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Note

Synthesis of tetrazoles from some per-O-benzoylaldononitriles*

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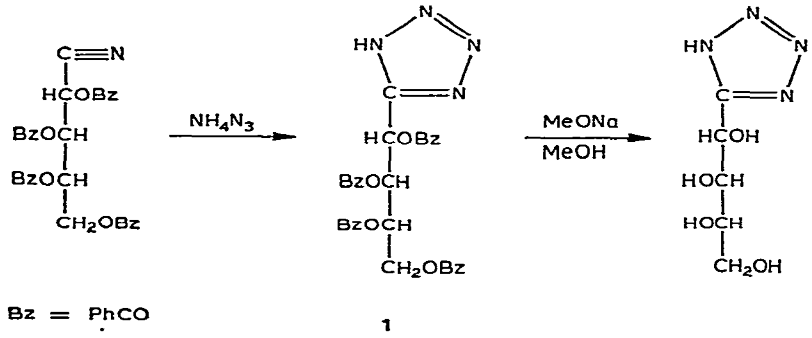
Synthesis of 5-[poly(acetoxy)alkyl]tetrazoles from acetylated aldononitriles by reaction with ammonium azide in *N*,*N*-dimethylformamide was described earlier[1,2]. Farkas *et al.*[3] described the preparation of some *C*-glycosyl derivatives of tetrazoles by a similar reaction.

We have now extended the reaction to some benzoylated aldononitriles, and the corresponding 5-[poly(benzoyloxy)alkyl]tetrazoles were obtained, in higher yields than the corresponding 5-[poly(acetoxy)alkyl]tetrazoles[2].

Debenzoylation of the 5-[poly(benzoyloxy)alkyl]tetrazoles with sodium methoxide in methanol gave the same 5-(polyhydroxyalkyl)tetrazoles as those obtained from the respective 5-[poly(acetoxy)alkyl]tetrazoles[2]. The reaction is formulated for 5-(tetra-*O*-benzoyl-L-*arabino*-tetritol-1-yl)tetrazole (**1**) in Scheme 1.



Scheme 1

By the same reaction, 5-(tetra-*O*-benzoyl-D-*arabino*-tetritol-1-yl)tetrazole (**4**), 5-(tetra-*O*-benzoyl-D-*xylo*-tetritol-1-yl)tetrazole (**6**), 5-(1,2,3,4-tetra-*O*-benzoyl-5-deoxy-L-*manno*-pentitol-1-yl)tetrazole (**8**), 5-(penta-*O*-benzoyl-D-*gluco*-pentitol-1-yl)tetrazole

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*Synthesis of Tetrazoles from Acylated Aldononitriles. Part III. For Part I, see ref. 1; for Part II, see ref. 2.

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(10), and 5-(penta-*O*-benzoyl-D-*manno*-pentitol-1-yl)tetrazole **(12)** were obtained, and these were debenzoylated.

EXPERIMENTAL

General procedures. — Melting points are not corrected. The optical rotations were determined at 20°. Ammonium azide was purified by sublimation. Thin–layer chromatography (t.l.c.) was performed on plates coated with silica gel G (Merck, Germany), with 19:1 chloroform–methanol as the eluant, and iodine vapor for detection.

Synthesis of 5-[poly(benzoyloxy)alkyl]tetrazoles. — These compounds were prepared by dissolving the benzoylated aldononitrile (5 g) in *N*,*N*-dimethylformamide (25–35 mL), and adding ammonium azide (0.6 g). The mixture was kept at room temperature, with occasional shaking, until the ammonium azide had completely dissolved. The reaction was monitored by t.l.c. until the nitrile had dissappeared (~7 days). The solution was evaporated under diminished pressure (bath temperature, 50°). The products were solids or syrups, which were purified as individually described.

Preparation of 5-(polyhydroxyalkyl)tetrazoles. — These compounds were obtained by dissolving the 5-[poly(benzoyloxy)alkyl]tetrazole (1.0 g) in methanol (70 mL), and adding 2% sodium methoxide solution to pH 8. The solution was kept for 24 h at room temperature, made neutral with Zeo Karb 225 (H^+) resin, the mixture filtered, the filtrate evaporated to dryness, and the product purified as individually described.

*5-(Tetra-O-benzoyl-*L-arabino*-tetritol-1-yl)tetrazole* **(1)**. — Tetra-*O*-benzoyl-L-arabinononitrile[4] gave compound **1** as a syrup, which was dissolved in ethanol, and the solution decolorized several times with charcoal, and concentrated. Crystallization could not be induced; after evaporation to dryness, compound **1** was obtained as a chromatographically homogeneous syrup (81.5%), $[\alpha]_D$ —13° (*c* 1, chloroform).

Anal. Calc. for $C_{33}H_{26}N_4O_8$: C, 65.34; H, 4.29; N, 9.24. Found: C, 65.01; H, 4.70; N, 9.10.

*5-(*L-arabino*-Tetritol-1-yl)tetrazole* **(2)**. — Compound **1** gave **2** as a white solid that crystallized from ethanol as rectangular prisms (58%), m.p. 200–202°, $[\alpha]_D$ +20° (*c* 1, water); lit.[2] m.p. 200–202°, $[\alpha]_D$ +22° (*c* 1, water).

*Tetra-O-benzoyl-*D*-arabinononitrile* **(3)**. — D-Arabinose oxime was benzoylated by the technique described for tetra-*O*-benzoyl-L-arabinononitrile[4]. After three precipitations from ethanol, compound **3** (64%) was obtained as a white, amorphous powder, m.p. 81–83°, $[\alpha]_D$ +13.8° (*c* 1, chloroform).

Anal. Calc. for $C_{33}H_{25}NO_8$: C, 70.33; H, 4.47; N, 2.49. Found: C, 70.10; H, 4.63; N, 2.30.

*5-(Tetra-O-benzoyl-*D-arabino*-tetritol-1-yl)tetrazole* **(4)**. — From **3**, compound **4** was obtained as a syrup. It was dissolved in ethanol, and the solution decolorized several times with charcoal, and concentrated, to give a chromatographically pure syrup (88%), $[\alpha]_D$ +15.4° (*c* 1, chloroform).

Anal. Calc. for $C_{33}H_{26}N_4O_8$: C, 65.34; H, 4.29; N, 9.24. Found: C, 65.68; H, 4.68; N, 9.16.

*5-(*D-arabino-*Tetritol-1-yl)tetrazole* (**5**). — From **4**, compound **5** was obtained as a white solid that crystallized from methanol as rectangular plates (69%), m.p. 200–203°, $[\alpha]_D$ —24.2° (*c* 1, water); lit.[2] m.p. 201–203°, $[\alpha]_D$ —24,5° (*c* 1, water).

*5-(Tetra-*O*-benzoyl-*D-xylo-*tetritol-1-yl)tetrazole* (**6**). — Tetra-*O*-benzoyl-D-xylononitrile[4] gave compound **6** as a syrup. It was dissolved in ethanol, and the solution decolorized several times with charcoal, and concentrated. Crystallization could not be induced, and, after evaporation to dryness, compound **6** was obtained as a chromatographically pure syrup (85%), $[\alpha]_D$ —13° (*c* 1, chloroform).

Anal. Calc. for $C_{33}H_{26}N_4O_8$: C, 65.34; H, 4 29, N, 9.24. Found: C, 65.46; H, 4.60; N, 9.59.

*5-(*D-xylo-*Tetritol-1-yl)tetrazole* (**7**). — Compound **6** gave **7** as a solid that crystallized from ethanol as needles (83%), m.p. 140–141°, $[\alpha]_D$ +22° (*c* 1, water); lit.[2] m.p. 139–140°, $[\alpha]_D$ +21.3° (*c* 1.2, water).

*5-(1,2,3,4-Tetra-*O*-benzoyl-5-deoxy-*L-manno-*pentitol-1-yl)tetrazole* (**8**). — Tetra-*O*-benzoyl-6-deoxy-L-mannononitrile[5] gave compound **8** as a syrup that crystallized from methanol as rectangular plates (74%), m.p. 92–95°, $[\alpha]_D$ —31.4° (*c* 1, chloroform).

Anal. Calc. for $C_{34}H_{28}N_4O_8$: C, 65.80; H, 4.51; N, 9.03. Found: C, 65.63; H, 4.57; N, 8.87.

*5-(5-Deoxy-*L-manno-*pentitol-1-yl)tetrazole* (**9**). — From **8**, compound **9** was obtained as a white material that crystallized from methanol as needles (96%), m.p. 204–205°, $[\alpha]_D$ +32.0° (*c* 0.5, water); lit [2] m.p. 204–205°, $[\alpha]_D$ +32.2° (*c* 1, water).

*5-(Penta-*O*-benzoyl-*D-gluco-*pentitol-1-yl)tetrazole* (**10**). — Using tetrahydrofuran instead of *N,N*-dimethylformamide as described under general procedures, penta-*O*-benzoyl-D-gluconconsole[5] gave compound **10** as a white material that crystallized from 9:1 ethanol–acetone as rhombic plates (87%), m.p. 106–108°, $[\alpha]_D$ +65.5° (*c* 1, chloroform).

Anal. Calc. for $C_{41}H_{32}N_4O_{10}$: C, 66.48; H, 4.32; N, 7.56. Found: C, 66.20; H, 4.45; N, 7.62.

*5-(*D-gluco-*Pentitol-1-yl)tetrazole* (**11**). — From **10**, compound **11** was obtained as a white material that crystallized from methanol as needles (70.5%), m.p. 194–196°, $[\alpha]_D$ +19.7° (*c* 1, water); lit.[2] m.p. 195–197°, $[\alpha]_D$ +19.2° (*c* 0.9, water).

*5-(Penta-*O*-benzoyl-*D-manno-*pentitol-1-yl)tetrazole* (**12**). — Penta-*O*-benzoyl-D-mannononitrile[5] gave compound **12** as a syrup that crystallized from ethanol as rectangular plates, m.p. 172–173°, $[\alpha]_D$ +50.4° (*c* 1, chloroform).

Anal. Calc. for $C_{41}H_{32}N_4O_{10}$: C, 66.48; H, 4.32; N, 7.56. Found: C, 66 09; H, 4.70; N, 7.33.

*5-(*D-manno-*Pentitol-1-yl)tetrazole* (**13**). — From **12**, compound **13** was obtained as a white material that crystallized from 9:1 ethanol–water as needles (68%), m p 200–202°, $[\alpha]_D$ —27° (*c* 0.5, water); lit.[2] m.p. 200–202°, $[\alpha]_D$ —29.6° (*c* 0.9, water).

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