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Dissolution of cellulose in lithium bromide–organic solvent systems and homogeneous bromination of cellulose with *N*-bromosuccinimide–triphenylphosphine in lithium bromide–*N*,*N*-dimethylacetamide

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ABSTRACT

Three solvent systems, namely lithium bromide in *N*,*N*-dimethylacetamide (DMA), *N*-methyl-2-pyrrolidone, or *N*,*N*-dimethylformamide, are able to dissolve cellulose. No appreciable decrease in molecular weight of cellulose was observed during the dissolution into the LiBr–DMA solvent system. The homogeneous bromination of cellulose with *N*-bromosuccinimide–triphenylphosphine in LiBr–DMA proceeded smoothly, and the degree of substitution by bromine of 0.9 was attained under appropriate conditions. Only the 6-hydroxyl groups were replaced with bromine, even for the sample having the highest degree of substitution. The effects of reaction conditions on the degree of substitution were studied in detail.

INTRODUCTION

Halodeoxycelluloses are of potential value for the preparation of functional cellulose derivatives. Although chlorination of cellulose under both homogeneous and heterogeneous conditions has been studied by many researchers, only few papers have dealt with bromination[1]. Bromination with molecular bromine and red phosphorus yielded bromodeoxycelluloses having bromine contents up to 16%, but the products also contained phosphorus, and showed carbonyl absorptions in their IR spectra[2]. Ziderman[3] used *N*-bromosuccinimide (NBS) and triphenylphosphine (Ph_3P) for the bromination of cotton, but the bromine content of the product was only 2.7%. These brominations were conducted heterogeneously. The degree of substitution of hydroxyl groups (ds, maximum 3) by bromine per glucose

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residue was much lower than 1, and the chemical structures of bromination products were not studied in detail.

Chlorination of cellulose proceeds smoothly under homogeneous conditions[4,5] or in systems that become homogeneous at a later stage of the reaction[6], and the ds by chlorine approaches 2 under appropriate reaction conditions. Usov et al.[7] brominated 2,3-di-*O*-acetylcellulose with NBS–Ph_3P under homogeneous conditions and obtained, after deacetylation, 6-bromo-6-deoxycellulose having ds by bromine of 0.8. These results imply that bromodeoxycelluloses having high ds values would be obtained directly from cellulose under homogeneous conditions.

We report here three solvent systems for cellulose, consisting of lithium bromide in either *N*,*N*-dimethylacetamide (DMA), *N*-methyl-2-pyrrolidone (NMP), or *N*,*N*-dimethylformamide (DMF). The homogeneous bromination of cellulose with NBS–Ph_3P in LiBr–DMA gave bromodeoxycelluloses having ds values by bromine up to 0.91. Only the 6-hydroxyl groups were replaced by bromine. The effects of reaction conditions on ds are described in detail.

RESULTS AND DISCUSSION

Solvent systems, containing lithium bromide, for cellulose.—Halogenation of cellulose usually involves the nucleophilic substitution by halide ions of suitably modified hydroxyl groups. In LiCl–organic solvent systems, chloride ions participate in the reaction. An attempted bromination of cellulose with NBS and Ph_3P in LiCl–DMA (a solvent system for cellulose[8]) yielded chlorodeoxycellulose almost exclusively. Only a trace amount of 6-bromo-6-deoxyglucose was found in the hydrolyzate. For the homogeneous bromination of cellulose, therefore, solvent systems containing bromide ions might be expected to be suitable. Salt–organic solvent systems other than LiCl–DMA and LiCl–NMP have been stated to be non-solvents for cellulose[9], but procedural details were not described. The chemical shifts of carbonyl carbons of organic amides in the presence of lithium chloride have been compared with those in the presence of lithium bromide, and the uniqueness of the LiCl-based systems as solvents for cellulose was explained in terms of the weaker nucleophilicity of chloride ions in these aprotic solvents as compared with that of bromide ions[9]. However, the chloride ion is a stronger nucleophile than the bromide ion in aprotic organic solvents[10]. We therefore examined some LiBr–organic-solvent systems.

Table I summarizes the results of the dissolution of microcrystalline cellulose in LiBr–organic-solvent systems in comparison with LiCl–organic-solvent systems. DMA, NMP, and DMF all dissolved cellulose in combination with lithium bromide. At a cellulose concentration of 10 g/L, the solutions were stable at room temperature and no gelation was observed. In the LiBr–DMA solvent system, 3.3 g of microcrystalline cellulose could be dissolved in 100 mL of the solvent, but the whole solution immediately solidified below $\sim 70°$. When diluted with an equal volume of DMA, the system remained homogeneous at room temperature, but on

TABLE I

Dissolution of microcrystalline cellulose in lithium halide–organic solvent systems

Organic solvent	LiBr–organic solvent				LiCl–organic solvent			
	Cellulose (g/L)	LiBr (mol/L)	[LiBr]/ [AGU]	Solubility [a]	Cellulose (g/L)	LiCl (mol/L)	[LiCl]/ [AGU]	Solubility [a]
DMA	10	2.53	41	○	10	2.36	38	○
	33	2.71	13	○ [b]				
NMP	10	2.22	36	○				
DMF	10	2.53	41	×	10	2.36	38	×
	10	6.38	104	○	10	9.26	150	×
TMU [c]	10	2.62	42	×				

[a] ○, Soluble; ×, insoluble. [b] Whole solution solidified below ~ 70°. [c] *N,N,N',N'*-Tetramethylurea.

dilution with an excess of DMA, the solution gelled at room temperature. Microcrystalline cellulose could not be dissolved in LiBr–DMF at a concentration of 2.53 mol/L of lithium bromide, but 1 g of cellulose was soluble in 100 mL of the solvent at a salt concentration of 6.38 mol/L. The LiCl–DMF system, on the other hand, did not dissolve microcrystalline cellulose even at a concentration of 9.26 mol/L of lithium chloride.

Strong intermolecular hydrogen-bonding is the cause of the insolubility of cellulose in common solvents, and the breakage of hydrogen bonds is necessary for the dissolution of cellulose. El-Kafrawy[9] proposed a mechanism of dissolution of cellulose into LiCl–DMA based on ^{13}C-NMR data, in which solvated lithium cations interacted with hydroxyl oxygen atoms. Chloride ions were supposed to interact with hydroxyl hydrogen atoms, thus promoting the breakage of intermolecular hydrogen-bonds in cellulose. The principal concept adopted in other proposed mechanisms is basically the same[11,12].

All of the organic solvents examined in this study are known to interact strongly with metal cations to form preferentially solvated cations and nonsolvated anions[10]. The order of nucleophilicity of nonsolvated halide ions is the same as that of the electronegativity of halogen atoms, namely $Cl^- > Br^- > I^-$. Table I shows that a slightly higher salt concentration was necessary for the smooth dissolution of cellulose in LiBr–DMA as compared with LiCl–DMA. This may be explained on the basis of weaker interaction of nonsolvated bromide ions with hydroxyl hydrogen atoms as compared with that of nonsolvated chloride ions.

Absorbent cotton dissolved in the LiBr–DMA solvent system, but its solubility was lower than that of microcrystalline cellulose. The intrinsic viscosities of absorbent cotton cellulose and microcrystalline cellulose dissolved in LiBr–DMA solution ([LiBr], 1.4 mol/L) at 50° were 8.26 and 1.88 dL/g, respectively. The low solubility of the former is probably due to its higher molecular weight.

Pretreatment of cellulose in organic solvents at 160° before the addition of lithium bromide was necessary for smooth dissolution, as in the case of dissolution[8] in LiCl–DMA. If the pretreatment was omitted, dissolution was slow, and the

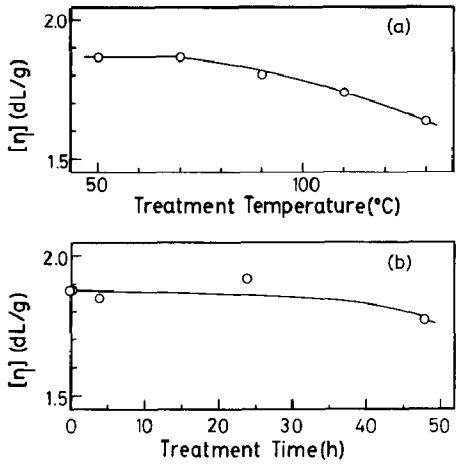


Fig. 1. Intrinsic viscosity of microcrystalline cellulose as a function of (a) heat treatment temperature and (b) heat treatment time. Treatment conditions: [Cell-OH], 5 g/L DMA; [LiBr], 1.26 mol/L DMA; (a) treatment time, 30 min; (b) treatment temperature, 70°.

samples recovered from such solutions showed extensive decrease in molecular weight. The possibility of partial depolymerization of cellulose was checked by viscometry. Both the untreated microcrystalline cellulose and a sample regenerated from a LiBr–DMA solution were converted into their *O*-phenylcarbamoyl derivatives[13]. The intrinsic viscosities measured at 50° in DMA were 0.81 and 0.83 dL/g for derivatives from untreated and regenerated samples, respectively. This finding shows that no depolymerization occurred during the dissolution process.

Cellulose samples were also heated in solution during bromination. The possibility of depolymerization of microcrystalline cellulose upon heating in the LiBr–DMA solution was also checked viscometrically. Fig. 1(a) shows that the intrinsic viscosity of microcrystalline cellulose dissolved in LiBr–DMA decreased at treatment temperatures $> 70°$. The viscosity also tended to decrease on prolonged heating at 70° as shown in Fig. 1(b). These findings show that the depolymerization of microcrystalline cellulose under mild conditions was negligible in this solution.

The solvent systems described in this study are easy to handle, and are useful for bromination and other reactions of cellulose, for which the presence of the bromide ion is favorable.

Bromination.—In this study, NBS and Ph_3P were used in equimolar amounts for the homogeneous bromination of microcrystalline cellulose in LiBr–DMA. This reagent system is recommended for the replacement of primary hydroxyl groups in carbohydrates with bromine[14]. It also replaced secondary hydroxyl groups with Walden inversion under suitable conditions[15]. Reaction conditions affected the extent of bromination of the products, as in the case of homogeneous chlorination[5] of cellulose with *N*-chlorosuccinimide–Ph_3P in LiCl–DMA.

Fig. 2 shows the effects of reaction temperature and time on ds by bromine and the recovery (based on repeating unit, %) of the product at the reagent ratio

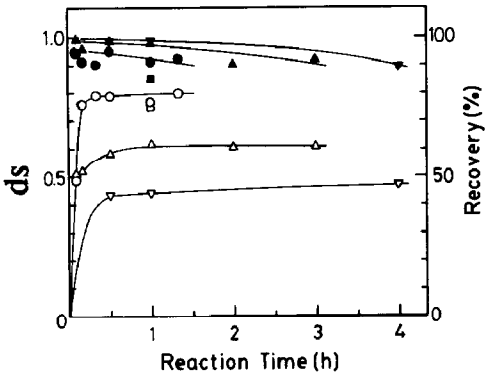


Fig. 2. Ds by bromine and recovery as a function of bromination time at [NBS, Ph_3P]:[AGU] = 2:1. Reaction temperature: ▽, 30°; △, 50°; ○, 70°; □, 90°. Open symbols denote ds and filled symbols denote recovery, respectively.

([NBS, Ph_3P]:[AGU]) of 2:1. Bromination under homogeneous conditions proceeded rapidly and leveled off in ~1 h at 50°. The ds increased as the reaction temperature rose and the final ds was ~0.8 at 70°. A further increase in ds was not observed at 90°. The recovery was higher than 85%, and white powdery bromodeoxycelluloses were obtained.

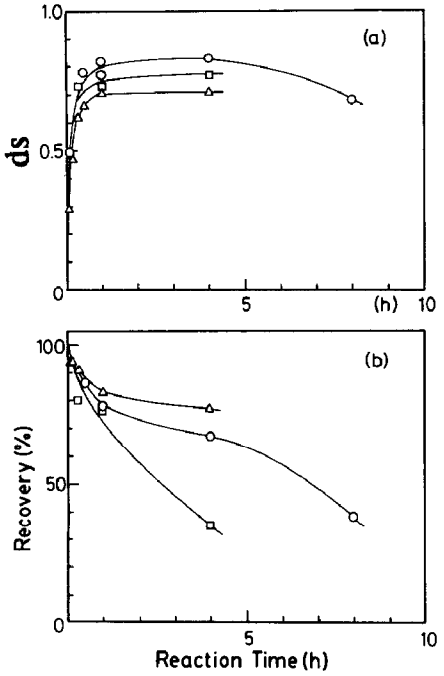


Fig. 3. (a) Ds by bromine and (b) recovery as a function of bromination time at [NBS, Ph_3P]:[AGU] = 5:1. Reaction temperature; △, 50°; ○, 70°; □, 90°.

TABLE II

Bromodeoxycelluloses obtained at 90°

Sample property	Acetone–water	
	Insoluble	Soluble
Recovery (%)	45	13
Br (%)	26.14 (29.35 / ds 0.77) [a]	27.62
Color	dark-brown solid (pale grey) [a]	pale-brown powder (white) [a]
$[\eta]$ [b] (dL/g)	0.18	0.06

[a] After treatment with a solution of sodium carbonate (pH 10, 1 week). [b] Measured at 50° in LiBr–DMA ([LiBr] 1.4 mol/L). Reaction conditions: 90° for 4 h, [NBS, Ph_3P]/[AGU] = 5:1.

Fig. 3 shows the results of bromination at the reagent ratio of 5:1. The ds values of the products obtained at 50° were higher than those obtained with the reagent ratio of 2:1. The ds by bromine at 70° was the same with both reagent ratios, and tended to decrease after a long period of reaction at 5:1. The recovery of bromodeoxycellulose decreased considerably at longer reaction times and at higher temperatures. Colored products were obtained at this reagent ratio, and the color deepened as the reaction temperature rose. The IR spectra of crude products showed a carbonyl absorption with fairly strong intensity at $\sim 1740\ cm^{-1}$ and an absorption at $\sim 1240\ cm^{-1}$ assignable to ester C–O.

The decrease in recovery was due to depolymerization during bromination. Bromodeoxycelluloses obtained at 90° and longer reaction-times were partially soluble in acetone–water ($\sim 7:3$ v/v). Table II summarizes the recoveries and some properties of the soluble and insoluble components of the bromodeoxycellulose sample obtained upon bromination for 4 h at 90°. The soluble part was recovered by dialysis against water. The bromine contents of the two components were not much different, but the intrinsic viscosities differed considerably. The intrinsic viscosity of the insoluble component, 0.18 dL/g, was still much lower than that of bromodeoxycellulose of comparable bromine content obtained under milder conditions (0.7–0.8 dL/g) as shown in Fig. 4. This Figure shows that the intrinsic viscosity of bromodeoxycellulose decreased with increase in ds and tended to level off at higher ds values. The reason for the decrease is considered to be the conformational and other changes caused by the change in chemical structure of cellulosic molecules and/or the depolymerization during bromination. A preliminary gel-permeation chromatographic measurement as *O*-phenylcarbamoyl derivatives[13] showed only a small decrease in the degree of polymerization of bromodeoxycelluloses of high ds values obtained under milder conditions.

Fig. 5 shows the effect of reagent ratio on ds by bromine and recovery. The data for the products obtained in the reaction for 30 min at 50° at a cellulose concentration of 5 g/L are plotted in circles. The ds increased steeply as the

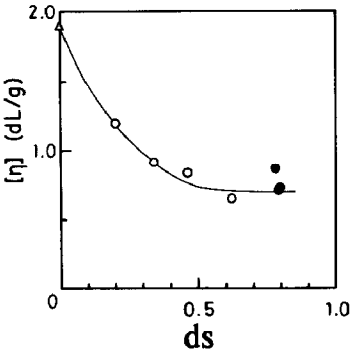


Fig. 4. Intrinsic viscosity of bromodeoxycellulose as a function of ds. ○, Samples obtained at 50°; ●, samples obtained at 70°.

reagent ratio increased from 1:1 to 2.5:1, and then rose slowly at higher reagent-ratios. The recovery was nearly quantitative at lower reagent-ratios. When the cellulose concentration was increased to 16.5 g/L (the concentration of lithium bromide was also increased from 2.53 to 2.71 mol/L), the bromination occurred more readily and bromodeoxycelluloses of corresponding ds values could be obtained at lower reagent-ratios as compared with the bromination at a cellulose concentration of 5 g/L. When the reaction temperature was raised to 70°, the ds further increased and a bromodeoxycellulose sample of ds of 0.91 was obtained at the reagent ratio of 2:1.

The bromination of absorbent cotton in LiBr–DMA was studied briefly. Table III summarizes the ds by bromine of products obtained at two levels of reagent ratio for 80 min at 70°. At the lower reagent-ratio, the ds was very low, whereas a sample of high ds was obtained at a reagent ratio of 6:1. This finding shows that the bromination system adopted in this study is useful for the preparation of high molecular-weight bromodeoxycellulose samples of high ds values.

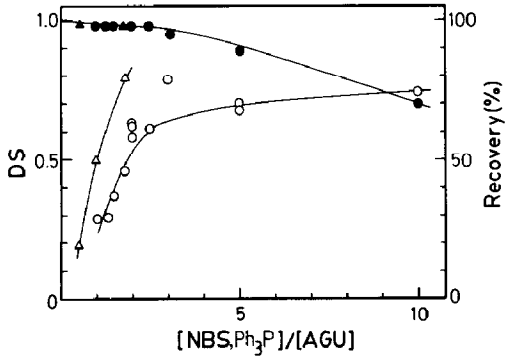


Fig. 5. Effect of reagent ratio on ds by bromine and recovery. Reaction conditions: temperature, 50°; ○, 30 min at [Cell-OH] 5 g/L; △, 40 min at [Cell-OH] 16.5 g/L. Open symbols denote ds and filled symbols denote recovery, respectively.

TABLE III

Bromination [a] of absorbent cotton

Cellulose (g/L)	[NBS, Ph_3P]:[AGU]	ds
2.7	3:1	0.02
3.3	6:1	0.90

[a] Reaction conditions: 70° for 80 min.

Position of bromination.—Bromodeoxycelluloses were hydrolyzed in sulfuric acid and the saccharides in the hydrolyzates were analyzed by gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS) as *O*-trifluoroacetyl (TFA) derivatives.

Fig. 6 shows gas chromatograms of the hydrolyzates of bromodeoxycelluloses of different ds values. Peaks 1 and 2 are attributable to α- and β-D-glucopyranose, respectively. Peak 3 is attributed to 3,6-anhydroglucose (3,6-AnG), and its peak area was dependent to some extent on the hydrolysis conditions. Peaks 4 and 5 are attributable to pyranose anomers of 6-bromo-6-deoxy-D-glucose (6-Br-Glc*p*). These three monosaccharides were identified by comparing their GC retention times and mass spectra with those of authentic samples. No peak was observed originating from a dibrominated monosaccharide, even for the samples having ds by bromine near 0.9. This result means that bromine atoms were homogeneously distributed at C-6 positions of glucose residues along the cellulose chains in the samples of high ds values obtained in this solvent system.

The replacement of hydroxyl groups by halogen in the reaction of an alcohol with *N*-halosuccinimide–Ph_3P is considered to proceed through the formation of alkoxyphosphonium salts followed by attack of the halide ions on to the phosphonium ester bonds[1,15] (Scheme 1). The ease of esterification of the three hydroxyl groups in the glucose residues is considered[16] to decrease in the order C-6 ≥ C-2

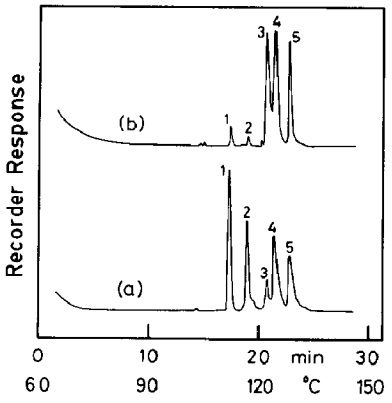
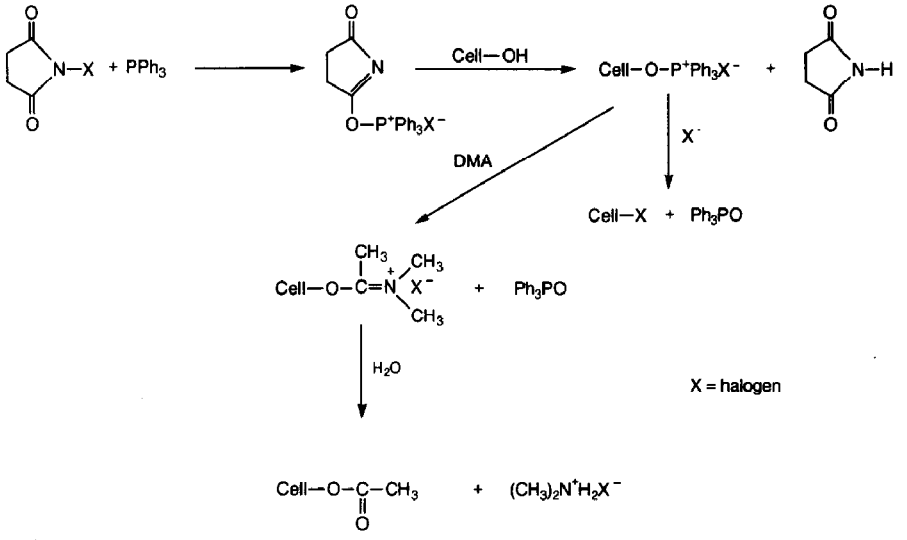


Fig. 6. Gas chromatograms of *O*-trifluoroacetyl derivatives of the hydrolyzates of bromodeoxycelluloses with ds of (a) 0.34 and (b) 0.91. Peak 1, α-glucopyranose; peak 2, β-glucopyranose; peak 3, 3,6-anhydroglucose; peaks 4 and 5, 6-bromo-6-deoxyglucopyranose.



Scheme 1.

≫ C-3, and therefore, excess amounts of reagents are necessary to effect replacement of 6-hydroxyl groups, as shown in Fig. 5. The susceptibility of modified hydroxyl groups towards nucleophilic substitutions with anions generally decreases[17] in the order C-6 > C-3 ≫ C-2 ~ 0. In the present study, no dibrominated monosaccharide was found in the hydrolyzates of the samples having high ds values by bromine of 0.8–0.9. In the chlorination of microcrystalline cellulose[5] with *N*-chlorosuccinimide–Ph_3P in LiCl–DMA, on the other hand, 3,6-dichloro-3,6-dideoxyallose units were formed in chlorodeoxycelluloses having ds values by chlorine higher than ~ 0.8.This difference between chlorination and bromination can be explained on the basis of the nucleophilicity[10] of the unsolvated halide ion formed in DMA, which decreases in the order $Cl^- > Br^-$.

The carbonyl absorption observed in the IR spectra of some bromodeoxycellulose samples is considered to be due mainly to acetate groups formed in the reaction between alkoxyphosphonium salts and DMA molecules to form iminium type ions[18] followed by hydrolysis during isolative treatment (Scheme 1). Vigo and Daigle[19] obtained cellulose formate by the reaction of cellulose with thionyl chloride in DMF. The formate was considered to be the hydrolysis product of an iminium ion formed from cellulose chlorosulfite and DMF. The carbonyl absorption disappeared or became weak after treatment with a solution (pH 10) of sodium carbonate at room temperature without loss of bromine, and the products became pale or colorless by the treatment (Table II). Samples obtained under severe conditions showed weak carbonyl absorption, even after treatment with sodium carbonate solution. NBS is itself an oxidizing reagent[20] and this carbonyl absorption remaining after the treatment was probably due to aldehyde and/or ketone groups formed by the oxidation of cellulose.

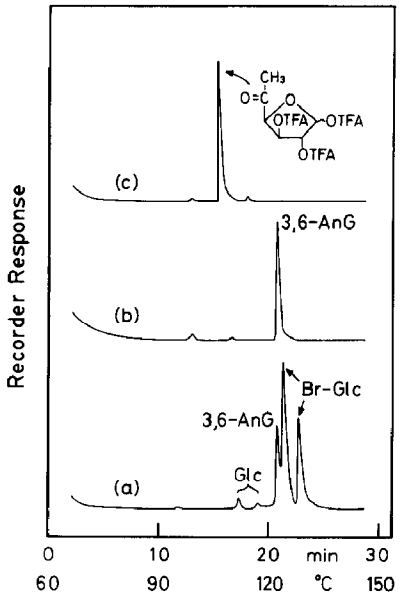


Fig. 7. Gas chromatograms for DBU- and NaOH-treated samples. (a) Original bromodeoxycellulose (ds 0.84, Br 31.20%); (b) NaOH-treated sample (Br 1.18%); (c) DBU-treated sample (Br 15.89%).

In the present bromination experiments, the maximum ds attained was 0.9. In an attempt to increase ds, bromodeoxycelluloses having several ds levels were brominated again under homogeneous conditions with NBS–Ph_3P in LiBr–DMA. For the samples having low ds values, the ds by bromine increased to 0.7–0.8, but no increase in ds was observed for the samples having ds around 0.8. Within the specified limits, however, bromodeoxycelluloses having desired ds values could be obtained by choosing appropriate reaction conditions.

Alkali treatment.—No loss of bromine from bromodeoxycellulose samples was observed in the treatment with aqueous sodium carbonate (pH 10) at room temperature, but dehydrobromination occurred under stronger alkaline conditions. A bromodeoxycellulose sample (ds 0.84, Br 31.20%) was treated with 0.2 M NaOH for 48 h at room temperature. The bromine content decreased to 1.18%, and the IR spectrum of the treated sample was quite different from that of the untreated sample. Ishii[21] obtained "5,6-cellulosene" by the reaction of acetylated 6-deoxy-6-iodocellulose with 1,8-diazabicyclo[5.4.0]-7-undecene (DBU). The conversion of bromodeoxycellulose into "cellulosene" was studied with the same bromodeoxycellulose sample. It was treated with DBU for 2 h at 50° after acetylation[21]. The bromine content decreased, and deacetylation gave another dehydrobrominated product (Br 15.89%).

Fig. 7 shows gas chromatograms of the hydrolyzates of DBU- and NaOH-treated samples. The DBU-treated sample was hydrolyzed for 2 h at 50° in 0.05 M sulfuric acid[21]. On the chromatogram for the hydrolyzate of the DBU-treated sample, a peak appeared at a column temperature lower than that for glucose. This peak

TABLE IV

Mass spectra of 6-deoxy-D-*xylo*-hexos-5-ulose (**A**) in hydrolyzate of DBU-treated sample and 3,6-anhydro-D-glucose (**B**) [a]

Ion	A		B [b]	
	m/z	r.a.	*m/z*	r.a.
M^+	450	0.02	450	0.2
$M-CH_3CO$	407	0.05		
$M-CF_3COO$ (I)	337	1.2	337	7.4
(I) $-CH_3CO$ (II)	294	3.1		
$C_3H_3(OCOCF_3)_2$	265	2.9	265	0.6
$C_2H_3(OCOCF_3)_2$			253	3.7
(I) $-CF_3COOH$	223	1.6	223	28.3
$(Ac)C_2H_2O(OCOCF_3)$	198	1.2		
$(Ac)C_3H_3(OCOCF_3)$	195	1.4		
$C_5H_5O(OCOCF_3)$			194	13.7
$C_4H_4O(OCOCF_3)$	181	2.5	181	17.8
(II) $-CF_3COOH$	180	9.6		
$C_3H_4O(OCOCF_3)$	169	2.6	169	2.7
$C_3H_4(OCOCF_3)$	153	2.6	153	15.9
$C_2H_3(OCOCF_3)$			140	14.9
(I) $-2\times CF_3COOH$	109	0.8	109	19.7
CF_3CO	97	3.4	97	19.1
C_5H_7O	83	4.7		
C_5H_5O	81	0.6	81	48.2
CF_3	69	27.3	69	100
C_2H_3O	43	100	43	9.9

[a] As *O*-trifluoroacetyl derivatives. [b] Authentic sample. **A**, 6-deoxy-D-*xylo*-hexos-5-ulofuranose; **B**, 3,6-anhydro-D-glucose: r.a., relative abundance (%). The assignments of some of the ions are tentative.

material was identified as 6-deoxy-D-*xylo*-hexos-5-ulose in its furanose form[22], based on its mass spectrum. This means that the DBU-treated sample contained 5,6-unsaturated units. 6-Deoxy-D-*xylo*-hexos-5-ulose could not be detected in the hydrolyzate of the DBU-treated sample hydrolyzed under reflux in 8% sulfuric acid. In the hydrolyzate of the NaOH-treated sample, 3,6-anhydro-D-glucose was the main product. When the sample was hydrolyzed under the conditions adopted for the DBU-treated sample, 6-deoxy-D-*xylo*-hexos-5-ulose and 1,6-anhydroglucose were found in the hydrolyzates along with 3,6-anhydro-D-glucose. Table IV compares the MS fragmentation pattern of trifluoroacetylated 6-deoxy-D-*xylo*-hexos-5-ulose found in the hydrolyzates with that of the *O*-trifluoroacetyl derivative of authentic 3,6-anhydro-D-glucose. The base ion at *m/z* 43 for trifluoroacetylated 6-deoxy-D-*xylo*-hexos-5-ulose corresponds to the acetyl moiety.

EXPERIMENTAL

Reagents.—Microcrystalline cellulose (Art. 2331 Cellulose mikrokrystallin, Merck) was dried in a desiccator under diminished pressure before use. NBS and Ph_3P were recrystallized from water and EtOH, respectively. DMA and DMF

were dried with CaH_2, distilled under diminished pressure and stored over molecular sieve (Linde type 4A). NMP and *N,N,N',N'*-tetramethylurea were dehydrated with CaH_2 and distilled under diminished pressure just before use. Lithium bromide (anhydrous) was dried at 180° under diminished pressure. Commercial D-glucose (α and β), 1,6-anhydroglucose, phenyl isocyanate and DBU were used without further purification. 6-Bromo-6-deoxy-D-glucose and 3,6-anhydro-D-glucose were synthesized according to the methods of Mogel' and Yurkevich[23] and of Fischer and Zach[24], respectively.

Dissolution of cellulose.—All dissolution and bromination experiments were carried out under N_2. In a typical dissolution experiment, 0.1 g of dried microcrystalline cellulose was placed in a flask containing 10 mL of DMA, and the mixture was heated for 1 h at 160° with stirring. The temperature was lowered to 90° and 2.2 g (25.3 mmol) of LiBr was added. The mixture was kept for a further 1 h at this temperature with stirring. The temperature was then lowered to 60°, and the mixture was kept at this temperature with stirring. A clear solution was obtained within 12 h. Cellulose samples were dissolved in LiBr–NMP and LiBr–DMF systems in the same way.

Bromination.—The cellulose solution just mentioned was stirred under cooling with ice–water, and calculated amounts of NBS and Ph_3P (both in DMA solution) were added in this order. The final volume of DMA was 20 mL. The solution was kept at a specified reaction temperature for a desired time with stirring. After the reaction, the solution was poured into 400 mL of acetone and the separated material was washed several times with acetone, dialyzed against tap water and then distilled water. The colored samples were treated with a solution of Na_2CO_3 (pH 10) at room temperature for more than a week. The samples were dried under diminished pressure and weighed.

Analyses.—Bromine contents of the products were determined by an oxygen-flask combustion method[25]. The ds by bromine was calculated from the bromine content. The recovery based on repeating unit was calculated from the weight recovery and ds.

Infrared spectra were recorded in KBr disks with a Fourier-transform IR spectrophotometer FT/IR-3 (Nihon Bunko Co.). A spectrum of ambient air was used as reference.

Solution viscosities of samples were measured at 50° in LiBr–DMA ([LiBr] 1.4 mol/L) with an Ubbelohde viscometer. Some of the samples were converted into *O*-phenylcarbamoyl derivatives[13], and their viscosities were measured at 50° in DMA.

For GC and GC–MS, samples were hydrolyzed in H_2SO_4 as described in the previous paper[5]. The saccharides in the hydrolyzate solutions were converted into *O*-trifluoroacetyl derivatives by the reaction with trifluoroacetic anhydride in CH_2Cl_2 for 20 min at 100°. Gas chromatograms were recorded on a Shimadzu GC-4BM dual-column gas chromatograph equipped with two flame-ionization detectors. The stationary phase used was Silicone GE SE-30 (3% on Gas chrom Q,

100–120 mesh) packed in a glass column (3 m × 3 mm). The flow rate of N_2 (carrier gas) was 60 mL/min, and the column temperature was raised from 60 to 250° at 3° min. A Shimadzu Chromatopac C-E1B was used for the data analysis. A Shimadzu LKB-9000 gas chromatograph–mass spectrometer was used for GC–MS analysis. The temperatures of the ion source and the separator were 290 and 280°, respectively. The acceleration voltages for the measurements of total-ion-current chromatograms and mass spectra were 20 and 70 eV, respectively. Helium was used for a carrier gas (flow rate, 30 mL/min), and other conditions for analysis were the same as those for the GC analysis. A Shimadzu GC-MSPAC 300 was used for the data processing.

REFERENCES

1 R.G. Krylova, *Russ. Chem. Rev.*, 56 (1987) 175–189.
2 H. Rath, J.H. Rau, and G. Brink, *Melliand Textilber.*, 47 (1966) 909–912.
3 I.I. Ziderman, *Text. Res. J.*, 51 (1981) 777–781.
4 S. Furubeppu, T. Kondo, and A. Ishizu, *Sen'i Gakkaishi*, 47 (1991) 592–597.
5 K. Furuhata, H.-S. Chang, N. Aoki, and M. Sakamoto, *Carbohydr. Res.*, 230 (1992) 151–164.
6 R.G. Krylova, A.I. Usov, and A.S. Shashkov, *Soviet J. Bioorg. Chem.*, 7 (1981) 871–877.
7 A.I. Usov, R.G. Krylova, and F.R. Suleimanova, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, (1975) 2009–2011.
8 A.F. Turbak, A. El-Karfrawy, F.W. Snyder, and A.B. Auerbach, *U.S. Pat.*, 4 302 252 (1981); *Chem. Abstr.*, 96 (1982) 54152b.
9 A. El-Kafrawy, *J. Appl. Polym. Sci.*, 27 (1982) 2435–2443.
10 A.J. Parker, *Chem. Rev.*, 69 (1969) 1–32.
11 C.L. McCormick, P.A. Callais, and B.H. Hutchinson, Jr., *Macromolecules*, 18 (1985) 2394–2401.
12 T.R. Dawsey and C.L. McCormick, *J. Macromol. Sci., Rev. Macromol. Chem.*, 30 (1990) 405–440.
13 Y.H. Suleman and R.A. Young, *Cellulose Chem. Technol.*, 22 (1988) 3–16.
14 S. Hanessian, M.M. Ponpipom, and P. Lavallee, *Carbohydr. Res.*, 24 (1972) 45–56.
15 A.K. Bose and B. Lal, *Tetrahedron Lett.*, (1973) 3937–3940.
16 S.P. Rowland, A.L. Bullock, V.O. Cirino, E.J. Roberts, D.E. Hoiness, C.P. Wade, M.A.F. Brannan, H.H. Janssen, and P.F. Pittman, *Text. Res. J.*, 37 (1967) 1020–1030.
17 A.C. Richardson, *Carbohydr. Res.*, 10 (1969) 395–402.
18 J.D. Albright, E. Benz, A.E. Lanzilotti, and L. Goldman, *Chem. Commun.*, (1965) 413–414.
19 T.L. Vigo and D.J. Daigle, *Carbohydr. Res.*, 21 (1972) 369–377.
20 R. Filler, *Chem. Rev.*, 63 (1963) 21–43.
21 T. Ishii, *Carbohydr. Res.*, 154 (1986) 63–70.
22 D.E. Kiely, J.W. Talhouk, J.M. Riodan, and K. Gray, *J. Carbohydr. Chem.*, 2 (1983) 427–438.
23 L.G. Mogel' and A.M. Yurkevich, *J. General Chem. USSR*, 40 (1970) 682.
24 E. Fischer and K. Zach, *Ber.*, 45 (1912) 456–465.
25 K. Kinoshita and K. Hozumi, *Bunseki Kagaku*, 14 (1965) 352–354.