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REACTION OF GLYCOSYL CHLORIDES WITH SILVER PERCHLORATE*

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ABSTRACT

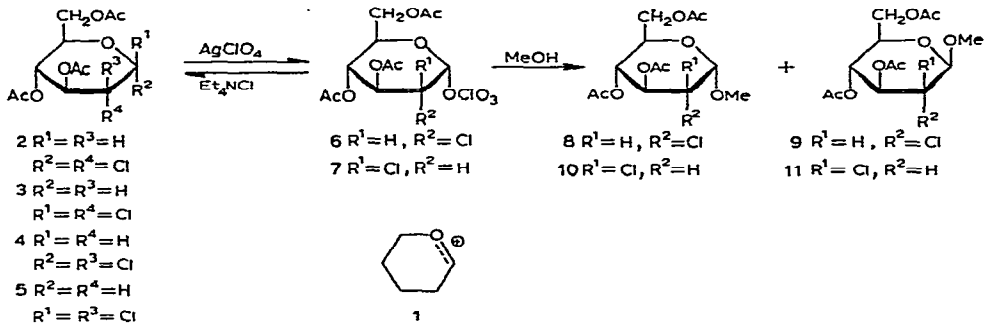
When 3,4,6-tri-*O*-acetyl-2-chloro-2-deoxy-D-gluco- and -manno-pyranosyl chlorides were treated with silver perchlorate in anhydrous toluene, ether, or liquid sulfur dioxide, the corresponding α-D-glycosyl perchlorate esters were obtained. Methanolysis of the perchlorate (**6**) having the D-*gluco* configuration gave a mixture of the methyl α- and β-D-glucopyranosides, the proportion of which varied with the conditions. Treatment of **6** with tetraethylammonium chloride gave predominantly the β-D-glucopyranosyl chloride. Methanolysis or treatment with tetraethylammonium chloride of the perchlorate (**7**) having the D-*manno* configuration gave preponderantly the methyl α-D-mannopyranoside and the α-D-mannopyranosyl chloride, respectively.

1,2-*O*-Acetoxonium-3,4,6-tri-*O*-acetyl-α-D-glucopyranose perchlorate (**13**) was obtained in the reaction of 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl chloride with silver perchlorate. Treatment of **13** with tetraethylammonium chloride gave 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl chloride in good yield. The proportion of the methyl α- and β-D-glucopyranosides obtained by methanolysis of **13** was solvent dependent.

INTRODUCTION

In a previous paper[1], it was found that the reaction of the anomeric 3,4,6-tri-*O*-acetyl-2-chloro-2-deoxy-D-manno- and -gluco-pyranosyl chlorides with silver tetrafluoroborate in anhydrous ether proceeded *via* a common intermediate such as an oxocarbonium ion (**1**). Although the oxocarbonium ion is often invoked as an intermediate in reactions of glycosyl halides with silver perchlorate, there are two possibilities when the reaction is carried out in the absence of other nucleophiles. One is the glycosyl perchlorate ester and the other is the corresponding ion. Methyl, ethyl, and propyl perchlorates are known to be esters, whereas triphenylmethyl perchlorate is a typical carbonium ion[2]. We now report on the reactions of glycosyl chlorides with silver perchlorate.

*Dedicated to Professor F. Micheel in celebration of his 70th birthday. This work was presented, in part, at a Joint Conference of the American Chemical Society and the Canadian Institute of Chemistry, Toronto, Canada, May 1970.



2 $R^1=R^3=H$, $R^2=R^4=Cl$
3 $R^2=R^3=H$, $R^1=R^4=Cl$
4 $R^1=R^4=H$, $R^2=R^3=Cl$
5 $R^2=R^4=H$, $R^1=R^3=Cl$

6 $R^1=H$, $R^2=Cl$
7 $R^1=Cl$, $R^2=H$

8 $R^1=H$, $R^2=Cl$
10 $R^1=Cl$, $R^2=H$

9 $R^1=H$, $R^2=Cl$
11 $R^1=Cl$, $R^2=H$

1

RESULTS AND DISCUSSION

The same, rather unstable, product was obtained in good yield when 3,4,6-tri-*O*-acetyl-2-chloro-2-deoxy-α- (**2**) or -β-D-glucopyranosyl chloride (**3**) was treated with silver perchlorate dissolved in anhydrous toluene or ether, or suspended in liquid sulfur dioxide. The reaction rate followed the solvent sequence sulfur dioxide > ether > toluene. The product showed a large, positive, specific rotation, and its n.m.r. spectrum (toluene-d_8, −5°), which resembles that of **2** (see Tables I and II), is consistent with the ester structure 3,4,6-tri-*O*-acetyl-2-chloro-2-deoxy-α-D-glucopyranosyl perchlorate (**6**) in the *C1* (D) conformation. For the oxocarbonium ion in

TABLE I

CHEMICAL SHIFTS (τ) OF GLYCOSYL CHLORIDES AND GLYCOSYL PERCHLORATES AT 60 MHz IN TOLUENE-d_8[a]

Compound	*H-1*	*H-2*	*H-3*	*H-4*	*H-5* *H-6*	*OAc*
2	4.43d	6.52q	4.43q	4.99t	5.6~6.2m	8.25 (2), 8.30
6	4.48d	6.98q	4.63t	5.02q	5.7~6.5m	8.23, 8.32 (2)
4	4.30d	5.67m	4.25~4.4m		5.8~6.0m	8.29, 8.30, 8.31
7	4.11d	6.27q	5.05q	4.34q	5.6~6.2m	8.31 (2), 8.41

[a]Observed multiplicities: d, doublet; t, triplet; q, quartet; m, multiplet.

TABLE II

FIRST-ORDER COUPLING CONSTANTS (Hz)[a] OF PROTONS OF GLYCOSYL CHLORIDES AND GLYCOSYL PERCHLORATES

Compound	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$
2	3.5	10.5	9.3	9.3
6	4.0	10.5	10.5	9.0
4	1.5			
7	1.5	3.5	10.0	9.0

[a]By direct measurement from spectra.

the half-chair conformation, the $J_{1,2}$ value is estimated to be *ca.* 2 Hz from inspection of models, and the H-2 and H-5 signals should appear at lower field than those of **2**. In the n.m.r. spectra[3] of α-chloroethers (neat) and their alkoxycarbonium ions ($R-\overset{2}{C}H_2-O^{\oplus}=\overset{1}{C}H-\overset{3}{C}H_2-R'$) in antimony pentafluoride–sulfur dioxide solution, the signals for the protons at positions 1, 2, and 3 appeared at lower field than those of the corresponding α-chloroether by *ca.* 4, 1.5, and 1.35 p.p.m., respectively. In the n.m.r. spectra of **2** and **6**, the H-1 signals appeared at an identical position and the H-2 signal for **6** appeared at a position 0.46 p.p.m. higher than that for **2**.

A similar, unstable product was obtained when 3,4,6-tri-*O*-acetyl-2-chloro-2-deoxy-α- (**4**) or -β-D-mannopyranosyl chloride (**5**) was treated with silver perchlorate. From the specific rotation value, solubility, and n.m.r. spectrum, the product was assigned the ester structure 3,4,6-tri-*O*-acetyl-2-chloro-2-deoxy-α-D-mannopyranosyl perchlorate (**7**). The n.m.r. spectrum of **7** (toluene-d_8, −5°) resembles that of **5**; the H-1 and H-2 signals for **7** appeared at positions 0.19 p.p.m. lower and 0.6 p.p.m. higher, respectively, than those of the corresponding protons in **5**.

In order to confirm the structures of the glycosyl perchlorates, methanolyses and reaction with tetraethylammonium chloride were carried out. As shown in Table III, methanolysis of **6** (obtained from both **2** and **3**) in toluene, ether, or sulfur dioxide at −20° gave identical results, in which methyl 3,4,6-tri-*O*-acetyl-2-chloro-2-deoxy-β-D-glucopyranoside (**9**) was obtained predominantly. These results also indicate that the perchlorate obtained is the ester and not the ion. In toluene and ether, the proportion of **9** decreased, and that of the α-D-glucopyranoside **8** increased, on raising the reaction temperature and reducing the amount of methanol; **8** preponderated when the methanolysis was carried out with 1.6 molar equivalents of methanol at 30°. It is known that organic perchlorate esters react similarly. For example, methyl perchlorate *p*-alkylates anisole, and benzyl perchlorate reacts rapidly with benzene to give a high yield of diphenylmethane. The ready formation of diphenylmethane has been ascribed to the high stability of the benzyl cation[2]. In the present case, it is reasonable that the extent of formation of oxocarbonium ion **1**, which reacts with methanol to give mainly methyl α-D-glucopyranoside, increases at a relatively high reaction temperature and a smaller amount of methanol since the ion is also known to be stable. Failure to detect a glucosyltoluene in these reactions may be ascribed to the difference in nucleophilicity between methanol and toluene.

Compound **6** reacted with tetraethylammonium chloride in acetonitrile–ether at −20° within 5 min to give a mixture of **2** and **3** (ratio 3.9:96.1 by g.l.c.), from which **3** was obtained in 75% yield. The reaction did not proceed when **2** was similarly treated with tetraethylammonium chloride for 4 h at 0°. Lemieux[4] reported that 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl chloride (**20**) was obtained by treatment of 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide with tetraethylammonium chloride in acetonitrile. Our method *via* perchlorate is more general for the preparation of unstable β-D-glucopyranosyl chlorides from the corresponding α-D-glucopyranosyl halides. The above data showed that **6** was almost completely pure α-D-glucopyranosyl

TABLE III

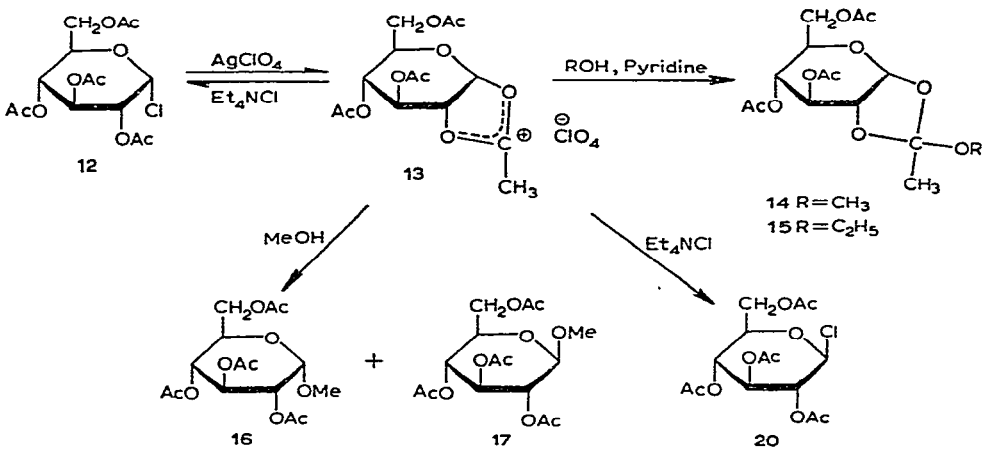
RESULTS OF METHANOLYSES OF GLYCOSYL PERCHLORATES[a]

Starting compound	*Solvent*	*MeOH (moles/mole)*	*Temperature (degrees)*	*Proportion[b] of methyl glycosides*		*Total yield (%)*
				α	*β*	
2	Toluene	85	−20	19.0	81.0	89
		85	0	36.6	63.4	88
		1.6	0	43.1	56.9	73.5
		370	30	23.0	76.0	89.3
	Ether	85	−20	18.1	81.9	92.7
		85	0	25.6	74.4	86.7
		1.6	0	72.2	27.8	90.1
		1.6	30	82.6	17.4	97.5
		370	30	10.4	89.6	88.6
	Sulfur dioxide	85	−20	22.5	77.5	81.5
3	Toluene	85	−20	20.1	79.9	92.8
		85	0	38.6	61.4	83
		1.6	0	44.5	55.5	78.6
		1.6	30	47.6	52.6	84.9
	Ether	85	−20	19.0	81.0	95.3
		85	0	23.9	76.1	90
		85	30	29.2	70.8	78.1
		1.6	0	71.6	28.4	90.3
		1.6	30	82.2	17.4	83.2
	Sulfur dioxide	85	−20	19.6	80.4	82.9
4	Toluene	85	−20	83.0	17.0	93.4
		85	0	86.6	13.4	78.5
		1.6	30	97.2	2.8	83.4
	Ether	85	−20	81.6	18.4	92.5
		85	0	83.0	17.0	88.5
		1.6	30	93.4	6.6	88.4
		370	30	78.0	22.0	72.5
	Sulfur dioxide	85	−20	96.4	3.6	86.5
5	Toluene	85	−20	83.6	16.4	96.5
		85	0	85.6	14.4	84
	Ether	85	−20	82.4	17.6	92.7
		85	0	84.9	15.1	87.1
	Sulfur dioxide	85	−20	94.7	5.3	86.4
2	Methanol		35	5.7	94.3[c]	
			20	18.0	82.0[d]	
3	Methanol		35	100	0[c]	
			20	86.0	14.0[d]	
4	Methanol		35	63.2	36.8[c]	
			20	55.0	45.0[d]	
5	Methanol		35	100	0[c]	
			20	96	4[d]	

[a]The glycosyl perchlorates were prepared by using 100 mg of the glycosyl chlorides and 4.0 ml of 148mM $AgClO_4$ in toluene, 4 ml of 80mM $AgClO_4$ in ether, or 66 mg of $AgClO_4$ suspended in 4 ml of sulfur dioxide under anhydrous conditions at 0 °C. [b]Analyzed by g.l.c. [c]Obtained by the methanolyses of the glycosyl chlorides (2–5) in methanol at 35 ±0.1° for 16.5 h, and acetylation of the products. [d]Obtained by the Koenigs–Knorr reaction of the glycosyl chlorides (2–5) with $AgClO_4$–Ag_2CO_3.

perchlorate. This may be attributed to the high reactivity and large anomeric effect of the perchlorate ester, which is expected from the large electronegativity of the perchlorate group.

By comparison with the glucose series, the course of the reaction in the mannose series was greatly changed. As shown in Table III, methanolysis of **7** gave predominantly methyl 3,4,6-tri-*O*-acetyl-2-chloro-2-deoxy-α-D-mannopyranoside (**10**), regardless of the conditions used. The proportion of **10** increased to over 90% when 1.6 molar equivalents of methanol were used in toluene and ether at 30° or when a large excess of methanol was used in sulfur dioxide at −20°. These results may be attributed to the easier formation of the mannosyl oxocarbonium ion, owing to so-called Δ2 effect[5]. The reaction of **7** with tetraethylammonium chloride gave **4** and **5** (ratio of 82.6:17.4) in 72.8% yield. Isolation by preparative t.l.c. gave **4** and **5** in 48 and 10% yields, respectively.



It was anticipated that 1,2-*O*-acetoxonium-3,4,6-tri-*O*-acetyl-α-D-glucopyranose perchlorate (**13**) would be obtainable when 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl chloride (**12**) was treated with silver perchlorate. In fact, **13** was obtained as a hygroscopic, unstable, crystalline solid, and the reaction rate followed the sequence nitromethane ≈ sulfur dioxide > ether > toluene. In toluene at 0°, decomposition of **13** was observed before all the starting chloride had disappeared. In ether at 0°, the rate of decomposition was slower but the mixture became brown-coloured when kept for 20 h at 0°. Isolation of the product gave a mixture of D-glucopyranose pentaacetates (50% yield), from which α-D-glucopyranose pentaacetate was isolated in 18% yield. Although a similar phenomenon was also observed when 1,2-*O*-acetoxonium-3,4,6-tri-*O*-acetyl-α-D-glucopyranose tetrafluoroborate was kept in 1,2-dichloroethane[1], the formation of the pentaacetates cannot yet be interpreted fully. Although the n.m.r. spectrum (nitromethane-d_3, −20°) of **13** was not well-resolved, the H-1 signal appeared at τ 2.63 as a doublet ($J_{1,2}$ 7.5 Hz) and the signal of the methyl group on the cationic carbon appeared at τ 6.94 as a singlet. On the other hand, in the n.m.r. spectrum of 3,4,6-tri-*O*-acetyl-1,2-*O*-(1-ethoxyethylidene)-α-D-glucopyranose

(**15**), the H-1 signal appeared at τ 4.28 as a doublet ($J_{1,2}$ 5 Hz) and the signal of the methyl group on the orthoester appeared at τ 8.3 as a singlet. Thus, the H-1 and the methyl protons on the acetoxonium ion of **13** resonated at positions 1.65 and 1.36 p.p.m. lower than the corresponding protons of **15**. The H-1 and methyl protons of 1,2-*O*-acetoxonium-3,4,6-tri-*O*-acetyl-α-D-glucopyranose tetrafluoroborate were observed[6] at τ 2.64 as a doublet ($J_{1,2}$ 7 Hz) and 6.92 as a singlet, respectively.

Treatment of **13** with methanol and ethanol in the presence of pyridine gave the corresponding methyl and ethyl orthoesters (**14** and **15**) in 67.3 and 60% yields, respectively. It is of interest to note that the proportion of methyl 2,3,4,6-tetra-*O*-acetyl-α- (**16**) and -β-D-glucopyranosides (**17**) obtained by the methanolysis of **13** with two molar equivalents of methanol varies with the solvent used. The results are summarized in Table IV. In ether, t.l.c. of the product showed mainly two spots. From the faster-moving zone, almost pure **17** (21%) was obtained, and from the slower-moving zone, a partially hydrolyzed syrup was obtained in 55.5% yield. Acetylation of the syrup gave **16** and **17** in a ratio of 60.6:39.4. The syrup is considered to be a mixture of methyl 3,4,6-tri-*O*-acetyl-α- (**18**) and -β-D-glucopyranosides (**19**). Lemieux[7] obtained a mixture of **18** and **19** in the reaction of 3,4,6-tri-*O*-acetyl-1,2-*O*-(1-alkoxyethylidene)-α-D-glucopyranose with a small amount of alcohol in the presence of *p*-toluenesulfonic acid. In nitromethane and sulfur dioxide, anomerization of the product was rapid, and after 3 h at 0° almost pure **16** was obtained in good yield.

TABLE IV

METHANOLYSES OF 1,2-*O*-ACETOXONIUM-3,4,6-TRI-*O*-ACETYL-α-D-GLUCOPYRANOSE PERCHLORATE (**13**) AND 2,3,4,6-TETRA-*O*-ACETYL-α-D-GLUCOPYRANOSYL CHLORIDE (**12**) WITH TWO MOLAR EQUIVALENTS OF METHANOL AT 0°

Compound	*$AgClO_4$ (moles/mole)*	*Reaction time (min)*	*Solvent*	*Ratio* **16** *to* **17**[a]	*Total*[b] *yield (%)*
13		60	Ether	42.4:57.6	78
13		5	CH_3NO_2	53:47	55.5
13		180	CH_3NO_2	90:10	49.6
13		180	SO_2	>95	53
12	1.2	90	Ether	44:56	77.5
12	1.2	5	CH_3NO_2	43:57	67.7
12	1.2	240	CH_3NO_2	90:10	47
12	1.2	180	SO_2	>95	60
12	1.2	180	SO_2	>95	71[c]

[a]Analyzed by g.l.c. after acetylation of the product. [b]Isolated by t.l.c. [c]400 mg of Drierite (anhydrous calcium sulfate as soluble anhydrite, W. A. Hammond Drierite Co., Xenis, Ohio) was added to 200 mg of **12**.

Treatment of **13** suspended in ether with tetraethylammonium chloride dissolved in acetonitrile gave 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl chloride (**20**) in 54.2% yield.

As shown above, the proportion of **16** and **17** obtained by the methanolysis of **13** varied with the solvent used. When **12** was treated with silver perchlorate in the presence of two molar equivalents of methanol, **16** and **17** were obtained in similar quantity. With sulfur dioxide as the solvent, pure **16** was obtained in 40% yield.

EXPERIMENTAL

Melting points were measured with a Monoscope (H. Boch, Frankfurt, Germany) and are uncorrected. N.m.r. spectra were measured with a Varian A-60 spectrometer. Tetramethylsilane was used as an internal reference unless otherwise stated. Specific rotations were measured with a Perkin–Elmer Model 141 polarimeter. Solvents were evaporated under reduced pressure below 35° with a rotatory evaporator. Silver perchlorate was purified according to a method of Pocker and Kevill[8]. Tetraethylammonium chloride was dissolved in anhydrous chloroform, and the traces of water were azeotropically removed. After cooling, the solution was filtered, and anhydrous benzene was added to the filtrate. The precipitated tetraethylammonium chloride was dried over phosphorus pentaoxide at 100°/1 mmHg for 20 h, and was thus obtained colourless and crystalline.

General procedure for the preparation of glycosyl perchlorates (**6** *and* **7**). — All experiments were carried out in a stream of dry nitrogen. The glycosyl chloride (**2–5**, ~200 mg) was placed in a flask, which was predried at 50°/1 mm Hg and then filled with dry nitrogen, and a solution of silver perchlorate dissolved in anhydrous toluene or ether was added. The mixture was stirred at 0° until the starting chloride disappeared (t.l.c.). In the case of sulfur dioxide, which did not dissolve silver perchlorate, the glycosyl chloride and silver perchlorate were placed in the flask, and sulfur dioxide was added by pipetting at −20°. The mixture was stirred at −20°. In toluene, the reaction was slow, and two molar equivalents of silver perchlorate (2.48 in the case of **2**) were used. Under these conditions, the reactions were complete within 40 min. In ether or sulfur dioxide, 1.1 equivalents of silver perchlorate are enough, and the reactions were complete within 30 and 5 min, respectively. When the reaction mixture in ether was filtered, and concentrated below 0°, both **6** and **7** were obtained as hygroscopic, unstable, crystalline compounds that were homogeneous on t.l.c. They were stable in these solvents below 0° but gradually decomposed at room temperature. For the n.m.r. measurements, the reaction was carried out in toluene-d_8, and the mixture was filtered to remove silver chloride. For the measurement of the specific rotation, the glycosyl chloride (100 mg) was treated with 4.0 ml of 80 mM ethereal silver perchlorate at 0°, the mixture was filtered, and the rotation of the filtrate was measured. The $[\alpha]_D^9$ values of **6** were +191.5° (from **2**) and +203.7° (from **3**). The $[\alpha]_D^9$ value of **7** was +92.6° (from **4** and **5**).

Methanolyses of the perchlorates (**6** *and* **7**). — A sealed ampoule, which contained an appropriate amount of methanol, was placed in the reaction flask for preparing the perchlorate, and after the reaction was complete the temperature of the reaction mixture was adjusted, the ampoule was crushed, and solid potassium

carbonate was added to neutralize perchloric acid formed. The results are summarized in Table III.

G.l.c. analyses of methyl glycosides (**8–11**). — G.l.c. analyses were carried out with a Yanagimoto Gas Chromatograph GCG-550F with a flame-ionization detector and a stainless-steel column (1.5 m × 3 mm i.d.) packed with 1.5% diethylene glycol succinate on Gaschrom *Q* (80–100 mesh) under the following conditions: column temperature, 180°; injection temperature, 200°; carrier gas, nitrogen (14 ml/min, 1.0 kg/cm^2). Methyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside was used as an internal standard. Areas were determined by the product of half-height width and height. Retention times (min) were as follows: **8**, 8.0; **9**, 9.25; **10**, 7.33; **11**, 17.25; internal standard, 12.83.

Reaction of **6** *with tetraethylammonium chloride.* — The reaction mixture obtained from 400 mg of **2** and 16 ml of 80 mM ethereal silver perchlorate for 30 min at 0°, was cooled to −20°. To the mixture was added, with stirring, a solution (at −20°) of 299.2 mg of tetraethylammonium chloride in 4 ml of anhydrous acetonitrile. After 10 min, 20 ml of dichloromethane was added, and the mixture was filtered to remove inorganic salts. The filtrate was washed with water, dilute, aqueous sodium hydrogen carbonate, and water, dried over sodium sulfate, and evaporated. G.l.c. analysis[9], showed that the residue (81.7%) contained **2** and **3** in a ratio of 3.9:96.1. Recrystallization of the residue from ether and light petroleum (b.p. 30–50°) gave 300 mg (75%) of **3**, m.p. 122–123°, $[\alpha]_D^{23}$ +40.2 ±0.8° (*c* 0.931, chloroform).

When **2** was treated with tetraethylammonium chloride in acetonitrile for 4 h at 0°, **3** was not detected by g.l.c., and only **2** was recovered.

Reaction of **7** *with tetraethylammonium chloride.* — Compound **7** obtained from 200 mg of **4** and 8 ml of 80 mM ethereal silver perchlorate for 30 min at 0° was similarly treated with tetraethylammonium chloride in acetonitrile. G.l.c. analysis of the product (72.8%) showed that **4** and **5** were obtained in a ratio of 82.6:17.4. Preparative t.l.c. on silica gel with benzene–ether (1:1) gave **4** and **5** in 48 and 10% yields, respectively.

*Preparation of 1,2-*O*-acetoxonium-3,4,6-tri-*O*-acetyl-α-D-glucopyranose perchlorate* (**13**). — When 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl chloride was treated with silver perchlorate, as described for **6** and **7**, **13** was obtained. Compound **13** is soluble in nitromethane and sulfur dioxide, less soluble in toluene and ether, and is more unstable than **6** or **7**. In toluene at 0°, the decomposition of **13** occurred before the reaction was finished. In ether at 0°, the rate of the decomposition was slower, since the spot of the decomposition product did not appear on a t.l.c. plate until 2 h after the reaction was finished. However, when the reaction mixture was kept for 20 h at 0°, the mixture assumed a dark-brown colour. Isolation of the product by preparative t.l.c. gave penta-*O*-acetyl-D-glucopyranoses in 50% yield, from which pure penta-*O*-acetyl-D-glucopyranose was obtained in 18% yield. In nitromethane and sulfur dioxide at −20°, **13** was more stable. For the n.m.r. measurement, the reaction was carried out in nitromethane-d_3 at −20°, and the mixture was filtered. N.m.r. (60 MHz, CD_3NO_2, tetramethylsilane as an external standard)

data: τ 2.63 (1-proton doublet, $J_{1,2}$ 7.5 Hz, H-1) and 6.94 (3-proton singlet, acetoxonium Me group).

Methanolyses of **13**. — Methanolyses of **13** were carried out as for **6** and **7**. The results are summarized in Table IV. G.l.c. analyses were carried out under the same conditions as for **8–11**, using **9** as an internal standard. The retention times (min) were as follows: **16**, 12.83; **17**, 14.9; **9**, 9.25.

Reaction of **12** *with silver perchlorate in the presence of methanol.* — Compound **12** (200 mg) was treated with 170 mg of silver perchlorate and 35 mg of anhydrous methanol. After isolation of the product in the usual manner, the product was acetylated with acetic anhydride and pyridine. The g.l.c. results are summarized in Table IV. In ether at 20°, 79 mg (39.9%) of **17** was obtained by fractional crystallization. In nitromethane and sulfur dioxide, **16** was obtained in 31.8 and 40% yields, respectively.

Reaction of **13** *with tetraethylammonium chloride.* — To a suspension of **13** in ether (obtained from 360 mg of **12** and 475 mg silver perchlorate in 30 ml of anhydrous ether for 60 min at 0°) was added, with stirring, 5.5 ml of 0.45M tetraethylammonium chloride in anhydrous acetonitrile at −20°. After 1 h at −20°, 50 ml of benzene was added, and the mixture was filtered to remove inorganic salts. The filtrate was washed with cold water (4 times), dried, and evaporated. The residue was crystallized from ether–light petroleum, with seeding, to give 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl chloride[10] (**20**; 195 mg, 54.2%), m.p. 93–96°. One recrystallization from the same solvent system gave the pure sample, m.p. 97–99°, $[\alpha]_D^{23}$ −6.5 ±5° (*c* 1, chloroform) (lit.[10], m.p. 99–100°, $[\alpha]_D^{17}$ −13° (chloroform).

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