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Preliminary communication

A new class of monosaccharide derivatives: O-phthalimidohexoses

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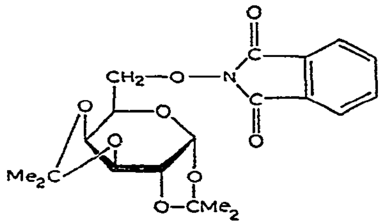
We recently reported that the use of *N*-hydroxyphthalimide as a nucleophilic reagent in reactions with alcohols in the presence of triphenylphosphine and diethyl azodicarboxylate leads to *O*-alkyl derivatives of hydroxylamine[1]. We now report on the application of this reaction to carbohydrate derivatives containing an "isolated" hydroxyl group to afford a new type of monosaccharide derivative, namely *O*-amino sugars.

Treatment of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose[2] with equimolar amounts of *N*-hydroxyphthalimide, triphenylphosphine, and diethyl azodicarboxylate in tetrahydrofuran at room temperature for 24 h, followed by concentration, and chromatography of the residue on a silica gel column with benzene–ether (9:1), gave 1,2:3,4-di-*O*-isopropylidene-6-*O*-phthalimido-α-D-galactopyranose (**1**, 54.3%), m.p. 121–122°; $\nu_{\max}^{\mathrm{KBr}}$ 1615, 1740 and 1795 (C=O), and 700 cm^{-1} (aromatic); no OH absorption. The p.m.r. spectrum (chloroform-*d*) was similar to that for 6-deoxy-1,2:3,4-



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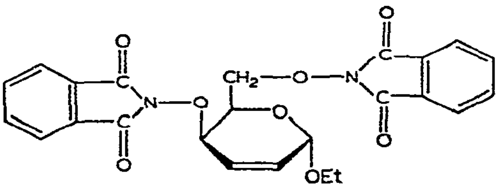

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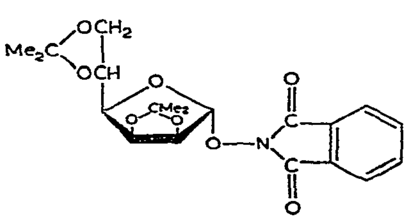

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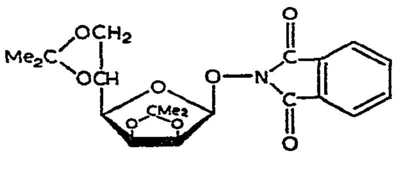

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di-*O*-isopropylidene-6-phthalimido-α-D-galactopyranose[3] except for the chemical shift of H-6,6′. Similarly, ethyl 2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside[4] with 2 moles of each reagent for 1 mole of sugar gave ethyl 2,3-dideoxy-4,6-di-*O*-phthalimido-α-D-*threo*-hex-2-enopyranoside (2, 78.5%), m.p. 250–252°, ν_{max}^{KBr} 1615, 1740 and 1790 (C=O), and 695 cm^{-1} (aromatic). The p.m.r. spectrum (pyridine-d_5) was similar to that for ethyl 2,3,4,6-tetradeoxy-4,6-diphthalimido-α-D-*threo*-hex-2-enopyranoside[3]; the coupling constants for H-4 ($J_{3,4}$ 5.0, $J_{4,5}$ 3.5 Hz) showed that inversion of configuration at C-4 had occurred in this reaction.

2,3:5,6-Di-*O*-isopropylidene-D-mannofuranose[5] was converted into two products that were isolated by chromatography on silica gel. The first was *N*-(2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranosyloxy)phthalimide (3, 11.0%), m.p. 128–129°; ν_{max}^{KBr} 1610, 1740 and 1795 (C=O), and 695 cm^{-1} (aromatic). The p.m.r. spectrum (chloroform-*d*) was similar to that recorded for *N*-(2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranosyl)phthalimide[6]. The α-configuration of this compound was established on the basis of the coupling constant $J_{1,2}$ ~0 Hz. The second product was *N*-(2,3:5,6-di-*O*-isopropylidene-β-D-mannofuranosyloxy)phthalimide (4, 65.0%), m.p. 146–147°; ν_{max}^{KBr} 1615, 1740 and 1795 (C=O), and 700 cm^{-1} (aromatic). The β-configuration followed from the coupling constant $J_{1,2}$ 4.0 Hz.

The new compounds described here had correct elemental analyses, and apparently constitute the first examples of carbohydrate *O*-derivatives of hydroxylamine.

ACKNOWLEDGMENT

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