Synthesis of Unsymmetrical 1,4-Diethers of Butadiene. A Ready Access to Normal and Ether-type Disaccharides with the β-*gulo*-Configuration

By **Serge David** * and **Jacques Eustache**, Laboratoire de Chimie Organique Multifonctionnelle,† Université de Paris-Sud, 91405 Orsay Cédex, France

The Wittig condensation of 3-benzyloxyacrolein with the phosphorane ROCH=PPh_3 derived from ' diacetone-glucose ' ROH, gives in the presence of iodide ions and excess of bases a 78 : 22 mixture of the all-*trans*-(2) and 1,2-*cis*-3,4-*trans*-(3) unsymmetrical 1,4-diethers of butadiene, RO·CH:CH·CH:CH·O·CH_2Ph. From the cycloaddition products of L-menthyl glyoxylate onto the diene (2), three 1,4,5-trisubstituted 2,3-dihydro-6*H*-pyrans with the all-*cis*-disposition, (4) (13.5%), (6) (24%), and (8) (19%) could be isolated. These were converted in good yield into completely functionalized disaccharides by lithium aluminium hydride reduction of the ester function, followed by *cis*-hydroxylation with osmium tetraoxide. Thus were obtained, starting respectively from compounds (4) and (6), 3-*O*-(4-*O*-benzyl-β-D- and L-gulopyranosyl)-1,2 ;5,6-di-*O*-isopropylidene-α-D-glucofuranose, (10) and (12). On the other hand, compound (8) gave *O*-(benzyl 4-deoxy-β-D-gulopyranosid-4-yl)-(4→3)-1,2 ;5,6-di-*O*-isopropylidene-α-D-glucofuranose (14). Thus binding of the oxygen atom of the dienophile to the diene (2) occurs on the sugar side, to give compounds (4) and (6), with the β-D- and β-L-sugar configuration, and on the benzyl side to give an ether of a benzyl β-D-hexopyranoside (8). The introduction of a 4-benzyloxy-substituent does not appear to change the relative reactivity towards cycloaddition of the two faces of the buta-1,3-dien-1-yl ether of ' diacetone-glucose '.

In previous papers,[1] we have shown that it was possible to build completely functionalized, chiral hexopyranosides starting from the cycloaddition products of glyoxylic esters onto the butadienyl ethers of protected sugars. Therefore it seemed desirable to examine the behaviour of ethers of substituted butadienes, with the hope of reducing the number of functionalization steps. We are aware of the existence of only three buta-1,3-dienes substituted by oxygen at positions 1 and 4: namely, 1,4-dimethoxy-,[2] 1,4-diphenoxy-,[3] and 1,4-diacetoxybuta-1,3-diene.[4] All three bear two identical substituents, and their mode of synthesis, which involves drastic steps, could not be readily extended to the preparation of butadienes with different, complicated oxygenated substituents on C-1 and C-4. The Wittig-type synthesis described below is obviously more versatile, and may be conducted so as to obtain the all-*trans*-isomer (2) as the main product. From the cycloaddition adducts, β-gulopyranosides may be prepared in two steps with very good yields, including a partially protected mixed ether of D-gulose and D-glucose.

RESULTS AND DISCUSSION

We have already reported [5] the preparation of a buta-1,3-dien-1-yl ether of the free secondary hydroxy-function of ' diacetone-glucose ', by a Wittig condensation of acrolein with the phosphorane derived from the phosphonium chloride (1). As the aldehyde partner, we have now chosen 3-benzyloxyacrolein. Although one isomer had already been prepared,[6] its configuration had not been elucidated. We found that its ^{1}H n.m.r. spectrum at 60 MHz was that of a pure *trans*-isomer ($J_{1.2}$ 13 Hz). Reaction with the same phosphorane as above gave in 62% yield a 2 : 3 mixture of dienyl diethers (2) and (3) with ' diacetone-glucose ' and benzyloxy-substituents at C-1 and C-4. This mixture could not be resolved, since even on t.l.c. plates, the two components were hardly separated in all the solvent systems used. The signals of the all-*trans* (2) and the 1,2-*cis*, 3,4-*trans* (3) dienes respectively could easily be located on the 240 MHz ^{1}H n.m.r. spectrum, the assumption being made that the *trans*-configuration of 3-benzyloxyacrolein was unaffected by the Wittig reaction. The signals of 1-H and 4-H in the *cis,trans*-diene (3) appear as doublets, at 5.90 and 6.56 p.p.m., with the coupling constants ^3J 6.2 and 12.6 Hz, respectively, characteristic of *cis*- and *trans*-orientations. On the other hand, because of the local symmetry of the all-*trans*-diene (2), the signals of 1-H and 4-H and those of 2-H and 3-H, are very near and appear as multiplets not amenable to first-order analysis.

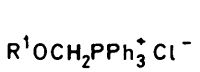
Preliminary experiments showed that the *cis,trans*-diene (3), although less reactive that its all *trans*-analogue (2), would still react with glyoxylic esters given on extended reaction times. This led to new adducts, and made the separation of pure products more difficult. Thus, we tried to lessen the proportion of the diene (3) in the Wittig condensation mixture. *In situ* equilibration of an intermediate betaine in the presence of strong bases and iodide ions has been claimed to be a good technique for the preparation of simple, *trans*-olefins [7] and, indeed, application of this technique in the present work raised from 40 to 78% the proportion of the all-*trans*-diene (2) formed.

In the cycloaddition of L-menthyl glyoxylate onto the above-prepared mixture the reaction was stopped when the main component (2) had disappeared (16 h at 80 °C), so as to minimize the production of the adducts of the diene (3). Chromatography then gave a mixture of three adducts (63%) one of which readily crystallized, m.p. 138 °C, upon addition of light petroleum; each of the others separated as an amorphous glass on chromatography of the mother-liquor.

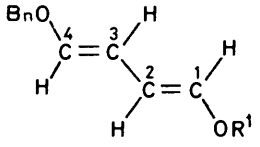
Because of the presence of two ether functions at each end of the diene system in (2), we were unable to decide upon the direction of the cycloaddition. We shall see below that the functionalization of the dihydropyran

† Equipe de recherches associée au C.N.R.S., n° 479.

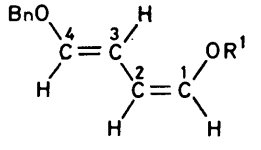
rings in the two glassy adducts leads to compounds which behave as typical, protected disaccharides. For instance, after removal of protecting groups they can be hydrolysed by moderate treatment with aqueous acid to



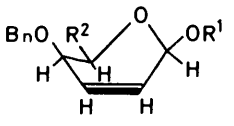
(1)



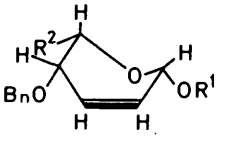
(2)



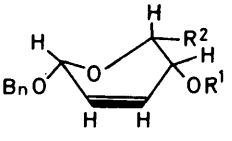
(3)



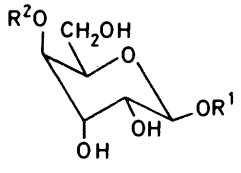
(4) R^2 = CO_2-L- Menthyl
(5) R^2 = CH_2OH



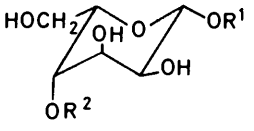
(6) R^2 = CO_2-L- Menthyl
(7) R^2 = CH_2OH



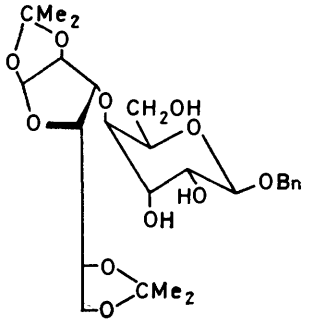
(8) R^2 = CO_2-L- Menthyl
(9) R^2 = CH_2OH



(10) R^2 = Bn
(11) R^2 = H

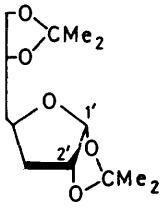


(12) R^2 = Bn
(13) R^2 = H



(14)

R^1 =



Bn = CH_2Ph

the component monosaccharides. Thus the dienophile oxygen atom is linked in these adducts to C-1 of the diene.

This being settled, the ^1H n.m.r. spectrum of the less-polar, glassy adduct obtained in 24% yield, points to either structure (4) or (6). The dihydropyran ring adopts the half-chair conformation in which the bulky L-menthoxycarbonyl substituent is equatorial. The axial. Thus the three substituents are on the same side of the ring. The alcohol obtained by lithium aluminium hydride reduction, (5) or (7), was *cis*-hydroxylated with osmium tetraoxide, to give, in high yield (89%), only one partially protected disaccharide. The likely assumption that the newly introduced *cis*-diol system would be *trans* to substituents already present was confirmed by the observation of high coupling, $J_{1.2}$ 8 Hz, an

indication that 1-H and 2-H are both axial. Thus the disaccharide is either a β-D- (10) or a β-L-glucoside (12). Hydrogenolytic removal of the benzyl ether function gave a new disaccharide (11) or (13), with a molecular rotation of +55, as estimated from the crude product. Calculations of molecular rotations from known values for methyl β-D-gulopyranoside [8] and ' diacetone-glucose ' respectively gave −218 and +121 for structures (11) and (13). Thus the disaccharide under study was the L-guloside (13). Acidic hydrolysis of the isopropylidene acetal and glycosidic bonds gave a mixture of gulose and glucose, which were characterized by v.p.c. It follows that the main adduct had structure (6) and was reduced to the alcohol (7) and *cis*-hydroxylated to the disaccharide (13).

The ^{1}H n.m.r. spectrum of the less-polar, glassy adduct, obtained in 13.5% yield, is almost superimposable on that of the adduct (6). This suggests that the dihydropyran moieties are enantiomeric in these compounds, so that this loss-polar adduct should have structure (4). Compound (4) may be reduced to the alcohol (5) and then *cis*-hydroxylated to the disaccharide (10). Hydrogenolysis of the benzyl ether function gives a disaccharide (11) the molecular rotation of which, −215, is in good agreement with the calculated value, −218. Complete, acidic hydrolysis of the disaccharide (11) gave a mixture of two hexoses, which were characterized as glucose and gulose by v.p.c.

In the ^{1}H n.m.r. spectrum of the crystalline adduct, m.p. 138 °C, of intermediate polarity, obtained in 19% yield, the values of the coupling constants are, once more, those expected for a β-*threo*-derivative in the half-chair conformation. This leaves as the only possibility an ether structure, resulting from a reverse cycloaddition. The signal of 3-H is shifted to low fields by 0.65 p.p.m. relative to its position in the spectra of the adducts (4) and (6), an indication of quite a different environment. The assumed β-D-guloside configuration (8) rests on the following evidence: lithium aluminium hydride reduction of the adduct (8) gave the alcohol (9) (93%), which was *cis*-hydroxylated with osmium tetraoxide in practically quantitative yield, to give the crystalline ether (14). Acid hydrolysis of the ether function in (14) would involve drastic, destructive conditions. However, the fact that the ether linkage is β to the potential aldehyde group of glucose suggested another possibility: mild hydrolysis with 90% aqueous trifluoroacetic acid removed the isopropylidene protecting groups. From the reducing disaccharide thus obtained, benzyl β-D-gulopyranoside was separated by alkaline β-elimination. Acidic hydrolysis of this guloside gave the free sugar which was characterized by v.p.c. The optical rotation was found to be $[\alpha]_D^{20}$ −15° while the values reported in the literature for D-gulose [9] vary between −10 and −20° according to the concentration.

Such derivatives as (14) (sometimes called anhydrides), where two reducing sugar units are linked by a true ether bond, are a very rare occurrence. To date, only three seem to have been reported: 6,6'-di-D-glucose anhydride,[10] D-glucose-D-galactose-6,6'-anhydride,[10] and methyl 4-*O*-(methyl 5-deoxy-β-D-ribofuranosid-5-yl)-β-D-glucopyranoside (and related derivatives),[11] a model of the core portion of the exotoxin from *Bacillus thuringiensis*.[12] In the latter case, the key step in the synthesis was the opening of a pyranose epoxide by the primary alcoholic function of a protected ribofuranose derivative. As the method looks somewhat laborious,[11] cycloaddition may provide a quicker approach to this barely-known class of carbohydrate derivatives.

A rigorous discussion of orientation in these additions is out of the question, since we can account for only 63% of the reaction products from the diene (2). Nevertheless, the proportions of isolated adducts are consistent with our former observations. As in the preceding paper,[13] we shall define the positive face of the diene *with respect to oxygen 3'-O of ' diacetone-glucose '*. Let us first consider the case when the dienophile oxygen atom binds itself to C-1 of the diene (2). We know that *endo*-additions on the positive and negative faces of the diene (2) lead respectively to β-D- and β-L-glycosides, while *exo*-additions result in α-glycosides. Assuming that the principle of *cis*-addition is still valid in our case, the benzyloxy-group will be *cis* to ' diacetone glucose ' in the adduct, giving products with the β-(D or L)-*threo*- and the α-(D or L)-*erythro*-configurations. The conclusion is that the adducts isolated only come from *endo*-addition, with a 64% preference for the negative face.

A similar reasoning shows that the disaccharide ether (8), β-D-*threo*, results from *endo*-addition on the negative face, which behaves in all cases as the more reactive one.

Altogether there is an 82% preference for the negative face, while in the case of the analogous diene not substituted on C-4, this preference was 73% with glyoxylic esters, and 68% with diethyl mesoxalate. Thus, in cycloadditions onto the diene (2), the chirality of the sugar near carbon C-1 once more appears to be the dominant factor in the selection of faces, while the benzyloxy-group seems to have little importance in this respect.

The sugar substituent in the diene (2) should be more electronegative than the benzyl, and a greater proportion of the ether-type adduct such as (8) would have been expected. Possibly the binding to C-1 of the dienophile carbonyl carbon is hindered by greater compression in the transition state.

EXPERIMENTAL

General Methods.—Chromatographic separations were made with the use of silica-gel columns, or, for analytical purpose only, plates coated with a thin layer of silica gel. ^{1}H N.m.r. spectra were recorded at 240 MHz, for solutions in the indicated solvent, and are reported in p.p.m. downfield from $SiMe_4$ (internal reference). Dashed figures refer to the atoms of the glucose unit. Ether refers to diethyl ether.

3-O-(EE *and* ZE-4-*Benzyloxybuta*-1,3-*dienyl*)-1,2;5,6-*di*-O-*isopropylidene*-α-D-*glucofuranose*, (2) *and* (3).—(a) A 1.7M-solution of phenyl-lithium (21 mmol) in benzene–ether (2 : 1) was slowly added to a suspension of the salt (1)

(11.41 g, 20 mmol) in dry ether (100 ml) under nitrogen. After 10 min, 3-benzyloxyacrolein (3.6 g, 22 mmol) was added, and after 5 min, the solution was filtered and evaporated to dryness. Chromatography of the residue (ether–light petroleum, 1 : 2) gave a 2 : 3 mixture (5.22 g, 62%), b.p. 150—160 °C at 0.01 mmHg, of the *EE*-(2) and *ZE*-(3) dienes, which appeared on t.l.c. (dichloromethane–hexane–acetone, 25 : 25 : 1) as two barely resolved spots; δ($CDCl_3$) for the *EE*-diene (2) 4.75 (2 H, s, $PhCH_2$), 5.46 (2 H, m, 2-H, 3-H), 6.37 (2 H, m, 1-H, 4-H); δ($CDCl_3$) for the *ZE*-diene (3) 4.83 (2 H, s, $PhCH_2$), 4.97 (1 H, q, $J_{1,2}$ 6.2 Hz, $J_{2,3}$ 11.2 Hz, 2-H), 5.73 (1 H, pseudo-t, $J_{3,4}$ 12.6 Hz, 3-H), 5.90 (1 H, d, 1-H), and 6.56 (1 H, d, 4-H). Intensity measurements on this spectrum allowed the estimation of the proportions of the dienes (2) and (3) in the mixture (Found: C, 66.3; H, 7.3; O, 26.8. $C_{23}H_{30}O_7$ requires C, 66.0; H, 7.2; O, 26.2%).

(b) To a solution of lithium iodide (575 mmol) in tetrahydrofuran (thf) (100 ml), prepared by *in situ* mixing of phenyl-lithium and methyl iodide, was first added the phosphonium salt (1) (18.6 g, 32.6 mmol), and then a 1.7M-solution of phenyl-lithium (34.2 mmol) in benzene-ether (2 : 1). After 10 min, the solution was cooled to −80 °C, and 3-benzyloxyacrolein (5.80 g) was slowly added. After 10 min, more phenyl-lithium (37.5 mmol) was slowly added, and the mixture was kept for 30 min at −80 °C. Potassium t-butoxide (75 mmol) and t-butyl alcohol (75 mmol) were then added and the mixture was allowed to warm to room temperature during 1 h. Most of the thf was then evaporated, light petroleum (200 ml) was added, the precipitate was filtered off on a silica-gel bed, and the solution was evaporated to dryness. Chromatography as above gave a 78 : 22 mixture of *EE*-(2) and *ZE*-(3) dienes (8.04 g, 59%).

Cycloaddition.—A mixture of the dienes (2) and (3) (78 : 22; 4.00 g) and L-menthyl glyoxylate (1.8 g) was heated at 80 °C for 16 h with exclusion of air, in the presence of hydroquinone (20 mg), when t.l.c. (dichloromethane–hexane–acetone, 25 : 25 : 1) indicated the disappearance of the diene (2), and the appearance of a major, composite spot corresponding to new compounds. These were separated by chromatography (ether–light petroleum, 1 : 1) as a purified mixture (3.02 g, 63%) which could be resolved by t.l.c. (dichloromethane–hexane–acetone, 15 : 15 : 1) into three components, called (A), (B), and (C) in order of increasing polarity. Dissolution of this mixture in boiling, light petroleum (10 ml) brought about the separation of (B) as a crystalline precipitate (0.91 g, 19%). Chromatography (dichloromethane–hexane–acetone, 15 : 15 : 1) of the mother-liquor of (B) first gave (A) (1.12 g, 24%) and then (C) (0.64 g, 13.5%).

O-(L-*Menthyl* 4-O-*benzyl*-β-L-threo-*hex*-2-*enopyranosyluronate*)-(1→3)-1,2;5,6-*di*-O-*isopropylidene*-α-D-*glucofuranose* (6).—This is component (A) of the mixture : glass (24%), $[\alpha]_D^{20}$ +32° (*c* 1.2 in CH_2Cl_2), δ(C_6D_6) 5.04 (1 H, s, with a fine structure, 1-H), 5.14 (1 H, d, $J_{1',2}$ 3.8 Hz, 2'-H), 5.64 (1 H, dd, $J_{2,3}$ 10.8 Hz, $J_{3,4}$ 5 Hz, 3-H), 5.80 (1 H, d, 2-H), and 5.86 (1 H, d, 1'-H) (Found: C, 66.3; H, 7.8; O, 25.3. $C_{35}H_{50}O_{10}$ requires C, 66.7; H, 7.9; O, 25.4%).

O-(L-*Menthyl* 4-O-*benzyl*-β,D-threo-*hex*-2-*enopyranosyluronate*)-(1→3)-1,2;5,6-*di*-O-*isopropylidene*-α-D-*glucofuranose* (4).—This is component (C) of the mixture : glass (13.5%), $[\alpha]_D^{20}$ −77° (*c* 5 in CH_2Cl_2), δ(C_6D_6) 5.07 (1 H, d, $J_{1',2'}$ 3.8 Hz, 2'-H), 5.11 (1 H, s with a fine structure, 1-H), 5.76 (1 H, dd, $J_{2,3}$ 10.5 Hz, $J_{3,4}$ 4.3 Hz, 3-H), 5.87 (1 H, d, 2-H), and 5.96 (1 H, d, 1'-H) (Found: C, 66.2; H, 8.1; O, 25.7. $C_{35}H_{50}O_{10}$ requires C, 66.7; H, 7.9; O, 25.4%).

O-[L-*Menthyl* (*benzyl* 4-*deoxy*-β-D-threo-*hex*-2-*enopyranosid*-4-*yl*)*uronate*]-(4→3)-1,2;5,6-*di*-O-*isopropylidene*-α-D-*glucofuranose* (8).—This is component (B) of the mixture (19%), m.p. 138 °C (from light petroleum), $[\alpha]_D^{20}$ −123° (*c* 1.4 in CH_2Cl_2), δ($CDCl_3$) 4.63 (1 H, d, $J_{1',2'}$ 3.8 Hz, 2'-H, 4.76, 4.91 (2 H, two d, $PhCH_2$), 5.30 (1 H, s, 1-H), 5.85 (1 H, d, 1'-H), 6.00 (1 H, d, $J_{2,3}$ 10.8 Hz, 2-H), and 6.35 (1 H, dd, $J_{3,4}$ 5.3 Hz, 3-H) (Found: C, 66.6; H, 8.1; O, 25.3. $C_{35}H_{50}O_6$ requires C, 66.7; H, 7.9; O, 25.4%).

O-(4-O-*Benzyl*-β-L-threo-*hex*-2-*enopyranosyl*)-(1→3)-1,2;5,6-*di*-O-*isopropylidene*-α-D-*glucofuranose* (7).—Lithium aluminium hydride (70 mg) was added to a solution of the ester (6) in ether (15 ml). After 1 h, the usual work-up gave the disaccharide (8) which, after chromatographic purification (ether–light petroleum, 3 : 1) was obtained as a glass (75%), $[\alpha]_D^{20}$ +50° (*c* 2 in CH_2Cl_2) (Found: C, 62.5; H, 7.1; O, 30.4. $C_{25}H_{34}O_9$ requires C, 62.8; H, 7.1; O, 30.1%).

Compounds (5) and (9) were prepared in the same way.

O-(4-O-*Benzyl*-β-D-threo-*hex*-2-*enopyranosyl*)-(1→3)-1,2;5,6-*di*-O-*isopropylidene*-α-D-*glucofuranose* (5).—From the reduction of the ester (4), obtained as a glass (63%), $[\alpha]_D^{20}$ −45° (*c* 1 in CH_2Cl_2) (Found: C, 62.6; H, 7.3; O, 30.3. $C_{25}H_{34}O_9$ requires C, 62.8; H, 7.1; O, 30.1%).

O-(*Benzyl* 4-*deoxy*-β-D-threo-*hex*-2-*enopyranosid*-4-*yl*)-(4→3)-1,2;5,6-*di*-O-*isopropylidene*-α-D-*glucofuranose* (9).—Obtained by reduction of the ester (6) as a glass (93%), $[\alpha]_D^{20}$ −88° (*c* 3 in CH_2Cl_2) (Found: C, 62.1; H, 7.1; O, 30.7. $C_{25}H_{34}O_9$ requires C, 62.8; H, 7.1; O, 30.1%).

O-(4-*Benzyl*-β-L-*gulopyranosyl*)-(1→3)-1,2;5,6-*di*-O-*isopropylidene*-α-D-*glucofuranose* (12).—A solution of osmium tetraoxide (0.27 g) in pyridine (2.7 ml) was added to a solution of the disaccharide (7) (0.47 g) in pyridine (4 ml), and the mixture was kept for 45 min at room temperature. Sodium hydrogen sulphite (0.60 g) in water (6 ml) and pyridine (2 ml) solution were then added. The mixture was stirred for 30 min, evaporated to dryness, and the residue was extracted with chloroform. Chromatographic purification (chloroform–methanol, 19 : 1) of this extract gave the *disaccharide* (12) as a foam, (0.45 g, 89%), homogeneous by t.l.c., $[\alpha]_D^{20}$ +7° (*c* 1 in CH_2Cl_2), δ($CDCl_3$) 4.54, 4.75 (2 H, two d, $PhCH_2$), 4.73 (1 H, d, $J_{1,2}$ 8 Hz, 1-H), 4.80 (1 H, d, $J_{1',2'}$ 3.8 Hz, 2'-H), and 6.00 (1 H, d, 1'-H) (Found: C, 58.2; H, 6.9; O, 34.8. $C_{25}H_{36}O_{11}$ requires C, 58.6; H, 7.1; O, 34.5%).

The disaccharides (10) and (14) were prepared in the same manner.

O-(4-O-*Benzyl*-β-D-*gulopyranosyl*)-(1→3)-1,2;5,6-*di*-O-*isopropylidene*-α-D-*glucofuranose* (10).—Prepared from (5), as a glass (83%), homogeneous by t.l.c., $[\alpha]_D^{20}$ −33° (*c* 1 in CH_2Cl_2), δ($CDCl_3$) 4.46, 4.64 (2 H, 2 d, $PhCH_2$), 4.60 (1 H, d, $J_{1,2}$ 8 Hz, 1-H), 4.78 (1 H, d, $J_{1',2'}$ 3.5 Hz, 2'-H), and 5.86 (1 H, d, 1'-H) (Found: C, 58.6; H, 7.3; O, 34.3. $C_{25}H_{36}O_{11}$ requires C, 58.6; H, 7.1; O, 34.5%).

O-(*Benzyl* 4-*deoxy*-β-D-*gulopyranosid*-4-*yl*)-(4→3)-1,2;5,6-*di*-O-*isopropylidene*-α-D-*glucofuranose* (14).—Obtained from compound (9) as crystals (98%), m.p. 148—150 °C (from ether), $[\alpha]_D^{20}$ −72° (*c* 1 in CH_2Cl_2), δ($CDCl_3$) 4.54 (1 H, d, $J_{1',2'}$ 3.7 Hz, 2'-H), 4.63, 4.95 (2 H, 2 d, $PhCH_2$), 4.79 (1 H, d, $J_{1,2}$ 8 Hz, 1-H), and 5.90 (1 H, d, 1'-H) (Found: C, 58.5; H, 7.0; O, 34.5. $C_{25}H_{36}O_{11}$ requires C, 58.6; H, 7.1; O, 34.3%).

Deprotection and Hydrolysis of Disaccharides (10) *and* (12).—A solution of compound (12) (90 mg) in 90% alcohol (10 ml) was shaken in a hydrogen atmosphere during 48 h at room temperature and normal pressure in the presence of palladium–charcoal (10%, 30 mg). Evaporation to dryness of the filtered solution then gave the crude disaccharide (13) (24.3 mg, 98%), $[\alpha]_D^{20}$ +13° (*c* 1 in water). A solution of this in 1M-aqueous sulphuric acid was refluxed for 90 min, then neutralized ($BaCO_3$), and filtered. The filtered solution was evaporated to dryness, and the residue was further dried *in vacuo*, taken over in pyridine, and silylated. V.p.c. (SE 30 column operating at 145 °C and 1.5 bar) then indicated the presence of two sugars with the same behaviour as glucose and gulose.

A similar treatment of the disaccharide (10) gave the crude debenzylated product (11), $[\alpha]_D^{20}$ −51° (*c* 1 in water), which was further hydrolysed to a mixture of glucose and gulose.

Degradation of the Ether (14) *to* D-*Gulose*.—A solution of compound (14) (52 mg) in 90% aqueous trifluoroacetic acid was kept for 20 min at room temperature, and then evaporated to dryness at room temperature at 0.01 mmHg. Molar, aqueous sodium hydroxide was then added, the mixture was heated at 100° for 1 h, and then evaporated to dryness. Chromatography of the residue (ethyl acetate–water–isopropyl alcohol, 65 : 11.5 : 23.3) gave benzyl D-guloside (20 mg, 60%), $[\alpha]_D^{20}$ −86° (*c* 1.6 in water). A solution of this in 1M-aqueous sulphuric acid was refluxed for 1 h, then neutralized ($BaCO_3$), filtered, and evaporated to dryness. The dried residue (9.45 mg, 72%), $[\alpha]_D^{20}$ −15° (*c* 1 in water) behaved like D-gulose in v.p.c. examination after silylation.

^1H *N.M.R. Spectrum of* E-3-*Benzyloxypropenal*.—δ(60 MHz, $CDCl_3$, $SiMe_4$) 4.95 (2 H, s, $PhCH_2$), 5.63 (1 H, dd, $J_{1,2}$ 7.5 Hz, $J_{2,3}$ 13 Hz, 2-H), 7.32 (5 H, Ph), 7.38 (1 H, d, 3-H), and 9.05 (1 H, d, CHO).

[8/1756 *Received*, 9*th October*, 1978]

REFERENCES

[1] (*a*) S. David, A. Lubineau, and J. M. Vatèle, *J.C.S. Perkin I*, 1976, 1831; (*b*) S. David and A. Lubineau, *Nouveau J. Chimie*, 1977, **1**, 376; (*c*) S. David, A. Lubineau, and J. M. Vatèle, *J.C.S. Chem. Comm.*, 1978, 535.

[2] H. Meister, *Chem. Ber.*, 1963, **96**, 1688.

[3] M. Julia and M. Baillarge, *Compt. rend.*, 1962, **254**. 4313.

[4] R. Criegee, W. Hörauf, and W. D. Schellenberg, *Chem. Ber.*, 1953, **86**, 126.

[5] S. David, J. Eustache, and A. Lubineau, *J.C.S. Perkin I*, 1974. 2274.

[6] V. T. Klimko, T. V. Protopopova, N. S. Smirnova, and A. P. Skoldinov, *J. Gen. Chem.* (*U.S.S.R.*), 1962, **32**, 2913.

[7] M. Schlosser, K. F. Christmann, and A. Piskala, *Chem. Ber.*, 1970, **103**, 2814.

[8] N. J. Antia and M. B. Perry, *Canad. J. Chem.*, 1960, **38**. 1917.

[9] L. Hough and A. C. Richardson, in ' Rodd's Chemistry of Carbon Compounds,' ed. S. Coffey, Elsevier, Amsterdam, 1967, vol. I, part F, p. 238.

[10] R. L. Whistler and A. Frowein, *J. Org. Chem.*, 1961, **26**, 3946.

[11] M. Prystas and F. Sorm, *Coll. Czech. Chem. Comm.*, 1971, **36**, 1448, 1472.

[12] H. de Barjac and M. R. Dedonder, *Compt. rend.*, 1965, **260**, 7050.

[13] S. David, J. Eustache, and A. Lubineau, *J.C.S. Perkin I*, 1979, 1795.