Reaction of Chlorosulphonyl Isocyanate with Unsaturated Sugars †

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Treatment of hex-2-enopyranosides with chlorosulphonyl isocyanate gives 3-alkoxycarbonylamino-3-deoxyglycals. 1,2-*O*-Isopropylidene groups in sugars are removed by the reagent and 1,2-carbonates are formed.

RECENT reviews [1,2] on the reaction of sulphonyl isocyanates with carbon–carbon double bonds suggested to us that the reaction of chlorosulphonyl isocyanate (CSI), the most reactive isocyanate known, with suitable unsaturated sugars might be used for the preparation of new branched-chain sugars. Depending on the structure of the starting material, CSI can react with carbon–carbon double bonds to give *N*-chlorosulphonyl β-lactams and either αβ- or βγ-unsaturated *N*-chlorosulphonyl amides. Reduction of the *N*-chlorosulphonyl group with iodide and hydrolysis, in the presence of base to neutralize liberated acid, gives the free β-lactam and amide in good yield.

In the expectation that 3,4,6-tri-*O*-acetyl-1,2-dideoxy-D-*arabino*-hex-1-enopyranose (tri-*O*-acetyl-D-glucal) (1) would react as an enol ether [3] to give such compounds, it was treated with CSI. An equimolar mixture of the reagents gave a single crystalline product, the dimer, 1,3,4,6-tetra-*O*-acetyl-2-*C*-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl)-2-deoxy-α-D-*erythro*-hex-2-enopyranose.[4,5] CSI contains a trace of sulphur trioxide [6] and this, acting as a Lewis acid, or the reagent itself, must have catalysed the dimerization in the same way as boron trifluoride [4] or iodine.[5]

The reactions of CSI with hex-2-enopyranosides were next studied. Ethyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside [7] (2) reacted with an equivalent of CSI in ether. After reduction and hydrolysis a dark mixture was obtained, from which two products, (A) and (B), could be separated by chromatography. The minor product (A) was obtained as an oil containing traces of impurities which could not be removed, but its spectral data indicated that it was the known 4,6-di-*O*-acetyl-2,3-dideoxy-αβ-D-*erythro*-hex-2-enopyranose [8] (3).

The i.r. spectrum of the major product (B) (60%), $C_{13}H_{19}NO_7$, showed peaks at $\nu_{max.}$ 3430 (NH), 1740 and 1720 (CO), and 1650 cm^{-1} (vinyl ether).[9] Two characteristic quartets [10] at τ 3·63 and 5·30 in the n.m.r. spectrum proved that (B) was a glycal with one hydrogen atom on C-3. The presence of two acetate groups, an ethoxy-group, and an NH group was also shown. In the mass spectrum the highest mass ion appeared at *m/e* 213 (*M* − 88). Catalytic hydrogenation of (B) gave a dihydro-product containing no double bond, as shown by its i.r. and n.m.r. spectra. It gave a molecular ion at *m/e* 303. These data established that (B) was a 4,6-di-*O*-acetyl-D-glycal with a substituent at C-3 comprising the elements $C_3H_6NO_2$ (88 mass units).

Alkaline hydrolysis of (B) and acetylation gave a compound (C), $C_{12}H_{17}NO_6$. The n.m.r. spectrum was similar to that of (B) except for a downfield shift of the NH signal and the replacement of the ethoxy-signals by a signal at τ 8·08 (NHAc; 3H, s). This showed that the substituent on C-3 in (B) was $NH{\cdot}CO_2Et$ which explains the ready loss of 88 mass units in the mass spectrum. A dihydro-product was also obtained on hydrogenation of (C).

Their n.m.r. spectra showed that (B) and (C) were substituted glucals and not the epimeric allals. The coupling constants $J_{2,3}$ (*ca.* 2 Hz) and $J_{1,3}$ (*ca.* 2 Hz) for both compounds are very close to those observed for

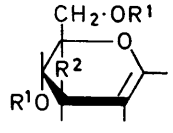
† Preliminary report, A. Jordaan and G. J. Lourens, *Chem. Comm.*, 1971, 581.

[1] R. Graf, *Angew. Chem. Internat. Edn.*, 1968, **7**, 172.
[2] H. Bestian, *Pure Appl. Chem.*, 1971, **27**, 611.
[3] F. Effenberger and R. Gleiter, *Chem. Ber.*, 1964, **97**, 1576.
[4] R. J. Ferrier and N. Prasad, *J. Chem. Soc.* (*C*), 1969, 581.
[5] I. Szczerek, J. S. Jewell, R. S. G. Richie, W. A. Szarek, and J. K. N. Jones, *Carbohydrate Res.*, 1972, **22**, 163.
[6] R. Graf, *Annalen*, 1963, **661**, 116.
[7] R. J. Ferrier and N. Prasad, *J. Chem. Soc.* (*C*), 1969, 570.
[8] S. Laland, W. G. Overend, and M. Stacey, *J. Chem. Soc.*, 1950, 738.
[9] R. J. Ferrier, *J. Chem. Soc.*, 1964, 5443.
[10] B. Fraser-Reid and B. Radatus, *Canad. J. Chem.*, 1969, **47**, 4905, and references therein.

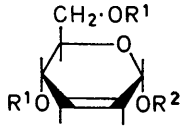
glucal derivatives [10] and differ considerably from those for allals.[10] An unambiguous synthesis of a derivative of (B) confirmed these findings.

4,6-*O*-Benzylidene-1,2-dideoxy-D-*ribo*-hex-1-enopyranose [11] (4,6-*O*-benzylidene-D-allal) was hydrogenated to give 1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-D-*ribo*-hexitol (4). The toluene-*p*-sulphonate derivative (5) was prepared and treated with sodium azide to give the azido-sugar (6). Reduction of (6) yielded an amine which reacted with ethyl chloroformate in pyridine to give 1,5-anhydro-4,6-*O*-benzylidene-2,3-dideoxy-3-ethoxycarbonylamino-D-*arabino*-hexitol (7); identical with the compound obtained on deacetylation and benzylidenation of dihydro-(B). The corresponding epimeric D-*ribo*-hexitol (8) was also prepared by a similar sequence from 4,6-*O*-benzylidene-D-glucal [11] (9). These syntheses proved unequivocally that (B) is 4,6-di-*O*-acetyl-1,2,3-trideoxy-3-ethoxycarbonylamino-D-*arabino*-hex-1-enopyranose (10) and (C) the corresponding 3-acetamido-compound (11). The dihydro-derivatives are the 1,5-anhydro-*arabino*-hexitols (12) and (13).

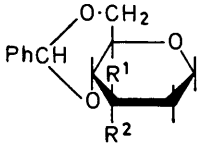
CSI was also treated with ethyl 2,3-dideoxy-4,6-di-*O*-methyl-α-D-*erythro*-hex-2-enopyranoside (14), obtained by methylation of ethyl 2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside [8] (15), to give the methyl analogues of (A) and (B), compounds (16) and (17). Unlike its acetyl analogue, (16) could be distilled and fully characterized. The marked similarity [12] of its n.m.r. spectrum to that



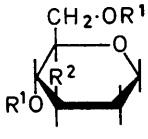
(1) R^1 = Ac, R^2 = OAc
(10) R^1 = Ac, R^2 = NH·CO_2Et
(11) R^1 = Ac, R^2 = NHAc
(17) R^1 = Me, R^2 = NH·CO_2Et



(2) R^1 = Ac, R^2 = Et
(3) R^1 = Ac, R^2 = H (+β-anomer)
(14) R^1 = Me, R^2 = Et
(15) R^1 = H, R^2 = Et
(16) R^1 = Me, R^2 = H (+β-anomer)
(19) R^1 = CH_2Ph, R^2 = Et
(20) R^1 = CH_2Ph, R^2 = H (+β-anomer)



(4) R^1 = H, R^2 = OH
(5) R^1 = H, R^2 = OTs
(6) R^1 = N_3, R^2 = H
(7) R^1 = NH·CO_2Et, R^2 = H
(8) R^1 = H, R^2 = NH·CO_2Et
(9) R^1 = OH, R^2 = H

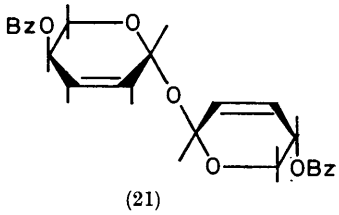


(12) R^1 = Ac, R^2 = NH·CO_2Et
(13) R^1 = Ac, R^2 = NHAc
(18) R^1 = Me, R^2 = NH·CO_2Et

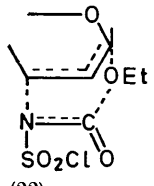
of (14) showed that mainly the α-anomer was present. Hydrogenation of (17) gave a dihydro-product (18), which was demethylated [13] and acetylated to give compound (12).

No amino-D-glucal derivative was obtained on treating CSI with ethyl 4,6-di-*O*-benzyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (19), prepared by the benzylation of compound (15). Only a low yield of the parent hex-2-enopyranose (20) was isolated.

Methyl 4-*O*-benzoyl-2,3-dideoxy-β-L-*glycero*-pent-2-enopyranoside [14] on treatment with CSI gave neither the parent pent-2-enopyranose nor the 3-alkoxycarbonylamino-derivative. The only product identified (35%) was the ββ′-disaccharide (21), the enantiomer of the compound obtained [15] on hydrolysis of 4-*O*-benzoyl-2,3-dideoxy-αβ-D-*glycero*-pent-2-enopyranosyl fluoride.



(21)



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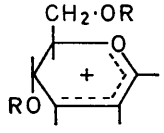
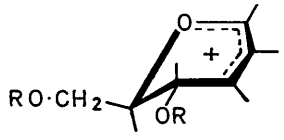


(23) R = Ac, Me



(24) R = Ac, Me

That the ethoxy-group present in compounds (10) and (17) was not introduced from ethanol during work-up was shown by employing aqueous methanol in the reduction step after the reaction of (2) with CSI. Compound (10) was again obtained, showing that transfer of the anomeric ethoxy-group must have taken place. An intramolecular transfer involving a six-membered transition state (22) similar to that envisaged by Fraser-Reid and Radatus [16] in the reductive rearrangement of hex-2-enopyranoses with lithium aluminium hydride, cannot be involved, as allal and not glucal derivatives would then have been formed by α-face attack. The formation of compounds (10) and (17) with the glucal configuration can be rationalized in terms of abstraction of the anomeric ethoxy-group by CSI to give the species $ClSO_2\cdot\bar{N}\cdot CO_2Et$ and the stable allylic oxo-carbonium ion (23). With $O{=}C(1)\overset{+}{-}C(2){=}C(3)$ in one plane the more energetically favourable form (24) has C-5 below the plane and the C-4 and C-5 substituents in pseudo-equatorial configuration, leaving the β-face accessible to attack at C-3 by the nitrogen species. This rationalization is supported by the other products, the parent hex-2-enopyranoses (3), (16), and (20) and the disaccharide (21). Attack at C-1 of the carbonium ion (23),

[11] M. Sharma and R. K. Brown, *Canad. J. Chem.*, 1966, **44**, 2825; R. U. Lemieux, E. Fraga, and K. A. Watanabe, *ibid.*, 1968, **46**, 61.
[12] B. Coxon, H. J. Jennings, and K. A. McLauchlan, *Tetrahedron*, 1967, **23**, 2395.
[13] A. B. Foster, D. Horton, N. Salim, M. Stacey, and J. M. Webber, *J. Chem. Soc.*, 1960, 2587.
[14] R. U. Lemieux, K. A. Watanabe, and A. A. Pavia, *Canad. J. Chem.*, 1969, **47**, 4413.
[15] K. Bock and C. Pedersen, *Acta Chem. Scand.*, 1971, **25**, 2757.
[16] B. Fraser-Reid and B. Radatus, *J. Amer. Chem. Soc.*, 1970, **92**, 6661.

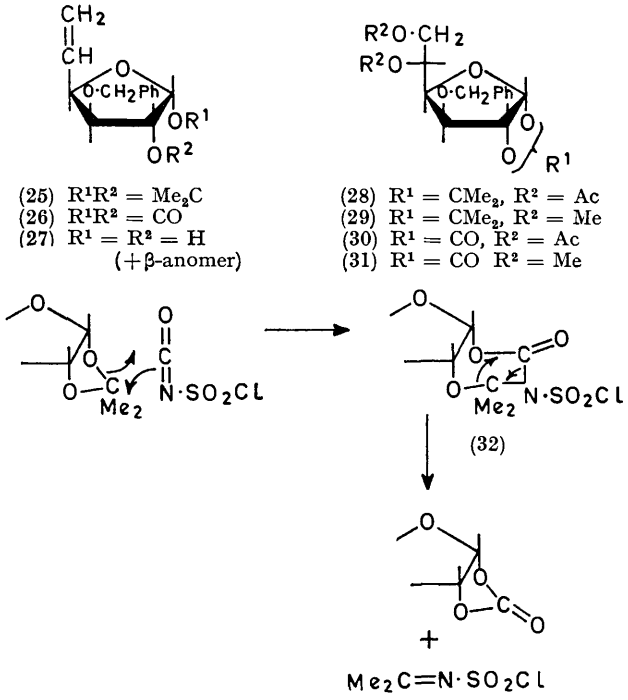
possibly by the nitrogen species or by some other species present in CSI as impurity, would give unstable compounds which would give the above products on hydrolysis.[15]

As an example of a terminally unsaturated sugar, 3-*O*-benzyl-5,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hex-5-enofuranose [17] (25) was treated with CSI. Chromatography of the resulting mixture of products gave unchanged (25) and a crystalline compound (D) in low yield. Bands at 1820 and 1840 cm^{-1} in the i.r. spectrum of (D) indicated the presence of a cyclic carbonate group.[18] The n.m.r. spectrum was similar to that of (25) except that the signals due to H-1 and H-2 had moved downfield and those due to the isopropylidene group had disappeared, showing that the double bond of (25) had not been affected by CSI and that the 1,2-*O*-isopropylidene group had been replaced by a 1,2-carbonate group to give (26). Analysis and mass spectrometry confirmed this assignment. On repeating the experiment for 2 days and leaving out the reduction step, the yield of (26) increased only slightly, from 30 to *ca.* 40%. The addition of traces of acid and variation of the reaction temperature did not improve the yield. Removal of the isopropylidene group from (25) by hydrolysis to give (27) and reaction of (27) with CSI again gave compound (26) in low yield.

Attempts to develop these reactions into a general method for the synthesis of 1,2-carbonate compounds proved unsuccessful owing to the reactivity of CSI with various protecting groups. Also, even with 1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranoses with non-reacting groups such as OMe or OAc at C-3, C-5, and C-6, the yields of carbonates were low (<10%). Thus the saturated sugar derivatives [19] (28) and (29), obtained by the acetylation and methylation respectively of 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose,[19] gave carbonates (30) and (31) although neither compound could be obtained pure. The unsaturated carbonate (26) was recovered unchanged (>90%) after treatment with CSI in ether or in refluxing benzene, emphasizing the unreactivity of the double bond to the reagent.

Graf [1] has shown that dimethoxymethane adds smoothly to CSI with fission of the MeO–CH_2·OMe bond. Attack by CSI at the anomeric oxygen atom of (25) to give a species (32) which collapses to give (26) can be envisaged (Scheme).

Some points of interest emerge from the n.m.r. spectra of the α-D-*xylo*-hexofuranoses (25)—(31) already described. Complete interpretation of the spectra of the 1,2-carbonates (26) and (30) (see Experimental section) shows that the furanose ring adopts the same configuration as in the analogous isopropylidene compounds [20] (25) and (28). Also, although only three closely related compounds, (26), (30), and (31), are involved, the τ values of H-1 (3·8 ± 0·1) and H-2 (5·05 ± 0·1) can be regarded as characteristic of α-D-xylofuranose 1,2-carbonates. Finally, the methylene protons of the benzyl group of compounds (25), (26), and (28)—(30) are non-equivalent [21] and give rise to AB-type spectra. All exhibit quartets



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except (26) in which the two protons are nearly equivalent and give rise to a slightly broadened singlet with two small side peaks. For all the derivatives, the coupling constants (12 ± 0·5 Hz) agree with those found [21] for similar compounds. The differences between the chemical shifts of the two protons (ν_{AB}) vary between 15·5 for (28) and <0·5 Hz in the case of (26).

Unsaturated sugars which were treated with CSI had to be of high purity as the presence of impurities drastically effected the yield of products.

Compound (10) has been employed in this laboratory in the preparation of nucleosides.[22]

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra were measured with a Perkin-Elmer model 257 spectrophotometer and n.m.r. spectra were recorded on a Varian HA-100 instrument with tetramethylsilane as internal standard for [^{2}H]chloroform solutions, unless otherwise stated. Optical rotations were measured for solutions in chloroform with a Bendix-NPL Automatic Polarimeter type 143 (*c* 1·0 ± 0·3). Mass spectra were determined with an A.E.I. MS-9 spectrometer by use of the

[17] D. Horton and C. G. Tindall, jun., *Carbohydrate Res.*, 1970, **15**, 215.
[18] L. Hough, J. E. Priddle, R. S. Theobald, G. R. Barker, T. Douglas, and J. W. Spoors, *Chem. and Ind.*, 1960, 148.
[19] A. S. Meyer and T. Reichstein, *Helv. Chim. Acta*, 1946, **29**, 152.
[20] R. J. Abraham, L. D. Hall, L. Hough, and K. A. McLauchlan, *J. Chem. Soc.*, 1962, 3699.
[21] R. C. Young, P. W. Kent, and R. A. Dwek, *Tetrahedron*, 1970, **26**, 3983.
[22] G. J. Lourens and A. Jordaan, *J. Heterocyclic Chem.*, in the press.

direct insertion technique. T.l.c. and p.l.c. were performed on silica gel GF_{254} (Merck); spots were detected with u.v. light at 254 nm, with iodine vapour, or with cerium(IV) sulphate. Silica gel for column chromatography refers to Merck reagent.

*Reaction of Tri-*O*-acetyl-*D*-glucal* (1) *with CSI*.—Tri-*O*-acetyl-D-glucal (1) (544 mg, 2 mmol) was intimately mixed with CSI (280 mg, 2 mmol) with cooling below 10°. The oil obtained was protected from moisture and air and kept at 10° for 2 h and then at room temperature for 16 h. After addition of ethanol (5 ml), the mixture was treated with aqueous sodium hydrogen carbonate solution (2N; 50 ml). Extraction with chloroform (2 × 50 ml), drying (Na_2SO_4), filtration, and removal of the solvent *in vacuo* gave an oil (290 mg) which slowly crystallized. Recrystallization from methanol gave needles, m.p. 182°, identical (m.p., mixed m.p., mass spectrum, and chromatographic behaviour) with authentic [4,5] 1,3,4,6-tetra-*O*-acetyl-2-*C*-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl)-2-deoxy-β-D-glucopyranose.

Reaction of Ethyl 4,6-*Di*-O-*acetyl*-2,3-*dideoxy*-α-D-erythro-*hex*-2-*enopyranoside* (2) *with CSI*.—To a solution of ethyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (2) (prepared [7] from tri-*O*-acetyl-D-glucal) (4·7 g, 18 mmol) in dry ether (30 ml), a solution of CSI (2·5 g, 18 mmol) in dry ether (20 ml) was added with stirring. The mixture was kept at room temperature for 18 h in a stoppered flask, then poured into an aqueous solution (100 ml) of sodium carbonate (10 g) and potassium iodide (2 g). The ether was removed with a stream of nitrogen and ethanol (*ca.* 50 ml) was added until all the organic precipitate had gone into solution. The solution was stirred for 10 min, diluted with water (200 ml), and extracted with chloroform (3 × 100 ml). The extracts were dried (Na_2SO_4) and filtered, and the solvent removed *in vacuo* to give a semicrystalline mass (4·8 g). Chromatography on silica (200 g) (elution with chloroform) gave an oil (400 mg), compound (A), identical (mass, i.r., and n.m.r. spectra) with authentic (3). The major component obtained from the column, 4,6-*di*-O-*acetyl*-1,2,3-*trideoxy*-3-*ethoxycarbonylamino*-D-arabino-*hex*-1-*enopyranose* (10) (3·2 g), crystallized from ether–hexane as needles, m.p. 113—115°, $[\alpha]_D^{22}$ +68°, $\nu_{max.}$ ($CHCl_3$) 3430 (NH), 1740 and 1720 (CO), and 1650 cm^{-1} (vinyl ether); *m/e* 213 ($M^+ - 88$); τ 3·63 (1H, q, $J_{1,2}$ 6·0 Hz, H-1) 5·16br (1H, NH, disappears on addition of D_2O), 5·30 (1H, q, $J_{2,3}$ 2 Hz, H-2), 5·90 (2H, q, *J* 7 Hz, O·CH_2·CH_3), 7·94 (6H, s, 2 × OAc), 8·89 (3H, t, *J* 7 Hz, O·CH_2·CH_3), and 4·80—6·10 (5H) (Found: C, 51·8; H, 6·3; N, 4·7. $C_{13}H_{19}NO_7$ requires C, 51·8; H, 6·4; N, 4·7%).

Catalytic Hydrogenation of Compound (10).—Compound (10) (90 mg) in ethanol (10 ml) was hydrogenated over palladium–charcoal (10 mg) (uptake 1 mol. equiv.). Filtration, evaporation, and recrystallization from acetone–hexane gave 4,6-di-O-*acetyl*-1,5-*anhydro*-2,3-*dideoxy*-3-*ethoxycarbonylamino*-D-arabino-*hexitol* (12), as needles, m.p. 130—132°, $[\alpha]_D^{21}$ +53°, M^+ 303, $\nu_{max.}$ ($CHCl_3$) 3410 (NH), 1735 (ester), and 1720 cm^{-1} (urethane), τ 5·10br (1H, NH, disappears on addition of D_2O), 5·90 (2H, q, O·CH_2·CH_3), 7·92 (6H, s, 2 × OAc), 8·78 (3H, t, *J* 7 Hz, O·CH_2·CH_3), and 5·00—6·70 (9H) (Found: C, 51·6; H, 6·9; N, 4·7. $C_{13}H_{21}NO_7$ requires C, 51·5; H, 7·0; N, 4·7%).

1,5-*Anhydro*-4,6-O-*benzylidene*-2-*deoxy*-D-ribo-*hexitol* (4).—A suspension of 4,6-*O*-benzylidene-D-allal [11] (3·3 g, 14 mmol) and Raney nickel (2 g) in 96% ethanol (100 ml) was stirred under positive hydrogen pressure. After 3 h the suspension was filtered and the filtrate evaporated to give an oil which slowly crystallized. Recrystallization from acetone–hexane gave the *hexitol* (1·7 g, 51%), m.p. 118—119°, $[\alpha]_D^{29}$ +22° (Found: C, 66·1; H, 6·8. $C_{13}H_{16}O_4$ requires C, 66·1; H, 7·1%).

1,5-*Anhydro*-4,6-O-*benzylidene*-2-*deoxy*-3-O-*tosyl*-D-ribo-*hexitol* (5).—A solution of the hexitol (4) (662 mg, 2·8 mmol) and toluene-*p*-sulphonyl chloride (591 mg, 3·1 mmol) in dry pyridine (6 ml) was left at 35° for 3 days, then poured into ice–water (50 ml) and extracted with chloroform (3 × 30 ml). The extract was washed with cold 0·2N-sulphuric acid (20 ml), saturated aqueous sodium hydrogen carbonate (20 ml), and water (20 ml), was dried (Na_2SO_4), and evaporated to give an oil which slowly crystallized. Recrystallization from methanol gave *compound* (5) (310 mg, 28%), m.p. 129—130°, $[\alpha]_D^{26}$ −2° (Found: C, 61·7; H, 5·7. $C_{20}H_{22}O_6S$ requires C, 61·5; H, 5·7%).

1,5-*Anhydro*-3-*azido*-4,6-O-*benzylidene*-2,3-*dideoxy*-D-arabino-*hexitol* (6).—A mixture of the *ribo*-hexitol (5) (488 mg, 1·25 mmol) and sodium azide (325 mg, 5 mmol) in dimethylformamide (5 ml) and water (2 ml) was kept at 120° under nitrogen for 24 h. It was then evaporated to dryness and the residue partitioned between chloroform (50 ml) and water (100 ml). The water layer was extracted with chloroform (2 × 20 ml) and the combined chloroform extracts were washed with water (50 ml), dried (Na_2SO_4), evaporated to give an oil (280 mg) which showed two spots on t.l.c. (chloroform). P.l.c. (chloroform) yielded *compound* (6) as an oil (240 mg, 73%), $[\alpha]_D^{28}$ −12°, $\nu_{max.}$ ($CHCl_3$) 2100 cm^{-1} (N_3) (Found: M^+, 261·110. $C_{13}H_{15}N_3O_3$ requires *M*, 261·110).

1,5-*Anhydro*-4,6-O-*benzylidene*-2,3-*dideoxy*-3-*ethoxycarbonylamino*-D-arabino-*hexitol* (7).—(a) *From compound* (12). Compound (12) (280 mg) was dissolved in methanol (200 ml) containing sodium methoxide (300 mg). After 18 h at room temperature the mixture was neutralized by passing it through a column of Bio-Rad Dowex 50 (20 g). The solvent was evaporated off, benzaldehyde (5 ml) was added to the residue, and the mixture was heated under carbon dioxide at 140° for 1 h. The mixture was passed down a column of silica (20 g), which was washed with benzene (500 ml) to remove excess of benzaldehyde. Elution with chloroform (250 ml) gave *compound* (7), which formed needles, m.p. 186° (from acetone), M^+ 307, $[\alpha]_D^{26}$ −36° (Found: C, 62·4; H, 6·9; N, 4·6. $C_{16}H_{21}NO_5$ requires C, 62·5; H, 6·9; N, 4·6%; *M*, 307).

(b) *From compound* (6). A mixture of the azide (6) (197 mg, 0·75 mmol) and zinc powder (300 mg) in 90% aqueous dimethylformamide (3 ml) was stirred under nitrogen at 140° for 18 h, then evaporated to dryness. The residue, after addition of water (100 ml), was extracted with chloroform (4 × 25 ml). The dried (Na_2SO_4) extract was evaporated to give an oil (180 mg). To a solution of this oil in dry cold pyridine (6 ml) ethyl chloroformate (1 ml) was added dropwise and the mixture was left at room temperature for 24 h. It was then poured into ice–water and extracted with chloroform (4 × 25 ml); the extract was washed successively with cold aqueous 0·5N-sulphuric acid (20 ml), saturated aqueous sodium hydrogen carbonate (20 ml), and water (20 ml), dried (Na_2SO_4), and evaporated to give crystalline material (235 mg). P.l.c. (chloroform as eluant) gave material which crystallized from acetone–hexane to give pure (7) (128 mg, 55% overall), identical (m.p., mixed m.p., mass spectrum, specific rotation, and analytical data) with the compound obtained by method (a).

1,5-*Anhydro*-4,6-O-*benzylidene*-2,3-*dideoxy*-3-*ethoxycarbonylamino*-D-ribo-*hexitol* (8).—The 3-*O*-tosylate of (9) [23] (2·5 g) was heated at 120° for 48 h under dry nitrogen with anhydrous hydrazine (20 ml). The hydrazine was then removed *in vacuo* (30° and 1 mmHg) to give semicrystalline material which was dissolved in ethanol (150 ml) and hydrogenated over Raney nickel at room temperature and 80 atm for 12 h. Filtration and evaporation left a crystalline sulphonate which was suspended in conc. aqueous potassium carbonate (100 ml) and extracted with dichloromethane (3 × 100 ml). Filtration of the extracts, drying (Na_2SO_4), and removal of solvent gave an oil which crystallized from hexane as needles, m.p. 85—86°, M^+ 235. A solution of this amine (470 mg) in dry pyridine (3 ml) was cooled in ice and a cold mixture of ethyl chloroformate (240 mg, 2·2 equiv.) and pyridine (2 ml) was added. The mixture was left at room temperature for 5 h and then poured into ice–water (50 ml). After stirring for 30 min the mixture was extracted with chloroform (3 × 25 ml) and the extract washed free of pyridine with ice-cold 0·2N-hydrochloric acid and then with a saturated solution of sodium hydrogen carbonate. Drying (Na_2SO_4), filtration, and evaporation yielded an oil (190 mg) which slowly crystallized. Recrystallization from acetone–hexane gave *needles*, m.p. 104—106°, M^+ 307, $[\alpha]_D^{26}$ +40° (Found: C, 62·3; H, 6·8; N, 4·4. $C_{16}H_{21}NO_5$ requires C, 62·5; H, 6·9; N, 4·6%).

3-*Acetamido*-4,6-*di*-O-*acetyl*-3-*deoxy*-D-*glucal* (11).—Compound (10) was refluxed for 18 h in anhydrous methanol (10 ml) in which sodium (0·5 g) has been dissolved. The solvent was removed *in vacuo*, acetic acid (2 ml) was added to the residue, and the mixture was then treated with acetic anhydride–pyridine (1 : 1) (20 ml) at 0°. The mixture was left at room temperature for 5 h, poured into ice–water (200 ml), and then (after 10 min) extracted with chloroform (3 × 100 ml). The extracts were washed with aqueous hydrochloric acid (2N; 2 × 150 ml), water (100 ml), and sodium hydrogen carbonate solution (N; 100 ml), dried (Na_2SO_4), filtered, and evaporated to give a semicrystalline solid (99 mg). P.l.c. [chloroform–methanol (97 : 3) as eluant] and crystallization from acetone–hexane gave *needles*, m.p. 156—158°, $[\alpha]_D^{18}$ +63°, $\nu_{max.}$ ($CHCl_3$) 3440 (NH), 1740 (OAc), 1670 (amide), and 1650 cm^{-1} (vinyl ether), τ 3·62 (1H, q, $J_{1,2}$ 6 Hz, H-1), 4·10 (1H, d, NH, disappears on addition of D_2O), 5·33 (1H, q, $J_{2,3}$ 2 Hz, H-2), 7·95 (6H, s, 2 × OAc), 8·08 (3H, s, NAc), and 4·8—6·0 (5H) (Found: C, 53·0; H, 6·0; N, 4·9. $C_{12}H_{17}NO_6$ requires C, 53·1; H, 6·3; N, 5·2%).

Hydrogenation of the Glucal (11).—Compound (11) absorbed 1 mol. equiv. of hydrogen when hydrogenated according to the procedure used to obtain (12). 3-*Acetamido*-4,6-*di*-O-*acetyl*-1,5-*anhydro*-2,3-*dideoxy*-D-arabino-*hexitol* (13) crystallized from acetone–hexane as needles, m.p. 166—168°, $[\alpha]_D^{22}$ +71°, M^+ 273, $\nu_{max.}$ ($CHCl_3$) 3404 (NH), 1738 (OAc), and 1667 cm^{-1} (amide), τ 4·05br (1H, d, NH, disappears on addition of D_2O), 7·95 (6H, s, 2 × OAc), 8·10 (3H, s, NAc), and 5·2—6·7 (9H) (Found: C, 52·9; H, 7·1; N, 5·4. $C_{12}H_{19}NO_6$ requires C, 52·7; H, 7·0; N, 5·1%).

Ethyl 2,3-*Dideoxy*-α-D-erythro-*hex*-2-*enopyranoside* (15).—Compound (2) (10·4 g, 4·03 mmol) was stirred with barium hydroxide octahydrate (25 g, 8·38 mmol) in water (250 ml) at room temperature (24 h). The excess of base was then neutralized with solid carbon dioxide. The mixture was filtered through a compact layer of filter aid and the water removed at 25° *in vacuo*. The residue was taken up in warm ethanol (200 ml) and the mixture filtered as before. The solvent was removed and the procedure was repeated with warm ethyl acetate. The residue crystallized from ethyl acetate to give compound (15) (7·8 g, 99%), m.p. 99—100° (lit.,[7] 100—101°); τ 4·05 (1H, doublet of narrow multiplets, $J_{3,2}$ 10 Hz, H-3), 4·29 (1H, doublet of narrow quartets, $J_{2,3}$ 10, $J_{2,1}$ 2·5, $J_{2,4}$ 2·0 Hz, H-2), 5·03 (1H, m, H-1), 5·83 (1H, triplet of narrow multiplets, $J_{4,5}$ 9, $J_{4,OH}$ 7·5 Hz, H-4, simplifies on addition of D_2O), 6·03—6·63 (5H, m, H-5, H-6*ax*, H-6*eq*, O·CH_2·CH_3, simplifies on addition of D_2O), 6·66 (1H, d, $J_{OH,4}$ 7·5 Hz, 4-OH disappears on addition of D_2O), 7·13 (1H, t, $J_{OH,6ax.6eq}$ 6 Hz, 6-OH disappears on addition of D_2O), and 8·80 (3H, t, J 7 Hz, O·CH_2·CH_3).

Ethyl 2,3-*Dideoxy*-4,6-*di*-O-*methyl*-α-D-erythro-*hex*-2-*enopyranoside* (14).—Sodium hydride (2·88 g, 60 mmol; 50% suspension in oil) was added in small amounts to compound (15) (5·23 g, 30 mmol) in dry dioxan (250 ml). When the evolution of hydrogen had ceased, methyl iodide (15 ml) was carefully added and the mixture was stirred at room temperature (3 h), filtered and evaporated *in vacuo* to give a pale yellow liquid. T.l.c. showed the presence of a trace of starting material (15) and a compound that was presumably monomethylated (15). Chromatography on silica (250 g) [elution with ethyl acetate–hexane (1 : 1)] gave the *dimethyl compound* (14) which was distilled (4·5 g, 74%), b.p. 62—67 at 0·1 mmHg, $[\alpha]_D^{22}$ +112°, τ 3·94 (1H, doublet of narrow multiplets, $J_{3,2}$ 10 Hz, H-3), 4·25 (1H, doublet of narrow multiplets, $J_{2,3}$ 10 Hz, H-2), 5·01 (1H, q, $J_{1,2}$ 2·5, $J_{1,4}$ <1 Hz, H-1), 6·02—6·74 (6H, m, H-4, H-5, H-6*ax*, H-6*eq*, O·CH_2·CH_3), 6·61 (3H, s, OMe), 6·64 (3H, s, OMe), and 8·80 (3H, t, J 7 Hz, O·CH_2·CH_3), *m/e* 157 (M^+ — OEt) (Found: C, 59·2; H, 8·9. $C_{10}H_8O_4$ requires C, 59·4; H, 9·0%).

Three successive Purdie methylations of (15), with excess of methyl iodide as solvent, also gave compound (14) (85%) on distillation.

Reaction of Compound (14) *with CSI*.—Compound (14) (5 g, 24·6 mmol) and CSI (3·54 g, 25 mmol) were treated in ether (50 ml) as described for compound (2). Similar work-up gave an oil (3·55 g). Chromatography on silica (250 g) [elution with ethyl acetate–hexane (1 : 1)] gave a pale yellow oil (1·54 g), which slowly crystallized. Recrystallization from cyclohexane–hexane gave 1,2,3-*trideoxy*-3-*ethoxycarbonylamino*-4,6-*di*-O-*methyl*-D-arabino-*hex*-1-*enopyranose* (17) as plates (1·35 g, 33%), m.p. 91—92°, $[\alpha]_D^{23}$ −10°, $\nu_{max.}$ ($CHCl_3$) 3430 (NH), 1710 (urethane), and 1650 cm^{-1} (vinyl ether), τ 3·66 (1H, q, $J_{1,2}$ 6, $J_{1,3}$ 2 Hz, H-1), 5·26 (1H, d, $J_{NH,3}$ 8·5 Hz, NH, disappears on addition of D_2O), 5·41 (1H, q, $J_{2,1}$ 6, $J_{2,3}$ 2 Hz, H-2), 5·57—6·72 (5H, m, H-3 to H-6*eq*, simplifies on addition of D_2O), 5·88 (2H, q, J 7 Hz, O·CH_2·CH_3), 6·51 (3H, s, OMe), 6·61 (3H, s, OMe), and 8·76 (3H, t, J 7 Hz, O·CH_2·CH_3), *m/e* 168 (M^+ — MeOH — MeO·CH_2) (Found: C, 54·0; H, 7·7; N, 5·6. $C_{11}H_{19}NO_5$ requires C, 53·9; H, 7·8; N, 5·7%).

Further elution gave a pale yellow oil (1·5 g) which on distillation (the apparatus employed did not allow the b.p. to be recorded) gave 2,3-*dideoxy*-4,6-*di*-O-*methyl*-αβ-D-erythro-*hex*-2-*enopyranose* (16) (1·11 g, 26%), ν_{max} ($CHCl_3$) 3400 cm^{-1} (OH), τ 3·97 (1H, doublet of narrow quartets, $J_{3,2}$ 10 Hz, H-3), 4·12—4·30 (1H, m, H-2), 4·65 (1H, m, H-1), 5·93—6·78 (4H, m, H-4 to H-6*eq*), 6·64 (3H, s, OMe), and 6·66 (3H, s, OMe), *m/e* 157 (M^+ — OH) (Found: C, 55·1; H, 7·9. $C_8H_{14}O_4$ requires C, 55·2; H, 8·1%).

[23] A. B. Foster, M. Stacey, and S. V. Vardheim, *Acta Chem. Scand.*, 1958, **12**, 1819.

1,5-*Anhydro*-2,3-*dideoxy*-3-*ethoxycarbonylamino*-4,6-*di*-O-*methyl*-D-ribo-*hexitol* (18).—Compound (17) (300 mg) was hydrogenated as in the preparation of (12). Recrystallization from cyclohexane–hexane gave *needles*, m.p. 63—64°, $[\alpha]_D^{22}$ +24°, $\nu_{max.}$ ($CHCl_3$) 3420 (NH) and 1710 cm^{-1} (urethane), τ 5·28 (1H, d, $J_{NH.5}$ 8 Hz, NH, disappears on addition of D_2O), 4·88 (2H, q, J 7 Hz, O·CH_2·CH_3), 6·02—7·05 (9H, m, simplifies on addition of D_2O), 6·66 (3H, s, OMe), 6·72 (3H, s, OMe), and 8·76 (3H, t, J 7 Hz, O·CH_2·CH_3), M^+ 247 (Found: C, 53·7; H, 8·4; N, 5·5. $C_{11}H_{21}NO_5$ requires C, 53·4; H, 8·6; N, 5·7%).

Demethylation and Acetylation of Compound (18) *to give Compound* (12).—Compound (18) (150 mg, 0·6 mmol) was treated with boron trichloride at −70° as described by Foster *et al.*[13] Acetic anhydride (2 ml) and pyridine (2 ml) were added to the residue and the solution was left at room temperature (16 h), then poured into ice–water (20 ml) and extracted with chloroform (2 × 10 ml). The extracts were washed [0·5N-sulphuric acid (2 × 10 ml), water (1 × 10 ml), saturated $NaHCO_3$ solution (2 × 10 ml), and water (1 × 10 ml)], dried (Na_2SO_4), and evaporated *in vacuo*. Recrystallization of the residue from acetone–hexane gave compound (12) (48 mg, 26%), m.p. and mixed m.p. 130—132°, identical (i.r. and n.m.r. spectra, t.l.c.) with the compound prepared before.

Ethyl 4,6-*Di*-O-*benzyl*-2,3-*dideoxy*-α-D-erythro-*hex*-2-*enopyranoside* (19).—Compound (15) (1·35 g, 7·7 mmol) was treated with sodium hydride (0·74 g, 15·5 mmol; 50% suspension in oil) and benzyl bromide (2·55 g, 15·5 mmol) in dioxan (75 ml) as in the preparation of (14) and the mixture was stirred at 100° (4 h). The solution was cooled, filtered, and evaporated to give a pale red syrup which on distillation (0·1 mmHg) (the apparatus employed did not allow the b.p. to be recorded) gave the *glycoside* (19) as a syrup (1·71 g, 78%), $[\alpha]_D^{22}$ +96°, τ 2·74 (5H, s, Ph), 2·78 (5H, s, Ph), 3·96 (1H, doublet of narrow multiplets, $J_{3,2}$ 10 Hz, H-3), 4·27 (1H, doublet of narrow quartets, $J_{2,3}$ 10, $J_{1,2}$ 2·5, $J_{2,4}$ 2·0 Hz, H-2), 5·45 (2H, q, J_{AB} 12, ν_{AB} 13·4 Hz, benzyl CH_AH_B), 5·51 (2H, q, $J_{A',B'}$ 12, $\nu_{A'B'}$ 13·4 Hz, benzyl $CH_{A'}H_{B'}$), 5·58 (1H, doublet of narrow multiplets, $J_{4,5}$ 9·5 Hz, H-4), 5·78—6·65 (5H, m, H-5, H-6*ax*, H-6*eq*, O·CH_2·CH_3), and 8·81 (3H, t, J 7 Hz, O·CH_2·CH_3), M^+ 354 (Found: C, 74·6; H, 7·6. $C_{22}H_{26}O_4$ requires C, 74·6; H, 7·4%).

Reaction of the Glycoside (19) *with CSI*.—Compound (19) (1 g, 2·8 mmol) and CSI (0·41 g, 2·9 mmol) in ether (20 ml) were treated as described for compound (2), to give an oil (635 mg). Chromatography on silica (75 g) (elution with hexane) gave unchanged (19) (75 mg, 7·5%) and an oil (0·148 g) which slowly crystallized. Recrystallization from acetone–hexane gave 4,6-*di*-O-*benzyl*-2,3-*dideoxy*-αβ-D-erythro-*hex*-2-*enopyranose* (20) as needles (0·13 g, 14%), m.p. 86—88°, $\nu_{max.}$ ($CHCl_3$) 3400 cm^{-1} (OH), τ 2·72 (5H, s, Ph), 2·77 (5H, s, Ph), 3·94 (1H, doublet of narrow multiplets, $J_{3,2}$ 5 Hz, H-3), 4·12—4·31 (1H, m, H-2), 4·62 (1H, m, H-1), 5·32—5·65 (4H, m, 2 × benzylic CH_AH_B), and 5·78—6·62 (4H, m, H-4 to H-6*eq*), *m/e* 308 ($M^+ - H_2O$) (Found: C, 73·5; H, 6·7. $C_{20}H_{22}O_4$ requires C, 73·6; H, 6·8%).

Reaction of Methyl 4-O-*Benzoyl*-2,3-*dideoxy*-β-L-glycero-*pent*-2-*enopyranoside with CSI*.—The pent-2-enopyranoside [14] (500 mg, 2·1 mmol) and CSI (312 mg, 2·2 mmol) in ether (10 ml) were treated as for compound (2), to give an oil (420 mg). Chromatography on silica (75 g) [elution with ethyl acetate–hexane (1 : 1)] gave an oil (192 mg) which slowly crystallized. Recrystallization from ethanol (96%) gave the ββ′-*disaccharide* (21) as needles (173 mg, 34·5%), m.p. 131° (lit.,[15] 125—126° for the enantiomeric compound), $[\alpha]_D^{23}$ −264° [lit.,[15] $[\alpha]_D^{23}$ +263° for the enantiomeric compound], *m/e* 301 ($M^+ - PhCO_2$), n.m.r. data identical with those for the enantiomer [15] (Found: C, 67·9; H, 5·3. $C_{24}H_{22}O_7$ requires C, 68·2; H, 5·3%).

Reaction of 3-O-*Benzyl*-5,6-*dideoxy*-1,2-O-*isopropylidene*-α-D-xylo-*hex*-5-*enofuranose* (25) *with CSI*.—Compound (25) [17] (1 g, 3·6 mmol) and CSI (0·55 g, 3·75 mmol) in ether (12 ml) were treated as described for compound (2) to give an oil (750 mg). P.l.c. [hexane–ethyl acetate (4 : 1) as eluant] gave unchanged (25) (157 mg, 15·7%) and a pale yellow gum which on recrystallization from ethanol (96%) gave 3-O-*benzyl*-5,6-*dideoxy*-α-D-xylo-*hex*-5-*enofuranose* 1,2-*carbonate* (26) as needles (291 mg, 31%), m.p. 71°, $[\alpha]_D^{21}$ −48°, $\nu_{max.}$ ($CHCl_3$) 1820 and 1840 cm^{-1} (cyclic carbonate), M^+ 262, τ 2·69 (5H, s, Ph), 3·80 (1H, d, $J_{1,2}$ 5 Hz, H-1), 4·00 (1H, septet, $J_{5,6\,trans}$ 17, $J_{5,6\,cis}$ 10, $J_{5,4}$ 7 Hz, H-5), 4·54 (1H, m, $J_{6\,trans,5}$ 17, $J_{6\,trans,6\,cis}$ 1·5, $J_{6\,trans,4}$ 1 Hz, H-6 *trans*), 4·60 (1H, m, $J_{6\,cis,5}$ 10, $J_{6\,cis,6\,trans}$ 1·5 Hz, H-6 *cis*), 5·02 (1H, d, $J_{2,1}$ 5 Hz, H-2), 5·40 (2H, s, with 2 small side peaks, J_{AB} 12, ν_{AB} <0·5 Hz, benzylic CH_AH_B), 5·41 (1H, m, H-4), and 5·95 (1H, d, $J_{3,4}$ 3 Hz, H-3) (Found: C, 64·1; H, 5·5. $C_{14}H_{14}O_5$ requires C, 64·1; H, 5·5%).

3-O-*Benzyl*-5,6-*dideoxy*-αβ-D-xylo-*hex*-5-*enofuranose* (27).—Compound (25) (0·89 g, 3·2 mmol) was kept at 90° (3 h) in aqueous acetic acid (60%; 15 ml). The solvent was removed *in vacuo* and the residue evaporated with toluene (3 × 5 ml) and carbon tetrachloride (2 × 5 ml) to remove all traces of acetic acid. The residue (0·72 g) crystallized from chloroform–hexane to give *compound* (27) as an amorphous solid (0·59 g, 78%), m.p. 65—67° (Found: C, 65·9; H, 6·9. $C_{13}H_{16}O_4$ requires C, 66·1; H, 6·8%).

Reaction of Compound (27) *with CSI*.—Treatment of (27) with CSI as already described gave compound (26) in 29% yield.

Reaction of Compound (26) *with CSI*.—Compound (26) (100 mg) was treated with CSI (0·5 ml) in ether (5 ml) in the usual manner. Work-up gave unchanged (26) (94 mg). The reaction was repeated in refluxing benzene (3 h) to give unchanged (26) in 91% yield.

Reaction of 5,6-*Di*-O-*Acetyl*-3-O-*benzyl*-1,2-O-*isopropylidene*-α-D-*glucofuranose* (28) *with CSI*.—Compound (28) [19] (500 mg, 1·27 mmol) and CSI (184 mg, 1·3 mmol) were treated in the usual manner to give a residue (304 mg). P.l.c. [ethyl acetate–hexane (1 : 1) as eluant] gave unchanged (28) (53 mg) and a pale yellow oil (61 mg). The oil was purified by p.l.c. to give 5,6-*di*-O-*acetyl*-3-O-*benzyl*-α-D-*glucofuranose* 1,2-*carbonate* (30) (45 mg, 9%) as an oil, $\nu_{max.}$ ($CHCl_3$) 1820 (cyclic carbonate) and 1740 cm^{-1} (acetate), M^+ 380, τ 2·69 (5H, s, Ph), 3·81 (1H, d, $J_{1,2}$ 5 Hz, H-1), 4·56 (1H, octet, $J_{5,4}$ 8·5, $J_{5,6}$ 4·5, $J_{5,6'}$ 2·5 Hz, H-5), 5·04 (1H, d, $J_{2,1}$ 5 Hz, H-2), 5·37 (1H, q, $J_{6',6}$ 12, $J_{6',5}$ 2·5 Hz, H-6′), 5·46 (2H, q, J_{AB} 12, ν_{AB} 10·6 Hz, $PhCH_AH_B$), 5·69 (1H, q, $J_{4,5}$ 8, $J_{4,3}$ 3·5 Hz, H-4), 5·89 (1H, d, $J_{3,4}$ 3·5 Hz, H-3), 5·93 (1H, q, $J_{6,6'}$ 12, $J_{6,5}$ 4·5 Hz, H-6), 7·97 (3H, s, OAc), and 8·10 (3H, s, OAc) (Found: M^+, 380·338. $C_{18}H_{20}O_9$ requires *M*, 380·340).

3-O-*Benzyl*-1,2-O-*isopropylidene*-5,6-*di*-O-*methyl*-α-D-*glucofuranose* (29).—Three successive Purdie methylations of 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose,[19] with excess of methyl iodide as solvent, gave an oil having no hydroxy-groups (i.r.). Distillation (0·1 mmHg) (the apparatus employed did not allow the b.p. to be recorded) gave *compound* (29) as an oil (1·2 g, 92%), $[\alpha]_D^{25}$ −21°, *m/e* 323

($M^+ - CH_3$), τ 2·69 (5H, s, Ph), 4·12 (1H, d, $J_{1,2}$ 4 Hz, H-1) 5·43 (1H, d, $J_{2,1}$ 4 Hz, H-2), 5·40 (2H, q, J_{AB} 12, ν_{AB} 9·0 Hz, $PhCH_AH_B$), 5·81 (1H, q, $J_{4,5}$ 9, $J_{4,3}$ 3 Hz, H-4), 5·96 (1H, d, $J_{3,4}$ 3 Hz, H-3), 6·17—6·60 (3H, m, H-5, H-6, H-6′), 6·62 (3H, s, OMe), 6·64 (3H, s, OMe), 8·54 (3H, s, CMe), and 8·72 (3H, s, CMe) (Found: C, 63·8; H, 7·7. $C_{18}H_{26}O_6$ requires C, 63·9; H, 7·7%).

Reaction of Compound (29) *with CSI*.—Compound (29) (950 mg, 2·8 mmol) and CSI (413 mg, 2·9 mmol) in ether (12 ml) were treated as before to give an oil (706 mg). P.l.c. [ethyl acetate–hexane (1 : 1) as eluant] gave unchanged (29) (384 mg, 40%) and a pale yellow oil (78 mg). The oil was purified by p.l.c. to give 3-O-*benzyl*-5,6-*di*-O-*methyl*-α-D-*glucofuranose* 1,2-*carbonate* (31) as an oil (52 mg, 8·3%), $\nu_{max.}$ ($CHCl_3$) 1820 cm^{-1} (cyclic carbonate), M^+ 324, τ 2·69 (5H, s, Ph), 3·86 (1H, d, $J_{1,2}$ 4 Hz, H-1), 5·10 (1H, d, $J_{2,1}$ 4 Hz, H-2), 5·37 (2H, s, $PhCH_AH_B$), 5·75—5·88 (2H, m, H-3, H-4), 6·07—6·68 (3H, m, H-5, H-6, H-6′), 6·62 (3H, s, OMe), and 6·64 (3H, s, OMe) (Found: M^+, 324·341. $C_{16}H_{20}O_7$ requires M, 324·320).

[2/1590 *Received*, 5*th July*, 1972]