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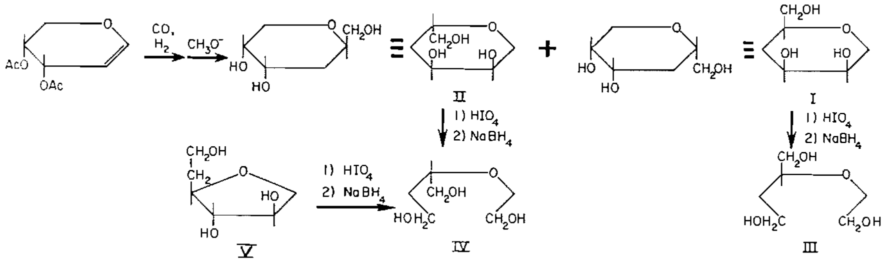
THE REACTION OF UNSATURATED CARBOHYDRATES WITH CARBON MONOXIDE AND HYDROGEN. III. STRUCTURE AND STEREOCHEMISTRY OF THE HEXITOLS FROM 3,4-DI-*O*-ACETYL-D-ARABINAL

ALEX ROSENTHAL AND HANS J. KOCH

In Part II of this series (1) it was shown that 3,4-di-*O*-acetyl-D-xylal reacted with carbon monoxide and hydrogen at a temperature of about 130° and at a pressure of about 4000 p.s.i. in the presence of dicobalt octacarbonyl to yield two anhydrodeoxyhexitols. This paper reports the results of an investigation of the application of a similar reaction to 3,4-di-*O*-acetyl-D-arabinal. The oxo product, first freed of catalyst, was deacetylated with methanolic sodium methoxide to afford a mixture of two hexitols contaminated with traces of sugars. Treatment of the mixture with sodium borohydride in water reduced the sugars to hexitols. Cellulose chromatography of the mixture gave the hexitols (I) and (II).



The structure and stereochemistry of the anhydrodeoxyhexitols (I) and (II) were determined in the same way as described in Part II of this series (1). Periodate oxidation of each hexitol (each consumed 1 molar equivalent of periodate) afforded sirupy dialdehydes. Sodium borohydride reduction of these dialdehydes yielded the triol ethers (III) and (IV), which had similar infrared spectra and equal but opposite optical rotations. Further confirmation that these triol ethers were enantiomers was provided by their characterization as crystalline *p*-nitrobenzoates with similar melting points. Direct comparison (m.p., mixed m.p., and infrared spectra) revealed that the *p*-nitrobenzoate of (IV) was identical with the *p*-nitrobenzoate of the triol ether obtained from 1,4-anhydro-5-deoxy-D-*arabino*-hexitol (V). Thus, the configuration of C-5 of the hexitol (II) is the same as that of C-4 of 1,4-anhydro-5-deoxy-D-*arabino*-hexitol (V), and compounds (I) and (II) are 1,5-anhydro-4-deoxy-D-*lyxo*-hexitol and 1,5-anhydro-4-deoxy-L-*ribo*-hexitol, respectively.

It is apparent that analysis of the nuclear magnetic resonance (n.m.r.) spectra (described in Experimental section) reveals the molecular structure of each of the anhydrodeoxyhexitols (I) and (II). Because each multiplet of peaks (equivalent to two hydrogens) occurs at about $\delta = 1.8$, it can be inferred from previous work (1) that each isomer possesses a methylene group on C-4. Thus, the two anhydrodeoxyhexitols must be linear and differ only in the configuration of C-5. The stereochemistry of C-5 of each of the anhydrodeoxyhexitols cannot be ascertained from the n.m.r. spectra because of overlapping peaks.

EXPERIMENTAL

General Considerations

These have been described previously (1).

*3,4-Di-O-acetyl-*D*-arabinal*

This was prepared following the procedure for the preparation of 3,4-di-*O*-acetyl-D-xylal (1).

*Reaction of 3,4-Di-O-acetyl-*D*-arabinal with Carbon Monoxide and Hydrogen to Yield 1,5-Anhydro-4-deoxy-*D*-lyxo-hexitol (I) and 1,5-Anhydro-4-deoxy-*L*-ribo-hexitol (II)*

The 3,4-Di-*O*-acetyl-D-arabinal (12 g) was allowed to react with 500 p.s.i. of carbon monoxide and 2500 p.s.i. of hydrogen in the presence of dicobalt octacarbonyl (2 g) for 1.5 h at 125°. The product (13 g), first freed of catalyst by filtration through Florisil, contained traces of reducing sugars. Reaction of the same substrate with carbon monoxide and hydrogen (1:8 by pressure) at 113° to 120° for 0.5 h yielded 33% reducing sugars and about 65% hexitols. The product was deacetylated with 0.1 *N* methanolic sodium methoxide. Sugars were reduced with sodium borohydride before separation of the hexitols by chromatography. Chromatography of 1.43 g of the deacetylated product on a powdered cellulose column (410 × 47 mm diam.) with water-saturated 1-butanol as developer yielded 0.80 g of fraction (I) and 0.55 g of fraction (II). Fractionation was also readily achieved using water-saturated 1-butanol containing 5% ethanol as developer.

Characterization of Fraction (I)

Fraction (I) (1,5-anhydro-4-deoxy-D-*lyxo*-hexitol) crystallized slowly when kept in a desiccator for several months over phosphorus pentoxide; m.p. 85–87°; $[\alpha]_D^{20}$ −50° (*c*, 1.7 water); $R_f = 0.26$. Attempts to crystallize (I) from methanol – isopropyl ether were unsuccessful. Anal. Calc. for $C_6H_{12}O_4$: C, 48.64; H, 8.17. Found: C, 48.38; H, 8.22. N.M.R. (deuterium oxide): multiplet of peaks, centered at $\delta = 1.68$ to 1.80, equal to 2 hydrogens. This spectrum was identical with that of a similar compound isolated by Gorin (2) from the hydrogenolysis of methyl-α-D-glucopyranoside.

Characterization of Fraction (II)

Fraction (II) (1,5-anhydro-4-deoxy-L-*ribo*-hexitol) solidified when kept in a desiccator over phosphorus pentoxide for several months. The substance was very hygroscopic. Attempts to crystallize (II) from various solvents were unsuccessful. $[\alpha]_D^{20}$ +29° (*c*, 2.5 water); $R_f = 0.36$. Anal. Calc. for $C_6H_{12}O_4$: C, 48.64; H, 8.17. Found: C, 48.49; H, 8.22. N.M.R. (deuterium oxide): multiplet of peaks, centered at $\delta = 1.60$ to 1.80, equal to 2 hydrogens.

*Preparation of 1,5-Anhydro-2,3,6-tri-O-benzoyl-4-deoxy-*D*-lyxo-hexitol*

Fraction (I) was benzoylated according to the procedure of Smith and Van Cleve (3) to yield sirupy 1,5-anhydro-2,3,6-tri-*O*-benzoyl-4-deoxy-D-*lyxo*-hexitol; $[\alpha]_D^{21}$ −63° (*c*, 3 ethanol). Anal. Calc. for $C_{27}H_{24}O_7$: C, 70.41; H, 5.25. Found: C, 70.60; H, 5.42.

*Preparation of 1,5-Anhydro-2,3,6-tri-O-benzoyl-4-deoxy-*L*-ribo-hexitol*

Fraction (II) was benzoylated in the usual way to yield 1,5-anhydro-2,3,6-tri-*O*-benzoyl-4-deoxy-L-*ribo*-hexitol, and the product was recrystallized from ethyl acetate – light petroleum ether, or methanol–water; m.p. 132–133°; $[\alpha]_D^{21}$ +79° (*c*, 1.58 chloroform). Anal. Calc. for $C_{27}H_{24}O_7$: C, 70.41; H, 5.25. Found: C, 70.75; H, 5.31.

Structure and Stereochemistry of Fractions (I) and (II)

Fraction (I) was oxidized, according to the procedure previously described (1), with 0.1 *M* periodic acid (1 molar equivalent consumed). The dialdehyde was immediately reduced with sodium borohydride to yield the triol ether (III); $[\alpha]_D^{21}$ −17° (*c*, 1 water). The triol ether was characterized as the *p*-nitrobenzoate; m.p. 102–102.5°; $[\alpha]_D^{22}$ −23° (*c*, 2 chloroform). Anal. Calc. for $C_{27}H_{23}N_3O_{13}$: C, 54.27; H, 3.88; N, 7.03. Found: C, 54.55; H, 3.96; N, 7.36.

Similarly fraction (II) was converted into the triol ether (IV); $[\alpha]_D^{24}$ +17° (*c*, 1 water). The infrared spectra of III and IV were similar. Reaction of the triol ether (IV) with *p*-nitrobenzoyl chloride in pyridine yielded the tris-*p*-nitrobenzoate; m.p. 102–102.5°; $[\alpha]_D^{22}$ +22.3 (*c*, 3.6 chloroform). Anal. Calc. for $C_{27}H_{23}N_3O_{13}$: C, 54.27; H, 3.88; N, 7.03. Found: C, 54.39; H, 3.98; N, 7.29.

The infrared spectra of the two *p*-nitrobenzoate derivatives were identical. The mixed m.p. of the tris-*p*-nitrobenzoate of compound (IV) and the tris-*p*-nitrobenzoate of 2-deoxy-3-*O*-(2-hydroxyethyl)-L-*glycero*-tetritol (1) (obtained by sodium borohydride reduction of the periodate oxidation product of authentic 1,4-anhydro-5-deoxy-D-*arabino*-hexitol (V)) was 101–103°. The infrared spectra of the two *p*-nitrobenzoates were identical.

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PROPYLENE GAS HYDRATE STABILITY[1]

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INTRODUCTION

Although the formation conditions for propane hydrate are well characterized (1, 2, 3), the comparable conditions for the formation of propylene hydrate from liquid water and propylene gas have been little studied and are known only approximately. From the three measurements available (3) it appears that the propylene hydrate is considerably less stable than the propane hydrate, in spite of the similar physical properties of the propylene and propane species. An experimental investigation of the propylene hydrate system has thus been made to better define the conditions for hydrate formation.

EXPERIMENTAL

The propylene was Matheson C.P. grade which was found by gas chromatography to contain 99.4 mole % propylene, 0.56 mole % propane, 127 p.p.m. ethane, and less than 10 p.p.m. of any other volatile impurity. The water was distilled and deionized by passage through a mixed ion exchange resin column, and subsequently outgassed in the hydrate cell prior to use.

The hydrate cell which was fabricated from stainless steel contained a stirrer operated by magnetic induction. The portion of the apparatus in which the hydrate was formed could be completely immersed in a large thermostat bath which could be regulated to ±0.001 °C. Pressure was measured using a 0–100 p.s.i., 10 in. diameter Heise gauge, which was calibrated by a dead-weight tester. The barometric pressure was recorded at each measurement. This procedure gave pressure accurate to ±0.1 p.s.i. or ±0.006 atm.

The temperature of the cell was measured relative to a block of stainless steel immersed in the same thermostat bath by means of a ten-junction copper-constantan thermocouple. The temperature of the block was measured by a platinum resistance thermometer which was calibrated at the triple point of water.

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[1] *Contribution No. 122.*