In compound III, the configurations of its carbon atoms confirm those expectations, and, from this, the structure of the aldol product could be predicted to be that of I. However, in the alkaline medium in which it is formed, such a compound theoretically might isomerize to other octuloses[4] that would be reduced to compound III. All of these possibilities were eliminated by degrading compound I with an equimolecular proportion of periodic acid,[5] and finding D-arabinose and D-glucono-1,5-lactone among the products. No octulose structure other than that proposed for compound I can give both products; and, of the remaining 5 ketoses, the 2-octulose could give only D-arabinose. Furthermore, compound I cannot be this 2-octulose, D-*glycero*-D-*gulo*-octulose, for it is a known substance[6] whose properties are different from those of I. Thus, the new sugar has structure I; and compound II, the new octitol, is D-*erythro*-L-*gulo*-octitol.

The readiness with which D-erythrose undergoes aldol reaction to afford compound I makes it seem odd that the new sugar (or its phosphate) has not yet been observed in biological systems. Perhaps, this nondetection is due to its low sensitivity to the orcinol–trichloroacetic acid spray, which produces a faint gray spot on paper chromatograms; however, under ultraviolet light a resulting yellow-orange fluorescence can be detected more readily. D-*manno*-3-Heptulose, which has been synthesized[1c] and crystallized,[7] reacts analogously. This behavior may be characteristic of 3-ketoses.

Further work on this and related aldol syntheses is in progress. Additional details will be published later.

Experimental

D-*gluco*-L-*glycero*-**3-Octulose** (I).—A solution of 2.4 g. of D-erythrose (prepared from 2,4-*O*-ethylidene-D-erythrose[1c]) in 200 ml. of a filtered, saturated solution of calcium hydroxide (prepared at 5°) was kept at room temperature until a maximum dextrorotation was reached (about 2 hr.), and then treated with excess carbon dioxide, filtered, and concentrated under reduced pressure. After removal of an additional precipitate, the concentrate was taken up in methanol, from which compound I crystallized; yield 16%, m.p. 164–165°, $[\alpha]^{26}D$ +59.3° (*c* 10, water), no mutarotation observed.

Anal. Calcd. for $C_8H_{16}O_8$: C, 40.0; H, 6.7. Found: C, 39.8; H, 6.7.

On being paper chromatographed, I traveled only a little more slowly than D-glucose in 1-butanol–ethanol–water (40:11:19) and in 1-butanol–pyridine–water (6:4:3). It reacts readily with silver nitrate and sodium hydroxide sprays, but poorly with orcinol and trichloroacetic acid (faint gray that is yellow-orange under ultraviolet light), and gives no reaction with aniline hydrogen phthalate.

Degradation with Periodic Acid.—At 0°, a solution of 5 mg. of compound I in 1 ml. of water was treated with 5 mg. of periodic acid. The mixture was allowed to warm to room temperature after 1 hr., and, an hour later, a sample was paper chromatographed using 1-butanol–ethanol–water (40:11:19) containing 1% of ammonium hydroxide. Aniline hydrogen phthalate spray gave a reddish pink color at a position corresponding to that for D-arabinose. The remainder of the oxidation mixture was neutralized with barium carbonate, treated with Amberlite IR-120 H^+, and concentrated under reduced pressure. The concentrate was dissolved in 2-methoxyethanol and reconcentrated, and this process was repeated several times. A sample of the concentrate was chromatographed in a solution of 1-butanol saturated with water and containing 2% of formic acid. Silver nitrate and sodium hydroxide sprays showed a spot corresponding to D-glucono-1,5-lactone. The 3-octulose and D-arabinose spots were near the spot for D-glucono-1,4-lactone, and this circumstance made difficult the positive identification of this D-gluconic acid derivative, too.

Reduction with Sodium Borohydride.—At 0°, a stirred solution of 1 g. of I in 50 ml. of water was treated with 1 g. of sodium borohydride, and allowed to warm to room temperature overnight. Excess borohydride was decomposed with Amberlite IR-120 H^+. Boric acid was removed by repeated evaporation with methanol; during this process, a new, crystalline material appeared. From the first crops, there was obtained D-*erythro*-L-*gulo*-octitol (II), m.p. 164.5–165°, $[\alpha]^{23}D$ 171° (in 5% ammonium molybdate[8]).

Anal. Calcd. for $C_8H_{18}O_8$: C, 39.7; H, 7.5. Found: C, 40.0; H, 7.7.

Acetylation with acetic anhydride in pyridine gave the octaacetate, m.p. 110–111°, $[\alpha]^{20}D$ 47° (*c* 0.4, chloroform).

Anal. Calcd. for $C_{24}H_{34}O_{16}$: C, 49.8; H, 5.9. Found C, 49.8; H, 5.8.

The mother liquor contained some of II, together with D-*erythro*-L-*galacto*-octitol (III). The latter was obtained crystalline from methanol–water. Its m.p. of 153–154°, undepressed mixture melting point, and the correspondence of its infrared spectrum with that of the authentic material[3c,d] established its identity. Its octaacetate, obtained from its interaction with acetic anhydride in pyridine, had m.p. 88–89°, an undepressed mixture melting point, and an identity of infrared spectrum with that of authentic D-*erythro*-L-*galacto*-octitol octaacetate.[3c,d]

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3,4,6-Tri-*O*-acetyl-2-*O*-nitro-α-D-glucopyranosyl Chloride and the Anomeric Tetraacetates of 2-*O*-Nitro-D-glucopyranose

M. L. WOLFROM, A. THOMPSON,[1,2] AND D. R. LINEBACK[2]

Department of Chemistry, The Ohio State University, Columbus, Ohio

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The synthesis of α-D-glucosides in a Koenigs–Knorr reaction[3] has been of great difficulty either because of the unavailability of stable poly-*O*-acyl-β-D-glucosyl halides or because of the tendency of these materials to react with hydroxylic compounds by a mechanism involving participation of the *trans* 2-*O*-acyl group in the displacement at C-1 leading to products of the β-D-configuration. Schlubach[4] prepared an unstable tetra-*O*-acetyl-β-D-glucopyranosyl chloride from the treatment of tetra-*O*-acetyl-α-D-glucopyranosyl bromide with "active" silver chloride. Lemieux and Brice[5] reported an improved synthesis of this material by the action of titanium tetrachloride on β-D-glucopyranose pentaacetate. The β-D-glucosyl chloride readily isomerized to the α-D-anomer and was thus unsuited for the synthesis of α-D-glucosides. Brigl[6] has shown that

(1) Deceased.

(2) Research Associate (A. T.) and Fellow of the Corn Industries Research Foundation.

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fusion of β-D-glucose pentaacetate and phosphorus pentachloride yields 3,4,6-tri-*O*-acetyl-2-*O*-trichloroacetyl-β-D-glucopyranosyl chloride, from which 3,4,6-tri-*O*-acetyl-β-D-glucopyranosyl chloride can be obtained. Wolfrom, Pittet, and Gillam[7] reported the synthesis of β-isomaltose octaacetate using stable 3,4,6-tri-*O*-acetyl-2-*O*-nitro-β-D-glucopyranosyl chloride as the glycosyl halide component of a modified Koenigs–Knorr reaction. This β-D-glucosyl chloride could not be anomerized[7] without concomitant cleavage of the 2-*O*-nitro group, thus illustrating the deactivating power of the 2-*O*-nitro moiety.

It was of interest to attempt the synthesis of a β-D-glucosyl bromide with a nonparticipating group substituted on C-2. Low temperature nitration of 3,4,6-tri-*O*-acetyl-α-D-glucopyranosyl chloride[8] yielded a sirupy product which resisted all efforts at crystallization. Elemental analysis and specific rotation indicated that this sirup was 3,4,6-tri-*O*-acetyl-2-*O*-nitro-α-D-glucopyranosyl chloride. Attempted conversion of this substance to the corresponding β-D-glucopyranosyl bromide using the conditions cited by Schlubach[4] yielded only recovered starting material. The nitrate group evidently deactivates the chloride to such an extent that halogen exchange would not occur, under the conditions used, with an "active" silver bromide prepared according to Schlubach.

Acetylation of 3,4,6-tri-*O*-acetyl-2-*O*-nitro-α-D-glucopyranosyl chloride with mercuric acetate and acetic acid[9] yielded crystalline 1,3,4,6-tetra-*O*-acetyl-2-*O*-nitro-β-D-glucopyranose and acetylation of 3,4,6-tri-*O*-acetyl-2-*O*-nitro-β-D-glucopyranosyl chloride[7] in the same manner yielded crystalline 1,3,4,6-tetra-*O*-acetyl-2-*O*-nitro-α-D-glucopyranose.

Experimental

3,4,6-Tri-*O*-acetyl-2-*O*-nitro-α-D-glucopyranosyl Chloride.—A mixture of 45 ml. of glacial acetic acid and 75 ml. of acetic anhydride was cooled to −20° (solid carbon dioxide–acetone), and 60 ml. of absolute nitric acid was added portionwise while maintaining the temperature below 0°. The solution was then cooled to −40° and 9.6 g. of 3,4,6-tri-*O*-acetyl-α-D-glucopyranosyl chloride[8] was added portionwise, with vigorous stirring, while maintaining the temperature between −36 and −42°. The mixture was allowed to warm to 0°, with stirring, and the clear solution was poured into 2 kg. of ice with stirring. The ice was allowed to melt over a 2- to 3-hr. period, and the solid material was separated by filtration. The amorphous product was dissolved in 250 ml. of ethylene dichloride, washed with aqueous sodium hydrogen carbonate, dried over calcium chloride, filtered, and the solvent removed under reduced pressure; yield, 7.47 g. of clear yellow sirup, $[\alpha]^{20}D$ +125° (*c* 1.18, chloroform).

Anal. Calcd. for $C_{12}H_{16}ClNO_{10}$: N, 3.79. Found: N, 4.15.

Attempted Synthesis of 3,4,6-Tri-*O*-acetyl-2-*O*-nitro-β-D-glucopyranosyl Bromide.—A solution of 3,4,6-tri-*O*-acetyl-2-*O*-nitro-α-D-glucopyranosyl chloride (5 g.) in 50 ml. of ether (dried according to Schlubach[4]) was refluxed, with stirring, for 5 hr. with 11 g. of "active" silver bromide (the silver bromide from 10 g. of silver nitrate according to Schlubach). The mixture was filtered and the residue washed with the same ether. The solvent was concentrated to a small volume under reduced pressure at low bath temperature. No crystalline material was obtained from this solution. Only sirupy starting material was recovered, 3.88 g., $[\alpha]^{18}D$ +130° (*c* 2.0, chloroform).

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1,3,4,6-Tetra-*O*-acetyl-2-*O*-nitro-β-D-glucopyranose.—The previously described, sirupy 3,4,6-tri-*O*-acetyl-2-*O*-nitro-α-D-glucopyranosyl chloride (2.5 g.) was dissolved in 20 ml. of glacial acetic acid containing 3.0 g. of mercuric acetate and maintained at room temperature for 1 hr. with occasional shaking. The mixture was diluted with 75 ml. of chloroform, washed thrice with water, the chloroform layer dried over anhydrous calcium chloride, filtered, and the solvent removed under reduced pressure. The resulting sirup was crystallized from ether–petroleum ether and recrystallized from hot ethanol; yield, 178 mg. (after three recrystallizations), m.p. 120–121°, $[\alpha]^{20}D$ +21° (*c* 2, chloroform); X-ray powder diffraction pattern[10]: 9.94 s (2), 7.56 s (1), 5.59 s (3), 5.40 vw, 4.87 m, 4.29 vw, 4.06 m, 3.88 w, 3.55 w, 3.25 w, 3.04 vw, 2.72 vw.

Anal. Calcd. for $C_{14}H_{19}NO_{12}$: C, 42.75; H, 4.83; N, 3.56. Found: C, 42.79; H, 4.95; N, 3.65.

1,3,4,6-Tetra-*O*-acetyl-2-*O*-nitro-α-D-glucopyranose.—3,4,6-Tri-*O*-acetyl-2-*O*-nitro-β-D-glucopyranosyl chloride[7] (2.5 g.) was treated with mercuric acetate as described before; yield, 1.43 g. (after three recrystallizations from ethanol), m.p. 92–93°, $[\alpha]^{22}D$ +107° (*c* 2, chloroform); X-ray powder diffraction pattern[10]: 8.31 s (2), 7.23 m, 6.68 w, 5.63 m, 5.05 vw, 4.68 vs (1), 4.24 m, 4.04 m, 3.91 w, 3.74 s (3), 3.54 w, 3.43 w, 3.24 w, 3.03 vw, 2.89 w, 2.72 vw, 2.51 vw, 2.27 vw, 2.18 w, 2.03 vw, 1.89 vw, 1.85 vw.

Anal. Calcd. for $C_{14}H_{19}NO_{12}$: C, 42.75; H, 4.83; N, 3.56. Found: C, 42.97; H, 5.13; N, 3.80.

(10) Interplanar spacing, Å., CuKα radiation. Relative intensities, estimated visually: s, strong; m, medium; w, weak; v, very. Strongest lines numbered, 1 strongest.

Oxidative Dimerization of Benzimidazole

JOHN H. M. HILL

Department of Chemistry, Hobart and William Smith Colleges, Geneva, New York

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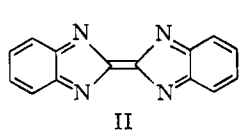
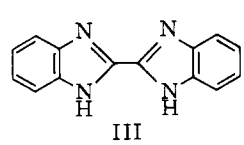
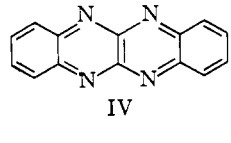
Benzimidazole (I) has been converted into $\Delta^{2,2'}$-biisobenzimidazolylidene (II), a nitrogen analog of the unknown 2,2′-biisoindene,[1,2] a dibenzofulvalene. Oxidation of I by potassium permanganate[3] or potassium dichromate[4] is known to produce imidazole-4,5-dicarboxylic acid. Prolonged oxidation of I by lead dioxide in refluxing benzene produces II, if azeotropic drying is carried out simultaneously. This reaction is slow and inefficient and the same product can be prepared more efficiently by oxidation of 2,2′-bibenzimidazole (III) under the same conditions. In this case the reaction is complete in twenty-four hours.



II



III



IV

In contrast to the fulvalenes,[5] which it resembles in its planarity and molecular structure, II is stable to heat.

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