45. *The Reactivity of the* O-*Acylglycosyl Halides. Part V.* The Catalysed and Uncatalysed Solvolysis of* 1 : 2-trans-2-O-*Acetylglycosyl Halides.*

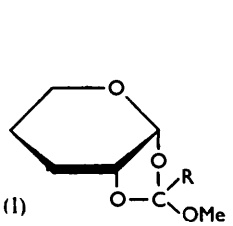
By G. L. Mattok and G. O. Phillips.

The kinetics and other general characteristics of the uncatalysed and catalysed solvolyses of 1 : 2-*trans*-2-*O*-acetylglycosyl halides show that the rate-determining stage is the removal of the halogen atom to form a carbonium ion. The nature of the products and the rate data are in accordance with the formation of a cyclic-ion intermediate.

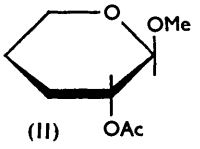
Anchimeric assistance due to the 2-acetyl group is shown to contribute to the enhanced rates of solvolysis of 1 : 2-*trans*-2-*O*-acetyl-1-halides compared with the corresponding 1 : 2-*cis*-compounds. However, a comparison of the solvolysis of tetra-*O*-acetyl-β-D-glucosyl 1-chloride and tetra-*O*-acetyl-α-D-mannosyl 1-chloride, both 1 : 2-*trans*-compounds, illustrates the importance of other factors, probably of steric origin, which govern the reactivity.

Neighbouring-group effects exert an important influence on the course of reactions at the lactol-carbon atom in the hexose molecule.[1,2] For example, it is well established that participation of the 2-acetyl group influences the nature of the product in the Koenigs–Knorr reaction.[3] Solvolysis of 1 : 2-*trans*-2-*O*-acetylglycosyl halides in methanol in the presence of certain electrophilic catalysts yields the 1 : 2-orthoacetate (I; R = Me), together with some anomeric glycosides; the corresponding reactions for the 1 : 2-*cis*-compounds give glycosides (II) with a high degree of inversion at the anomeric centre.

According to Frush and Isbell[4] the orthoester is formed by attack of the methanol at the 2-acetyl group, and of this group at the lactol-carbon atom with simultaneous dissociation of the *C*-halogen bond. The transition state is shown in (III).



(I)



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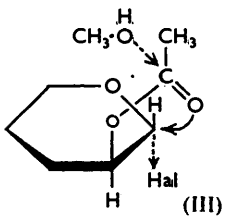


(III)

Simultaneous glycoside formation was attributed to the competition of a direct S_N2 replacement at $C_{(1)}$. However, kinetic studies on the solvolysis of *trans*-2-acetoxy*cyclo*hexyl toluene-*p*-sulphonate led Winstein, Hanson, and Grunwald[5] to rule out this mechanism of orthoester formation. Subsequently Frush and Isbell[6] presented additional evidence in support of the " solvated orthoester intermediate " mechanism from a study of the effects of mixed solvents and temperature on the reaction products.

The previous paper in this series describes the mechanism of the Koenigs–Knorr reaction for tetra-*O*-acetyl-α-D-glucosyl 1-chloride. In the present paper the uncatalysed and the catalysed solvolysis of 1 : 2-*trans*-acetoxyhalides are examined kinetically. The results show that the reactions are of the S_N1 type, and support existence of a cyclic-ion intermediate. There is evidence for anchimeric assistance due to the *trans*-2-acetyl group,

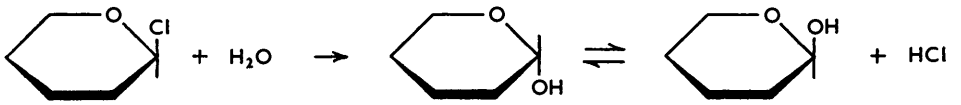
* Part IV, *J.*, 1956, 1836.

[1] Lemieux, *Adv. Carbohydrate Chem.*, 1954, **9**, 1.
[2] Isbell, *Ann. Rev. Biochem.*, 1940, **9**, 65.
[3] Winstein and Buckles, *J. Amer. Chem. Soc.*, 1942, **64**, 2780, 2787.
[4] Frush and Isbell, *J. Res. Nat. Bur. Stand.*, 1945, **34**, 111.
[5] Winstein, Hanson, and Grunwald, *J. Amer. Chem. Soc.*, 1948, **70**, 812.
[6] Frush and Isbell, *J. Res. Nat. Bur. Stand.*, 1949, **43**, 161.

a behaviour commonly observed by Winstein and his co-workers [7] in similar reactions. Comparison of two 1 : 2-*trans*-acetoxy-halides emphasises the importance of other factors which govern the reactivity.

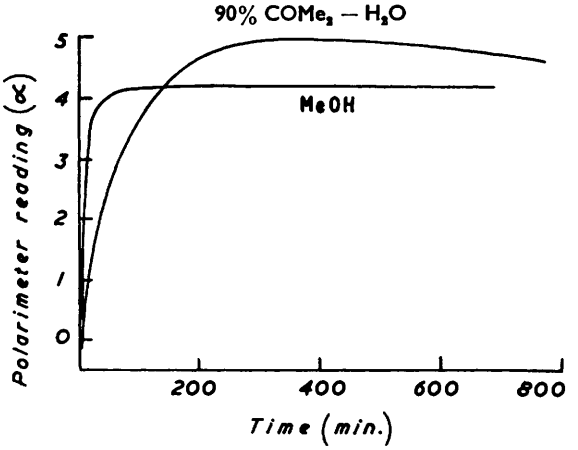
Results

Reactions of Tetra-O-acetyl-β-D-glucosyl 1-Chloride.—In acetone–water, this chloride gives tetra-*O*-acetyl-α-D-glucose which subsequently mutarotates :



This secondary reaction presents difficulties when polarimetric methods are used for rate measurements, but by using initial rates this complication may be avoided as described in an earlier paper. The mutarotation is, however, not as marked as for the 1 : 2-*cis*-acetoxy-halides.

In methanol, methyl 2 : 3 : 4 : 6-tetra-*O*-acetyl-α-D-glucoside is formed in the absence and presence of mercuric chloride, and mutarotation presents no difficulty. Consequently rate



constants could be calculated either by using initial rates or from the conventional first-order rate expression; the agreement was excellent.

The Figure shows the change in rotation (degrees) with time for the solvolysis of tetra-*O*-acetyl-β-D-glucosyl 1-chloride in methanol and acetone–water; the final decrease in rotation in acetone–water indicates the small amount of secondary mutarotation.

In certain solvents, notably acetone, tetra-*O*-acetyl-β-D-glucosyl 1-chloride spontaneously rearranges to the α-anomer, and it has been suggested that this may even take place in solvents which react with the halogen atom, such as acetone–water or methanol, at a rate comparable with that of the main reaction.[8] Although this in our view was unlikely we have sought confirmation since such anomerisation, if it occurred, would cast doubt on polarimetric rate measurements. Table 1 shows a comparison of typical rate constants obtained polarimetrically and by titration of the acid liberated during the reaction for the solvolysis of tetra-*O*-acetyl-β-D-glucosyl 1-chloride in methanol–acetone and in aqueous acetone at 25·5°. The good agreement rules out the possibility of appreciable anomerisation.

Addition of hydroxyl ions in the solvolysis of tetra-*O*-acetyl-β-D-glucosyl 1-chloride in 90% acetone–water does not influence the reaction rate (Table 2).

Increasing the ionising power of the solvent has a marked enhancing effect on the rate. Table 3 shows the effect of increasing the proportion of water in an aqueous-acetone medium on the solvolysis of tetra-*O*-acetyl-β-D-glucosyl 1-chloride. The reaction rates are correlated

[7] Winstein, Grunwald, Buckles, and Hanson, *J. Amer. Chem. Soc.*, 1948, **70**, 816.
[8] Ref. 1, p. 20.

with a constant (Y value) expressing the ionising power of the solvent.[9] There is a linear dependence between log k and Y which, expressed by the relation $\log k = mY + \log k_0$, gives the constants $m = 0{\cdot}5$, $\log k_0 = -2{\cdot}74$.

TABLE 1.

[RCl] = 0·05M.

Method	Polarimetric	Titrimetric	Polarimetric	Titrimetric
10^4k_1 (sec.$^{-1}$)	3·0 *	2·9	3·2	3·4
Solvent	25% Methanol–acetone		90% Acetone–water	

* Value obtained at 25·5° from Arrhenius plot.

TABLE 2.

[RCl] = 0·05M.

[OH$^-$] (M)	0	0·025	0·05
10^4k_1 (sec.$^{-1}$)	3·16 *	3·20	3·1

* By extrapolation.

TABLE 3.

Water (%)	10	20	30	40
Y value	−1·850	−0·673	+0·130	+0·796
10^4k_1 (sec.$^{-1}$)	2·57	9·25	22·0	51·4
$4 + \log k$	0·4102	0·9661	1·3430	1·7112

TABLE 4.

Temp.	10^4k_1 (sec.$^{-1}$)	E (kcal. mole^{-1})	Temp.	10^4k_1 (sec.$^{-1}$)	E (kcal. mole^{-1})	Temp.	10^4k_1 (sec.$^{-1}$)	E (kcal. mole^{-1})
Water 10%			Water 20%			Water 30%		
23·7°	2·57	20·7	23·6°	9·25	21·0	23·8°	22·0	21·6
26·7	3·95		26·7	13·2		26·8	31·6	
29·8	5·03		29·6	18·7		29·7	44·5	

TABLE 5.

Water (%)	10	20	30
$\Delta G‡$ (kcal. mole^{-1}) (at 25°)	22·4	21·6	21·1
$\Delta H‡$ (kcal. mole^{-1}) (at 25°)	20·1	20·4	21·0
$\Delta S‡$ (e.u.) (at 25°)	−7·70	−4·03	−0·34

TABLE 6.

Temp.	10^5k_1 (sec.$^{-1}$)	E (kcal. mole^{-1})	Temp.	10^5k_1 (sec.$^{-1}$)	E (kcal. mole^{-1})	Temp.	10^5k_1 (sec.$^{-1}$)	E (kcal. mole^{-1})	Temp.	10^5k_1 (sec.$^{-1}$)	E (kcal. mole^{-1})
Methanol: 10%			Methanol: 50%			Methanol: 25%			Methanol: 100%		
23·5°	6·91	20·3	23·0°	60·6	23·0	23·4°	23·0	22·5	23·7°	265	23·0
26·1	8·64		26·4	93·3		23·9	23·4		26·2	382	
27·6	10·7		29·1	132		26·3	33·8		29·0	489	
29·2	12·7					29·0	44·5				

TABLE 7.

Methanol (%)	10	25	50	100
$\Delta G‡$ (kcal. mole^{-1}) (at 25°)	23·2	22·4	21·8	21·0
$\Delta H‡$ (kcal. mole^{-1}) (at 25°)	19·7	21·9	11·4	22·4
$\Delta S‡$ (e.u.) (at 25°)	−11·7	−1·68	+3·00	+4·70

The effect of temperature on the solvolysis of tetra-*O*-acetyl-β-D-glucosyl 1-chloride in aqueous acetone is shown in Tables 4 and 5. Increasing the proportion of methanol in methanol–acetone produces similar results (Tables 6 and 7).

Addition of Mercuric Chloride.—When mercuric chloride is added in the solvolysis of tetra-*O*-acetyl-β-D-glucosyl 1-chloride there is a large increase in rate. The order with respect to

[9] Winstein and Grunwald, *J. Amer. Chem. Soc.*, 1948, **70**, 846.

the reactants, sugar halide, mercuric chloride, and water was determined as described in the previous paper. As for the 1 : 2-*cis*-acetoxy-halides, the reaction is of first order with respect to the sugar halide and mercuric chloride, and independent of the water (Table 8).

The effect of temperature on the catalysed methanolysis of tetra-*O*-acetyl-β-D-glucosyl 1-chloride is shown in Tables 9 and 10.

Reactions of Tetra-O-acetyl-α-D-mannosyl 1-Chloride.—Rate data and thermodynamic constants for the catalysed and uncatalysed solvolysis of tetra-*O*-acetyl-α-D-mannosyl 1-chloride are shown in Table 11.

TABLE 8. *Second-order rate constants for the solvolysis of tetra-O-acetyl-β-D-glucosyl 1-chloride catalysed by mercuric chloride.*

	Acetone–water at 25°			25% Methanol–acetone at 25·5°		
Solvent	99%	98%	97%			
[RCl] (10^3M)	5·00	5·00	5·00	5·03	5·0	4·38
[$HgCl_2$] (10^3M)	5·00	5·00	5·00	4·94	4·05	3·68
10^3k_2 (l. mole^{-1} sec.$^{-1}$) ...	3·24	3·13	3·14	3·46	3·46	3·38

TABLE 9. *Effect of temperature and solvent on the solvolysis catalysed by mercuric chloride* (0·05M) *in methanol–acetone.*

Methanol (%)	Temp.	10^3k_2 (l. mole^{-1} sec.$^{-1}$)	*E* (kcal. mole^{-1})	Methanol (%)	Temp.	10^3k_2 (l. mole^{-1} sec.$^{-1}$)	*E* (kcal. mole^{-1})
10	22·5°	2·24	14·4	50	23·4°	4·08	15·8
	23·5	3·07			26·5	5·22	
	26·9	4·18			26·8	5·45	
	28·0	4·55			29·4	6·73	
	29·8	5·03			30·9	7·83	
	31·8	6·04			32·5	8·83	

TABLE 10. *Solvolysis catalysed by mercuric chloride in methanol–acetone at* 25°.

Methanol (%)	10	50	$\Delta H^{\ddagger}$ (kcal. mole^{-1})	13·8	15·2
$\Delta G^{\ddagger}$ (kcal. mole^{-1})	19·6	19·4	$\Delta S^{\ddagger}$ (e.u.)	−19·5	−14·1

TABLE 11. *Methanolysis of tetra-O-acetyl-α-D-mannosyl 1-chloride in the absence and presence of mercuric chloride.*

[$HgCl_2$] = nil			[$HgCl_2$] = 0·05M		
Temp.	10^6k_1 (sec.$^{-1}$)	*E* (kcal. mole^{-1})	Temp.	10^4k_2 (l. mole^{-1} sec.$^{-1}$)	*E* (kcal. mole^{-1})
23·5°	6·9	30·8	23·1°	3·19	21·4
26·6	12·7		26·0	4·41	
28·2	14·4		28·9	6·59	
29·8	17·7		32·7	9·67	

[$HgCl_2$] (M)	nil	0·05
$\Delta G^{\ddagger}$ (kcal. mole^{-1}) at 25°	24·6	22·2
$\Delta H^{\ddagger}$ (kcal. mole^{-1}) at 25°	30·2	20·8
$\Delta S^{\ddagger}$ (e.u.) at 25°	+18·8	−4·7

DISCUSSION

The mechanism of the Koenigs–Knorr reaction for a 1 : 2-*cis*-2-*O*-acetylglycosyl halide shows features similar to those of a S_N1 reaction, the catalyst assisting in the removal of the halogen atom to form a carbonium ion. In the absence of an electrophilic catalyst solvolysis of these compounds is strictly of S_N1 type.[10] The results presented for the corresponding solvolytic reactions of 1 : 2-*trans*-*O*-acetylglycosyl halides indicate that a similar mechanism is operative for these compounds, and do not support the mechanism postulated by Frush and Isbell involving simultaneous attack by the reagent and release of the halogen.[4,6]

The solvolysis of tetra-*O*-acetyl-β-D-glucosyl 1-chloride in the absence of a catalyst is of the first order, and the rate is unaffected by addition of alkali (Table 2). Since the strong nucleophilic reagent has no influence on the rate, it is unlikely that it takes part in

[10] Mattok and Phillips, *J.*, 1956, 1846.

the rate-determining stage of the reaction. Solvent effects are characteristic of the S_N1 process; increases in the ionising power of the solvent are accompanied by large increases in reaction rate (Table 3). The variations in rate are due almost entirely to changes in entropy of activation as a result of changing the solvent composition (Table 5). During the solvolysis of tetra-*O*-acetyl-β-D-glucosyl 1-chloride in various acetone–water and methanol–acetone media, the activation energy remains constant at each solvent composition, but the entropy of activation becomes less negative to allow the observed enhanced rates. This is a general behaviour for S_N1 reactions, and was suggested in the previous paper as a suitable criterion for this mechanism.

Addition of mercuric chloride in the solvolysis of tetra-*O*-acetyl-β-D-glucosyl 1-chloride causes large increases in the rate; the reaction is of the first order with respect to the sugar halide and to the catalyst, but is independent of the reagent concentration. Solvent effects for the catalysed solvolysis show similarities to those observed for a 1 : 2-*cis*-acetoxy-halide.[10] As for tetra-*O*-acetyl-α-D-glucosyl 1-chloride, solvent effects are not so pronounced in the presence of a catalyst; for example, changing the medium from 10% to 50% methanol–acetone increases the catalysed rate 1·3 times, compared with a ten-fold increase for the non-catalysed reaction.

Thus, in the main features, the kinetic behaviour of the 1 : 2-*trans*- is similar to that of the 1 : 2-*cis*-acetoxy-halide. For each, the rate-determining stage in independent of the solvent molecules and is characteristic of the S_N1 reaction type:

$$\text{R—Cl} \longrightarrow \text{R}^+ + \text{Cl}^-$$

or

$$\text{R—Cl} + \text{HgCl}_2 \longrightarrow \text{R}^+ + \text{HgCl}_3^-$$

However, for the following reasons it is clear that for the 1 : 2-*trans*-acetoxy-halide, there is participation of the 2-acetyl group in the initial stage of the reaction, which is likely to modify the structure of the intermediate ion.

Lemieux and Brice [11] showed that tetra-*O*-acetyl-β-D-glucosyl 1-chloride reacts with methanol in the presence of silver carbonate, to give methyl α-D-glucopyranose 3 : 4 : 6-triacetate 1 : 2-orthoacetate, and we have confirmed this result. Treatment with silver acetate in dry acetic acid gives β-glucose penta-acetate but when a small amount of water is added the product is 2 : 3 : 4 : 6-tetra-*O*-acetyl-α-D-glucose. The same product is formed in the solvolytic reactions we have carried out in aqueous media; in methanol, methyl 2 : 3 : 4 : 6-tetra-*O*-acetyl-α-D-glucoside is formed. Formation of the orthoester is a definite indication of participation of the neighbouring acetyl group, and, in addition, the definite change in stereochemical path with added water is an established criterion for carbonium ions derived from neighbouring-group participation.[12]

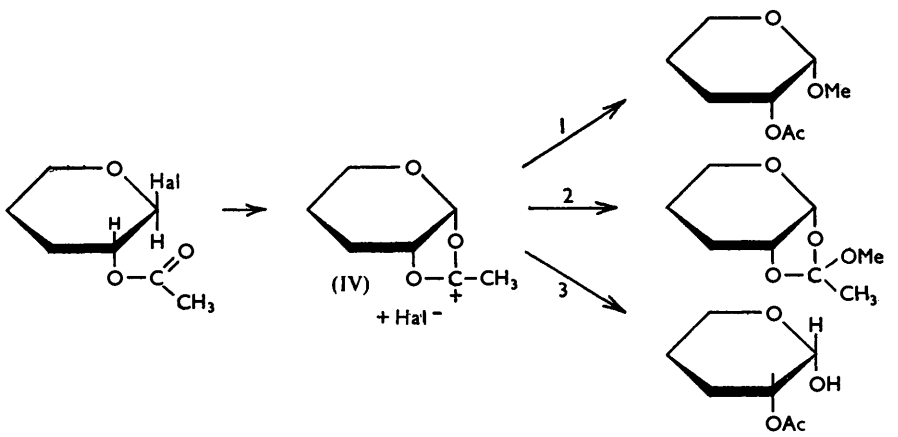
Further evidence is provided by the rate data. The rate of solvolysis of the 1 : 2-*trans*-β-D-anomer is 1000 times greater than for the corresponding 1 : 2-*cis*-α-D-compound. A similar behaviour is given during the acetolysis of 2-substituted *cyclo*hexyl *p*-bromobenzenesulphonates and toluenesulphonates where the *trans*-acetoxy-group anchimerically assists the removal of the replaced group.[5] For these compounds the *trans*-2-acetyl derivative is $1{\cdot}5 \times 10^3$ times more reactive than its *cis*-counterpart. Significant also is the large difference in reactivity between the anomeric D-glucopyranose penta-acetates noted by Lemieux and Brice.[11]

Therefore we can distinguish between two types of the intermediate ion, formed from a 1 : 2-*cis*- and the 1 : 2-*trans*-acetoxy-halide respectively. For the latter, the ionisation may lead to a cyclic intermediate with Walden inversion at $C_{(1)}$ by a one-stage closure (IV), or for the former to the carbonium ion (V).

For the 1 : 2-*cis*-acetoxy-halides the disposition of the carbonyl-oxygen atom of the 2-acetyl group is unlikely to be suitable for the formation of a cyclic ion, since the most

[11] Lemieux and Brice, *Canad. J. Chem.*, 1955, **33**, 109.
[12] Winstein and Roberts, *J. Amer. Chem. Soc.*, 1953, **75**, 2297.

energetically favourable position would have the oxygen directed away from the halogen at the glycosidic carbon centre because both atoms bear residual negative charges. Brauns [13] has set out the most favourable positions for the acetyl groups in the *O*-acetylglycosyl halides, and our postulate is in agreement with his conclusions.



Reagents: 1, MeOH, $HgCl_2$. 2, MeOH, Ag_2CO_3. 3, Acetone–H_2O ± $HgCl_2$.

As a further test for the formation of two different types of intermediate ion from the 1 : 2-*cis*- and 1 : 2-*trans*-acetoxy-halides, we have examined the solvent effects, because ions from (I) and (II) would present different opportunities for solvation, on steric considerations alone. This is in fact the case; varying the solvent from 80% to 60% acetone–water results in a ten-fold increase in rate for tetra-*O*-acetyl-α-D-glucosyl 1-chloride, but only a 5·5-fold increase for the β-anomer. Expressed as constants by Winstein and Grunwald's method (Table 3), for the former $m = 0{\cdot}7$ and for the latter $m = 0{\cdot}5$.

(V)

Tables 5, 7, and 10 give the thermodynamic constants for the catalysed and uncatalysed solvolysis of tetra-*O*-acetyl-β-D-glucosyl 1-chloride. Comparison with the corresponding values for the α-anomer given in the previous paper show that the large difference in

TABLE 12. *Thermodynamic constants for the solvolysis of tetra*-O-*acetyl-α- and -β-*D-*glucosyl 1-chloride.*

	Uncatalysed in 80% acetone–water		Catalysed in 50% methanol–acetone	
	E	$\Delta S^{\ddagger}$	*E*	$\Delta S^{\ddagger}$
1 : 2-*trans*-β-D-Anomer ...	21·0	— 4·0	15·8	—14·1
1 : 2-*cis*-α-D-Anomer	20·0	—27·2	12·9	—36·9

reactivity between the two compounds is due almost entirely to the more favourable entropies of activation for the 1 : 2-*trans*-acetoxy-halide. A typical set of results for comparison is given in Table 12. In each case the heat term is slightly less favourable for

[13] Brauns, *J. Res. Nat. Bur. Stand.*, 1931, **7**, 573.

the 1 : 2-*trans*-anomer, but the entropy is much more favourable, leading to the enhanced rates.

This is in accord with the larger solvation effects associated with the open ion (V). In this structure more water molecules can arrange themselves around the open carbonium ion than is possible for the cyclic ion (IV). The more ordered system resulting leads to a much less favourable entropy. By building scale models of the two types of ion this conclusion can be verified.

Winstein, Grunwald, and Ingraham [14] found that, in the compounds they studied, variations in rate as a result of neighbouring group participation are due mainly to changes in $\Delta H\ddagger$, although there is a small contribution from $\Delta S\ddagger$. In the sugar molecule, however, more complex steric conditions operate.

Comparison of the two 1 : 2-*trans*-acetoxy-halides, tetra-*O*-acetyl-α-D-mannosyl and -β-D-glucosyl 1-chloride, illustrates the importance of factors other than " anchimeric assistance " of the 2-acetyl group which control the reactivity of the halogen. At 23·5°, the solvolysis rate of the D-glucose derivative is 380 times more than that of the D-mannose derivative, although both reactions proceed by the same mechanism. Evidence of the S_N1 solvolysis of tetra-*O*-acetylmannosyl halides was given earlier.[15] Large differences in reactivity of the methyl 1 : 2-orthoacetates of glucose and mannose were observed by Lemieux and Brice, who suggested that it was due to steric inhibition to resonance in the D-mannose carbonium-ion, not present in the D-glucose ion.[11] Similar consideration would apply to the solvolysis rates of the 1 : 2-*trans*-acetoxy-halides, since the difference in reactivity is directly due to the unfavourable activation energy for the D-mannose halide; the entropy factor is more favourable for this compound. The introduction of another large group on the same side of the ring as two previously *cis*-erected groups in the reacting conformation of the 1 : 2-*trans*-glucose anomer would account for the higher activation energy.

Thus although anchimeric assistance of a *trans*-2-acetyl group undoubtedly contributes to the reactivity of the 1 : 2-*trans*-acetoxy-halides discussed, the importance of steric factors is also considerable. This has been emphasised previously, and the large steric effects shown by the *O*-acylglycosyl halides may be attributed to hindrance by the large groups to the realisation of a planar configuration of the ion or perhaps steric hindrance to the solvation of the ion. This point will be discussed further later.

Experimental

Solvents.—Methanol and acetone were purified by the methods described in earlier papers of this series. The solvent compositions are given according to the convention given in the preceding paper of this series.

Tetra-O-acetyl-α-D-mannosyl 1-Chloride.—This was prepared from β-penta-*O*-acetylmannose by treatment with sublimed aluminium chloride and phosphorus pentachloride in chloroform; the m. p. was 81° and $[\alpha]_D$ + 88·9° (*c* 2·1 in $CHCl_3$).

Tetra-O-acetyl-β-D-glucosyl 1-Chloride.—This was prepared from β-penta-*O*-acetylglucose by treatment with titanium tetrachloride in benzene, at 40°; the m. p. was 95—96° and $[\alpha]_D$ −22° (*c* 2 in $CHCl_3$).

Reaction Products. Catalysed Solvolysis of Tetra-O-acetyl-β-D-glucosyl 1-Chloride in Methanol.—(i) *Mercuric chloride catalyst.* Tetra-*O*-acetyl-β-D-glucosyl 1-chloride (2 g.) and mercuric chloride (1·5 g.) were dissolved in methanol (150 ml.) at room temperature. After 0·5 hr. the solvent was removed under reduced pressure and the resulting mixture of syrup and mercuric chloride extracted with chloroform. The mercuric chloride was filtered off and the chloroform evaporated under reduced pressure. The syrup eventually crystallised, to give methyl 2 : 3 : 4 : 6-tetra-*O*-acetyl-α-D-glucoside, m. p. 100°, $[\alpha]_D$ +129° (*c* 0·8 in $CHCl_3$).

[14] Winstein, Grunwald, and Ingraham, *J. Amer. Chem. Soc.*, 1948, **70**, 821.
[15] Newth and Phillips, *J.*, 1953, 2404, 2896, 2900.

(ii) *Silver carbonate catalyst.* The method used was that of Lemieux and Brice.[11] Tetra-*O*-acetyl-β-D-glucosyl 1-chloride (1 g.) was shaken with methanol (50 ml.) containing freshly prepared silver carbonate (1·5 g.) for 50 min. at room temperature. The solids were filtered off and washed with benzene. The combined filtrates were evaporated, below 12°, to a syrup which was dissolved in benzene. The solution was clarified by filtration and evaporated to a syrup, $[\alpha]_D$ +165° (*c* 1 in $CHCl_3$).

Rate Measurements.—The technique was the same as that described in Part IV of this series. All runs were carried out at temperatures close to room temperature.

The rate constants were evaluated from the initial rates of the solvolysis. Tables 13—16 show typical runs, only a part of the experimental observations being given.

TABLE 13. *Solvolysis of tetra-O-acetyl-β-D-glucosyl 1-chloride in 50% methanol–acetone at 26·8° catalysed by mercuric chloride.*

[RCl] = 0·05M. [$HgCl_2$] = 0·05M.

Time (min.) ...	1¼	2	2½	3	3½	4	4½	5	10	15	20	∞
α	0·31°	0·84°	1·14°	1·41°	1·62°	1·82°	2·07°	2·22°	3·37°	3·92°	4·16°	4·45°

$(d\alpha/dt)_{t=0}$ = 0·73 degree min.$^{-1}$. k_2 = 5·45 × 10^{-2} l. mole^{-1} sec.$^{-1}$.

TABLE 14. *Solvolysis of tetra-O-acetyl-β-D-glucosyl 1-chloride in 80% acetone–water at 26·7°.*

[RCl] = 0·05M.

Time (min.)	1½	2	3	3½	4	4½	4	6	10	20	∞
α	0·15°	0·35°	0·69°	0·91°	1·03°	1·20°	1·41°	1·66°	2·56°	3·93°	5·13°

$(d\alpha/dt)_{t=0}$ = 0·415 degree min.$^{-1}$. k_1 = 1·32 × 10^{-3} sec.$^{-1}$.

TABLE 15. *Solvolysis of tetra-O-acetyl-α-D-mannosyl 1-chloride in 100% methanol at 23·5°.*

[RCl] = 0·05M.

Time (min.)	5	49	97	132	173	278	320	370	417	466	∞
α	3·55°	3·49°	3·44°	3·40°	3·35°	3·25°	3·21°	3·15°	3·10°	3·05°	0·65°

$(d\alpha/dt)_{t=0}$ = 1·2 × 10^{-3} degrees min.$^{-1}$. k_1 = 6·9 × 10^{-6} sec.$^{-1}$.

TABLE 16. *Solvolysis of tetra-O-acetyl-α-D-mannosyl 1-chloride in 100% methanol at 28·9° catalysed by mercuric chloride.*

[RCl] = 0·049M. [$HgCl_2$] = 0·05M.

Time (min.)	5	23	34	48	59	76	97	118	141	145	325	∞
α	3·43°	3·32°	3·25°	3·20°	3·15°	3·09°	2·98°	2·90°	2·83°	2·39°	2·09°	0·65°

$(d\alpha/dt)_{t=0}$ = 5·5 × 10^{-3} degree min.$^{-1}$. k_2 = 6·59 × 10^{-4} l. mole^{-1} sec.$^{-1}$.

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