Carbohydrate Research, 211 (1991) 173–178
Elsevier Science Publishers B.V., Amsterdam

Note

Preparation of acetylated 2,6-anhydrohept(hex)-2-enononitriles (1-cyano-2-hydroxyglycals)

László Somsák*, Etelka Papp, Gyula Batta, and István Farkas
Department of Organic Chemistry, Lajos Kossuth University, H-4010 Debrecen, P.O.B. 20 (Hungary)

(Received June 29th, 1990; accepted for publication, September 3rd, 1990)

The reactions of acetylated 1-bromo-D-glycosyl cyanides[1,2] (**1–4**) with acetate[3] and thiolates[4] have been described, and reactions with cyanides are now reported.

TABLE I

Data on **5–12**

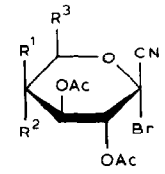
Compound	*Yield* (%)	*M.p.* (*degrees*)	$[\alpha]_D^{20a}$ (*degrees*)	*Formula*	*Anal.*		*I.r. data* (cm^{-1})
					Calc.	*Found.*	$\nu_{C\equiv N}$ $\nu_{C=C}$
5[b]	67	syrup	−49	$C_{15}H_{17}NO_9$	C 50.70	50.14	2219[j] 1666
					H 4.82	4.76	
					N 3.94	3.89	
6[c]	70	99–101 (from ethanol)	−68	$C_{15}H_{17}NO_9$	C 50.70	50.19	2215[k] 1671
					H 4.82	4.71	
					N 3.94	3.91	
7[d]	83	60–61 (from ethanol)	−268	$C_{12}H_{13}NO_7$	C 37.60	37.50	2218[k] 1660
					H 3.41	3.29	
					N 4.94	4.95	
8[e]	82	syrup	+162	$C_{12}H_{13}NO_7$	C 37.60	37.10	2219[j] 1664
					H 3.41	3.20	
					N 4.94	4.55	
9[f]	20	syrup	−4	$C_{14}H_{18}O_{10}$	C 48.55	47.91	$\nu_{C=O}$ (lactone)
					H 5.23	5.16	1810[j]
10[g]	27[l] 54[m]	100–101 (from ethanol)	−68	$C_{11}H_{14}O_8$	C 48.17	48.45	1786[k]
					H 5.14	5.50	
11[h]	33	syrup	+45	$C_{11}H_{14}O_8$	C 48.17	47.85	1807[j]
					H 5.14	5.01	
12[i]	64	107–108 (from ethanol)	−141	$C_{11}H_{14}O_8$	C 48.17	48.51	1776[k]
					H 5.14	5.45	

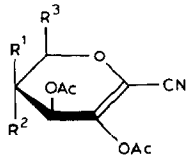
[a] $CHCl_3$. [b] 3,4,5,7-Tetra-*O*-acetyl-2,6-anhydro-D-*arabino*-hept-2-enononitrile. [c] 3,4,5,7-Tetra-*O*-acetyl-2,6-anhydro-D-*lyxo*-hept-2-enononitrile. [d] 3,4,5-Tri-*O*-acetyl-2,6-anhydro-D-*threo*-hex-2-enononitrile. [e] 3,4,5-Tri-*O*-acetyl-2,6-anhydro-D-*erythro*-hex-2-enononitrile. [f] For comparison, see refs. 17 and 10. [g] See refs. 19 and 20. [h] See ref. 21. [i] 2,3,4-Tri-*O*-acetyl-D-arabinono-1,5-lactone. [j] Nujol. [k] KBr. [l] $Hg(CN)_2$–Me_2SO. [m] $Hg(OAc)_2$–Me_2SO.

* Author for correspondence.

0008-6215/91/$ 03.50

The reactions of **2** with sodium cyanide in acetonitrile, acetone, or methyl sulfoxide or with mercury(II) cyanide in hexamethylphosphoric triamide gave multicomponent mixtures. No reaction occurred with sodium cyanide in 1,2-dimethoxyethane and with mercury(II) cyanide in acetonitrile, acetone, or nitromethane. However, in the presence of a catalytic amount of silver tosylate, one product was formed (reflux, 3 h) in each of the reactions of **1–4** with mercury(II) cyanide–nitromethane and the time of reaction decreased to 5 min on using silver triflate. The respective products **5–8** (Table I) were obtained by elimination of hydrogen bromide and not by cyanide substitution.





	R^1	R^2	R^3	
1	H	OAc	CH_2OAc	5
2	OAc	H	CH_2OAc	6
3	H	OAc	H	7

4 8

Compounds **5–8** each had one ^{13}C resonance (Table II) and a sharp i.r. band for CN (Table I). The ^1H-n.m.r. spectra (Table III) each contained one less resonance than those of the starting compounds and the same number of resonances for OAc groups. The presence of a double bond was proved by the resonances at 124–127 and 137–138 p.p.m. in the ^{13}C-n.m.r. spectra (Table II) and by the i.r. bands at 1660–1670 cm^{-1} (Table I). The 1,2-positions of the double bonds were supported by the CN resonances (singlets) and the i.r. bands for CN. The CN group in glycosyl cyanides is only Raman-active[5,6], and 2,6-anhydro-3,4-dideoxyhept-3-enononitriles[7] have only very weak i.r. bands at ~2200 cm^{-1}. The presence of the double bond on the carbon bearing the CN counteracts quenching by the alkoxy substituent and makes the cyanide stretching vibration i.r.-active in **5–8**. Compounds of the type PhCH=C(OR)CN exhibit[8] i.r. bands for CN at 2215–2240 cm^{-1}. The preferred conformations of **5–8** were identified by c.d. spectroscopy[9].

The reactions of **2–4** with mercury(II) cyanide in methyl sulfoxide each gave two products, namely, the corresponding unsaturated compound (**6–8**) and the acetylated

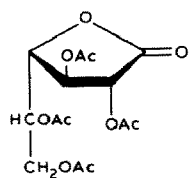
TABLE II

^{13}C-N.m.r. data[a] for **5–12**

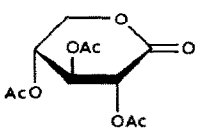
Compound	*CN*	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*Acetyl*	
								C=O	*CH$_3$*
5	110.11	124.99	137.62	75.83[d]	66.44[d]	65.48[d]	59.82	167.50	19.78
								168.74	20.00
								169.16	20.12
								169.81	
6	110.31	124.66	138.03	74.99[d]	63.86[d]	62.66[d]	60.80	167.60	20.09
								169.20	20.16
								169.69	20.34
								170.16	20.51
7	110.45	126.75	137.40	66.45[d]	63.05[d]	65.08	–	167.98	20.00
								168.96	20.27
								169.17	20.34
8[b]	111.14	126.50	137.90	64.08[d]	63.81[d]	65.44	–	167.86	19.51
								168.97	19.52
								169.38	
9[c]	–	169.73	71.83[d]	71.57[d]	76.05[d]	67.96[d]	61.16	167.55	19.78
								168.81	19.92
								169.15	20.04
								169.23	
10[c]	–	165.32	72.37[d]	70.11[d]	68.95[d]	66.28[d]	–	168.96	20.09
								169.18	20.36
								169.32	20.38
11	–	168.13	72.46[d]	72.11[d]	77.27[d]	61.98	–	169.30	20.12
								169.66	20.31
								170.05	20.33
12	–	162.52	68.71[d]	68.66[d]	67.89[d]	66.97[d]	–	169.61	20.39
								169.93	20.46
									20.58

[a] $CDCl_3$. [b] C_6D_6. [c] For comparison, see ref. 18. [d] Interchangeable assignments.

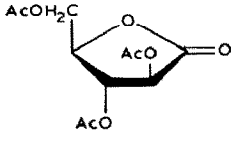
aldonolactones (**9–11**). The physical and spectral parameters of these compounds (Tables, I, II, and IV) agreed well with literature data. Using mercury(II) acetate in methyl sulfoxide, **3** and **4** reacted to give the aldonolactones **10** and **12**, respectively, as the only products.



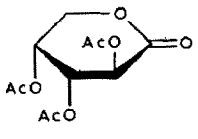
9



10



11



12

TABLE III

^{1}H-N.m.r. data[a] (δ in p.p.m., J in Hz) for **5–8**

Compound	*H-3* ($J_{3,4}$, $J_{3,5}$)	*H-4* ($J_{4,5}$)	*H-5* ($J_{5,6b}$)	*H-6a* ($J_{5,6a}$)	*H-6b* ($J_{6a,6b}$)	Ac
5	5.61 (4.5)	5.23 (6)	4.41 (6)	4.45 (5)	4.20 (16)	2.11 2.15 2.78 2.83
6	5.96 (4.6, 1)	5.53 (1.5)	4.55 (6.3)	4.26 (6.3)		2.20 2.26 2.34 2.40
	H-3 ($J_{3,4}$, $J_{3,5eq}$)	*H-4* ($J_{4,5eq}$)	*H-5*eq ($J_{5eq,5ax}$)	*H-5*ax ($J_{4,5ax}$)		
7	5.44 (2.4, 1.7)[b]	5.01 (2.5)	4.37 (12.5)	4.07 (1.5)		1.99 2.06 2.20
8	5.82 (4.5, 1.2)	5.32 (3.4)	4.21 (11.2)	4.12 (8)		2.12 2.18 2.23

[a] $CDCl_3$. [b] $J_{3,5ax}$ 0.6.

TABLE IV

^{1}H-N.m.r. data[a] (δ in p.p.m., J in Hz) for **9–12**

Compound	*H-2* ($J_{2,3}$)	*H-3* ($J_{3,4}$)	*H-4* ($J_{4,5b}$)	*H-5* (*H-5a*) ($J_{4,5a}$ *or* $J_{5,6a}$)	*H-5b or H-6a* ($J_{5a,5b}$ or $J_{5,6b}$)	*H-6b* ($J_{6a,6b}$)	*Ac*
9[b]	5.58 (7.2)	5.39 (7)	4.62 (3)	5.33 (7)	4.34 (5.5)	4.22 (12)	2.09 2.14 2.17 2.21
10	5.51 (8.5)	5.21 (2.5)	5.13 (2.7)	4.59 (2.3)	4.42 (13.2)	–	2.12 2.15 2.21
11[c]	5.52 (7)	5.39 (7)	4.51 (5)	4.41 (2.8)	4.22 (12.5)	–	2.05 2.08 2.13
12	5.32 (10.2)	5.47 (3)	5.55 (2.2)	4.53 (1.7)	4.44 (12.5)	–	2.10 2.18 2.20

[a] $CDCl_3$. [b] For comparison, see ref. 17. [c] See ref. 21.

The mechanism of the formation of the lactones is unclear. Oxidative decyanation of nitriles to give ketones and other carbonyl compounds in the presence of a strong base is well documented[10–14]. Compounds of the type ArRC(I)CN were converted[15] into ArRC=O with silver oxide in tetrahydrofuran, whereas the corresponding bromides were inert. In these reactions, air is the source of the oxygen. Since the transformations reported here give the lactones in an atmosphere of nitrogen, methyl sulfoxide may be the oxidising agent[16].

EXPERIMENTAL

Melting points were measured in open capillary tubes and are uncorrected. Optical rotations were measured with a Perkin–Elmer 241 polarimeter, i.r. specta with a Perkin–Elmer 283B spectrophotometer, and n.m.r. spectra with a Bruker WP 200 SY (^{1}H, 200 MHz; ^{13}C, 50.3 MHz) spectrometer (the n.m.r. data are given in Tables II–IV). T.l.c. was performed on Kieselgel 60 F_{254} (Merck), with benzene–ether–hexane (6:3:1) and detection by gentle heating, and column chromatography was performed on Kieselgel 40 (Merck) or 60 (Reanal). Solutions were dried over anhydrous $MgSO_4$ and solvents were evaporated under diminished pressure at $< 50°$.

Acetylated 2,6-anhydrohept(hex)-2-enononitriles (**5–8**). — To a solution of acetylated 1-bromo-D-glycosyl cyanide (**1–4**; 1 mmol) in dry nitromethane (5 mL) were added mercury(II) cyanide (1.5 mmol) and silver triflate (0.1 mmol). Each mixture was boiled for 5 min, then concentrated, and a solution of the residue in chloroform was washed with water, aqueous 5% potassium iodide, and water, dried, and concentrated. The product was either crystallised from ethanol (**6** and **7**) or purified by column chromatography (**5** and **8**). The details are given in Table I.

Acetylated 2,6-anhydrohept(hex)-2-enononitriles (**6–8**) *and acetylated aldonolactones* (**9–11**). — To a solution of acetylated 1-bromo-D-glycosyl cyanide (**2–4**) (2 mmol) in methyl sulfoxide (10 ml) was added mercury(II) cyanide (3 mmol), and each mixture was heated on a boiling water bath until the starting material disappeared (t.l.c., 0.5–1 h). Each mixture was cooled to room temperature, diluted with chloroform, washed with water, aqueous 5% potassium iodide, and water, dried, and evaporated. The residue was subjected to column chromatography. The details are given in Table I.

Acetylated aldonolactones (**10, 12**). — To a solution of the acetylated 1-bromo-D-glycosyl cyanide (**3** or **4**; 2 mmol) in methyl sulfoxide (20 mL) was added mercury (II) acetate (6 mmol). Each mixture was stored at room temperature for 2 days, then worked-up as described above, to give a syrup that solidified on the addition of ether. The products were recrystallised from ethanol. The details are given in Table I.

REFERENCES

1 L. Somsák, Gy. Batta, and I. Farkas, *Carbohydr. Res.*, 124 (1983) 43–51.
2 F. W. Lichtenthaler and P. Jarglis, *Angew. Chem. Suppl.*, (1982) 1449–1459.
3 L. Somsák, Gy. Batta, and I. Farkas, *Carbohydr. Res.*, 132 (1984) 342–344.
4 L. Somsák, Gy. Batta, I. Farkas, L. Párkányi, A. Kálmán, and Á. Somogyi, *J. Chem. Res.* (*S*), (1986) 436–437; (*M*), (1986) 3543–3566.

5 R. W. Myers and Y. C. Lee, *Carbohydr. Res.*, 132 (1984) 61–82.
6 A. T. Tu, W. K. Liddle, Y. C. Lee, and R. W. Myers, *Carbohydr. Res.*, 117 (1983) 291–297.
7 G. Grynkiewicz and J. N. BeMiller, *Carbohydr. Res.*, 108 (1982) 229–235.
8 M. Cariou, G. Mabon, G. le Guillanton, and J. Simonet, *Tetrahedron*, 39 (1983) 1551–1558.
9 I. Farkas, G. Snatzke, and L. Somsák, *Liebigs Ann. Chem.*, (1989) 599–600.
10 M. S. Kharasch and G. Sosnovsky, *Tetrahedron*, 3 (1958) 105–112.
11 S. J. Selikson and D. S. Watt, *J. Org. Chem.*, 40 (1975) 267–268.
12 A. Donetti, O. Boniardi, and A. Ezhaya, *Synthesis*, (1980) 1009–1011.
13 S. S. Kulp and M. J. McGee, *J. Org. Chem.*, 48 (1983) 4097–4098.
14 H. G. Aurich, *Tetrahedron Lett.*, (1964) 657–658.
15 D. S. Watt, *J. Org. Chem.*, 39 (1974) 2799–2800.
16 D. Martin and H. G. Hauthal, *Dimethylsulfoxid*, Akademie Verlag, Berlin, 1971, pp. 313–316.
17 Z. Wałaszek and D. Horton, *Carbohydr. Res.*, 105 (1982) 131–143.
18 K. Bock, I. Lundt, and C. Pedersen, *Acta Chem. Scand., Ser B*, 35 (1981) 155–162.
19 G. O. Aspinall and R. R. King, *Can. J. Chem.*, 51 (1973) 394–401.
20 W. J. Humphlett, *Carbohydr. Res.*, 4 (1967) 157–164.
21 C. R. Nelson, *Carbohydr. Res.*, 68 (1979) 55–60.