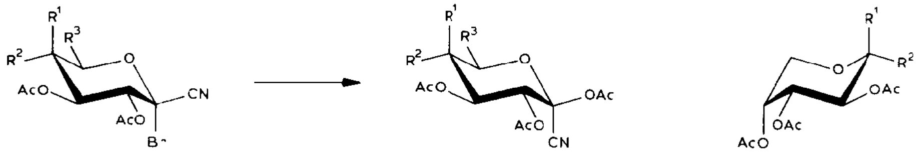
Carbohydrate Research, 132 (1984) 342–344
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

Preparation of acetylated 2-heptulo- and 2-hexulo-pyranosononitriles from acetylated 1-bromo-D-glycosyl cyanides

LÁSZLÓ SOMSÁK, GYULA BATTA, AND ISTVÁN FARKAS
Department of Organic Chemistry, Kossuth Lajos University, H-4010 Debrecen (Hungary)
(Received December 14th, 1983; accepted for publication, February 27th, 1984)

Reaction of the recently reported acetylated 1-bromo-D-glycosyl cyanides[1–3] **1–3** with silver acetate or mercury(II) acetate in acetic acid–acetic anhydride gave 2,3,4,5,7-penta-*O*-acetyl-β-D-*galacto*-2-heptulopyranosononitrile (**4**), 2,3,4,5-tetra-*O*-acetyl-β-D-*xylo*-2-hexulopyranosononitrile (**5**), and 2,3,4,5-tetra-*O*-acetyl-α-D-*arabino*-2-hexulopyranosononitrile (**6**), respectively, in good yields[4] (Table I). It is remarkable that, whereas for some other brominated sugar derivatives[5,6], the reaction proceeds quickly and under mild conditions, **1–3** need significantly longer times and reflux temperature to complete the transformation.



1 $R^1 = OAc, R^2 = H, R^3 = CH_2OAc$
2 $R^1 = R^3 = H, R^2 = OAc$
4 $R^1 = OAc, R^2 = H, R^3 = CH_2OAc$
5 $R^1 = R^3 = H, R^2 = OAc$
3 $R^1 = Br, R^2 = CN$
6 $R^1 = CN, R^2 = OAc$

The ^1H- and ^{13}C-n.m.r. spectra (Tables II and III) contain signals of 5 acetyl groups for **4**, and 4 for **5** and **6**. The H,H coupling constants indicate that **4–6** exist in the conformations depicted. The H,C coupling constants[7,8] for H-3 and the CN carbon (Table III) reflect a *trans*-diaxial relationship, indicating that the reactions of **1–3** to give **4–6** proceed with inversion of configuration at C-2.

Compounds **4–6** can be regarded as 2-keto-3-deoxyoctulosonic acid (KDO) analogues.

EXPERIMENTAL

Melting points are uncorrected. Optical rotations were measured with a Perkin–Elmer 241 polarimeter. N.m.r. spectra were recorded with a Bruker WP 200 SY spectrometer (^1H, 200 MHz; ^{13}C, 50.3 MHz).

Preparation of acetylated 2-heptulo- and 2-hexulo-pyranosononitriles. —To a

0008-6215/84/$ 03.00

TABLE I

ACETYLATED 2-HEPTULO- AND 2-HEXULO-PYRANOSONONITRILES

Compound	*Reaction time (h)*	*Yield (%)*	*M.p. (degrees)*	$[\alpha]_D^{20a}$ *(degrees)*	*Formula*	*Analytical data (%)*	
						Calc.	*Found*
4	8	59	130–131	+99	$C_{17}H_{21}NO_{11}$	N, 3.37	3.54
						C, 49.16	48.81
						H, 5.09	5.19
5	3	73	143–144	+83	$C_{14}H_{17}NO_9$	N, 4.08	4.12
						C, 48.98	49.10
						H, 4.99	4.87
6	4.5	65	117–118	−158	$C_{14}H_{17}NO_9$	N, 4.08	3.98
						C, 48.98	48.89
						H, 4.99	4.91

[a] In chloroform.

TABLE II

^{1}H-N.M R. DATA[a] (δ SCALE, J IN Hz) FOR ACETYLATED 2-HEPTULO- AND 2-HEXULO-PYRANOSONONITRILES

Compound	*H-3* $(J_{3,4})$	*H-4* $(J_{4,5})$	*H-5* $(J_{5,6})$	*H-6*	*H-7*	*H-7'*	*Me*
4	5.50	5.28	5.52	4.43	4.20	4.17	2.00–2.20
	(11)	(3)	(1.2)				(15 H, 5 Me)
			H-5 $(J_{5,6e})$	*H-6e* $(J_{6e,6a})$	*H-6a* $(J_{5,6a})$		
5	5.27	5.34	5.02	4.26	3.83		2.03–2.16
	(9)	(8)	(5.2)	(12.2)	(9.2)		(12 H, 4 Me)
6	5.90	5.54	5.20	3.61[b]	3.49[b]		1.40–1.72
	(10.5)	(3.3)	(1.3)	(14)	(2)		(12 H, 4 Me)

[a] First-order analysis, 200 MHz, $CDCl_3$, internal Me_4Si. [b] Interchangeable assignments.

solution of acetylated 1-bromo-D-glycosyl cyanide (1 g, **1**–**3**) in acetic acid (12 mL) and acetic anhydride (3 mL) was added 1.2 mol of silver acetate or 0.6 mol of mercury(II) acetate. The mixture was boiled under reflux for the time given in Table I and then cooled to room temperature, the solids were collected and washed with a little acetic acid, and the combined filtrate and washings were concentrated *in vacuo*. The residue was triturated with ice–water, stored at room temperature for 1 h, and then extracted with chloroform (2 × 10 mL). The combined extracts were washed with water, aqueous sodium hydrogencarbonate, and water, dried, and concentrated. The residue was crystallised from ether–light petroleum.

TABLE III

^{13}C-N.M.R. DATA[a] FOR ACETYLATED 2-HEPTULO- AND 2-HEXULO-PYRANOSONONITRILES

Compound	*C-2*	*C-3–C-7*	*CN* ($^3J_{CN,H-3}$)	*C=O*	*Me*
4	92.09	72.48	111.64	170.10	20.79
		69.14	(6.5 Hz)	169.75	20.54
		68.04		169.30	20.49
		66.17		168.81	20.45
		66.17		166.20	20.33
		C-3–C-6			
5	91.77	69.79	111.30	169.30	20.41
		69.60	(5.3 Hz)	168.80	20.32
		66.95		168.35	20.21
		62.82		166.29	20.11
6	92.56	68.64	111.71	169.80	20.74
		68.16	(6.0 Hz)	169.32	20.66
		66.78		168.81	20.49
		65.30		166.20	20.37

[a] 50.3 MHz, $CDCl_3$, internal Me_4Si.

ACKNOWLEDGMENT

The authors thank their student Miss E. Papp for assistance.

REFERENCES

1 L. Somsák, Gy. Batta, and I. Farkas, *Carbohydr. Res.*, 106 (1982) c4–c5.
2 L. Somsák, Gy. Batta, and I. Farkas, *Carbohydr. Res.*, 124 (1983) 43–51.
3 F. W. Lichtenthaler, and P. Jarglis, *Angew. Chem. Suppl.*, (1982) 1449–1459.
4 L. Somsák, Gy. Batta, and I. Farkas, *Abstr. Eur. Symp. Carbohydr. Glycoconjugates, 2nd*, Budapest, August 9–12, 1983, A-7.
5 R. J. Ferrier and R. H. Furneaux, *J. Chem. Soc., Perkin Trans. 1*, (1977) 1996–2000.
6 R. J. Ferrier and P. Tyler, *J. Chem. Soc., Perkin Trans. 1*, (1980) 2767–2773.
7 A. S. Perlin, *M.T.P. Int. Rev. Sci., Org. Chem. Ser. Two*, 7 (1976) 24–26.
8 C. H. Wang and C. A. Kingsbury, *J. Org. Chem.*, 40 (1975) 3811–3820.