

*The Action of Grignard Reagents on Anhydro-sugars of Ethylene Oxide Type. Part III.\* The Behaviour of Methyl 2 : 3-Anhydro-4 : 6-O-benzylidene- $\alpha$ -D-mannoside towards Methyl-, Ethyl-, and Phenyl-magnesium Iodide.*

By G. N. RICHARDS.

[Reprint Order No. 5623.]

Methyl 2 : 3-anhydro-4 : 6-O-benzylidene- $\alpha$ -D-mannoside with methyl- or phenyl-magnesium iodide gives as only product the expected methyl 4 : 6-O-benzylidene-3-deoxy-3-iodo- $\alpha$ -D-altroside (II) (cf. Parts I, II), but with ethylmagnesium iodide it yields, in relative amounts dependent on conditions, the products (II), methyl 4 : 6-O-benzylidene-3-deoxy- $\alpha$ -D-mannoside, methyl 4 : 6-O-benzylidene-2-deoxy-2-iodo- $\alpha$ -D-glucoside, and methyl 4 : 6-O-benzylidene-2 : 3-didehydro-2 : 3-dideoxy- $\alpha$ -D-glucoside. Reference is made to reactions leading to each of these different types of compound in Grignard reactions with simpler molecules.

PREVIOUS papers of this series have emphasised the difficulties of establishing fixed rules for the direction of scission of the epoxide ring of anhydro-sugars by a given type of reagent. Thus, whereas methylmagnesium iodide and methyl 2 : 3-anhydro-4 : 6-O-benzylidene- $\alpha$ -D-alloside gave mainly methyl 4 : 6-O-benzylidene-3-deoxy-3-iodo- $\alpha$ -D-glucoside (Part I, *J.*, 1950, 2356), the same anhydro-sugar with ethyl- or phenyl-magnesium iodide yielded the corresponding 2-deoxy-2-iodoaltroside (Part II \*). However, a similar series of experiments has now been carried out with methyl 2 : 3-anhydro-4 : 6-O-benzylidene- $\alpha$ -D-mannoside (I), in which the main product was always methyl 4 : 6-O-benzylidene-3-deoxy-3-iodo- $\alpha$ -D-altroside (II), although methyl-, ethyl-, and phenyl-magnesium iodides were all used. It therefore appears possible that only in the former anhydro-sugar is the oxide ring so situated that the nature of the alkyl group may affect the direction of scission and that some factor is operative other than the suggested preferential formation of the axial derivative (see, for example, Cookson, *Chem. and Ind.*, 1954, 223).

Foster, Overend, Stacey, and Vaughan (*J.*, 1953, 3308) showed that the anhydro-mannoside (I) with diethylmagnesium yields methyl 4 : 6-O-benzylidene-3-deoxy-3-C-ethyl- $\alpha$ -D-altroside, but with diphenylmagnesium it yields methyl 4 : 6-O-benzylidene-2-deoxy-2-C-phenyl- $\alpha$ -D-glucoside (Richards, Thesis, Birmingham, 1951). Although the possibility cannot be entirely eliminated at present that a rearrangement has occurred (cf. Gaylord and Becker, *Chem. Reviews*, 1951, 49, 413) with formation of an isomeric branched-chain sugar which would be difficult to distinguish conclusively, this apparent reversal of the direction of scission of the epoxide ring may be related to the case previously described.

Owing to the effects of temperature and excess of reagent on the reaction of the mannoside (I) with ethylmagnesium iodide (see below), the reaction with methylmagnesium iodide was studied under various conditions (Table 1); in each case, however, the only product isolated was methyl 4 : 6-O-benzylidene-3-deoxy-3-iodo- $\alpha$ -D-altroside (II) identical with that obtained by reaction of the anhydro-sugar with magnesium iodide (Richards, Wiggins, and Wise, unpublished work), but the variations of yield suggested that some reduction may have occurred at room temperature. The structure (II) was confirmed by reduction of the compound to methyl 3-deoxy- $\alpha$ -D-mannoside (III) (cf. Richards, Wiggins, and Wise, *loc. cit.*), identical with the product of the reduction of the anhydro-sugar by the procedure of Bollinger and Prins (*Helv. Chim. Acta*, 1946, 29, 1061). The product obtained by Bollinger and Prins was, however, amorphous, and when treated with benzaldehyde and zinc chloride yielded, apart from the expected methyl 4 : 6-O-benzylidene-3-deoxy- $\alpha$ -D-mannoside (IV), three other crystalline compounds, none of which was positively identified. One of these, however (m. p. 137—138°), was almost certainly methyl 4 : 6-O-benzylidene-

\* Part II, *J.*, 1953, 2442.

2-deoxy- $\alpha$ -D-glucoside (VII), since prepared by Hughes, Overend, and Stacey (*J.*, 1949, 2846) (m. p. 137—139°) and derived from the alternative product to be expected from the original reduction, *viz.*, methyl 2-deoxy- $\alpha$ -D-glucoside (VIII).

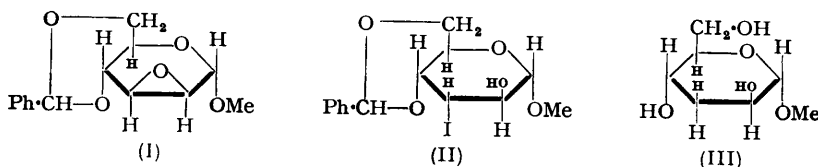


TABLE 1. Reaction of methyl 2:3-anhydro-4:6-O-benzylidene- $\alpha$ -D-mannoside (I) with methylmagnesium iodide.

Solvent	Reaction time (hr.)	Temp.	MeMgI used (moles/mole)	Recovery of (I) (%)	Yield of (II) (%)
Ether .....	5	35°	1.1	70	14
Ether .....	1	35	5.5	31	61
Tetrahydropyran .....	1	81	1.1	28	51
Ether .....	120	15—20	2.5	25	44

Although the mannoside (I) with ethylmagnesium iodide gave methyl 4:6-O-benzylidene-3-deoxy-3-iodo- $\alpha$ -D-altroside (II) as the chief halogeno-sugar, several other products were simultaneously formed, in amounts dependent on temperature and excess of reagent, and identified as described below. Each of these is analogous with a product obtained under suitable conditions by the action of Grignard reagents on simpler molecules; the increase in reducing power of ethyl- compared with methyl-magnesium iodide, as shown by the formation of methyl 4:6-O-benzylidene-3-deoxy- $\alpha$ -D-mannoside (IV), agrees with Kharasch and Weinhouse's observations (*J. Org. Chem.*, 1937, 1, 209) on the effect of the nature of the alkyl group in Grignard reductions, as does the absence of reduction in the reaction of the anhydro-sugar (I) with phenylmagnesium iodide (see below).

Methyl 4:6-O-benzylidene-3-deoxy- $\alpha$ -D-mannoside (IV) was formed predominantly (53%) at room temperature with 2.5 equivalents of ethylmagnesium iodide, but in lower yield at higher temperature (*e.g.*, 5% in boiling ether for 30 min.). This product crystallised when purified through its crystalline 2-O-benzoyl derivative, and the yield indicated that the syrup first obtained was homogeneous; the crystalline product (and its 2-O-toluene-*p*-sulphonyl derivative) agreed in properties with those described by Bollinger and Prins (*loc. cit.*), and it was shown to yield methyl 3-deoxy- $\alpha$ -D-mannoside (III) by partial acidic hydrolysis. The behaviour of Grignard reagents as reducing agents is well known (*cf.* Kharasch, Morrison, and Urry, *J. Amer. Chem. Soc.*, 1944, 66, 368; Kharasch and Weinhouse, *loc. cit.*).

When the anhydro-sugar (I) was treated with a large excess (10 equivalents) of ethylmagnesium iodide in boiling ether for 1½ hr. a very small amount of an unsaturated compound was formed, which is tentatively identified as methyl 4:6-O-benzylidene-2:3-

TABLE 2.

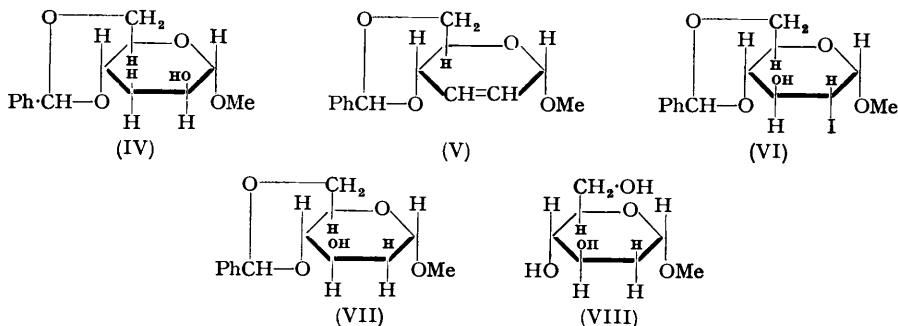
Compound	$\lambda_{\max}$ (Å)	$\epsilon_{\max}$	Compound	$\lambda_{\max}$ (Å)	$\epsilon_{\max}$
Supposed methyl 4:6-O-benzylidene-2:3-didehydro-2:3-dideoxy- $\alpha$ -D-glucoside	2120 *	11.6	Ethyl 2:3-didehydro-2:3-dideoxy- $\alpha$ -D-glucoside	2120	5.29
	2200	17.2		2170	5.33
	2350	17.9		2550	2.78
	2450	17.3			
	2600	18.1	Methyl 4:6-O-benzylidene- $\alpha$ -D-glucoside	2150	0.50
				2550	0.79
				2650	0.71

\* Submerged maximum.

didehydro-2:3-dideoxy- $\alpha$ -D-glucoside (V). This structure rests on analysis, the fact that the compound slowly reduced bromine, and the formation of benzaldehyde by warm dilute acid. The melting point, but not the rotation, agreed with those recorded by Bollinger and Prins (*loc. cit.*). The ultra-violet absorption (Table 2) was rather greater than would be expected from summation of the curves for methyl 4:6-O-benzylidene- $\alpha$ -D-glucoside and

ethyl 2 : 3-didehydro-2 : 3-dideoxy- $\alpha$ -D-glucoside (Laland, Overend, and Stacey; *J.*, 1950, 738), but occurred at similar wave-lengths. Formation of an ethylenic linkage by the action of magnesium on halides has previously been observed (*e.g.*, by Robinson and Smith, *J.*, 1936, 196) and, by analogy, the product (V) may arise by action of excess of magnesium in the unfiltered solution on methyl 4 : 6-*O*-benzylidene-3-deoxy-3-iodo- $\alpha$ -D-altroside (II), which under these conditions was obtained in reduced yield. In view of this the action of magnesium on the halogeno-sugars under similar conditions should prove of interest.

A very small amount of a further isomeric iodo-sugar obtained when the anhydro-sugar (I) was heated for 30 min. with ethereal ethylmagnesium iodide was almost certainly methyl 4 : 6-*O*-benzylidene-2-deoxy-2-iodo- $\alpha$ -D-glucoside (VI) since this is the only other isomer possible from simple scission of the epoxide ring.



The anhydro-sugar (I) was also treated with phenylmagnesium iodide, but in agreement with the general absence of reducing power in aryl Grignard reagents (see above) methyl 4 : 6-*O*-benzylidene-3-deoxy-3-iodo- $\alpha$ -D-altroside (II) was the only product isolated.

#### EXPERIMENTAL

Methyl 2 : 3-anhydro-4 : 6-*O*-benzylidene- $\alpha$ -D-mannoside was prepared by the method of Bollinger and Prins (*Helv. Chim. Acta*, 1945, 28, 465).

*Reaction of Methyl 2 : 3-Anhydro-4 : 6-O-benzylidene- $\alpha$ -D-mannoside with Methylmagnesium Iodide.*—In a typical reaction a solution of the mannoside (1.37 g.) in dry ether (100 ml.) was stirred with the reagent (from 0.3 g. of magnesium and 1.8 g. of methyl iodide in 20 ml. of ether) at room temperature for 5 days. Powdered ice was then added, followed by a small excess of dilute hydrochloric acid, and the ethereal solution was separated, washed with sodium hydrogen carbonate solution and water, dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated to dryness. The white crystalline residue, when recrystallised from ethanol-water, yielded methyl 4 : 6-*O*-benzylidene-3-deoxy-3-iodo- $\alpha$ -D-altroside (0.53 g., 26%), m. p. 163—163.5° alone or on admixture with the product from the similar reaction with anhydrous magnesium iodide (Richards, Wiggins, and Wise, *loc. cit.*).

The mother-liquors from the recrystallisation were evaporated to dryness and the residue chromatographed on a column of alumina, resulting in a recovery of the unchanged anhydride (0.34 g., 24.5%) and a further 0.36 g. (17.8%) of the iodo-altroside. The results obtained by varying the solvent, temperature, and ratio of reactants are summarised in Table 1.

*Derivatives of Methyl 4 : 6-O-Benzylidene-3-deoxy-3-iodo- $\alpha$ -D-altroside.*—The esters were prepared by standard procedures, in pyridine: 2-*toluene-p-sulphonate*, m. p. 127.5—129°,  $[\alpha]_D^{25} +46.4^\circ$  (c, 1 in  $\text{CHCl}_3$ ) (Found: C, 45.9; H, 4.75.  $\text{C}_{21}\text{H}_{23}\text{O}_7\text{IS}$  requires C, 46.1; H, 4.2%); 2-*acetate*, m. p. 123—124°,  $[\alpha]_D^{25} +72.4^\circ$  (c, 2 in  $\text{CHCl}_3$ ) (Found: C, 44.2; H, 4.57.  $\text{C}_{16}\text{H}_{19}\text{O}_6\text{I}$  requires C, 44.2; H, 4.4%); 2-*benzoate*, m. p. 140.5—141°,  $[\alpha]_D^{25} -11.7^\circ$  (c, 2 in  $\text{CHCl}_3$ ) (Found: C, 51.0; H, 4.1.  $\text{C}_{21}\text{H}_{21}\text{O}_6\text{I}$  requires C, 50.8; H, 4.3%).

*Methyl 3-Deoxy- $\alpha$ -D-mannoside.*—Methyl 2 : 3-anhydro-4 : 6-*O*-benzylidene- $\alpha$ -D-mannoside (4.00 g.) was reduced over Raney nickel according to the procedure of Bollinger and Prins (*loc. cit.*) to yield methyl 3-deoxy- $\alpha$ -D-mannoside (1.47 g.), which crystallised on complete removal of solvent. Recrystallised from acetone, it had m. p. 123.5—124°, alone or on

admixture with the product obtained by reduction of methyl 4 : 6-*O*-benzylidene-3-deoxy-3-iodo- $\alpha$ -D-altroside with Raney nickel (Richards, Wiggins, and Wise, *loc. cit.*), and  $[\alpha]_D^{22} + 129.6^\circ$  (*c*, 1 in MeOH) (Found: C, 47.5; H, 8.05. Calc. for  $C_{14}H_{14}O_5$ : C, 47.2; H, 7.9%). An alternative preparation by Bollinger and Prins (*loc. cit.*) from methyl 4 : 6-*O*-benzylidene-3-deoxy- $\alpha$ -D-mannoside also yielded amorphous material,  $[\alpha]_D^{15} + 108.9^\circ$  (*c*, 2 in MeOH).

*Reaction of Methyl 2 : 3-Anhydro-4 : 6-O-benzylidene- $\alpha$ -D-mannoside with Ethylmagnesium Iodide.*—(a) At 35°. A solution of the above mannoside (2.64 g.) in ether (250 ml.) was added with stirring at room temperature to a solution of the Grignard reagent (from 15.6 g. of ethyl iodide and 2.4 g. of magnesium) in ether (50 ml.), then heated with stirring under reflux for 1½ hr. during which an amorphous white solid was deposited, then cooled to room temperature; ice was added, followed by a slight excess of dilute hydrochloric acid. The aqueous phase, when neutralised with sodium hydrogen carbonate, evaporated to dryness and extracted with chloroform, yielded a yellow syrup (0.081 g.) which was not further investigated.

The ethereal phase from the reaction mixture was washed with sodium hydrogen carbonate solution and with water, dried ( $Na_2SO_4$ ), and evaporated to dryness. The residual syrup crystallised partly on trituration with ethyl acetate and when recrystallised therefrom yielded methyl 4 : 6-*O*-benzylidene-3-deoxy-3-iodo- $\alpha$ -D-altroside (0.37 g., 9.4%), m. p. and mixed m. p. 162.5—163.5°. The mother-liquors from the recrystallisation were evaporated to a colourless syrup and transferred to alumina (40 × 1 cm.). Fractions were obtained as follows:

(i) Ether-light petroleum (b. p. 60—80°) (1 : 5) gave a colourless pungent liquid (5 mg.),  $\alpha$  0°, which was not further investigated.

(ii) A second fraction obtained with the same eluant yielded yellow crystals (51 mg., 2%), which when recrystallised from ethanol had m. p. 119.5—120°,  $[\alpha]_D^{26} + 129^\circ$  (*c*, 0.7 in  $CHCl_3$ ) (Found: C, 67.8; H, 6.5. Calc. for  $C_{14}H_{14}O_4$ : C, 67.7; H, 6.5%), tentatively identified as methyl 4 : 6-*O*-benzylidene-2 : 3-didehydro-2 : 3-dideoxy- $\alpha$ -D-glucoside, for which Bollinger and Prins (*loc. cit.*) reported m. p. 119°,  $[\alpha]_D + 90^\circ$ . It gave a positive Molisch reaction; for the ultra-violet absorption spectrum see Table 2. It slowly absorbed bromine in carbon tetrachloride, and liberated the odour of benzaldehyde on acidic hydrolysis.

(iii) Elution with the same solvents (2 : 1) gave a mixture of the original anhydride (0.26 g., 9.9%) and methyl 4 : 6-*O*-benzylidene-3-deoxy-3-iodo- $\alpha$ -D-altroside (0.041 g.), resolved by crystallisation from ethanol-water.

(iv) Elution with ether yielded a colourless syrup (0.42 g.), apparently a mixture containing the preceding substances.

A similar reaction, with a smaller excess (2.5 equivs.) of Grignard reagent and the same anhydride (1.37 g.), heated for only 30 min. and then stirred at room temperature for 2 hr., yielded a crystalline product without resort to fractionation. Fractional recrystallisation from ethyl acetate-light petroleum, however, gave unchanged anhydride (0.28 g., 20.5%) and methyl 4 : 6-*O*-benzylidene-3-deoxy-3-iodo- $\alpha$ -D-altroside (0.51 g., 26%). Mother-liquors from the recrystallisations were evaporated to a syrup and subjected to chromatography as above, the first fraction obtained being the original anhydride (0.068 g.). Further elution with ether-light petroleum (b. p. 60—80°) (2 : 1) yielded a colourless syrup (0.040 g., 2%) which crystallised on trituration with ether. This was probably methyl 4 : 6-*O*-benzylidene-2-deoxy-2-iodo- $\alpha$ -D-glucoside, having m. p. 154.5—156° when recrystallised from ether (Found: C, 42.8; H, 4.6.  $C_{14}H_{17}O_5I$  requires C, 42.85; H, 4.4%). Further elution with the same mixture of solvents yielded crude methyl 4 : 6-*O*-benzylidene-3-deoxy- $\alpha$ -D-mannoside as a colourless syrup (0.38 g.) (iodine-free); treatment with toluene-*p*-sulphonyl chloride (0.5 g.) in pyridine (5 ml.) for 2 days at room temperature yielded crystalline methyl 4 : 6-*O*-benzylidene-2-deoxy-2-*O*-toluene-*p*-sulphonyl- $\alpha$ -D-mannoside (0.109 g., 5% calc. from the original anhydride), having m. p. 120.5—121°, alone or on admixture with an authentic sample (see below), and  $[\alpha]_D^{21} + 40.9^\circ$  (*c*, 2 in  $CHCl_3$ ), when recrystallised from ethanol-water (Found: C, 60.0; H, 5.7. Calc. for  $C_{21}H_{24}O_7S$ : C, 60.0; H, 5.8%).

(b) At 20°. Methyl 2 : 3-anhydro-4 : 6-*O*-benzylidene- $\alpha$ -D-mannoside (5.48 g.) was treated with ethylmagnesium iodide (2.5 equivs.) at room temperature for 21 hr. Thereafter the hydrolysis procedure was the same but the product finally obtained was amorphous and chromatography on alumina yielded only the original anhydride (0.86 g., 16%) and syrupy methyl 4 : 6-*O*-benzylidene-3-deoxy- $\alpha$ -D-mannoside (2.92 g., 53%). The latter readily yielded the 2-toluene-*p*-sulphonate, m. p. and mixed m. p. 120.5—121°, in good yield.

*Benzoylation of Crude Methyl 4 : 6-O-Benzylidene-3-deoxy- $\alpha$ -D-mannoside.*—The crude product (0.147 g.) of the previous reaction was treated in pyridine (2 ml.) with benzoyl chloride (0.2 ml.) at room temperature for 22 hr. The 2-benzoate (0.179 g., 91%), isolated in the usual

way and recrystallised from ethanol-water, had m. p. 139—140°,  $[\alpha]_D^{21} - 3.0^\circ$  (*c.* 4 in  $\text{CHCl}_3$ ) (Found: C, 67.9; H, 5.9.  $\text{C}_{21}\text{H}_{22}\text{O}_6$  requires C, 68.1; H, 6.0%).

*Alkaline Hydrolysis of Methyl 2-O-Benzoyl-4 : 6-O-benzylidene-3-deoxy- $\alpha$ -D-mannoside.*—(a) *By sodium methoxide.* A solution of the 2-benzoate (0.527 g.) in methanol (10 ml.) and chloroform (5 ml.) was treated with a solution of sodium (0.15 g.) in methanol (5 ml.) at room temperature for 20 hr. Reaction, made evident by a white precipitate, began immediately. Water (20 ml.) was next added and the mixture extracted with chloroform. The extract was washed repeatedly with water saturated with carbon dioxide, dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated to a yellow syrup which contained methyl benzoate (persistent even when the product was dried at 60°/0.01 mm.), and the syrup (0.391 g., 100.5%) could not be crystallised, although the rotation,  $[\alpha]_D^{20} + 94.0^\circ$  (*c.* 2 in  $\text{CHCl}_3$ ), indicated that it was essentially methyl 4 : 6-O-benzylidene-3-deoxy- $\alpha$ -D-mannoside.

(b) *By sodium hydroxide.* The same 2-benzoate (1.267 g.) was heated under reflux for 2 hr. with a solution of sodium hydroxide (1 g.) in ethanol (40 ml.) and chloroform (10 ml.), sodium benzoate separating. The product was isolated as described for the previous experiment and methyl 4 : 6-O-benzylidene-3-deoxy- $\alpha$ -D-mannoside crystallised readily. Recrystallised from benzene-light petroleum it (0.429 g., 46%) had m. p. 107.5—108.5,  $[\alpha]_D^{23} + 96.5^\circ$  (*c.* 2 in  $\text{CHCl}_3$ ),  $[\alpha]_D^{19} + 88.6^\circ$  (*c.* 1 in EtOH) (Found: C, 63.3; H, 6.6. Calc. for  $\text{C}_{14}\text{H}_{18}\text{O}_5$ : C, 63.1; H, 6.8%). Bollinger and Prins (*loc. cit.*), for the same compound prepared from methyl 3-deoxy- $\alpha$ -D-mannoside, recorded m. p. 110—111°,  $[\alpha]_D^{12} + 95.0^\circ$  (*c.* 3 in  $\text{CHCl}_3$ ).

The 2-toluene-*p*-sulphonate had m. p. 120.5—121°, alone or on admixture with the product obtained from the amorphous material. Bollinger and Prins (*loc. cit.*) record for this compound m. p. 121—122°,  $[\alpha]_D^{13} + 45.2^\circ$ .

*Partial Acidic Hydrolysis of Methyl 4 : 6-O-Benzylidene-3-deoxy- $\alpha$ -D-mannoside.*—The mannoside (0.316 g.) in acetone (25 ml.) was heated under reflux with aqueous oxalic acid (0.7 g. of the dihydrate in 2.5 ml. of water) to constant rotation (3 hr.;  $[\alpha]_D^{20} + 77.7^\circ \longrightarrow + 92.3^\circ$ ). After neutralisation with barium carbonate and filtration, the solution was evaporated to dryness and the residue distilled in steam until free from benzaldehyde. The remaining aqueous solution was evaporated to a colourless syrup, which crystallised on trituration with chloroform and when recrystallised from ethyl acetate had  $[\alpha]_D^{24} + 132^\circ$  (*c.* 0.7 in EtOH) and m. p. 123—124° alone or on admixture with the compound obtained by reduction of methyl 4 : 6-O-benzylidene-3-deoxy-3-iodo- $\alpha$ -D-altroside.

*Reaction of Methyl 2 : 3-Anhydro-4 : 6-O-benzylidene- $\alpha$ -D-mannoside with Phenylmagnesium Iodide.*—A solution of the mannoside (1.37 g.) in ether (125 ml.) was added slowly with vigorous stirring to the Grignard solution prepared from iodobenzene (2.55 g.), magnesium (0.3 g.), and ether (20 ml.). A white granular precipitate separated immediately. After 1 hour's heating with stirring, the usual acidification and extraction yielded a crystalline product which was resolved by fractional recrystallisation from ethanol-water and ethyl acetate-light petroleum into unchanged anhydromannoside (0.57 g., 42%) and methyl 4 : 6-O-benzylidene-3-deoxy-3-iodo- $\alpha$ -D-altroside (0.69 g., 34%), m. p. and mixed m. p. 163—163.5°. Chromatography of the mother-liquors on alumina yielded only further amounts of the same compounds (0.04 and 0.275 g. respectively).

The author is grateful to Professor M. Stacey, F.R.S., for his interest and advice and to the Department of Scientific and Industrial Research for a maintenance grant.

THE CHEMISTRY DEPARTMENT, THE UNIVERSITY, EDGBASTON,  
BIRMINGHAM, 15.

[Present address: THE BRITISH RAYON RESEARCH ASSOCIATION,  
HEALD GREEN, MANCHESTER.]

[Received, August 6th, 1954.]