopropylidene*-3-O-*methyl*-α-D-*glucofuranose*-5,6-(N-p-*tolylsulphonyl*)*iminocarbonate* (28).—Freshly recrystallised toluene-*p*-sulphonyl chloride (950 mg) was added all in one portion to a stirred solution of freshly prepared 1,2-*O*-isopropylidene-3-*O*-methyl-α-D-glucofuranose-5,6-iminocarbonate (736.2 mg) in chloroform (4 cm) containing triethylamine (350 mg) and the reaction was stirred at room temperature for 48 h, diluted with chloroform, washed with water, brine, dried (Na_2SO_4), and the solvent removed to give a brown oil (1.740 g). Purification by column chromatography on silica gel gave the *title compound* as a foam (990.2 mg, 84%); $[\alpha]_D^{21}$ −36.8° (*c* 0.5, $CHCl_3$); $\nu_{max.}$ 1 640 (C=NTs) cm^{-1}; τ 2.18 and 2.73 (4 H, AB q, aromatic), 4.14 (1 H, d, $J_{1,2}$ 3.5 Hz, H-1), 4.70—5.08 (1 H, m, H-5), 5.23—5.58 (4 H, m, H-2, -4, -6, and -6′), 6.18 (1 H, d, $J_{3,4}$ 3.8 Hz, H-3), 6.65 (3 H, s, OMe), 7.60 (3 H, s, CH_3), and 8.55 and 8.72 (6 H, 2 s, CMe_2); *m/e* 413 (M^+ weak) (Found: C, 52.0; H, 5.7; N, 3.45. $C_{18}H_{23}NO_8S$ requires C, 52.3; H, 5.6; N, 3.4%).

N-p-*Tolylsulphonyloxazolidin*-2-*one Derivative of* 6-*Amino*-6-*deoxy*-1,2-O-*isopropylidene*-3-O-*methyl*-α-D-*glucofuranose* (29).—Sodium iodide (49 mg) was added to a solution of the tosyliminocarbonate (28) (126.6 mg) in [$^2H_6$]acetone (0.5 ml) and the mixture was sealed in an n.m.r. tube and heated at a temperature of 70 °C for 5 h. The tube was cooled, opened, and solvent was evaporated. The residue was taken up in chloroform and water, and the aqueous phase was thoroughly extracted with chloroform. The combined organic extracts were washed with brine, dried (Na_2SO_4), and the solvent removed to give a crude product (137.8 mg) which was purified by short-column chromatography on silica gel to yield the rearranged *title derivative* (92.6 mg, 73%), as a foam; $[\alpha]_D^{21}$ −28.8° (*c* 0.29 $CHCl_3$); $\nu_{max.}$ 1 790 (C=O) cm^{-1}; τ 2.11 and 2.64 (4 H, AB q, aromatic), 6.13 (1 H, d, $J_{1,2}$ 3.8 Hz, H-1), 6.84—5.24 (1 H, m, H-5), 5.44 (1 H, d, $J_{1,2}$ 3.8 Hz, H-2), 5.70 (1 H, m, H-4), 5.90 and 6.06 (2 H, H-6 and -6′), 6.21 (1 H, d, $J_{3,4}$ 4 Hz, H-3), 6.60 (3 H, s, OMe), 7.55 (3 H, s, CH_3), and 8.55 and 8.69 (6 H, 2 s, CMe_2); *m/e* 398 (M^+ − 15) (Found: C, 52.7; H, 5.75; N, 3.1. $C_{18}H_{23}NO_8S$ requires C, 52.3; H, 5.6; N, 3.4%).

Attempted Formation and Characterization of Methyl-4,6-O-*benzylidene*-α-D-*glucopyranoside*-2,3-*iminocarbonate*.—To a magnetically stirred solution of methyl-4,6-*O*-benzylidene-α-D-glucopyranoside (281.7 mg) in tetrahydrofuran (2 ml) under nitrogen was added a solution of butyl-lithium in hexane (0.75 ml, 1.46M). The mixture was stirred at room temperature for 1 h and then cooled in an ice-bath. A solution of cyanogen bromide (144.0 mg) in tetrahydrofuran (1 ml) was added *via* a syringe and stirring was continued for a further 2 h. The solvent was removed *in vacuo* and the residue was taken up in benzene and washed with water. The aqueous phase was thoroughly extracted with chloroform and the combined organic extracts were washed with brine, dried (Na_2SO_4), and the solvent removed to yield a crude product (299.2 mg); $\nu_{max.}$ 1 720 (C=NH) and 1 565 (cyanurate) cm^{-1}.

A solution of oxalic acid dihydrate (67.6 mg) in tetrahydrofuran (0.5 ml) was added *via* a syringe to a magnetically stirred solution of the above freshly prepared iminocarbonate (299.2 mg) in tetrahydrofuran (2.5 ml) and stirring was continued at room temperature for 2.5 h under nitrogen. Solvent was removed *in vacuo* and the residue was taken up in chloroform, washed with brine, dried (Na_2SO_4), and the solvent evaporated to yield a crude product (282.5 mg) whose i.r. spectrum displayed no carbonyl absorption at 1 800 cm^{-1}, $\nu_{max.}$ 1 560 (cyanurate) cm^{-1}.

[9/1124 *Received*, 17*th July*, 1979]

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