Synthetic Studies with Carbonates. Part 11.[1] D-Glucopyranose 1-Carbonate Derivatives; Pyrolytic Behaviour and Use for Glucosylation of Phenols

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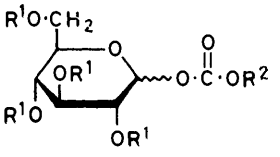
2,3,4,6-Tetra-*O*-acetyl-1-*O*-phenoxycarbonyl-β-D-glucopyranose (1), its 1-*O*-methoxycarbonyl analogue (3), and 2,3,4,6-tetra-*O*-benzoyl-1-*O*-phenoxycarbonyl-β-D-glucopyranose (5) underwent pyrolysis to give mixtures of various products whose composition depended on the structure of the starting material. However, the α-anomers of (1) and (3) were not susceptible to pyrolysis, even under more drastic conditions. Glucosylation reactions of phenols with the β-D-glucopyranose 1-carbonates were conducted autocatalytically to give the corresponding phenyl β-D-glucopyranoside derivatives in moderate yields. Especially useful was the synthesis of *o*-nitrophenyl and *o*-chlorophenyl glucopyranoside derivatives, which cannot be prepared through the Helferich's procedure, even under acid-catalysis conditions. A reaction mechanism involving an orthoester intermediate is suggested; such an intermediate was isolated and transformed into the corresponding glucopyranoside derivatives *etc.*

A NEW glycosylation process for the synthesis of phenyl glycosides, purine and pyrimidine nucleosides, and related compounds involves an autocatalytic reaction of sugar 1-carbonate derivatives with nucleophiles such as phenols, purines, and pyrimidinones, *etc.*[2] We now report detailed results of its application to the synthesis of a series of phenyl glucopyranoside derivatives and a



(1) R^1 = Ac, R^2 = Ph; β-anomer
(2) R^1 = Ac, R^2 = Ph; α-anomer
(3) R^1 = Ac, R^2 = Me; β-anomer
(4) R^1 = Ac, R^2 = Me; α-anomer
(5) R^1 = Bz, R^2 = Ph; β-anomer

comparison of the results with those of the autocatalytic or acid-catalysed fusion reaction of fully acetylated sugars with phenols originally developed by Helferich *et al.*[3]

Pyrolysis.—Prior to the glycosylation reaction, we examined the pyrolytic behaviour of D-glucopyranose 1-carbonate derivatives. Alkyl aryl carbonates have been shown to afford the corresponding alkyl aryl ethers or olefins and alcohols on pyrolysis at an elevated temperature, with evolution of carbon dioxide.[4]

2,3,4,6-Tetra-*O*-acetyl-1-*O*-phenoxycarbonyl-β- (1) and -α-D-glucopyranose (2), 2,3,4,6-tetra-*O*-acetyl-1-*O*-methoxycarbonyl-β- (3) and -α-D-glucopyranose (4), and 2,3,4,6-tetra-*O*-benzoyl-1-*O*-phenoxycarbonyl-β-D-glucopyranose (5) were prepared from the corresponding 2,3,4,6-tetra-*O*-acyl-D-glucopyranoses with pyridine–phenyl or –methyl chloroformate. Pyrolytic conditions for each sugar 1-carbonate were settled by finding the temperature at which carbon dioxide evolution was induced.

TABLE 1

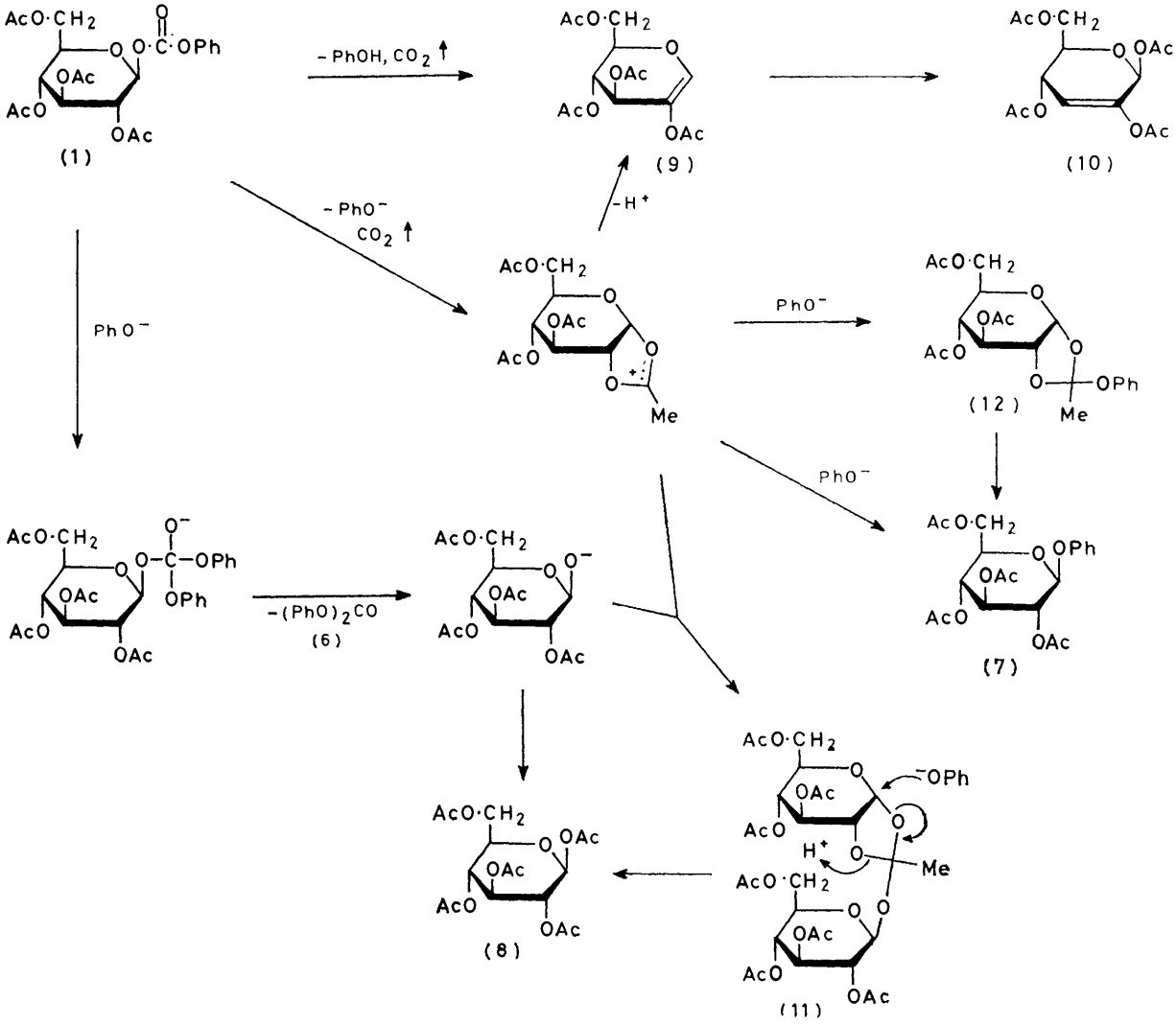
Pyrolyses of 2,3,4,6-tetra-*O*-acetyl-1-*O*-phenoxycarbonyl-β-D-glucopyranose (1) at 160—165 °C [a]

Reaction period (h)	Yields (%) (6)	(7)	(8)	(9) + (10) [b]	(11)
2	7	27	9	7 (4 : 3)	8
3	11	46	17	8 (1 : 1)	
4 [c]	3	36	13	18 (7 : 1)	7

[a] All performed by use of 5 mmol (2.34 g) of (1). [b] The ratios in parentheses were calculated by n.m.r. integration. [c] Performed *in vacuo*.

[1] Part 10, Y. Ishido, H. Tsutsumi, and S. Inaba, *J.C.S. Perkin I*, 1977, 521.
[2] S. Inaba, M. Yamada, T. Yoshino, and Y. Ishido, *J. Amer. Chem. Soc.*, 1973, **95**, 2062.
[3] (*a*) B. Helferich and R. Gootz, *Ber.*, 1929, **62**, 2788; (*b*) B. Helferich and E. Schmitz-Hillebrecht, *ibid.*, 1933, **66**, 378, *etc.*
[4] (*a*) A. Einhorn and L. Rothlauf, *Annalen*, 1911, **382**, 237; (*b*) K. Tsou, *J. Amer. Chem. Soc.*, 1954, **76**, 6108, *etc.*

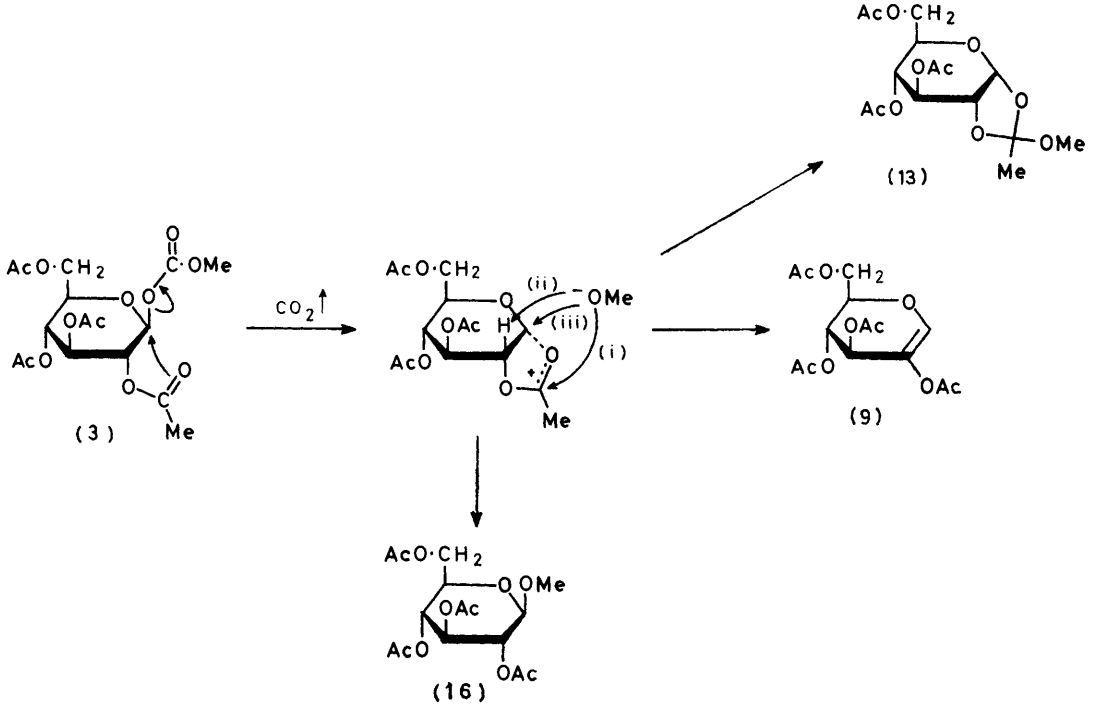
Pyrolysis of the carbonate (1) at 160—165 °C for 2, 3, or 4 h (*in vacuo*) gave diphenyl carbonate (6), phenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (7), 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose (8), 2,3,4,6-tetra-*O*-acetyl-2-hydroxy-D-glucal (9), 1,2,4,6-tetra-*O*-acetyl-3-deoxy-β-D-*erythro*-hex-2-enopyranose (10), and 3,5,6-tri-*O*-acetyl-α-D-glucopyranose 1,2-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl orthoacetate) (11) in the yields as shown in Table 1. At least 3 h was needed for completion of the reaction; the orthoester (11) was not obtained in this case but was isolated from reactions performed for 2 and 4 h (*in vacuo*). The reaction mechanism shown in Scheme 1 is suggested. Compound (7) is formed by the nucleophilic attack of phenoxide ion on C-1 of the 1,2-dioxolanylium ion formed from (1) by loss of phenoxide ion and carbon dioxide either directly or *via* the 1,2-(phenyl orthoacetate) (12). Nucleophilic attack of the phenoxide ion on the carbonyl group of the carbonate function of (1) leads, with loss of diphenyl carbonate (6), to the glucopyranosyloxide ion, which may afford (8) *via* (11) or abstract one acetyl group from another sugar derivative to give (8). The pathway from (1) to (8) *via* (11) acquires some support from the reaction of 3,4,6-tri-*O*-acetyl-α-D-glucopyranose 1,2-(1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranos-6-yl orthoacetate) with phenol (3 mol. equiv.), giving compounds (7) (42% yield) and (8) (23% yield), together with two products which behave in t.l.c. as if they were hydroxy-derivatives such as 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranose; because of difficulty in their chromatographic separation, they were isolated as (7) and (8) after acetylation. The monohydroxy-compound isolated as (7) is considered to be phenyl 3,4,6-tri-*O*-acetyl-β-D-glucopyranoside, which should be formed in the course of the reaction from (11) according to the mechanism shown in Scheme 1. We must emphasize that this reaction is not as simple as we expected, perhaps involving other pathways for the formation of (8) as judged from t.l.c., which indicated the formation of several unidentified products. The elimination of phenol and carbon dioxide gas from (1) may initially give the glucal (9), which may then be isomerized to (10); the isomerization mechanism may be the same as has been



SCHEME 1

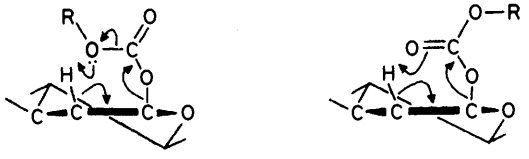
proposed by Ferrier *et al.*[5] for that occurring in nitrobenzene under reflux.

The pyrolysis of the methyl carbonate (3), on the other hand, was successfully induced by heating at *ca.* 190 °C



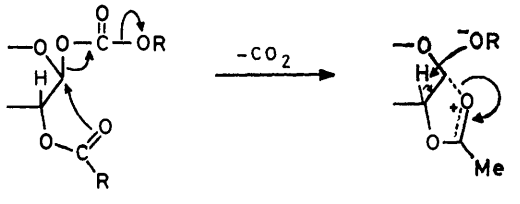
SCHEME 2

to give a mixture of the corresponding elimination products (9) and (10) (33% yield) together with the



SCHEME 3

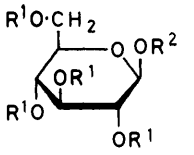
penta-acetate (8) (23% yield) and 3,4,6-tri-*O*-acetyl-α-D-glucopyranose 1,2-(methyl orthoacetate) (13) (23% yield). A trace of residual syrup gave a ^{1}H n.m.r. spectrum with



SCHEME 4

a singlet signal at δ 3.4, characteristic of *O*-methyl protons and suggesting the formation of methyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (16). Probable pathways for the formation of compounds (9), (13), and (16), shown in Scheme 2, involve a 1,2-dioxolanylium ion as intermediate; nucleophilic attack of the methoxide ion in the modes (i), (ii), and (iii) may give compounds (13), (9), and (16), respectively. The formation of (8) and (10) can be interpreted as in Scheme 1. The difference in pyrolytic susceptibility between (1) and (3) can be explained either by a difference in nucleophilicity of the carbonyl oxygen as for Chugaev-type elimination reactions, or in that of the resulting phenoxide or methoxide ion, as illustrated in Schemes 3 and 4, respectively.

The phenyl carbonate tetrabenzoate (5) on pyrolysis at *ca.* 190 °C gave phenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (14) in 80% yield by direct crystallization of the resulting mixture from ethanol. The



(14) R^1 = Bz, R^2 = Ph
(15) R^1 = Ac, R^2 = *p*-ClC$_6$H$_4$
(16) R^1 = Ac, R^2 = Me

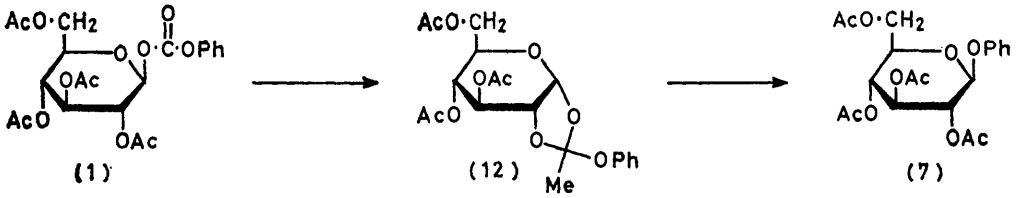
residual syrup was almost entirely composed of (14), as indicated by t.l.c. (19 : 1 benzene–ethyl acetate), which also showed a small spot corresponding to 2,3,4,6-tetra-*O*-benzoyl-D-glucopyranose. The preponderent formation of (14) is likely to arise from chemical or stereochemical instability of the postulated orthobenzoate intermediate.

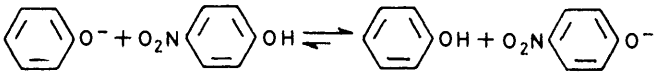
The carbonates (2) and (4) were not susceptible to pyrolysis up to 200 °C; these results suggest that for pyrolysis to occur the 1-*O*-phenoxy- or -methoxy-carbonyl group should exist in a *trans* relation with the 2-*O*-acetyl group.

[5] R. J. Ferrier, N. Prasad, and G. H. Sankey, *J. Chem. Soc.* (*C*), 1968, 974.

Glucosylation of Phenols.—The foregoing results demonstrate that sugar 1-carbonate derivatives surpass the corresponding 1-acetates in reactivity; * we therefore subsequently investigated the glucosylation of a variety of phenols by the sugar carbonates under autocatalytic conditions. The results of the reaction of the carbonate (1) with 3 mol. equiv. of phenol are summarized in Table 2. Since carbon dioxide evolution was observed to begin at *ca.* 75 °C, the reaction was first performed at 85—90 °C, giving a 65% yield of the orthoester (12); this was successfully isolated by use of a column of silica gel previously washed with dilute aqueous ammonia, then distilled water, and dried azeotropically with benzene. Reactions performed at 125—130 °C for 1 h, and at 170 °C for 10 min gave compounds (7) and (12) in 30 and 70% and 35 and 60% yields, respectively. Extension of reaction period in the latter case from 10 min to 1 h resulted in the isolation of (7) in 90% yield. Therefore, transformation of (12) into (7) was attempted by heating the former in phenol at 170 °C for 1 h; (7) was isolated in 71% yield as expected. Thus the reaction proceeds *via* (12) as intermediate, drastic conditions afford glucosylation and mild conditions the phenyl orthoester, and problems in glucosylation may be overcome by use of the orthoester (12).† All subsequent glucosylations of phenols were performed with 3 mol. equiv. of the phenol to minimize the formation of the unsubstituted phenyl glucoside (7) (6% yield) which was obtained together with *p*-nitrophenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (87% yield) in an equimolar fusion of (1) with *p*-nitrophenol at 110 °C for 1 h; this is accepted in view of the equilibrium between *p*-nitrophenoxide and phenoxide shown in Scheme 5. The conditions used and the results are summarized in Table 3. All the nitrophenols gave the corresponding β-D-glucopyranoside acetates in good yields. The possibility of obtaining the corresponding nitrophenyl orthoacetates in these reactions was examined by studying the reaction with *p*-nitrophenol at 70—80 °C. However, the orthoester was not detected by ^{1}H n.m.r. spectroscopy; this may reflect the instability of the nitrophenyl orthoacetates under these conditions. Reactions with *o*- and *p*-chlorophenol also afforded the corresponding β-D-glucopyranoside acetates in moderate yields; the formation of the corresponding chlorophenyl orthoacetates was not detected.

Glucosylation reactions by use of the methyl carbonate (3) were performed in the expectation that the yields of the phenyl glucosides would be improved, since methanol should readily be expelled from the system on account of its low b.p. and thus the formation of the methyl glycoside corresponding to (7) could be avoided. The reaction of (3) with phenol at 130 °C, however, gave the phenyl orthoacetate (12) (19% yield), the methyl orthoacetate (13) (42% yield), and the phenyl glucoside (7) (8% yield), unexpectedly. Moreover, a reaction conducted at 140—150 °C gave no phenyl orthoacetate (12), but compounds (13) (10% yield), (7) (26% yield), and (8) (26% yield). These results can be explained in terms of the phenyl





SCHEME 5

TABLE 2

Glucosylation of phenol with 2,3,4,6-tetra-*O*-acetyl-1-*O*-phenoxycarbonyl-β-D-glucopyranose (1) [a]

Conditions		Yields (%)	
Temp. (°C)	Period (min)	(12) [b]	(7)
85—90	240	65	
125—130	60	(70)	30
170	10	(65)	35
170	60		90 [c]

[a] All reactions performed by use of 3.3 mmol of (1) and 10 mmol of phenol. [b] Yields in parentheses calculated in terms of the total weight of the products and their n.m.r. spectra. [c] In this case, 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose (8) was isolated in 3% yield.

TABLE 3

Glucosylation of a series of phenols with 2,3,4,6-tetra-*O*-acetyl-1-*O*-phenoxycarbonyl-β-D-glucopyranose (1) [a]

	Conditions		Yield of aryl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside
Phenol	Temp. (°C)	Period (min)	(%)
2,4-Dinitro-	120—125	30	86 [b]
o-Nitro-	135—140	60	95 [b]
m-Nitro-	135—140	45	87 [b]
p-Nitro-	90—95	60	91 [c]
o-Chloro-	130—135	40	65 [d]
p-Chloro-	120—135	50	41 [b]

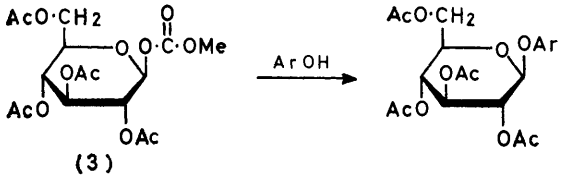
[a] All reactions were performed by use of 3.3 mmol of (1) and 10 mmol of the phenol. [b] Isolated by direct crystallization of the resultant syrup from ethanol. [c] Chromatography of the resulting syrup afforded 4% yield of (7). [d] Chromatography of the resulting syrup also afforded 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose (8) (11%) and (7) (8%).

* Decomposition of 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose could not be induced by heating up to 200 °C in a capillary tube; the acetate has been shown to condense with *p*-nitrophenol autocatalytically on heating at 180—185 °C (*cf.* ref. 6).

† An investigation of the utilization of this species is in progress.

[6] Y. Ishido, T. Matsuba, A. Hosono, K. Fujii, H. Tanaka, K. Iwabuchi, S. Isome, A. Maruyama, Y. Kikuchi, and T. Sato, *Bull. Chem. Soc. Japan*, 1965, **38**, 2019

orthoacetate (12) as intermediate; its absence in the reaction at 140—150 °C may reflect its instability with respect to (13) under these conditions. The mechanism



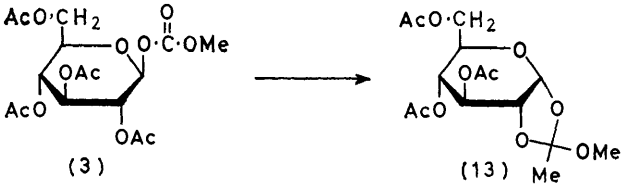
of this reaction can be deduced to be the same as that of the phenyl carbonate (1) with phenols from the foregoing facts as well as from the isolation of *p*-methoxyphenyl methyl carbonate in the reaction with *p*-methoxyphenol which indicates the formation of (11) as a precursor of (8). The conditions and results are summarized in Table 4, together with those for other phenols. The

TABLE 4

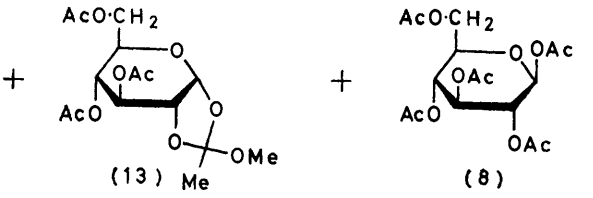
Glucosylation of phenols with 2,3,4,6-tetra-*O*-acetyl-1-*O*-methoxycarbonyl-β-D-glucopyranose (3) [a]

	Conditions		Yields (%)		
Phenol	Temp. (°C)	Period (min)	Aryl glucoside acetate	(13)	(8)
o-Chloro-	140—150	120	60 [b]		
p-Chloro-	150	80	44		25 [c]
H-	145—150	60	26	10	26
p-Methyl-	155—160	40	26	7	24
p-Methoxy-	155—160	60	23	21	10 [d]

[a] All reactions performed by use of 5 mmol of (3) and 25 mmol of the phenol. [b] Obtained by direct crystallization of the resulting syrup from ethanol. [c] Reaction continued until the g.l.c. peak of the orthoester (13) had disappeared. [d] *p*-Methoxyphenyl methyl carbonate was isolated and identified.

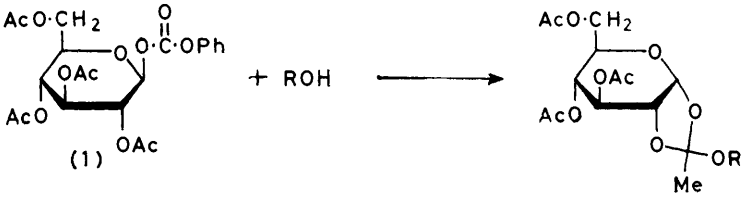


reactions with phenol, *p*-cresol, and *p*-methoxyphenol were confirmed to give compounds (8) and (13) as well as the corresponding β-D-glucopyranoside acetates, and that with *p*-chlorophenol gave (8) as well as *p*-chlorophenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (15). The reactions with nitrophenols, on the other hand, gave neither (8) nor (13), but methyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (16) as well as the corresponding nitrophenyl glucoside acetates in the yields shown in Table 5. Subsequently, the reactions of the methyl carbonate (3) with *p*-chlorophenol and with *m*-nitrophenol were examined by g.l.c. and ^{1}H n.m.r. The former was demonstrated by g.l.c. to proceed by initial formation of the methyl



orthoacetate (13), with the glycoside (15) appearing later. When starting material (3) had disappeared (after *ca.* 20 min), the amount of penta-acetate (8) was still small, and prolongation of the reaction gave a final mixture composed only of (8) and (15), as shown in the Figure. The behaviour of the *C*-methyl ^{1}H n.m.r. signal of (13) (δ 1.71) paralleled that observed in the g.l.c. experiment. If we postulate the formation of the orthoester (11) in this reaction, the increase in the amount of the penta-acetate (8) with time can be explained in parallel with the loss of (13) and formation of (15). Examination of the reaction with *m*-nitrophenol at 90 °C, on the other hand, showed the involvement of (13) as intermediate and gave a final mixture (after 5 h) composed of (3), (13), (16), and *m*-nitrophenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (17). The ^{1}H n.m.r. spectrum of the mixture showed three *O*-methyl signals [(3) (δ 3.83), (13) (δ 3.28), and (16) (δ 3.50)] in addition to the *C*-methyl signal of (13) (δ 1.71).

The differences amongst these reactions are likely to arise from differences in acidity and nucleophilicity of the phenols. Less acidic phenols may preferentially attack the carbonyl carbon of the methoxycarbonyl group of (3) to give the corresponding aryl methyl carbonates and 2,3,4,6-tetra-*O*-acetyl-D-glucopyranosyl-oxide ion, which could give (8) *via* (11). More acidic phenols may preferentially protonate the carbonyl oxygen of the methoxycarbonyl group to give the corresponding aryl orthoacetates, which may readily be transformed into the more stable (13). The transformation of (13) into (16) resembles the transformation [7] of 3,4,6-tri-



[7] R. U. Lemieux and A. R. Morgan, *Canad. J. Chem.*, 1965, **43**, 2199.

O-benzyl-β-D-mannopyranose 1,2-(methyl orthoacetate) into methyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (82% yield) and methyl 3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (7% yield) by toluene-*p*-sulphonic acid in anhydrous methylene chloride at 47 °C.

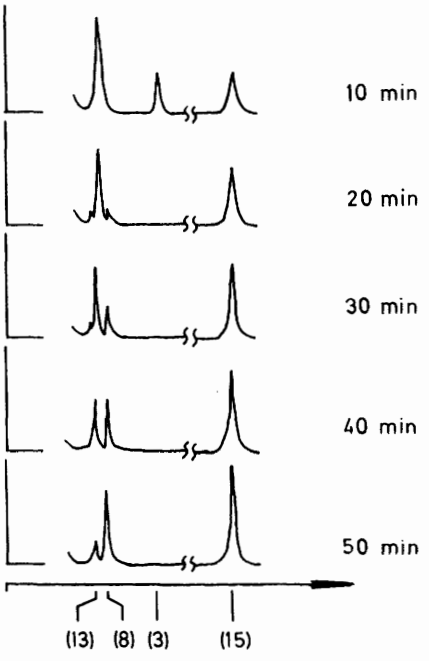
TABLE 5

Glucosylation of nitrophenols with 2,3,4,6-tetra-*O*-acetyl-1-*O*-methoxycarbonyl-β-D-glucopyranose (3) [a]

	Conditions		Yields (%)	
Phenol	Temp. (°C)	Period (h)	Aryl glucoside acetate	(16)
p-Nitro-	90—95	4	15	59
	120	1	61	38
m-Nitro-	100—105	5	16	61
	160	0.5	83	11
o-Nitro-	190—195	1.5	84 [b]	
2,4-Dinitro-	110—120	2	93 [b]	

[a] All reactions performed by use of 3.3 mmol of (3) and 10 mmol of the phenol. In all reactions, the formation of the orthoester (13) was confirmed by g.l.c. and n.m.r. spectroscopy. [b] Obtained by direct crystallization of the resulting syrup from ethanol.

In contrast with the reactions of the carbonate tetra-acetates (1) and (3), the reactions of the tetrabenzoate (5) with phenols were expected to proceed without formation of the corresponding aryl orthobenzoates which are equivalent to (12), since pyrolysis of (5) afforded



G.l.c. traces of the mixture from the reaction of the carbonate (3) with *p*-chlorophenol

no detectable amounts of products other than (14) and 2,3,4,6-tetra-*O*-benzoyl-D-glucopyranose (t.l.c.). Consequently, its reactions with *p*-nitrophenol, phenol, and *p*-methoxyphenol were performed under autocatalytic conditions. The results and conditions are summarized in Table 6. In every case, the reaction gave only the corresponding aryl glucopyranoside, as expected. The reaction with *p*-methoxyphenol also gave the phenyl glucopyranoside of (14), as expected from the equilibrium between phenol and *p*-methoxyphenoxide.

The reactions of the carbonate (1) with alcohols were investigated in view of the reactivity of the less acidic phenols in the previous reactions. Heating (1) in methanol or in cyclohexanol under reflux gave the corresponding 3,4,6-tri-*O*-acetyl-α-D-glucopyranose 1,2-(alkyl orthoacetates) in 69 and 74% yields, respectively. The conditions and results are summarized in Table 7. An apparent temperature dependence of these reactions was observed. Moreover, the latter reaction also gave the penta-acetate (8) (10% yield). The mechanism of these reactions may be the same as discussed for the reactions with phenols. Sugar 1-carbonates may thus be applicable in coupling reactions with sugar derivatives bearing a free hydroxy-group for the synthesis of intermonosaccharide orthoester derivatives.[8]

TABLE 6

Reactions of 2,3,4,6-tetra-*O*-benzoyl-1-*O*-phenoxycarbonyl-β-D-glucopyranose (5) with phenols [a]

	Conditions		Yield of aryl
Phenol	Temp. (°C)	Period (h)	β-D-glucopyranoside benzoate (%)
p-Nitro-	130	1	78
H-	130	2	82
p-Methoxy-	130	2	57 [b]

[a] All reactions performed by use of 2 mmol of (5) and 6 mmol of the phenol. [b] This reaction afforded (14) (17%) as a by-product.

TABLE 7

Reactions of 2,3,4,6-tetra-*O*-acetyl-1-*O*-phenoxycarbonyl-β-D-glucopyranose (1) with alcohols [a]

	Conditions		Yields (%)		Recovery of
Alcohols	Temp. (°C) [b]	Period (h)	Orthoacetate	(8)	(1) (%)
Methyl	65	34	69		17
Cyclohexyl	161	1	74	10	

[a] Both reactions performed by use of (1) (2 mmol) and the alcohol (10 ml). [b] Both were performed under reflux in the alcohols.

In conclusion, the autocatalytic glycosylation of phenols by use of sugar 1-carbonates such as (1) has thus been established as easy to perform; and is advantageous for the coupling reactions with *o*-chlorophenol and *o*-nitrophenol, which have not been achieved previously;[6,9] such reactions have only been brought about by the use of polyacylglycosyl halides rather than fully acetylated sugars.[9] Moreover, the reaction described here has been deduced to proceed *via* a 1,2-dioxolanylium ion intermediate, which should effectively be converted into the corresponding glycosyl compound under the conditions used. Sugar 1-carbonates such as (1) are reactive enough with ordinary alcohols to give the corresponding 1,2-(alkyl orthoacetates) in good yields.

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EXPERIMENTAL

Solvents were evaporated off *in vacuo*. T.l.c. was performed on Wako-gel B-5F and DC-Alufolien Kieselgel 60 F254 (Merck), and column chromatography on Wako-gel C-300. G.l.c. was performed with a Hitachi K-53 instrument [column of 10% SE-30 on Chromosorb W(60—80 mesh) with nitrogen at 1.5 atm as carrier gas; oven temperature, 200 °C; injection temperature 300 °C]. I.r. spectra were taken with a Hitachi 215 or 218 spectrometer for potassium bromide pellets. ^{1}H N.m.r. spectra were recorded with a Varian T-60 instrument for solutions in deuteriochloroform (tetramethylsilane as internal standard). Specific rotation values were determined with a Hitachi PO-B polarimeter.

2,3,4,6-*Tetra*-O-*acetyl*-1-O-*phenoxycarbonyl*-β-D-*glucopyranose* (1).—To a solution of 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranose [10] (13.9 g, 40 mmol) in pyridine (6 ml, 70 mmol) and chloroform (20 ml) cooled in ice, phenyl chloroformate (7.1 g, 45 mmol) was added dropwise. The resulting mixture was then kept at room temperature overnight, then successively washed with aqueous M-sodium hydroxide, water, M-hydrochloric acid, saturated aqueous sodium hydrogen carbonate, and water, dried ($MgSO_4$), and evaporated. Recrystallization of the residue gave the *carbonate* (1) (15.3 g, 82%), m.p. 114—115 °C (from diethyl ether), $[\alpha]_D^{22}$ −11° (*c* 1.0 in $CHCl_3$) (Found: C, 53.8; H, 5.25. $C_{21}H_{24}O_{12}$ requires C, 53.85; H, 5.15%), δ 5.73 (1 H, d, $J_{1,2}$ *ca.* 7 Hz, H-1), $\nu_{C=O}$ 1 779 (acyclic carbonate), 1 750, and 1 730 cm^{-1} (acetate).

2,3,4,6-*Tetra*-O-*acetyl*-1-O-*phenoxycarbonyl*-α-D-*glucopyranose* (2).—The glucose tetra-acetate [10] (34.8 g, 100 mmol) mentioned above was stirred in pyridine (15 ml, 175 mmol) and chloroform (50 ml) overnight, after which phenyl chloroformate (17.8 g, 110 mmol) was added with cooling in ice. The resulting mixture was further stirred overnight, and treated as above to give a syrup, which gradually crystallized at 0 °C. Recrystallization gave the *carbonate* (2) (22 g, 47%), m.p. 81—82 °C (from diethyl ether), $[\alpha]_D^{22}$ +88° (*c* 1.0 in $CHCl_3$) (Found: C, 53.85; H, 5.3%), δ 6.24 (1 H, d, $J_{1,2}$ 3.0 Hz, H-1), $\nu_{C=O}$ 1 768 (acyclic carbonate), 1 750, and 1 740 cm^{-1} (acetate).

2,3,4,6-*Tetra*-O-*acetyl*-1-O-*methoxycarbonyl*-β-D-*glucopyranose* (3).—The same glucose tetra-acetate [10] (69.6 g, 200 mmol) was treated as in the first experiment with methyl chloroformate (16 ml, 220 mmol) in pyridine (18 ml, 220 mmol) and chloroform (200 ml) and the product was worked up as before to give crystals. Recrystallization gave the *carbonate* (3) (67 g, 83%), m.p. 120 °C (from diethyl ether), $[\alpha]_D^{22}$ −8° (*c* 1 in $CHCl_3$) (Found: C, 47.2; H, 5.25. $C_{16}H_{22}O_{12}$ requires C, 47.3; H, 5.45%), δ 5.60 (1 H, d, $J_{1,2}$ *ca.* 8 Hz, H-1) and 3.83 (3 H, s, O-CH_3), $\nu_{C=O}$ 1 770 (acyclic carbonate), 1 750, and 1 740 cm^{-1} (acetate).

2,3,4,6-*Tetra*-O-*acetyl*-1-O-*methoxycarbonyl*-α-D-*glucopyranose* (4).—The glucose tetra-acetate [10] (7.0 g, 20 mmol) was treated as in the second experiment with methyl chloroformate (1.6 ml, 22 mmol) to give the *carbonate* (4) (3.4 g, 43%), m.p. 77.5—78.5 °C (from diethyl ether), $[\alpha]_D^{22}$ +83° (*c* 1.0 in $CHCl_3$) (Found: C, 47.55; H, 5.5%), δ 6.18 (1 H, d, $J_{1,2}$ 2.8 Hz, H-1) and 3.85 (3 H, s, *O*-CH_3), $\nu_{C=O}$ 1 770 (acyclic carbonate), 1 755, and 1 740 cm^{-1} (acetate).

2,3,4,6-*Tetra*-O-*benzoyl*-1-O-*phenoxycarbonyl*-β-D-*glucopyranose* (5).—2,3,4,6-Tetra-*O*-benzoyl-α-D-glucopyranosyl bromide [11] (22.2 g, 30 mmol) was treated with silver carbonate (8.2 g, 30 mmol) in water (0.4 ml) and acetone (25 ml) with vigorous stirring at room temperature for 30 min, after which the mixture was heated on a steam-bath (50—60 °C) for 5 min and the insoluble mass was filtered off (glass filter). Evaporation of the filtrate gave, as a syrup, 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranose (17 g, quantitative), which was cooled in ice and treated with phenyl chloroformate (7.2 g, 50 mmol) in pyridine (6.6 ml, 65 mmol) and chloroform (75 ml) as above. The resulting mixture was further stirred at room temperature overnight; treatment as above gave a syrup, whose solution in a small volume of chloroform on addition of diethyl ether gave crystals. Recrystallization gave the *carbonate* (5) (11 g, 51%), m.p. 185—186 °C, $[\alpha]_D^{22}$ +42° (*c* 1.0 in $CHCl_3$) (Found: C, 68.4; H, 4.6. $C_{41}H_{32}O_{12}$ requires C, 68.7; H, 4.5%), δ 6.12 (1 H, d, $J_{1,2}$ 6.8 Hz, H-1), $\nu_{C=O}$ 1 774 (acyclic carbonate), 1 742, and 1 728 cm^{-1} (benzoate).

The mother liquor on evaporation gave a small amount of the α-*anomer*, m.p. 174.5—175.5 °C (from ethanol), $[\alpha]_D^{22}$ +81° (*c* 1.0 in $CHCl_3$) (Found: C, 69.0; H, 4.4%), δ 6.57 (1 H, d, $J_{1,2}$ 3.8 Hz, H-1), $\nu_{C=O}$ 1 769 (acyclic carbonate), 1 736, and 1 720 cm^{-1} (benzoate).

Pyrolysis of the Carbonate (1).—(*a*) On heating the carbonate (1) (2.34 g, 5.0 mmol) in an oil-bath, it melted at *ca.* 114 °C, and began to evolve carbon dioxide at *ca.* 160 °C; evolution had ceased after 3 h. The mixture was dissolved in chloroform (50 ml), and the solution successively washed with aqueous M-sodium hydroxide and water, dried ($MgSO_4$), and evaporated. Chromatography of the residual syrup (2.22 g) on a silica gel column (99 : 1 chloroform–ethyl acetate) gave diphenyl carbonate (160 mg, 11%) [i.r. spectrum identical with that of a commercial sample (Aldrich), m.p. 78—80.5 °C]; the phenyl glucoside (7) (975 mg, 46%), m.p. 125—126 °C (from ethanol), $[\alpha]_D^{22}$ −20° (*c* 1.0 in $CHCl_3$) {lit.,[3] m.p. 124—125 °C, $[\alpha]_D$ −22° (in $CHCl_3$)}; 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose (8) (340 mg, 17%), m.p. 129.5—130 °C (from ethanol), $[\alpha]_D^{22}$ +1° (*c* 1.0 in $CHCl_3$ [lit.,[12] m.p. 132 °C (corr.)]; and an equimolar mixture of 2,3,4,6-tetra-*O*-acetyl-2-hydroxy-D-glucal (9) and 1,2,4,6-tetra-*O*-acetyl-3-deoxy-β-D-*erythro*-hex-2-enopyranose (10) (138 mg, 8%), re-chromatography of which afforded pure samples. The ^{1}H n.m.r. spectra of (9) and (10) [m.p. 82—83 °C (from ethanol), $[\alpha]_D^{22}$ +150° (*c* 1.0 in $CHCl_3$)] {lit.,[5] m.p. 81—83 °C, $[\alpha]_D$ +156° (in $CHCl_3$)} were identical with those reported.[5,13] Quantitative determination was performed by integration of the anomeric proton signals [δ 6.67(s) for (9) and 6.31(s) for (10)].

(*b*) Pyrolysis of the carbonate (1) (5 mmol) at 160—165 °C for 2 h gave 3,4,6-*tri*-O-*acetyl*-α-D-*glucopyranose* 1,2-(2,3,4,6-*tetra*-O-*acetyl*-β-D-*glucopyranosyl orthoacetate*) (11) (135 mg, 8%), m.p. 122—124 °C (from ethanol), $[\alpha]_D^{22}$ +79° (*c* 1.0 in $CHCl_3$) (Found: C, 49.6; H, 5.6. $C_{28}H_{38}O_{19}$ requires C, 49.55; H, 5.65%), δ 1.75 (3 H, s, *C*-CH_3), 2.1 (21 H, seven OAc), 5.58 (1 H, d, $J_{1',2'}$ 9.7 Hz, H-1′), and 5.70 (1 H, d, $J_{1,2}$ 5.5 Hz, H-1), in addition to compounds (6) (7%), (7) (27%), and (8) (9%), and a 4 : 3 mixture of (9) and (10) (7%).

(*c*) Pyrolysis of (1) at 160—165 °C *in vacuo* for 4 h afforded the same products as above in the yields shown in Table 1.

Pyrolysis of the Carbonate (3).—Similar pyrolysis of the

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carbonate (3) at 190 °C for 4 h gave compound (8) (420 mg, 23%), an equimolar mixture of (9) and (10) (540 mg, 33%), and 3,4,6-tri-*O*-acetyl-α-D-glucopyranose 1,2-(methyl orthoacetate) (13) (204 mg, 23%), a syrup (Found: C, 49.6; H, 6.1. Calc. for $C_{15}H_{22}O_{10}$: C, 49.7; H, 6.1%), n.m.r. spectrum identical with that of an authentic specimen.[6]

Reaction of 3,4,6-*Tri*-O-*acetyl*-α-D-*glucopyranose* 1,2-(1,2,3,4-*Tetra*-O-*acetyl*-β-D-*glucopyranos*-6-*yl orthoacetate*) *with Phenol*.—The orthoacetate * (679 mg, 1 mmol) was heated with phenol (280 mg, 3 mmol) at 150—160 °C for 5 h. Column chromatography of the resulting mixture (benzene–acetone, 97 : 3 to 9 : 1) gave compound (7) (178 mg, 0.42 mmol), 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose (8) (89 mg, 0.23 mmol), and hydroxy-compounds [R_F 0.30 and 0.25 after two developments (19 : 1 benzene–methanol) in t.l.c.; *cf.* R_F 0.75 for (7) and 0.70 for (8)] as an inseparable mixture. Chromatographic separation of the mixture resulting from acetylation of the latter mixture with acetic anhydride–pyridine gave (7) (34 mg, 0.80 mmol) and (8) (220 mg, 0.56 mmol).

Pyrolysis of the Carbonate (5).—Pyrolysis of the carbonate (5) (1.43 g, 2 mmol) at 180—190 °C for 1 h, followed by direct crystallization of the resulting mixture from hot ethanol, gave *phenyl* 2,3,4,6-*tetra*-O-*benzoyl*-β-D-*glucopyranoside* (14); recrystallization afforded a specimen (1.06 g, 80%), m.p. 115—117 °C (from ethanol), $[\alpha]_D^{22}$ +27.7° (*c* 1.0 in $CHCl_3$) (Found: C, 71.4; H, 4.65. $C_{40}H_{32}O_{10}$ requires C, 71.4; H, 4.8%).

3,4,6-*Tri*-O-*acetyl*-α-D-*glucopyranose* 1,2-(*Phenyl orthoacetate*) (12).—A stirred mixture of the carbonate (1) (1.56 g, 3.3 mmol) and phenol (0.96 g, 10 mmol) was heated at 85—90 °C for 4 h, then dissolved in chloroform (50 ml); the solution was successively washed with aqueous M-sodium hydroxide and water, dried (Na_2SO_4), and evaporated. The resulting syrup (1.5 g) was chromatographed (19 : 1, benzene–ethyl acetate) on a silica gel column previously subjected to a neutralization procedure,† to give the *orthoester* (12) (0.85 g, 65%), a syrup, $[\alpha]_D^{22}$ +36.5° (*c* 1.0 in $CHCl_3$) (Found: C, 56.55; H, 5.6. $C_{20}H_{24}O_{10}$ requires C, 56.6; H, 5.7%), δ 1.80 and 1.60 (3 H, two s, *C*-CH_3), 2.10 (9 H, s, three OAc), 3.8—4.4 (4 H, m, H-2 and -5 and 6-H_2), 4.93 (1 H, dd, $J_{4,5}$ 10 Hz, H-4), 5.23 (1 H, d, $J_{2,3}$ 2.3 Hz, H-3), 5.72 (1 H, d, $J_{1,2}$ 5 Hz, H-1), and *ca.* 7.2br (5 H, s, Ph).

Phenyl 2,3,4,6-*Tetra*-O-*acetyl*-β-D-*glucopyranoside* (7).—(*a*) From the orthoester (12). The syrup (12) was heated with phenol (0.96 g, 10 mmol) at 170 °C for 1 h, and the resulting mixture was washed as above after dissolving in chloroform (50 ml). Evaporation of the dried ($MgSO_4$) solution afforded a syrup (1.5 g); crystallization and recrystallization gave the product (7) (980 mg, 71%).

(*b*) Treatment of the carbonate (1) (1.56 g, 3.3 mmol) with phenol (0.96 g, 10 mmol) at 170 °C for 1 h, followed by similar washing, drying, and chromatography afforded compounds (8) (40 mg, 3.4%) and (7) (1.27 g, 90%).

Reaction of the Carbonate (1) *with a Series of Phenols*.—All the reactions of the carbonate (1) (1.56 g, 3.3 mmol) with phenol derivatives (10 mmol) were conducted under the conditions shown in Table 3, which also summarizes the results. 2,4-Dinitrophenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside had m.p. 176—177 °C (from ethanol), $[\alpha]_D^{22}$ +30° (*c* 1.0 in $CHCl_3$) {lit.,[14a] m.p. 173—177 °C, $[\alpha]_D$ +34.5° (*c* 4 in $CHCl_3$); lit.,[14b] m.p. 176—177°C, $[\alpha]_D^{20}$ +34.9° (*c* 1.09 in $CHCl_3$)}. *o*-Nitrophenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside had m.p. 157—158 °C (from ethanol), $[\alpha]_D^{22}$ +37° (*c* 1.0 in $CHCl_3$) {lit.,[14b] m.p. 160.5—161.5 °C, $[\alpha]_D^{20}$ +43° (*c* 1.2 in $CHCl_3$); lit.,[15] m.p. 150—152 °C, $[\alpha]_D^{20}$ +45° (*c* 2 in $CHCl_3$)}. *m*-Nitrophenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (17) had m.p. 138—139 °C (from ethanol), $[\alpha]_D^{22}$ −40° (*c* 1.0 in $CHCl_3$) {lit.,[14b] m.p. 136—137 °C, $[\alpha]_D^{20}$ −34.8° (*c* 0.5 in $CHCl_3$)}. *p*-Nitrophenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside had m.p. 175—177 °C (from ethanol), $[\alpha]_D^{22}$ −27° (*c* 1.0 in $CHCl_3$) {lit.,[16] m.p. 174—175 °C, $[\alpha]_D$ −20.17° (in $CHCl_3$)}. *o*-Chlorophenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside had m.p. 145—146 °C (from ethanol), $[\alpha]_D^{22}$ −34° (*c* 1.0 in $CHCl_3$) {lit.,[17] m.p. 141—143 °C, $[\alpha]_D$ −46.5° (in $CHCl_3$)}. *p*-Chlorophenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (15) had m.p. 123—124 °C (from ethanol), $[\alpha]_D^{22}$ −23° (*c* 1.0 in $CHCl_3$) {lit.,[18] m.p. 123—124 °C, $[\alpha]_D$ −20 °(*c* 2 in $CHCl_3$)}.

Reactions of the Carbonate (3) *with Chlorophenol, Phenol,* p-*Cresol, and* p-*Methoxyphenol*.—These reactions are exemplified by that of (3) (2.04 g, 5 mmol) with phenol (2.45 g, 25 mmol), which was conducted at 145—150 °C for 1 h; the resulting mixture was dissolved in chloroform (50 ml), and the solution was washed with aqueous M-sodium hydroxide solution, dried ($MgSO_4$), and evaporated to give a syrup. This was chromatographed to give compounds (7) (560 mg, 26%), (13) (185 mg, 10%), and (8) (470 mg, 26%). The results similarly obtained with other phenols are summarized in Table 4. *p*-Cresyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside had m.p. 113.5—114 °C (from ethanol), $[\alpha]_D^{22}$ −16° (*c* 0.75 in $CHCl_3$) (lit.,[19a] m.p. 116—118 °C; lit.,[19b] 119—120 °C) (Found: C, 57.35; H, 5.95. $C_{21}H_{26}O_{10}$ requires C, 57.55; H, 6.0%). *p*-Methoxyphenyl methyl carbonate was a colourless, transparent liquid, $\nu_{C=O}$ 1 560, ν_{aryl} 1 500, ν_{C-O-C} 1 262, 1 250, and 1 210 cm^{-1}, δ 3.60 (3 H, s, $ArOCH_3$), 3.75 (3 H, s, CO_2Me), and 6.80 (2 H, d) and 7.07 (2 H, d) (A_2B_2, *J* 9.6 Hz), isolated by chromatography and identical spectroscopically with a specimen prepared from *p*-methoxyphenol and methyl chloroformate–pyridine. *p*-Methoxyphenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside had m.p. 102.5—103.5 °C (from ethanol), $[\alpha]_D^{22}$ −16° (*c* 1.0 in $CHCl_3$) (lit.,[20] m.p. 102—104 °C, $[\alpha]_D$ −17°).

Reactions of the Carbonate (3) *with Mononitrophenols*.—The reactions are exemplified by that of (3) (1.36 g, 3.3 mmol) with *p*-nitrophenol (1.39 g, 10 mmol), conducted at 120 °C for 1 h; the resulting mixture was dissolved in hot ethanol and allowed to cool at room temperature to give *p*-nitrophenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (0.91 g). Chromatography of the syrup obtained by

* Prepared by fusion of (1) with 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranose at 160—170 °C for 90 min *in vacuo* (*cf.* ref. 7).

† Wako-gel C-300 was washed on the column with aqueous M-ammonia until the eluate showed an alkaline colour reaction, and then with distilled water until the eluate showed a weakly acidic colour reaction. Remaining moisture in the silica gel was azeotropically removed by heating in an excess of benzene under reflux with stirring, after which the silica gel was further dried.

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evaporation of the mother liquor gave additionally the glucoside (40 mg) and methyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (16) (0.46 g, 38%), m.p. 103—104 °C, n.m.r. spectrum identical with that of an authentic specimen [21] (m.p. 104 °C). The total yield of *p*-nitrophenyl glucoside acetate was up to 61%. A reaction conducted at 90—95 °C for 4 h gave the glucoside (15%) and methyl glucoside acetate (59%).

Reaction of the Carbonate (3) *with* 2,4-*Dinitrophenol*.—Treatment of (3) (3.3 mmol) with 2,4-dinitrophenol (1.84 g, 10 mmol) at 110—120 °C for 2 h, and dissolution of the resulting mixture in hot ethanol gave crystals, recrystallization of which afforded 2,4-dinitrophenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (1.58 g, 93%).

Monitoring the Reactions of the Carbonate (3) *with* p-*Chlorophenol and with* m-*Nitrophenol*.—Each fused reaction mixture was examined by g.l.c. and n.m.r. under the conditions described in the general method. The Figure shows gas–liquid chromatograms obtained from the *p*-chlorophenol reaction. Relative retention times with reference to (3) (1.00) are 0.91 for (13), 0.69 for (8), 7.1 for (15), and 12 for (17).

Reactions of the Carbonate (5) *with* p-*Nitrophenol, Phenol, and* p-*Methoxyphenol*.—These reactions are exemplified by the reaction of (5) (1.43 g, 2 mmol) with *p*-nitrophenol (830 mg, 6 mmol) at 130 °C for 1 h; the resulting mixture was dissolved in hot ethanol and the solution kept at room temperature to give p-*nitrophenyl* 2,3,4,6-*tetra*-O-*benzoyl*-β-D-*glucopyranoside* (1.12 g, 81%), m.p. 148—150 °C, $[\alpha]_D^{22}$ +18° (*c* 1.0 in $CHCl_3$) (Found: C, 67.35; H, 4.2; N, 1.85. $C_{40}H_{31}NO_{12}$ requires C, 66.95; H, 4.4; N, 1.95%). *Phenyl* 2,3,4,6-*tetra*-O-*benzoyl*-β-D-*glucopyranoside* had m.p. 115—117 °C, $[\alpha]_D^{22}$ +27.7° (*c* 1.0 in $CHCl_3$) (Found: C, 71.4; H, 4.65. $C_{40}H_{32}O_{10}$ requires C, 71.4; H, 4.8%). p-*Methoxyphenyl* 2,3,4,6-*tetra*-O-*benzoyl*-β-D-*glucopyranoside* had m.p. 170—171 °C, $[\alpha]_D^{22}$ +27.6° (*c* 1.0 in $CHCl_3$) (Found: C, 69.9; H, 4.95. $C_{41}H_{34}O_{11}$ requires C, 70.1; H, 4.9%). The results and conditions are summarized in Table 6. In the reaction with *p*-methoxyphenol, the resulting mixture was chromatographed to give phenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranoside (17%) in addition to the desired product.

Reactions of the Carbonate (1) *with Alcohols;* 3,4,6-*Tri*-O-*acetyl*-α-D-*glucopyranose* 1,2-(*Alkyl orthoacetates*).—The carbonate (1) (940 mg, 2 mmol) was heated in the anhydrous alcohol under reflux under the conditions summarized in Table 7, which also gives the results. 3,4,6-*Tri*-O-*acetyl*-α-D-*glucopyranose* 1,2-(*cyclohexyl orthoacetate*) had m.p. 82—83 °C (from ethanol), $[\alpha]_D^{22}$ +13° (*c* 0.6 in $CHCl_3$) (Found: C, 55.55; H, 7.05. $C_{20}H_{30}O_{10}$ requires C, 55.8; H, 7.05%); δ 1.73 (3 H, s, C-CH_3), 4.34 (1 H, dd, $J_{2,3}$ 3.0 Hz, H-2), 4.92 (1 H, dd, $J_{4,5}$ 9.1 Hz, H-4), 5.19 (1 H, t, $J_{3,4}$ 3.0 Hz, H-3), and 5.68 (1 H, d, $J_{1,2}$ 5.2 Hz, H-1), $\nu_{C=O}$ 1 750 and 1 735 cm^{-1}.

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