Carbohydrate Research, 106 (1982) C4–C5
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

Preliminary communication

Bromination of acetylated 2,5-anhydro-aldononitriles at the anomeric centre using *N*-bromosuccinimide: synthesis of 2,3,4,6-tetra-*O*-acetyl-1-bromo-D-galactopyranosyl cyanide and its D-xylopyranosyl analogue

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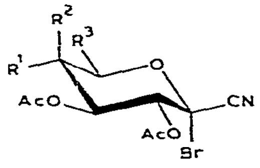
(Received April 20th, 1982; accepted for publication, June 8th, 1982)

Ferrier and his co-workers brominated acylated hexo- and pento-pyranosides[1–4], some glucopyranuronic acid derivatives[5], and acylated 1-thioglycopyranosides[6] and glycopyranosides[7] by a radical process to obtain, in most cases, products monobrominated at C-5. In the light-induced reaction of penta-*O*-acetyl-β-D-glucopyranose with bromine, 2,3,4,6-tetra-*O*-acetyl-D-glucopyranosyl bromide and 2,3,4,6-tetra-*O*-acetyl-1-bromo-D-glucopyranosyl bromide were isolated in low yields by column chromatography[3].

During experiments on the bromination of some *C*-glycosyl heterocycles with *N*-bromosuccinimide, it was found that bromination occurred on the sugar moieties, and the reaction has now been extended to glycosyl cyanides.

The reaction of 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl cyanide (**1**) or 2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl cyanide (**2**) with *N*-bromosuccinimide in refluxing carbon tetrachloride in the presence of benzoyl peroxide gave, respectively, the 1-bromoglycosyl cyanides **3** (82%) {m.p. 117–118° (from ethanol), $[\alpha]_D$ +184° (*c* 1.5, chloroform) (*Anal.* Calc. for $C_{15}H_{18}BrNO_9$: N, 3.21; Br, 18.34. Found: N, 3.18; Br, 18.14)} and **4** (42%) {m.p. 182–184° (from ethanol), $[\alpha]_D$ +148° (*c* 1.5, chloroform) (*Anal.* Calc. for $C_{12}H_{14}BrNO_7$: N, 3.84; Br, 21.94. Found: N, 3.92; Br, 21.64)}. Compounds **3** and **4**, if pure and dry, are stable in air. No further bromination could be achieved with *N*-bromosuccinimide–benzoyl peroxide or bromine–u.v. light in refluxing carbon tetrachloride.

The 200-MHz, ^{1}H-n.m.r. data (internal Me_4Si, room temperature) for **3** [acetone-d_6: δ 5.47 (dd, 1 H, $J_{2,3}$ 10.4, $J_{2,4}$ 0.4 Hz, H-2), 5.33 (dd, 1 H, $J_{3,4}$ 3.2 Hz, H-3), 5.61



3 $R^1 = H, R^2 = OAc, R^3 = CH_2OAc$
4 $R^1 = OAc, R^2 = H, R^3 = H$

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(dd, 1 H, $J_{4,5}$ 1.4 Hz, H-4), 4.73 (m, 1 H, $J_{5,6}$ 5.4, $J_{5,6'}$ 6.7 Hz, H-5), 4.30 (m, 1 H, H-6), 4.23 (m, 1 H, $J_{6,6'}$ 11.8 Hz, H-6')] and 4 [$CDCl_3$: δ 5.23 (d, 1 H, $J_{2,3}$ 9.5 Hz, H-2), 5.45 (dd, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 5.08 (m, 1 H, $J_{4,5a}$ 11, $J_{4,5e}$ 6 Hz, H-4), 4.24 (dd, 1 H, H-5*e*), and 3.80 (dd, 1 H, $J_{5a,5e}$ 12 Hz, H-5*a*)] in comparison with those of **1** and **2** unambiguously indicate that bromination had occurred at C-1, since the signals for H-1 had disappeared and those for H-2 had become doublets, and that the compounds existed in the $^4C_1$ conformation. These data suggest that the bromine atom is *axial*, since an *equatorial* bromine would be expected to destabilise the $^4C_1$ conformer because of the strong anomeric effect.

The ^{13}C-n.m.r. data (50.3 MHz, $CDCl_3$, room temperature, internal Me_4Si) of **1**–**4** showed that the introduction of the bromine substituent caused a downfield shift of ~15 p.p.m. for the C-1 signal (**1**, 66.54; **3**, 81.84; **2**, 65.70; **4**, 81.81 p.p.m.). The assignments of the carbon signals were made by low-power, single-frequency, off-resonance decoupling experiments. The splitting of the C≡N carbon resonances provided further proof of the site of substitution and of the orientation of the substituents at C-1 These resonances were double doublets for **1** ($J_{CN,H\text{-}1}$ 7.2, $J_{CN,H\text{-}2}$ 3.9 Hz) and **2** ($J_{CN,H\text{-}1}$ 8.1, $J_{CN,H\text{-}2}$ 2.0 Hz); for the brominated compounds, they were doublets (**3**, $J_{CN,H\text{-}2}$ 2.7; **4**, $J_{CN,H\text{-}2}$ 2.2 Hz). The values of $J_{CN,H\text{-}2}$ for **3** and **4** are consistent with a *gauche* orientation[8,9] of H-2 and CN, and indicate that the CN group has retained the original *equatorial* position; therefore, Br-1 must be *axial*.

The ^2J and ^3J couplings of the C≡N carbon resonances were identified by continuous wave, selective decoupling.

An X-ray crystallographic determination of structure for **3** and **4** is in progress.

ACKNOWLEDGMENTS

The authors thank Dr. A. Liptak and Dr. L. Szilagyi for advice on the ^{13}C-n.m.r. spectra.

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