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Note

Synthesis of polymerizable anhydrodeoxyribose derivatives

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2-Deoxy-D-*erythro*-pentose ("deoxyribose") is an important constituent of DNA. It has been shown that selective ring-opening polymerization of anhydroribose derivatives can afford stereoregular (1→4)-β-D-ribopyranan or (1→5)-α-D-ribofuranan[1,2]. Synthesis of poly(deoxyribose) is, therefore, of interest in the field of both biochemistry and polymer chemistry. We report herein the syntheses of anhydrodeoxyribose (2-deoxy- and 3-deoxy-D-*erythro*-pentose) derivatives as starting materials for synthesis of poly(deoxyribose)s.

Vacuum pyrolysis of 2-deoxy-D-*erythro*-pentose failed to afford 1,5-anhydro-2-deoxy-β-D-*erythro*-pentofuranose (= 1,4-anhydro-2-deoxy-α-D-*erythro*-pentopyranose), even though the pyrolysis of monosaccharides is a normal method for preparing 1,5-anhydro sugars[3]. Consequently, deoxygenation of 1,5-anhydro-β-D-ribofuranose was attempted.

1,5-Anhydro-β-D-ribofuranose (**1**) was treated with 1.2 eq. of *tert*-butylchlorodimethylsilane, affording mainly a 1:1 mixture (^{1}H-n.m.r.) of the monosilylated anhydroroboses (**2** and **3**); the disilylated compound[6] **4** was a minor product.

The mixture of **2** and **3** was treated with *N,N'*-thiocarbonyldiimidazole to give the corresponding imidazolylthiocarbonyl derivatives **5** and **6**, which were readily separated by column chromatography. Reduction of **5** and **6** with tributyltin hydride gave the anhydro-2-deoxy-D-*erythro*-pentose derivative **7** and the anhydro-3-deoxy-D-*erythro*-pentose derivative **8**, respectively.

TABLE I

^{1}H Chemical shifts of 1,5-anhydro-β-D-ribopyranose derivatives[a]

Compound	*H-1*	*H-2a*	*H-2b*	*H-3a*	*H-3b*	*H-4*	*H-5exo*	*H-5endo*
7	5.69(d)	2.20(q)	1.65(q)	4.06(q)		4.58(d)	3.46(q)	3.32(d)
8	5.33(s)	4.05(q)		2.00(q)	1.59(m)	4.84(q)	3.44(q)	3.36(d)
4 (ref. 6)	5.31(s)	3.94(d)		3.99(d)		4.55(d)	3.42(q)	3.34(d)

[a] s, singlet; d, doublet; q, quartet; m, multiplet.

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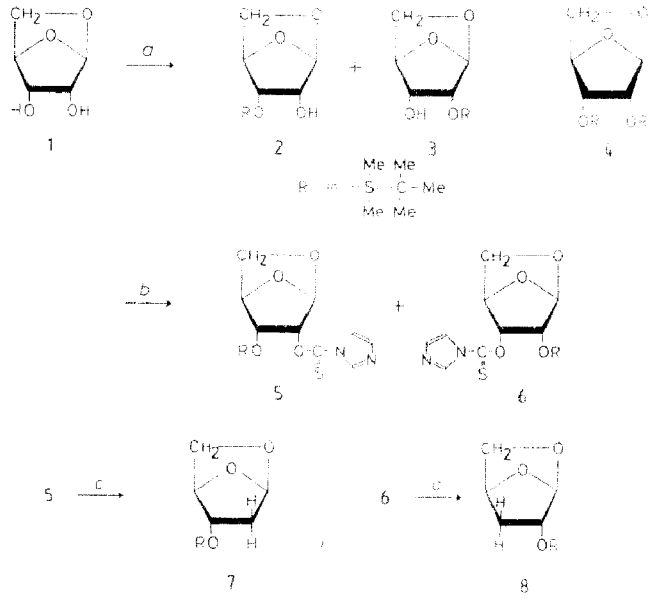
TABLE II

Coupling constants of **7** and **8**

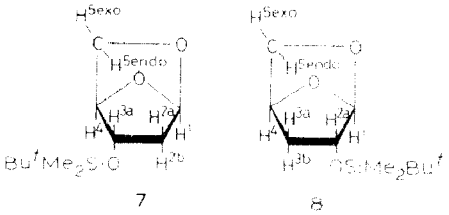
Compound	$J_{1,2a}$	$J_{1,2b}$	$J_{2a,2b}$	$J_{2a,3a}$	$J_{2b,3a}$	$J_{3a,3b}$	$J_{3a,4}$	$J_{3b,4}$	$J_{4,5exo}$	$J_{4,5endo}$	$J_{5,5}$
7	0	2.1	12.9	6.4		1.7		0		4.1	0	6.6
8	0			6.6	2.3		12.4	0	5.2	2.9	0	6.2

The ^{1}H-n.m.r. chemical shifts of **7**, **8**, and **4** (ref. 6) are given in Table I. The downfield shift of H-1 in **7** may be attributed to the deoxygenation at C-2. Similarly, H-4 of **8** shows a downfield shift owing to the deoxygenation at C-3.



Reagents: *a*, Bu^tMe_2SiCl (1.2 equiv.), $AgNO_3$, pyridine; *b*, *N*,*N*′-thiocarbonyldiimidazole, 1,2-dichloromethane; *c*, Bu_3SnH, toluene

Coupling constants are summarized in Table II. The values of $J_{1,2a}$, $J_{3a,4}$ and $J_{4,5endo}$ were close to zero, indicating that dihedral angles between the respective protons are ~90°.



The silylated anhydro-deoxyriboses **7** and **8** underwent polymerization with a cationic initiator to give novel poly(deoxyribose)s; the results will be reported in detail elsewhere.

EXPERIMENTAL

General methods. — Column chromatography and t.l.c. were conducted on silica gel (Merck Silica Gel 60). ^{1}H-N.m.r. spectra were recorded at 270 MHz with a Jeol GX-270 spectrometer, with Me_4Si as internal standard; peak assignments were performed by H–H COSY determinations.

*1,5-Anhydro-3-*O-tert-*butyldimethylsilyl-2-deoxy-* (**7**) *and 2-*O-tert-*butyldimethylsilyl-3-deoxy-β-*D-erythro-*pentofuranose* (**8**). — A solution of 1,5-anhydro-β-D-ribofuranose (**1** 10 g, 76 mmol, prepared by vacuum pyrolysis of D-ribose[2]) in THF (140 mL) was added dropwise to a stirred mixture of $AgNO_3$ (15.4 g, 91 mmol) and pyridine (30 mL), and then Bu^tMe_2SiCl (13.7 g, 91 mmol) was added at room temperature by a modification of the method of Hakimelahi[4]. The mixture was stirred in the dark overnight at room temperature and filtered. The filtrate was mixed with $NaHCO_3$, and the solution extracted with $CHCl_3$. The extract was concentrated *in vacuo* and the syrupy product chromatographed on silica gel, with 6:1 (v/v) hexane–EtOAc as eluent to afford a mixture of monosilylated anhydro-riboses (**2** and **3** R_F 0.26 and 0.31) containing a minor proportion of disilylated product **4**, R_F 0.57.

Deoxygenation of **2** and **3** was performed by the method of Rasmussen[5]. *N,N'*-Thiocarbonyldiimidazole (10 g, 56 mmol) was added to a solution of the monosilylated derivatives **2** and **3** (6.9 g, 28 mmol) in 140 mL of 1,2-dichloromethane. The mixture was stirred for 3 h at reflux temperature. The cooled solution was concentrated and by use of silica gel column chromatography [4:1 (v/v) hexane–EtOAc] 1,5-anhydro-3-*O-tert*-butyldimethylsilyl-2-*O*-imidazolylthiocarbonyl-β-D-ribofuranose (**5**) and 1,5-anhydro-2-*O-tert*-butyldimethylsilyl-3-*O*-imidazolyl-thiocarbonyl-β-D-ribofuranose (**6**) were separated and purified. The yields of **5** and **6** were 4.7 and 5.6 g, respectively (total yield, 98%).

Compound **5** (297 mg) was treated with 0.4 mL of Bu_3SnH in refluxing toluene (14 mL) for 6 h. After cooling, the solution was concentrated. 1,5-Anhydro-3-*O-tert*-butyldimethylsilyl-2-deoxy-β-D-*erythro*-pentofuranose (**7**) was purified by preparative t.l.c. with 6:1 (v/v) hexane–EtOAc as eluent; yield 74 mg (39%). Compound **6** (407 mg) was also reduced with 0.8 mL of Bu_3SnH. The syrupy product was chromatographed on t.l.c. with 6:1 (v/v) hexane–EtOAc as eluent to afford syrupy 1,5-anhydro-2-*O-tert*-butyldimethylsilyl-3-deoxy-β-D-*erythro*-pentofuranose (**8**); yield 109 mg (42%).

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