1011. *Carbohydrate Carbonates. Part III.* The Transformation of Some 1,2-Isopropylidene-α-D-glucofuranose 5,6-Carbonates into 3,6-Anhydro-derivatives.*

By L. D. HALL and L. HOUGH.

Improved methods for the preparation of 5,6-carbonate derivatives of 1,2-O-isopropylidene-α-D-glucofuranose are described. Attempts to convert these carbonates into the corresponding 5,6-episulphides and 5,6-epoxides by fusion with potassium thiocyanate and sodium hydrogen carbonate, respectively, were unsuccessful and resulted in the formation of derivatives of 3,6-anhydro-1,2-O-isopropylidene-α-D-glucofuranose. A mechanistic rationalisation of these observations is given. Propane-1,2-diol carbonate gave propylene sulphide on fusion with potassium thiocyanate.

SEARLES and LUTZ[1] found that aliphatic cyclic carbonates could be converted, with loss of carbon dioxide, into episulphides by heating them with potassium thiocyanate at *ca.* 170°. In view of the recent improvements[2] in the preparation of carbohydrate cyclic carbonates, this method offered a potential route to the carbohydrate episulphides. With the exception of ethylene carbonate, the derivatives that Searles and Lutz

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* Part II, *J.*, 1962, 1934.

[1] Searles and Lutz, *J. Amer. Chem. Soc.*, 1958, **80**, 3168.
[2] Hough, Priddle, and Theobald, *Adv. Carbohydrate Chem.*, 1960, **15**, 91.

investigated were all six-membered cyclic 1,3-carbonates which are less stable thermally than the five-membered cyclic carbonates. When propane-1,2-diol carbonate was heated at *ca.* 170° with potassium thiocyanate, a 30% yield of propylene sulphide was obtained.* On this basis it seemed highly probable that five-membered monosaccharide 5,6-carbonates could be similarly converted into the corresponding 5,6-episulphides.

Treatment of 1,2-*O*-isopropylidene-α-D-glucofuranose (I) with carbonyl chloride, in the conditions of Haworth and Porter,[3a] gave 1,2-*O*-isopropylidene-α-D-glucofuranose 5,6-carbonate (II) in *ca.* 7% yield. A 15% yield has been obtained on a smaller scale.[3b] Acetylation of the 5,6-carbonate (II) with acetic anhydride–pyridine gave 3-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose 5,6-carbonate (III). As in the general method of Hough *et al.*,[2] addition of aqueous sodium hydroxide to a stirred mixture of benzyl chloroformate and aqueous 1,2-*O*-isopropylidene-α-D-glucofuranose gave the 5,6-carbonate (II), but in only 10% yield. When this reaction was repeated with aqueous dioxan as solvent, crystalline 3-*O*-benzyloxycarbonyl-1,2-*O*-isopropylidene-α-D-glucofuranose 5,6-carbonate (IV) was formed in 52% yield, together with some syrupy acyclic-ester derivatives. Catalytic hydrogenolysis of the 3-*O*-benzyloxycarbonyl group afforded the 5,6-carbonate [3,4] (II) in 75% yield. Reist, Spencer, and Baker [3b] have prepared the 5,6-carbonate (II) in 58% yield from the isopropylidene derivative (I) by formation of the 6-*O*-methoxycarbonyl derivative followed by cyclisation in pyridine at 60°.

The general method adopted for the decomposition of the carbonates was to fuse an intimate mixture of the carbonate with finely powdered potassium thiocyanate (or other base) and continue heating at *ca.* 170° until no further carbon dioxide was evolved. When 1,2-*O*-isopropylidene-α-D-glucofuranose 5,6-carbonate (II) was fused with potassium thiocyanate at 170° for *ca.* four minutes, a high yield of 3,6-anhydro-1,2-*O*-isopropylidene-α-D-glucofuranose (V) was obtained. Although Freudenberg *et al.*[5] claimed that this decomposition occurred when the 5,6-carbonate (II) was heated alone, attempts to repeat this were unsuccessful unless a weakly basic catalyst was included. Since no reaction occurred when the 5,6-carbonate (II) was heated in a dry Pyrex-glass flask, whereas a smooth decomposition followed the addition of finely powdered soda-glass, the potassium thiocyanate must have acted solely as a basic catalyst in the above experiments. This is supported by the base-catalysed thermal decomposition of carbonate esters of 1,2-, 1,3-, 1,4-, and 1,5-diols to anhydro-derivatives.[6,7] In addition, Reist, Spencer, and Baker [3b] have shown that heating the 5,6-carbonate (II) at 140° in dimethylformamide in the presence of sodium methoxide affords the 3,6-anhydro-derivative (V) in 64% yield.

Two mechanisms are possible for the formation of the 3,6-anhydro-compounds; either (*a*) the elimination of carbon dioxide with concomitant formation of 5,6-anhydro-1,2-*O*-isopropylidene-α-D-glucofuranose (X), followed by attack of O-3 on C-6, although Mills [8a] has pointed out that this reaction is sterically unfavourable, or (*b*) the direct attack on C-6 by the anionoid O-3, resulting in the formation of the 3,6-anhydro-ring with elimination of carbon dioxide. Accordingly, the reaction between the 5,6-anhydro-derivative (X) and base was investigated, but with potassium thiocyanate a syrup with negative $[\alpha]_D$ was isolated which could not be further characterised (the 3,6-anhydro-derivative has a positive rotation). In the presence of sodium hydrogen carbonate under more vigorous

* We are indebted to Dr. Scott Searles (Kansas State University) for communicating similar results to us before their publication.

[3] (*a*) Haworth and Porter, *J.*, 1929, 2796; (*b*) Reist, Spencer, and Baker, *J. Org. Chem.*, 1958, **23**, 1958.

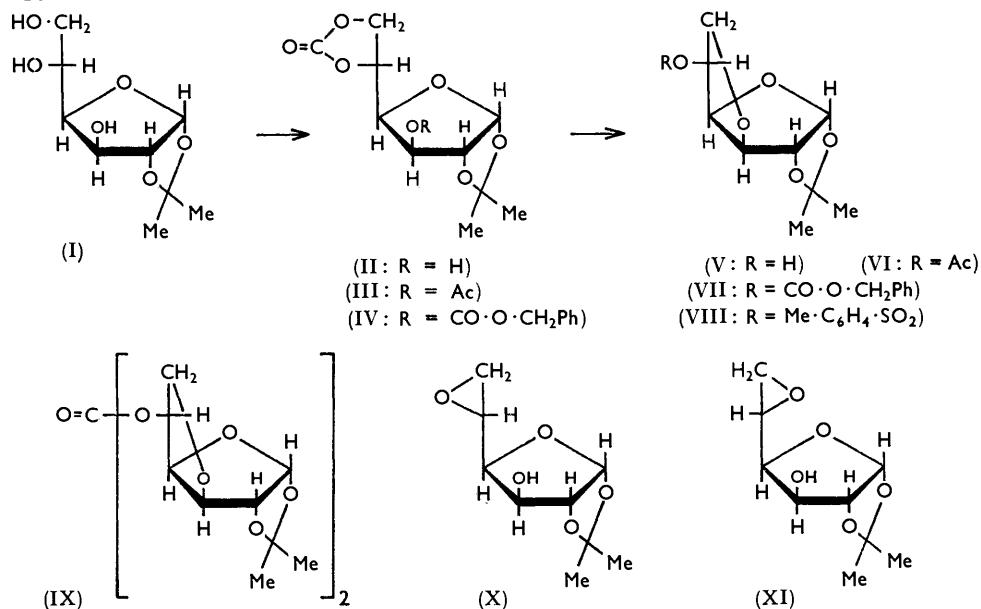[4] Overend, *J.*, 1949, 1358.

[5] Freudenberg, Eich, Knoevenagel, and Westphal, *Ber.*, 1940, **73**, 441.

[6] Searles, Hummel, Nukina, and Throckmorton, *J. Amer. Chem. Soc.*, 1960, **82**, 2928, and references therein.

[7] Pattison, *J. Amer. Chem. Soc.*, 1957, **79**, 3455.

[8] (*a*) Mills, *Adv. Carbohydrate Chem.*, 1955, **10**, 8; (*b*) Ohle and von Vargha, *Ber.*, 1929, **62**, 2435; (*c*) Montgomery and Wiggins, *J.*, 1946, 390.

conditions than the above elimination, the 5,6-anhydro-derivative was recovered unchanged; hence decomposition of the 5,6-carbonate follows route (*b*). Support for this mechanism follows from conversion of 1,2-*O*-isopropylidene-5,6-di-*O*-tosyl-α-D-gluco-furanose with base into 3,6-anhydro-1,2-*O*-isopropylidene-5-*O*-tosyl-α-D-glucofuranose in high yield.[8] Whistler and Frowlin [9] have reported that heating 5,6-anhydro-1,2-*O*-iso-propylidene-α-D-glucofuranose with a base such as pyridine or sodium methoxide results

(I)

(II: R = H)
(III: R = Ac)
(IV: R = CO·O·CH₂Ph)

(V: R = H)   (VI: R = Ac)
(VII: R = CO·O·CH₂Ph)
(VIII: R = Me·C₆H₄·SO₂)

(IX)   (X)   (XI)

in polymerisation, but their conditions were considerably more vigorous than those described here. It is noteworthy that attempts to convert methyl 4,6-*O*-benzylidene-α-D-mannopyranoside 2,3-carbonate into the corresponding 2,3-epoxide by basic, thermal decomposition were unsuccessful.[10]

The decomposition of 3-*O*-benzyloxycarbonyl-1,2-*O*-isopropylidene-α-D-glucofuranose 5,6-carbonate (IV) was not investigated since 3,6-anhydro-formation might have been excluded by the 3-*O*-substituent. Reaction as above yielded a mixture from which two compounds were separated by fractional crystallisation. From elemental analyses and infrared spectra these were tentatively identified as a monoanhydro-monobenzyloxy-carbonyl derivative and a bis(monoanhydro-1,2-*O*-isopropylidene-α-D-glucofuranose) carbonate. It seemed possible that these were 5,6-anhydro-derivatives since Bruson and Riener [11] have shown that the thermal decomposition of glycerol 1,2-carbonate produces 2,3-epoxypropan-1-ol (glycidol), whereas 3,6-anhydro-formation did not appear to be feasible without concomitant elimination of the oxo-atom. However, comparison of their proton magnetic resonance spectra with known [12] 3,6-anhydro- (V; VIII) and 5,6-anhydro-derivatives (X; XI) showed that, instead of the expected 5,6-epoxy-ring, a 3,6-anhydro-ring was present in each compound. Further, catalytic hydrogenation of the monoanhydro-monobenzyloxycarbonyl derivative afforded 3,6-anhydro-1,2-*O*-isopropyl-idene-α-D-glucofuranose (V). So the products from the decomposition of the 3-*O*-benzyl-oxycarbonyl derivative (IV) are assigned the structures 3,6-anhydro-5-*O*-benzyloxy-carbonyl-1,2-*O*-isopropylidene-α-D-glucofuranose (VII) and di-(3,6-anhydro-1,2-*O*-isopropyl-idene-α-D-glucofuranose) 5,5'-carbonate (IX).

[9] Whistler and Frowlin, *J. Org. Chem.*, 1961, **26**, 3946.
[10] Hough and Priddle, unpublished results.
[11] Bruson and Riener, *J. Amer. Chem. Soc.*, 1952, **74**, 2100.
[12] Abraham, Hall, Hough, and McLauchlan, *Chem. and Ind.*, 1962, 213; *J.*, 1962, 3699.

Chemical shifts (τ-values) of ring hydrogen atoms.

Hydrogen	5,6-Anhydro-derivative [12]		3,6-Anhydro-derivative [12]		Monomer
	(X)	(XI)	(V)	(VIII)	(VII)
H_1	4·06	4·06	4·06	4·06	4·09
H_2	5·44	5·48	5·45	5·45	5·44
H_3	5·76	5·74	5·54	5·58	5·50
H_{61}	7·17	7·26	6·37	6·19	6·01
H_6	7·26	7·34	6·90	6·56	6·29

Further evidence in favour of these structures followed an investigation of the ester-exchange of the compounds in methanol. Theobald [13] found that polymeric sucrose carbonates slowly dissolved in boiling methanol in the presence of a weak base and suggested that this was caused by an ester exchange. Preliminary studies on the de-esterification of propane-1,2-diol carbonate with methanol containing a little sodium hydrogen carbonate showed that the reaction exhibited the " mass action " characteristics of an ester exchange since complete de-esterification occurred only when a large excess of
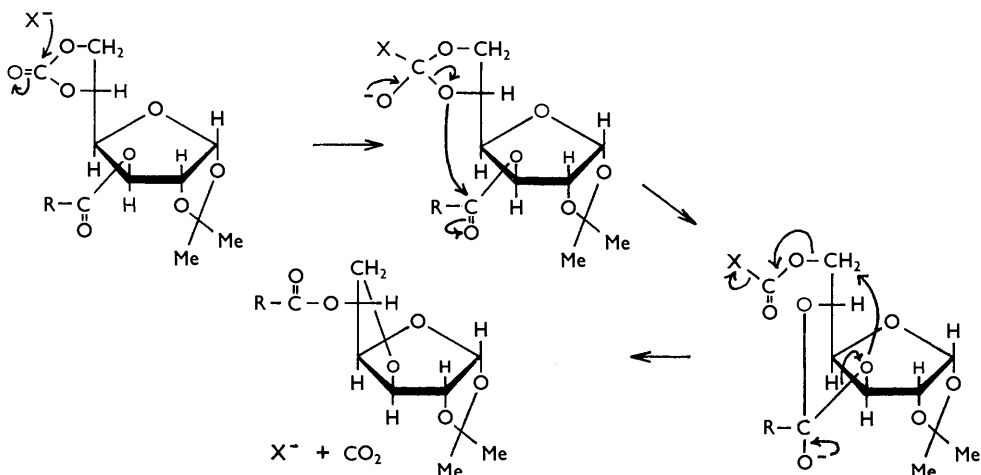
methanol was used. In a suitably dilute solution, 3-*O*-benzyloxycarbonyl-1,2-*O*-iso-propylidene-α-D-glucofuranose 5,6-carbonate was fully de-esterified, giving 1,2-*O*-iso-propylidene-α-D-glucofuranose. In similar conditions, the 5-*O*-benzyloxycarbonyl deriv-ative (VII) and the 5,5'-carbonate (IX) were converted into 3,6-anhydro-1,2-*O*-isopropyl-idene-α-D-glucofuranose (V). Since 5,6-anhydro-1,2-*O*-isopropylidene-αD-glucofuranose (X) was not converted into the 3,6-anhydro-derivative in these conditions, thereby invalidating the 5,6-epoxide as an intermediate, the presence of a 3,6-anhydro-ring in both products (VII and IX) was confirmed.

Although the formation of the 5,5'-carbonate (IX) from the 5-*O*-benzyloxycarbonate (VII) could be readily explained by the elimination of dibenzyl carbonate between two monomer units, the formation of the monomer is less obvious. A rational explanation of

$$2Ph·CH_2·O·CO·O-R \longrightarrow (Ph·CH_2·O)_2CO + OC(OR)_2$$
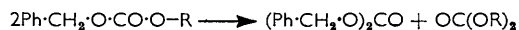
the latter reaction follows from the observations of Searles *et al.*,[6] by initial attack of base at the carbonate-carbonyl carbon atom rather than at the primary carbon atom. Once attack by the nucleophile has occurred, a rearrangement can follow, so that the benzyloxy-carbonyl group can migrate from O-3 to O-5, leaving a nucleophilic atom O-3 to attack C-6 and thus form the 3,6-anhydro-derivative.

Two relevant examples of anomalous migrations have previously been observed with derivatives of 1,2-*O*-isopropylidene-α-D-glucofuranose. Freudenberg *et al.*[5] found that

[13] Theobald, unpublished results.

in moist air 3-O-chloroformyl-1,2:5,6-di-O-isopropylidene-α-D-glucofuranose was converted into 1,2-O-isopropylidene-α-D-glucofuranose 5,6-carbonate, and Smith[14] showed that the action of phosphorus pentachloride on 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose produced 6-chloro-6-deoxy-1,2:3,5-di-O-isopropylidene-α-D-glucofuranose.

The decomposition of 3-O-acetyl-1,2-O-isopropylidene-α-D-glucofuranose 5,6-carbonate was of interest in this case since dimerisation could not occur. However, this carbonate proved to be far more stable than those described above. Under more vigorous conditions than those used for the 3-O-benzyloxycarbonyl derivative (IV), a syrup was obtained whose infrared spectrum and elemental analysis was consistent with formulation as 5-O-acetyl-3,6-anhydro-1,2-O-isopropylidene-α-D-glucofuranose (VI). The extra stability of the 3-O-acetate (III) compared with the 3-O-benzyloxycarbonyl derivative (IV) is compatible with the mechanism outlined earlier, in which it might be expected that an aryl substituent would migrate more readily than an alkyl substituent.

EXPERIMENTAL

Concentrations were carried out under reduced pressure. M. p.s were determined on a Kofler microscope stage. Optical rotations were determined at $25° \pm 1°$ for $CHCl_3$ solutions unless otherwise stated. Light petroleum of b. p. 60—80° was used throughout. Unless otherwise stated, infrared spectra were determined for Nujol mulls. The proton magnetic resonance spectra were recorded on a Varian 60 Mc./sec. 4200 B spectrometer at $\sim25°$. Calibration was by the usual side-band technique with tetramethylsilane as internal reference.

3-O-*Benzyloxycarbonyl*-1,2-O-*isopropylidene*-α-D-*glucofuranose* 5,6-*Carbonate* (IV).—1,2-O-Isopropylidene-α-D-glucofuranose (6·0 g.), in 2 : 1 aqueous dioxan (37 ml.), and benzyl chloroformate (18·0 ml.), were stirred vigorously and cooled in ice–salt. Aqueous 3N-sodium hydroxide (36·5 ml.) was added dropwise so that the temperature did not exceed 2°, and stirring was continued overnight. Water (200 ml.) and chloroform (300 ml.) were added to the resultant emulsion, and the chloroform layer was separated, washed with water, and dried ($CaSO_4$). The chloroform solution was concentrated to a thick syrup which was heated at 180° (bath)/6×10^{-3} mm. until no more dibenzyl carbonate distilled. Trituration of the resultant syrup with ethanol produced crystals (5·5 g., 52%), m. p. 125—131°, and recrystallisation from ethanol afforded the *benzyloxycarbonyl derivative* (4·7 g., 45%), m. p. 136—137·5°, $[\alpha]_D$ −23·7° (c 2·58), $\nu_{max.}$ 1747, 1794 (C=O) (Found: C, 56·7; H, 5·3. $C_{18}H_{20}O_9$ requires C, 56·8; H, 5·3%).

1,2-O-*Isopropylidene*-α-D-*glucofuranose* 5,6-*Carbonate* (II).—(a) *From* D-*glucose.* Carbonyl chloride was passed into a stirred suspension of D-glucose (32 g.) in dry acetone (280 ml.) until all the glucose had dissolved (3·5 hr.). The solution was kept over anhydrous calcium sulphate for 11 hr. at room temperature and then neutralised with lead carbonate. The insoluble lead salts were filtered off and washed with acetone, and the combined filtrates were concentrated. Crystals which separated were filtered off and recrystallised from aqueous ethanol as colourless needles (2·27 g., 7%), m. p. 218—220°. Recrystallisation from methanol gave 1,2-O-isopropylidene-α-D-glucofuranose 5,6-carbonate, m. p. 224—225° (sublimes at ca. 210°), $[\alpha]_D$ −31·8° (c 0·5 in acetone) (Found: C, 48·95; H, 5·9. Calc. for $C_{10}H_{14}O_7$: C, 48·75; H, 5·75%) (lit.,[3] m. p. 223—224°, $[\alpha]_D$ −36°).

(b) *From* 1,2-O-*isopropylidene*-α-D-*glucofuranose* (I). Treatment of 1,2-O-isopropylidene-α-D-glucofuranose (6 g.) under conditions similar to those employed in the preparation of the benzyloxycarbonyl derivative (IV), but without the dioxan, afforded the 5,6-carbonate (II) as needles (0·68 g., 10%), m. p. 177—192°. Recrystallised from ethanol–light petroleum, the carbonate had m. p. 215—216°, mixed m. p. with a sample from (a) 215—224°.

(c) *From* 3-O-*benzyloxycarbonyl*-1,2-O-*isopropylidene*-α-D-*glucofuranose* 5,6-*carbonate* (IV). The benzyloxycarbonyl derivative (9·4 g.) was hydrogenated at atmospheric pressure in dioxan (100 ml.) with 10% palladium–charcoal (1·0 g.) (uptake 1·0 mol. in 1·5 hr.). The catalyst was filtered off and washed with acetone, and the combined filtrates were concentrated, affording the carbonate (II) as needles (4·55 g., 75%), m. p. 220° (sublimes at ca. 210°), $[\alpha]_D$ −31·1° (c 0·6 in acetone), $\nu_{max.}$ 1790 (C=O) and 3420 (OH).

3-O-*Acetyl*-1,2-O-*isopropylidene*-α-D-*glucofuranose* 5,6-*Carbonate* (III).—1,2-O-Isopropylidene-α-D-glucofuranose 5,6-carbonate (2·0 g.) in dry pyridine (12 ml.) and acetic anhydride

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[14] Smith, *J.*, 1956, 1244.

(12 ml.) was kept at room temperature for 16 hr. Concentration produced a crystalline residue which recrystallised from ethanol–light petroleum as needles (2·2 g., 94%), m. p. 129—130°. Further recrystallisation from ethanol afforded the acetate (III), m. p. 130—131°, $[\alpha]_D$ —44·5° (*c* 1·9), $\nu_{max.}$ 1747 (OAc) and 1804 (C=O) (Found: C, 50·25; H, 5·65. Calc. for $C_{12}H_{16}O_8$: C, 50·0; H, 5·55%) {lit.[5] m. p. 128—129°, $[\alpha]_D$ —43·2° (*c* 2·5)}.

Base-catalysed Thermal Decomposition of Carbonates

Propane-1,2-*diol Carbonate*.—(*a*) *To propylene sulphide*. Propylene carbonate (10·7 g.) and anhydrous potassium thiocyanate (11·0 g.) were heated at 170° (bath) under a Dufton fractionating column (1 × 10 cm.). Potassium cyanate gradually separated from the initially clear solution and a colourless mobile liquid distilled off. The propylene sulphide (2·44 g., 31%) had b. p. 74—76°, n_D^{20} 1·4783 ± 0·0002 (Found: C, 48·4; H, 8·15. Calc. for C_3H_6S: C, 48·6; H, 8·1%) (lit.,[15] b. p. 75—76°, n_D^{15} 1·4780).

(*b*) *To propylene oxide*. When propylene carbonate was heated at 220° (bath) for *ca.* 75 min. with potassium carbonate or sodium cyanide, no distillable product was obtained. An amber-coloured gel which remained in the flask appeared to be polymeric since it was insoluble in both water and chloroform.

1,2-*O-Isopropylidene-α-*D*-glucofuranose* 5,6-*carbonate* (II).—The carbonate (0·75 g.) and sodium hydrogen carbonate (0·005 g.) were heated under nitrogen at 240° (bath) for 3 min. A sublimate was collected and crystallised from ether as needles (0·48 g., 78%), m. p. 52—54°. Recrystallisation from light petroleum gave 3,6-anhydro-1,2-*O*-isopropylidene-α-D-gluco-furanose (0·414 g., 67%), m. p. 53·2—54·6°, $[\alpha]_D$ +28·7° (*c* 1·6 in H_2O); mixed m. p. and infrared spectrum were identical with those of authentic material. Similar results were obtained by using either ground soda-glass or anhydrous potassium thiocyanate as the basic catalyst. If the catalyst was omitted and the experiment carried out in a " Pyrex " flask, starting material was recovered unchanged.

3-*O-Benzyloxycarbonyl*-1,2-*O*-*isopropylidene*-α-D-*glucofuranose* 5,6-*Carbonate* (IV).—The benzyloxycarbonyl derivative (IV) (1·49 g.) and anhydrous potassium thiocyanate (0·39 g.) were thoroughly mixed, dried over phosphorus pentoxide, and heated at 166° (bath) for 4 min. The fused mass was extracted with chloroform (80 ml.), and the chloroform solution was washed with water (20 ml.) and dried ($CaSO_4$). Potassium thiocyanate was recovered in quantitative yield from the combined aqueous solutions.

Concentration of the chloroform extract gave a brown syrup (1·33 g.), an ethanolic solution of which was decolorised (charcoal) and concentrated to give crystals (0·51 g.), m. p. 153—155·5° (fraction A). Successive additions of light petroleum to the ethanolic mother-liquors yielded further crystals, (0·25 g.) m. p. 71—75° (fraction B), and (0·08 g.) m. p. 67—73° (fraction C).

Fraction A was thrice recrystallised from ethanol, to yield di-(3,6-*anhydro*-1,2-*O-isopropyl-idene-α*-D*-glucofuranose*) 5,5′-*carbonate* (IX), m. p. 155—157°, $[\alpha]_D$ +97·7° (*c* 1·14), $\nu_{max.}$ 1760 (C=O) (Found: C, 53·2; H, 6·05. $C_{19}H_{26}O_{11}$ requires C, 53·0; H, 6·1%).

Fractions B and C were combined and digested with boiling ethanol, the residual crystals were filtered off, and the solution was concentrated and mixed with light petroleum. The crystals thus obtained had m. p. 71—73·8° and were recrystallised from the same solvents, to yield 3,6-*anhydro*-5-*O-benzyloxycarbonyl*-1,2-*O*-*isopropylidene-α*-D*-glucofuranose* (VII) (0·18 g.), m. p. 73·5—74·5°, $[\alpha]_D$ +50·1° (*c* 1·04), $\nu_{max.}$ 700, 767 (Ph), and 1750 (C=O) (Found: C, 60·25; H, 5·8. $C_{17}H_{20}O_7$ requires C, 60·65; H, 6·0%).

3-*O-Acetyl*-1,2-*O*-*isopropylidene-α*-D*-glucofuranose* 5,6-*Carbonate* (III).—The carbonate (0·295 g.) and potassium carbonate (0·22 g.) were heated under nitrogen at 186° (bath) for *ca.* 16 min. The resultant fused mass was extracted with chloroform, and the solution was concentrated to a syrup (0·142 g.), $\nu_{max.}$ (in $CHCl_3$) 1747 (OAc) (Found: C, 55·0; H, 7·0. $C_{11}H_{16}O_6$ requires C, 54·1; H, 6·55%).

The carbonate (III) was recovered unchanged after being heated at 170° (bath) with potassium thiocyanate for 20 min. or with sodium hydrogen carbonate for 6 min.

Ester-exchange

The general method consisted of heating a solution of the compound and sodium hydrogen carbonate in methanol under reflux for *ca.* 30 min. The solution was then concentrated to

[15] Culvenor, Davies, and Pausacker, *J.*, 1946, 1050.

dryness, the residue extracted with either ether or chloroform, and the product obtained from the extract by concentration, followed by recrystallisation from a suitable solvent.

Propane-1,2-diol Carbonate.—The carbonate (6 g.) and sodium hydrogen carbonate (0·06 g.) in methanol (200 ml.) were heated under reflux for 30 min. Filtration followed by concentration afforded a viscous liquid (4·1 g., 92%) which was characterised as propane-1,2-diol by the formation of the di-*O-p*-nitrobenzoate, m. p. 120—122° undepressed on admixture with authentic material.

*3-O-Benzyloxycarbonyl-1,2-O-isopropylidene-α-*D*-glucofuranose 5,6-Carbonate* (IV).—The benzyloxycarbonyl derivative (0·185 g.) and sodium hydrogen carbonate (0·02 g.) in methanol (10 ml.) were treated as described above, affording crystals (0·06 g., 57%), m. p. 145—158°. Recrystallised from chloroform–light petroleum, the product had m. p. 158—160° undepressed on admixture with 1,2-*O*-isopropylidene-α-D-glucofuranose.

*5,6-Anhydro-1,2-O-isopropylidene-α-*D*-glucofuranose.*—The 5,6-anhydro-derivative (0·19 g.) and sodium hydrogen carbonate (0·018 g.) in methanol (25 ml.) were treated as above, affording unchanged starting material.

*Di-(3,6-anhydro-1,2-O-isopropylidene-α-*D*-glucofuranose) 5,5′-Carbonate* (IX).—The compound (0·18 g.) and sodium hydrogen carbonate (0·013 g.) in methanol (10 ml.), as described above, gave a syrup which slowly crystallised (m. p. *ca.* 55°). Recrystallisation from ether–light petroleum afforded long needles (0·095 g., 56%), m. p. 52—56°, undepressed on admixture with 3,6-anhydro-1,2-*O*-isopropylidene-α-D-glucofuranose. The infrared spectrum ($CHCl_3$ solution) was also identical with that of an authentic specimen.

*3,6-Anhydro-5-O-benzyloxycarbonyl-1,2-O-isopropylidene-α-*D*-glucofuranose* (VII).—The compound (0·06 g.) and sodium hydrogen carbonate (*ca.* 0·05 g.) in methanol (15 ml.) afforded a syrup, $[\alpha]_D$ +14·9° (*c* 1·9 in H_2O). Vacuum-sublimation at 80° (bath) afforded needles, m. p. 51—54° undepressed on admixture with 3,6-anhydro-1,2-*O*-isopropylidene-α-D-glucofuranose.

*Hydrogenation of 3,6-Anhydro-5-O-benzyloxycarbonyl-1,2-O-isopropylidene-α-*D*-glucofuranose* (VII).—The compound (VII) (0·07 g.) in dioxan (30 ml.) was hydrogenated with 10% palladium–charcoal (*ca.* 0·5 g.) for 4 hr. The catalyst was filtered off and washed with methanol, and the combined filtrates were concentrated to a colourless syrup (0·04 g., 100%), $[\alpha]_D$ +26·0° (*c* 2·1 in H_2O). The syrup crystallised with difficulty from ether–light petroleum as needles, m. p. 50—54° undepressed on admixture with 3,6-anhydro-1,2-*O*-isopropylidene-α-D-glucofuranose.

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