Carbohydrate Research, 76 (1979) 131–140

THE SYNTHESIS AND THE ^{1}H- AND ^{13}C-NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY OF THE CYCLIC SULFITES OF SOME SUGARS

YUEH WANG AND HARRY P. C. HOGENKAMP*
Department of Biochemistry, The University of Minnesota, Minneapolis, Minnesota 55455 (U.S.A.)
(Received March 26th, 1979; accepted for publication, April 10th, 1979)

ABSTRACT

Treatment of methyl β-D-ribofuranoside with thionyl chloride in hexamethylphosphoric triamide gives two diastereoisomeric methyl 5-chloro-5-deoxy-β-D-ribofuranoside 2,3-cyclic sulfites. Similar cyclic sulfites are formed from benzyl β-D-ribofuranoside and 1,4-anhydro-DL-ribitol. If acetonitrile is substituted for hexamethylphosphoric triamide, the cyclic sulfites are the main products, and only traces of the chlorinated sugars are formed. ^{1}H- and ^{13}C-n.m.r.-spectral analysis of these reactions demonstrated that one of the diastereomers preponderates. The structure of these cyclic sulfites was established by comparison of the ^{1}H-n.m.r. spectra with those of the propylene sulfites. Treatment of 1,2-*O*-isopropylidene-α-D-glucofuranose (**14**) with thionyl chloride in hexamethylphosphoric triamide yields 3-chloro-3-deoxy-1,2-*O*-isopropylidene-α-D-allofuranose 5,6-cyclic sulfite. In contrast to the 2,3-cyclic sulfites, which are stable, the cyclic sulfites derived from **14** slowly decompose at room temperature.

INTRODUCTION

Several years ago, Kikugawa and Ichino[1] reported a very convenient method for the preparation of 5′-deoxy-5′-haloribonucleosides. Thionyl bromide or chloride in hexamethylphosphoric triamide was found to halogenate C-5′ of ribonucleosides specifically, thus obviating protection of the vicinal hydroxyl groups on C-2′ and C-3′. These 5′-deoxy-5′-halonucleosides are precursors of several biologically important compounds that had hitherto been synthesized by rather lengthy procedures. For instance, reaction of 5′-chloro-5′-deoxyribonucleosides with cob(I)alamin yields adenosylcobalamin and numerous of its analogs, differing in the base, or the sugar moiety, or both[2], and reaction with either homocysteine thiolactone in aqueous alkali[3], or homocystine in sodium–liquid ammonia[4], affords *S*-adenosylhomocysteine in excellent yield. Furthermore, dechlorination of 5′-chloro-5′-deoxyribonucleosides with tributyltin hydride affords the 5′-deoxyribonucleosides[5].

We intended to explore the utility of the thionyl chloride–hexamethylphosphoric triamide reagent for the preparation of specifically chlorinated sugars that would, in turn, be suitable precursors for deoxy sugars or unsaturated sugars. However,

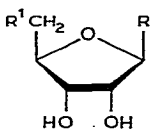
reaction of methyl β-D-ribofuranoside (**1**), which differs from adenosine in being a glycoside, with thionyl chloride in hexamethylphosphoric triamide did not yield methyl 5-chloro-5-deoxy-β-D-ribofuranoside, but the two diastereomeric 2,3-cyclic sulfites (**2** and **3**). Cyclic sulfites of diols had been prepared before; for instance, Honeyman and Morgan[6] treated methyl 4,6-*O*-benzylidene-α-D-glucopyranoside with thionyl chloride in pyridine, to yield the 2,3-cyclic sulfites, and Robertson and Neish[7] reported the isolation of the cyclic sulfites of *levo*- and *meso*-2,3-butanediol. These derivatives are unstable, and decompose slowly on standing.

More recently, Sowa and Tsunoda[8,9] described the preparation of the 2′,3′-sulfites of purine and pyrimidine nucleosides by treating the parent nucleosides with thionyl chloride in acetonitrile, and Beranek and Hrebabecky[10,11] reported the synthesis of similar esters of adenosine, cytidine, and uridine by use of the thionyl chloride–hexamethylphosphoric triamide reagent. The cyclic sulfites of nucleosides are also rather labile, and, in earlier syntheses, presumably decomposed during processing.

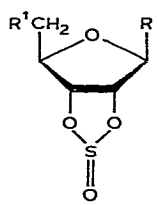
We now describe the synthesis of reasonably stable cyclic sulfites of several sugar derivatives by use of thionyl chloride in either hexamethylphosphoric triamide or acetonitrile. The structure of these cyclic sulfites has been established by comparison of their ^{1}H- and ^{13}C-n.m.r. spectra with those of propylene sulfites.

DISCUSSION

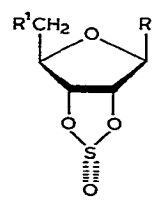
Sugars bearing *cis*-vicinal hydroxyl groups react with thionyl chloride in hexamethylphosphoric triamide or acetonitrile to give the cyclic sulfites. In contrast to



1 R = OMe, R^1 = OH
8 R = OCH_2Ph, R^1 = OH
11 R = H, R^1 = OH

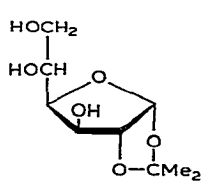


a

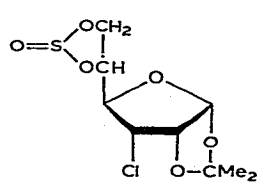


b

2,3 R = OMe, R^1 = Cl
4,5 R = OMe, R^1 = OH
6,7 R = OMe, R^1 = OBz
9,10 R = OCH_2Ph, R^1 = Cl
12,13 R = H, R^1 = Cl



14



15

the 2′,3′-cyclic sulfites of the ribonucleosides, the cyclic sulfites of sugars are quite stable, and may be isolated in good yield. Thus, reaction of methyl β-D-ribofuranoside (**1**), benzyl β-D-ribofuranoside (**8**), or 1,4-anhydro-DL-ribitol (**11**) with thionyl chloride in hexamethylphosphoric triamide yields the corresponding 5-chloro-5-deoxy 2,3-cyclic sulfites (**2** and **3**, **9** and **10**, and **12** and **13**); under the same conditions, 1,2-*O*-isopropylidene-α-D-glucofuranose (**14**) gives 3-chloro-3-deoxy-1,2-*O*-isopropylidene-α-D-allofuranose 5,6-cyclic sulfite (**15**). If acetonitrile is substituted for hexamethylphosphoric triamide, the cyclic sulfites are the main products, and only traces of the chlorinated sugars can be detected. Whereas the ribofuranose derivatives **2** and **3** are sufficiently stable to be isolable by sublimation at 100°, the cyclic sulfite **15** slowly decomposes at room temperature.

The ^{13}C- and ^{1}H-n.m.r. spectra of these preparations clearly demonstrate that both of the diastereomeric cyclic sulfites are formed. It is also evident from these spectra that one of the diastereomers preponderates (see Fig. 1). The ^{13}C-n.m.r. spectra show occurrence of chlorination at C-5 of **2**, **3**, **8**, **9**, **12**, and **13**, the replacement of the hydroxyl group by a chlorine atom resulting in a large, upfield shift (~19 p.p.m.) of the C-5 resonance. Similarly, the chlorination of **14** causes a large upfield shift of the C-3 signal; as this reaction occurs with inversion of configuration, the C-2 resonance is also shifted upfield, because a *cis* orientation of vicinal substituents is associated with a substantial increase in shielding[12], whereas a *trans* relationship with the substituent on C-4 causes a downfield shift (—2.55 p.p.m.) of that

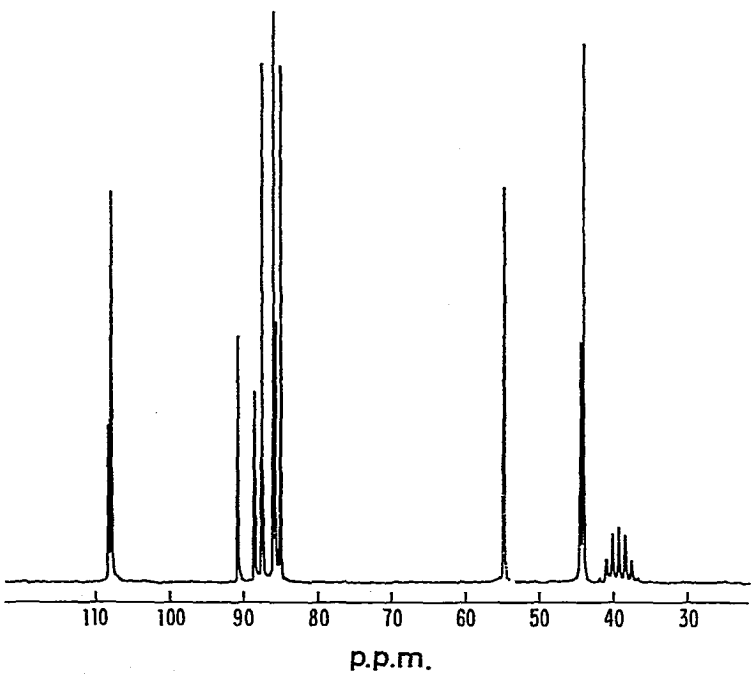


Fig. 1. F.t., ^{13}C-n.m.r., proton-decoupled spectrum (at 25.15 MHz) of **2** and **3** in Me_2SO-d_6.

TABLE I

^{13}C-N.M.R. CHEMICAL-SHIFTS[a] OF FURANOID DERIVATIVES

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*Other*
1[b]	108.30	74.42	71.13	83.79	63.31	54.38 (OMe)
2	107.78	87.50	86.01	85.06	44.47	55.01 (OMe)
3	108.14	90.73	88.53	85.69	44.83	55.01 (OMe)
4	107.26	87.46	86.60	85.91	61.85	54.63 (OMe)
5	107.67	90.67	88.78	86.15	62.24	54.63 (OMe)
6	107.29	87.63	85.70	82.72	64.65	54.75 (OMe), 128.95, 129.48, 133.69 (aromatic), 165.60 (C=O)
7	108.15	90.76	88.18	83.56	64.97	54.75 (OMe), 128.95, 129.48, 133.69 (aromatic), 165.60 (C=O)
8	106.42	74.61	71.21	83.96	63.33	68.20 (benzyl), 127.59, 127.93, 128.41, 138.29 (aromatic)
9	105.07	87.55	85.93	84.99	44.47	69.24 (benzyl), 127.83, 128.04, 128.32, 136.63 (aromatic)
10	105.32	90.69	88.42	85.70	44.85	69.24 (benzyl), 127.83, 128.04, 128.32, 136.63 (aromatic)
11[c]	72.13	70.55	71.70	83.32	61.87	
12	70.88	85.40	86.20	83.19	42.15	
13	72.14	88.71	88.85	83.86	43.03	
14[d]	104.66	84.87	73.45	80.25	68.62	63.81 (C_6), 110.58 (CMe_2), 26.14, 26.71 (Me)
15	104.70	73.62	44.48	82.80	75.05	69.85 (C_6), 112.26 (CMe_2), 26.11, 26.42 (Me)

[a]Chemical shifts are given in p.p.m. downfield from internal Me_4Si: in Me_2SO-d_6 (39.6 p.p.m.). [b]For peak assignments in D_2O, see ref. 13. [c]For peak assignments in D_2O, see ref. 14. [d]For peak assignments, see ref. 15.

TABLE II

^{13}C SHIELDING DIFFERENCES ASSOCIATED WITH SUBSTITUENT AND CONFIGURATIONAL EFFECTS OF FURANOID DERIVATIVES

Compound	*Δδ[a] C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*
2 *vs.* 1	+0.52	−13.08	−14.88	−1.27	+18.84	
3 *vs.* 1	+0.16	−16.31	−17.40	−1.90	+18.48	
2 *vs.* 3	+0.36	+ 3.23	+ 2.52	+0.63	+ 0.36	
4 *vs.* 5	+0.41	+ 3.21	+ 2.18	+0.24	+ 0.39	
6 *vs.* 7	+0.86	+ 3.13	+ 2.48	+0.84	+ 0.32	
9 *vs.* 8	+1.35	−12.94	−14.72	−1.03	+18.86	
10 *vs.* 8	+1.10	−16.08	−17.21	−1.74	+18.48	
9 *vs.* 10	+0.25	+ 3.14	+ 2.49	+0.71	+ 0.38	
12 *vs.* 11	+1.25	−14.85	−14.50	+0.13	+19.72	
13 *vs.* 11	−0.01	−18.16	−17.15	−0.54	+18.84	
12 *vs.* 13	+1.26	+ 3.31	+ 2.65	+0.67	+ 0.88	
15 *vs.* 14	−0.04	+11.25	+28.97	−2.55	− 6.43	−6.04

[a]Key: +, shielding; −, deshielding (in p.p.m.).

TABLE III

270 MHz, ^{1}H-N.M.R. SPECTRAL DATA[a] OF FURANOID DERIVATIVES

Compound	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*Other*
1[b]	4.62 (s,1)	3.70		3.81 (m)	3.49 (m,1,H_R)	3.22 (s,3,OMe)
					3.35 (m,1,H_S)	
2	5.20 (s,1)	5.65 (d,1)	5.44 (d,1)	4.40 (t,1)	3.73 (d,2)	3.33 (s,3,OMe)
		$J_{2,3} = 6.14$		$J_{4,5} = 7.60$		
3	5.31 (s,1)	5.49 (d,1)	5.27 (d,1)	4.55 (t,1)	3.70 (d,2)	3.34 (s,3,OMe)
		$J_{2,3} = 6.71$		$J_{4,5} = 7.63$		
6	5.21 (s,1)	5.84 (d,1)	5.47 (d,1)	4.66 (q,1)	4.46 (q,1,H_R)	3.29 (s,3,OMe)
				$J_{4,5H_R} = 5.88$	4.35 (q,1,H_S)	7.56 (t,2,*meta*)
						$J_{m,o} = J_{m,p} = 7.6$
		$J_{2,3} = 5.88$		$J_{4,5H_S} = 6.62$	$J_{5H_R,5H_S} = -11.76$	7.68 (t,1,*para*)
						8.03 (d,2,*ortho*)
7	5.32 (s,1)	5.68 (d,1)	5.31 (d,1)	4.80 (q,1)	4.46 (q,1,H_R)	same as above
		$J_{2,3} = 5.88$		$J_{4,5H_R} = 5.88$	4.35 (q,1,H_S)	
				$J_{4,5H_S} = 6.62$	$J_{5H_R,H_S} = -11.76$	
8	4.88 (s,1)	3.86		3.98 (m)	3.63 (q,1,H_R)	4.42 (d,1,benzyl)
					3.45 (q,1,H_S)	4.70 (d,1,benzyl)
						$J_{benzyl} = -11.77$
					$J_{4,5H_R} = 2.94$,	
					$J_{4,5H_S} = 6.25$	7.34 (s,5,aromatic)
					$J_{5H_R,H_S} = -11.77$	
9	5.40 (s,1)	5.69 (d,1)	5.51 (d,1)	4.46 (t,1)	3.78 (d,2)	4.73 (d,1,benzyl)
		$J_{2,3} = 5.88$		$J_{4,5} = 7.36$		4.55 (d,1,benzyl)
						$J_{benzyl} = -11.03$
						7.36 (s,5,aromatic)

TABLE III *(continued)*

Compound	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*Other*
10	5.50 (s,1)	5.53 (d,1) $J_{2,3} = 6.62$	5.35 (d,1)	4.59 (t,1) $J_{4,5} = 7.35$	3.76 (d,2)	4.73 (d,1,benzyl) 4.55 (d,1,benzyl) $J_{benzyl} = -11.03$ 7.36 (s,5,aromatic)
11[c]	3.53 (m,1,H_S) 3.39 (m,1,H_R)	4.01 (m,1)	~3.88 (m,1)	3.79 (m,1)	3.62 (m,1,H_R) ~3.53 (m,1,H_S)	
12	4.04 (q,1,H_R) 4.12 (q,1,H_S) $J_{1H_R,1H_S} = -11.76$ $J_{1H_R,2}$ $J_{1H_S,2}$	5.68 (0,1) $J_{2,3} = 6.62$	5.48 (q,1) $J_{3,4} = 1.70$	4.26 (sextet 1) $J_{4,5H_R} = J_{4,5H_S}$ $= 6.62$	3.79 (q,1,H_R) 3.71 (q,1,H_S) $J_{5H_R,5H_S}$	
14[d]	5.78 (d,1) $J_{1,2} = 3.68$	4.37 (d,1)	4.03 (d,1) $J_{3,4} = 2.2$	3.83 (q,1) $J_{4,5} = 8.09$ $J_{3,4} = 2.20$	3.70 (m,1)	3.55 (d,1,6H_R) 1.36 (s,3,Me) 3.37 (d,1,6H_S) 1.22 (s,3,Me) $J_{6H_R,6H_S} = -11.70$
15	6.05 (d,1) $J_{1,2} = 3.80$	4.83 (d,1)	5.04 (d,1) $J_{3,4} = 2.30$	4.47	4.49 (m)	4.16 (q,1,6H_R) 1.45 (s,3,Me) 4.70 (q,1,6H_S) 1.30 (s,3,Me) $J_{5,6H_R} = 5.97$ $J_{5,6H_S} = 6.63$ $J_{6H_R,6H_S} = -12.5$

[a]Chemical shifts are given in p.p.m. downfield from internal Me_4Si, in Me_2SO-d_6; coupling constants are given in Hz. [b]For data assignments in deuterium oxide, see ref. 16. [c]D_2O was added to sample solution; chemical shifts of H-3 and H-5 may not be accurate, due to peak overlap. [d]For data assignments in chloroform, see ref. 17.

resonance. The formation of the cyclic sulfites is accompanied by a substantial, downfield shift of both the C-2 and the C-3 resonances. For one diastereomer, these resonances are shifted ~13 and 15 p.p.m., whereas the other isomer shows downfield shifts of 16 and 17 p.p.m. These carbon-13 data are summarized in Table I, and the ^{13}C-shielding differences associated with chlorination and formation of cyclic sulfites are presented in Table II.

The ^{1}H-n.m.r. spectra are also in accord with the structures assigned (see Table III). The chlorination at C-5 of **1**, **8**, and **11**, or at C-3 of **14**, causes downfield shifts of the methylene protons on C-5, or of H-3 of the D-glucose derivative. Furthermore, on chlorination, the two prochiral hydrogen atoms on C-5 of **1** and **8** become magnetically equivalent, and give rise to a doublet. The *pro-R* hydrogen atom at C-1 of **11** and of the cyclic sulfite **12** is assigned to the upfield resonance, because this hydrogen atom is shielded by the *cis*-2-hydroxyl group. Similarly, the H-2 resonance of **15** is shifted downfield, because the chlorination occurs with inversion of configuration, and thus H-2 is no longer shielded by the hydroxyl group.

The assignment of structure to the two diastereomeric, cyclic sulfites (*e.g.*, **2** *versus* **3**) is based on both the ^{1}H- and the ^{13}C-n.m.r. spectra. Pritchard and Lauterbur[18] provided the basis for these assignments; their analysis of the ^{1}H-n.m.r. spectra of the two isomers of propylene sulfite indicated that hydrogen atoms *trans* to the double-bonded oxygen atom resonate upfield from those *cis* to that oxygen atom. Inspection of the ^{1}H-n.m.r. spectra of isomers **2** and **3** reveals that, for one isomer (**3**), H-2 and H-3 resonate at higher field, whereas H-1 and H-4 resonate at lower field, suggesting that, for this isomer, H-2 and H-3 are *trans* to the oxygen atom doubly bonded to sulfur, whereas H-1 and H-4 are *cis* to this oxygen atom.

Perlin[13] pointed out that an increase in the shielding of carbon is generally accompanied by a decrease in the shielding of the attached proton. Comparison of the ^{13}C-n.m.r. spectra of **2** and **3** reveals that the resonances of C-2 and C-3 of isomer **3** do, indeed, occur at lower field than the corresponding resonances of isomer **2**. Thus, on the basis of the ^{1}H- and ^{13}C-n.m.r. spectra, **2** is identified as the *exo* isomer *a*, and **3** as the *endo* isomer *b*. The carbon-13 shielding differences (see Table II) between the *exo* and *endo* diastereomers clearly demonstrate that the preponderant isomers **2**, **4**, **6**, **9**, and **12** all have the *exo* configuration.

Only one isomer could be isolated from the reaction between **14** and thionyl chloride in hexamethylphosphoric triamide, and thus, no structural assignment can be made for isomer **15**.

EXPERIMENTAL

General methods. — Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., except that sulfur analyses were made by Dr. C. W. Carr, University of Minnesota. Melting points were determined on a hot stage equipped with a microscope, and are not corrected. Pulse, ^{1}H-n.m.r. spectra were recorded with a Bruker 270-MHz spectrometer, and pulse, ^{13}C-n.m.r. spectra with a Varian

XL-100-15 spectrometer; chemical shifts are recorded in p.p.m. downfield from an external standard of tetramethylsilane.

Materials. — Methyl β-D-ribofuranoside[19], benzyl β-D-ribofuranoside[20], 1,4-anhydro-DL-ribitol[21], and 1,2-*O*-isopropylidene-α-D-glucofuranose[22] were prepared by published procedures.

Synthesis of cyclic sulfites

Methyl 5-chloro-5-deoxy-β-D-ribofuranoside 2,3-cyclic sulfites (**2** *and* **3**). — To a solution of thionyl chloride (3 mL, 41.7 mmol) in hexamethylphosphoric triamide (25 mL) was added methyl β-D-ribofuranoside (**1**; 3.0 g, 18.3 mmol), and the mixture was stirred, with exclusion of moisture, for 20 h at room temperature. The mixture was then poured into ice–water (200 mL), made neutral with sodium hydrogencarbonate, and stored at 4°. The white precipitate resulting was collected by filtration, washed with cold water, and purified by vacuum sublimation at 100°; yield 2.72 g (64%); m.p. 59–62°.

Anal. Calc. for $C_6H_9ClO_5S$ (228.6): C, 31.52, H, 3.97; Cl, 15.51; S, 14.02. Found: C, 31.70; H, 3.94; Cl, 15.66; S, 14.00.

Separation of the two diastereomers by fractional recrystallization, or by diffusion crystallization (ethanol–water) was unsuccessful. In one preparation, a pure diastereomer was isolated from the filtrate of the crude reaction-mixture; recrystallization from ethanol gave 0.27 g of a product having m.p. 127–130°; ν_{max}^{KBr} 1220 cm^{-1} (S=O).

Methyl 5-O-benzoyl-β-D-ribofuranoside 2,3-cyclic sulfites (**6** *and* **7**). — To a solution of thionyl chloride (3.95 mL, 55 mmol) in dry acetonitrile (20 mL, distilled from calcium hydride), prepared at 0°, was slowly added methyl β-D-ribofuranoside (**1**; 3.0 g, 18.3 mmol), and the mixture was stirred for 3 h at room temperature with exclusion of moisture, poured over crushed ice (100 g), and extracted twice with chloroform. The extracts were combined, successively washed with 10% aqueous sodium hydrogencarbonate (100 mL) and water (100 mL), dried (anhydrous sodium sulfate), and evaporated to an amber syrup (2.6 g). The ^{13}C-n.m.r. spectrum of this material indicated a mixture of both diastereomeric methyl β-D-ribofuranoside 2,3-cyclic sulfites (**4** and **5**) in the ratio of ~2.4 to 1, as well as traces of the 5-chloro derivatives **2** and **3**. A solution of the syrup in dry pyridine (15 mL) was treated with benzoyl chloride (1.5 mL, 12.5 mmol); after 20 h at room temperature, ice was added, and the mixture was extracted with chloroform. The extract was successively washed with cold, 3M hydrochloric acid and water, dried (sodium sulfate), and evaporated to dryness. The residual syrup was crystallized from ethanol–water with the aid of charcoal, to yield 2.44 g (66%) of colorless needles, m.p. 67–70°.

Anal. Calc. for $C_{13}H_{14}O_6S$ (298.3): C, 49.68; H, 4.49; S, 10.20. Found: C, 49.97; H, 4.59; S, 10.32.

Benzyl 5-chloro-5-deoxy-β-D-ribofuranoside 2,3-cyclic sulfites (**9** *and* **10**). — Benzyl β-D-ribofuranoside (**8**; 3.0 g, 12.5 mmol) was treated with thionyl chloride in hexamethylphosphoric triamide as already described. The crude product was

crystallized from ethanol with the aid of charcoal, to yield 3.3 g (87%) of the cyclic sulfites **9** plus **10**, m.p. 94–97°. The ^{13}C-n.m.r. spectrum of this preparation showed a ratio of 2.6 to 1 for the two isomers. The main isomer could be isolated by three recrystallizations from ethanol; m.p. 111–112°.

Anal. Calc. for $C_{12}H_{13}ClO_5S$ (304.7): C, 47.29; H, 4.30; Cl, 11.63; S, 10.52. Found (mixture): C, 47.13; H, 4.28; Cl, 11.72; S, 10.05; pure isomer: C, 47.22; H, 4.28; Cl, 11.56; S, 10.83.

*1,4-Anhydro-5-chloro-5-deoxy-*DL*-ribitol 2,3-cyclic sulfites* (**12** *and* **13**). — 1,4-Anhydro-DL-ribitol (**11**, 3.0 g, 22.4 mmol) was treated with thionyl chloride (4.3 mL, 60 mmol) in hexamethylphosphoric triamide (30 mL) as just described. Crystallization of the crude product from aqueous ethanol gave only a single diastereomer (**12**); yield 2.53 g (57%), m.p. 96–98°.

Anal. Calc. for $C_5H_7ClO_4S$ (198.6): C, 30.24; H, 3.55; Cl, 17.85; S, 16.14. Found: C, 30.50; H, 3.66; Cl, 17.77; S, 15.80.

The ^{13}C-n.m.r. spectrum of the mother liquor showed that a small proportion of the other diastereomer (**13**) was also produced. However, attempts to isolate pure **13** as a crystalline preparation were unsuccessful.

*3-Chloro-3-deoxy-1,2-*O*-isopropylidene-α-*D*-allofuranose 5,6-cyclic sulfite* (**15**). — 1,2-*O*-Isopropylidene-α-D-glucofuranose (**14**; 3.0 g, 13.6 mmol) was treated with thionyl chloride (2.6 mL, 36 mmol) in hexamethylphosphoric triamide (20 mL) as just described. The crude product (3.7 g, 95%) was crystallized from aqueous ethanol with the aid of charcoal, to yield 1.9 g (49%) of one of the diastereomers of **15**, m.p. 92–93°. The low value found for %S in **15** is attributed to its decomposition during the analysis.

Anal. Calc. for $C_9H_{13}ClO_6S$ (284.7): C, 37.97; H, 4.60; Cl, 12.45; S, 11.26. Found: C, 38.28; H, 4.77; Cl, 12.13; S, 10.66.

ACKNOWLEDGMENTS

This work was supported by U.S. Public Health Research Grant GM-23773 from the National Institutes of Health, and by a Grant from the Minnesota Medical Foundation.

REFERENCES

1 K. KIKUGAWA AND M. ICHINO, *Tetrahedron Lett.*, (1971) 87–90.
2 H. P. C. HOGENKAMP, *Biochemistry*, 13 (1974) 2736–2740.
3 M. LEGRAVEREND AND R. MICHELOT, *Biochimie*, 58 (1976) 723–729.
4 R. T. BORCHARDT, J. A. HUBER, AND Y. S. WU, *J. Org. Chem.*, 41 (1976) 565–567.
5 Y. WANG, H. P. C. HOGENKAMP, R. A. LONG, G. R. REVANKAR, AND R. K. ROBINS, *Carbohydr. Res.*, 59 (1977) 449–457.
6 J. HONEYMAN AND J. W. W. MORGAN, *J. Chem. Soc.*, (1955) 3660–3674.
7 F. M. ROBERTSON AND A. C. NEISH, *Can. J. Res. Sect. B*, 25 (1947) 491–493.
8 T. SOWA AND K. TSUNODA, *Bull. Chem. Soc. Jpn.*, 48 (1975) 505–507.
9 T. SOWA AND K. TSUNODA, *Bull. Chem. Soc. Jpn.*, 48 (1975) 3243–3245.
10 J. BERANEK AND H. HREBABECKY, *Nucleic Acids Res., Spec. Publ.*, 4 (1978) 125–128.

11 H. HREBABECKY AND J. BERANEK, *Nucleic Acids Res., Spec. Publ.*, 4 (1978) 131–134.
12 R. G. S. RITCHIE, N. CYR, B. KORSCH, H. J. KOCH, AND A. S. PERLIN, *Can. J. Chem.*, 53 (1975) 1424–1433.
13 A. S. PERLIN, *MTP Int. Rev. Sci.: Org. Chem. Ser. Two*, 7 (1976) 1–34.
14 L. QUE, JR., AND G. R. GRAY, *Biochemistry*, 13 (1974) 146–153.
15 W. A. SZAREK, A. ZAMOJSKI, A. R. GIBSON, D. M. VEJAS, AND J. K. N. JONES, *Can. J. Chem.*, 54 (1976) 3783–3793.
16 T. E. WALKER, Ph.D. Thesis, University of Iowa, 1974.
17 R. J. ABRAHAM, L. D. HALL, L. HOUGH, AND K. A. MCLAUCHLAN, *J. Chem. Soc.*, (1962) 3699–3705.
18 J. G. PRITCHARD AND P. C. LAUTERBUR, *J. Am. Chem. Soc.*, 83 (1961) 2105–2110.
19 R. BARKER AND H. G. FLETCHER, JR., *J. Org. Chem.*, 26 (1961) 4605–4609.
20 K. HEYNS AND T. LENZ, *Chem. Ber.*, 94 (1961) 348–352.
21 D. L. MACDONALD, J. D. CRUM, AND R. BARKER, *J. Am. Chem. Soc.*, 80 (1958) 3379–3381.
22 O. T. SCHMIDT, *Methods Carbohydr. Chem.*, 2 (1963) 318–325.