Some Rearrangements of 2-Deoxy-3,4,6-tri-*O*-methyl-2-methylamino-D-glucose and Related Compounds in Basic Solution; a Novel Base-promoted N→O Migration of a Phosphonate Ester

C. Richard Hall, Thomas D. Inch,* and Nancy E. Williams
Chemical Defence Establishment, Porton Down, Salisbury, Wiltshire SP4 0JQ

Treatment of 2-deoxy-2-methylamino-3,4,6-tri-*O*-methyl-D-glucose (1) with sodium alkoxides affords 1-methyl-5-methoxymethylpyrrole-2-carbaldehyde (2) presumably by a series of elimination reactions and keto–enol equilibrations which precede ring closure and elimination of water. Substitution of nitrogen in (1) to give *e.g.* 2-*N*-[(*R*)-*O*-ethyl(phenyl)phosphoryl]-2-deoxy-2-methylamino-3,4,6-tri-*O*-methyl-D-glucose (8) interferes with the elimination sequence at an early stage so that when (8) is treated with sodium ethoxide a novel N→O migration of the phosphonate ester group occurs in a rapid reaction sequence which results in the conversion of (8) into 3-deoxy-2*N*-methyl-4,6-di-*O*-methyl-α,β-D-*erythro*-hexofuran-2-ulosylamine 1,1-diethyl acetal in high yield. The N→O migrations in this type of reaction involve P–N bond cleavage with retention of configuration at phosphorus, an unusual if not unique occurrence for reactions under basic conditions.

2-Amino-2-deoxy-D-glucose derivatives in which the amino group is unsubstituted are sensitive to base.[1] This sensitivity has been utilised with advantage in the quantitative determination of 2-amino-2-deoxy-sugars [2] but has frequently caused problems during their alkylation. Although these problems are well recognised there has been little definitive work in identifying the products from alkaline rearrangements in marked contrast to the very extensive work on free sugars that do not contain nitrogen.[3] It was anticipated therefore that during basic hydrolysis of phosphonate ester groups involving 2-deoxy-2-methylamino-D-glucose and which are described in the previous paper,[4] product identification might be complicated by rearrangements of the sugar. Steps were taken therefore to carry out control experiments which would help identify any rearrangement products. Thus, 2-deoxy-2-methylamino-3,4,6-tri-*O*-methyl-D-glucose (1) was treated with methanolic sodium methoxide and was ethylated in sodium hydroxide. The results are described below. Also described is an entirely novel rearrangement which resulted when (1), substituted on nitrogen with a phosphonate ester group, was treated with ethoxide.

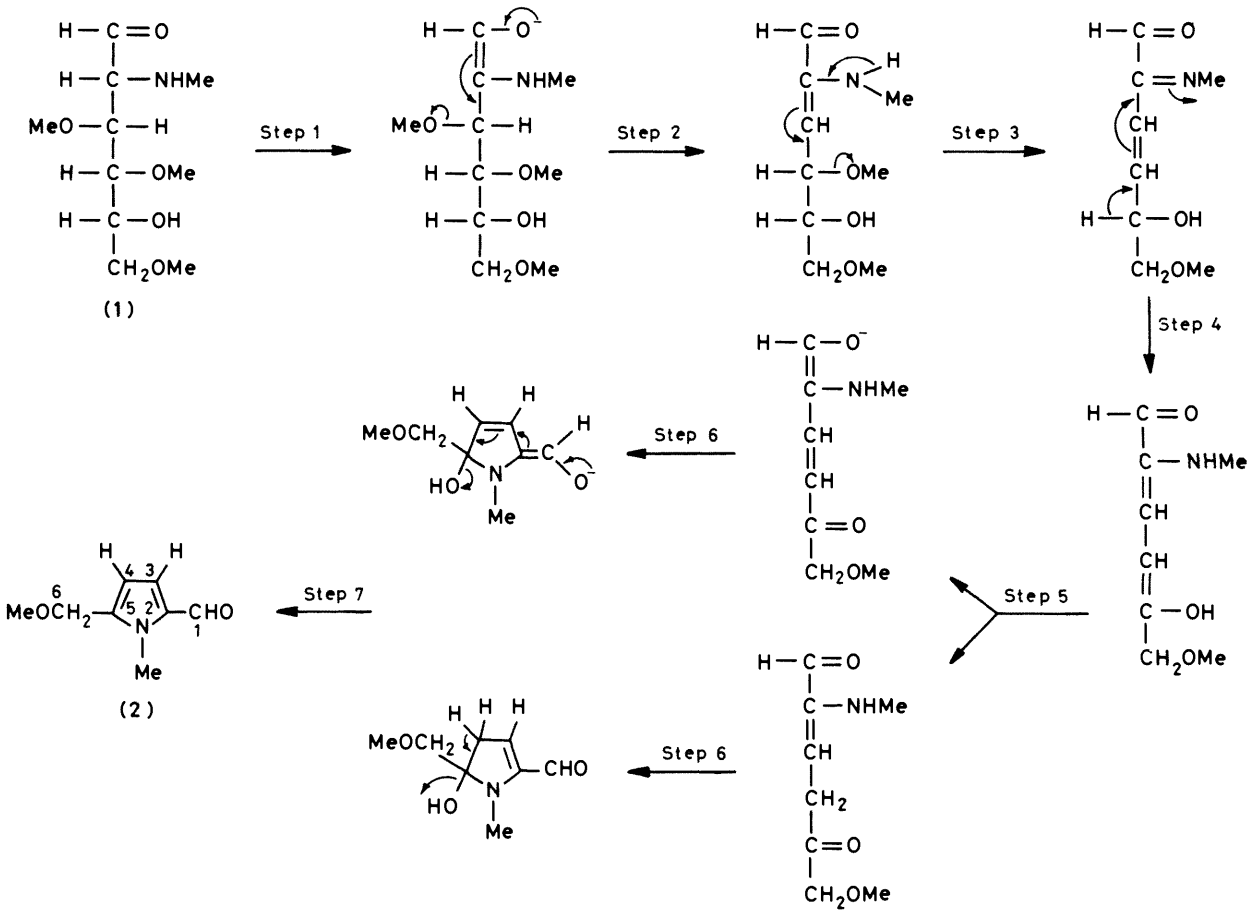
Reaction of (1) *with Sodium Methoxide.*—On treatment of (1) with 0.4 M-sodium methoxide at room temperature for 48 h there was only one t.l.c.-mobile product which was isolated in 45% yield. This product with M^+ 153.0787 was spectroscopically consistent with 1-methyl-5-methoxymethylpyrrole-2-carbaldehyde (2). A possible mechanism for the reaction is shown in Scheme 1.

The first step is formation of an enolate anion; [5] then in step 2 β-elimination of the 3-*O*-methyl group occurs. There are many precedents for these steps in non-amino sugars.[6] In step 3 the abstraction of the amine proton causes elimination of the 4-*O*-methyl substituent. Abstraction of 5-H in step 4 gives a conjugated enol which in step 5 can form various keto derivatives which are well suited for subsequent ring closure and elimination (steps 6 and 7). Since the only product isolated was the pyrrole (2) little further investigation of the reaction and its mechanism was carried out. It was shown however that whereas the protons at C-3 and C-4 in (2) did not exchange with deuterium in $NaOCD_3$–CD_3OD some incorporation of deuterium was observed (80% at C-3 and 60% at C-4) when (2) was formed from (1) in this medium. This partial exchange of 3-H and 4-H during the elimination process is fully consistent with the many possibilities for keto–enol equilibrations.

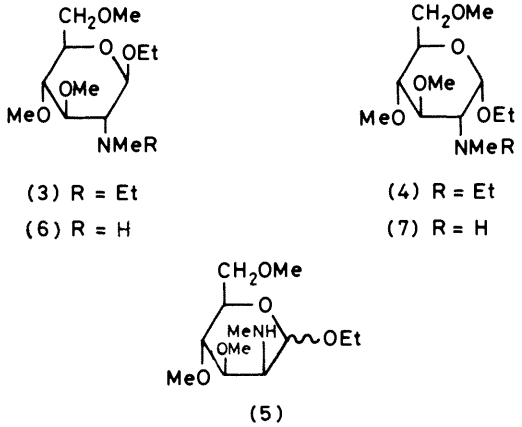
Ethylation of (1) *with Ethyl Bromide in Sodium Hydroxide.*—Ethyl glucosides of (1) were required to determine whether or not 1-*O*-phosphates of (1) gave ethyl glucosides on treatment with sodium ethoxide.[4] Since conventional glycosidation reactions using acidic alcohol are not applicable to 2-deoxy-2-amino sugars, basic alkylation reaction conditions were chosen. Thus a mixture of (1) and ethyl bromide in dichloromethane and aqueous sodium hydroxide was stirred vigorously. When product formation was observed to be slow, tetrabutylammonium hydrogen sulphate was included in the mixture as a phase-transfer catalyst. Using this procedure the following were formed and isolated following chromatography over silica: ethyl 2-deoxy-2-ethylmethylamino-3,4,6-tri-*O*-methyl-β-D-glucopyranoside, (3) (5.1%), ethyl 2-deoxy-2-ethylmethylamino-3,4,6-tri-*O*-methyl-α-D-glucopyranoside (4) (3.3%), ethyl 2-deoxy-2-methylamino-3,4,6-tri-*O*-methyl-D-mannopyranoside (5) (4.6%), ethyl 2-deoxy-2-methylamino-3,4,6-tri-*O*-ethyl-β-D-glucopyranoside (6) (5.2%) and ethyl 2-deoxy-2-methylamino-3,4,6-tri-*O*-methyl-α-D-glucopyranoside (7) (7.2%). The low yields reflect the difficulty of the separation rather than the low efficiency of the reaction.

Other minor products were present in the complex reaction mixture but were not isolated. The mannose derivative results presumably *via* the enolic intermediate (as from step 1, Scheme 1), which is analogous to the enolic intermediates that are well accepted for the equilibration of *N*-acetylglucosamine and *N*-acetylmannosamine.[5] Presumably *N*-ethylation or *O*-ethylation occurs more rapidly under the reaction conditions than the subsequent eliminations shown in Scheme 1. Since of the three glycosides (5), (6), and (7) which might have been formed from reactions of 1-*O*-phosphonate esters with sodium ethoxide only the ethyl β-D-glucopyranoside derivative (6) was detected,[4] no attempt was made to assign the anomeric configuration to the ethyl D-mannopyranoside derivative (5) where the small $J_{1,2}$ coupling constant is not diagnostic of configuration.[7]

Reactions of some 2-N-[(R)-O-*Ethyl(phenyl)phosphoryl*]-2-*deoxy*-2-*methylamino*-3,4,6-*tri*-O-*methyl*-D-*glucose Derivatives with Sodium Alkoxides.*—On treatment of the phosphorylglucose (8) with dilute sodium ethoxide in ethanol under carefully controlled conditions the only phosphorus-containing product was ethyl phenylphosphonic acid. The major carbohydrate product detected in the reaction mixture was (9) but after processing and chromatography (10) (38%) as well as (9), (36%) was isolated.



Scheme 1.

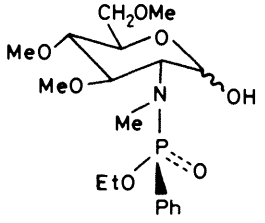


Compound (10) was identified as a mixture of anomers of 3-deoxy-4,6-di-O-methyl-αβ-D-*erythro*-hexafuran-2-ulose 1,1-diethyi acetal on the basis of ^1H and ^{13}C n.m.r. spectral data (see Experimental section). For example, each anomer showed only two OMe signals, consistent with the elimination of one methoxy group. There were no anomeric proton signals but there were ^{13}C signals at 106.7 and 107.1 p.p.m. which showed no coupling to any proton. Each anomer showed a singlet proton consistent with the diethyl acetal group. The spectra did not show distinct signals for endocyclic methylene groups for each anomer; however there were a broad pair of quartets at 2.08 p.p.m. (*J* 13.3 and 6.4 Hz) and 2.40 p.p.m. (*J* 13.3 and 2.8 Hz) with couplings consistent with those for an endocyclic methylene group in a five-member ring. Presumably the signals for each anomer are essentially superimposed.

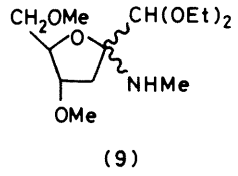
Similarly ^1H and ^{13}C n.m.r. data for (9) were consistent with it being a mixture of anomers of 3-deoxy-2-*N*-methyl-4,6-di-*O*-methyl-αβ-D-*erythro*-hexofuran-2-ulosylamine 1,1-diethyl acetal. The easy conversion of (9) into (10) on chromatography over silica is not unreasonable for such a compound.

Further confirmation of the structure of (10) was provided by its reactions. Thus, on acetylation with acetic anhydride in pyridine, (10) gave the acylic monoacetate (11) as a single isomer. The formation of an acyclic rather than a cyclic, acetate is unusual particularly since in pyridine it may be shown by ^1H n.m.r. that (10) exists essentially in the five-member ring form. Compound (11) was also formed from (10) when acetyl chloride was the reagent.

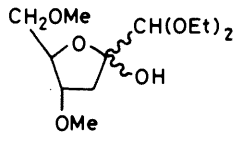
Treatment of (10) or its acetate (11) with methylmagnesium iodide gave a mixture of the isomers (12) and (13). These products were unstable in chloroform, rapidly rearranging into ethyl glucopyranoside derivatives. This rearrangement proceeded more rapidly when hydrogen chloride was present giving four isomers (14), (15), (16), and (17), two of which were isolated in pure form. No attempt has been made to assign anomeric or C-2 configurations to these isomers. Their ^1H and ^{13}C n.m.r. characteristics (see Experimental section) are, however, fully consistent with the assigned structures providing confirmation of the structure of (10) and therefore also of (9).



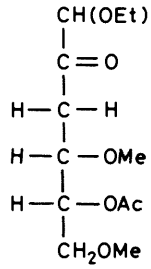
(8)



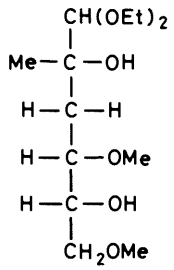
(9)



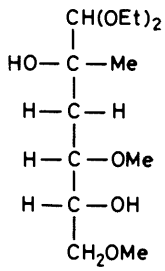
(10)



(11)



(12)



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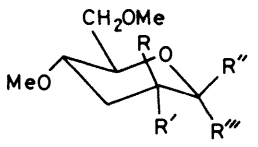
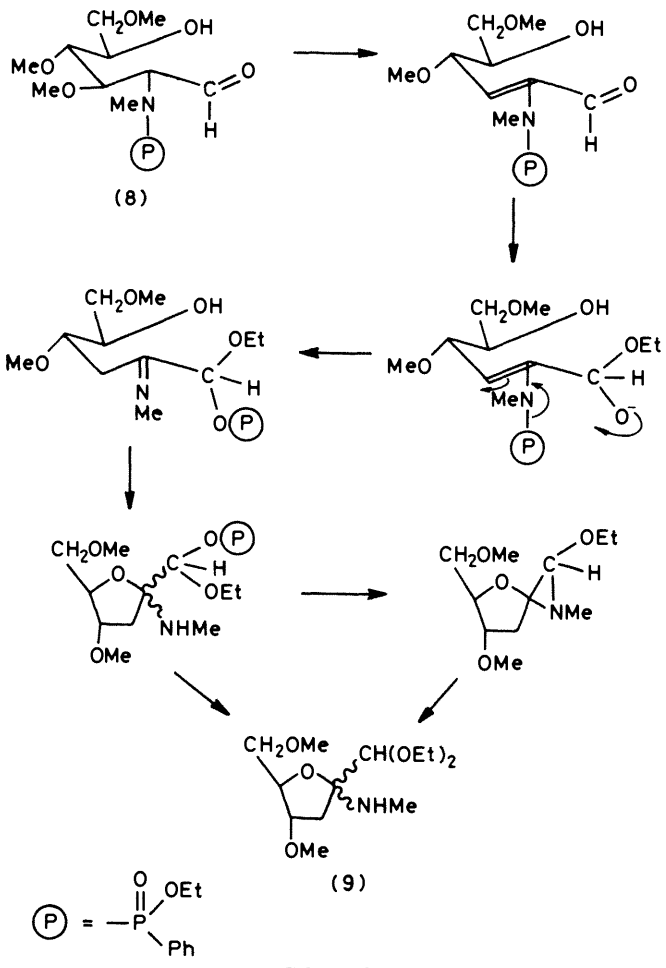


	R	R′	R″	R‴
(14)	Me	OH	OEt	H
(15)	Me	OH	H	OEt
(16)	OH	Me	OEt	H
(17)	OH	Me	H	OEt



Scheme 2.

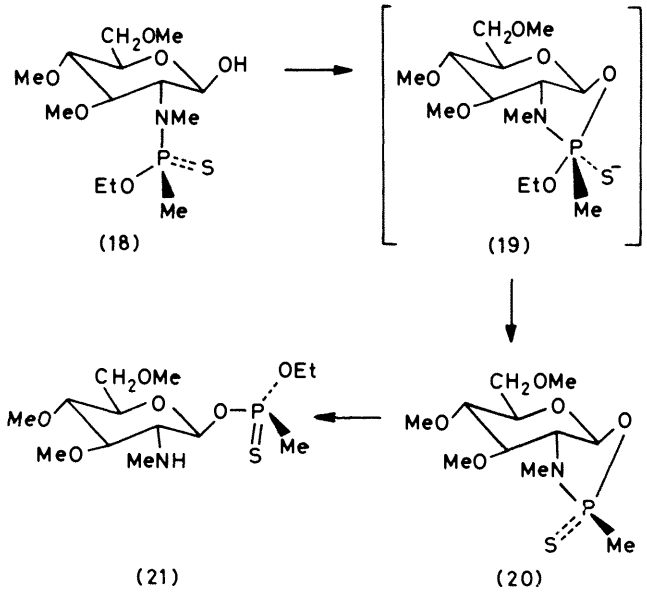
In considering possible mechanisms for the formation of (9) from the phosphorylglucose (8) attention was first given to the fact that a P–N bond had been broken and ethyl phenylphosphonic acid liberated. The formation of ethyl phenylphosphonic acid precluded P–N bond cleavage by ethoxide attack at phosphorus as an early step in the rearrangement since this reaction would generate diethyl phenylphosphonate; such a reaction was in any event of low probability because of the resistance to base of the phosphorylamino compounds. Further, reactions which involve migration of the phosphorus ester group from N→O-1 were also precluded because the 1-O-phosphonate so formed would then react with ethoxide to afford either (*a*) ethyl phenylphosphoric acid and the ethyl glucoside derivative (6) or (*b*) diethyl phenylphosphonate and the pyrrole (2) (*cf.* Schemes 3 and 4 previous paper [5]). Neither the pyrrole (2) nor the glucoside (6) were present to any significant extent in the reaction mixture.

A mechanism which appears to fit the experimental results and which uses the acyclic rather than the pyranoid form of the sugar is shown in Scheme 2.

The first step, as in the case of pyrrole formation (Scheme 1), involves the elimination of the 3-*O*-methyl substituent. At this point, because nitrogen is fully substituted, further eliminations do not occur. Instead, ethoxide attacks the carbonyl group (there are precedents in carbohydrate chemistry [8]) and the anion so generated attacks phosphorus intramolecularly so that migration of phosphorus occurs with the formation of a 3-deoxy-2-imino sugar. This step is followed by attack of the 5-OH group on the imine carbon to form a furanoid derivative with a free amino group that may participate in displacement of ethyl phenylphosphonic acid with formation of an aziridine. Attack on the aziridine by ethoxide generates the diethyl acetal.

It must be pointed out that under suitably controlled reaction conditions the formation of (9) from (8) is the high-yielding reaction described in the Experimental section. However by slight changes in the reaction conditions or of the substituents on phosphorus other reactions can be enhanced. Thus migration of phosphorus from nitrogen to O-1 of the pyranoid derivative occurs and in the product mixture can be detected diethyl phenylphosphonate and the pyrrole (2) and ethyl phenylphosphonic acid and the ethyl β-glycoside (6). The conditions which favour one reaction over another have not been investigated.

In the previous paper [4] it was reported that 2-*N*-[(*S*)-thiophosphoryl]glucosamine (18) with the *S*-configuration at phosphorus [compound (8*S*) in the previous paper], on treatment with ethanolic sodium ethoxide afforded, following methylation of the product, ethyl *S*-methyl methylphosphonothioate in which there was a 5 : 1 ratio of *S* : *R* enantiomers. The implication of this result was that ethyl methylphosphonothioic acid was displaced from (18) preponder-

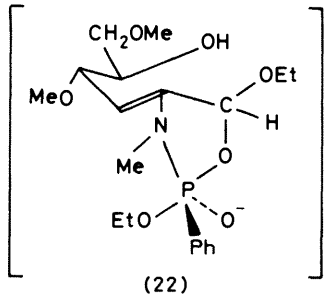


Scheme 3.

antly with retention of configuration. This is not consistent stereochemically with the migration of the phosphonothioate group from N to O-1 in the pyranoid sugar (18) and subsequent C–O bond cleavage (Scheme 3). Such a migration would involve a five-co-ordinate intermediate formed by attack of O-1 *trans*-apical to the ethoxy group, *i.e.* (19) (illustrated for the β-anomer). Such intermediates are identical with those formed during ring opening of the parent cyclic esters by P–O bond cleavage and do not undergo any significant pseudorotation as shown by the fact that in (20) for example no P–N bond cleavage by ethoxide occurs with retention of configuration. Thus, for migration to occur the five-co-ordinate intermediate (19) must eliminate the ethoxy group, re-forming (20), with the migration to O-1 being the result of re-ring opening by P–N bond cleavage which is with inversion of configuration. This mechanism requires the ethyl *S*-methyl methylphosphonothioate eventually isolated to have the *R* configuration (see Scheme 2 previous paper [4]).

The mechanism shown in Scheme 2 however does allow for the formation of ethyl methylphosphonothioic acid with retention of configuration. There is no experimental evidence to preclude pseudorotation of the trigonal bipyramidal intermediate (22) prior to cleavage of an apical P–N bond, *i.e.* a reaction with retention of configuration. In fact the concerted mechanism may facilitate such a step providing an additional driving force for P–N bond cleavage. Alternatively, the unusual electronic character of nitrogen (for displacements at phosphorus) as the phosphorylamino compound is converted into an imine may provide a situation where P–N bond cleavage occurs from a basal rather than apical position in the trigonal bipyramidal intermediate; such a reaction would also proceed with retention of configuration.

In summary, the results for the formation of (9) from (8) and of ethyl methylphosphonothioic acid with retention of configuration from (18) are consistent with the mechanism in Scheme 2 as the preponderant pathway. The identification of the pyrrole (2), the ethyl β-D-glucopyranoside derivative (6), and the detection of a small amount of ethyl methylphosphonothioic acid formed with inversion of configuration from (18) show that the migration mechanism illustrated in Scheme 3 may also play a part which might be enhanced under other reaction conditions.



Experimental

General procedures are described in the previous paper.[4] ^{13}C spectra were recorded on a JEOL FX60 spectrometer at 15.0 MHZ in $CDCl_3$ using the deuterium signal as an internal lock and with $SiMe_4$ as internal standard. Signal assignment was facilitated where possible by off-resonance decoupling.

Treatment of 2-*Deoxy*-2-*methylamino*-3,4,6-*tri*-O-*methyl*-α,β-D-*glucose Hydrochloride* (1) *with Sodium Methoxide*.—A solution of (1) (0.6 g) in methanolic sodium methoxide (0.4 M; 25 ml) was stored at 25 °C for 48 h and then poured into water and extracted with chloroform. Concentration of the organic layer and chromatography of the residue, benzene–acetone–methanol (12 : 1 : 1) gave 1-*methyl*-5-*methoxymethylpyrrole*-2-*carbaldehyde* (2) (0.15 g, 45%) as a clear oil, δ 3.34 (NMe), 3.95 (OMe), 4.43 (CH_2), 6.22 (1 H, d, *J* 4.0 Hz 4-H), 6.85 (1 H, d, *J* 4.0 Hz, 3-H), and 9.54 (CHO); $\nu_{max.}$ 1 660 cm^{-1} (CHO) (M^+, 153.0787. $C_8H_{11}NO_2$ requires M^+, 153.0790).

When the above experiment was repeated using (1), which had previously been stored in D_2O, and deuteriomethanol–methoxide, the resulting pyrrole had *ca.* 80% deuterium incorporation at position 3 and *ca.* 60% incorporation at position 4.

Storage of a solution of the pyrrole (2) in deuteriomethanol–methoxide (0.4 M) for 24 h did not result in any deuterium incorporation.

Phase Transfer Ethylation of (1).—A mixture of (1) (2 g), ethyl bromide (2 ml), tetrabutylammonium hydrogen sulphate (0.3 g), and aqueous sodium hydroxide solution (50%; 30 ml) was stirred vigorously for 5 h. The organic layer was then separated and concentrated. Chromatography of the residue, benzene–acetone–methanol (85 : 18 : 2) gave *ethyl* 2-*deoxy*-2-*ethylmethylamino*-3,4,6-*tri*-O-*methyl*-β-D-*glucopyranoside* (3) (0.11 g, 5.1%) as a syrup, $[\alpha]_D$ −2.65° (*c* 0.9), δ 1.04 (CH_3CH_2N), 1.21 (CH_3CH_2O), 2.40 (NMe), 3.37, 3.51, 3.59 (3 × OMe), 4.38 (1 H, d, *J* 8.0 Hz, 1-H); *ethyl* 2-*deoxy*-2-*ethylmethylamino*-3,4,6-*tri*-O-*methyl*-α-D-*glucopyranoside* (4) (0.07 g, 3.3%) as a syrup, $[\alpha]_D$ +109° (*c* 0.4), δ 1.04 (CH_3CH_2N), 1.18 (CH_3CH_2O), 2.45 (NMe), 3.38, 3.51, and 3.58 (3 × OMe), 4.78 (1 H, d, *J* 3.3 Hz, 1-H); *ethyl* 2-*deoxy*-2-*methylamino*-3,4,6-*tri*-O-*methyl*-α-D-*mannopyranoside* (5) (0.09 g, 4.6%) as a syrup, m.p. (hydrochloride salt), 128—129 °C (from benzene–light petroleum), $[\alpha]_D$ +40° (*c* 2.0), δ 1.20 (CH_3CH_2O), 2.45 (NMe), 2.88 (1 H, dd, *J* 4.2 and 1.5 Hz, 1 H), 3.40, 3.43, and 3.49 (3 × OMe), 4.84 (1 H, d, *J* 1.5 Hz, 1-H); *ethyl* 2-*deoxy*-2-*methylamino*-3,4,6-*tri*-O-*methyl*-β-D-*glucopyranoside* (6) (0.10 g, 5.2%) as a syrup, m.p. (hydrochloride salt) 127 °C (from benzene–light petroleum), $[\alpha]_D$ −6.7° (*c* 1.0), δ 1.21 (CH_3CH_2O), 2.36 (1 H, dd, *J* 9.5 and 8.0 Hz, 2-H), 2.53 (NMe), 3.38, 3.50, and 3.59 (3 × OMe), 4.20 (1 H, d, *J* 8.0 Hz, 1-H); and *ethyl* 2-*deoxy*-2-*methylamino*-3,4,6-*tri*-O-*methyl*-α-D-*glucopyranoside* (7) (0.14 g, 7.2%)

as a syrup, $[\alpha]_D$ +143° (*c* 0.9), δ 1.21 (CH_3CH_2O), 2.44 (NMe), 2.54 (1 H, dd, *J* 9.3 and 3.5 Hz, 2-H), 3.39, 3.51, and 3.60 (3 × OMe), and 4.89 (1 H, d, *J* 3.5 Hz, 1-H).

Reaction of 2-N-[(R)-O-*Ethyl*(*phenyl*)*phosphoryl*-2-*deoxy*-(2-*methylamino*)-3,4,6-*tri*-O-*methyl*-D-*glucose* (8) *with Sodium Ethoxide*.—A solution of (8) (1.8 g) and sodium (0.3 g) in ethanol (60 ml) was stored overnight and then poured into water and extracted with chloroform. The combined extracts were concentrated and the residue was subjected to fast chromatography, with benzene–acetone (7 : 3) as eluant, to give (10) as a mixture of isomers (0.45 g, 38%, clear oil), R_F 0.35, $[\alpha]_D$ +14.6° (*c* 0.4), δ_H (C_6D_6) 1.51 and 1.54 (2 × CH_3CH_2O), 2.08 (2 H, dd, $J_{3,3'}$ 13.3, $J_{3,4}$ 6.4 Hz, 2 × 3-H), 2.40 (2 H, dd, $J_{3',3}$ 13.3, $J_{3'4}$ 2.8 Hz, 2 × 3'-H), 3.05, 3.09, 3.13, and 3.15 (2 × 2, OMe), 4.38 and 4.40 (2 × $CH(OEt)_2$); δ_C (C_6D_6) 37.8 and 39.6 (2 × C-3), 103.9 and 104.4 (2 × C-1), and 106.7 and 107.1 (2 × C-2); $\nu_{max.}$ (film) 3 475 cm^{-1}; and (9) as a mixture of isomers (0.45 g, 36%, clear oil), R_F 0.3, $[\alpha]_D$ +36.5° (*c* 0.8), δ_H 1.23 (2 × CH_3CH_2O), 1.87 (dd, 2 × 3-H), 2.23 (dd, 2 × 3'-H), 2.34 (NMe), 2.41 (NMe), 3.31 and 3.33 (2 × OMe), 3.38 (2 × OMe), 4.37 and 4.44 (2 × $CH(OEt)_2$); δ_C 34.0 and 35.3 (2 × C-3), 98.5 and 98.9 (2 × C-2), and 103.6 and 105.2 (2 × C-1).

^{31}P Monitoring showed that the sodium salt of ethyl hydrogen phenylphosphonic acid was essentially the only phosphorus-containing product of the above reaction.

Conversion of (9) *into* (10).—A suspension of (9) (0.24 g) and silica (5 g) in chloroform (25 ml) was stored overnight, and then filtered and the silica was washed with more chloroform. Concentration of the organic fraction gave (10) (0.19 g, 84%).

Acetylation of (10).—A solution of (10) (0.2 g) in pyridine–acetic anhydride (1 : 1) (2 ml) was stored for 48 h and then carefully poured into cool, dilute aqueous sodium carbonate. The mixture was extracted with chloroform and the combined extracts concentrated; the residue was chromatographed with light petroleum–acetone (9 : 1) as eluant to give (11) (0.1 g, 54% clear oil), $[\alpha]_D$ −10.0° (*c* 0.6) δ_H 1.24 (CH_3CH_2O), 2.07 (COMe), 2.66 (1 H, dd, $J_{3,3'}$ 17.1 $J_{3,4}$ 4.0 Hz, 3-H), 2.94 (dd, $J_{3,3'}$ 17.1, $J_{3'4}$, 7.7 Hz. 3'-H), 3.33 and 3.37 (2 × OMe), 3.99 (1 H, ddd, *J* 7.7, 4.0 and 4.0 Hz, 4-H), 4.59 (1-H), 5.13 (1 H, ddd, 4.5, 4.5 and 4.0 Hz, 5-H); δ_C 102.4 (C-1), 170.1 (C-2), and 203.3 (acetate); $\nu_{max.}$ (film) 1 740 cm^{-1} (Found: C, 54.9; H, 8.7. $C_{14}H_{26}O_7$ requires C, 54.9; H, 8.6%).

Reaction of (10) *with* MeMgI.—A solution of (10) (0.4 g) and an excess of methylmagnesium iodide in ether (50 ml) was boiled under reflux for 4 h and then carefully poured into a concentrated aqueous ammonium chloride and extracted with ether. The combined extracts were concentrated and the residue chromatographed, with benzene–acetone–methanol (85 : 13 : 2) as eluant, to give (12) and (13) as a mixture of isomers (0.15 g, 36%, clear oil), $[\alpha]_D$ −1.3° (*c* 2.4), δ_H (C_6D_6) 1.10 and 1.11 (6 H), 1.12 (4 × CH_3CH_2O), 1.33 (2 × CMe), 1.70—2.22 (m, 2 × 3-H, 3'-H), 3.13, 3.16, 3.27, and 3.29 (4 × OMe), 4.14 (1-H), and 4.21 (1'-H); δ_C (C_6D_6) 74.5 (C-2) and 109.0 and 109.6 (2 × C-1); $\nu_{max.}$ (film) 3 450 cm^{-1}.

Ring Closure of (12) *and* (13).—A solution of (12) and (13) (1 g) in chloroform (25 ml) that also contained a trace of anhydrous hydrogen chloride was stored for ½ h and then washed twice with water. Concentration of the organic layer gave a mixture of four isomers (14), (15), (16), and (17) (0.8 g, 96%, clear oil), δ_H 4.24, 4.28, 4.34, and 4.38 (1 H, s, 1-H). Chromatography, with light petroleum–acetone (4 : 1) as eluant, resulted in the isolation of two of the isomers: $[\alpha]_D$ +17.4° (*c* 0.2), δ_H 1.21 (CH_3CH_2O), 1.24 (CMe), 1.65 (1 H, dd, *J* 12 and 12 Hz, 3-H), 2.11 (1 H, dd, *J* 12 and 5 Hz, 3'-H), 3.29, 3.35 (2 × OMe), 4.38 (1-H); $\nu_{max.}$ (film) 3 475 cm^{-1} (Found: C, 56.6; H, 9.5. $C_{11}H_{22}O_5$ requires C, 56.4; H, 9.4%); and $[\alpha]_D$ +142° (*c* 1.0), δ_H 1.14 (CMe), 1.18 (CH_3CH_2O), 1.59 (1 H, dd, *J* 12 and 10.2 Hz, 3-H), 2.10 (1 H, dd, *J* 12 and 4 Hz, 3'-H), 3.28 and 3.36 (2 × OMe), and 4.34 (1-H); $\nu_{max.}$ (film) 3 450 cm^{-1}.

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