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Note

2,3,4,6-Tetra-*O*-acetyl-α- and -β-D-gluco- and -galacto-pyranosyl isocyanides

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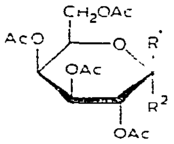
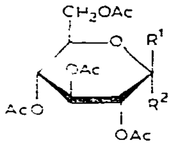
As part of a study of the reaction of 2,3,4,6-tetra-*O*-acetyl-α-D-galacto- and gluco-pyranosyl bromide with metallic cyanides[1], we report the isolation of 2,3,4,6-tetra-*O*-acetyl-β- and -α-D-galacto- and -gluco-pyranosyl isocyanides (**1**–**4**). Glycosyl isocyanides have been previously detected[2], and have been prepared very recently by reaction of benzyl halogenated glycosides with silver cyanide[3].



1 $R^1 = N\equiv C$, $R^2 = H$
2 $R^1 = H$, $R^2 = N\equiv C$



3 $R^1 = N\equiv C$, $R^2 = H$
4 $R^1 = H$, $R^2 = N\equiv C$

The reaction of 2,3,4,6-tetra-*O*-acetyl-α-D-gluco- and -galacto-pyranosyl bromides with silver cyanide in boiling xylene gave a complex mixture of products. In the galactose series, crystallization of the concentrated reaction mixture afforded 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl isocyanide (**1**, 20%). Analytical and m.s. data were consistent with the proposed structure. The i.r. spectrum of **1** showed a sharp band of medium intensity at 2155 cm^{-1}, in contrast to the glycosyl cyanides which show no detectable absorption in this region. The p.m.r. spectrum of **1** showed a doublet for H-1 at δ 4.80 ($J_{1,2}$ 9.0 Hz), and the ^{13}C-n.m.r. spectrum showed a peak at 164.4 p.p.m. for the isocyanide carbon atom.

In the glucose series, 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl isocyanide (**3**, 12%) and 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl isocyanide (**4**, 10%) were separated by column chromatography.

Compounds **3** and **4** gave satisfactory analytical and m.s. data, and showed i.r. bands at 2150 and 2130 cm^{-1}, respectively. The p.m.r. spectra showed doublets for H-1 at δ 4.78 ($J_{1,2}$ 9.0 Hz) and 5.53 ($J_{1,2}$ 5.0 Hz) for **3** and **4**, respectively.

2,3,4,6-Tetra-*O*-acetyl-α-D-galactopyranosyl isocyanide (**2**) was isolated as a syrup contaminated with 3,4,6-tri-*O*-acetyl-1,2-*O*-(1-cyanoethylidene)-α-D-galactopyranose, and the i.r. (2130 cm^{-1}) and p.m.r. (δ 5.59, $J_{1,2}$ 4.2 Hz) spectra strongly support the assigned structure.

EXPERIMENTAL

General. — Melting points were measured on a Kofler hot-stage and are uncorrected. T.l.c. was performed on silica gel G (Merck) with detection by charring with sulphuric acid. Column chromatography was performed on silica gel Merck (60–230 mesh). I.r. spectra were recorded for KBr discs with a Perkin–Elmer 457 spectrometer. ^{1}H-N.m.r. spectra were recorded for solutions in $CDCl_3$ (internal Me_4Si) with a Varian XL-100 spectrometer operating at 100 MHz. ^{13}C-N.m.r. spectra were recorded with a Bruker Spectrospin spectrometer operating at 15.08 MHz for $CDCl_3$ solutions (internal Me_4Si). Mass spectra were determined on an Hitachi–Perkin–Elmer RMU 6 MG apparatus (direct inlet system). Optical rotations were determined with a Perkin–Elmer 141 polarimeter.

*2,3,4,6-Tetra-*O*-acetyl-β-* (**1**) *and -α-D-galactopyranosyl isocyanide* (**2**). — A mixture of 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (4.14 g, 10 mmol), silver cyanide (6 g, 24 mmol), and dry xylene (40 ml) was heated under reflux with stirring for 1 h, and then cooled, filtered, and concentrated to dryness. Crystallization of the syrupy residue from methanol afforded **1** (0.75 g, 20%), m.p. 164–165°, $[\alpha]_D^{25}$ +32° (*c* 1.5, chloroform), ν_{max}^{KBr} 2155 cm^{-1} (N≡C). ^{1}H-N.m.r. data: δ 4.80 (d, 1 H, $J_{1,2}$ 9.0 Hz, H-1), 5.01 (q, 1 H, $J_{2,3}$ 10.0, $J_{3,4}$ 3.2 Hz, H-3), 5.42 (q, 1 H, H-2), 5.43 (q, 1 H, $J_{4,5}$ 1.0 Hz, H-4), 4.15 and 3.97 (3 H, A_2B system, $J_{5,6}$ 6.3 Hz, H-5,6,6′), 1.97, 2.03, 2.10, and 2.15 (12 H, 4 OAc). ^{13}C-N.m.r. data: 164.4 p.p.m. (N≡C).

Anal. Calc. for $C_{15}H_{19}NO_9$: C, 50.41; H, 5.36; N, 3.92. Found: C, 50.04; H, 5.04; N, 3.64.

The mother liquors were concentrated and the residue was subjected to column chromatography. Elution with 95:5 benzene–ethyl acetate yielded first a fraction which gave one spot on t.l.c. (6:4 benzene–ethyl acetate), ν_{max}^{KBr} 2130 cm^{-1}. The n.m.r. spectrum indicated the presence of two compounds: 3,4,6-tri-*O*-acetyl-1,2-*O*-(1-cyanoethylidene)-α-D-galactopyranose and **2**. By repeated p.l.c. (6:4 benzene–ethyl acetate), **2** (70% pure by n.m.r.) was obtained as a syrup, ν_{max}^{KBr} 2130 cm^{-1} (N≡C). ^{1}H-N.m.r. data: δ 5.57 (d, 1 H, $J_{1,2}$ 4.2 Hz, H-1).

*2,3,4,6-Tetra-*O*-acetyl-β-* (**3**) *and -α-D-glucopyranosyl isocyanide* (**4**). — A mixture of 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (2.07 g, 5 mmol), silver cyanide (3 g, 12 mmol), and dry xylene (20 ml), was heated under reflux with stirring for 1 h, filtered, and concentrated *in vacuo*. The residue (2.14 g) was subjected to column chromatography. Elution with 95:5 benzene–ethyl acetate first gave a fraction which, after crystallization from ethanol, afforded 3,4,6-tri-*O*-acetyl-1,2-*O*-(1-cyanoethylidene)-α-D-glucopyranose (0.96 g, 60%), m.p. 77°, $[\alpha]_D^{20}$ +13.5° (*c* 1.21, chloroform); lit.[4] m.p. 77–78°, $[\alpha]_D^{20}$ +13.8°. Subsequently, fractions containing first **4** and then **3** were eluted. Pure **4** and **3** were obtained after several recrystallizations from ethanol.

Compound **4** (0.16 g, 10%) had m.p. 107–109°, $[\alpha]_D^{20}$ +99° (*c* 0.12, chloroform), ν_{max}^{KBr} 2150 cm^{-1} (N≡C). ^{1}H-N.m.r. data: δ 5.53 (d, 1 H, $J_{1,2}$ 5.0 Hz, H-1), 5.44 (q, 1 H, $J_{2,3}$ 9.0, $J_{3,4}$ 9.5 Hz, H-3), 5.07 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-4), 4.89 (q, 1 H, H-2), 4.40 and 4.00 (3 H, A_2B system, H-5,6,6′), 2.11, 2.07, 2.03, and 2.01 (4 s, 12 H, 4 OAc).

Anal. Calc. for $C_{15}H_{19}NO_9$: C, 50.41; H, 5.36; N, 3.92. Found: C, 50.42; H, 5.37; N, 3.95.

Compound **3** (0.19 g, 12%) had m.p. 102–104°, $[\alpha]_D^{20}$ +4° (*c* 0.11, chloroform), ν_{max}^{KBr} 2150 cm^{-1} (N≡C). ^{1}H-N.m.r. data: δ 4.78 (d, 1 H, $J_{1,2}$ 9.0 Hz, H-1), 4.24 (q, 1 H, $J_{5,6}$ 4.5, $J_{6,6'}$ 12.7 Hz, H-6), 4.10 (q, 1 H, $J_{5,6'}$ 2.7 Hz, H-6′), 3.72 (m, 1 H, H-5), 2.10, 2.02, 2.00 (3 s, 12 H, 4 OAc).

Anal. Found: C, 50.32; H, 5.36; N, 3.72.

ACKNOWLEDGMENTS

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