581. *The Reactivity of the O-Acylglycosyl Halides. Part III.* Steric Effects.*

By F. H. Newth and G. O. Phillips.

The reactivity of *O*-acylglycosyl 1-halides has been related to structure by a kinetic examination of selected compounds, all of which undergo unimolecular solvolysis. The difference between the methanolysis rate of 3 : 4 : 6-tri-*O*-acetyl-2-trichloroacetyl-β-D-glucosyl 1-chloride and 3 : 4 : 6-tri-*O*-acetyl-β-D-glucosyl 1-chloride is attributed to the steric effect of the 2-trichloroacetyl group. The effect of the acetyl group at positions 2 and 4, and the 6-acetoxymethyl group in tetra-*O*-acetyl-α-D-glucosyl 1-bromide has been assessed by examining the α-acetobromo-derivatives of mannose, galactose, and xylose. The methanolysis rate is directly proportional to the amount of " crowding " about $C_{(1)}$ as shown by accurate scale models.

It was shown in Part I (*J.*, 1953, 2896) that the solvolytic reactions of tetra-*O*-acetyl-α-D-glucosyl 1-bromide operate through the S_N1 mechanism, and in this paper several other *O*-acetylglycosyl 1-halides are shown to behave similarly. In the reactions of these compounds, the S_N1 mechanism is followed in preference to any other because of the strong electron-releasing capacity of the lactol ring oxygen atom (Part II). In S_N2 reactions the effects of steric factors have been evaluated by Dostrovsky, Hughes, and Ingold (*J.*, 1946, 173). Steric hindrance in the transition states of these reactions is unfavourable to the bimolecular reaction; it is very pronounced in the *neo*pentyl system where compressions of the order of 1·0 Å were observed. For unimolecular reactions, the effects of steric factors on reaction rates are not nearly so definite. According to Hughes and Ingold (Hughes, *Quart. Reviews*, 1951, **5**, 245) steric factors seem to have no marked effect on the unimolecular solvolysis rates of tertiary halides. Baddeley and Chadwick (*J.*, 1951, 368), however, have shown that the ionisation of an aralkyl halide is subject to steric hindrance, but, in the compounds they studied, pure steric effects were difficult to recognise because of superimposed polar effects. With cyclic structures also there is evidence to indicate that steric factors effect unimolecular solvolysis. Winstein and his co-workers (*J. Amer. Chem. Soc.*, 1948, **70**, 812) examined the acetolysis of *cis*- and *trans*-2-acetoxy*cyclo*hexyl toluene-*p*-sulphonates in which the rate-determining stage is the initial ionisation of the sulphonic ester, and found that the rate of acetolysis of the *trans*- is much greater than that of the *cis*-ester.

By varying the size and position of the groups in the *O*-acylglycosyl 1-halides, effects have been observed which can be attributed directly to steric factors without the danger of ambiguity due to superimposed polar factors. Such a structural investigation was carried out with two aims. First, to obtain quantitative information about the relative reactivity of the *O*-acylhexosyl 1-halides and, secondly, to observe the steric characteristics of the S_N1 mechanism. The importance of these steric factors in the reactivity of the *O*-acylglycosyl 1-halides was demonstrated by a comparison of 3 : 4 : 6-tri-*O*-acetyl-2-*O*-trichloroacetyl-β-D-glucosyl 1-chloride (I) and 3 : 4 : 6-tri-*O*-acetyl-β-D-glucosyl 1-chloride (II). Provided that both compounds react by the same mechanism, the difference in solvolysis rate can be due mainly to the decrease in steric hindrance at $C_{(1)}$ in the latter compound caused by the absence of the bulky trichloroacetyl group at $C_{(2)}$. The polar effect of the trichloroacetyl group would be damped considerably on passing through the saturated carbon atom $C_{(2)}$. The chloride (I) was first prepared by Brigl (*Z. physiol. Chem.*, 1921, **116**, 1) by the interaction of penta-*O*-acetyl glucose and phosphorus pentachloride, and Brigl found that selective hydrolysis of the trichloroacetyl group occurred with ammonia, to give (II). The reactions of both compounds with methanol were of the first order and, in the range investigated, no acid catalysis was observed. The rate constants obtained in various media are summarised in Table 1, and there was the same type of variation as with tetra-*O*-acetylglucosyl 1-bromide when the polarity of the medium

* Part II, preceding paper.

was altered. Furthermore, the rate of solvolysis of each compound in 60% aqueous acetone was unaltered by adding alkali, which establishes the reactions as unimolecular.

TABLE 1.—*The rate of solvolysis of* 3 : 4 : 6-*tri*-O-*acetyl*-2-O-*trichloroacetyl*-β-D-*glucosyl* 1-*chloride and* 3 : 4 : 6-*tri*-O-*acetyl*-β-D-*glucosyl* 1-*chloride in various media.*

Medium	Temp.	10^5k_1(sec.$^{-1}$)
Tri-*O*-acetyl-2-*O*-trichloroacetyl-β-D-glucosyl 1-chloride		
MeOH	21·2°	1·18
,,	27·4	2·48
,,	34·9	3·48
90% Aq. MeOH	27·4	6·74
80% ,,	27·4	11·79
90% MeOH–$COMe_2$	27·4	1·34
80% ,,	27·4	1·02
60% ,,	27·4	0·48
80% Aq. $COMe_2$	34·9	0·61
60% ,,	34·9	5·64
,, ,,	18	1·41 *
,, ,,	18	1·44 * †
3 : 4 : 6-Tri-*O*-acetyl-β-glucosyl 1-chloride		
MeOH	21·2°	66·6
,,	34·8	229
80% Aq. $COMe_2$	21·2	24·6
60% ,,	21·2	120
,, ,,	*ca.* 24	195 *
,, ,,	*ca.* 24	196 * †

* Measurements made simultaneously by the polarimetric method.
† [Alkali] = 0·025N.

The Arrhenius activation energy for the methanolysis of tri-*O*-acetyl-2-trichloroacetyl-β-D-glucosyl 1-chloride is 20·8 kcal., whereas that for 3 : 4 : 6-tri-*O*-acetyl-β-D-glucosyl 1-chloride is 16·3 kcal., a value deduced from measurements at two temperatures only and so subject to error. The lower reactivity of the 2-trichloroacetyl derivative is largely due to this increase in the activation energy of the reaction.

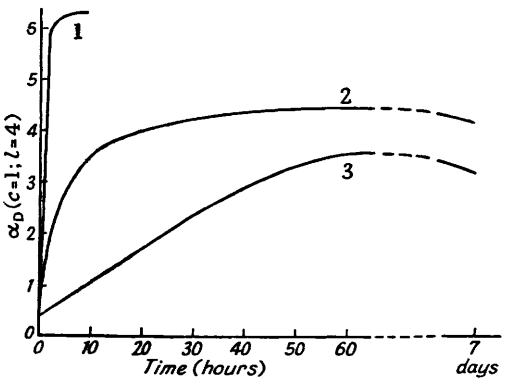
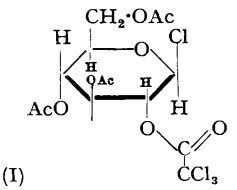


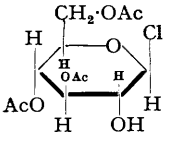
FIG. 1. *Methanolysis of* 3 : 4 : 6-*tri*-O-*acetyl*-2-O-*trichloroacetyl*-β-D-*glucosyl* 1-*chloride and* 3 : 4 : 6-*tri*-O-*acetyl*-β-D-*glucosyl* 1-*chloride.*

1, 3 : 4 : 6-*Tri*-O-*acetyl*-β-D-*glucosyl* 1-*chloride in* 100% MeOH.
2, 3 : 4 : 6-*Tri*-O-*acetyl*-2-O-*trichloroacetyl*-β-D-*glucosyl* 1-*chloride in* 80% *aqueous* MeOH.
3, *As* 2, *but in* 100% MeOH.

The products of the reaction of the two compounds with alcohols were fully studied by Hickinbottom (*J.*, 1929, 1676) whose results show that during certain reactions racemisation had occurred. Tri-*O*-acetyl-2-trichloroacetyl-β-D-glucosyl 1-chloride, for example, with methanol in the presence of silver carbonate gave 70% of α- and 30% of β-methyl



(I)



(II)

glucoside, whereas in the corresponding reaction of 3 : 4 : 6-tri-*O*-acetyl-β-D-glucosyl 1-chloride the product was almost completely the α-glucoside. This result was confirmed by a polarimetric examination of the reaction. In Fig. 1 is shown the variation of optical rotation during the reaction of (I) and (II) with methanol. From the much higher value of the rotation in the second case, the presence of a higher proportion of α-isomer may be inferred. With the 2-trichloroacetyl derivative (I) it was noted that the addition of

water had an effect similar to that observed with tetra-*O*-acetyl-α-D-glucosyl 1-bromide (Part I, *loc. cit.*). It is not unexpected that the alcoholysis of tri-*O*-acetyl-2-*O*-trichloroacetyl-β-D-glucosyl 1-chloride leads to a certain amount of β-glucoside since the large trichloroacetyl group would exert a shielding influence on the side at which the entering group leads to the formation of the α-glucoside. 3 : 4 : 6-Tri-*O*-acetyl-β-D-glucosyl 1-chloride, on the other hand, in which the hydroxyl group at $C_{(2)}$ is not acylated is able to produce the α-glucoside in the normal manner. Although discussion of the formation of 1 : 2-orthoesters is being reserved for a subsequent communication, it is pertinent that it does not occur in solvolysis of the 2-trichloroacetyl compound. Although the acyl group is *trans* to the halogen atom at $C_{(1)}$, the inductive effect of the trichloromethyl group will so diminish the polarisation of the carbonyl group that the cyclic orthoester cation is not formed. Although both compounds (I) and (II) undergo solvolysis by the unimolecular mechanism, that of (II) with methanol is over 60 times as fast at 21° as that of (I). This demonstrates the large steric effect operating here.

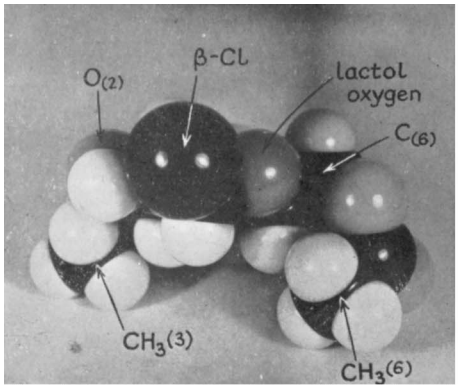
In order to ascertain the extent to which each acetyl group affects the reactivity of the halogen atom, a systematic variation of the configuration of the groups in the molecule was undertaken by choosing appropriate compounds.

The Acetyl Group at $C_{(2)}$.—A change in configuration at position 2 to make the acetyl group *trans* to the 1-halogen atom in the α-configuration is found in the mannose series. In Table 2 the rate constant for the methanolysis of tetra-*O*-acetyl-α-D-mannosyl 1-bromide (III) is given and, compared with tetra-*O*-acetyl-α-D-glucosyl 1-bromide at the same temperature, there is a ten-fold increase in the solvolysis rate. To confirm the unimolecular character of the reaction, the effect of alkali on the solvolysis in 60% aqueous acetone was examined and only a small increase in rate was observed. The amount of alkali used was insufficient to maintain alkalinity throughout the reaction and it became acidic during the measurements; nevertheless this had no effect on the kinetic form of the reaction. It is safe to conclude therefore that the solvent molecules do not function as reagents in the rate-determining stage of the reaction.

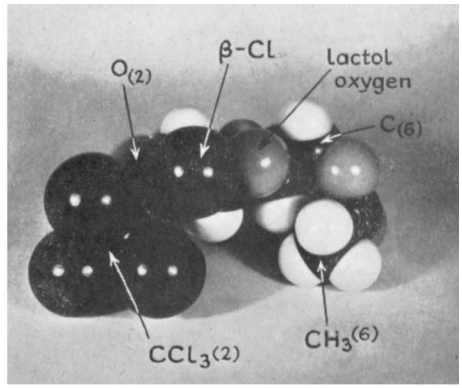
The Acetyl Group at $C_{(3)}$.—In the present series the effect of the acetyl group at position 3 could not be ascertained. A change of configuration at this position gives allose, and neither this sugar nor its appropriate derivatives were available. Howard (*J.*, 1950, 1045), however, has suggested that in a *cis*-2 : 3-diacetoxy-system, the 3-acetoxy-group would restrict the movement of the 2-acetoxy-group to the neighbourhood of $C_{(1)}$, and examination of scale models showed that this effect is likely in the *trans*-system also.

The Acetyl Group at $C_{(4)}$.—If the configuration of *O*-glucose is inverted at position 4, D-galactose results. A first-order rate constant for the methanolysis of tetra-*O*-acetyl-α-D-galactosyl 1-bromide (IV) was obtained by both the polarimetric method and titration of the acid liberated with standard alkali (Table 2). Catalysis by liberated acid was noticed during the later stages of the reaction. The rate of methanolysis of this derivative is 4·5 times greater than that of the corresponding glucose compound, an increase which can only be attributed to the acetyl group at $C_{(4)}$. Solvent effects were observed similar to those with tetra-*O*-acetyl-α-D-glucosyl 1-bromide. A change of medium from 80% to 60% aqueous acetone produced an eight-fold increase in rate, compared with a nine-fold increase for the glucose derivative. The possibility of a bimolecular reaction was again eliminated by the failure of added alkali to affect the rate constant in 60% aqueous acetone (Table 2).

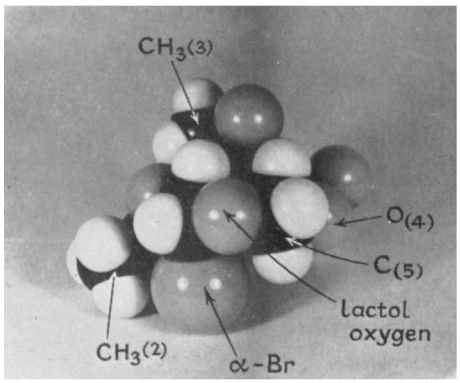
Position 6. *The Acetoxymethyl Group.*—There is little doubt that $C_{(1)}$ and $C_{(6)}$ can approach each other in some substituted compounds since 1 : 6-anhydrides can be formed. For instance, tetra-*O*-acetyl-α-glucosyl 1-bromide reacts with trimethylamine, to give a quaternary bromide from which 1 : 6-anhydro-β-D-glucose is formed by treatment with barium hydroxide solution (Micheel, *Ber.*, 1929, **62**, 687; Karrer and Smirnoff, *Helv. Chim. Acta*, 1921, **4**, 819); and 1 : 6-anhydro-β-D-galactose is obtained in a similar way. It was therefore expected that the acetoxymethyl group in the hexose series would influence the properties of the 1-halogen atom. A direct experimental test was made by investigating tri-*O*-acetyl-α-D-xylosyl 1-bromide (V) in which, apart from the absence of the acetoxymethyl group attached to $C_{(5)}$, the rest of the molecule is identical with the glucosyl bromide.



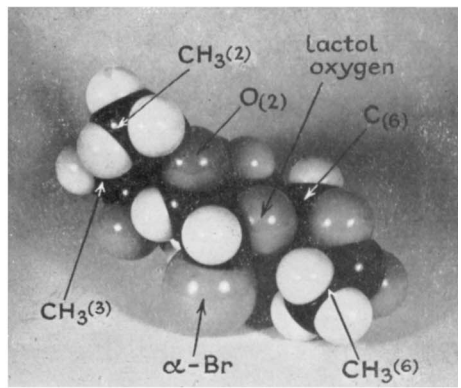
1, 3 : 4 : 6-*Tri*-O-*acetyl*-β-D-*glucosyl* 1-*chloride*.



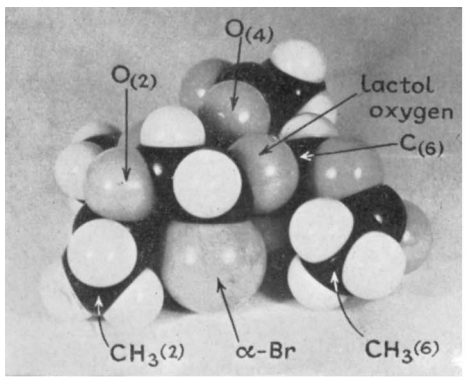
2, 3 : 4 : 6-*Tri*-O-*acetyl*-2-O-*trichloroacetyl*-β-D-*glucosyl* 1-*chloride*.



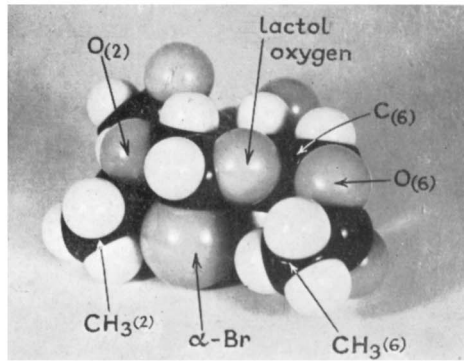
3, *Tri*-O-*acetyl*-α-D-*xylosyl* 1-*bromide*.



4, *Tetra*-O-*acetyl*-α-D-*mannosyl* 1-*bromide*.



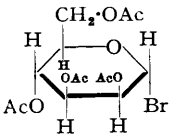
5, *Tetra*-O-*acetyl*-α-D-*galactosyl* 1-*bromide*.



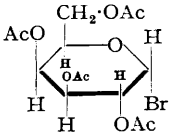
6, *Tetra*-O-*acetyl*-α-D-*glucosyl* 1-*bromide*.

[*To face p.* 2907.

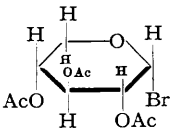
The methanolysis rate was found to be 50 times greater than that of the glucose derivative (Table 2)—a striking confirmation of the prediction by Hassel and Ottar (*Acta Chem. Scand.*, 1947, **1**, 929) that tetra-*O*-acetylxylosyl bromide should be more reactive than the glucose derivative. As with tetra-*O*-acetyl-α-D-mannosyl 1-bromide, there was a small increase in rate of the solvolysis in 60% aqueous acetone in the presence of alkali. Here again, the possibility of a bimolecular reaction could be eliminated because no change in kinetic form was observed when the alkali had been consumed and the medium became acidic.



(III)



(IV)



(V)

The foregoing experiments show that the geometrical position of the acetyl groups has a pronounced effect on the reactivity of the halogen atom which throughout follows a unimolecular mechanism in solvolysis. Since the conventional sugar formulæ give no indication of the size of the groups or of their disposition in the molecule, it was necessary to consider the more precise structure of the *O*-acetylglycosyl 1-halides which have been investigated. This was done by assigning a ring conformation and then, with the aid of accurate scale models and consideration of the intramolecular interactions in the molecule,

TABLE 2. *Comparison of the rate of solvolysis of several O-acetyl-α-glycosyl 1-halides with that of tetra-O-acetyl-α-glucosyl 1-bromide.*

Tetra-*O*-acetyl-α-D-glycosyl 1-bromide	Medium	Temp.	10^5k_1 (sec.$^{-1}$)	Tetra-*O*-acetyl-α-D-glycosyl 1-bromide	Medium	Temp.	10^5k_1 (sec.$^{-1}$)
Glucosyl ...	MeOH	21·2°	2·80	Galactosyl	MeOH	21·2°	12·4
Mannosyl ...	MeOH	21·2	30·0		,,	35·0	45·3
	60% Aq. $COMe_2$	16	13·1 *		,,	16	8·5 *
	,, ,,	16	16·9 †		80% Aq. $COMe_2$	21·2	1·69
Xylosyl	MeOH	21·2	139 *		60% ,,	21·2	13·5
	,, ,,	16	94 *		,, ,,	21	13·7 *
	60% Aq. $COMe_2$	16	76·3 *		,, ,,	21	13·7 * †
	,, ,,	16	82·0 * †				

* Polarimetric method employed.
† [Alkali] = 0·025N; measurements were made at the same time as those in which alkali was absent.

the most likely relative arrangement of the substituent groups was determined. The *cyclo*hexane molecule has been shown by many workers (Hermanns, *Rec. Trav. chim.*, 1938, **57**, 333; Kohlrausch and Wittek, *Z. physikal. Chem.*, 1941, **48**, *B*, 177; Geoding, Smit, and Westrik, *Rec. Trav. chim.*, 1942, **61**, 561; Aston, Schumann, Fink, and Doty, *J. Amer. Chem. Soc.*, 1941, **63**, 2029; Beckett, Pitzer, and Spitzer, *ibid.*, 1947, **69**, 2488) to exist predominantly in the rigid chair form. A similar conclusion has been drawn concerning the ring conformation in the pyranose form of the sugars, both from theoretical (Gorin, Kanzmann, and Walter, *J. Chem. Phys.*, 1939, **7**, 327; Cox, *J.*, 1935, 1495) and experimental considerations (Reeves, *J. Amer. Chem. Soc.*, 1949, **71**, 215, 1737; *Adv. Carbohydrate Chem.*, 1952, **6**, 108). From a study of the cuprammonium–glycoside complexes Reeves reduced the number of possible conformations to not more than three and in the sugars under discussion the conformation at $C_{(1)}$ (Fig. 2) is sufficient to explain their behaviour as complex-forming glycosides. This is assumed to be present in the *O*-acylglycosyl 1-halides and was adopted in the models. In the acetyl group, the carbonyl charge distribution $>C\overset{\curvearrowright}{=}O$ is well established and hyperconjugation permits allocation of a fractional positive charge to the hydrogen atoms of the methyl group. The other polar link in the *O*-acylglycosyl 1-halides is $C_{(1)}$–Hal. In the models constructed, the groups

were assigned to positions based on these fractional charges, so that the resultant molecule would have the minimum potential energy, a methyl group for example being directed towards a carbonyl-oxygen atom. By means of this convention, the precise structures of the *O*-acylglycosyl 1-halides were built up (Phillips, Thesis, University of Wales, 1952). The various structures are illustrated in the Plate and it is seen that each presents a different amount of hindrance in the neighbourhood of the halogen atom. A correlation between this variation in steric hindrance and rate of methanolysis is shown in Table 3. As the hindrance at $C_{(1)}$ increases so does the rate constant decrease.

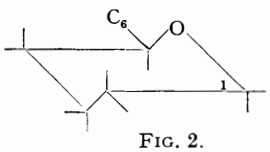
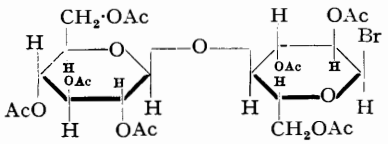


FIG. 2.

TABLE 3. *Variation in rate constant with steric hindrance.*

Compound	Hindrance at $C_{(1)}$	Relative rate constant
Tri-*O*-acetyl-α-D-xylosyl 1-bromide	Least	50
Tetra-*O*-acetyl-α-D-mannosyl 1-bromide	↓	10
Tetra-*O*-acetyl-α-D-galactosyl 1-bromide		4·5
Tetra-*O*-acetyl-α-D-glucosyl 1-bromide	Greatest	1

Further confirmation that the variation in unimolecular solvolysis rate is a direct function of the steric hindrance at $C_{(1)}$ was obtained from a study of hepta-*O*-acetyl-α-cellobiosyl 1-bromide (VI) and hepta-*O*-acetyl-α-gentiobiosyl 1-bromide (VII). These may



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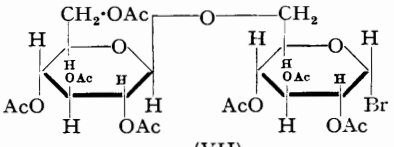

(VII)

be considered as tetra-*O*-acetylglucosyl 1-bromide in which an acetylated glucosyl residue has been substituted at position 4 or 6. Examination of their scale models showed that the orientation of the groups in the neighbourhood of the halogen is similar to that in tetra-*O*-acetyl-α-D-glucosyl 1-bromide, except that in the gentiobiose derivative it is slightly less because of the biose linkage at position 6. The first-order constants for their methanolysis are compared in Table 4 and completely support the relation between steric hindrance and reactivity.

TABLE 4. *Methanolysis of hepta-*O*-acetyl-α-cellobiosyl 1-bromide, hepta-*O*-acetyl-α-gentiobiosyl 1-bromide and tetra-*O*-acetyl-α-glucosyl 1-bromide at* 35°.

Compound	10^4k_1 (sec.$^{-1}$)
Tetra-*O*-acetyl-α-glucosyl 1-bromide	1·21
Hepta-*O*-acetyl-α-cellobiosyl 1-bromide	1·12
Hepta-*O*-acetyl-α-gentiobiosyl 1-bromide	2·98

EXPERIMENTAL

Materials.—3 : 4 : 6-Tri-*O*-acetyl-2-*O*-trichloroacetyl-β-D-glucosyl 1-chloride, m. p. 139—140°, was prepared by the action of phosphorus pentachloride on β-penta-*O*-acetylglucose (Brigl, *Z. physiol. Chem.*, 1921, **116**, 1; Hickinbottom, *J.*, 1929, 1676; Abramovitch, *J.*, 1951, 2996). The purity of the phosphorus pentachloride noted by Farrar (*J.*, 1949, 3131) was not found to be important, but no product was obtained when the α-penta-acetate was used. Selective deacylation gave 3 : 4 : 6-tri-*O*-acetyl-β-D-glucosyl 1-chloride, m. p. 153—155° (after five recrystallisations from ethyl acetate) (Brigl; Hickinbottom, *locc. cit.*). The *O*-acetylglycosyl 1-bromides were prepared from the sugar acetates by the standard procedure. Tetra-*O*-acetyl-α-D-galactosyl 1-bromide had m. p. 82—83°, $[\alpha]_D^{20}$ +237° (*c*, 1·22 in benzene). Tri-*O*-acetyl-α-*O*-xylosyl 1-bromide had m. p. 100—101°, $[\alpha]_D^{20}$ +210° (*c*, 1·17 in $CHCl_3$); to avoid decomposition it was kept under ether until required. Tetra-*O*-acetyl-α-D-mannosyl 1-bromide could not be crystallised. Isolated by methods of Micheel and Micheel (*Ber.*, 1930, **63**, 386) and Levene and Tipson (*J. Biol. Chem.*, 1931, **90**, 89) the products showed $[\alpha]_D^{20}$

$+111\cdot2°$ and $115\cdot6°$ (*c*, 1·64 and 1·37 in $CHCl_3$) (Found : Br, 19·0 and 19·3. Calc. for $C_{14}H_{19}O_9$: Br, 19·5%). Hepta-*O*-acetyl-α-cellobiosyl 1-bromide and hepta-*O*-acetyl-α-gentiobiosyl 1-bromide had respectively m. p. 180° and 143—144° and $[\alpha]_D^{20}$ $+95\cdot4°$ (*c*, 1·26 in $CHCl_3$) and $[\alpha]_D^{18}$ $+100\cdot3°$ (*c*, 1·46 in $CHCl_3$).

Solvents were purified by the methods described in the preceding papers.

Rate Measurements.—The technique was the same as that employed in the preceding papers. The following record of detailed experiments is typical of the series of solvolytic reactions studied. The concentration of the halides is expressed in equivalent ml. of standard alcoholic alkali per 5 ml. of solution, and the first-order rate constants are in sec.$^{-1}$.

Methanolysis of the O-*acylglycosyl* 1-*halides at* 21·2° (*except where otherwise stated*).

3 : 4 : 6-*Tri*-O-*acetyl*-2-O-*trichloroacetyl*-β-D-*glucosyl* 1-*chloride*

t (min.)	0	50	80	140	270	330	450	500	575
[Halide]	8·70	8·35	8·10	7·87	7·22	6·85	6·31	6·10	5·79

[Halide] = 0·0216M. Alkali = 0·025N. Slope : $-3\cdot07 \times 10^{-4}$ min.$^{-1}$. $10^5k = 1\cdot18$.

Tetra-O-*acetyl*-α-D-*mannosyl* 1-*bromide* (21·3°)

t (min.)	0	2	5	10	20	25	30	35	40	45	50
[Halide]	8·40	7·41	7·02	6·40	5·43	4·90	4·43	4·12	3·76	3·43	3·14

[Halide] = 0·0252M. Alkali = 0·0151N. Slope : $-7\cdot80 \times 10^{-3}$ min.$^{-1}$. $10^4k = 3\cdot00$.

Tri-O-*acetyl*-α-D-*xylosyl* 1-*bromide*.

t (min.)	0	2	5	7·5	10	12	15	17·5	20	22	25
[Halide]	12·00	10·35	8·33	6·53	5·27	4·47	3·25	2·82	2·21	1·95	1·51

[Halide] = 0·0247M. Alkali = 0·0102N. Slope : $-3\cdot61 \times 10^{-2}$ min.$^{-1}$. $10^3k = 1\cdot39$.

Hepta-O-*acetyl*-α-*gentiobiosyl* 1-*bromide* (35·0°).

t (min.)	0	4	10	12·5	15	19	25	30	35	40	50
[Halide]	5·66	5·35	4·87	4·61	4·45	4·11	3·71	3·39	3·10	2·76	2·37

[Halide] = 0·011M. Alkali = 0·010N. Slope : $-7\cdot75 \times 10^{-3}$ min.$^{-1}$. $10^4k = 2\cdot98$.

Certain reactions (Tables 1 and 2) were followed polarimetrically according to the details given in Part I. The following results are typical.

Solvolysis of tetra-O-*acetyl*-α-D-*galactosyl* 1-*bromide in* 60% *aqueous acetone at* 21°.

t (min.)	7	15	30	40	65	80	105	125	160	180	220	∞
α	4·62°	4·42°	3·98°	3·79°	3·41°	3·21°	2·89°	2·68°	2·34°	2·18°	1·93°	1·35°

c, 1·0875. *l* = 2. Slope : $-3\cdot575 \times 10^{-3}$ min.$^{-1}$. $10^4k = 1\cdot37$.

The same containing 0·03N-*alkali*.

t (min.)	5	15	30	45	60	85	110	140	180	200	220	∞
α	3·51°	3·28°	3·03°	2·87°	2·70°	2·43°	2·23°	1·97°	1·76°	1·66°	1·60°	1·21°

c, 1·1565. *l* = 2. Slope : $-3\cdot576 \times 10^{-3}$ min.$^{-1}$. $10^4k = 1\cdot37$.

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