ELSEVIER

Carbohydrate Research 275 (1995) 17–24

CARBOHYDRATE RESEARCH

Synthesis of methyl 3,6-dibromo-3,6-dideoxy-β-D-allopyranoside and -glucopyranoside, and their interconversion in the presence of bromide ion

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Received 18 August 1994; accepted in revised form 24 November 1994

Abstract

The bromination of methyl β-D-glucopyranoside with tribromoimidazole and triphenylphosphine in toluene–acetonitrile (2:1 v/v) for 4 h at 110°C gave methyl 3,6-dibromo-3,6-dideoxy-β-D-alloside in low yield, while the bromination in toluene under otherwise comparable conditions gave methyl 3,6-dibromo-3,6-dideoxy-β-D-glucoside. Examination of the time course of the reaction in toluene showed that the dibromoalloside was initially formed and was converted into the dibromoglucoside during the bromination. The rate constants of the interconversion between the dibromoglycosides in LiBr–*N,N*-dimethylacetamide (DMA) were about 10^3 times as large as those of the interconversion of the corresponding dichloroglycosides in LiCl–DMA. The results are discussed in relation to the presence of 3,6-dibromo-3,6-dideoxyglucose residues, in addition to 3,6-dibromo-3,6-dideoxyallose and 6-bromo-6-deoxyglucose residues, in bromodeoxycellulose samples having high ds values obtained by the bromination of cellulose with tribromoimidazole–triphenylphosphine.

Keywords: Methyl 3,6-dibromo-3,6-dideoxy-β-D-allopyranoside; Methyl 3,6-dibromo-3,6-dideoxy-β-D-glucopyranoside

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SSDI 0008-6215(95)00005-4

1. Introduction

We reported previously [1,2] the halogenation of cellulose with *N*-halosuccinimide and triphenylphosphine (PPh_3) under homogeneous conditions in lithium halide-*N,N*-dimethylacetamide (DMA). In the chlorination [1], the ds value reached 1.9 and 3,6-dichloro-3,6-dideoxyallose residues (**10**) were present together with 6-chloro-6-deoxyglucose residues (**11**) in the samples having high ds values. We later showed [3] that the conversion of residues of **10** into 3,6-dichloro-3,6-dideoxyglucose (**12**) residues in LiCl–DMA was negligible under the chlorination conditions adopted. In the bromination [2], on the other hand, the ds value did not exceed 1 and only C-6 hydroxyl groups were substituted with bromine. Krylova et al. [4] brominated 6-*O*-tritylcellulose with tribromoimidazole (Br_3Im), PPh_3, and imidazole in toluene and obtained, after detritylation, a sample containing 3-bromo-3-deoxyallose (**13**) residues having a ds of 0.63. In the course of studies on the synthesis of bromodeoxycellulose samples having high ds values, we examined the Br_3Im–PPh_3 reagent system for the bromination of cellulose under both homogeneous [5] and heterogeneous [6] conditions. Bromodeoxycellulose samples having high ds values were obtained under appropriate conditions, and both 3,6-dibromo-3,6-dideoxyallose (**14**) and 3,6-dibromo-3,6-dideoxyglucose (**15**) residues were present in these samples, together with 6-bromo-6-deoxyglucose (**16**) residues. Halodeoxycelluloses, especially bromodeoxycellulose samples having high ds values, are expected to be useful for the introduction of functional groups into cellulose through nucleophilic substitution with suitable nucleophiles having functional substituents [7–9].

The aim of this paper is to find out the reason for the presence of both **14** and **15** repeating units in bromodeoxycellulose samples brominated with Br_3Im–PPh_3. The syntheses of methyl 3,6-dibromo-3,6-dideoxy-β-D-alloside (**1**) and methyl 3,6-dibromo-3,6-dideoxy-β-D-glucoside (**2**) from methyl β-D-glucoside (**3**) and Br_3Im–PPh_3 as model compounds are described first. The kinetic study on the interconversion between **1** and **2** in LiBr–DMA is described next. The values of rate constants obtained were large enough to explain the presence of both **14** and **15** units in the bromodeoxycellulose samples having high ds values obtained with Br_3Im–PPh_3.

2. Results

Bromination of methyl β-D-glucopyranoside (**3**) *with* Br_3Im *and* PPh_3.—The reaction of methyl α-D-glucopyranoside (**9**) with Br_3Im–PPh_3 for 1 h at 75° C and then for 4 h at 110°C in toluene [10] or in toluene–acetonitrile (2:1 v/v) [11] was apparently heterogeneous and gave methyl 3,6-dibromo-3,6-dideoxy-α-D-alloside (**7**) in a yield over 70%. We applied these synthetic procedures to **3**. The reaction in toluene–acetonitrile (2:1 v/v) for 1 h at 75° C and then for 4 h at 110° C gave the expected compound **1**. The yield of purified **1** was below 5%, and methyl 6-bromo-6-deoxy-β-D-glucoside (**4**) [12] was the main product (yield, about 60%). When the reaction was carried out in toluene, under otherwise the same conditions, compound **2** was isolated from the reaction mixture in pure form, instead of **1**. Apparently, both reactions proceeded heterogeneously, and most of the solid mass remained undissolved throughout the reaction.

Table 1
^{1}H NMR chemical shifts and coupling constants for methyl 3,6-dibromo-3,6-dideoxyglycosides

Compound	Solvent–standard	^{1}H Chemical shift (δ)								Coupling constant (Hz)						
		1	2	3	4	5	6	6′	OCH_3	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$
1	D_2O,D^+–DSS [a]	4.80	3.62	4.84	3.89	4.07	3.80	3.69	3.59	7.3	3.7	3.0	9.2	2.5	4.9	11.6
	$CDCl_3$–Me_4Si	4.65	3.58	4.86	3.69	3.91	3.76	3.59	3.58	6.7	3.4	3.1	8.6	3.1	6.1	11.6
2	D_2O–DSS	4.46	3.58	3.94	3.77	3.65	3.82	3.70	3.58	7.9	10.1	9.8	9.4	2.2	5.0	11.6
	$CDCl_3$–Me_4Si	4.26	3.63	3.89	3.72	3.50	3.79	3.60	3.61	7.3	10.3	9.8	9.1	2.5	6.1	11.0
8	D_2O,D^+–DSS [a]	4.80	3.89	4.10	3.74	3.84	3.82	3.71	3.45	3.6	10.8	10.3	9.2	6.0		12.1
	$CDCl_3$–Me_4Si	4.82	3.81	4.11	3.68	3.78	3.77	3.61	3.49	3.7	10.5	9.8	9.5	6.1		11.0

[a] A small amount of trifluoroacetic acid was added to aviod the overlapping of HOD and C-1 proton absorptions.

The structures of **1** and **2** were determined by their ^{1}H and ^{13}C NMR spectra. The assignments were confirmed by ^{1}H homonuclear and ^{1}H–^{13}C heteronuclear two-dimensional spectra. ^{1}H and ^{13}C NMR parameters are summarized in Tables 1 and 2, respectively. The $J_{1,2}$ values show that **1** and **2** are in the $^4C_1$ conformation, and $J_{2,3}$ and $J_{3,4}$ values confirm their *allo* and *gluco* configurations [3], respectively. The carbon chemical shifts confirm the bromine substitution at C-3 and C-6 [10].

*Interconversion between methyl 3,6-dibromo-3,6-dideoxy-β-*D*-alloside* (**1**) *and methyl 3,6-dibromo-3,6-dideoxy-β-*D*-glucoside* (**2**) *in LiBr–DMA.*—The time course of the heterogeneous reaction of **3** with Br_3Im–PPh_3 in toluene was examined by TLC. Only compound **1** was found both in the toluene solution and in the solid at the earliest stage of the reaction, whereas **2** became prominent in both phases at the later stages. This finding indicates that **1** was initially formed from **3** and was converted into **2** by an S_N2 reaction. In the bromination of cellulose with Br_3Im–PPh_3, units of **14** are considered to be formed initially and converted into residues of **15** during the bromination at a rate comparable to that of bromination. To examine this, the interconversion between **1** and **2** (eq 1) was studied kinetically at 60–90° C under homogeneous conditions in LiBr–DMA;

$$\mathbf{1} + Br^- \underset{k_{GA}}{\overset{k_{AG}}{\rightleftharpoons}} \mathbf{2} + Br^- \qquad (1)$$

Table 2
^{13}C NMR chemical shifts for methyl 3,6-dibromo-3,6-dideoxyglycosides

Compound	Solvent–standard	^{13}C Chemical shift (ppm)						
		1	2	3	4	5	6	OCH_3
1	D_2O,D^+–DSS [a]	104.93	71.75	65.15	70.46	76.19	35.62	60.18
	$CDCl_3$–Me_4Si	101.81	69.63	62.18	68.43	74.70	32.20	57.13
2	D_2O–DSS	106.24	76.37	60.94	74.61	78.10	35.25	60.12
	$CDCl_3$–Me_4Si	103.88	73.94	59.66	72.92	75.77	32.20	57.34
8	D_2O,D^+–DSS [a]	101.82	74.56	60.23	74.78	73.61	35.74	57.88
	$CDCl_3$–Me_4Si	99.19	72.68	60.57	73.05	70.97	32.78	55.57

[a] A small amount of trifluoroacetic acid was added.

Table 3
Kinetic parameters [a] for the reversible conversion between compounds **1** and **2**

Starting compound	Temp. (°C)	[Sac] [b] (g/L)	[LiX] (mmol/L)	$\alpha^G(\infty)$	$k_{AG} \times 10^3$ (L mol^{-1} min^{-1})	$k_{GA} \times 10^3$ (L mol^{-1} min^{-1})	Activation energy (kJ mol^{-1}) k_{AG}	Activation energy (kJ mol^{-1}) k_{GA}
1 [c]	60	1.00	82.6	0.897	17.5	2.02		
	70	1.03	42.1	0.854	101	17.2	143	145
	80	1.00	40.5	0.880	264	36.1		
	90	0.93	4.15	0.885	1470	192		
2 [c]	70	0.86	42.2	0.870	114	17.0		
7 [c]	90	1.02	83.6	> 0.98	33.0 [d]			
5 [e]	80	1.65	2.14×10^3	0.856	0.19	0.03	175	177
	90	1.58	2.04×10^3	0.855	0.77	0.13		
6 [e]	90	2.49	2.01×10^3	0.861	0.64	0.10		

[a] k_{AG} is the rate constant for the conversion of an alloside to a glucoside and k_{GA} vice versa.
[b] Saccharide concentration.
[c] In LiBr–DMA.
[d] From the inital slope.
[e] In LiCl-DMA. Data from ref. [3].

where k_{AG} and k_{GA} are the rate constants for the substitution of bromine at C-3. It was analyzed in the same way as for the interconversion between methyl 3,6-dichloro-3,6-dideoxy-β-D-alloside (**5**) and methyl 3,6-dichloro-3,6-dideoxy-β-D-glucoside (**6**) in LiCl–DMA [3]. The substitution at C-6 is assumed not to affect the substitution at C-3. If the starting material is pure **1**, the rate equation for this interconversion becomes [3];

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

where t is time, $\alpha^G(t)$ is the mole fraction of **2** in the dibromoglycosides at time t, and $\alpha^G(\infty)$ is that at equilibrium. The values of k_{AG} and $\alpha^G(\infty)$ were calculated with a non-linear least-squares regression method. The experimental values satisfactorily fitted the theoretical curves as in the case of the interconversion between **5** and **6** in LiCl–DMA [3]. The value of k_{GA} is obtained from k_{AG} and $\alpha^G(\infty)$ as;

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

Table 3 summarizes the values of k_{AG}, k_{GA}, $\alpha^G(\infty)$ and the activation energy. The values of k_{AG}, k_{GA}, and $\alpha^G(\infty)$ obtained at 70°C using **1** as the starting material agree very well with those using **2** as the starting material. This finding shows that the reaction is reversible, as in the case for **5** and **6** [3]. The values for the conversion of **7** into methyl 3,6-dibromo-3,6-dideoxy-α-D-glucoside (**8**) at 90°C and some values of the rate constants for the interconversion between **5** and **6** [3] are also shown for comparison. The value for the conversion of **7** was calculated from the initial slope because, in this case, the $\alpha^G(\infty)$ value was close to unity and the numerical calculation of $\alpha^G(\infty)$ and k_{GA} with eqs (2) and (3) became unrealistic. The kinetic analysis of the conversion of **8** into **7** was not possible because of the very small equilibrium fraction of **8**. The NMR parameters for compound **8** are listed also in Tables 1 and 2. The values of coupling

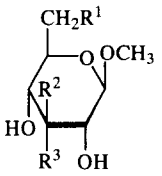
constants confirm the *gluco* configuration in the $^4C_1$ conformation and ^{13}C chemical shifts indicate the substitution of C-3 and C-6 hydroxyl groups with bromine.

3. Discussion

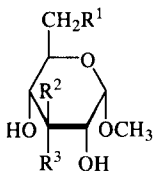
The key step in the bromination of alcohols with the Br_3Im–PPh_3 system is no doubt the S_N2 replacement of the phosphonium ester moiety of the intermediate complex with bromine [10], as in the case of the iodination of alcohols with reagent systems based on iodine and PPh_3 [13]. For the I_2–PPh_3 system in toluene–acetonitrile, the addition of a base such as imidazole or triethylamine was necessary to attain high yields of products. The details of the reaction mechanisms for the Br_3Im–PPh_3 system, however, are not fully understood. It is not known, for example, which of the three bromine atoms in a Br_3Im molecule is incorporated in the substitution, nor what is the active species that participates in the substitution as the bromine source.

Sulfuryl chloride or methanesulfonyl chloride gave **5** and methyl 4,6-dichloro-4,6-dideoxy-β-D-galactoside from **3** after desulfation [14,15], whereas methyl 4,6-dichloro-4,6-dideoxy-α-D-galactoside was the only product from **9** [15,16]. This can be explained in terms of the 1,3-diaxial interaction in the activated complex between glycoside bond and bonds formed at C-3 (between C-3 carbon and nucleophiles) in the α anomer in the $^4C_1$ conformation [16]. Characteristic of the Br_3Im–PPh_3 system is that it yields only 3,6-dibromo-3,6-dideoxyglycosides from both **3** and **9**. Classon et al. [10] assumed that an intermediate in the $^1C_4$ conformation was formed through formation of a cyclic phosphonium diester bridging O-2 and O-4. Although this mechanism is, as they stated, "highly tentative", it explains the lower reactivity of **3** to form **1** than that of **9** to form **7**, as observed in this study.

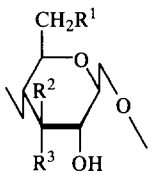
Compound **1** was converted into **2** almost completely in toluene under the synthetic conditions in 4 h, whereas only a small amount of **2** (less than 10% of **1**) was detected by GLC for the reaction in toluene–acetonitrile under otherwise the same conditions. It is not known whether the bromine substitution is caused by bromide ion (or an anion



1 R^1=Br, R^2=H, R^3=Br
2 R^1=Br, R^2=Br, R^3=H
3 R^1=OH, R^2=OH, R^3=H
4 R^1=Br, R^2=OH, R^3=H
5 R^1=Cl, R^2=H, R^3=Cl
6 R^1=Cl, R^2=Cl, R^3=H



7 R^1=Br, R^2=H, R^3=Br
8 R^1=Br, R^2=Br, R^3=H
9 R^1=OH, R^2=OH, R^3=H



10 R^1=Cl, R^2=H, R^3=Cl
11 R^1=Cl, R^2=OH, R^3=H
12 R^1=Cl, R^2=Cl, R^3=H
13 R^1=OH, R^2=H, R^3=Br
14 R^1=Br, R^2=H, R^3=Br
15 R^1=Br, R^2=Br, R^3=H
16 R^1=Br, R^2=OH, R^3=H

that donates bromine) or by a neutral molecule that generates bromine. However, the facile substitution at C-3 in toluene as compared with the case in the more polar toluene–acetonitrile medium is consistent with an S_N2 reaction between a neutral molecule and an anion [17]. In the reaction between **1** and Br^- (or other anion), the initial state is polarized while the charge becomes dispersed in the activated complex. A polar solvent-system would decrease the energy of the initial state to a considerable extent, resulting in an increase in the activation energy. It is concluded that compound **1** is a kinetically controlled product whereas **2** is a thermodynamically stable product.

The rate constants for the interconversion between **1** and **2** in LiBr–DMA at 80 and 90° C are about 10^3 times as large as those between **5** and **6** (Table 3). This can not be explained fully because kinetic data for halogen substitution at high temperatures in polar aprotic solvents such as DMA are not found in the literature. The C–Br bond is more susceptible to nucleophilic substitution as compared with the C–Cl bond. In *N,N*-dimethylformamide at 25°C, the rate constant for the substitution of CH_3Br with SCN^- is 60 times as large as that of CH_3Cl, and the rate constant for the substitution of CH_3OTs with Br^- is about three times as large as that with Cl^- [18]. The values of the activation energies show that the bromine substitution in LiBr–DMA is less affected by the reaction temperature than the chlorine substitution in LiCl–DMA.

The value of the rate constant (k_{AG}) of the conversion of compound **7** into **8** is about 1/45 of that of **1** into **2** in LiBr–DMA at 90°C (Table 3). This can be ascribed to the 1,3-diaxial interaction operating in the α-anomer. Although the formation of **7** only was reported for the reaction between **9** and Br_3Im–PPh_3 [10,11], we found by GLC and GLC-MS analyses (as *O*-trifluoroacetyl derivatives on Dexsil 300 GC) that compound **8** was present before crystallization ($\sim$ 10% of **7**) in the mixture obtained under the reaction conditions reported. Compound **8** could not be separated from **7** in TLC with several solvent systems examined as eluents. This is probably the reason for the fact that the formation of **8** has not been reported [10,11].

The bromodeoxycellulose samples having high ds values obtained from cellulose with Br_3Im–PPh_3, under homogeneous conditions in LiBr–DMA [5] and under heterogeneous conditions in organic solvents [6], contained residues of both **14** and **15**. This may be explained based on the large rate-constants for the interconversion between **1** and **2**. Some of the residues of **14** are converted into residues of **15** during the bromination. For the dibromoglycosides, the equilibrium mole fractions of **2** are larger than 0.85 whereas the amounts of **15** residues in the bromodeoxycellulose samples obtained were about double those of residues of **14** [5]. A similar tendency was observed for the reaction of a chlorodeoxycellulose sample (ds, 1.54) with LiCl in DMA [3], where the amount of **10** residues at equilibrium was almost equal to that of **12** residues. The equilibrium mole fractions of **5** in LiCl–DMA, on the other hand, were larger than 0.85 (Table 3).

4. Experimental

General methods.—Tribromoimidazole (Br_3Im) was synthesized according to the reported method [19]. LiBr was dried at 180° C under diminished pressure, and

commercial DMA was purified conventionally. Kieselgel 60 F_{254} (Merck) was used for TLC and Wakogel C-100 (silica gel, Wako Pure Chemical Ind., Ltd.) was used for column chromatography. Ethyl acetate–toluene (1:1 v/v) was used as the eluent for both column chromatography and TLC. A JNM-A500 spectrometer (Jeol Ltd.) was used for the measurements of both normal and two-dimensional ^1H and ^{13}C NMR spectra. D_2O (internal standard, DSS) and $CDCl_3$ (Me_4Si) were used as NMR solvents. The samples were heated with D_2O before dissolving into NMR solvents. The optical rotations were measured with a Jasco DIP-370 digital polarimeter (Jasco Ltd.). GLC analyses of the interconversion between **1** and **2** and of the conversion of **7** into **8** were carried out as *O*-trifluoroacetyl derivatives using Dexsil 300 GC as a stationary phase. The operation conditions were the same as those for the measurement of the interconversion between **5** and **6** [3]. Melting points were not corrected.

*Methyl 3,6-dibromo-3,6-dideoxy-β-*D*-allopyranoside* (**1**).—The synthesis was carried out following the synthetic method for **7** reported by Garegg et al. [11]. Compound **3** (3.0 g, 15 mmol), Br_3Im (9.5 g, 31 mmol) and PPh_3 (16.2 g, 62 mmol) were placed in a flask containing 330 mL of toluene–acetonitrile (2:1 v/v). The mixture was kept for 1 h at 75° C and then for 4 h at 110°C with stirring. After the reaction, the mixture was extracted with water several times. The aqueous layers were combined, evaporated under diminished pressure, and the residue was chromatographed. The product **1** obtained (160 mg, 3%) was recrystallized from 1:1 $CHCl_3$–EtOAc. mp 138°C (decomp). $[\alpha]_D^{25}$ −38° (*c* 0.52, EtOAc). R_f value in TLC, 0.39. Anal. Calcd for $C_7H_{12}O_4Br_2$: C, 26.28; H, 3.78; Br, 49.94. Found: C, 26.14; H, 3.78; Br, 50.18. The NMR parameters are listed in Tables 1 and 2.

*Methyl 3,6-dibromo-3,6-dideoxy-β-*D*-glucopyranoside* (**2**).—The synthesis was carried out following the synthetic method for **7** reported by Classon et al. [10]. Compound **3** (3.0 g), Br_3Im (9.4 g), and PPh_3 (16.2 g) were placed in a flask containing 300 mL of toluene. The mixture was kept for 1 h at 75°C and then for 4 h at 110°C with stirring. After the reaction, a saturated solution of $NaHCO_3$ was added, and the mixture was stirred for 10 min. Iodine was added until the color of iodine remained in the organic phase, and the excess of iodine was reduced with aqueous $Na_2S_2O_3$. The toluene layer was separated and extracted with water. All the aqueous layers were combined and the combined solution was extracted with CH_2Cl_2. The CH_2Cl_2 solution was dried with $MgSO_4$ and evaporated under diminished pressure. The residue was chromatographed and 390 mg of syrup (R_f value in TLC, 0.51) was obtained. Two further recrystallizations from 1:1 $CHCl_3$–EtOAc gave hygroscopic crystals (95 mg, 2%). mp 117–118°C. $[\alpha]_D^{25}$ 12° (*c* 0.30, EtOAc). Anal. Calcd for $C_7H_{12}O_4Br_2$: C, 26.28; H, 3.73; Br, 49.94. Found: C, 26.11; H, 3.77; Br, 50.19. The NMR parameters are listed in Tables 1 and 2. Acetate: mp 146–147° C. $[\alpha]_D^{25}$ −6° (*c* 0.25, EtOAc). Anal. Calcd for $C_{11}H_{16}O_6Br_2$: C, 32.70; H, 3.99; Br, 39.55. Found: C, 32.70; H, 3.99; Br, 39.44.

Interconversion between **1** *and* **2** *in LiBr–DMA*.—The reactions were carried out under homogeneous conditions in LiBr–DMA under a nitrogen atmosphere. Aliquots were taken from the mixture at predetermined intervals. The pipetted solution was poured into water containing silver lactate in an amount equimolar to LiBr in the aliquot, and the resultant AgBr was filtered off. The filtrate was evaporated to dryness and the residue was trifluoroacetylated with trifluoroacetic anhydride–CH_2Cl_2. Details of the

measurements of rate constants with GLC were the same as for the interconversion between **5** and **6** described in the previous paper [3].

*Conversion of methyl 3,6-dibromo-3,6-dideoxy-α-*D*-alloside* (**7**) *into methyl 3,6-dibromo-3,6-dideoxy-α-*D*-glucoside* (**8**) *in LiBr–DMA*.—Compound **7** [10,11] was heated in LiBr–DMA at 90°C, and the mixture was treated and analyzed by the same procedures just described. A hygroscopic syrup was obtained from the mixture afier 48 h. GLC and GLC-MS analyses showed that the syrup contained **8** and **7** (mol ratio, about 98:2). The R_f values of **8** in TLC for several solvent systems were very close to those of **7**. Compound **8** could not be obtained crystalline, and the structure was analyzed by NMR spectroscopy only. NMR parameters are listed in Tables 1 and 2.

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