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# Reaction of dichloroallose units in a chlorodeoxycellulose with lithium chloride under homogeneous conditions in *N*,*N*-dimethylacetamide

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**Abstract**

The reaction of methyl 3,6-dichloro-3,6-dideoxy-β-D-allopyranoside with lithium chloride in *N*,*N*-dimethylacetamide (DMA) was studied in relation to the possible conversion of 3,6-dichloro-3,6-dideoxy-D-allose units in a chlorodeoxycellulose during synthesis in a LiCl–DMA solvent system. Methyl 3,6-dichloro-3,6-dideoxy-β-D-glucoside was formed; the reaction was reversible and the equilibrium was on the glucoside side. GLC analysis of the hydrolyzates of chlorodeoxycellulose samples after treatment with LiCl showed that the dichloroallose units were partly converted into 3,6-dichloro-3,6-dideoxy-D-glucose units. A kinetic study showed that the rate of conversion of the dichloroallose unit into the dichloroglucose unit was lower than that of the dichloroalloside into the dichloroglucoside, and the amounts of the two units at equilibrium were calculated to be close to each other. Based on the values of the kinetic parameters obtained, the conversion of the dichloroallose units into the dichloroglucose units during the chlorination of cellulose in LiCl–DMA was estimated to be negligibly small under typical reaction conditions.

## 1. Introduction

Several reagent systems [1–3] have been reported for the chlorination of cellulose to yield chlorodeoxycellulose ("Cell-Cl") samples having ds values with chlorine much higher than 1. These Cell-Cl samples contained 3,6-dichloro-3,6-dideoxyallose ("3,6-$Cl_2$-All") units in addition to 6-chloro-6-deoxyglucose ("6-Cl-

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Glc") units. We reported previously [4] the chlorination of cellulose with *N*-chlorosuccinimide and triphenylphosphine under homogeneous conditions in LiCl–*N*,*N*-dimethylacetamide (DMA). Under appropriate conditions, the ds of chlorine reached 1.9, and 3,6-$Cl_2$-All and 6-Cl-Glc units were present in Cell-Cl samples with high ds values.

A characteristic feature of our chlorination system is that it contained a high concentration of LiCl. Nucleophilic substitution of chlorine atoms in Cell-Cl by chloride ion might have occurred during the chlorination because chloride ion is highly nucleophilic in such polar aprotic solvents as DMA [5]. The same configuration is retained after substitution at C-6, whereas that at C-3 will be inverted. The expected substitution product, 3,6-dichloro-3,6-dideoxyglucose ("3,6-$Cl_2$-Glc"), was not detected by GLC analysis of the hydrolyzates (as trifluoroacetate) of Cell-Cl samples obtained, for example, for 4 h at 70°C or for 1 h at 90°C. However, this does not necessarily mean the absence of 3,6-$Cl_2$-Glc in the hydrolyzates because the GLC behavior of 3,6-$Cl_2$-Glc was not known at that time. We found later [6] that 3,6-$Cl_2$-All units in Cell-Cl were partly converted into 3-chloro-6-bromo-3,6-dideoxyallose and 3,6-dibromo-3,6-dideoxyaldohexose units when the sample was heated under homogeneous conditions in LiBr–DMA for 24 h at 90°C. Although this reaction was not analyzed kinetically, the formation of substitution compounds suggests that the reaction of 3,6-$Cl_2$-All units with LiCl will occur to an appreciable extent at higher temperatures and with longer reaction times, because chloride ion is a stronger nucleophile than bromide ion in DMA [5].

In this paper, we first show that methyl 3,6-dichloro-3,6-dideoxy-β-D-alloside [7] ("Me $Cl_2$-All") is converted into methyl 3,6-dichloro-3,6-dideoxy-β-D-glucoside ("Me $Cl_2$-Glc") by heating in LiCl–DMA. The kinetics of the replacement at C-3 is described next and the result is compared with that of the conversion of 3,6-$Cl_2$-All units in Cell-Cl into 3,6-$Cl_2$-Glc units. The extent of replacement of chlorine at C-3 in Cell-Cl with chloride ion during the chlorination can be estimated for the reaction conditions used [4].

## 2. Results and discussion

*Reaction of Me $Cl_2$-All with LiCl.*—The reaction of Me $Cl_2$-All with LiCl at 80–100°C in DMA yielded a new compound, "Me $Cl_2$-Glc". Its $^1H$ and $^{13}C$ NMR parameters are summarized in Tables 1 and 2, respectively, together with those of Me β-D-glucoside (Me Glc), Me $Cl_2$-All, and methyl 4,6-dichloro-4,6-dideoxy-β-D-galactoside [7] ("Me $Cl_2$-Gal"). All of the peak assignments are based on the correlation observed in $^1H$ homonuclear and $^1H$–$^{13}C$ heteronuclear two-dimensional spectra.

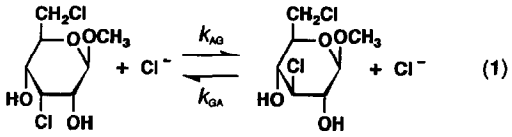
The $J_{1,2}$ value in the $^1H$ NMR spectrum shows that Me $Cl_2$-Glc is in the same $^4C_1$ conformation as other glycosides in the table, and the $J_{2,3}$, $J_{3,4}$, and $J_{4,5}$ values show that protons at C-2–C-5 are all axially oriented [8], confirming the *gluco* configuration. High-field shifts of C-3 (9.79 ppm) and C-6 (16.85 ppm) in the $^{13}C$ NMR spectrum as compared with the corresponding carbons of Me Glc confirm

the substitution of hydroxyl groups by chlorine at these positions [9,10]. The chemical shift of C-2 of methyl 2-chloro-2-deoxy-β-D-glucoside is 10.2 ppm higher than that of Me Glc [9].

Table 3 summarizes the mass fragmentation patterns of Me $Cl_2$-Glc and Me $Cl_2$-All as their trifluoroacetates. These two fragmentation patterns resemble each other and daughter ions formed by the loss of trifluoroacetic acid are characteristic of trifluoroacetyl derivatives [4]. The 9:6:1 triplet ions indicate the presence of two chlorine atoms in the molecule, and the 3:1 doublet at $m/z$ 373 and 375 indicates substitution of the C-6 hydroxyl group by chlorine.

Simple heating of Me $Cl_2$-All in LiCl–DMA causes an $S_N2$ reaction at C-3, and this method should be generally applicable to the synthesis of epimeric chlorodeoxysaccharides, for example, methyl 4,6-dichloro-4,6-dideoxy-β-D-glucoside from Me $Cl_2$-Gal.

*Kinetics of substitution.*—The conversion of Me $Cl_2$-All to Me $Cl_2$-Glc in the presence of LiCl in DMA is considered to be a reversible process;




(1)

**Me $Cl_2$-All** **Me $Cl_2$-Glc**

where $k_{AG}$ and $k_{GA}$ are the rate constants for the substitution at C-3. In this case, the concentration of chloride ion is constant throughout the reaction, and eq. *1* can be analyzed as a simple first-order reversible reaction. The substitution at C-6 is considered to be faster than that at C-3, and is assumed not to affect the substitution at C-3.

If the starting material is Me $Cl_2$-All, the rate equation for this reversible reaction becomes [11],

$$\alpha^G(t)/\alpha^G(\infty) = 1 - \exp\{-k_{AG}[Cl^-]t/\alpha^G(\infty)\} \quad (2)$$

where $t$ is the reaction time, $\alpha^G(t)$ is the mole fraction of Me $Cl_2$-Glc in the dichloroglycosides at time $t$, and $\alpha^G(\infty)$ is that at equilibrium. The rate constant $k_{GA}$ is calculated from $k_{AG}$ and $\alpha^G(\infty)$ as;

$$k_{GA} \cdot \alpha^G(\infty) = k_{AG}[1 - \alpha^G(\infty)] = k_{AG} \cdot \alpha^A(\infty) \quad (3)$$

If the starting material is Me $Cl_2$-Glc, the mole fraction of Me $Cl_2$-All at time $t$ becomes;

$$\alpha^A(t)/\alpha^A(\infty) = 1 - \exp\{-k_{GA}[Cl^-]t/\alpha^A(\infty)\} \quad (4)$$

Fig. 1(a) shows $\alpha^G(t)$ as a function of reaction time at 80, 90, and 100°C with Me $Cl_2$-All as the starting material, and Fig. 1(b) shows $\alpha^A(t)$ starting with Me $Cl_2$-Glc, both determined by GLC analysis on a Dexsil 300 GC column after trifluoroacetylation. The values of the rate constants and the mole fractions at equilibrium were calculated for each temperature by applying a nonlinear least-

Table 1
$^1$H NMR chemical shifts and coupling constants for chlorinated methyl β-glycosides

| Compound | Solvent–standard | $^1$H Chemical shift (δ) | | | | | | | | Coupling constant (Hz) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 6′ | $OCH_3$ | $J_{1,2}$ | $J_{2,3}$ | $J_{3,4}$ | $J_{4,5}$ | $J_{5,6}$ | $J_{5,6'}$ | $J_{6,6'}$ |
| Me Glc | $D_2O$–DSS | 4.36 | 3.24 | 3.47 | 3.36 | 3.44 | 3.91 | 3.71 | 3.56 | 7.9 | 9.2 | 9.2 | 9.8 | 2.5 | 6.1 | 12.2 |
| Me $Cl_2$-Glc | $D_2O$–DSS | 4.47 | 3.49 | 3.86 | 3.74 | 3.74 | 3.96 | 3.87 | 3.57 | 7.9 | 10.4 | 9.8? | | 1.6 | 4.0 | 12.5 |
| | $CDCl_3$–$Me_4Si$ | 4.27 | 3.55 | 3.80 | 3.69 | 3.56 | 3.92 | 3.78 | 3.60 | 7.6 | 9.9 | 9.5 | 9.5 | 2.5 | 6.1 | 11.9 |
| Me $Cl_2$-All | $D_2O$, $D^+$–DSS | 4.77 | 3.77 | 4.75 | 4.10 | 4.13 | 3.95 | 3.86 | 3.58 | 7.9 | 3.0 | 2.5? | 9.5 | 2.4 | 4.0 | 12.5 |
| | $CDCl_3$–$Me_4Si$ | 4.63 | 3.72 | 4.75 | 3.92 | 3.93 | 3.90 | 3.75 | 3.58 | 7.3 | 3.1 | 3.1 | 8.6? | 2.4 | 5.5 | 11.6 |
| Me $Cl_2$-Gal | $D_2O$-DSS | 4.41 | 3.57 | 3.94 | 4.54 | 4.12 | 3.78 | 3.75 | 3.57 | 7.9 | 9.8 | 3.7 | < 0.6 | 7.5 | 5.9 | 11.6 |
| | $CDCl_3$–$Me_4Si$ | 4.24 | 3.70? | 3.84 | 4.53 | 3.87 | 3.75 | 3.72 | 3.58 | 7.9 | 9.7? | 3.6 | < 0.6 | 7.4 | 6.7 | 11.0 |

Table 2
$^{13}C$ NMR chemical shifts for chlorinated methyl β-glycosides

| Compound | Solvent–standard | $^{13}C$ Chemical shift (ppm) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | $OCH_3$ |
| Me Glc | $D_2O$–DSS | 105.79 | 75.65 | 78.34 | 72.22 | 78.47 | 63.33 | 59.76 |
| Me $Cl_2$-Glc | $D_2O$–DSS | 106.14 | 76.18 | 68.55 | 73.16 | 78.00 | 46.48 | 60.11 |
| | $CDCl_3$-$Me_4Si$ | 103.88 | 73.87 | 67.01 | 71.74 | 75.77 | 43.94 | 57.39 |
| Me $Cl_2$-All | $D_2O$–DSS | 103.64 | 71.78 | 69.07 | 69.07 | 75.03 | 46.64 | 60.03 |
| | $CdCl_3$–$Me_4Si$ | 101.09 | 70.21 | 66.22 | 67.96 | 74.16 | 44.12 | 57.21 |
| Me $Cl_2$-Gal | $D_2O$–DSS | 106.65 | 72.88 | 74.23 | 64.86 | 76.13 | 45.16 | 60.02 |
| | $CDCl_3$–$Me_4Si$ | 104.38 | 71.55 | 72.48 | 61.41 | 73.96 | 42.07 | 57.40 |

Table 3
Mass fragmentation patterns of Me $Cl_2$ – Glc and me $Cl_2$-All as trifluoroacetates

| Fragment [a] | $m/z$ [b] | Relative abundance (%) | |
|---|---|---|---|
| | | Me $Cl_2$-Glc | Me $Cl_2$-All |
| $M^+$ | 422(t) | 0.0 | 0.0 |
| M – H | 421(t) | 0.6 | 0.8 |
| M – Cl | 387(d) | 9.1 | 21.2 |
| M – $CH_2Cl$ | 373(d) | 0.6 | 1.8 |
| 373 – MeOH | 341(d) | 0.0 | 0.4 |
| 387 – $HCOOCH_3$ | 327(d) | 28.0 | 52.6 |
| $C_4H_4(OCOCF_3)_2(OCH_3)$ | 309(s) | 3.9 | 6.2 |
| 327 – HCl | 291(s) | 12.3 | 20.8 |
| $C_3H_3(OCOCF_3)_2$ | 265(s) | 1.8 | 3.8 |
| 373 – $CF_3COOH$ | 259(d) | 0.7 | 0.9 |
| 309 – $HCOOCH_3$ | 249(s) | 1.0 | 1.2 |
| $C_4H_4Cl(OCOCF_3)(OCH_3)$ | 231(d) | 0.3 | 0.8 |
| 327 – $CF_3COOH$ | 213(d) | 30.2 | 46.2 |
| 213 – HCl | 177(s) | 27.4 | 40.3 |
| $C_2H_2(OCOCF_3)(OCH_3)$ | 170(s) | 10.4 | 11.1 |
| $CH(OCOCF_3)(OCH_3)$ | 157(s) | 31.4 | 40.0 |
| $C_3H_4(OCOCF_3)$ | 153(s) | 11.6 | 11.6 |
| | 149(s) | 11.2 | 13.9 |
| 249 – $CF_3COOH$ | 135(s) | 1.7 | 2.5 |
| | 129(s) | 10.6 | 13.3 |
| | 117(s) | 16.7 | 19.4 |
| $C_5H_4Cl$ | 99(d) | 29.4 | 30.4 |
| $CF_3CO$ | 97(s) | 14.2 | 14.6 |
| | 89(s) | 8.5 | 9.8 |
| $C_3H_4O(OCH_3)$ | 87(s) | 9.8 | 6.3 |
| $C_5H_5O$ | 81(s) | 37.1 | 42.9 |
| | 77(s) | 9.8 | 10.1 |
| $C_3H_2Cl$ | 73(d) | 14.0 | 11.7 |
| $CF_3$ | 69(s) | 100 | 100 |

[a] Some of the assignments are tentative.
[b] Mass numbers are based on $^{35}Cl$: t, 9:6:1 triplet at $m$, $m+2$, and $m+4$; d, 3:1 doublet at $m$ and $m+2$; s, singlet.

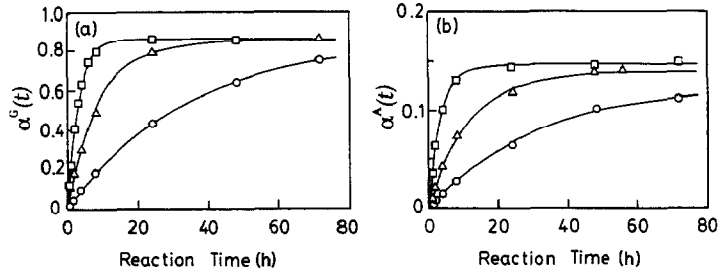



Fig. 1. Reaction of (a) methyl 3,6-dichloro-3,6-dideoxy-β-D-allopyranoside ("Me $Cl_2$-All") and (b) methyl 3,6-dichloro-3,6-dideoxy-β-D-glucopyranoside ("Me $Cl_2$-Glc") with LiCl in DMA. Temperature: 80 (○), 90(△), and 100°C (□).

square regression method to eqs. 2 and 4. Solid lines in the figures show theoretical curves calculated with the rate equations using the values obtained. The coincidence between experimental and theoretical values as shown in both figures indicates that eqs. 2 and 4 satisfactorily describe this substitution.

Table 4 summarizes the values of $k_{AG}$, $k_{GA}$, $\alpha^G(\infty)$, and the activation energies. The values of kinetic parameters obtained in experiments with Me $Cl_2$-Glc as a starting material agree well with those obtained with Me $Cl_2$-All. The $\alpha^G(\infty)$ values show that Me $Cl_2$-Glc is thermodynamically more stable than Me $Cl_2$-All.

*Reaction of "Cell-Cl" with LiCl.*—The reaction of 3,6-$Cl_2$-All units in Cell-Cl with LiCl was studied in DMA. The system was homogeneous throughout the reaction. The reaction products were analyzed by GLC after hydrolysis and conversion to their volatile trifluoroacetates [4]. Cell-Cl samples having ds by

Table 4
Kinetic parameters for the reversible conversion between Me $Cl_2$-All and Me $Cl_2$-Glc

| Starting compound | Temperature (°C) | [Saccharide] (g/L) | [LiCl] (mol/L) | $\alpha^G(\infty)$ | $k_{AG} \times 10^4$ ($L \cdot mol^{-1} \cdot min^{-1}$) | $k_{GA} \times 10^4$ ($L \cdot mol^{-1} \cdot min^{-1}$) | Activation energy ($kJ \cdot mol^{-1}$) | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | $k_{AG}$ | $k_{GA}$ |
| $MeCl_2$-All | 80 | 1.65 | 2.14 | 0.856 | 1.9 | 0.3 | | |
| | 90 | 1.58 | 2.04 | 0.855 | 7.7 | 1.3 | 175 | 177 |
| | 100 | 1.68 | 0.99 | 0.853 | 46.7 | 8.0 | | |
| Me $Cl_2$-Glc | 80 | 1.62 | 2.31 | 0.872 | 1.9 | 0.3 | | |
| | 90 | 2.49 | 2.01 | 0.861 | 6.4 | 1.0 | 163 | 171 |
| | 100 | 1.72 | 1.08 | 0.855 | 37.5 | 6.4 | | |
| Cell-Cl [a] | 80 [b] | 10.0 | 2.12 | | 0.9 | | | |
| | 90 [c] | 10.0 | 2.10 | 0.46 | 2.3 | 2 ~ 3 | 77 | |
| | 100 [b] | 10.0 | 2.12 | 0.52 | 3.7 | 3.4 | | |

[a] Cell-Cl samples were prepared under homogeneous conditions in LiCl/DMA usinjg N-chlorosuccinimide (NCS) and triphenylphosphine in excess of the amount of repeating unit (RU) of cellulose.
[b] Ds by chlorine, 1.35: reaction conditions; 70°C for 6 h, [NCS]:[$PPh_3$]:[RU] = 5:5:1.
[c] Ds by chlorine, 1.54: reaction conditions; 50°C for 6 h, [NCS]:[$PPh_3$]:[RU] = 20:25:1.

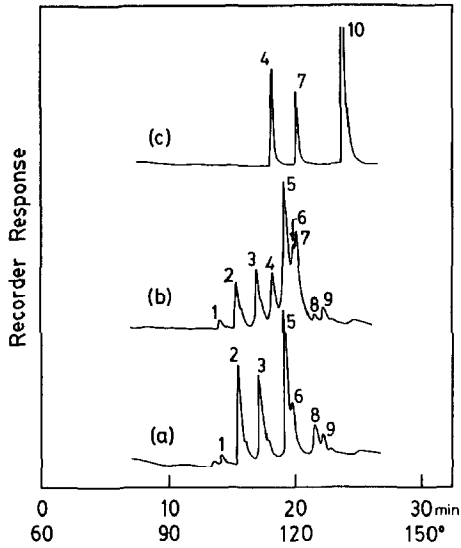



Fig. 2. GLC chromatograms (on SE-30) of hydrolyzates of Cell-Cl with ds by chlorine of 1.54 (a) before and (b) after treatment in LiCl-DMA at 90°C for 48 h, and (c) GLC chromatogram of the hydrolysis product of Me $Cl_2$-Glc: Peak 1, $\alpha$-Glc*p*; 2, $\beta$-Glc*p* + 6-Cl-Glc*p*; 3,6-Cl-Glc*p*; 4 and 7, 3,6-$Cl_2$-Glc*p*; 5 and 8, 3,6-$Cl_2$-All*p*; 6 and 9, 3,6-$Cl_2$-All*f*, 10, Me $Cl_2$-Glc.

chlorine of 1.5 were used because samples having ds by chlorine close to 2 are very resistant towards hydrolysis [4,12]. NMR analysis of Cell-Cl samples would be better for examining the formation of Me $Cl_2$-Glc units and their quantitation. However, it could not be carried out because the samples were insoluble in the NMR solvents available.

Fig. 2 shows chromatograms on an SE-30 column of the hydrolyzates of the sample before and after treatment with LiCl for 48 h at 90°C. New peaks appear on the chromatogram for the treated sample (peaks 4 and 7) near the peaks of the pyranose and furanose anomers of 3,6-$Cl_2$-All [4]. These new peaks were ascribed to the pyranose anomers of the expected 3,6-$Cl_2$-Glc by comparing their retention times on both SE-30 and Dexsil 300 GC columns and their EI mass spectra with those of the hydrolysis product of Me $Cl_2$-Glc. The mass fragmentation pattern of the trifluoroacetate [4] of 3,6-$Cl_2$-Glc is compared in Table 5 with that of 3,6-$Cl_2$-All [4]; the nomenclature of fragment ions proposed by Kochetkov and Chizhov [13] is used. The two fragmentation patterns resemble each other. The triplet ions, such as $A_1$, show that they carry two chlorine atoms and the doublet E-series ions indicate that one of the chlorine atoms is attached to C-6.

The total area of 3,6-$Cl_2$-Glc relative to that of 3,6-$Cl_2$-All was measured as a function of treatment time, and the relative molar response values of the two compounds on a flame-ionization detector were assumed to be the same. The kinetic parameters of the conversion of 3,6-$Cl_2$-All units into 3,6-$Cl_2$-Glc units were obtained by the same method as for Me $Cl_2$-All. However, the appearance of

Table 5
Mass fragmentation patterns of 3,6-$Cl_2$-Glc and 3,6-$Cl_2$-All as trifluoroacetates

| Fragment [a] | $m/z$ [b] | Relative abundance (%) | |
|---|---|---|---|
| | | 3,6-$Cl_2$-Glc*p* | 3,6-$Cl_2$-All*p* [c] |
| $M^+$ | 504(t) | 0.0 | 0.0 |
| $A_1$ | 391(t) | 6.9 | 3.7 |
| $A_2$ | 355(d) | 2.3 | 2.5 |
| | 277(t) | 1.9 | 2.3 |
| $A_3$ | 319(s) | 0.2 | 0.3 |
| | 241(d) | 19.6 | 10.6 |
| | 163(t) | 3.0 | 1.8 |
| $E_1$ | 455(d) | 1.0 | 3.8 |
| $E_2$ | 419(s) | 0.0 | 0.1 |
| | 341(d) | 0.3 | 1.3 |
| $E_3$ | 305(s) | 1.7 | 2.4 |
| | 227(d) | 1.2 | 3.0 |
| $C_2$ | 405(s) | 0.0 | 0.1 |
| | 327(d) | 15.7 | 9.2 |
| $F_1$ | 265(s) | 34.8 | 35.0 |
| | 187(d) | 7.2 | 5.7 |
| $CF_3CO$ | 97(s) | 19.3 | 23.5 |
| $C_5H_5O$ | 81(s) | 15.5 | 14.6 |
| $CF_3$ | 69(s) | 100 | 100 |

[a] Nomencalture for fragment ions, see refs 4 and 13.
[b] Mass numbers are based on $^{35}Cl$.
[c] From ref 4.

each saccharide in the maximal four peaks and the overlapping of peaks lowered the accuracy in quantitation of 3,6-$Cl_2$-Glc at lower temperatures.

The values of $k_{AG}$, $k_{GA}$, $\alpha^G(\infty)$, and the apparent activation energy calculated from $k_{AG}$ are also listed in Table 4. The substitution at 80°C is too slow to obtain a reliable value for $k_{GA}$. It is also slow at 90°C causing a large fluctuation in the determination of the value of $k_{GA}$. The values of the rate constants for the conversion of dichlorodideoxy units in Cell-Cl at 100°C are about one order of magnitude smaller than those for the conversion of dichloroglycosides. The energy difference between 3,6-$Cl_2$-Glc and 3,6-$Cl_2$-All units is smaller than that between the monomeric glycosides. The activation energy for Cell-Cl is lower than those for the glycosides. This shows that the substitution of chlorine atoms at C-3 of 3,6-$Cl_2$-All units in Cell-Cl with chloride ions is less affected by the change in temperature.

The substitution of chlorine by chloride ion at C-3 of 3,6-$Cl_2$-All units during the synthesis of Cell-Cl is negligible at lower temperatures based on the $k_{AG}$ values at these temperatures, estimated by extrapolating the Arrhenius plot of the values in Table 4. For example, less than 1% of 3,6-$Cl_2$-All units will be converted into 3,6-$Cl_2$-Glc units at 70°C for 2 h at a LiCl concentration of 1.18 mol/L, which are typical conditions for the chlorination described in our previous paper [4].

## 3. Experimental

*General methods.*—The reactions of methyl dichloroglycosides and Cell-Cl with LiCl were performed under $N_2$ in DMA containing a known amount of LiCl. Commercial DMA was dried with $CaH_2$ and distilled under diminished pressure. LiCl was dried at room temperature under diminished pressure over silica gel. Wakogel C-100 (silica gel, Wako Pure Chemical Ind., Ltd.) was used for column chromatography and Kieselgel 60 $F_{254}$ (Merck) was used for TLC. Butyl acetate was used as eluent for both column chromatography and TLC.

$^1H$ and $^{13}C$ NMR spectra (normal and two-dimensional) were recorded on a JNM-A500 spectrometer (500 MHz for $^1H$, Jeol Ltd.). When necessary, a small quantity of trifluoroacetic acid was added to shift the HOD absorption (at ~4.8 ppm) to a lower field (~5.2 ppm). Some of the $^{13}C$ NMR spectra were also measured with a JNM-FX90Q spectrometer at 22.53 MHz. Glycosides were treated with $D_2O$ before the NMR measurement. NMR solvents used were $D_2O$ (internal standard, DSS) and $CDCl_3$ ($Me_4Si$).

A GC 4BMP gas chromatograph (Shimadzu Corp.) equipped with two flame-ionization detectors was used for detection and quantitation of the saccharides as trifluoroacetates [4]. The stationary phases used were Dexsil 300 GC coated on Chromosorb G-HP (80-100 mesh, 1.5 wt%) and SE-30 on Gas Chrom Q (100–120 mesh, 3 wt%). The operation conditions for the GLC instrument were the same as those previously described [4].

*Synthesis of methyl 3,6-dichloro-3,6-dideoxy-β-D-glucopyranoside ("Me $Cl_2$-Glc").* —Methyl 3,6-dichloro-3,6-dideoxy-β-D-allopyranoside (2.0 g) was heated in LiCl–DMA (17 g/200 mL) at 90°C for 28 h. The solution was concentrated and the saccharides were extracted with EtOAc. A new compound was found in the extract ($R_f$ value in TLC, 0.53) together with Me $Cl_2$-All ($R_f$, 0.39). The separation by column chromatography gave 1.1 g of chromatographically pure sample, which was recrystallized slowly from 3:4 $CHCl_3$–hexane to give colorless and transparent pillars. The crystals showed an absorption at 1634 $cm^{-1}$ in the IR spectrum, which can be attributed to lattice water [14] and lost weight corresponding to ~1 mol of water on heating to ~100°C. The origin of water is difficult to explain, but it might have come from the ambient air. The absorption at 1634 $cm^{-1}$ did not disappear for samples after repeated recrystallization or by extensive drying although its relative intensity varied. The compound had a broad mp 84–91°C, and was volatile at ~100°C/3 torr. The crystals became glassy after melting or drying over $P_2O_5$ under diminished pressure. Anal. Calcd for $C_7H_{12}Cl_2O_4 \cdot H_2O$: C, 33.75; H, 5.67; Cl, 28.47. Found: C, 33.98; H, 5.85; Cl, 29.91; N, 0.00. Acetylation of Me $Cl_2$-Glc and recrystallization from 3:2 water–EtOH gave needles; mp 117.5–118°C. Anal. Calcd for $C_{11}H_{16}Cl_2O_6$: C, 41.92; H, 5.12; Cl, 22.50. Found: C, 42.29; H, 5.21; Cl, 22.30. The structure of Me $Cl_2$-Glc was confirmed by its $^1H$ and $^{13}C$ NMR spectra (Tables 1 and 2).

*Kinetics of substitution with chloride ion.*—Both Me $Cl_2$-All and Me $Cl_2$-Glc were used as starting materials for the treatment in LiCl-DMA at 80–100°C. Aliquots were pipetted from the solution at predetermined time intervals and

poured into an excess amount of BuOAc to separate LiCl. The ratio of two glycosides was determined by GLC analysis on a Dexsil 300 GC column.

A Cell-Cl sample obtained by the homogeneous chlorination [4] was dissolved in DMA containing a known amount of LiCl at the treatment temperature (80–100°C). Aliquots were taken from the solution at predetermined time intervals and poured into an excess amount of water. The separated polymer was washed with water and MeOH, several times each, dialyzed against water, and dried under diminished pressure. The cellulose samples for analysis were hydrolyzed [4] in $H_2SO_4$ and the ratios of 3,6-$Cl_2$-Glc to 3,6-$Cl_2$-All in the hydrolyzates were determined by GLC on an SE-30 column.

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