655. *Structure and Reactivity of Anhydro-sugars. Part I. Branched-chain Sugars. Part I. Action of Diethylmagnesium on Methyl 2 : 3-Anhydro-4 : 6-O-benzylidene-α-D-mannoside.*

By A. B. Foster, W. G. Overend, M. Stacey, and G. Vaughan.

The action of diethylmagnesium on methyl 2 : 3-anhydro-4 : 6-*O*-benzylidene-α-D-mannoside (I) under a variety of conditions has been investigated. The sole product of the reaction in ether is methyl 4 : 6-*O*-benzylidene-3-deoxy-3-*C*-ethyl-α-D-altroside (II) whereas the use of toluene leads to a complex mixture of products. Graded acid hydrolysis of (II) gave methyl 3-deoxy-3-*C*-ethyl-α-D-altroside (IV), the structure of which was proved by oxidation with lead tetra-acetate. Complete acidic hydrolysis of (IV) or (II) afforded a mixture of 3-deoxy-3-*C*-ethyl-D-altrose and -D-altrosan (V and VI), and ionophoretic studies and osazone formation confirmed these structures. The behaviour of the mixture (V–VI) was closely analogous to that of an authentic D-altrose–D-altrosan mixture. A preliminary comment, on the basis of conformational analysis, on the scission of ethylene oxide rings in anhydro-sugars is given.

Although many examples of the interaction of Grignard reagents and molecules containing epoxide rings have been studied (cf. Gaylord and Becker, *Chem. Reviews*, 1951, **49**, 413) investigations with anhydro-sugars of the ethylene oxide type have been limited in scope. In previous publications from this laboratory, Wiggins and his co-workers (Newth, Richards, and Wiggins, *J.*, 1950, 2356; Richards and Wiggins, *J.*, 1953, 2442) have described the action of methyl-, ethyl-, and phenyl-magnesium halides on derivatives of methyl 2 : 3-anhydro-α-D-alloside. In this communication an extension of this work is reported.

As is well known, Grignard reagents may be represented by the equation :

$$2RMgX \rightleftharpoons \begin{bmatrix} \overset{+}{M}gX & R^- \\ \overset{+}{M}gR & X^- \end{bmatrix} \rightleftharpoons MgR_2 + MgX_2$$

The equilibrium lies predominantly to the right, and indeed in certain cases (cf. Huston and Agett, *J. Org. Chem.*, 1941, **6**, 123; Gaylord and Becker, *loc. cit.*) addition of dioxan precipitates the magnesium halide as a complex which can be removed, thereby leaving the dialkylmagnesium as the main component in solution. When methyl 2 : 3-anhydro-4 : 6-*O*-benzylidene-α-D-mannoside (I) was added to a Grignard reagent (in this case ethylmagnesium iodide) which had been treated with dioxan but without removal of the precipitated complex, reaction occurred exclusively with the dialkylmagnesium in the solution since the sole product was methyl 4 : 6-*O*-benzylidene-3-deoxy-3-*C*-ethyl-α-D-altroside (II). This member of a novel class of branched-chain sugars (cf. Newth, Richards, and Wiggins, *loc. cit.*; see also Hudson, *Adv. Carbohydrate Chem.*, 1949, **4**, 57; Cunningham, Hutchinson, Manson, and Spring, *J.*, 1951, 2299; Bentley, Cunningham, and Spring, *ibid.*, 1951, 2301, for details of other types of branched-chain sugars) was initially isolated by Richards (Ph.D. Thesis, University of Birmingham, 1951) but its structure was not elucidated.

The yields of (II) produced under various reaction conditions are shown in Table 1. Apparently in ether the reaction is relatively simple, and the yield of (II) is then a function of the time of reaction. Anomalous reactions occur, however, since in some cases methyl 4 : 6-*O*-benzylidene-3-deoxy-3-iodo-α-D-altroside (III) was obtained (see Table 1). When the reaction was carried out in tetrahydropyran (II) was not isolated, but (III) was obtained in 88·5% yield indicating that it was the major product of the reaction. The magnesium iodide, although largely precipitated as the dioxan complex, evidently reacts preferentially with (I) under these conditions. The use of toluene as the reaction medium gave a complex variable mixture of products, but in some cases (II) could be isolated in 11·8% yield.

Various pieces of evidence indicated that (II) was correctly designated as methyl

4 : 6-*O*-benzylidene-3-deoxy-3-*C*-ethyl-α-D-altroside. Although it did not yield a crystalline toluene-*p*-sulphonyl derivative or acetate, a crystalline methanesulphonyl derivative was obtained. Mild hydrolysis of (II) with oxalic acid afforded syrupy methyl 3-deoxy-3-*C*-ethyl-α-D-altroside (IV) which on acetylation gave a syrupy triacetate. The glycoside (IV) in dry benzene solution was resistant to oxidation by lead tetra-acetate

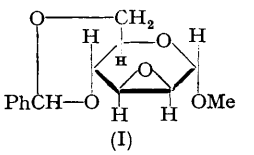
TABLE 1. *Reaction of methyl* 2 : 3-*anhydro*-4 : 6-O-*benzylidene*-α-D-*mannoside* (I) *with diethylmagnesium, in the presence of the precipitated magnesium iodide–dioxan complex.*

Solvent	Duration of reaction, hr.	Temp., °c	Wt. of (I) recovered, g.	Wt. of (II) isolated, g.	Wt. of (III) isolated, g.	% Yield of (II) *
Ether	8—9	70	0·839	0·325	—	67·3
Ether	12	70	0·686	0·562	—	90·6
Ether	24	70	0·457	0·724	—	83·5
Ether	48	70	0·810	trace	0·517	— †
Tetrahydropyran	9	81	0·890	—	0·560	—
Toluene	8	112	—	0·174	—	11·8 ‡

The amount of (I) used in each case was 1·32 g. (see Experimental section).

* Based on the amount of (I) not recovered.
† Reaction mixture was set aside at room temperature for 24 hr. before being heated.
‡ Three unidentified syrupy products were also obtained.

which clearly indicated that the *C*-ethyl group was located at $C_{(3)}$. More drastic treatment of (II) with oxalic acid removed both benzylidene and glycosidic groups and gave a syrupy product which was only weakly reducing towards Fehling's solution. This property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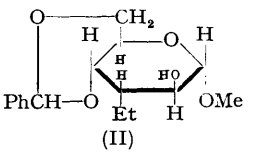
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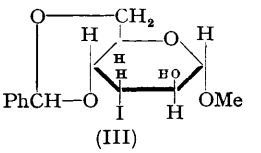
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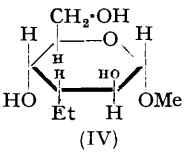
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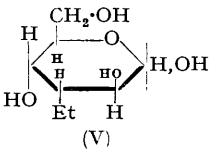
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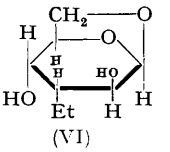

(VI)

together with the elemental analysis suggested that the product was a mixture of the free sugar and an anhydro-derivative, with the latter predominating. This evidence supports the allocation of the D-altrose configuration to (II), since it is well known that acidic hydrolysis of methyl α-D-altroside or its derivatives leads to the formation of a mixture of the free sugar and its 1 : 6-anhydro-derivative (altrosan) (Newth and Wiggins, *J.*, 1950, 351; Hudson and Richtmyer, *J. Amer. Chem. Soc.*, 1935, **57**, 1716). If, as is exceedingly probable, the scission of the epoxide ring in (I), by diethylmagnesium in ether, involves Walden inversion at the carbon atom where the ethyl group is introduced (cf. Peat, *Adv. Carbohydrate Chem.*, 1946, **2**, 37) then of the two products theoretically derivable that with the new substituent at $C_{(3)}$ would be expected to have the D-altrose configuration. The weakly reducing product isolated after complete hydrolysis of (II) is therefore most probably a mixture of 3-deoxy-3-*C*-ethyl-αβ-D-altrose (V) and its 1 : 6-anhydro-derivative (VI).

Treatment of the mixture (V–VI) with 2 : 4-dinitrophenylhydrazine (3 mol.) under mild conditions gave a low yield (18%) of 3-deoxy-3-*C*-ethyl-D-altrose 2 : 4-dinitrophenylhydrazone. With 3 mol. of the 2 : 4-dinitrophenylhydrazine under more drastic conditions an osazone was obtained in 35% yield. The low yields are in agreement with the small amount of the D-altrose derivative in the mixture (see below), since molecules of the D-altrosan type are known to be very stable (Peat, *loc. cit.*). It is extremely unlikely that osazone formation would have occurred had the *C*-ethyl group been located at $C_{(2)}$. In

model experiments it was shown that whereas 3-deoxy-D-mannose formed an osazone, 2-deoxy-D-glucose underwent decomposition and yielded only tarry products.

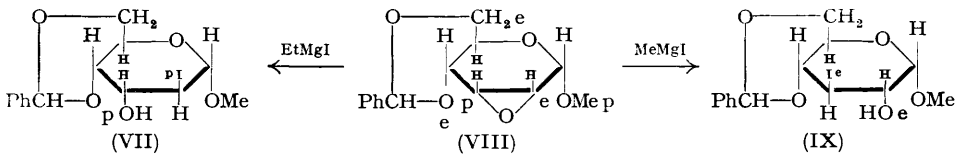
Further support for the allocation of the D-altrose configuration to (II) follows from the ionophoretic behaviour of the mixture (V–VI). The favoured interaction of hydroxylated pyran structures with borate ions at pH 10, under the conditions of filter-paper ionophoresis previously described (Foster, *Chem. and Ind.*, 1952, 1050), involves vicinal *cis*-hydroxyl groups (Foster, *J.*, 1953, 982, and unpublished results). Such a structural feature is present in the β-form of (V) and absent in the altrosan structure (VI), and so (VI) would be expected to have zero ionophoretic migration (M_G value; Foster, *loc. cit.*; Foster and Stacey, *J. Appl. Chem.*, 1953, **3**, 19). The M_G values recorded in Table 2 demonstrate the closely similar and expected ionophoretic behaviour of the mixture (V–VI) to that of a 3-deoxy-3-iodo-αβ-D-altrose–altrosan mixture of proved structure (Richards, *loc. cit.*). The important rôle of the hydroxyl group at $C_{(2)}$ in the interaction of reducing (pyranose and furanose) sugars with borate ions enables the location of a substituent at $C_{(2)}$ to be easily determined (Foster, *loc. cit.*). The M_G value of the altrose component of the mixture (V–VI) in comparison with the various 2- and 3-substituted derivatives listed in Table 2 is clear evidence for the absence of a substituent at $C_{(2)}$ in (V).

TABLE 2. M_G *values of some carbohydrate derivatives.*

Derivative	M_G	Derivative	M_G
3-Deoxy-3-iodo-D-altrose–altrosan ...	0·00, 0·73	2-Deoxy-D-glucose	0·24
3-Deoxy-3-*C*-ethyl-D-altrose–altrosan	0·00, 0·73	2-Methyl-D-glucose	0·24 *
2-Methyl-D-galactose	0·32 *	3-Methyl-D-glucose	0·78
2-Deoxy-D-galactose	0·37 *	3-Deoxy-D-mannose	0·76

* Values described by Foster (*J.*, 1953, 982).

Although numerous examples of the scission of epoxide rings in ethylene oxide anhydro-sugar derivatives, under the influence of a variety of reagents, have been recorded, the underlying principles governing the manner of opening of the epoxide rings have not been fully elucidated. Mills (Addendum to Newth and Homer, *J.*, 1953, 989) has suggested that sugar epoxides may behave in a manner analogous to steroid epoxides in undergoing scission to products with the new substituents in polar positions. If the anhydro-sugar is able to oscillate freely between its possible conformations then cleavage of the epoxide ring will give a mixture of the two possible isomeric products in more or less equal amounts. Any excess of one isomer over the other will depend on the general symmetry of the particular sugar. However the presence for example of a 4 : 6-*O*-benzylidene residue will effectively stabilise one particular conformation and on scission of the epoxide ring one of the two possible isomeric products will predominate according to the conformational requirements.



e = equatorial; p = polar.

There are other factors however which cannot be neglected. This is effectively demonstrated by the action of Grignard reagents on certain 2 : 3-anhydro-sugars. As stated, the action of diethylmagnesium in ether on (I) leads exclusively to the formation of (II). Since the benzylidene residue in (I) is best accommodated when the hydroxyl and hydroxymethyl groups at $C_{(4)}$ and $C_{(5)}$ respectively are equatorially situated, the sole product (II) subsequently isolated has the groups at $C_{(2)}$ and $C_{(3)}$ in polar positions. This result is in agreement with Mills's suggestion (*loc. cit.*). The action of ethylmagnesium iodide in tetrahydropyran on methyl 2 : 3-anhydro-4 : 6-*O*-benzylidene-α-D-alloside (VIII) (Richards and Wiggins, *loc. cit.*) also follows the predicted course in yielding as sole product methyl 4 : 6-*O*-benzylidene-2-deoxy-2-iodo-α-D-altroside (VII). On the other hand methylmagnesium iodide in a similar reaction (Newth, Richards, and Wiggins, *loc. cit.*) gives as the sole product methyl 4 : 6-*O*-benzylidene-3-deoxy-3-*C*-iodo-α-D-glucoside (IX) with the

new substituents both equatorial. It is significant that the course of the reaction is completely altered and not partly so as might normally be expected following the use of such apparently closely related reagents as methyl- and ethyl-magnesium iodide. A full analysis of the reaction of sugar epoxides will be published later.

Experimental

Reaction of Methyl 2 : 3-*Anhydro*-4 : 6-O-*benzylidene*-α-D-*mannoside with Diethylmagnesium.*—(a) *In ether at* 70°. To an ethereal solution of ethylmagnesium iodide [from ethyl iodide (15·6 g.; 8·08 ml.), magnesium turnings (2·4 g.), and ether (50 ml.)], in an open Carius tube, dioxan (12 ml.) was added at room temperature with vigorous stirring. To the resultant white paste was added a solution of methyl 2 : 3-anhydro-4 : 6-*O*-benzylidene-α-D-mannoside (1·32 g.) in ether (50 ml.) containing dioxan (2 ml.; to facilitate dissolution); meanwhile stirring was continued. The white suspension was heated under reflux for 1 hr., and after being cooled with liquid air, the Carius tube was sealed off. The tube was then heated at 70° for 8 hr. [In subsequent experiments varying periods of heating were used. For the effects see Table 1.] After cooling, the contents of the tube were poured into water (200—300 ml.), and the mixture worked up in the usual manner to give a white solid, a solution of which, in ether–light petroleum (b. p. 60—80°)–chloroform (2 : 1 : 2; v/v/v; 25 ml.), was passed through alumina (30 × 1 cm.). Elution with ether–light petroleum (b. p. 60—80°) (2 : 1; v/v; 300 ml.) and concentration of the eluate yielded starting material (0·839 g.). Concentration of a subsequent chloroform eluate (200 ml.), decolorisation of the pale brown syrupy residue with activated charcoal in methanol, and evaporation of the solvent afforded a syrup which rapidly crystallised. The product was extracted with hot light petroleum (b. p. 60—80°) and on cooling the extract deposited methyl 4 : 6-*O*-benzylidene-3-deoxy-3-*C*-ethyl-α-D-hexoside (altroside) (*A*) (0·325 g.) as white needles, m. p. 97—98°, $[\alpha]_D^{16}$ +113° (*c*, 0·91 in $CHCl_3$) (Found: C, 65·0; H, 7·5. Calc. for $C_{16}H_{22}O_5$: C, 65·3; H, 7·5%). [Richards, Ph.D. Thesis, Univ. of Birmingham, 1951, reports m. p. 97—98°, $[\alpha]_D^{23}$ +113·5° (*c*, 0·82 in chloroform).]

(b) *In tetrahydropyran.* Diethylmagnesium was prepared as described above. The ether was removed by distillation and immediately replaced by tetrahydropyran (50 ml.). Methyl 2 : 3-anhydro-4 : 6-*O*-benzylidene-α-D-mannoside (1·32 g.) dissolved in tetrahydropyran (100 ml.) was added and the mixture stirred and heated under reflux for 9 hr. It was set aside at room temperature overnight and then poured into ice–water (300 ml.) and worked up in the usual manner to give a yellow solid. Extraction of this material with ether–light petroleum (2 : 1; v/v; 15 ml.) left starting material (0·32 g.). The soluble fraction (1·23 g.) was passed through alumina (30 × 1 cm.), wet packed in ether–light petroleum (b. p. 60—80°; 2 : 1; v/v). Elution with ether–light petroleum (b. p. 60—80°; 2 : 1; v/v) afforded more starting material (0·57 g.). Elution with chloroform and concentration of the eluate yielded a yellow syrup (0·56 g.) which was crystallised by trituration with methanol. Recrystallisation from methanol gave methyl 4 : 6-*O*-benzylidene-3-deoxy-3-*C*-iodo-α-D-altroside (0·4 g.), m. p. 162·5—163° (undepressed on admixture with an authentic specimen), $[\alpha]_D^{20}$ +114° (*c*, 1·01 in $CHCl_3$) (Found: C, 42·9; H, 4·6. Calc. for $C_{14}H_{17}O_5I$: C, 42·85, H, 4·4%). [Richards, *loc. cit.*, reports m. p. 163—163·5°, $[\alpha]_D^{22}$ +111·4° (*c*, 4·19 in $CHCl_3$).] No other compound was isolable from the mother liquors.

(c) *In toluene.* Dioxan (12·0 ml.) was added with vigorous stirring to an ethereal solution of ethylmagnesium iodide [from magnesium (2·4 g.) and ethyl iodide (8·08 ml.)]. Ether was removed carefully by slow distillation and was simultaneously replaced by dry tolueue (100 ml.). Thereafter the solution was cooled and the methyl anhydro-D-mannoside derivative (1·32 g.) in dry toluene (100 ml.) added. The mixture was stirred continuously and heated under reflux for 8 hr. Hydrolysis followed by extraction of the reaction mixture as previously described afforded a pale yellow syrup, which was dissolved in the minimum of ether–light petroleum (b. p. 60—80°; 2 : 1; v/v) and chromatographically separated on alumina (30 × 1·5 cm.); four fractions were obtained:

(i) Elution with ether–light petroleum (b. p. 60—80°)–chloroform (2 : 1 : 2; v/v/v; 200 ml.) gave methyl 4 : 6-*O*-benzylidene-3-deoxy-3-*C*-ethyl-α-D-hexoside (*A*), m. p. 97°, $[\alpha]_D^{19}$ +113° (*c*, 1·5 in $CHCl_3$). Fraction (ii), obtained by elution with ether (100 ml.), was a pale yellow unidentified syrup (0·102 g.) which failed to crystallise. Fraction (iii) (0·192 g.) was obtained by subsequent elution with chloroform (200 ml.). This was also an unidentified syrup. (iv) Finally, elution with methanol (100 ml.) gave syrup (1·154 g.) (Found: C, 67·2; H, 9·0%).

Derivatives of Methyl 4 : 6-O-*Benzylidene*-3-*deoxy*-3-C-*ethyl*-α-D-*hexoside* (A).—(a) 2-O-

Toluene-p-*sulphonyl derivative.* Methyl 4 : 6-*O*-benzylidene-3-deoxy-3-*C*-ethyl-α-D-hexoside (0·147 g.) in dry pyridine (3 ml.) was treated with toluene-*p*-sulphonyl chloride (0·105 g., 1·15 mol.). The 2-O-*toluene*-p-*sulphonyl* derivative (0·15 g., 67% of theory) was obtained as a syrup, n_D^{19} 1·5000, $[\alpha]_D^{19}$ +75° (*c*, 0·8 in $CHCl_3$) (Found : C, 61·7; H, 6·6; S, 7·3. $C_{23}H_{28}O_7S$ requires C, 61·5; H, 6·3; S, 7·2%).

(b) 2-O-*Methanesulphonyl derivative.* Likewise the 2-O-*methanesulphonyl* derivative was prepared; it had m. p. 136—137° (after recrystallisation from ethanol), $[\alpha]_D^{19}$ +61·5° (*c*, 3·26 in $CHCl_3$) (Found : C, 55·1; H, 6·8; S, 8·6. $C_{17}H_{24}O_7S$ requires C, 54·9; H, 6·5; S, 8·6%).

Hydrolysis of Methyl 4 : 6-O-*Benzylidene*-3-*deoxy*-3-C-*ethyl*-α-D-*hexoside* (A).—(a) *Partial acidic hydrolysis.* Methyl 4 : 6-*O*-benzylidene-3-deoxy-3-*C*-ethyl-α-D-hexoside (0·4 g.) was dissolved in acetone (50 ml.), and a solution of oxalic acid (0·7 g. of hydrate) in water (2·5 ml.) was added. The mixture was heated under reflux and the ensuing hydrolysis was followed polarimetrically. It was complete in 400 min.

The solution was diluted with water, made slightly alkaline with aqueous barium hydroxide and then neutralised with solid carbon dioxide. After filtration, the solution was concentrated to a syrupy residue. Extraction with ethyl acetate followed by evaporation of the extracts afforded a pale yellow non-reducing syrup (B) (0·24 g.). Acetylation by use of acetic anhydride in pyridine gave syrupy methyl 2 : 4 : 6-tri-*O*-acetyl-3-deoxy-3-*C*-ethyl-α-D-hexoside, $[\alpha]_D^{20}$ −15·0° (*c*, 1·2 in $CHCl_3$) (Found : C, 54·3; H, 7·1. Calc. for $C_{15}H_{24}O_8$: C, 54·2; H, 7·3%) (Richards, *loc. cit.*, described this compound as amorphous, $[\alpha]_D^{16}$ −14·1°).

The syrupy product (B) (20 mg.) was dissolved in boiling dry benzene (49 ml.), and after cooling, a standard solution of lead tetra-acetate [50 ml. of a solution prepared by dissolving lead tetra-acetate (7·25 g.) in dry benzene (250 ml.)] was added and the volume was made up to 100 ml. The solution was placed in a thermostat at 25°, and aliquots (10 ml.) were removed at intervals and the uptake of oxidant determined titrimetrically. Results obtained were as follows :

Time (days)	1	2·5	4	6	8	10
Uptake of $Pb(OAc)_4$ (mol.)	0·013	0·036	0·043	0·050	0·055	0·060

(b) *Complete acidic hydrolysis.* Methyl 4 : 6-*O*-benzylidene-3-deoxy-3-*C*-ethyl-α-D-hexoside (altroside) (0·81 g.) dissolved in oxalic acid solution [81 ml. of a solution prepared by dissolving oxalic acid hydrate (9·0 g.) in water (30 ml.) and acetone (270 ml.)] was heated under reflux for 8·6 hr. The ensuing hydrolysis was followed polarimetrically and was complete in 8 hr. The solution was neutralised as previously described, filtered, and concentrated to a syrup. Water was distilled several times over this material to remove benzaldehyde and thereafter the syrup was extracted with ethyl acetate (3 × 20 ml.). Evaporation of the extract afforded a syrup (0·45 g.) which after decolorisation (activated charcoal) in ethanolic solution was slightly reducing, $[\alpha]_D^{20}$ +65° (*c*, 1·0 in methanol) (Found : C, 55·1; H, 8·4. $C_8H_{16}O_5$ requires C, 50·0; H, 8·3. $C_8H_{14}O_4$ requires C, 55·2; H, 8·05%). It seemed that the product was a mixture of a 3-deoxy-3-*C*-ethyl-D-hexose (altrose) and a 3-deoxy-3-*C*-ethyl-D-hexosan (altrosan). The Keller–Kiliani test was negative. This product (0·14 g.), dissolved in a small amount of water, was treated with a solution of 2 : 4-dinitrophenylhydrazine [prepared by dissolving the hydrazine derivative (0·45 g.) in glacial acetic acid (10 ml.), water (10 ml.), and methanol (5 ml.) and filtering the solution] at 100° for 1 hr., and the reddish-brown solid (0·05 g.; 18%) was removed by filtration while the solution was still hot and was washed with methanol. Recrystallisation from a large volume of methanol gave 3-*deoxy*-3-C-*ethyl*-D-*hexose* (*altrose*) 2 : 4-*dinitrophenylhydrazone* as orange-red microcrystals, m. p. 218° (Found : C, 45·6; H, 5·6; N, 15·3. $C_{14}H_{20}O_8N_4$ requires, C, 45·2; H, 5·4; N, 15·1%).

Formation of Osazones with 2 : 4-*Dinitrophenylhydrazine.*—The general method adopted was to treat an aqueous solution of the sugar (1 mol.) with 2 : 4-dinitrophenylhydrazine (3 mol.) dissolved in 60 times its weight of 2N-hydrochloric acid containing 1% of methanol, and to heat the mixture at 100° for 6 hr. The flocculent product was filtered off at 80°, and was washed successively with 2N-hydrochloric acid, water, and methanol. In this way 3-*deoxy*-D-*mannose* 2 : 4-*dinitrophenylosazone* was prepared in microcrystalline form (recrystallisation from ethyl acetate and ethanol), m. p. 205° (with decomp.) (Found : N, 21·7. $C_{18}H_{18}O_{11}N_8$ requires, N, 21·5%). 2-Deoxy-D-glucose when subjected to the above procedure rapidly decomposed with the formation of tarry products.

The hydrolysate of compound (A) yielded an orange-coloured solid, which after recrystallisation from absolute ethanol had m. p. 196° (Found : N, 20·4. $C_{20}H_{22}O_{11}N_8$ requires N, 20·4%). It was most probably 3-*deoxy*-3-C-*ethyl*-D-*altrose* 2 : 4-*dinitrophenylosazone*.

Ionophoretic Experiments.—The experiments were performed in the apparatus and by the technique described by Foster (*Chem. and Ind.*, 1952, 1050). Whatman No. 3 paper was used throughout, and the buffer employed was 0·2M-sodium borate (pH 10). The duration of the ionophoreses was 1·5 hr. in all cases under an applied potential of 900 v, which gave a final current of 32—35 mA. Detection of the sugar derivatives on the ionophoretogram was achieved by use of aniline hydrogen phthalate (Partridge, *Nature*, 1948, **164**, 443). The sugars employed are listed in Table 2, and in each case 40—60 γ were placed on the ionophoretogram.

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