method of Tejima, *et al.*,[20] by comparison of rotation value and infrared spectrum and by mixture melting point determination.

Another crystalline compound (**9**) was obtained as fine needles: mp 78–79°; $[\alpha]^{24}D$ +89.5 ± 1.3° (*c* 0.966, $CHCl_3$); λ_{max}^{Nujol} 1734 (*O*-acetates), 1691 (*S*-acetate), and 1657 cm^{-1} (C=C, weak); CD max $[\theta]_{265}$ +2090°, $[\theta]_{228}$ −6760°, and $[\theta]_{210}$ +26,100° (CH_3OH); nmr (100 MHz) τ 3.84(one-proton multiplet, H_1), 4.08 (two-proton singlet with satellites, H_2 and H_3), 4.73 (one-proton doublet of quartets, $J_{4,5}$ = 6.8 Hz, H_4), 5.79 (two-proton multiplet, 2 H_6), 6.02 (one-proton multiplet, $J_{5,6}$ = 4 Hz, $J_{5,6'}$ = 5.5 Hz), 7.63 (three-proton singlet, SAc), and 7.93 (six-proton singlet, 2 OAc).

Anal. Calcd for $C_{12}H_{16}O_6S$: C, 49.99; H, 5.59; S, 11.12. Found: C, 50.21; H, 5.60; S, 11.14.

1,5-Anhydro-4,6-*O*-benzylidene-2,3-dideoxy-D-*erythro*-hexitol[17] was obtained from **7**, **8**, and **9** by Raney nickel reduction and hydrolysis followed by benzylidation.

Desulfurization of 2 and 3 with Raney Nickel.—To a solution of 348 mg (1 mmol) of **2** dissolved in 4 ml of methanol was added 2.2 ml of freshly prepared Raney nickel[38] and the mixture was refluxed for 20 min. The catalyst was filtered off and the filtrate was evaporated to dryness. The residue was dissolved in ether and the ethereal solution was treated with charcoal to remove the insoluble material. The filtrate showed one spot on a thin layer plate. The solvent was evaporated and the residue (85.5% yield) was partially crystallized when it was dried over phosphorous pentoxide at room temperature under reduced pressure (0.1 mm) for several days. Crystallization was completed by scratching it after addition of small amounts of *n*-hexane and ether. Recrystallization from the same solvent mixture gave the pure **4** as colorless prisms in 60% yield: mp 41–42.5°; $[\alpha]^{24}D$ +34.5 ± 0.7° (*c* 0.985, ethanol), $[\alpha]^{24}D$ +27.7 ± 0.7° (*c* 1.011, $CHCl_3$).

Anal. Calcd for $C_{12}H_{18}O_7$: C, 52.55; H, 6.62. Found: C, 52.72; H, 6.66.

This compound was hydrolyzed with methanolic ammonia, and the product was recrystallized from acetone–ethyl acetate, giving 1,5-anhydro-2-deoxy-D-*arabino*-hexitol (dihydro-D-glucal), mp 87–88°, $[\alpha]^{24}D$ +16.2 ± 0.4° (*c* 1.004, water). Reduction of **1** with platinum black in glacial acetic acid[37,39] followed by fractionation by preparative tlc on silica gel using *n*-hexane–ethyl acetate (7:3) as the developer gave 4,6-di-*O*-acetyl-1,5-anhydro-2,3-dideoxy-D-*erythro*-hexitol (2%) as a syrup and 3,4,6-tri-*O*-acetyl-1,5-anhydro-2-deoxy-D-*arabino*-hexitol (dihydro-D-glucal triacetate) (93.3%), mp 41–42.5°, $[\alpha]^{23}D$ +34.5 ± 0.4° (*c* 1.080, ethanol). The latter compound was found to be identical with **4** by comparison of their ir spectra and by mixture melting point determination. Fischer[13] reported **4** as a syrup, $[\alpha]^{24}D$ +34.5° (EtOH). The former was characterized by converting it into a crystalline 1,5-anhydro-4,6-*O*-benzylidene-2,3-dideoxy-D-*erythro*-hexitol, mp 141.5–142° (lit.[17] mp 137°), $[\alpha]^{25}D$ −4.0 ± 0.8° (*c* 1.032, $CHCl_3$).

Desulfurization of **3** in a similar manner also gave crystalline **4**.

Lithium Aluminum Hydride Reductions of 3,4,6-Tri-*O*-acetyl-2-deoxy-2-thiocyanato-α-D-mannopyranosyl Chloride (5) and -α-D-glucopyranosyl Chloride (6).—To a suspension of 200 mg of lithium aluminum hydride in 4 ml of anhydrous ether was added dropwise a solution of 358 mg of **5**,[6c] $[\alpha]^{23}D$ +98.4°, in 8 ml of anhydrous ether under cooling with ice, and the mixture was stirred for 30 min. Water was added to decompose the excess of lithium aluminum hydride, and the mixture was filtered to remove a precipitate. The precipitate was washed with water. The combined filtrate and washings were evaporated to dryness. The residue was acetylated with 10 ml of pyridine and 5 ml of acetic anhydride. The product was fractionated by preparative tlc on silica gel using benzene–ether (1:1) as the developer. From the upper zone, 218 mg (63.8%) of a syrup was obtained. The syrup was recrystallized from ether–petroleum ether, giving 146 mg (42.8%) of prisms, mp 65–67°, $[\alpha]^{24}D$ −10.4 ± 0.4° (*c* 1.048, $CHCl_3$), which were identical with **2**.

Reduction of **6**[6c] with lithium aluminum hydride in a similar manner gave prisms, mp 59–61°, $[\alpha]^{24}D$ +8.4 ± 0.4° (*c* 0.995, $CHCl_3$) (18.6% yield), which were identical with **3**.

Registry No.—**1**, 2873-29-2; **2**, 20746-41-2; **3**, 20746-42-3; **4**, 13035-12-6; **7**, 22931-86-8; **8**, 4631-35-0; **9**, 23025-38-9; thiolacetic acid, 507-90-5.

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Addition Reactions of Glycals. V.[1] Solvent Effects in the Chlorine Addition to D-Glucal Triacetate[2]

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The four possible isomers of D-glucal triacetate dichloride were obtained in crystalline form by the heterolytic addition of chlorine to D-glucal triacetate (**1**) in various solvents. The structure of the dichlorides were clarified from their nmr spectra and chemical reactions. The proportions of the dichlorides were dependent upon the polarity of the solvent used. In nonpolar solvents such as carbon tetrachloride, diethyl ether, chloroform, dichloromethane, and 1,2-dichloroethane, *cis*-addition products, 3,4,6-tri-*O*-acetyl-2-chloro-2-deoxy-α-D-glucopyranosyl chloride (**2**) and -β-D-mannopyranosyl chloride (**3**), were predominantly obtained. In polar solvents, such as nitromethane and propylene carbonate, *trans*-addition products, 3,4,6-tri-*O*-acetyl-2-chloro-2-deoxy-β-D-glucopyranosyl chloride (**15**) and -α-D-mannopyranosyl chloride (**4**), were predominantly obtained. The logarithms of the ratios of (**2** + **15**)/(**3** + **4**) were linearly related to the dielectric constants ϵ, $(\epsilon - 1)/(2\epsilon + 1)$, and the Et values of the solvents.

It has been reported that the polar addition of chlorine to olefins, such as *cis*- and *trans*-2-butene,[3,4] 1-butene,[4b] *cis*- and *trans*-di-*t*-butylethylene,[5a] cyclohexene,[5b] and pentenes,[5c] proceeded in the *trans* sense. However, since Cristol, Stermitz, and Ramey[6] found that the addition of chlorine to acenaphthylene in nonpolar solvents unexpectedly gave only *cis*-dichloroacenaphthane, several examples of *cis* addition of chlorine were reported. Summerbell and Lunk[7] reported that the addition of chlorine to *p*-dioxene in carbon tetrachloride gave *cis*-2,3-dichloro-*p*-dioxane

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(2) Preliminary communications on portions of this work have appeared: K. Igarashi and T. Honma, *Tetrahedron Lett.*, 755 (1968); Abstracts, the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, No. 27C.
(3) H. J. Lucas and C. W. Gould, *J. Amer. Chem. Soc.*, **63**, 2541 (1941).
(4) (a) R. C. Fahey and C. Schubert, *ibid.*, **87**, 5172 (1965); (b) M. L. Poutsma, *ibid.*, **87**, 2172 (1965).
(5) (a) R. C. Fahey, *ibid.*, **88**, 4681 (1966); (b) M. L. Poutsma, *ibid.*, **87**, 2161 (1965); (c) M. L. Poutsma and J. L. Kartch, *ibid.*, **89**, 6595 (1967).
(6) S. J. Cristol, F. R. Stermitz, and P. S. Ramey, *ibid.*, **78**, 4939 (1956).
(7) R. K. Summerbell and H. E. Lunk, *ibid.*, **79**, 4802 (1957).

TABLE I

CHEMICAL SHIFTS (τ) OF PROTONS OF CHLORINATION PRODUCTS OF D-GLUCAL TRIACETATE AT 100 MHz IN $CDCl_3$[a]

	H_1		H_2		H_3,	H_4,	H_5,	
Compd	e[b]	a[c]	e	a	a	a	a	2 H_6
2	3.84 d			5.84 q	4.45 q	4.90 q	5.57 m	~5.83 m
3		4.40 d	5.45 q		4.94 q	4.60 t	6.24 m	5.81 m
4	3.83 d		5.36 q		4.34 q	4.55 m	~5.61 m	~5.75 m
15		4.69 d		6.07 t	4.74 t	4.94 t	6.14 m	5.69 q, 5.87 q

[a] Observed multiplicities: d, doublet; t, triplet; q, quartet; m, multiplet. In the case of a complex, overlapping, or incompletely resolved multiplet, the chemical shifts given may be approximate values. [b] Equatorial. [c] Axial.

predominantly. Cristol and Bly[8] reported that the chlorination of *trans*-stilbene gave a mixture of the *dl* and *meso* dichloride. de la Mare, Klasseu, and Koenigsberger[9] reported that the addition of chlorine to phenanthrene gave more of *cis*-9,10-dichloro-9,10-dihydrophenanthrene than of the corresponding *trans* dichloride. Fahey and Schubert[4a] reported that the addition of chlorine to *cis*- and *trans*-1-phenylpropylene in various solvents gave a mixture of the dichlorides. Recently, in his extensive studies of chlorine addition to olefins, Poutsma[10] postulated that olefins and chlorine might combine initially to form a complex which was either rearranged to an ion pair, which was committed to polar-product formation, or was treated with more olefins to form a pair of radicals, which initiated chain reactions.

In the sugar field, Fischer, Bergmann, and Schotte[11] investigated the addition of chlorine to D-glucal triacetate (**1**) in carbon tetrachloride and isolated a crystalline compound named triacetyl glucal dichloride. Lemieux and Fraser-Reid[12] clarified the structure of the dichloride as 3,4,6-tri-*O*-acetyl-2-chloro-2-deoxy-α-D-glucopyranosyl chloride (**2**) and explained the result by an oxocarbonium ion mechanism. They also suggested the possibility of a four-centered transition mechanism. Lefar and Weill[13] reinvestigated this addition reaction using chloroform as the solvent and isolated **2** and another crystalline dichloride. They assigned the structure of the latter dichloride as 3,4,6-tri-*O*-acetyl-2-chloro-2-deoxy-α-D-mannopyranosyl chloride from its nmr spectrum. This paper describes the isolation and quantitative analyses of the four possible isomers of the dichloride and discusses the stereochemistry of the addition reaction.

Results

When D-glucal triacetate (**1**) was chlorinated in carbon tetrachloride in a manner described in the literature[11] and the product was fractionated by preparative tlc or column chromatography on silica gel, **2** and another crystalline dichloride (**3**) were obtained in good yield (Scheme I). The melting point and nmr spectrum of **3** were identical with those of 3,4,6-tri-*O*-acetyl-2-chloro-2-deoxy-α-D-mannopyranosyl chloride assigned by Lefar and Weill.[13] However, we assigned the structure as 3,4,6-tri-*O*-acetyl-2-chloro-2-deoxy-β-D-mannopyranosyl chloride from the rotation value and the nmr spectrum (the results of the nmr spectra of the four isomeric dichlorides are summarized in Tables I and II). In the nmr spectrum at 100 MHz

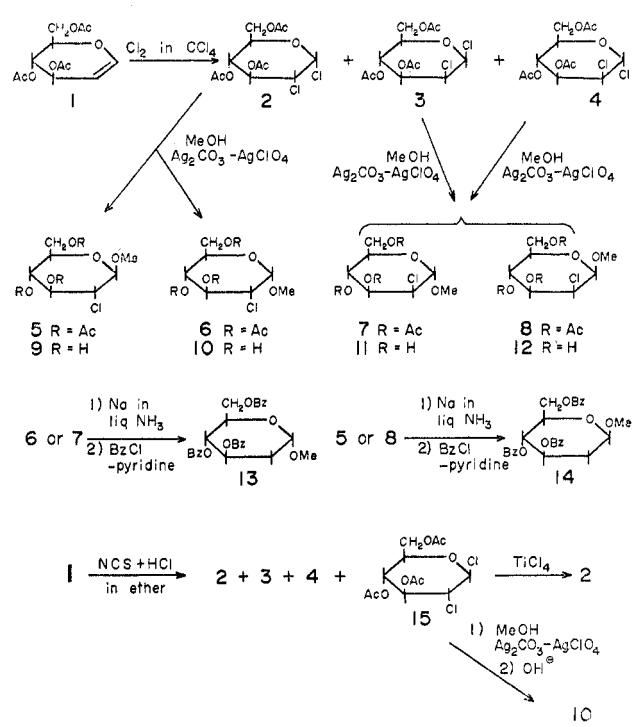
TABLE II

FIRST-ORDER COUPLING CONSTANTS (HERTZ)[a] OF PROTONS OF CHLORINATION PRODUCTS OF D-GLUCAL TRIACETATE

Compd	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{6,6'}$	$J_{6,6'}$
2	3.5	10.5	9.3	10.0			
3	1.2	3.5	9.5	9.5	4.5		
4	1.5	3.0	9.5				
15	9.3	9.3	9.3	9.3	4.6	2.5	12.6

[a] By direct measurement from spectra.

SCHEME I



in deuteriochloroform solution, the H_1 signal appeared at τ 4.40 as a doublet ($J_{1,2}$ = 1.2 Hz). Although Lefar and Weill[13] assigned the structure from the small $J_{1,2}$ value, the α-D- or β-D-manno configuration cannot be assigned with certainty from the $J_{1,2}$ value, since in both cases the $J_{1,2}$ values are very small.[14] If this compound has the α-D-manno configuration, H_1, H_3, and H_5 should appear at positions similar to those of **2**, since H_1 in **2** and **3** is equatorial and H_3 and H_5 in both compounds are axial and are deshielded by the axial chlorine substituent at C_1. In the results obtained, however, all of the H_1, H_3, and H_5 signals

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(9) P. B. D. de la Mare, N. V. Klasseu, and R. Koenigsberger, *J. Chem. Soc.*, 5285 (1961).
(10) M. L. Poutsma, *Science.*, **157**, 997 (1967), and references cited therein.
(11) E. Fischer, M. Bergmann, and H. Schotte, *Chem. Ber.*, **53**, 509 (1920).
(12) R. U. Lemieux and B. Fraser-Reid, *Can. J. Chem.*, **43**, 1460 (1965).
(13) M. S. Lefar and C. E. Weill, *J. Org. Chem.*, **30**, 954 (1965).
(14) R. U. Lemieux and J. D. Stevens, *Can. J. Chem.*, **43**, 2059 (1965).

TABLE III

PRODUCT DISTRIBUTION IN THE CHLORINATION OF D-GLUCAL TRIACETATE (1) IN VARIOUS SOLVENTS[a]

Solvent	ϵ[b]	$(\epsilon - 1)/(2\epsilon + 1)$	*Et*[c]	2	3	4	15	Total yield, %
CCl_4	2.23	0.25	32.5	85.3	8.6	4.5	1.6	94.1
CCl_4[d]	2.23	0.25	32.5	73.6	15.6	6.0	4.8	94.3
Et_2O	4.22	0.34	34.6	77.4	9.8	9.1	3.7	82.8
$CHCl_3$	4.70	0.35	39.1	73.5	10.1	10.5	5.9	95.5
CH_2Cl_2	8.90	0.42	41.1	55.5	14.1	18.7	11.7	92.0
CH_2Cl | CH_2Cl	10.37	0.43	41.9	54.2	18.3	16.4	11.1	92.2
CH_3NO_2	35.57	0.48	46.3	28.1	12.4	40.1	19.4	61.4
PC[e]	65.1	0.49	46.6	8.6	4.1	45.6	41.7	70.3
PC[d,e]	65.1	0.49	46.6	9.4	6.4	45.1	39.1	88.3

[a] Reactions were carried out in oxygen atmosphere in the dark at 2° in a thermostated bath with a constant concentration of 1 (0.073 *M*) except where noted. Each experiment was repeated twice and in each run the areas were determined by the mean values of duplication of the chromatogram. The values shown are the mean values of the above data. [b] Dielectric constant: "Landolt-Börnstein Zahlwerte und Funktionen," 6th ed, Vol. II, Spinger, Berlin, 1959, p 613. [c] *Et* value: C, Reichardt, *Angew. Chem. Intern. Ed. Engl.*, **4**, 29 (1965). [d] The concentration of 1 was 0.365 *M*. [e] Propylene carbonate.

of **3** appeared at *ca.* 0.5 ppm higher than those of **2**. When the structure of **3** is assigned as β-D-mannosyl chloride, all of the discrepancies disappeared. The structure of **3** was further confirmed by the chemical reactions.

When **3** was refluxed with titanium tetrachloride in chloroform for 2.5 hr, another crystalline dichloride (**4**) was obtained in 90% yield. The dextrorotatory value and the nmr spectrum of **4**, in which the H_1, H_3, and H_5 signals appear at positions similar to those of **2** as expected, also support the conclusion that the structure of **4** is 3,4,6-tri-*O*-acetyl-2-chloro-2-deoxy-α-D-mannopyranosyl chloride, *i.e.*, that **3** is the β-D anomer. Methanolysis of **3** using silver carbonate and silver perchlorate as catalysts gave a syrupy methyl 3,4,6-tri-*O*-acetyl-2-chloro-2-deoxy-α-D-mannopyranoside (**7**),[15] which was further confirmed by conversion into crystalline methyl 3,4,6-tri-*O*-benzoly-2-deoxy-α-D-*arabino*-hexopyranoside (**13**)[16] by reduction with sodium in liquid ammonia followed by benzoylation, and another methyl mannoside (**8**) in 88.5 and 3.2% yields, respectively. The structure of **8** was proved to be that of methyl 3,4,6-tri-*O*-acetyl-2-chloro-2-deoxy-β-D-mannopyranoside from the elemental analyses of **8** and its deacetylated product (**12**), the nmr spectrum, and its conversion into methyl 3,4,6-tri-*O*-benzoyl-2-deoxy-β-D-*arabino*-hexopyranoside (**14**).[16] Methanolysis of **4** in a similar condition gave **7** and **8** in 50.5 and 37% yields, respectively. These results apparently indicate that the above structural assignments for **3** and **4** are correct.

Methanolysis of **2** gave methyl 3,4,6-tri-*O*-acetyl-2-chloro-2-deoxy-β-D-glucopyranoside (**5**)[15] in 81% yield. Deacetylation of the mother liquor and fractionation of the product gave a small amount of a deacetylation product of **5** and another crystalline methyl glucopyranoside (**10**) in 15% yield based on **2**. Acetylation of **10** gave a syrupy acetate (**6**). The structure of **10** was proved to be that of methyl 2-chloro-2-deoxy-α-D-glycopyranoside from the elemental analyses, the large dextrorotatory value, the nmr spectrum of the acetate, and conversion into **13**.

Kent, *et al.*,[17] and Hall and Manville[18] reported that the reaction of **1** with *N*-bromosuccinimide and hydrogen fluoride gave 3,4,6-tri-*O*-acetyl-2-bromo-2-deoxy-α-D-mannopyranosyl fluoride and -α-D-glucopyranosyl fluoride as the major products. When **1** was chlorinated with *N*-chlorosuccinimide and hydrogen chloride and the product was fractionated, **2**, **3**, **4**, and another crystalline dichloride (**15**) were obtained in 15.7, 4.4, 1.4, and 10.7% yields, respectively. The structure of **15** was proved to be that of 3,4,6-tri-*O*-acetyl-2-chloro-2-deoxy-β-D-glucopyranosyl chloride from the nmr spectrum and conversion into **2**.

As the four possible isomers of the dichloride were obtained in crystalline form, the quantitative analysis of the dichlorides using glpc techniques was investigated. Up to now there has been no report of glpc analysis of glycosyl halide, probably because of the instability. We found that the four isomeric dichlorides could quantitatively be analyzed when a rather short column was used at relatively low temperature. Despite the fact that, even under these conditions, the peaks of **2**, **4**, and **15** did not resolve completely and very small amounts of **3** and **15** were anomerized to **4** and **2**, respectively, it was found that the calculation by a method of Bartlet and Smith[19] gave a satisfactory result. The results obtained from several mixtures of the known amounts of the dichlorides agreed with the calculated values within ±1%. We also found the interesting fact that the proportion of the dichlorides was changed with the polarity of the solvent used. The results are summarized in Table III. All of the reactions were carried out in oxygen atmosphere in the dark at 2° with a constant concentration of **1** (0.073 *M*) unless otherwise stated, and chlorocyclohexane could not be detected in any measurable extent in the product when the reactions were carried out with the addition of cyclohexane. These facts show that the reactions do not proceed *via* a free-radical process.[20] The four isomeric dichlorides were not affected to any measurable extent under the reaction condition in all solvents. This fact shows that the reactions are kinetically controlled. In non-

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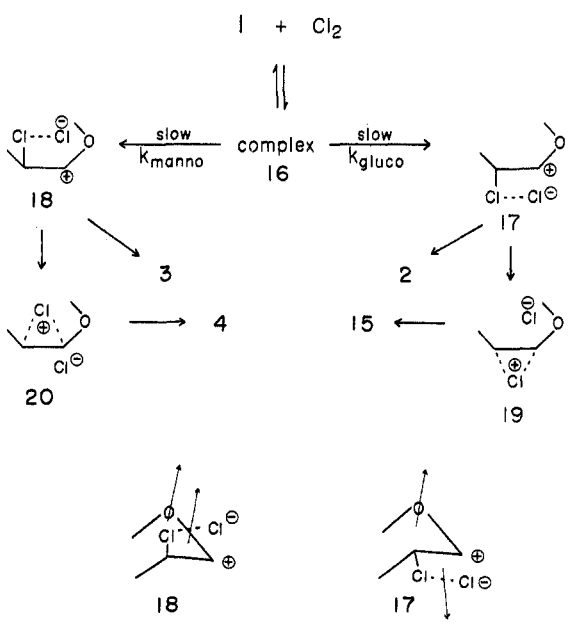
(16) K. Igarashi and T. Honma, *J. Org. Chem.*, **32**, 2521 (1967).
(17) P. W. Kent, F. O. Robson, and V. A. Welch, *J. Chem. Soc.*, 3273 (1963); J. C. Campbell, R. A. Dwex, P. W. Kent, and C. K. Prout, *Chem. Commun.*, 34 (1968).
(18) L. D. Hall and J. F. Manville, *Chem. Commun.*, 35 (1968).
(19) J. C. Bartlet and D. M. Smith, *Can. J. Chem.*, **38**, 2057 (1960).
(20) M. L. Poutsma and R. L. Hinman, *J. Amer. Chem. Soc.*, **86**, 3807 (1964).

polar solvents, *cis* dichlorides, **2** and **3**, were predominantly obtained. Conversely, in polar solvents, *trans* dichlorides **4** and **15** were predominantly obtained. With increasing solvent polarity, the proportion of *cis* dichlorides was decreased and that of *trans* dichlorides was increased. It is interesting to note that the proportion of **3** in the *cis* products is increased with increasing solvent polarity. In carbon tetrachloride, the product ratio was not affected when the reaction was carried out with a concentration of less than 0.073 *M* **1**, but the amounts of the *trans* dichlorides and **3** were increased when the reaction was carried out with a concentration of 0.365 *M* of **1**. These results are reasonable, since it was observed that the dielectric constant of the solution in the former case did not change compared with that in 0.073 *M* **1** but that in the latter case was found to increase. In the case of polar propylene carbonate, such difference could not be observed, since the change of the concentration of **1** did not affect the polarity of the solution.

Discussion

With these results at hand, we would like to discuss the stereochemistry of the chlorine addition to **1**. As shown in Table III, the addition reactions are not stereospecific, but *cis* and *trans* additions with higher stereoselectivity are observed in carbon tetrachloride and propylene carbonate, respectively. The results can be interpreted by a mechanism[21] which involves rapid, reversible formation of a chlorine–olefin complex (**16**) followed by rate-determining ionization to ion pairs, **17** and **18**, in which the chlorine ion is associated on the same side of the original plane from which chlorine attack first occurred (Scheme II). Collapse of **17** and **18** give *cis*-addition products **2** and **3**, respectively. Alternatively, **17** and **18** may rearrange to free ions **19** and **20**, respectively, in which the chlorine ion is now on the opposite side of the plane. The free ions, **19** and **20**, give *trans*-addition products **15** and **4**, respectively. The predominant *cis* addition in nonpolar solvents and *trans* addition in polar solvents are reasonable, since the charge separation is unfavorable in nonpolar solvent but favorable in polar solvent.

SCHEME II



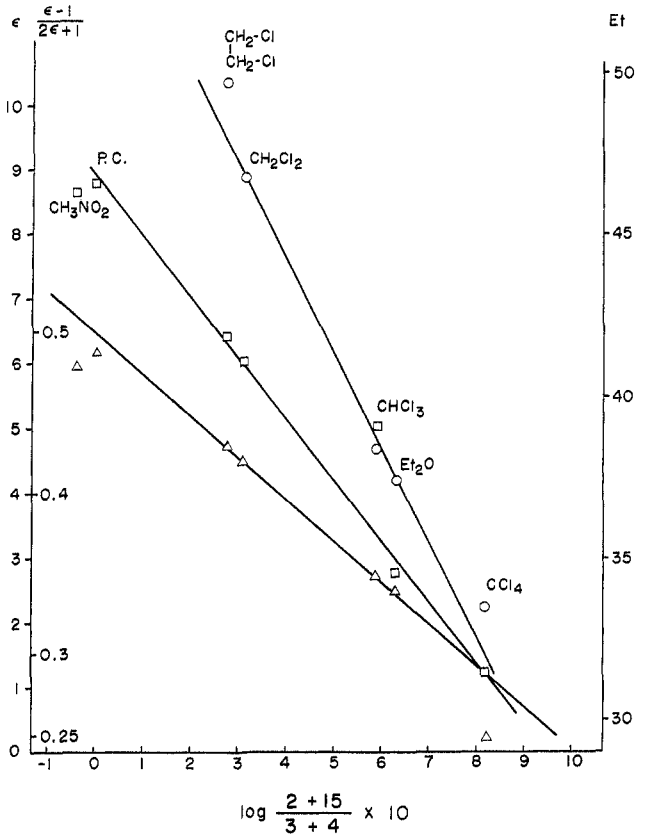


Figure 1.—Correlation of log (2 + 15)/(3 + 4) with solvent parameters: ○, dielectric constants (see Table III, footnote *b*); △, (ε − 1)/(2ε + 1); □, *Et* values.[20]

When the logarithms of the product ratio (2 + 15)/(3 + 4) are plotted against the solvent parameters, dielectric constant ε, (ε − 1)/(2ε + 1), and *Et* value,[20] fairly good linear relationships are observed (Figure 1). When plotted against ε, the points of nonpolar solvents are well related, whereas those of nitromethane and propylene carbonate are seriously off to the upper side of the line. When plotted against Et values, only the chloroform point is not well related. If these points are omitted, it is reasonably assumed that the product ratio (2 + 15)/(3 + 4) is equal to the ratio of the specific rate coefficients k_{gluco}/k_{manno}. Furthermore, the ground-state reactants leading to a pair of isomeric transition states for the formation of the ion pairs **17** and **18** are identical, so that log k_{gluco}/k_{manno} is directly proportional to the free-energy difference between the two transition states. It is interesting to note that the free-energy difference depends upon the polarity of the solvent. If the structures of the transition states resemble those of the ion pairs **17** and **18**, and the ion pairs collapse to **2** and **3**, respectively, with very little change of the conformations, the results can be reasonably explained.

(21) We thank a referee for a comment about the mechanism. We previously[2] proposed a four-centered transition mechanism for this addition reaction, but there is no clear example of it and the process is known to be symmetry forbidden.

Berson, Hamlet, and Muelle[22] reported that in kinetically controlled Diels–Alder reactions of dienophiles, such as methyl acrylate, methyl methacrylate, and methyl *trans*-crotonate, to cyclopentadiene, the logarithm of the ratio of *endo* and *exo* products was linear in *Z* value[23] and the proportion of the *endo* product was increased with increasing solvent polarity, whereas that of the *exo* product was decreased with increasing solvent polarity. The results were explained by the consideration that in the transition state the dipoles of cyclopentadiene and dienophile to form the *endo* product were roughly in the same direction and those to form the *exo* product were roughly in opposite direction. In the present study, in the formation of the ion pair **17**, the group moments of C_5–O–C_1 of the ring and carbon–chlorine at C_1 and C_2 are roughly in opposite direction, and consequently the net moment is expected to be smaller than that in the formation of the ion pair **18**, where the group moments are roughly in the same direction. The observed dipole moments of **2** and **3** were 2.38 and 3.63 D, respectively, in benzene solution. In sugar chemistry, it is well known that the dipole–dipole interactions between the C_5–O–C_1 bonds and the equatorial carbon–halogen bond at the C_1 position are much more unfavorable than those between the C_5–O–C_1 bonds and the axial carbon–halogen bond at C_1 (anomeric effect).[24,25] From these facts it is reasonably understood that the formation of **17** is much more favored than that of **18** in nonpolar solvent and the ratio of **17**/**18** is decreased with increasing solvent polarity, since the formation of **18** in polar solvent is more favorable than in nonpolar solvent. Furthermore, the predominant formation of **4** over **15** is also reasonable, since in comparing the ion pairs **17** and **18** and the *cis*-addition products **2** and **3**, **18** and **3** are less stable than **17** and **2**, respectively, and the rate of rearrangement of **18** to **20** should be faster than that of **17** to **19**.

Let us now consider the structures of the free ions leading to *trans*-addition products. In the chlorination of simple olefins, the stereochemical evidence[3–5] has shown that a chloronium ion was involved. Olah and Bollinger[26] reported that nmr spectra of trimethylethylene and tetramethylethylene chloronium ions supported a bridged structure but nmr spectra of chloro-*t*-butyl cation supported an open structure. On the other hand, the addition of chlorine to *cis*- and *trans*-1-phenylpropene[4a] and methyl *trans*-cinnamate[27] were found to occur *via* an open benzylic cation. In the present study, it is expected that resonance stabilization by the participation of the lone-pair electrons of the ring oxygen would favor an open oxocarbonium ion intermediate.[28,29] It is not clear, however, whether the addition of chlorine to **1** should occur *via* a chloronium ion or an oxocarbonium ion, since phenyl is a better neighboring group than oxygen. The result in propylene carbonate supports chloronium ions. If the addition proceeds *via* open oxocarbonium ions and an anomeric effect governs the direction of chlorine-ion attack at C_1 position,[12] the ratio of **4**/**3** and **2**/**15** should be similar. The facts that **4** (C_1 chlorine, axial) was obtained over **3** (C_1 chlorine, equatorial), while **15** (C_1 chlorine, equatorial) was obtained over **2** (C_1 chlorine, axial) cannot be explained by the open oxocarbonium ion intermediates. If the addition proceeds *via* chloronium ion intermediates, the result, in which **4** and **15** were obtained in almost equal amounts, can reasonably be explained, since there is no remarkable steric hindrance to form **19** and **20** and it is reasonable to consider that the chloronium ions should be opened at the C_1 position regardless of the configuration by the participation of the lone-pair electrons of the ring oxygen.[30] In nonpolar solvents and nitromethane, however, the possibility that oxocarbonium ions are involved, although perhaps not exclusively, as free ions cannot be excluded. It would be very interesting to know a real solvent effect on ion structure, but there does not at present appear to be any evidence on this point.

Experimental Section

Melting points were measured on a Monoscope (H. Boch, Frankfurt am Main, Germany) and were uncorrected. The nmr spectra were obtained, unless otherwise stated, in deuteriochloroform with Varian A-60 and HA-100 spectrometers using tetramethylsilane as an internal standard. The infrared spectra were measured using a Koken Model DS-301 infrared double-monochromatic spectrophotometer. The rotations were measured using a Perkin-Elmer Model 141 polarimeter in chloroform unless otherwise stated. Dipole moments were measured at 25° in benzene solution. Preparative tlc was carried out using silica gel G (E. Merck, AG, Darmstadt, Germany). The zones were detected[31] as bright yellow by ultraviolet light after spraying 0.01% morin solution in methanol, collected, and extracted with ether. Solvents were evaporated below 40° using a rotatory evaporator.

Materials.—D-Glucal triacetate (**1**) was prepared by a method of Helferich, Mulcahy, and Ziegler:[32] mp 55–55.5°; $[\alpha]^{28}D$ −14.1 ± 0.5° (*c* 1.050, EtOH), $[\alpha]^{26}D$ −24.9° (*c* 0.982) [lit.[32] mp 54–55°; $[\alpha]^{19}D$ −15.7° (EtOH)]. Solvents were purified and redistilled just prior to use and center cuts were used. Carbon tetrachloride was washed with concentrated potassium hydroxide solution (twice), water, concentrated sulfuric acid (five times), and water, dried over calcium chloride, and distilled. Diethyl ether was refluxed over metallic sodium for a day, distilled, refluxed over lithium aluminum hydride for a day, and distilled. Chloroform, dichloromethane, and 1,2-dichloroethane were washed with concentrated sulfuric acid, water, 10% sodium hydroxide solution, and water, dried over calcium chloride, and distilled. Nitromethane was washed with 10% sodium bicarbonate, water, sodium bisulfite, water, concentrated sulfuric acid, and water, dried over calcium chloride, and distilled. Propylene carbonate was distilled under reduced pressure twice.

Chlorination of 3,4,6-Tri-*O*-acetyl-D-glucal (1) in Carbon Tetrachloride.—A 10.00-g sample of **1** was dissolved in 80 ml of carbon tetrachloride, and 10 ml of the solvent was evaporated to remove the moisture. To the solution cooled at 0° was bubbled chlorine gas in the dark with stirring until a yellow color appeared.

(22) J. A. Berson, Z. Hamlet, and W. A. Mueller, *J. Amer. Chem. Soc.*, **84**, 297 (1962).

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(26) G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, **89**, 4744 (1967); **90**, 947 (1968).

(27) M. C. Catabiro and M. D. Johnson, *J. Chem. Soc., B*, 565 (1967).

(28) R. U. Lemieux and G. Huber, *Can. J. Chem.*, **33**, 128 (1955).

(29) G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, **89**, 2993 (1967).

(30) It is known that epoxides of enol ether and enol acetate are opened at carbon bearing the enol oxygen regardless of the configurations of the epoxides: C. L. Stevens, E. Farkas, and B. Gillis, *ibid.*, **76**, 2695 (1954); N. S. Leeds, D. F. Fukushima, and T. F. Gallagher, *ibid.*, **76**, 2943 (1954); P. Brigl, *Z. Phys. Chem.*, **122**, 245 (1922).

(31) V. Cerny, J. Joska, and L. Labler *Collect. Czech. Chem. Commun.* **26**, 1658 (1961).

(32) B. Helferich, E. N. Mulcahy, and H. Ziegler, *Chem. Ber.*, **87**, 233 (1954).

After 5 min, nitrogen was bubbled into the solution to remove the excess chlorine, and the solvent was evaporated. The residual syrup was chromatographed on 1 kg of silica gel G with benzene–ether (1:1) as the solvent using a Toyo SF-200A fraction collector. Each eluate was regulated to 10 g of the weight. The residue (9.668 g) from fractions 15–62 was recrystallized from ether–petroleum ether (bp 30–50°) to give 7.867 g (62.5%) of 3,4,6-tri-*O*-acetyl-2-chloro-2-deoxy-α-D-glucopyranosyl chloride (**2**) as colorless, silky needles: mp 99–101°; $[\alpha]^{24}D$ +227.6 ± 2° (*c* 1.023); dipole moment μ = 2.38 D [lit.[12] mp 96–97°; $[\alpha]D$ +218° ($CHCl_3$)]. The nmr spectrum at 60 MHz was identical with that of **2** reported.[12] The residue (3.0 g) from fractions 63–131 was recrystallized from ether–petroleum ether to give 1.571 g (12.5%) of 3,4,6-tri-*O*-acetyl-2-chloro-2-deoxy-β-D-mannopyranosyl chloride (**3**) as colorless needles: mp 145.5–146°; $[\alpha]^{23}D$ −44.0 ± 2° (*c* 1.077); dipole moment μ = 3.63 D. The nmr spectrum at 60 MHz was identical with that of a compound which Lefar and Weill[13] assigned as 3,4,6-tri-*O*-acetyl-2-chloro-2-deoxy-α-D-mannopyranosyl chloride, mp 139–140°.

Anal. Calcd for $C_{12}H_{16}O_7Cl_2$: C, 42.00; H, 4.74; Cl, 20.66. Found: C, 41.84; H, 4.60; Cl, 20.56.

Anomerization of 3,4,6-Tri-*O*-acetyl-2-chloro-2-deoxy-β-D-mannopyranosyl Chloride (3).—A 500-mg sample of **3** was dissolved in 15 ml of chloroform, and 5 ml of the chloroform was evaporated to remove the moisture. To the solution was added 425 mg of titanium tetrachloride and the mixture was refluxed for 2.5 hr, poured onto ice, and extracted with dichloromethane. The dichloromethane solution was washed with water, dried over sodium sulfate, and evaporated. The residue was crystallized from ether–petroleum ether to give 450 mg of crude 3,4,6-tri-*O*-acetyl-2-chloro-2-deoxy-α-D-mannopyranosyl chloride (**4**), mp 57–61°, as colorless plates. A pure sample was obtained, mp 62–62.5°, $[\alpha]^{24}D$ +62.7 ± 0.9° (*c* 1.028). In another run, **4** was obtained from the same solvent as prisms, mp 85.5–86°, $[\alpha]^{21}D$ +62.4 ± 1.0° (*c* 1.041). These are considered to be dimorphous by comparison of nmr and ir spectra.

Anal. Calcd for $C_{12}H_{16}O_7Cl_2$: C, 42.00; H, 4.74; Cl, 20.66. Found: C, 42.22; H, 4.70; Cl, 20.49.

Methanolysis of 3.—A mixture of 250 mg of freshly prepared silver carbonate, 50 mg of silver perchlorate, 1.75 g of Drierite,[33] and 5 ml of anhydrous methanol was stirred in the dark for 10 min, 500 mg of **3** was added, and the mixture was stirred for 2 hr. The insoluble inorganic salts were filtered off and washed with methanol. The combined filtrate and washings were evaporated. The residue was fractionated by preparative tlc with benzene–ether (1:1) as the developer. From the faster moving zone (R_f 0.57), 437 mg (88.5%) of syrupy methyl 3,4,6-tri-*O*-acetyl-2-chloro-2-deoxy-α-D-mannopyranoside (**7**) was obtained. This syrup showed $[\alpha]^{24}D$ +45.1 ± 0.7° (*c* 1.021) [lit.[15] $[\alpha]D$ +45.2° (*c* 1.7, $CHCl_3$)]; nmr (60 MHz) τ 5.14 (one-proton doublet, $J_{1,2}$ = 1.5 Hz, H_1), 5.61 (one-proton quartet, $J_{2,3}$ = 2.0 Hz, H_2), 6.58 (three-proton singlet, OCH_3), 7.92, 7.93, and 7.97 (three-proton singlets, OAc). Deacetylation of **7** with methanolic ammonia gave syrupy methyl 2-chloro-2-deoxy-α-D-mannopyranoside (**11**): $[\alpha]^{24}D$ +81.1 ± 1.1° (*c* 0.947, CH_3OH); nmr (60 MHz, D_2O) τ 5.04 (one-proton doublet, $J_{1,2}$ = 1.5 Hz, H_1), 5.62 (one-proton quartet, $J_{2,3}$ = 3.5 Hz, H_2), and 6.58 (three-proton singlet, OCH_3). From the more slowly moving zone (R_f 0.36), 32 mg of syrup was obtained. The syrup was recrystallized from acetone–*n*-hexane to give 16 mg (3.2%) of crystalline compound, mp 120.5–121°, $[\alpha]^{22.5}$ −86.9 ± 1.2° (*c* 0.976). This was identical with an authentic sample of methyl 3,4,6-tri-*O*-acetyl-2-chloro-2-deoxy-β-D-mannopyranoside (**8**) (see below) by a mixture melting point determination and comparison of their infrared spectra.

Methanolysis of 4.—Methanolysis of 626 mg of **4** and fractionation of the product in a similar manner as described above gave 312 mg (50.5%) of **7** and 228 mg (36.9%) of **8**, mp 119–121°. The pure sample (plates) of **8** was obtained by recrystallization from acetone–*n*-hexane: mp 120.5–121.5°; $[\alpha]^{23}D$ −87.2 ± 1.5° (*c* 1.037); nmr (60 MHz) τ 4.60 (one-proton triplet, $J_{3,4}$ = $J_{4,5}$ = 9.5 Hz, H_4), 4.96 (one-proton quartet, $J_{2,3}$ = 3.5 Hz, H_3), 5.37 (one-proton doublet, $J_{1,2}$ = 1.0 Hz, H_1), 5.53 (one-proton quartet, H_2), 6.42 (three-proton singlet, OCH_3), and 7.90 7.91, and 7.95 (three-proton singlets, OAc).

Anal. Calcd for $C_{13}H_{19}O_8Cl$: C, 46.09; H, 5.65; Cl, 10.47. Found: C, 46.34; H, 5.70; Cl, 10.48.

(33) Anhydrous calcium sulfate as soluble anhydrite, W. A. Hammond Drierite Co., Xenis, Ohio.

Deacetylation of **8** with methanolic ammonia and recrystallization of the product from ethyl acetate gave methyl 2-chloro-2-deoxy-β-D-mannopyranoside (**12**) as plates: mp 134–134.5°; $[\alpha]^{24}D$ −78.6 ± 1° (*c* 1.049, CH_3OH); nmr (60 MHz, D_2O) τ 5.18 (one-proton doublet, $J_{1,2}$ = 1.0 Hz, H_1), 5.52 (one-proton quartet, $J_{2,3}$ = 3.5 Hz, H_2), and 6.43 (three-proton singlet, OCH_3).

Anal. Calcd for $C_7H_{13}O_5Cl$: C, 39.54; H, 6.16; Cl, 16.68. Found: C, 39.23; H, 6.04; Cl, 16.75.

Methyl 3,4,6-Tri-*O*-benzoyl-2-deoxy-α-D-*arabino*-hexopyranoside (13) from 7.—To a solution of 250 mg of **7** dissolved in 10 ml of redistilled liquid ammonia at −50° was added small pieces of metallic sodium with stirring at −50° until the blue color of sodium persisted. The solution was further stirred for 30 min, ammonium chloride was added, and the ammonia was evaporated. The residue was benzoylated with 0.6 ml of benzoyl chloride and 3 ml of pyridine. The product was fractionated by preparative tlc using benzene–ethyl acetate (9:1) as the developer. From the R_f 0.60 portion, 202 mg (55.8%) of crystalline compound was obtained. This was recrystallized from ether–petroleum ether to give colorless needles, mp 110.5–111°, $[\alpha]^{24}D$ +50.9 ± 1.4° (*c* 0.591, CH_2ClCH_2Cl), which were identical with an authentic specimen[16] of **13**, mp 110.5–111°, $[\alpha]^{22}D$ +49.4 ± 2° (CH_2ClCH_2Cl), by a mixture melting point determination and comparison of their infrared spectra.

Methyl 3,4,6-Tri-*O*-benzoyl-2-deoxy-β-D-*arabino*-hexopyranoside (14) from 8.—A similar treatment of **8** as described above gave a crystalline compound, mp 96–97.5°, $[\alpha]^{24}D$ −51.1 ± 2° (*c* 1.040, CH_2ClCH_2Cl), in 60% yield. This was identical with an authentic sample[16] of **14**, mp 95.5–97.5°, $[\alpha]^{22}D$ −53.1 ± 2° (*c* 1.031, CH_2ClCH_2Cl), by a mixture melting point determination and comparison of their infrared spectra.

Methanolysis of 3,4,6-Tri-*O*-acetyl-2-chloro-2-deoxy-α-D-glucopyranosyl Chloride (2).—Methanolysis of 3.0 g of **2** in a manner described above gave a syrupy product. The product was recrystallized from acetone–*n*-hexane to give 2.394 g (81.1%) of methyl 3,4,6-tri-*O*-acetyl-2-chloro-2-deoxy-β-D-glucopyranoside (**5**) as colorless needles, mp 151–156°. Recrystallization from the same solvent gave the pure sample: mp 154–155°; $[\alpha]^{23}D$ +48.6 ± 0.4° (*c* 1.014) [lit.[15] mp 149–150°; $[\alpha]D$ +53° (*c* 1.0, $CHCl_3$)]; nmr (60 MHz) τ 4.75 (one-proton quartet, $J_{2,3}$ = 8.5 Hz, $J_{3,4}$ = 9.0 Hz, H_3), 5.03 (one-proton triplet, $J_{4,5}$ = 9.0 Hz, H_4), 5.58 (one-proton doublet, $J_{1,2}$ = 8.5 Hz, H_1), and 6.42 (three-proton singlet, OCH_3). Deacetylation of **5** gave methyl 2-chloro-2-deoxy-β-D-glucopyranoside (**9**), mp 168–169°, $[\alpha]^{24}D$ −11.9 ± 0.3° (*c* 1.27, H_2O) [lit.[15] mp 164–165°, $[\alpha]D$ −12.9° (H_2O)]. The mother liquor (513 mg) obtained after removal of crystalline **5** was deacetylated with methanolic ammonia at room temperature for 20 hr and the mixture was evaporated. The residue showed two spots on a silica gel thin layer plate using ethyl acetate–methanol (9:1) as the developer. Fractionation of the residue was carried out by the same solvent system. In this case, however, the zones could not be detected by morinn and ultraviolet light and the fractionation was carried out by detecting the zones in a part of the plate with sulfuric acid and cutting the same position of the major part of the plate. Ethyl acetate–methanol (9:1) was used for the extraction of the products. From the faster moving zone (R_f 0.61), a small amount of **9** was obtained. From the more slowly moving zone (R_f 0.51), 279 mg (15%) of crystalline material, mp 139–142°, was obtained. Recrystallization from ethyl acetate gave the pure methyl 2-chloro-2-deoxy-α-D-glucopyranoside (**10**): mp 143–143.5°; $[\alpha]^{24}D$ +182.6 ± 2° (*c* 1.067, CH_3OH); nmr (60 MHz, D_2O), τ 5.07 (one-proton doublet, $J_{1,2}$ = 3.0 Hz, H_1), and 6.57 (three-proton singlet, OCH_3).

Anal. Calcd for $C_7H_{13}O_5Cl$: C, 39.54; H, 6.16; Cl, 16.68. Found: C, 39.60; H, 6.23; Cl, 16.53.

Acetylation of **10** with acetic anhydride and pyridine gave the syrupy acetate (**6**): $[\alpha]^{24}D$ +171.2 ± 2° (*c* 0.972); nmr (60 MHz) τ 4.54 (one-proton quartet, $J_{2,3}$ = 10.5 Hz, $J_{3,4}$ = 9.0 Hz, H_3), 5.01 (one-proton triplet, $J_{4,5}$ = 9.0 Hz, H_4), 5.16 (one-proton doublet, $J_{1,2}$ = 3.5 Hz, H_1), 6.08 (one-proton quartet, H_2), and 6.53 (three-proton singlet, OCH_3).

Methanolysis of the Mother Liquor of 2.—Methanolysis of the mother liquor (1.801 g), which was obtained after removal of crystalline **2** in the chlorination described above and did not contain **3** at all in the nmr spectrum and thin layer plate, was carried out with 900 mg of silver carbonate, 180 mg of silver perchlorate, 6.3 g of Drierite,[33] and 20 ml of anhydrous methanol in a similar manner as described above. The product was frac-

tionated by preparative tlc using benzene–ether (1:1) as the developer. From the faster moving zone (R_f 0.57), 240 mg (3.7% based on 1) of crystalline **5** was obtained. The nmr spectrum of the mother liquor showed that it contained **5–7**.

Chlorination of 1 with *N*-Chlorosuccinimide and Hydrogen Chloride.—A 4.72-g sample of hydrogen chloride gas dried with sulfuric acid was bubbled into 20 ml of anhydrous ether at −75°, and to the solution was added portionwise a powdered mixture of 2.50 g of **1** and 1.50 g of *N*-chlorosuccinimide over a period of 10 min with stirring at −75°. After 5 min, 50 ml of cold dichloromethane was added, and the solution was washed with ice-cold water, cold, saturated sodium bicarbonate, and water, dried over sodium sulfate, and evaporated to dryness. The residue was chromatographed on 500 g of silica gel with benzene–ether (1:1) as the developer using a Toyo SF-200A fraction collector. Each eluate was regulated to 10 g of weight. Fractions 1–13 (292 mg) were not studied further. Fractions 14–18 (1.244 g) were recrystallized from ether–petroleum ether to give 376 mg of **2**, mp 99–101°. The mother liquor was fractionated by preparative tlc using benzene–ether (1:1) as the developer. The chromatogram appeared as only one but a somewhat long and narrow zone. The zone was divided into three parts. From the upper part, 41 mg (1.4%) of **4**, mp 61–62.5°, was obtained after recrystallization from ether–petroleum ether. From the middle part, 28 mg of **2**, mp 99–101°, was obtained. From the lower part, 35 mg of 3,4,6-tri-*O*-acetyl-2-chloro-2-deoxy-β-D-glucopyranosyl chloride (**15**), mp 118–122°, was obtained after recrystallization from ether–petroleum ether. Fractions 19–28 (675 mg) were recrystallized from ether–petroleum ether to give 293 mg of **15**, mp 119–122°. The mother liquor was further fractionated by preparative tlc as described above. From the upperzone, 64 mg of **2**, mp 98–100°, was obtained. The lower zone was not treated further. From fractions 21–54, 131 mg (4.4%) of **3**, mp 143–145°, was obtained. Total yields of **2** and **15** were 468 mg (15.7%) and 321 mg (10.7%), respectively. Compound **15** was recrystallized from the same solvent, giving the pure sample as prisms, mp 122.5–123°, $[\alpha]^{24}D$ +42.7 ± 0.7° (*c* 1.089).

Anal. Calcd for $C_{12}H_{16}O_7Cl_2$: C, 42.00; H, 4.74; Cl, 20.66. Found: C, 42.12; H, 4.75; Cl, 20.46.

Anomerization of 3,4,6-Tri-*O*-acetyl-2-chloro-2-deoxy-β-D-glucopyranosyl Chloride (15).—To a solution of 50 mg of **15** in 5 ml of chloroform was added 100 mg of titanium tetrachloride and the mixture was refluxed for 3.5 hr. The mixture was poured onto ice and the organic layer was separated. The water layer was extracted with chloroform. The combined chloroform solutions were washed with saturated sodium bicarbonate and water, dried, and evaporated. The residue was crystallized from ether–petroleum ether, giving 35 mg (70%) of colorless, silky needles, mp 99–100°, which were identical with **2** described above.

Methanolysis of 15.—Methanolysis of 90 mg of **15** was carried out as described above. The product was dissolved in 4 ml of anhydrous methanol, and to the solution ammonia gas was bubbled in at −20° for 15 min. The solution was allowed to stand at room temperature for 20 hr. The excess of ammonia and methanol was evaporated and the residue was purified by preparative thin layer chromatography using ethyl acetate–methanol (9:1) as the developer. In this case the zones could not be detected by morin and ultraviolet light and the separation was carried out as described in the case of methanolysis of **2**, From the upper zone (R_f 0.61), 3 mg (5%) of crystalline material. mp 168–169°, was obtained after recrystallization from ethyl acetate. This was identical with **9** described above. From the lower zone (R_f 0.51), 33.5 mg (60%) of crystalline material was obtained after recrystallization from ethyl acetate. This was identical with **10** described above.

Chlorination of 1 in Propylene Carbonate.—Chlorine gas was slowly bubbled into a solution of 2.0 g of **1** in 40 ml of propylene carbonate in the dark at 0° with stirring until a yellow color appeared. The solution was poured onto ice and the mixture was extracted with carbon tetrachloride. The carbon tetrachloride solution was washed with water, dried, and evaporated. The residue was fractionated by chromatography on 250 g of silica gl G using a Toyo SF-200A fraction collector and repeated preparative tlc using benzene–ether (1:1) as the solvent as described in the chlorination of **1** with *N*-chlorosuccinimide and hydrogen chloride. In one run, **2–4** and **15** were obtained in 0.8, 3.6, 18.3, and 17.8% yields, respectively.

Quantitative Analysis of the Chlorination Products in Various Solvents.—*Ca.* 100 mg of **1** was accurately weighed and dissolved in a freshly purified solvent. The solution measured just 5 ml in a foil-covered 25-ml flask equipped with a gas-inlet tube and a drying tube. All glass apparatus was dried in an oven and assembled hot under a slow stream of oxygen before the solution was made. For a higher concentration run, about 700 mg of **1** was dissolved in a solvent and the solution, was made to 5 ml. The solution was cooled to 2° using a thermostated bath with a slow stream of oxygen to prevent the entering of moisture. Chlorine was condensed in a calibrated tube using a Dry Ice–acetone bath and swept into the reaction mixture by a stream of oxygen (30 ml/min) which was passed through concentrated sulfuric acid. The reaction was complete in 2–2.5 min, the excess chlorine was removed by bubbling oxygen, and the appropriate amount of the internal standard, penta-*O*-acetyl-β-D-mannopyranose, accurately weighed, was added. The solvent was evaporated, the residue was dissolved in carbon disulfide containing a small amount of dichloromethane, and the solution was analyzed by glpc. In the case of propylene carbonate, carbon disulfide was added to the solution without the evaporation because of the high boiling point of propylene carbonate and the solution was analyzed.

Analyses were carried out with a Yanagimoto gas chromatograph GCG-550F with a flame ionization detector using 75 cm × 3 mm i.d. stainless steel column packed with 1.5% XE-60 on Gaschrom Q (80–100 mesh) under the following conditions: column temperature, 155°; injection temperature, 155–160°; nitrogen as the carrier gas, 1.03 kg/cm², 89 ml/min; hydrogen, 30 ml/min. Areas were determined by a method of Bartlet and Smith.[19] Retention times in minutes follow: **4**, 2.45; **2**, 3.58; **15**, 4.25; **3**, 8.50; the internal standard, 12.00. Calibration curves for the four isomeric dichlorides were linear and the lines crossed their origins. Under the above conditions, **3** and **15** were anomerized to **4** and **2** in 1.5 and 1.3% yields, respectively. Preliminary experiments with mixtures of known amounts of the dichlorides had a reproducibility of 1% in the absolute value of the per cent of a given component in a given sample for the mixture compositions. To establish identity by glpc analysis, comparisons were made both by retention times and by simultaneous injection of a standard with the mixture to observe peak enhancement.

The results are summarized in Table III. In each solvent the experiment was repeated twice, and in each run areas were shown by the mean value of duplication of the chromatogram. The values shown in Table III are the mean value of the above data.

Registry No.—**1**, 2873-29-2; **2**, 3067-57-0; **3**, 20512-20-3; **4**, 3067-58-1; **5**, 23025-29-8; **6**, 20513-90-0; **7**, 22931-82-4; **8**, 20512-22-5; **9**, 14685-78-0; **10**, 20513-89-7; **11**, 20512-21-4; **12**, 20513-88-6; **13**, 13145-23-8; **14**, 13145-18-1; **15**, 20513-91-1.