1353. *Branched-chain Sugars. Part V.*[1] *Structure and Reactivity of Anhydro-sugars. Part VI.*[2] *The Synthesis of Branched-chain Deoxy-sugars*

By A. A. J. Feast, W. G. Overend, and N. R. Williams

The preparation of branched-chain deoxy-sugars by the action of organo-lithium reagents on methyl 2,3-anhydro-β-D-ribopyranoside and some of its derivatives has been investigated. With the exception of methyl-lithium, which led to unidentified unsaturated products, the various reagents examined led to cleavage of the epoxide to give 3-*C*-substituted derivatives of methyl 3-deoxy-β-D-xylopyranoside. By appropriate conversions the 3-*C*-formyl and 3-*C*-hydroxymethyl derivatives were obtained from methyl 3-deoxy-3-*C*-(2,2-dimethylvinyl)- or (*cis*- or *trans*-2-phenylethenyl)-β-D-xylopyranoside. Although methyl-lithium cleaves the epoxide in methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-mannoside in normal fashion to give a product with a methyl branch at *C*-3, with the corresponding alloside it gives a 4,6-*O*-benzylidene-glycal.

Recently we described general methods for the preparation of branched-chain sugars.[1,3] We have been concerned also with the synthesis of branched-chain deoxy-sugars, and in an earlier Paper some experiments on the conversion of branched-chain sugars into their deoxy-analogues (*i.e.*, $\rangle C(OH)-R \longrightarrow \rangle CH-R$) were outlined. However, the method developed was not general, and so we have examined other possible routes to these deoxy-sugars. In particular, the action of organo-lithium compounds on methyl 2,3-anhydroglycosides has been studied.

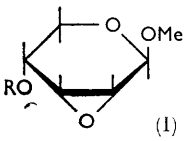
Little has been reported in the literature concerning the scission of epoxides with these reagents, and in the case of sugar epoxides the results did not permit general conclusions to be drawn about the mode of reaction. Thus, working with anhydrides in which there was no fused ring system, English and Levy [4] obtained 1,2-*O*-isopropylidene-3-*O*-benzyl-5-deoxy-5,6-glucoseen from the treatment of either 1,2-*O*-isopropylidene-3-*O*-benzyl-5,6-anhydro-D-glucose or L-idose with methyl-lithium. However, reaction of the 5,6-anhydro-glucose derivative with phenyl-lithium yielded the 6-deoxy-6-*C*-phenyl compound. With ethyl-lithium and the same anhydride an unidentified sugar which was not unsaturated was obtained.

The major part of our work has been carried out with methyl 2,3-anhydro-β-D-ribo-pyranoside (I; R = H), and for the reasons given previously [3] we were interested in introducing as branch a formyl, hydroxymethyl, or methyl group. At the outset it was considered advisable to protect the free hydroxyl group in the anhydride, and so the 4-*O*-tosyl, 4-*O*-methyl,[5] 4-*O*-trimethylsilyl,[6] and 4-*O*-benzyl derivatives were prepared. Some difficulty was encountered with the benzylation, and no etherification was achieved from the action of benzyl chloride on the sodio-derivative of (I; R = H), which was prepared by adding sodium in dry xylene, or the sodium-naphthalene reagent [7] to the anhydride (I). (Cf. the recent preparation of methyl 2,3-anhydro-4-*O*-benzyl-β-L-riboside by adding benzyl bromide to the sodio-derivative obtained by treating the parent anhydride with the sodium-naphthalene reagent.[8]) The derivative (I; R = CH_2Ph) was eventually obtained

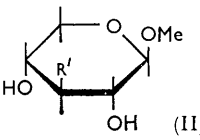
[1] Part IV, W. G. Overend and N. R. Williams, *J.*, 1965, 3446.
[2] Part V, E. J. Hedgley, W. G. Overend, and R. A. C. Rennie, *J.*, 1963, 4701.
[3] J. S. Burton, W. G. Overend, and N. R. Williams, *J.*, 1965, 3433.
[4] J. English and M. F. Levy, *J. Amer. Chem. Soc.*, 1956, **78**, 2846.
[5] Prepared by the procedure of J. C. Irvine and A. Cameron, *J.*, 1904, 1071.
[6] Prepared by the method of E. J. Hedgley and W. G. Overend, *Chem. and Ind.*, 1960, 378.
[7] N. D. Scott, J. F. Walker, and V. L. Hansley, *J. Amer. Chem. Soc.*, 1936, **58**, 2442.
[8] N. F. Taylor and G. M. Riggs, *Chem. and Ind.*, 1963, 209.

by a modification of the benzylation procedure of Croon and Lindberg,[9] by treating the anhydride at room temperature with benzyl bromide in dimethylformamide in the presence of silver oxide.

First 2,2-dimethylvinyl-lithium was used as reagent for cleavage of the epoxide, because ozonolysis of a 2,2-dimethylvinyl branch would yield a formyl group from which the hydroxymethyl and methyl branches are derivable (see Burton *et al.*[3]). When the lithium reagent was added to the 4-*O*-methyl derivative (I; R = Me) a syrup was obtained which analysed correctly for a methyl deoxy-*C*-(2,2-dimethylvinyl)-*O*-methyl-β-D-pentoside, but which contained two components in the ratio of 93 : 7. An attempt to dealkylate this mixture or the product obtained on reduction of the double bond in the branching group, by the procedure of Bonner *et al.*,[10] led only to black material. When the 4-*O*-benzyl



(I)



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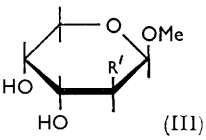


(III)

derivative (I; R = CH_2Ph) was treated with 2,2-dimethylvinyl-lithium a crystalline methyl 4-*O*-benzyl-2 or 3-deoxy-2 or 3-*C*-(2,2-dimethylvinyl)-β-pentoside was obtained which would be either the 2-deoxy-2-*C*-(2,2-dimethylvinyl)arabinoside (III; R″ = $CH{=}CMe_2$) or the 3-deoxy-3-*C*-(2,2-dimethylvinyl)xyloside (II; R′ = $CH{=}CMe_2$) derivative. Attempts to determine the configuration by successive debenzylation and periodate oxidation were unsuccessful. Debenzylation was not achieved by treatment with hydrogen and either Adams catalyst in glacial acetic acid or ethanol, or palladium–charcoal, or by treatment in ethanol with sodium or sodium amalgam. Consequently, experiments with methyl 2,3-anhydro-4-*O*-benzyl-β-D-riboside were not pursued further.

In other attempts to determine the direction of scission of the epoxide the 4-*O*-tosyl derivative (I; R = Ts) was treated with phenyl-lithium. [This reagent was selected rather than methyl-lithium because preliminary experiments with the latter had given anomalous results (see later).] Two compounds were isolated. An amorphous substance gave a crystalline diacetate which analysed correctly for a methyl di-*O*-acetyl-deoxy-*C*-phenyl-β-D-pentoside, and which underwent smooth deacetylation to afford a crystalline glycoside which consumed no periodate. Taken in conjunction with its method of formation, this stability to periodate indicated that it was methyl 3-deoxy-3-*C*-phenyl-β-D-xylopyranoside (II; R′ = Ph). The other product was identified as phenyl *p*-tolyl sulphone. Consequently, detosylation had occurred in the reaction, and cleavage of the epoxide had taken place in normal fashion to give a product with the *xylo*-configuration.

In view of these results, methyl 2,3-anhydro-β-D-ribopyranoside (I; R = H) was treated with phenyl-lithium, and this reaction also yielded methyl 3-deoxy-3-*C*-phenyl-β-D-xylopyranoside, which could be converted into a 2,4-diacetate identical with that obtained previously. Hydrolysis of the glycoside (II; R′ = Ph) by Wadman's method [11] gave crystalline 3-deoxy-3-*C*-phenyl-D-xylose. The direction of mutarotation indicated that the sugar most probably had the β-configuration. With 2,2-dimethylvinyl-lithium the anhydride (I; R = H) afforded in good yield a syrupy mixture of methyl 3-deoxy-3-*C*-(2,2-dimethylvinyl)-β-D-xylopyranoside (II; R′ = $CH{=}CMe_2$) and methyl 2-deoxy-2-*C*-(2,2-dimethylvinyl)-β-D-arabinopyranoside (III; R′ = $CH{=}CMe_2$); the latter was present to the extent of 20% as determined by periodate oxidation. The aqueous phase obtained on work-up was shown by thin-layer chromatography to contain unreacted

[9] I. Croon and B. Lindberg, *Acta Chem. Scand.*, 1959, **13**, 593.
[10] T. G. Bonner, E. J. Bourne, and S. McNally, *J.*, 1960, 2929.
[11] W. H. Wadman, *J.*, 1952, 3051.

anhydride (I; R = H), compounds (II; R′ = CH=CMe_2) and (III; R′ = CH=CMe_2), and a substance later identified as methyl 2-bromo-2-deoxy-β-D-arabinopyranoside (III; R″ = Br) by comparison with crystalline material obtained from experiments with the anhydride (I; R = H) and phenylacetylene-lithium; all were present in small amount. Separation of compounds (II; R′ = CH=CMe_2) and (III; R′ = CH=CMe_2) was achieved by acetonation of (III; R′ = CH=CMe_2) followed by chromatography on a column of neutral alumina. Pure xyloside (II; R′ = CH=CMe_2) was obtained, but the acetonated arabinoside could not be freed from contaminants.

The anhydride (I; R = H) was treated also with phenylacetylene-lithium and *trans*-styryl-lithium. When the phenylacetylene-lithium was prepared *in situ* from n-butyl bromide, lithium, and phenylacetylene *via* n-butyl-lithium a reasonable yield (based on anhydride) of methyl 3-deoxy-3-*C*-(phenylethynyl)-β-D-xylopyranoside (II; R′ = C≡C·Ph) was obtained, accompanied by a small amount of a syrupy mixture of unreacted anhydride (I; R = H) and methyl 2-bromo-2-deoxy-β-D-arabinoside (III; R′ = Br). However, if the phenylacetylene-lithium was prepared by treating phenyl-lithium (from bromobenzene and lithium) with phenylacetylene a very poor yield of methyl 3-deoxy-3-*C*-(phenylethynyl)-β-D-xyloside (II; R′ = C≡C·Ph) was obtained, together with methyl 2-bromo-2-deoxy-β-D-arabinoside (III; R′ = Br). The structure and configuration of the latter compound followed from its elemental analysis, consumption of 1·04 mol. of periodate, and sequential reductive dehalogenation and hydrolysis to give a sugar chromatographically indistinguishable from 2-deoxy-D-ribose, and the fact that it was derived from a 2,3-anhydroriboside. There are two features of interest about the production of this halogenated glycoside, (i), it is formed in greater amount than compound (II; R = C≡C·Ph) and (ii), on the basis of what is known [12] about epoxide-cleavage reactions of the anhydride (I; R = H) it is not the isomer that would be expected. However, no trace of methyl 3-bromo-3-deoxy-β-D-xyloside (II; R′ = Br) could be detected amongst the reaction products. Presumably the methyl 2-bromo-2-deoxy-β-D-arabinoside (III; R′ = Br) arises from reaction of lithium bromide with the anhydride (I; R = H), but it cannot be a direct reaction because we showed that the action of anhydrous lithium bromide on the anhydride (I; R = H) in dry ether under an atmosphere of pure dry nitrogen gave mainly methyl 3-bromo-3-deoxy-β-D-xylopyranoside (II; R′ = Br), and only a chromatographic amount of methyl 2-bromo-2-deoxy-β-D-arabinoside (III; R′ = Br). This result is akin to that of Kent *et al.*,[12b] who found that treatment of the anhydride (I; R = H) with hydrobromic acid in acetone afforded predominantly the xyloside derivative (II; R′ = Br). In the preparation of phenylacetylene-lithium *in situ* from bromobenzene, lithium, and phenylacetylene, the lithium bromide will be present as part of a complex containing also ether and the organo-lithium reagent,[13] but it is not known whether cleavage of the 2,3-anhydride (I; R = H) by this complex would give an anomalous reaction leading to the 2-bromo-2-deoxyarabinoside. This problem is being investigated further.

Partial reduction of the acetylenic compound (II; R′ = C≡C·Ph) afforded methyl 3-deoxy-3-*C*-(*cis*-2-phenylethenyl)-β-D-xylopyranoside (II; R′ = *cis*-CH=CHPh). The corresponding *trans*-isomer (II; R′ = *trans*-CH=CHPh) was obtained by treating the anhydride (I; R = H) with *trans*-styryl-lithium. It was shown to differ from the *cis* form by melting point, mixed melting point, specific rotation, and infrared spectral measurements. A single substance, methyl 3-deoxy-3-*C*-(2-phenylethyl)-β-D-xylopyranoside (II; R′ = $(CH_2)_2$Ph), was obtained on reduction of both compounds. That these compounds (II, R′ = C≡C·Ph, $-(CH_2)_2$Ph, and *cis*- and *trans*-CH=CHPh) have been correctly designated as 3-*C*-substituted derivatives of methyl 3-deoxy-β-D-xylopyranoside was indicated by the

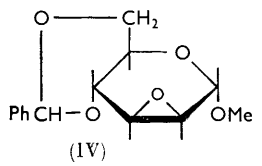
[12] (*a*) J. Honeyman, *J.*, 1946, 990; S. Mukherjee and A. R. Todd, *J.*, 1947, 969; R. Allerton and W. G. Overend, *J.*, 1951, 1480; B. R. Baker and R. E. Schaub, *J. Org. Chem.*, 1954, **19**, 646; F. H. Newth, *Quart. Rev.*, 1959, **13**, 30; (*b*) P. W. Kent, M. Stacey, and L. F. Wiggins, *J.*, 1949, 1232.

[13] See T. V. Talalaeva, A. N. Rodionov, and K. A. Kocheschkov, *Doklady Akad. Nauk S.S.S.R.*, 1961, **140**, 847 (*Chem. Abs.*, 1962, **56**, 5989*f*).

isolation of the same *C*-formyl compound (II, R′ = CHO) (characterised as its 2,4-dinitrophenylhydrazone) from the ozonolysis of the *cis* and *trans* forms of methyl 3-deoxy-3-*C*-(2-phenylethenyl)-β-D-xyloside as was obtained from the ozonolysis of methyl 3-deoxy-3-*C*-(2,2-dimethylvinyl)-β-D-xyloside (II; R′ = $CH{=}CMe_2$). The structure of methyl 3-deoxy-3-*C*-(2,2-dimethylvinyl)-β-D-xylopyranoside follows from its preparation from the anhydride (I; R = H) and its demonstrated stability towards periodate. Since reduction of the *cis* form of methyl 3-deoxy-3-*C*-(2-phenylethenyl)-β-D-xylopyranoside gives methyl 3-deoxy-3-*C*-(2-phenylethyl)-β-D-xylopyranoside and is itself obtained from the acetylenic compound (II; R′ = C≡C·Ph), it follows that the saturated (II; R′ = $(CH_2)_2Ph$) and acetylenic (II; R′ = C≡C·Ph) compounds have the D-xylo configuration.

Reduction of methyl 3-deoxy-3-*C*-formyl-β-D-xylopyranoside with lithium aluminium hydride gave methyl 3-deoxy-3-*C*-hydroxymethyl-β-D-xylopyranoside (II; R′ = CH_2OH). An attempt to convert the formyl group in compound (II; R′ = CHO) into a methyl group by Burton's method [3] was unsuccessful, and so the action of methyl-lithium on the anhydride (I; R = H) was examined. Difficulty was experienced in isolating products which were completely free from inorganic material, as, rather unexpectedly, a large part of the product remained in the aqueous layer after ether extraction. Acetylation of the syrupy product from the aqueous phase gave a small amount of a crystalline substance which analysed as a methyl 2 or 3,4-di-*O*-acetyl-3 or 2-deoxy-3 or 2-iodo-β-D-pentoside, and more syrup which contained at least four components. On distillation, this syrup afforded two fractions which displayed no absorption at 3500 cm.$^{-1}$ but did so at 1680 and 1650 cm.$^{-1}$ (C=C). Both cuts rapidly decolourised bromine in carbon tetrachloride and potassium permanganate in 50% aqueous acetone. Various procedures for work-up of the aqueous extract were employed, but always mixtures of products were obtained which showed positive tests for unsaturation.

To determine whether treatment of other methyl 2,3-anhydroglycosides with methyl-lithium gave unsaturated products, the action of this reagent on methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-mannoside and -alloside (IV and V, respectively) was studied. From the reaction with the mannoside and methyl-lithium in ether a good yield of a methyl *O*-benzylidene-monodeoxy-*C*-methyl-α-D-hexoside (A) was obtained. Removal of the benzylidene residue by hydrogenolysis gave a methyl monodeoxy-*C*-methyl-hexopyranoside (B) which did not undergo oxidation with periodate and which had, therefore, bearing in mind its mode of formation, the D-*altro* configuration [*i.e.*, A = (VI) and B = (VII)]. Epoxide cleavage had occurred to give, as expected, a product with the substituents at *C*-2 and *C*-3 in a diaxial relationship. Similar reaction with the alloside (V)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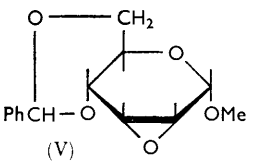
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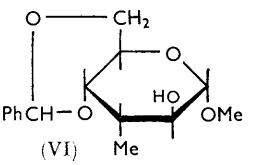
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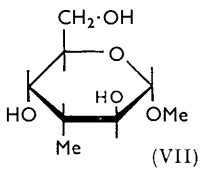
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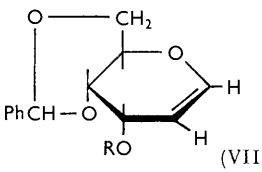
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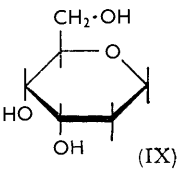
(IX)

gave a good yield of a crystalline material (C) which still contained the benzylidene residue, and which showed an intense absorption at 1645 cm.$^{-1}$ (C=C) and a broad band at 3230 cm.$^{-1}$ (OH). It afforded a crystalline monoacetate which had no hydroxyl absorption. Neither compound (C) nor its acetate contained a methoxyl group. The n.m.r. spectrum of the acetate was similar in certain respects to that of tri-*O*-acetyl-D-glucal, and integration

of the peak areas showed that the acetate contained 16 protons per molecule. Compound (C) is considered to be 4,6-*O*-benzylidene-D-allal (VIII; R = H) which gives the 3-acetate (VIII; R = $COCH_3$). On hydrogenation and hydrogenolysis it afforded a crystalline compound which consumed periodate (1·04 mol./mol.) and which analysed correctly for 1,5-anhydro-2-deoxy-D-*ribo*-hexitol. The configuration is based on the assumption that, since there is a hydroxyl group located at *C*-3, the initial bond broken during epoxide cleavage was the *C*-2–O bond, and so no inversion would occur at *C*-3. Further study of this reaction is in progress.

Experimental

Chromatography.—For paper chromatograms the descending method was used with Whatman No. 1 paper. The solvent systems employed were (A), n-butanol–ethanol–water (4 : 1 : 5); (B), n-butanol–acetic acid–water (4 : 1 : 5); (C), n-butanol–pyridine–water (6 : 2 : 5) (all compositions are v/v and the organic phase was employed). The spots were detected by dipping in silver nitrate–acetone and subsequently spraying with sodium hydroxide in ethanol.[14]

Silica gel G (supplied by Merck A.G., Darmstadt) was used as absorbent phase for thin-layer chromatography (t.l.c.) with benzene–methanol (19 : 1) as solvent. The chromatograms were sprayed with the anisaldehyde reagent.[15]

Gas–liquid chromatographic separations were carried out with an argon gas chromatograph built in this laboratory by Dr. G. B. Gill and employing a high-sensitivity β-ionisation detector. The straight column (length 4 ft.) was packed with 10% Apiezon " L " grease on Celite (100—120 mesh).

Spectra.—Unless stated otherwise infrared spectra were measured with an Infracord spectrophotometer, model 137. Potassium bromide discs were used. N.m.r. spectra were measured in deuterochloroform with a Varian Associates A-60 instrument equiped with an integrator.

Periodate Oxidations.—These were followed by Aspinall and Ferrier's method.[16]

Methods.—Unless otherwise stated all solutions were dried over anhydrous Na_2SO_4 and all solvents were evaporated under reduced pressure (bath temperature below 50°). All reactions involving the use of organo-lithium compounds were carried out in an atmosphere of dry oxygen-free nitrogen. For the preparation of organo-lithium reagents the metal was weighed under liquid paraffin, beaten into thin sheets (*ca.* 1 mm. thick) while still retaining a protective layer of paraffin, and then cut into small pieces into dry ether. The pieces of lithium were washed several times with dry ether and were then transferred into dry ether in the reaction flask under an atmosphere of dry oxygen-free nitrogen.

The light petroleum used was the fraction with b. p. 40—60°.

Derivatives of Methyl 2,3-Anhydro-β-D-ribopyranoside.—The anhydride [m. p. 52·5—53°, $[\alpha]_D^{23}$ −47° (*c* 1·8 in EtOH)] was prepared by the method of Kent *et al.*[12b]

(*a*) *Benzylation.* Benzyl bromide (70·8 g.) was added to a solution of the anhydride (6·0 g.) in dry redistilled dimethylformamide (50 ml.). Freshly prepared silver oxide (24 g.) was added with stirring over 1 hr., and stirring was continued for 16 hr. longer. After filtration, the residue was washed successively with dimethylformamide (20 ml.) and chloroform (20 ml.). The addition of chloroform to the filtrate gave a sticky precipitate which was removed and washed with chloroform (20 ml.). Filtrates and washings were combined, washed with water (3 × 50 ml.), and dried. Distillation of the residue obtained after removal of solvent and excess of benzyl bromide gave a colourless oil (b. p. 114—116°/0·08 mm.) which crystallised. Recrystallisation of the solid from ether–light petroleum gave the 4-O-*benzyl* derivative (8·1 g., 83·5%) with m. p. 42—43°, $[\alpha]_D^{22}$ +9·1° (*c* 2·7 in EtOH)(Found: C, 65·6; H, 6·8. $C_{13}H_{16}O_4$ requires C, 66·1; H, 6·8%).

(*b*) *Methylation.* The anhydride (12 g.) was methylated with methyl iodide (60 ml.) and silver oxide (19 g.) in standard fashion. Recrystallisation from light petroleum gave colourless needles of the 4-O-*methyl* derivative (10·7 g., 81%), m. p. 74·5—75·5°, $[\alpha]_D^{22}$ −14·9° (*c* 1·1 in EtOH) (Found: C, 52·9; H, 7·6; OMe, 38·7. $C_7H_{12}O_4$ requires C, 52·5; H, 7·6; OMe, 38·7%).

(*c*) *Tosylation.* The 4-O-*tosyl* derivative (8·7 g., 85%), m. p. 91·5—92° (from ethanol),

[14] W. E. Trevelyan, F. P. Procter, and J. S. Harrison, *Nature*, 1950, **166**, 444.
[15] E. Stahl and U. Kaltenbach, *J. Chromatog.*, 1961, **5**, 351.
[16] G. O. Aspinall and R. J. Ferrier, *Chem. and Ind.*, 1957, 1216.

$[\alpha]_D^{20}$ −16·4° (*c* 1·0 in EtOH) (Found: C, 51·8; H, 5·4; S, 10·9. $C_{13}H_{16}O_6S$ requires C, 52·0; H, 5·4; S, 10·7%), was obtained by treatment at room temperature of a solution of the anhydride (5 g.) in dry pyridine (25 ml.) with a solution of tosyl chloride (7·25 g.) in pyridine (25 ml.).

(*d*) *Trimethylsilylation.* Dry, redistilled trimethylchlorosilane (7·5 g.) was added to a solution of the anhydro-riboside (1·0 g.) in dry pyridine (10 ml.). After shaking for 6 hr. and storage for 12 hr. and work-up the 4-*O*-trimethylsilyl derivative was obtained as a mobile colourless oil (1·1 g., 72%), b. p. 116—118°/10 mm., $\nu_{max.}$ 1250, 840, 760 (Si–C) cm.$^{-1}$, negligible absorption at 3500 cm.$^{-1}$ (OH). After storage for several days in an airtight container under an atmosphere of nitrogen the oil deposited crystals of methyl 2,3-anhydro-β-ribopyranoside; the trimethylsilyl group had been hydrolysed off.

All the derivatives described above gave a positive epoxide test.[17]

Reaction of Derivatives of Methyl 2,3-Anhydro-β-D-riboside with Organolithium Reagents.—(1) *2,2-Dimethylvinyl-lithium.* (*a*) 4-O-*Methyl derivative.* 2,2-Dimethylvinyl-lithium was prepared by Braude and Timmon's method [18] from lithium (0·95 g.) and 2,2-dimethylvinyl bromide (8·9 g.) in dry ether (70 ml.). The methylated anhydride (2·5 g.) in dry ether (50 ml.) was added slowly with cooling and stirring. On completion of the addition the mixture was stirred and boiled for 2 hr. After filtration through glass wool, water was added to the stirred filtrate until two clear layers were formed. The layers were separated and the aqueous portion was washed with ether (4 × 20 ml.). The combined ethereal layer and washings were dried and evaporated to a dark yellow syrup which was distilled. The main fraction [b. p. 80—82°/0·01 mm., $[\alpha]_D^{23}$ −65·8° (*c* 0·9 in EtOH), $\nu_{max.}$ 3500 (OH), 1680 (C=C) cm.$^{-1}$ (Found: C, 60·9; H, 8·9. $C_{11}H_{20}O_4$ requires C, 61·1; H, 9·3%)] was a pale yellow mobile syrup (2 g., 60%), which rapidly decolourised (i), bromine in carbon tetrachloride without formation of hydrogen bromide and (ii), a solution of potassium permanganate in 50% aqueous acetone. G.l.c. showed that the fraction contained two components (in amounts of about 93% and 7%). Presumably these were methyl 2-deoxy-2-*C*-(2,2-dimethylvinyl)-4-*O*-methyl-β-D-*arabo*-pentoside and methyl 3-deoxy-3-*C*-(2,2-dimethylvinyl)-4-*O*-methyl-β-D-*xylo*-pentoside. When a solution of the fraction (0·1 g.) in dichloromethane (1 ml.) was cooled to −80° and treated under anhydrous conditions with boron trichloride (1·0 g.) for 12 hr., only a black residue was obtained on work-up. Paper chromatography (system A) of a methanolic solution indicated that the residue contained some unreacted starting material.

(*b*) 4-O-*Benzyl derivative.* This reaction was carried out by the same procedure as for the 4-*O*-methyl derivative. The amounts of reactants used were: lithium (1·20 g.), 2,2-dimethylvinyl bromide (11·5 g.), benzylated anhydroriboside (5·0 g.). The product was distilled as a pale yellow syrup (4 g., 65%), b. p. 128—130°/0·01 mm., which crystallised. Recrystallisation from aqueous ethanol gave colourless *methyl* 4-O-*benzyl*-(2 *or* 3)-*deoxy*-(2 *or* 3)-C-(2,2-*dimethylvinyl*)-β-D-*pentoside*, m. p. 50—51°, $[\alpha]_D^{23}$ −43·6° (*c* 2·1 in EtOH), $\nu_{max.}$ 3500 (OH), 1680 (C=C) cm.$^{-1}$ (Found: C, 69·8; H, 8·3; OMe, 10·1. $C_{17}H_{24}O_4$ requires C, 69·8; H, 8·3; OMe, 10·6%). The compound gave a positive test for unsaturation.

(2) *Phenyl-lithium.* (*c*) 4-O-*Tosyl derivative.* Phenyl-lithium was prepared from lithium (1·28 g.) in dry ether (15 ml.) and bromobenzene (6·5 g.) in dry ether (30 ml.). The 4-*O*-tosyl derivative (2·5 g.) was added slowly to the cooled and stirred solution of the organo-lithium compound, and, after completion of the addition, stirring and boiling were continued for a further 3 hr. After filtration, water was added to the filtrate until two clear layers were formed. The layers were separated and the aqueous portion extracted with ether (5 × 20 ml.). The combined ether extracts were washed with water (2 × 10 ml.), and the washings were added to the aqueous layer. The combined ethereal solution was dried, filtered, and evaporated to a syrup, from which crystals (0·23 g.) were obtained after washing with light petroleum and trituration with ether. Recrystallisation (twice) from ethanol gave the material as colourless plates, m. p. 127—128°, $\nu_{max.}$ 1600 and 1500 (Ph), 1300 and 1160 (S=O of sulphone) cm.$^{-1}$. The compound was identified as phenyl *p*-tolyl sulphone (m. p. 127—128° [19]).

The aqueous layer was neutralised (dilute H_2SO_4) and evaporated. The residue was extracted with boiling ethyl acetate (5 × 20 ml.). Evaporation of the filtered extract gave a

[17] W. C. J. Ross, *J.*, 1950, 2257.
[18] E. A. Braude and C. J. Timmons, *J.*, 1950, 2000, 2007; see also E. A. Braude and J. A. Coles, *J.*, 1950, 2012.
[19] See W. R. Gaythwaite, J. Kenyon, and H. Phillips, *J.*, 1928, 2283.

hygroscopic amorphous material [1·65 g., $[\alpha]_D^{20}$ −32·3° (*c* 1·2 in EtOH)] which could not be induced to crystallise. This substance (1·2 g.) in dry pyridine (30 ml.) was acetylated at room temperature for 3 days with acetic anhydride (15 ml.). Usual work-up yielded *methyl* 2,4-*di*-O-*acetyl*-3-*deoxy*-3-C-*phenyl*-β-D-*xyloside* (0·68 g.), which after recrystallisation from ethanol had m. p. 149·5°, $[\alpha]_D^{20}$ −33·3° (*c* 0·7 in EtOH), $\nu_{max.}$ 1600 and 1500 (Ph), 1750 (C=O, acetate), 1225 cm.$^{-1}$, no absorption at 3500 cm.$^{-1}$ (Found: C, 62·5; H, 6·2; OMe, 10·0. $C_{16}H_{20}O_6$ requires C, 62·3; H, 6·5; OMe, 10·1%).

Methyl 3-*Deoxy*-3-C-*phenyl*-β-D-*xylopyranoside*.—The acetate (0·5 g.) in 0·05N-sodium methoxide (15 ml.) was kept for 18 hr. at room temperature; the solution was then neutralised (CO_2) and evaporated. The residue was extracted with hot ethyl acetate (5 × 10 ml.), and the filtered extract was evaporated to a residue which was retreated with cold ethyl acetate. The residue finally obtained was recrystallised from benzene–light petroleum, when needles of *methyl* 3-*deoxy*-3-C-*phenyl*-β-D-*xylopyranoside* (0·33 g., 91%) were obtained, m. p. 102—102·5°, $[\alpha]_D^{20}$ −38·7° (*c* 0·44 in EtOH), $\nu_{max.}$ 3450 (OH), 1600 and 1500 (Ph) cm.$^{-1}$ (Found: C, 63·3; H, 6·75; OMe, 13·8. $C_{12}H_{16}O_4$ requires C, 64·3; H, 7·2; OMe, 13·8%). The glycoside was slightly hygroscopic and consumed no periodate in 24 hr.

Reaction of Methyl 2,3-*Anhydro*-β-D-*ribopyranoside with Organo-lithium Reagents*.—(1) *Phenyl-lithium*. The reaction was carried out according to the procedure outlined above, and with the following amounts of reactants: lithium (1·06 g.), bromobenzene (10·8 g.), methyl 2,3-anhydro-β-D-riboside (2·0 g.).

The dark viscous syrup obtained from the ether extract was washed with light petroleum and extracted with hot water (5 × 20 ml.). Evaporation of the extract gave a colourless glass (0·5 g., 16·3%) which crystallised from benzene–light petroleum to yield methyl 3-deoxy-3-*C*-phenyl-β-D-xyloside, m. p. 100—101°, $[\alpha]_D^{21}$ −41·2° (*c* 0·74 in EtOH). The glycoside showed no depression of m. p. with the material described previously, and its i.r. spectrum was identical.

Evaporation of the neutralised (dil. H_2SO_4) aqueous extract and extraction of the residue with boiling ethyl acetate (5 × 50 ml.) gave on removal of solvent a residue which was dried in cold ethyl acetate. Evaporation gave an amorphous hygroscopic material from which crystals (1·9 g.) were obtained by ether extraction. After purification by recrystallisation from benzene–light petroleum the substance was found to be methyl 3-deoxy-3-*C*-phenyl-β-D-xyloside, which thus was obtained in 78·2% overall yield. The glycoside could be acetylated readily to give the diacetate, which was identical with that prepared as already described.

The glycoside (0·5 g.) in hot water (25 ml.) was hydrolysed by stirring under reflux with Amberlite IR-120 (H^+) (*aci*-form) ion-exchange resin. After 2 hr. the optical rotation was constant, and the resin was filtered off and washed with water. Solvent removal from the combined filtrate and washings gave a colourless viscous syrup which crystallised. Recrystallisation from ethyl acetate gave 3-*deoxy*-3-C-*phenyl*-D-*xylose* (0·4 g., 85%) as colourless needles, m. p. 151—152°, $[\alpha]_D^{25}$ +5·07° (4 min. and 24 hr.) (*c* 1·97 in H_2O), $\nu_{max.}$ 1600 and 1500 (Ph) cm.$^{-1}$ (Found: C, 63·0; H, 6·9. $C_{11}H_{14}O_4$ requires C, 62·9; H, 6·7%).

In 75% aqueous ethanol (5 ml.) at 25° the compound (0·0825 g.) showed the following changes in optical rotation:

Time (min.)	1	2	3	4	5	6	60
$[\alpha]_D$	−4·85°	−1·82°	+1·21°	+3·03°	+4·24°	+4·85°	+4·85°

(2) *Methyl-lithium*. To a stirred suspension of small pieces of lithium metal (0·43 g.) in dry ether (9 ml.) under an atmosphere of dry oxygen-free nitrogen, a few drops of methyl iodide were added. The solution became turbid and the ether commenced to reflux gently. Methyl iodide (3·97 g.) in dry ether (9 ml.) was added slowly to the stirred solution so that gentle reflux was maintained. When addition was complete, stirring and heating were continued for a further 30 min. After cooling, methyl 2,3-anhydro-β-D-ribopyranoside (2·0 g.) in dry ether (40 ml.) was added slowly, and the mixture was stirred and heated under reflux for 3 hr. Excess of lithium was removed, and water was added until two clear layers were obtained. These layers were separated, and the aqueous phase was extracted with ether (6 × 5 ml.). The ether extracts were combined and washed with water (2 × 5 ml.), and the washings were combined with the aqueous phase. A light brown mobile oil was obtained by evaporation of the dried ethereal solution, which was distilled under diminished pressure to give a yellow oil. This

material, which gave a positive test for unsaturation [and had $\nu_{max.}$ 1650 cm.$^{-1}$ (C=C)] was shown by paper chromatography to contain three components (R_F 0·53, 0·73 and 0·86 in system A).

The neutralised (dil. H_2SO_4) aqueous layer was taken to dryness and the residue extracted with boiling ethyl acetate. The yellow syrup (5·0 g.) obtained from the extract was acetylated [Ac_2O (20 ml.), C_5H_5N (40 ml.), 22 hr., room temperature] to afford a crystalline acetate (0·1 g.), which on sodium fusion gave a positive test for iodine. Recrystallisation from ethanol yielded *methyl* 2 *or* 3,4-*di*-O-*acetyl*-3 or 2-*deoxy*-3 *or* 2-*iodo*-β-D-*pentoside*, m. p. 153—154°, $[\alpha]_D^{24}$ −48·7° (*c* 0·72 in EtOH), $\nu_{max.}$ 1750 (C=O acetate), 1250—1220 (C–O acetate), no absorption at 3500 cm.$^{-1}$ (OH) (Found: C, 33·7; H, 4·3; OMe, 8·7. $C_{10}H_{15}IO_6$ requires C, 33·5; H, 4·2; OMe, 8·7%).

A dried chloroform extract (6 × 25 ml.) of the filtrate from the acetylation mixture gave on evaporation a dark brown syrup. This was distilled and two cuts were taken, (i), a pale yellow, fairly mobile oil (0·4 g.), b. p. 92—94°/0·04 mm., $\nu_{max.}$ 1750 and 1230 cm.$^{-1}$ and (ii), a dark yellow, viscous syrup (0·53 g.), b. p. 107—109°/0·07 mm. $\nu_{max.}$ 1750, 1680, 1580, and 1230 cm.$^{-1}$. Both cuts showed no absorption at 3500 cm.$^{-1}$. Gas–liquid chromatography showed both cuts to be mixtures.

(3) 2,2-*Dimethylvinyl-lithium*. Lithium metal (1·6 g.), 2,2-dimethylvinyl bromide (14 g.) and the anhydro-riboside (5·0 g.) were used for the reaction which was conducted according to the usual procedure.

From the dried ether phase a pale yellow viscous syrup was obtained, which on distillation gave an unidentified dark yellow mobile oil (0·2 g.), b. p. 38—40°/0·03 mm., and two fractions, (A), [a pale yellow viscous syrup (4·12 g.), b. p. 93—95°/0·007 mm., $\nu_{max.}$ 3450 (OH), 1680 (C=C) cm.$^{-1}$] and, (B), [also a pale yellow viscous syrup (1·14 g.), b. p. 103—105°/0·007 mm., $\nu_{max.}$ 3450 and 1680 cm.$^{-1}$]. The infrared spectra of fractions (A) and (B) were almost identical. Both fractions gave positive tests for unsaturation; on periodate oxidation fraction A consumed 0·215 mole of oxidant/mole and fraction B 0·221 mole of periodate/mole. The fractions were apparently mixtures of methyl 2-deoxy-2-*C*-(2,2-dimethylvinyl)-β-D-arabinopyranoside (*ca.* 20%) and methyl 3-deoxy-3-*C*-(2,2-dimethylvinyl)-β-D-xylopyranoside (*ca.* 80%). When a portion (1·5 g.) of the original mixture from the ether phase was acetonated by Honeyman's method [12a] a pale yellow viscous syrup (1·7 g.) was obtained. This contained some acetone autocondensation products, and the mixture was separated by chromatography on a column (18 × 2 cm.) of neutral alumina (100—120 mesh). The eluting solvents were benzene (50 ml.) followed by benzene–ethanol (1 : 1) (50 ml.) and 24 fractions (each 5 ml.) were collected. Fractions 12—20 were combined, and removal of solvent afforded *methyl* 3-*deoxy*-3-C-(2,2-dimethylvinyl)-β-D-*xylopyranoside* (1·1 g.) as a colourless viscous syrup, b. p. 88—90°/0·01 mm., $[\alpha]_D^{24}$ −71·8° (*c* 0·42 in EtOH), $\nu_{max.}$ 3500 and 1680 cm.$^{-1}$ (Found: C, 59·1; H, 9·0; OMe, 14·7. $C_{10}H_{18}O_4$ requires C, 59·4; H, 9·0; OMe, 15·3%). The compound consumed no periodate during 24 hr.

Separation of the mixture by cyclohexylidenation gave the same result.

From the aqueous phase derived from the original reaction mixture a light brown viscous syrup (0·35 g.) was obtained after extraction by the ethyl acetate procedure. This was shown by thin-layer chromatography to contain unchanged methyl 2,3-anhydro-β-D-riboside, the methyl deoxy-(2,2-dimethylvinyl)-pentosides, and methyl 2-bromo-2-deoxy-β-D-arabino-pyranoside.

(4) *Phenylacetylene-lithium*. (*a*) A solution of phenyl-lithium in ether was prepared as already described from lithium (0·53 g.) and bromobenzene (5·4 g.). Phenylacetylene (4·5 g.) in dry ether (20 ml.) was added slowly to the solution with stirring. After stirring and heating under reflux for 2 hr., the anhydroriboside (1·0 g.) in dry ether (25 ml.) was added slowly. After the addition was complete the mixture was stirred and heated under reflux for a further 3 hr., and then worked up in the usual manner to give ethereal and aqueous extracts.

Removal of solvent from the ethereal extract afforded a brown solid which was washed several times with light petroleum and recrystallised from ether–light petroleum to yield colourless needles of *methyl* 3-*deoxy*-3-C-(*phenylethynyl*)-β-D-*xylopyranoside* (0·14 g., 8·3%), m. p. 125·5—126°, $[\alpha]_D^{19}$ −40° (*c* 0·41 in EtOH) (Found: C, 67·2; H, 6·6; OMe, 12·6. $C_{14}H_{16}O_4$ requires C, 67·7; H, 6·5; OMe, 12·5%).

Work-up of the aqueous extract by the ethyl acetate procedure gave a viscous syrup. Soxhlet extraction of the syrup with ether and evaporation of the extract gave colourless crystals (0·21 g.), m. p. 151—152°, which sublimed at 110°/0·03 mm. to give *methyl* 2-*bromo*-2-*deoxy*-

β-D-*arabinoside*, m. p. 152·5—153°, $[\alpha]_D^{20}$ −20·5° (*c* 0·39 in MeOH), R_F = 0·78 (system A), 0·71 (system B), 0·83 (system C) on paper chromatography, and R_F = 0·15 on thin-layer chromatography (Found: C, 31·4; H, 4·8; Br, 35·9; O, 28·1; OMe, 13·7. $C_6H_{11}BrO_4$ requires C, 31·7; H, 4·9; Br, 35·2; O, 28·2; OMe, 13·5%). The compound consumed 1·04 mole of periodate per mole.

(*b*) The experiment was repeated, but with the phenylacetylene-lithium prepared from n-butyl-lithium [obtained from n-butyl bromide (9·5 g.) and lithium (1·05 g.) in ether (15 ml.)] and phenylacetylene (8·3 g.) in dry ether (20 ml.). The organo-lithium compound so obtained acted on the anhydro-riboside (2 g.) in dry ether (50 ml.) to give, after work-up in the usual way, methyl 3-deoxy-3-*C*-(phenylethynyl)-β-D-xylopyranoside (2 g., 59%), m. p. 126—126·5°, and a syrup (0·4 g.) which contained unreacted anhydroriboside and methyl 2-bromo-2-deoxy-β-D-arabinopyranoside.

(5) trans-*Styryl-lithium*. This reagent was prepared by Wright's method.[20] A commercial sample of β-bromostyrene (10%, *cis*- and 90% *trans*-forms, m. p. −7·5° and +6·5°, respectively) was solidified and then allowed to melt partially on a suction filter. At +6° the *trans*-isomer was retained. The process was repeated on the *trans*-enriched mixture and then repeated twice more. A few drops of the *trans*-β-bromostyrene were added to a stirred suspension of small pieces of lithium (1·24 g.) in dry ether (20 ml.) in an atmosphere of pure nitrogen. After reaction had commenced, more *trans*-β-bromostyrene (13 g.) in dry ether (30 ml.) was added at a rate which maintained gentle reflux. After addition, heating was continued for 1·5 hr., when the anhydroriboside (3·0 g.) in dry ether (60 ml.) was added slowly. The reaction mixture was worked up normally to give ethereal and aqueous phases.

From the ether extract a pale yellow syrupy residue was isolated. Evaporation of a hot water extract (6 × 30 ml.) of this residue gave a colourless syrup (1·5 g., 29%) which crystallised on trituration with ether. Recrystallisation from ether–light petroleum gave *methyl* 3-*deoxy*-3-C-(trans-2-*phenylethenyl*)-β-D-*xylopyranoside*, m. p. 140—141° [mixed m. p. with *cis*-isomer (see later), 102—118°], $[\alpha]_D^{24}$ −49·1° (*c* 0·34 in EtOH) (Found: C, 66·8; H, 6·8; OMe, 11·7. $C_{14}H_{18}O_4$ requires C, 67·2; H, 7·25; OMe, 12·4%). This substance on hydrogenation gave methyl 3-deoxy-3-*C*-(2-phenylethyl)-β-D-xylopyranoside identical (m. p., mixed m. p., and i.r. spectrum) with material prepared by the alternative procedure described below.

The syrup remaining after the hot water extraction was shown to contain more of the *product*, but it could only be obtained in impure amorphous form.

The original aqueous extract was passed through an ion-exchange column containing a mixed-bed resin, and evaporated to a syrup (0·25 g.). Thin-layer chromatography showed the syrup to contain four components, none of which was methyl 3-deoxy-3-*C*-(*trans*-2-phenylethenyl)-β-D-xylopyranoside. Two of the components were identified as methyl 2,3-anhydro-β-D-riboside and methyl 2-bromo-2-deoxy-β-D-arabinoside. In another experiment the aqueous extract was worked up by the usual ethyl acetate-extraction procedure and the bromo-arabinoside (0·14 g., 4·5%) was isolated.

Methyl 3-*Deoxy*-3-C-(cis-2-*phenylethenyl*)-β-D-*xylopyranoside*.—A solution of methyl 3-deoxy-3-*C*-(phenylethynyl)-β-D-xylopyranoside (0·6 g.) in ethanol (20 ml.) was shaken at room temperature and pressure in an atmosphere of hydrogen with a Lindlar-type catalyst (Pd on $BaSO_4$, 0·02 g.) and synthetic quinoline (0·01 g.) until hydrogen uptake ceased. Filtration and removal of solvent gave colourless *methyl* 3-*deoxy*-3-C-(cis-2-*phenylethenyl*)-β-D-*xylopyranoside* (0·59 g., 97·5%), m. p. 127—127·5° (from ether–light petroleum) (mixed m. p. with starting material 96—102°), $[\alpha]_D^{24}$ −105° (*c* 0·77 in EtOH) (Found: C, 67·2; H, 7·4. $C_{14}H_{18}O_4$ requires C, 67·2; H, 7·25%).

Methyl 3-*Deoxy*-3-C-(2-*phenylethyl*)-β-D-*xylopyranoside*.—A solution of methyl 3-deoxy-3-*C*-(*cis*-2-phenylethenyl)-β-D-xylopyranoside (0·035 g.) in ethanol (10 ml.) was hydrogenated normally with palladium (10%)–charcoal as catalyst. The named *product* (0·03 g., 85%) was obtained from ether–light petroleum as colourless needles, m. p. 104—105°, $[\alpha]_D^{20}$ −56° (*c* 0·4 in EtOH) (Found: C, 66·1; H, 7·8; OMe, 12·9. $C_{14}H_{20}O_4$ requires C, 66·6; H, 8·0; OMe, 12·3%). The compound gave negative tests for unsaturation.

Methyl 3-*Deoxy*-3-C-*formyl*-β-D-*xylopyranoside*.—(*a*) Ozonised oxygen was bubbled slowly through a solution of methyl 3-deoxy-3-*C*-(2,2-dimethylvinyl)-β-D-xylopyranoside (0·69 g.) in dry ethyl acetate (30 ml.) at room temperature until it could be detected by starch–iodide

[20] G. F. Wright, *J. Org. Chem.*, 1937, **1**, 457.

paper at the outlet of the apparatus. The solution was shaken in hydrogen at room temperature and atmospheric pressure with Adams catalyst (0·05 g.) until uptake of hydrogen ceased. Removal of catalyst and solvent gave a colourless viscous syrup (0·58 g., 96·5%) [$\nu_{max.}$ 1730 cm.$^{-1}$ (C=O), R_F 0·70 (system A)] which could not be induced to crystallise, and which decomposed on attempted distillation. The syrup was strongly reducing to Fehling's solution in the cold, and was considered to be methyl 3-deoxy-3-*C*-formyl-β-D-xylopyranoside. The syrup (0·07 g.) in absolute ethanol (2 ml.) was heated at 40° for 0·5 hr. with a solution of 2,4-dinitrophenylhydrazine (0·069 g.) in absolute ethanol (5 ml., 0·15N in HCl). On storage overnight at room temperature, crystals (0·06 g.) separated and were collected and washed with cold ethanol. Recrystallisation from ethanol gave the 2,4-*dinitrophenylhydrazone* (0·03 g.) as orange-yellow plates, m. p. 210°, $[\alpha]_D^{24}$ +16·7° (*c* 0·2 in EtOH) (Found: C, 43·85; H, 4·9; N, 15·65. $C_{13}H_{16}N_4O_8$ requires C, 43·8; H, 4·5; N, 15·7%).

(*b*) Similarly, the *cis*- (0·15 g.) and *trans*- (0·18 g.) forms of methyl 3-deoxy-3-*C*-(2-phenylethenyl)-β-D-xylopyranoside in dry ethyl acetate (each in 15 ml.) each gave on ozonolysis syrupy methyl 3-deoxy-3-*C*-formyl-β-D-xylopyranoside (0·05 and 0·10 g., respectively) identical (i.r. spectra and chromatography) with the sample described above.

Methyl 3-*Deoxy*-3-C-*hydroxymethyl*-β-D-*xylopyranoside*.—Methyl 3-deoxy-3-*C*-formyl-β-D-xylopyranoside (0·2 g.) in dry ether (50 ml.) was added slowly to a stirred solution of lithium aluminium hydride (0·43 g.) in dry ether (50 ml.). The stirred mixture was heated under reflux for 5 hr., cooled, and ethyl acetate added, followed by water. The ether layer was decanted, and the residue washed with ether (5 × 10 ml.). The combined layer and washings were dried, filtered, and evaporated to a viscous non-reducing syrup (0·06 g.), which crystallised on trituration with ethyl acetate. Recrystallisation from ethyl acetate gave colourless *methyl* 3-*deoxy*-3-C-*hydroxymethyl*-β-D-*xylopyranoside* (0·02 g.), m. p. 147·5—148·5°, $[\alpha]_{5461}^{25}$ −135° (*c* 0·047 in EtOH) (Found: C, 46·8; H, 7·6. $C_7H_{14}O_5$ requires C, 47·2; H, 7·9%).

Reactions of Methyl-lithium with Methyl Anhydro-benzylidene-hexosides.—(*a*) *Methyl* 2,3-*anhydro*-4,6-O-*benzylidene*-α-D-*alloside*. The anhydro-hexoside (1·5 g.) was placed in a vapour-jacketted Soxhlet apparatus, and extracted for 1 hr. into a solution of methyl-lithium (4·0 g.) in dry ether (100 ml.). The solution was heated under reflux for a further 8 hr. and then was worked up as described for the reactions with methyl anhydroriboside. The pale yellow viscous syrup so obtained crystallised on storage. Recrystallisation from light petroleum yielded colourless needles of 4,6-O-*benzylidene*-D-*allal* (1·0 g., 75%), m. p. 84—84·5°, $[\alpha]_D^{25}$ +210° (*c* 0·44 in EtOH) (Found: C, 66·5; H, 6·0; OMe,[21] nil. $C_{13}H_{14}O_4$ requires C, 66·7; H, 6·0%). The compound gave positive unsaturation tests.

Acetic anhydride (5 ml.) was added to a solution of the compound (0·091 g.) in dry pyridine (10 ml.). The acetylation was conducted and worked up in the usual manner, and the solid (0·081 g., 76%) obtained was recrystallised from ethanol. The 3-O-*acetyl*-4,6-O-*benzylidene*-D-*allal* had m. p. 121—121·5°, $[\alpha]_D^{24}$ +253° (*c* 0·17 in EtOH) (Found: C, 65·6; H, 5·8. $C_{15}H_{16}O_5$ requires C, 65·3; H, 5·8%).

1,5-*Anhydro*-2-*deoxy*-D-*allitol*. A solution of 4,6-*O*-benzylidene-D-allal (0·5 g.) in ethanol (50 ml.) was shaken overnight (17 hr.) in an atmosphere of hydrogen at room temperature and pressure in the presence of palladium (5%)–charcoal (0·05 g.) until uptake of hydrogen (168 ml.) ceased. Removal of the catalyst and solvent gave a clear syrup, which crystallised to a sticky solid. Recrystallisation from acetone yielded needles of 1,5-*anhydro*-2-*deoxy*-D-*allitol* (0·2 g., 65%), m. p. 105·5—106·5°, $[\alpha]_D^{22}$ +90·7° (*c* 0·25 in EtOH), R_F 0·45 (system A) (Found: C, 48·5; H, 8·1. $C_6H_{12}O_4$ requires C, 48·6; H, 8·2%). The compound consumed 1·04 mole of periodate per mole.

(*b*) *Methyl* 2,3-*Anhydro*-4,6-O-*benzylidene*-α-D-*mannoside*. The procedure was that used for the alloside derivative, except that a vapour-jacketted Soxhlet apparatus was not used. The amounts of reactants were: methyl-lithium (4·0 g.), methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-mannoside (1·0 g.). A pale yellow crystalline compound (0·82 g., 77%) was obtained, which was recrystallised from ether–light petroleum to yield colourless needles of *methyl* 4,6-O-*benzylidene*-3-*deoxy*-3-C-*methyl*-α-D-*altroside*, m. p. 114·5—116°, $[\alpha]_D^{20}$ +115·9° (*c* 0·28 in EtOH), $\nu_{max.}$ 3500 (OH), 770, 700 and 685 cm.$^{-1}$ (monosubstituted Ph), R_F 0·55 (t.l.c.) (Found: C, 64·6; H, 7·3; OMe, 11·1. $C_{15}H_{20}O_5$ requires C, 64·3; H, 7·2; OMe, 11·1%). Stevens and Wiggins [22] find m. p. 114—115° for this compound. When the reaction was carried out in

[21] Determination by the method of F. Vieböck and C. Brecher, *Ber.*, 1930, **63**, 3207.
[22] R. Stevens and L. F. Wiggins, personal communication.

either ether or benzene with only a five-fold excess of methyl-lithium the starting material was recovered unchanged.

Methyl 3-*Deoxy*-3-C-*methyl*-α-D-*altropyranoside*.—The benzylidene derivative (0·35 g.) in ethanol (20 ml.) was hydrogenolysed at room temperature and pressure with a palladium (5%)–charcoal (0·035 g.) catalyst for 16 hr. (observed uptake of hydrogen 70 ml.). Normal work-up led to a colourless, fairly mobile syrup (0·23 g., 97%), b. p. 165° (bath temp.)/0·04 mm., $[\alpha]_D^{21}$ +117° (*c* 1·3 in EtOH), R_F 0·14 (t.l.c.). The compound consumed no periodate during 24 hr.

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